CRystalline RADIATION-CROSSLINKED HYDROGELS OF POLY (VINYL-ALCOHOL) AS POTENTIAL BIOMATERIALS

A Study of the Properties of Poly(Vinyl-Alcohol) Hydrogels in Relation to Conditions of Primary Crosslinking by Irradiation, and of Secondary Network Reinforcement by Crystallization

By

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Diploma of Chem. Eng., National Technical University of Athens, Greece (1971)

Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Science at the Massachusetts Institute of Technology

October 3, 1973

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JAN 28 1974
ABSTRACT

CRYSTALLINE RADIATION-CROSSLINKED HYDROGELS OF POLY (VINYL-ALCOHOL) AS POTENTIAL BIOMATERIALS

A Study of the Properties of Poly (Vinyl-Alcohol) Hydrogels in Relation to Conditions of Primary Crosslinking by Irradiation, and of Secondary Network Reinforcement by Crystallization

by

NIKOLAOS A. PEPPAS

Submitted to the Department of Chemical Engineering on October 3, 1973 in partial fulfillment of the requirements for the Degree of Doctor of Science

Aqueous poly (vinyl-alcohol) solutions of wt. concentrations 10% and 15% were crosslinked via electron beam and Y-radiation at 0° and 30° to form transparent hydrogels of varying crosslinking densities. Gamma radiation favored crosslinking, leading to more dense networks than electron beam radiation, for the same dose delivered. Oxygen generally led to degradation, but the final crosslinking density depended on the dose rate as well.

Typical crosslinked hydrogels with crosslinking densities varying between 10 and 25 crosslinks per polymer unit (M_r =3500-8000) were weak, easy to shatter, non extensible materials. Moduli of the swollen hydrogels varied between 10-70 psi, strength at break between 1-10 psi and elongation was not more than 100%. They could not be used for practical applications, unless reinforced in some way.

Reinforcement of PVA hydrogels by induction of partial crystallization was accomplished by a two stage drying process. This comprised (1) a dehydration stage, after which the crystallinity increased to 15-20%, and the polymer volume fraction after swelling to 25-30%, and (2) an annealing stage which was mainly responsible for the reinforcement of the material. The swollen hydrogels after the annealing process had crystallinities widely varying between 30 and 65% and polymer volume fraction between 30 and 60% depending on the temperature-time history of the specimens. Temperatures in the range of 30-200°C and times of 5 minutes to two hours produced materials with moduli up to 1500 psi, strengths at break up to 2500 psi and elongations at break as high as 600%. These materials showed very high tear strength. In practical applications, they could be used in water at temperatures up to 40°C.
The physical properties of the crystallized hydrogels (swelling ratio, degree of crystallinity, polymer volume fraction), as well as the mechanical properties (modulus, ultimate tensile strength, elongation at break, tear strength, creep behavior) were functions of the initial cross-linking density.

The materials were proposed to be used, after heparinization, as potential nonthrombogenic biomaterials.

Thesis Supervisor: Edward W. Merrill
Title: Professor of Chemical Engineering
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Cambridge, Massachusetts 02139  
October 3, 1973

Professor David B. Ralston  
Secretary of the Faculty  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

Dear Professor Ralston:

In accordance with the regulation of the Faculty, I herewith submit a thesis, entitled "Crystalline Radiation-Crosslinked Hydrogels of Poly (Vinyl-Alcohol) as Potential Biomaterials" in partial fulfillment of the requirements for the Degree of Doctor of Science in Chemical Engineering at the Massachusetts Institute of Technology.

Respectfully submitted,

Nikolaos A. Peppas

NAP/mt
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DEDICATED

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CHAPTER 1

SUMMARY

For the purpose of ultimately achieving a superior material to be used in prolonged contact with blood, to the surface of which the naturally anticoagulant heparin could be covalently bonded, this thesis was concerned with the synthesis of a cross-linked network of poly (vinyl alcohol) produced from concentrated aqueous solution of PVA by irradiation, subsequently dehydrated and annealed to induce micellar crystallization and thereby reinforcement, and finally allowed to come to equilibrium in water at 30°C. The properties of the intermediate and final materials were evaluated by appropriate analytical methods, with particular reference to the superposition of crystallization on a precisely crosslinked network.

A. INTRODUCTION

A wide variety of biomaterials have been developed for use in many applications of hemodialysis. The most important problem in the development of these materials is the absence of a successful blood-compatible biomaterial and especially one that will prevent coagulation, without the continuous administration of heparin solution.
Heparin is a natural anticoagulant polysaccharide with molecular weight between 8000 - 15000. Its anticoagulant action is a direct result of the fact that it combines with a wide variety of proteins because of strong electrostatic charges (81). It participates in the intrinsic mechanism of coagulation (194) by complexing with antithrombin to form a complex, which finally reacts with thrombin to form an inactive complex (306). Thus heparin blocks the formation of fibrin or platelet thrombi and it maintains the blood fluidity, when it is pumped through extracorporeal devices (169).

Certain authors (223, 376) have proposed some guidelines for the evaluation of potential biomaterials. According to them, a biomaterial should be:

(1) non toxic
(2) non carcinogenic
(3) non inflammatory

In combination, the above-mentioned three requirements imply:

(4) chemical inertness in contact with living tissue
(5) absence of elutable substance, e.g. catalyst fragments

For convenience, one may also specify as desiderata:

(6) appropriate mechanical durability (317)
(7) processability, i.e., easily molded or casted films
(8) sterilizability, without any change in properties or form (47)
In the particular case of materials to be used in contact with blood *in vivo*, the special properties sought in addition to the forgoing, are:

(9) lack of thrombogenic action
(10) lack of damage to red cells, white cells or platelets.

Current research on nonthrombogenic materials is connected with the theories of minimum surface energy (Lyman 224, 226), of the energy of interaction of the molecules at a surface (Baier 21) and of the zeta potential (Leininger 213, 214).

Among other nonthrombogenic biomaterials, heparinized hydrogels are preferable because evidence in the literature (317) shows that a network in the rubbery or solvated state is less thrombogenic than in a semicrystalline state.

Ionically bound heparin on certain surfaces is a common practice, but these surfaces generally show greater nonthrombogenicity than those with covalent bonding or crosslinked heparin due to some release of heparin by ion exchange with proteins from the contacting blood (452).

Heparinized PVA hydrogels are the subject of extensive work under the direction of Merrill and Wong at MIT. A PVA heparin hydrogel "G" (256) crosslinked via gluteraldehyde was the first biomaterial to be produced. Improvement of this hydrogel was achieved by the so-called "solid state" method, according to which, heparin was reacted only on the surface of the PVA hydrogel (260).
However, by either method, the reaction whereby heparin was coupled to the PVA network, namely acetal bond formation, served also to crosslink the PVA molecules and convert them into copolymer (poly-vinyl alcohol-co-formal) at indefinite composition. A major purpose of this thesis was to find an alternative to acetal crosslinking, in order to better define the relation between structure and properties.

A study of the substrate and its properties, as well as methods of reinforcement is needed.

Statement of Objectives

(1) synthesis of crosslinked PVA hydrogel via irradiation

(2) study of the effect of radiation condition on the crosslinking density and processability of the hydrogels

(3) investigation of the effects of crosslinking on the mechanical properties of the hydrogel

(4) development of a reinforcement method of dehydration and annealing of the original hydrogel

(5) characterization of the degree of crystallibility of the produced gels

(6) study of the mechanical behavior of the semicrystalline PVA hydrogel

B. PROPERTIES OF PVA

Poly (vinyl alcohol), from now on designated also as PVA, has the structure (i)

\[
\text{CH}_2 - \text{CH (OH)} \overset{\text{i}}{\longrightarrow} \text{n} - 37 -
\]
It is commercially produced by polymerization of vinyl acetate and subsequent hydrolysis of the produced polymer. There are three principal stereoregular forms, the isotactic, the syndiotactic and the atactic. Commercial PVA as used in this thesis is mostly atactic. Head-to-head addition, containing 1,2-glycol and leading to linkages of structure (ii), is usually around 1-2%

\[ \pm \text{CH}_2 - \text{CH(OH)} - \text{CH(OH)} - \text{CH}_2 \overset{\n}{\smile} \]  

(ii)

The chemical properties of PVA are affected by its degree of hydrolysis. Commercial PVA of high degree of hydrolysis has less than 1.5% acetate groups (91).

Fully hydrolyzed PVA has a melting point between 210°C and 240°C and glass transition temperature of 85°C (101). The solubility in water is a function of the degree of hydrolysis and highly hydrolyzed PVA dissolves in water only above 70°C (426).

Aqueous PVA solutions behave as non-Newtonian fluids (370). The thermodynamic aspects of PVA in aqueous solution are usually complicated and not well understood. For example, aqueous PVA solutions were assigned to systems with a lower critical miscibility temperature (LCMT) by Dieu (82) who reported a θ—temperature of 97°C. Phase separation occurred when the temperature was increased above 97°C. On the contrary Tager et al. (418) assigned a LCMT of 241°C and noticed that PVA solubility became poorer in the whole range of increasing temperatures. This phenomenon was explained by crosslinking
reactions during the separation of the system into phases (418) and by slight gelation and formation of semicrystalline structures (394).

Dilute solutions of PVA undergo marked "retrogradation" (i.e. spontaneous precipitation of PVA from water solution upon standing) in 2-3 days (192). Klenin's data (192) are the most accurate one. The behavior of the PVA-H₂O system, and they show that this system is a peculiar one with upper and lower miscibility temperatures, complicated by crystallization depending on the stereoregular tacticity of the initial PVA.

Light scattering measurements (201) and electron microscope investigations (198, 199) showed that the particles are almost spherical with dimensions up to 1000Å.

Supermolecular structures in PVA solutions have been also observed upon continuous heating, or upon freezing-thawing processes.

The knowledge of the phase behavior in PVA-H₂O systems in this thesis is important because of (i) reproducibility during preparation of PVA solutions (ii) accurate determination of weight average molecular weight M₆ and (iii) complication on the treatment of the crosslinking and swelling of the gels produced from these solutions.

Poly (vinyl alcohol) undergoes typical chemical reaction of polyhydric alcohols and can be crosslinked by any difunctional agent including gluteraldehyde (256). The use of electron-beam and γ-radiation for the production of PVA hydrogels has been reported (339).
As noted earlier, a major object of this thesis was to produce a network hydrogel from PVA without the complication of graft copolymerization inherent with aldehydes; and a second objective was to undertake a pioneering study of the effect of crystallization, subsequent to crosslinking, on the mechanical properties of PVA. A future objective is to provide a substance to which heparin may be coralement bound.

C. RADIATION EFFECTS ON PVA AND PVA SOLUTIONS

Ionizing radiation includes different types of radiation of moving particles, from primary or secondary sources, which carry enough energy to ionize simple molecules (55) either in air or in water. Electron beams and gamma-rays are mainly used for macromolecular studies. Electron beams are emitted usually by Co-60 sources.

Irradiated polymers primarily either crosslink or degrade according to their chemical structure. Both crosslinking and degradation may occur simultaneously and many authors have considered that the radiation effects are a kinetic phenomenon, where the rate of crosslinking or degradation predominates (458).

According to Sakurada's (328, 333, 335, 336, 339, 340, 341, 347) and Danno's (72, 75) studies, when PVA solutions are irradiated, the following events can occur (where PH is PVA long chain)
Activation

(1) \( \text{PH} + \text{PH}^* \)
(2) \( \text{H}_2\text{O} + \text{HOH}^* \)

Free Radical Formation

(3) \( \text{PH}^* + \text{P}^* + \text{H}^* \)
(4) \( \text{HOH}^* + \text{HO}^* + \text{H}^* \)

Gas Evolution

(5) \( \text{H}^* + \text{H}^* \rightarrow \text{H}_2 \)

Recombination

(6) \( \text{P}^* + \text{H}^* \rightarrow \text{PH} \)
(7) \( \text{HO}^* + \text{H}^* \rightarrow \text{H}_2\text{O} \)

Energy Transfer

(8) \( \text{PH} + \text{HOH}^* \rightarrow \text{PH}^* + \text{H}_2\text{O} \)
(9) \( \text{PH}^* + \text{H}_2\text{O} \rightarrow \text{PH} + \text{HOH}^* \)

Radical Transfer

(10) \( \text{PH} + \cdot\text{OH} \rightarrow \text{P}^* + \text{H}_2\text{O} \)
(11) \( \text{P}^* + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{PH} \)

Crosslinking

(12) \( \text{P}^* + \text{PH} \rightarrow \text{P}^* + \text{PH} \)

Degradation

(13) \( \text{P}^* - \text{PH} \rightarrow \text{P}^* + \text{PH} \)
The chemical changes occurring during irradiation of PVA solution result either from direct or from indirect effects via the solvent. When the dilute solution is irradiated, its viscosity rises and suddenly a gel structure is formed. This gel may be removed and further swollen in water. If the gel structure is further irradiated, the equilibrium degree of swelling is reduced until the gel exudes the excess water and breaks away from the container wall.

Gas evolution of hydrogen, according to reaction (5) is a common phenomenon, during the irradiation of PVA solution and it is a matter of rate of formation of hydrogen and diffusion of it through the continuously becoming more viscous PVA solution, which of the two rates will be predominant, leading either to clear PVA gel or to a gel with entrapped hydrogen bubbles (173).

Polymer radicals are formed either by reaction (3) or by reaction (10) and a large number of solvent radicals can lead to a large increase in the number of polymer radicals formed.

Oxygen usually favors the formation of weak peroxide bonds in the main chain of PVA and these bonds can decompose and cause oxidative degradation of the main chain. This process too, will depend on the relative rate of diffusion of oxygen through the irradiated PVA solution and the rate of irradiation dose (286, 388).

The relative effects of crosslinking and degradation are discussed by Saito (326) who gives the mathematical models and solutions of them in different cases of initial molecular weight distributions (321).
Numerous workers have studied the effects of radiation on aqueous PVA solutions (30, 72, 75, 83, 243, 340).

Danno (75) irradiated dilute PVA solutions with γ-radiation and he proved that the critical concentration of gelation varies with the initial degree of polymerization and that the gelation dose depends on the degree of polymerization and the concentration. In other studies (72) he found that the molecular weight increases monotonically with the dose.

Dieu and Desreux (83) verified the previous data and concluded that gamma-irradiation of aqueous PVA solutions leads to crosslinking.

Berkowitch et al. (30) studied the effects of electron beam and gamma irradiation and he found that the gelation dose decreased linearly with the concentration of the polymer and that it was lower in the case of γ-irradiation.

Sakurada (340) showed that when aqueous solutions were irradiated in air at 25°C, scission of the main chain predominated because of degradation phenomena due to formation of peroxidic bonds from radicals like HO₂⁺, HO⁻ etc., formed in the presence of oxygen. Matsumoto (243) studied quantitatively this effect.

Hirano (148, 149, 150) showed that selective main chain scission of PVA occurs if the 1, 2 - glycol content of the samples is higher than 1%.
Danno (75) observed entrapped bubbles of gas in irradiated samples and Bray (42) proposed that they were hydrogen bubbles. Petrov and Karpov (303), studied the gas evolution from PVA, as a function of dose and they showed that the gas consists of hydrogen in percent as high as 95.1%.

A number of additives used in irradiation of deaerated and aerated aqueous PVA solutions by Sakurada (335) protected polymers against degradation by radical transfer (acceptance) and recombination of radicals produced from irradiation of water.

Finally, quantitative analysis of the effects of electron beam radiation on aqueous PVA solutions was done by Bray and Merrill (42, 43) and Bauer (28) for solution of 5 - 30% in PVA, irradiated at 0-85°C with doses of 3 - 15 Mgrads. It was shown that higher doses, lower concentration and lower temperature favored the crosslinking density.

D. RUBBER ELASTICITY THEORY

The characterization of a crosslinked network can be done by the average molecular weight between crosslinks $M_c$, or the corresponding crosslinking density $\rho = \frac{M}{M_c}$. The theory developed by Flory (104) assumes ideal tetrafunctional crosslinks. The theoretical study of a hydrogel network has the purpose of revealing the structure and mechanical and chemical properties.
If an uncrosslinked polymer is soluble in a liquid, then the same polymer when crosslinked, will swell in the liquid. Swelling is expressed by the swelling ratio $Q$, defined as the ratio of the volume of the swollen gel to the volume of the unswollen one. Flory (104) developed an expression for the calculation of $M_c$ in a swollen network, where the crosslinks were introduced in the solid state.

$$\frac{1}{M_c} = \frac{2}{M_n} - \frac{\bar{V}}{V_1} \left[ \ln(1-u_{2,s}) + u_{2,s} + x_1 u_{2,s}^2 \right] \frac{1}{(u_{2,s}^{1/3} - \frac{u_{2,s}}{2})} \quad (1-1)$$

In the case of a swollen network, where the crosslinks have been introduced in the presence of a diluent, Bray and Merrill (42) developed a similar relation, which takes into account the fact that $u_{2,r} \neq 1$.

$$\frac{1}{M_c} = \frac{2}{M_n} - \frac{\bar{V}}{V_1} \left[ \ln(1-u_{2,s}) + u_{2,s} + x_1 u_{2,s}^2 \right] \frac{1}{u_{2,r} \left[ \left( \frac{u_{2,s}}{u_{2,r}} \right)^{1/3} - \frac{1}{2} \left( \frac{u_{2,s}}{u_{2,r}} \right) \right]} \quad (1-2)$$

where

- $u_{2,r}$ = polymer volume fraction in relaxed state
- $u_{2,s}$ = polymer volume fraction in swollen state
- $\bar{V}$ = specific volume of polymer
- $V_1$ = polar volume of solvent
- $M_n$ = number average molecular weight
- $x_1$ = Flory polymer-solvent interaction parameter
The $\chi$ factor is a function of temperature and polymer volume fraction and it controls in a great extent the final calculated value of $M_c$ as well as of other thermal properties that will be discussed later.

The assumptions made during the development of the rubber elasticity theory are, that the crosslinks here have been introduced randomly into the amorphous polymer, that the subunits of the network are long enough, that the deformation of the sample occurs at constant volume, that the contributions of the effective subunits to the total retractive force are additive and that the deformation of a sample is thermodynamically reversible. Thus the equation developed by Flory (113, 114) and modified by Treloar (430) is

$$\tau = \frac{RT}{M_c}(1 - \frac{2M_c}{M_n} \frac{r_i}{r_0}^2)(\alpha - \frac{1}{\alpha})$$  \hspace{1cm} (1-3)

where

- $\tau$ = tensile stress (force per initial cross-sectional area)
- $\rho$ = density of the sample
- $\alpha$ = elongation = $L/L_0$
- $T$ = temperature
- $\frac{r_i^2}{r_0^2}$ = ratio of the mean square end to end distance for the network subunits in the undeformed...
isotropic state to the corresponding
mean-square end-to-end distance for the
undeformed subunits in the absence of
crosslinks.

The last ratio is called "the front factor" and in most
practical application it is assumed as one.

The above-mentioned equation does not apply in the case of
hydrogels, where the crosslinks were introduced in the presence of
solvent. In that case a similar expression has been developed by
Sillman and Merrill (394).

\[
\tau = RT \frac{Q^{2/3}}{M_c} \left(1 - \frac{2M_c}{M_n} \frac{r_i^2}{r_o^2}(a - \frac{1}{a^2})\right) \quad (1-4)
\]

where \( Q \) is the swelling ratio as defined earlier.

E. THEORY OF CRYSTALLIZATION OF HYDROGELS

Crystallization of many polar polymers is associated with
strong kinetic hindrances and production of microscopic crystalline
phase in the form of spherulites or single crystals is practically im-
possible. The usual method of crystallization of difficult to solu-
bilize polymers, consists of crystallizing them in the presence of a
plasticizer, which is a poor solvent for the given polymer.
Although PVA is soluble in hot water, its resistance to water can be improved by heat treatment. This happens due to the formation of crystallites that do not dissolve in water. The crystallites are generally shorter than the polymer molecules and a single molecule may pass through several crystallites separated by amorphous regions.

The state of an unoriented semicrystalline polymer is defined by the degree of crystallinity (x) and the average dimension of the crystallite (length ξ).

When a crosslinked polymer, like a PVA network produced via irradiation is heat-treated, the chains are aligned and they form oriented chain regions of higher density. These regions are the crystallites and they act as additional multifunctional in contradistinction to tetrafunctional cross-links produced by, for example, irradiation crosslinks redistributing the stress applied on the network between the crosslinks and the crystallites.

The formation of the crystallites in crosslinked polymers depends on the crosslinking density and an internal relation between the maximum crystallite length ξ and the corresponding to the average $M_c$ length, controls the formation of crystallites in the network.

Poly (vinyl alcohol) is a semi-crystalline polymer with melting point of 220°C (32, 267). It is usually about 20-35% crystalline, but with drawing or annealing above Tg, its crystallinity can increase up to 70%. The Tg is 85°C for dry PVA films, but it decreases significantly in the presence of water (294).
Single crystals of PVA were first formed by Tsubo and Mechizuki (434) by isothermal crystallization from the solution. The crystals belong the monoclinic system and the lamella thickness is around 100-150Å.

Packter and Nerurkar (295) have noticed spherulite growth when crystallizing PVA films from concentrated polyol solutions.

Crystallizability is a strong function of stereoregularity (139). According to the PVA model, proposed by Bunn (50) the atactic form of PVA is easily crystallizable, because the hydrogel group can easily substitute for the hydrogen group and there is no steric hindrance. Kenney and Willcockson (186) showed that within the range 100-180°C, crystallization proceeded in the order atactic > syndiotactic > isotactic.

The swelling phenomena of crystalline polymers are treated with the hypothesis that a crystalline region is not affected at all by the solvent and that this region plays the role of crosslink in a network of a polymer. As the volume of the non-crystalline region increases, the volume of the solid polymer as a whole also increases. Finally, the swelling equilibrium point is reached (350, 360). Sakurada (360) found that the swelling ratio is independent of degree of polymerization and temperature of heat treatment and that the crystallinity was not change through swelling.
In a gel formation, depending on the solvent nature and the crystallizability of polymer in it, both crystalline and amorphous PVA gels are formed. The gelation is clearly related to tacticity (127) and it is apparently associated with the formation of some order with intermolecular forces, probably hydrogen bonding. From the calculation of $\Delta H$ (229), the number of hydrogen bonds involved can be calculated.

**Methods of Evaluation of Crystalline and Thermal Properties of PVA**

The methods of evaluation of crystallinity are based on the estimation of the arithmetic values of certain properties that vary due to the existence of amorphous (non-crystalline) and crystalline phases. These arithmetic values can be generally expressed with the additivity principle, so that the corresponding values of the 100% amorphous materials can be calculated. These methods include:

(i) Density measurements: Using the principle of additivity of volumes and the densities of the fully crystalline and amorphous PVA reported as 1.345 gr/cm$^3$ and 1.269 gr/cm$^3$ respectively by Sakurada et al. (357), the degree of crystallinity can be calculated. The method is accurate (401) provided that no bubbles or voids exist in the hydrogel (415).

(ii) Calorimetric methods: They include differential thermal analysis (DTA) and differential scanning calorimetry (DSC). By an indirect method, the heat of crystallization is compared to the heat of crystallization of 100% crystalline PVA and the degree of crystallinity is reported. The heat
of crystallization of a semi-crystalline PVA hydrogel is a function of its heat-history and can be calculated from a relation developed by Flory (104).

(iii) Spectroscopic Methods: The intensity of the peak at 1141 cm\(^{-1}\) of the infrared spectrum of PVA is dependent upon the crystallinity of the sample tested (204). Krimm suggested (204) that this band is associated with the \(\nu(CO)\) mode of a portion of a chain, where an intramolecular hydrogen bond is formed between two neighboring OH groups that are on the same side of the plane of the carbon chain.

(iv) X-rays analysis: Sakurada \textit{et al.} (350) developed a method of measurement of diffracted x-ray beam by a Geiger counter, by medium of which he was able to calculate the crystallinity of PVA fibers and films. In the case of swollen PVA films the quantitative analysis is somewhat more complicated, because of the existence of the pattern of water (357).

(v) Other methods: They include acoustical methods as the pulse-echo-overlap method (296), NMR analysis (396), etc.

F. MECHANICAL BEHAVIOR OF HIGH POLYMERS

The behavior of polymeric materials upon application of transient or steady mechanical stresses depends on the internal structure of the material, the orientation and the crosslinking and on the temperature of test relative to \(T_g\) or \(T_m\).
Among the different tests used, the tensile strength tests provide information about the strength and the maximum elongation of a material, as well as its modulus of elasticity which is a measure of its rigidity and hardness. The creep experiments provide information on the extension and the time of rupture of specimens subjected to constant tensile load. The tear propagation experiments refer to the force necessary to propagate a tear in plastic films, especially in cases of practical application under shear stresses.

Reinforcement of weak polymeric material for improvement of their mechanical properties, can be achieved by different methods including introduction of crystallites, crosslinks or inert fillers.

In general, increasing degree of crystallinity increases the tensile strength, the initial modulus, the hardness and the density whereas it decreases the extensibility, the flexibility and the toughness.

Crosslinking effects the elongation at break, because of the restrictions in extensibility. Closely related is also the stress at break. However, depending on the orientation and the contribution of crosslinks, crystalline and amorphous regions on the final structure of the polymer, the stress at break can be higher or lower than that of an uncrosslinked polymer.
The mechanical properties of PVA film and hydrogels have not been studied by many authors. The effect of crosslinking (3, 162) and crystallinity (32) on the modulus of elasticity and ultimate tensile strength of PVA films has been studied and found to be as predicted from the previous discussion.

G. EXPERIMENTAL WORK

The experimental work described here includes the crosslinking process in respect to concentrated acqueous solution of PVA, the crystallization process as affected by condition of temperature and rate of water removal and the evaluation of the mechanical properties of the materials, with particular emphasis on additional mechanical reinforcement produced by crystallization after crosslinking.

Preparation and Supermolecular Order of PVA Solution

The PVA used in this thesis was supplied by duPont de Nemours (91) and it was Elvanol Grade 73-125G. The number average degree of polymerization was \( \bar{DP}_n = 2020 \) and the number average molecular weight \( \bar{M}_n = 88,880 \). It had less than 1% glycol groups and was above 70% atactic. Since the degree of hydrolysis was higher than 99.3% all samples were prepared by dissolving PVA in water at 90°C for six hours. Premeasured portions of PVA were placed in culture dishes, they were degassed, distilled water was added, they were covered and put in an
oven. Concentrations of 5, 10 and 15% at PVA were prepared in this way.

A freezing-thawing process of the initial PVA solution has been undertaken for the prevention of bubbles formation during irradiation. The supermolecular structures produced during this process were studied by preparing solutions of 2.5, 5, 10, 15% wt. PVA and testing their turbidimetric properties. Five ml cylindrical cells of a Colemen II Spectrophotometer-Model 6/35 were filled with different concentration of PVA solutions and they were frozen at \(-20^\circ\text{C}\) for 45, 60, 75, 105, 120 minutes. After the freezing process they were thawed for long periods of time at \(23 \pm 1^\circ\text{C}\). During this thawing process the cells were placed in the spectrophotometer and the transmittance of visible light was recorded as a function of thawing time. Wavelengths used were \(5000-8000 \text{ Å}\). Processing of the data and determination of the parameters of the supermolecular particles in the polymer solution was done with the theory developed by Klenin et al. (191).

Crosslinking of Aqueous Solutions of PVA Via Irradiation.

1. For electron beam irradiation a Van de Graaff accelerator was used. The accelerator delivered 3 Mev electrons and the dose rate was between 89,000 and 222,000 rads/sec. depending on the position of the samples irradiated.
PVA solutions of 10% and 15% concentration, prepared under nitrogen atmosphere, were frozen at -20°C for 60 minutes and then they were thawed at room temperature of 23 ± 2°C for 6 hours. These samples were irradiated at 0 and 30°C (by immersion either in an ice bath or in a preheated glycerol-water bath). The radiation doses were 5 and 10 Mgrads, sometimes also 3, 8, 13 and 15 Mgrads.

2. For the effect of dose rate, using electron beam irradiation, a series of irradiations of 10%, PVA solution irradiated at 30°C with 3 Mgrads were performed. The dose rate varied between 413-4130 rads/sec.

3. For γ-irradiation, a Cobalt -60 source delivering 3600 rads/minute was used. The samples were prepared in small tubings of 13 x 100 mm, which were sealed in atmosphere or under vacuum. They were irradiated at 0º or 30ºC in an ice or glycerol-water bath placed in the radiation chamber of dimension 22" x 17" x 7" which could be immersed 12 feet under water, where the two Cobalt -60 bars were located.

4. Determination of the molecular weight between cross-links \( M_c \) via swelling experiments is done by allowing the already prepared samples to equilibrate in water at 30°C for long periods of time, till they reach constant weight at constant temperature.
For the calculation of $M_c$ by the method developed by Bray and Merrill (42), information on the volume fraction of polymer in the relaxed state (immediately after irradiation) $\nu_{2,r}$ and the volume fraction after the sample was swollen in water at 30°C, $\nu_{2,s}$ (See equation 1-2).

Volume fractions were calculated by determining the relaxed and swollen volumes by weighing the samples in air and in distilled water. From these experiments the following values can be obtained:

(i) the relaxed volume fraction of polymer

$$\nu_{2,r} = \frac{v_p}{v_r} \quad (1-5)$$

(ii) the swollen volume fraction of polymer

$$\nu_{2,s} = \frac{v_p}{v_s} \quad (1-6)$$

(iii) the weight percentage of PVA in the swollen hydrogel $w_{PVA}$

(iv) the swelling ratio (weight) $q.q = \frac{1}{w_{PVA}} \quad (1-7)$

(v) the swelling ratio (volume) $Q = \frac{1}{\nu_{2,s}} \quad (1-8)$

Determination of the swelling properties at different temperatures can be done by placing the gels in water at different temperatures.
Determination of the Elastic Behavior of the Hydrogels

PVA hydrogels prepared by irradiation of 10 and 15% PVA solutions at 0°C and 30°C with 3, 5, 8, 10, 15 Mgrads, in cultured dishes of dimensions 150 x 20 mm., were used for determination of the mechanical properties after swelling at 30°C.

Crystallization Procedure

The crystallization procedure was done in a two-stage procedure:

(1) The dehydration stage was done by drying the samples immediately after radiation in a dust free environment, by a slow drying rate process at 23 ± 2°C and relative humidity 40% for 24 hours. Other experiments with the intention of revealing the effect of dehydration condition on the crystallinity of the samples were done by drying samples of M_c 5715 and 4770 at 25 ± 1°C using the following drying media SiO_2, Ca(NO_3)_2, MgCl_2, KB_r, and K_2Cr_2O_7.

(2) The annealing stage followed the previous stage. After dehydration the samples were placed in an oven at temperatures of 90, 105, 120 and 135% for 30-120 minutes. Other samples were placed in the oven at
165, 175, 185 and 195°C for significantly shorter periods of time.

With this procedure the whole process of crystallization has occurred. Figure 8-4 shows the complete process.

Evaluation of Crystallinity of Heat-treated Films

(1) Swelling experiments lead to calculation of the polymer volume fraction, the swelling ratio and the water percentage in the hydrogel, parameters which depend on the degree of crystallinity. The swelling experiments were done at 30°C and they were reported earlier.

(2) Evaluation via density measurements was done by weighing the already swollen PVA hydrogels, in air and water at 30°C. This way the density of the hydrogels \( \rho_n \) was obtained. Then the samples were placed in a vacuum desiccator and dried for 48 hours at 100°C. This way the degree of crystallinity could be calculated as:

\[
\frac{1}{\rho_n} = w_{PVA} \left( \frac{x}{\rho_c} + \frac{1-x}{\rho_{\alpha}} \right) + \frac{1-w_{PVA}}{\rho_w} \quad (1-9)
\]
where

\[ \rho_h \] = density of the swollen hydrogel after crystallization
\[ \rho_a \] = density of 100% amorphous PVA = 1.269 gr/cm³
\[ \rho_c \] = density of 100% crystalline PVA = 1.345 gr/cm³
\[ \rho_w \] = density of water at 30°C = 0.996 gr/cm³
\[ w_{PVA} \] = percentage of PVA in swollen hydrogel
\[ x \] = crystallinity (%) defined as the ratio of crystalline PVA to the total PVA (weight)

(3) Differential scanning calorimetry was used to calculate the heat of fusion of PVA hydrogels and, via this, the degree of crystallinity. The instrument used was a Perkin-Elmer Differential Scanning Calorimeter DSC-1, with a programmer permitting the linear increase of the temperature. The hydrogel to be analyzed was cut with a round die of internal diameter 6 mm. (weight of sample between 8 and 15 mgs), it was placed in the pan, covered with an aluminum dish and pressed in the sample pan crimper. The pellet was placed on the right-hand sample holder, while an empty pan was placed on the left-hand sample holder. The low-temperature cover was placed on top and liquid nitrogen was used for the cooling process. The thermogram was recorded from -100°C to +250°C with scanning speed 5°C/min.
The instrument was calibrated with indium. The area under the peak expressed as calories/mole was the heat of fusion \( \Delta H^\circ \) of the particular sample.

The heat of fusion \( \Delta H_u \) of 100\% crystalline sample was calculated using Flory's (104) equation:

\[
\frac{(\frac{1}{T_m} - \frac{1}{T_m^0})}{v_u} = \frac{R V_u}{\Delta H_u V_1} \left(1 - \frac{B V_1 u_1}{R T_m} \right) \tag{1-10}
\]

where

\( V_u \) is the molar volume of the polymer repeat unit

\( v_1 \) is the molar volume of the solvent

\( u_1 \) is the solvent volume fraction

\( B \) is the interaction energy between polymer and solvent

\( T_m^0 \) is the melting point of the polymer

\( T_m \) is the melting point of the polymer in the presence of diluent.

Plot of \( \frac{(\frac{1}{T_m} - \frac{1}{T_m^0})}{v_u} \) versus \( u_1/T_m \) gave straight lines from which \( \Delta H_u \) was calculated.

Then the crystallinity could be calculated as

\[
x = \frac{\Delta H^\ast}{\Delta H_u} \tag{1-11}
\]
(4) IR Spectroscopy: Microscope slides 3 x 1 inch were treated with a 1% siliclad solution and drops of 10% or 15% PVA solutions were placed on one of them and another microscope slide was put on top, separated at the ends by two small square glasses 20 mil thick. Film casted in this way were irradiated at 3, 5, and 10 Mgrads at 0°C and 30°C, using the same technique as before.

The intensity of the 1141 cm⁻¹ band was recorded using a Perkin Elmer 237 IR spectrophotometer. By determination of the baseline a linear relationship between the crystallinity and the peak intensities of the above mentioned band and the band at 1425 cm⁻¹ (d and c respectively) was established

\[ x(\%) = A' \left( \frac{d}{c} \right) - B' \]  

(1-12)

where A' and B' are constants.

**Tensile Experiments**

PVA hydrogels prepared in 150 x 20 mm culture dishes, crosslinked by electron beam irradiation, crystallized at different temperatures and swollen at 30°C, were tested on a Table Model Instron in distilled water at 30°C using an extension rate of 1"/min. The samples were stretched to break, and the initial modulus, the
elongation at break and the ultimate tensile strength were determined.

**Creep Experiments**

PVA hydrogels prepared, crosslinked, crystallized and swollen as previously, were subjected to creep experiments using load of 500-1000gms in cylinders filled with water and kept at 70°C for prevention of drying out of the samples.

The samples were cut using a dumbbell shape die, the load was applied and the elongation was recorded as a function of time up to 30 hours, when the load was removed and the recovery was studied up to 15 hours.

The creep compliance, the permanent elongation after recovery and the exponent "n" of Nutting's equation were reported.

**Tear Strength Experiments**

The force necessary to propagate a tear in plastic-films was studied by testing 3 x 1 in specimens cut from the previously prepared swollen crystallized PVA hydrogels. These specimens had a 2 in longitudinal slit so that the one tongue of the specimen could be fixed on one grip and the other on the other. The grip separation rate used was 1 in/min. The load was recorded as a function of time and reported per mil of the thickness.
H. RESULTS AND DISCUSSION

Electron-beam Radiation Effects on PVA Solutions

The crosslinking density (expressed as $M_c$, molecular weight between crosslinks), of PVA hydrogels was studied by irradiating PVA solutions of concentrations 5-20% at 0°C and 30°C by delivering doses of 3-15 Mrads. The purpose of this part of the thesis was to increase the reliability of data reported by Bray, in view of some modifications in the method of irradiation, the thickness of the films and the absence of visible bubbles after the irradiation. The method used for the evaluation of $M_c$ is via the relation developed by Bray and Merrill (43)(See Eq. 1-2)

Figure 9-7 shows a typical plot of $M_c$ as a function of dose delivered for different concentrations of initial solutions. As the dose increases the crosslinking density increases. By plotting

$\rho( = \frac{M_n}{M_c})$ versus the dose delivered, a linear relationship can be obtained as shown in Figure 9-12.

$M_c$ is a function of temperature and concentration of irradiation and it decreases with decreasing concentration of initial solution and temperature.

Hydrogels with $M_c$ between 3500 and 6000 are considered moderately crosslinked and can be used for further applications.
For purposes of prevention of formation of bubbles during irradiation a freezing-thawing process has been undertaken. Determination of the size of the supermolecular particles has been done using Klenina's method (191). The size depends on the initial concentration and the freezing time and it is a function of the thawing time. A typical diagram of the variation of the average radius of the particles \( \bar{r}_w \) is shown in Figure 9-5. The particles have sizes between 1.8 - 2.2 \( \mu \). The size of the supermolecular particles increased with thawing time, showing gelling of the particles but as the thawing treatment continued, the average radius was reduced, showing a breakdown of previously swollen particles. The formation of PVA gels may be accompanied by a partial crystallization of the polymer, which also explains the progressive clouding of the gel.

\( M_c \) is a function of the depth of irradiation, and Figure 9-14 shows the variation of \( M_c \) with thickness of sample as well as with distance from the "center" of the irradiating unit.

It is now clear the the formation of gas bubbles is a diffusion rate limited phenomenon, depending mainly on the diffusion coefficient of hydrogen through viscous PVA solutions. During irradiation of pre-treated gelled PVA samples, gas bubbles are not formed, prevented by the immobility and the solid-like state of the material.

The effect of dose rate of electron beam irradiation or cross-linking has been studied. Dose rate from 400-80,000 rads/sec. was studied.
TABLE 1-1

CONDITIONS OF IRRADIATION OF PVA SAMPLES AND CROSSLINKING PARAMETERS.

<table>
<thead>
<tr>
<th>Condition of Irradiation</th>
<th>C_c (%)</th>
<th>T_c (°C)</th>
<th>D_c (Mgrads)</th>
<th>M_c</th>
<th>ρ</th>
<th>u</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0</td>
<td>3</td>
<td></td>
<td>7650</td>
<td>11.6</td>
<td>174</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>5</td>
<td></td>
<td>3765</td>
<td>23.6</td>
<td>86</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>10</td>
<td></td>
<td>1495</td>
<td>59.4</td>
<td>34</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>3</td>
<td></td>
<td>9370</td>
<td>9.5</td>
<td>213</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>5</td>
<td></td>
<td>4770</td>
<td>18.6</td>
<td>108</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>10</td>
<td></td>
<td>1395</td>
<td>63.7</td>
<td>32</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>3</td>
<td></td>
<td>8420</td>
<td>10.6</td>
<td>191</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>5</td>
<td></td>
<td>3960</td>
<td>22.4</td>
<td>90</td>
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<td>10</td>
<td></td>
<td>1790</td>
<td>49.6</td>
<td>41</td>
</tr>
<tr>
<td>15</td>
<td>30</td>
<td>3</td>
<td></td>
<td>9850</td>
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<td>224</td>
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<td>5</td>
<td></td>
<td>5715</td>
<td>15.5</td>
<td>130</td>
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<td>15</td>
<td>30</td>
<td>10</td>
<td></td>
<td>2190</td>
<td>40.6</td>
<td>50</td>
</tr>
</tbody>
</table>
Because of the slow rate, the hydrogen molecules diffuse out without forming bubbles by supersaturation and nucleation. At the same time the crosslinking density increases. This can be explained by reference to the direct effect at radiation on PVA which is predominant only at high dose rates, producing shorter chains and thus favoring degradation.

In any way the variation of the crosslinking density with dose rate is not that important, considering other significant parameters affecting the radiation phenomenon.

**Gamma-Radiation Effects on PVA Solution**

Gamma radiation was proposed as an alternative to electron beams for solving the problem of bubble formation and for achieving a higher crosslinking density.

The effect of \( \gamma \)-radiation was studied only to samples irradiated *in vacuo* or under nitrogen because in the presence of oxygen which continuously diffuses through the solution, degradation predominates.

The crosslinking density is almost double in some cases, than the corresponding one of the electron-beam irradiated samples.

Gamma-irradiation is thus preferred for more crosslinked materials, but technical difficulties (relatively small radiation chambers) as well as very long time of irradiation are the disadvantages of the method. Electron-beam irradiation was the principal mode used in this thesis, principally because of the short time doses
that could be delivered.

Evaluation of $M_C$ from Tensile Measurements

The mechanical properties have been studied on selected, electron beam radiation crosslinked swollen uncrystallized PVA hydrogels. Table 1-2 includes the properties studied for different samples. The modulus, the UTS and the elongation at break are functions of $M_C$. The initial modulus, characterizing the rigidity of the hydrogel, increases linearly with the crosslinking density as shown in Figure 9-22.

Even with 100 crosslinks per chain, the crosslinking is not very dense so that the applied stress is equally distributed among the crosslinks.

UTS is higher for higher degrees of crosslinking $\rho$, whereas the elongation at break decreases.

Using the tensile data of the previous experiments, an $M_C$ can be calculated and compared to the $M_C$ from swelling experiments (referred in Table 1-2).

The relation used for this calculation is:

$$
\tau = RT \frac{e^{2i}}{M_C} \cdot \frac{1}{Q^{1/3}} \left(1 - \frac{2M_C}{M_n}(\alpha - \frac{1}{\alpha^2})\right) \quad (1-13)
$$
TABLE 1-2

TENSILE DATA FOR UNCRYSTALLIZED PVA HYDROGELS

<table>
<thead>
<tr>
<th>Radiation Conditions</th>
<th>Initial Mod</th>
<th>UTS (psi)</th>
<th>Elong. break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C_c (%)</td>
<td>T(°C)</td>
<td>D_c (Mgrads)</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>3</td>
<td>7650</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>5</td>
<td>3765</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>8</td>
<td>1990</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>10</td>
<td>1495</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>15</td>
<td>950</td>
</tr>
</tbody>
</table>
where

\[ \tau \quad \text{is the tensile stress} \]

\[ c_{2,i} = \frac{u_{2,i}}{V} = \frac{\text{volume fraction of polymer in relaxed state}}{\text{molar volume of polymer}} \]

\[ Q \quad \text{volumetric swelling ratio} \]

\[ \alpha = \frac{\lambda}{\lambda_0} \]

The tensile stress is directly proportional to the extension term \( \alpha - \frac{1}{\alpha^2} \) and from plots of the \( \tau \) versus \( \alpha - \frac{1}{\alpha^2} \), \( M_c \) can be calculated in an independent way. The experimental points of five tested samples (previously mentioned in Table 1-3) fit on straight lines, as shown in Figure 9-27. \( M_c \) is calculated in this way and it is found to be two to three times higher than the one calculated from swelling experiments, for the same samples. The thermodynamic swelling experiments possibly give more reliable results of \( M_c \) than the tensile experiments, because in the latter case, entanglements and other defects of the chains affect the mechanical properties, the stress and finally the calculated values of \( M_c \). On the other hand, the Flory \( \chi \) factor, necessary to interpret the swelling experiments, is recognized to be in fact a variable determinable with poor precision. As Flory notes (104) agreement within a factor of 2 is good in view of postulates necessary made. Oversimplified treatment of the network structure is thus recognized. The differences of \( M_c \) will be greater at lower degrees of crosslinking, where entanglements and other restraints are predominant.
Dehydration Experiments

During dehydration, most of the water of the hydrogels is removed by slow rate evaporation. Dehydration experiments have been performed, to show the effect of drying rate on the crystallization. The effects of relative humidity and temperature of drying have been studied. As is obvious, expected lower relative humidity and higher temperature increased the drying rate. The degree of crystallinity has been calculated to a function of time for different drying media, as shown in Figure 9-39. There is an induction time of crystallization \( t \) of 10-118 hours depending on the drying rate.

The initiation of crystallization is a function of water percent in the polymer and this can be seen in Figure 9-40, where crystallinity is introduced only when the film tested have above 77-84% PVA.

Thus a short 24-hours dehydration at room temperature (25-30°C) does not introduce any crystallites and the main procedure of crystallization is the annealing stage at temperatures higher than 90°C.

Annealing Experiments

The polymer concentration in hydrogels, after reswelling in water, as a function of annealing conditions, has great practical value in the case of biomedical applications. Since water does not enter the crystalline regions, the grossly observed polymer weight percent is an
approximate means of judging for the variation of crystallinity as a function of annealing condition.

Very high degrees of crosslinking do not favor crystallinity because a critical minimum length is necessary for a crystalline to form. Thus very low values of equilibrium polymer percent and degrees of crystallinity are reported for $\rho > 40$. The variation of these two terms with $\rho$ is shown in Figures 9-43 and 9-59. In both cases the curves reach a maximum and then as $\rho$ decreases crystallinity decreases too. This somewhat puzzling phenomenon can be explained, considering that the crosslinks act to protect and maintain the crystalline regions, so that, if $\rho$ gets very low, the crystallites will be dissolved and the crystallinity will be lower.

The crystallites formed by these annealing processes dissolve at higher temperatures as it can be seen by the change of the water percent of swollen hydrogels as the swelling temperature increases (see Figure 9-48). The "limits" of the melting region of the crystallites are functions of the crosslinking density, i.e., the size of the crystallites. For practical purpose and especially in uses in the body, the swelling temperature of 37ºC does not change significantly the physical and mechanical properties. However, heat sterilization and reactions at high temperatures cannot be performed.

The degree of crystallinity varies with the temperature and time of annealing. A typical plot of the degree of crystallinity as a function of these two parameters is shown in Figure 9-57.
Differential Scanning Calorimetry

Using DSC, different samples of PVA hydrogels were studied. The melting points of PVA as a function of crosslinking density were studied and Figure 9-60 shown the variation of the melting point depression with crosslinking density.

From the thermograms obtained, plots of $(\frac{1}{T_m} - \frac{1}{T_o})/u_2$ versus $u_1/T_m$ give a straight line as shown in Figure 9-64. From this figure $\Delta H_u$ is calculated using Equation (1-10) as 1.05 kcal/mole which is in reasonable agreement with values reported by other investigators (101).

During the evaluation of DSC data as well as swelling data a serious problem is faced in calculating the $\chi$ factor. For this purpose the $\chi$ factor of PVA-$H_2O$ systems was studied via swelling experiments on noncrystallized samples. Figure 9-67 shows the variation of $\chi$ factor with $u_2$. This value at 30°C in the range of $u_2 = 0.04 - 0.14$ varies between 0.475 - 0.495 versus the value of 0.494 used in all the calculations.

Calculation of the degree of crystallinity of different samples from the DSC-data was done by evaluation of the heat fusion $\Delta H^*$ of the individual samples and using equation (1-11). Table 1-3 includes some of the final results of crystallinity as compared to the degree of crystallinity from density measurements. The precision
<table>
<thead>
<tr>
<th>$M_c$</th>
<th>Annealing Condition</th>
<th>Crystallinity from DSC</th>
<th>Crystallinity from Density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T(\degree C)$</td>
<td>$t$(min)</td>
<td></td>
</tr>
<tr>
<td>3765</td>
<td>90</td>
<td>60</td>
<td>30.02</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>90</td>
<td>31.59</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>30</td>
<td>49.65</td>
</tr>
<tr>
<td>4770</td>
<td>90</td>
<td>30</td>
<td>35.61</td>
</tr>
<tr>
<td></td>
<td>105</td>
<td>60</td>
<td>46.80</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>30</td>
<td>50.12</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>90</td>
<td>71.10</td>
</tr>
<tr>
<td>3370</td>
<td>90</td>
<td>30</td>
<td>29.93</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>60</td>
<td>49.10</td>
</tr>
</tbody>
</table>
of ± 5% is satisfactory in most of the cases. The second method seems more reliable, since in DSC, false drawing of the baseline is always a problem and it can lead to certain errors.

**IR Spectroscopy**

Using the intensities of the peaks of the PVA-IR spectrum at 1141 cm⁻¹ and 1425 cm⁻¹ the following equation was derived for samples of $M_C = 4770$

\[
\text{Crystallinity } \% = 26.7 + 102.6 \left[ \frac{d}{c} - 0.36 \right] \tag{1-14}
\]

The arithmetic values of the crystallinities are surprisingly close. Some of the results were shown in Table 1-4. The difference is higher for higher crystallization, probably because of slight etherification, induced by high temperature annealing at long times, although these samples do not show any evidence of CO groups.

**Tensile Experiments**

The mechanical properties are a strong function of the crystalline regions of the hydrogels. Increase of the swelling temperature causes a significant change in the degree of crystallinity of the hydrogel and subsequent decrease of the arithmetic values of the mechanical properties, i.e., the initial modulus, the UTS and the elongation at break as shown in Fig. 9-71, 9-76 and 9-78. The shape of the curves of modulus versus temperature as well as the order of magnitude, clearly
TABLE 1-4

CRYSTALLINITY OF PVA HYDROGELS AS JUDGED FROM IR SPECTROSCOPY

<table>
<thead>
<tr>
<th>Annealing Conditions</th>
<th>Crystallinity from IR</th>
<th>Crystallinity from Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>T(°C)</td>
<td>t(min)</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>30</td>
<td>31.10</td>
</tr>
<tr>
<td>90</td>
<td>60</td>
<td>41.80</td>
</tr>
<tr>
<td>90</td>
<td>90</td>
<td>51.60</td>
</tr>
<tr>
<td>105</td>
<td>90</td>
<td>52.67</td>
</tr>
<tr>
<td>120</td>
<td>90</td>
<td>62.70</td>
</tr>
</tbody>
</table>
that some of the fine chemical viscoelastic regions can be recognized in the mechanical behavior of these materials (see Fig. 9-71).

Similar behavior is shown by the ultimate tensile strength and the elongation at break.

The results of tensile tests on crystallized PVA hydrogels show that the properties are functions of (i) annealing temperature (ii) annealing time (iii) crosslinking density (iv) percent PVA in initial solution. Some characteristic curves are shown in Figs. 9-80, 9-81 (modulus) 9-85, 9-86 (UTS) 9-91, 9-92 and 9-93 (elongation).

The initial modulus increases with increasing time and temperature of annealing, the values varying between 200 and 1500 psi, while the corresponding values of the noncrystalline materials are very low, i.e., between 5 and 25 psi. The ultimate tensile strength and the elongation at break show the same behavior. The values of UTS vary between 500 and 1500 psi, whereas the uncrystallized materials have UTS up to 40 psi. The elongation at break varies between 120% and 500%, whereas the uncrystallized materials do not elongate more than 100%.

Within the range of crystallization of 10-25%, the initial modulus is a linear relation of the crystalline PVA weight percent of the hydrogel, leveling off at higher percentages of crystallinity (Fig. 9-95).
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Within the range of crystallization of 10-25%, the initial modulus is a linear relation of the crystalline PVA weight percent of the hydrogel, leveling off at higher percentages of crystallinity (Fig. 9-95).
The effect of the crosslinking density $\rho$ on the mechanical properties is shown in Figs. 9-100, 9-101 and 9-102.

As it has been explained, a critical length of chain is needed before a crystallite can be formed, with larger crystallites arising from larger segments. As the crystallinity affects directly the mechanical properties, lower crosslinking densities should lead to higher moduli, UTS and elongations. However, when the stress gets sufficiently high and in the case of low crosslinking, the crystallites can be "melted out" and the mechanical properties are lower.

**Creep Experiments**

In Figure 9-103 the results of a typical creep experiment are shown, where the strain is plotted against time elapsed since the application of load. A region of instantaneous elongation is followed by a rapid rate of creep region and the constant rate of creep region. After 30 hours, the load is removed and the recovery process is studied.

The creep experiments were performed not under identical stress, but under identical force, this being unavoidable because of the thickness and the different buoyancy forces of the loads used, during the in-water creep experiments. Experiments on the permanent elongation after recovery showed that partial recrystallization is possible in the direction of relieving the stress.
Application of Nuttins equation (1-14)

\[ J = \psi t^\eta \]  \hspace{1cm} (1-14)

where \( J \) is the creep compliance, \( t \) is the time elapsed and \( \psi, \eta \) constants, lead to the exponent "n" which is a measure of the degree of crystallinity. Fig. 9-119 shows the variation of n on the annealing conditions and crosslinking density. The behavior of n is of the same trend as the crystallinity-crosslinking density curve (Fig. 9-59).

Tear Propagation Experiments

The load necessary to tear PVA film annealed at different temperatures is reported as a function of the different annealings parameters as well as the crosslinking density \( \rho \), and normalized as load per thickness, as is reported in Fig. 9-123. Increasing crystallinity increases the tear strength, because the crystallites act as additional crosslinks. For the same reason, increasing \( M_c \) favors the formation of the crystallites and the tear strength is higher. Typical values of tear strength are between 2 and 4 gram per inch thickness.

I. CONCLUSIONS

1. Poly (vinyl alcohol) solutions of wt concentration 10% and 15% were crosslinked via electron beam and \( \gamma \)-radiation under different radiation conditions and the effects of dose, dose rate,
oxygen and method used, on the crosslinking parameters were studied. The crosslinked materials (10-25 crosslinks per polymer unit) were swollen in water at 30°C and their mechanical properties tested. They showed initial moduli between 10-70 psi ultimate tensile strength 1-10 psi and elongation at break not more than 100%. These hydrogels had more than 85% water and they were rather "weak" inadequate for many practical applications.

2. Reinforcement of PVA hydrogels was done by induction of crystallinity by a two shape drying process (dehydration-annealing). The dehydration was done in air or different drying media at temperatures 25-45°C and did not increase significantly the degree of crystallinity. The annealing step was done by heating at temperatures of 90-200°C and periods of time between 5 minutes and 2 hours. The crystallized hydrogels had moduli up to 1500 psi, ultimate tensile strengths 2500 psi and elongations at break as high as 600%. The water content was 40-70% and the crystallinity varied widely between 30 and 65%, depending on the temperature-time history of the specimen.

The crystallites acted as additional crosslinks redistributing the stress equally among them and the physical and the mechanical properties were functions of the initial crosslinking density.

The materials are proposed to be used, after heparization, as potential nonthrombogenic biomaterials.
J. RECOMMENDATIONS

1. Study of the dynamic mechanical properties of crystallized and uncrystallized materials for purpose of detection of their behavior under repeated deformations.

2. Study of the heparinization reaction with special interest on the rate of heparinization on crystallized hydrogels.

3. Investigation of the *in vivo* and *in vitro* properties of heparinization PVA hydrogels.

4. Study of crosslinked copolymers of PVA with other polymers (less number of hydroxyl groups).
CHAPTER 2

INTRODUCTION

A. MOTIVATION AND PURPOSE

One of the most exciting and challenging fields of research is that of biomedical polymers. For the past 15-20 years, innumerable investigators have devoted their time and experience in designing, studying, and evaluating various complex biological materials, that could be used for substitution of human organs. A wide variety of mainly-polymeric materials has been studied and tested for uses either as simple artificial parts (heart valves, tendons, lenses, and vitreous fluid of eyes, etc.), as assist devices (sutures, artificial veins) or as more complex devices (such as artificial heart, artificial lungs, artificial kidneys, etc.) (46,234).

A wide range of biomedical polymers has been developed for solution of the many problems that arise from hemodialysis. This procedure, which is administered to most of the patients, who suffer from chronic renal failure, is accomplished by the diffusion of the patient's blood through certain well characterized polymeric membranes. It is with the cooperation of chemists, physicists, physicians, and engineers that the production of successful polymeric materials for use as membranes, veins, etc., has been achieved.

The foremost problem in the development of these materials is the absence of a successful blood-clotting biomaterial. For the past ten years the study has turned towards the development of biomaterials that will prevent blood coagulation, when blood comes in contact with them,
without the continuous administration of heparin solution, as it is a practice these days.

Many investigators under the direction of Prof. E.W. Merrill and Dr. P.S.L. Wong have been working in the Biomedical Engineering Laboratories of the Chemical Engineering Department at M.I.T., on the production of new non-thrombogenic biomaterials and many articles have already been published (45, 255, 256, 258, 259, 261, 262, 378, 379).

Among them, heparinized poly-(vinyl alcohol) hydrogels, from now on designated also as PVA hydrogels, have been proposed (256, 257, 259, 260, 261, 262). These hydrogels were prepared by crosslinking of PVA by a mixture of aldehydes via an acid-catalyzed acetal formation with the secondary hydroxyls on the polymer backbone, and by subsequent heparinization on the matrix by acetalization with the secondary hydroxyls of heparin.

An alternative method of production was proposed in this thesis. According to this method, crosslinking of PVA occurs via electron beam or gamma rays, followed by the reaction of heparinization. However, it has been recognized that poly-(vinyl alcohol) hydrogels have not been satisfactorily characterized, with reference to their chemical and mechanical properties.

It was the purpose of this Sc.D. thesis to study the development of a crosslinked PVA hydrogel substrate, to study its chemical and mechanical properties, to investigate modes of reinforcement of this hydrogel, and finally to deliver the biomaterial for heparinization and biomedical in vitro and in vivo tests.

B. NONTHROMBOGENIC POLYMERIC MATERIALS

The most serious problem that arises in devices used to transport
blood, as in hemodialysis units, "heart - lung machines" and cardiac assist devices (380), is that of thrombosis resulting from activation of the plasma protein clotting factors, and platelet aggregation. Activation of these processes of blood coagulation and the adhesion of platelets by "foreign" surfaces is not well understood. As a consequence the selection and the development of nonthrombogenic biomaterials has been largely empirical (217).

**Blood Coagulation**

In order to understand the way nonthrombogenic biomaterials function, it is necessary to present some general information on the mechanism of blood coagulation. However it is not the author's purpose to go into these subjects in any great deal. They have been very well presented in critical reviews (98, 306, 376, 377, 383, 384, 464) to which the reader should refer for further information.

Blood clotting can be initiated by two separate ways:

1) by the extrinsic mechanism in which an extract from the damaged tissue is mixed with the blood;

2) by the intrinsic mechanism in which the blood itself is traumatized.

It is now well established that the production and growth of thrombi depends on the surface conditions and the flow over the surface. However, at the present time, the knowledge of the exact conditions under which these thrombi are formed and the parameters that control their formation is obscure (304).
It is primarily the intrinsic mechanism that is responsible for the coagulation of blood that has been placed on a "foreign" surface (vessel, container) after removal from the body. It is a fact that non-wettability (siliconized walls) favors the thrombo-resistance of a material and coagulation can be delayed as long as one hour or more (36, 376) otherwise, clotting starts after five minutes.

A short description of the mechanism of intrinsic and extrinsic systems of blood clotting, illustrating the different factors that are involved in these two systems, is shown in Figure 2-1, as taken from (98). A full explanation of the clotting factors that are necessary for the explanation of these mechanisms is shown in Table 2-1.

Some investigators have noticed (168) that the primary stage of hemostasis (prevention of blood loss) is the formation of an enzyme-acceptor complex, which is an effective intermediate in platelet-collagen adhesion and is used for further studies of this step.

In the case of the intrinsic mechanism, and as shown in Figure 2-2, factor X is activated to form Xa, via a series of activations of other factors, and it excites factor II to become IIa. This is the step of prothrombin to thrombin formation (194). Thrombin acts on the platelets that become activated and they agglutinate to form the white thrombus. Thrombin also activates fibrinogen (I), converting it to fibrin (Iₐ), which finally makes the crosslinked form of fibrin network (Iₐ). The last agglomeration is known as a red thrombus (98).

Thus, it is obvious that platelets play an integral part in thrombus
Extrinsic System

- Tissue Damage
  - Tissue Factor + Factor VII
  - Factor X
  - Factor V
  - Phospholipid
  - Calcium

Intrinsic System

- Surface contact
  - Factor XII
  - Factor XI
  - Factor IX
  - Factor VIII
  - Factor X
  - Factor V
  - Phospholipid
  - Calcium

Platelet changes

Thrombin

Fig. 2-1: The factors concerned with the activation of Factor II following surface contact and tissue damage.
### TABLE 2-1: THE BLOOD COAGULATION FACTORS AND SOME OF THEIR PROPERTIES

<table>
<thead>
<tr>
<th>Roman Numerals</th>
<th>Common Synonyms</th>
<th>Molecular Weight</th>
<th>Concentration (mg/100ml)</th>
<th>Derivative</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Fibrinogen</td>
<td>340,000</td>
<td>200 - 600</td>
<td>Fibrin monomer, Fibrin polymer</td>
</tr>
<tr>
<td>II</td>
<td>Prothrombin</td>
<td>69,000</td>
<td>10 - 15</td>
<td>IIα, thrombin</td>
</tr>
<tr>
<td>V</td>
<td>Ac-globulin, labile factor</td>
<td>290,000</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>VII</td>
<td>Proconvertin, autoprothrombin I</td>
<td>35,000</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>VIII</td>
<td>Antihemophilic globulin</td>
<td>400,000</td>
<td>0.012</td>
<td></td>
</tr>
<tr>
<td>IX</td>
<td>Christmas factor, autoprothrombin II</td>
<td>50,000</td>
<td>----</td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>Stuart factor, autoprothrombin III</td>
<td>86,000</td>
<td>1.2</td>
<td>Xα, thrombokinase</td>
</tr>
<tr>
<td>XI</td>
<td>P.T.A.</td>
<td>200,000</td>
<td>----</td>
<td></td>
</tr>
<tr>
<td>XII</td>
<td>Hageman factor</td>
<td>20,000</td>
<td>1.2</td>
<td>XIIα</td>
</tr>
<tr>
<td>XIII</td>
<td>Fibrin stabilizing factor, fibrinase</td>
<td>350,000</td>
<td>0.7</td>
<td>XIIIα</td>
</tr>
</tbody>
</table>
Fig. 2-2: A scheme of the interaction of clotting factors. The subscript indicates the activated form or product.

$\text{II}_a = \text{thrombin}; \, \text{I}_a = \text{fibrin}; \, \text{I}_b = \text{stabilized fibrin}$

Transformation; --- Enzymic action;

.....Cofactor action
formation (290). The thrombus formation on foreign surfaces has been studied by many people as a fluid mechanics problem (304), with some interesting results. However, extensive study is necessary.

The role of heparin

Among the many anticoagulant drugs used to prevent coagulation, heparin has been widely used with good results.

Heparin is a polysaccharide with molecular weight between 8,000 - 15,000. Its chemical structure is shown in Fig. 2-3. Its anticoagulant action is a direct result of the fact that it combines with a wide variety of proteins because of strong electrostatic charges (81). With respect to the repeating tetramer of heparin, each carbon-3 (four in total) and one carbon-2 carries a secondary hydroxyl. It is because of this hydroxyl that heparin can be covalently attached to synthetic polymeric surfaces, as it will be discussed later (23,219).

As it is shown in Fig. 2-4, when thrombin (I,IIα) is produced, naturally circulating antithrombin (A) reacts with it and produces the complex (AT), which is inactive as to the conversion of fibrinogen to fibrin. However, when heparin (H) is added to blood, it complexes with antithrombin (A) to form the complex (HA). This complex reacts with thrombin and it forms the inactive complex (HAT) (306, 464). The distribution of heparin along the plasma proteins has been well studied (309) and the identification of the plasma cofactor responsible for the antithrombogenic activity of heparin has been done. The rate of
**HEPARIN TETRAMER**

![Chemical structure of heparin tetramer](image)

Fig. 2-3: Chemical structure of heparin tetramer
Fig. 2-4: Effect of heparin on the blood clotting mechanism
complex HAT is 30 times faster than the rate of formation of HA. Thus when heparin is added to blood, it blocks the formation of fibrin or platelet thrombi and it maintains the blood fluid, so that it can be pumped through extracorporeal devices (169) (see Fig. 2-5). In practice, intravenous heparin may be administered by continuous infusion or by intermittent injection (474). A steady blood concentration is best achieved by a continuous infusion following a loading dose (290). After a large intravenous dose as much as 50% may be excreted unmetabolized in the urine.

However, long administration of heparin to a patient can produce severe effects. These include:

a) Hematoma: slow and variable absorption of heparin from subcutaneous and intramuscular sites can lead to hematoma formation (290).

b) Osteoporosis

c) Derangement of metabolism of calcium and lipids.

These are the chronic disadvantages of heparin administration.

Current evidence suggests that the problem can be partially overcome if heparin is covalently bound on the foreign surface (substrate). It is not clear, however, that heparin, when bound to a surface, has the same biological/biochemical action as it does in free solution. It is also a fact that heparinized surfaces rapidly become coated with protein layers when brought into contact with blood in vivo. The protein layer may in fact be the ultimate "non-thrombogenic" surface.
Fig. 2-5: Surface contact of blood and action of heparin
C. CRITERIA FOR DEVELOPMENT OF BIOMATERIALS

Considerable empirical information is available on the use and application of many polymeric materials. \textit{In vitro} and \textit{in vivo} tests and their results have been reported, but it is quite difficult to translate them into some basic characteristics that a candidate - biomaterial should have. Thus, the biomaterial researcher is faced with a dilemma of trying to design a material, having little idea about the properties that it should have.

Certain authors in successful critical reviews (223,376) have proposed some guidelines for the evaluation of potential biomaterials. A compilation of information from the above mentioned and other reviews (234,410) leads to the following characteristics that a potential biomaterial should have:

1. Chemical and Mechanical Requirements

They should be:

i) Free from elutable impurities, additives, catalyst residues, emulsifiers, etc., from the initial polymerization reaction. These can give rise to toxicity, other biological reactions, and artifacts in blood coagulation testing. For example, it is now recognized that the phthalate ester plasticizers used in polyvinyl chloride blood bags can accumulate in the contained blood to a potentially harmful level.

ii) Chemically inert (e.g., not subjected to slow hydrolytic cleavage).
iii) One with reasonably good mechanical properties: The proper design of a device or part made of a polymer, must take into account the individual characteristics of the polymer. Failure of prostheses often results from lack of basic information about the polymer and the physiological environment (223). Some parameters to be considered include the geometry of the part, the type of stresses, the environment in which the part will be exposed, and different processing variables. In conclusion, the elastic properties of the biomaterial, its behavior in tensile and compressive stresses, its tear properties, and its fatigue resistance are the properties of concern (317).

iv) Processable: It must be easily casted or molded in films, rods, tubings, etc. Also, it must be processable without being degraded or adversely changed.

2. Biological Requirements (46,48,223)

They should be:

i) Non toxic

ii) Non carcinogenic

iii) Sterilizable, without any change in properties or form. The problem of sterilization of biomaterials still remains, despite the many methods tested (47,223).

iv) Non biodegradable: generally speaking, its physical, chemical and mechanical properties should not be altered by the biological environment; specifically, naturally circulating enzymes should
not interfere with the material.

v) A material that does not induce inflammatory reactions when in contact with tissue.

3. Hematological Requirements:

They should not cause:

i) Thrombosis

ii) Alteration of the stability of any soluble or cellular materials in the blood (RBC, WBC, platelets, albumin, globulin, fibrinogen, etc.), that would lead to allergic, toxic, aging, or cell fragility reactions.

Unfortunately, the problem still remains, because the proposed biomaterials do not fulfill the above mentioned characteristics. This is the reason that a wide variety of nonthrombogenic biomaterials has been proposed.
D. CURRENT RESEARCH ON NONTHROMBOGENIC MATERIALS

As already mentioned, the development of nonthrombogenic biomaterials has for the most part been empirical or based on unproven theoretical hypotheses.

Lyman, for example (224, 226, 227), has postulated that the less the surface energy, the less is the absorptivity of a surface. Thus, considering the critical surface tension, he was able to develop a variety of hydrophobic polymers which are less likely to change the configuration of absorbed proteins. When the log of the surface free energy is plotted against the coagulation time for different surfaces, a linear relationship is shown (227).

Mason et al (239) have tried to correlate the chemistry of different polymers with their hematological properties. Baier et al (21) suggested that adhesion of a liquid to a solid is a function of the energy of interaction of the molecules at the surface. Thus, he proposed a correlation between the contact angle of a liquid drop on a surface and the hematological properties.

Following Lyman's and Baier's theories, the tested polymers were divided in hydrophobic and hydrophilic and preference was given to the former group. However, the problem was still unsolved, since it was observed that silicone rubber membranes became water-wettable after a brief contact with blood, may be because of absorption of plasma proteins.

On the other side, many investigators proposed hydrophilic gels that showed extended compatibility with blood (377).

Two other classes of materials have been studied. These include sur-
faces having a fixed negative charge and surfaces coated with heparin.

The negatively charged surfaces were initiated by Leiningen and his collaborators (213, 214) who tried to correlate the zeta potential (and the related to its streaming potential) to blood compatibility (410). They suggested that endothelium owes its blood compatibility to its negative charges and that \textit{in vivo} thrombosis results from development of local positive charges attracting blood elements. It was claimed (155) that surfaces able to activate factor XII are negatively charged, that exposure to certain cationic molecules inhibits the activation of the intrinsic clotting system (whereas it is well known that most cationic surfaces are active in provoking blood clotting and platelet adhesion) and that platelets adhere to both negatively and positively charged surfaces.

On the above basis the current literature is concerned with the following categories of biomaterials (48).

1. Synthetic Materials:
   i) Silicone rubbers (284)
   ii) Segmented polyurethanes
   iii) Pyrolitic carbon (38,39)
   iv) Ionic, polarized, and neutral polymers. A very successful example is an elastomer terpolymer (216) with negative charges.
   v) Polyelectrolyte complexes.

Polyelectrolyte complexes (Ioplex TM) as nonthrombogenic biomaterials have been developed by Amicon (37). There is a definite correlation between the polyanionic density and the thromboreistant characteristics. The complexes are reinforced by
using polyester or special glass fabrics. Other polyelectrolyte complexes appear to be non-irritating to body tissue (237). Excellent in vivo thromboresistance has been claimed for prepared electronegative surfaces using the electret effect (273).

2. Additive Containing Synthetic Materials, Such as Heparinized Surfaces

Heparinized surfaces are quite promising, but the mode of their action has been disputed. Gott et al (129) were the pioneers to succeed in attaching heparin on graphite. This graphite—benzalkonium—heparin (GBH) material had in vitro coagulation time more than 600 minutes and it was further improved and characterized by Milligan (264) and Fourt et al (115) with special interest in the preparation methods and properties. At the same time, some observations on the physico-chemical role played by glass surfaces in light of nonmigratable negative ionic charge which appears on leached glass surfaces, were made (145). They led to an ionic linking of heparin to borosilicate glass via an amine silane.

Flexible and rigid epoxy and urethane polymers containing heparin ionically complexed to quaternized amine groups were prepared (375) and claimed to have excellent thromboresistance in vitro and in vivo (up to 2 weeks). Ionically bound heparin on quaternized polyurethanes was also achieved (471). Heparinized polyester fibers have been developed by a thermofixation process (146) i.e., the fixation of heparin into the polyester fiber by application of heat. An easy method for the attachment of hepar-
arin including TDMAC (tridodecyl methylaminochloride) via impregnation was applied to silicone rubber surfaces (131). It is the author's opinion that this is one of the most promising materials although there is some evidence that TDMAC is not sufficiently permanently absorbed in silicone.

3. Hydrogels

i) Neutral hydrogels, including one of the most successful hydrophilic materials, hydron (ethyleneglycomethacrylate gel network) (218).

ii) Negatively charged hydrogels (37)

iii) Positively charged hydrogels (45)

4. Woven Prostheses to form a neointimal layer of cellular material (223,410). The prostheses are made on a mesh of Teflon, Dacron, etc.

5. Composites based on various components of the above, as the initial PVA-Heparin hydrogel G (256)

For normalization of the thromboresistance results of the materials, there have been proposed (459) standard methods of evaluation - for example, the amount of thrombus formation is measured gravimetrically (158) - applied to unheparinized and heparinized materials.

The big problem of current research remains the platelets interaction with polymer surfaces. Lyman et al (225) noticed the fact and they explained it as resulting from a denatured protein layer deposition formed by the movement of the polymer surface
through an air/blood interface.

Characteristically enough, Dutton et al (93) found that platelets are not adherent to the foreign surfaces directly, but that a thin film "conditions" the surface before platelet adhesion. Mason et al (239) evaluated the platelet - interface interaction and blood compatibility of 58 polymers in an in vitro test system. Although many investigators have faced this serious problem (257) during the development of their proposed biomaterials, Leininger insists that in his in vivo work, platelet absorption does not appear to be a problem when the polymer is treated in an one-step TDMAC - heparin complex. This is a contradiction to the results of Grode (131) who noticed the same aggregates with TDMAC covered surfaces. Further observations concerning the initial absorptive events (21) dominated by fibrinogen deposition and the interactions of blood cells on the surfaces (170) are of some interest.

The very promising heparinized hydrogels deserve a closer look and analysis.
E. HEPARINIZED HYDROGELS

Among other nonthrombogenic biomaterials, heparinized hydrogels are preferred because of the speculation that endothelium owes its compatibility with blood to a lining of heparin (39)- theory without serious scientific evidence- but mainly because of the easy binding of heparin on the surface of many polymers.

Hydrogels

Hydrogels are amorphous polymers containing a high content of water, usually above 80%. Evidence available in the literature (317) shows that when a network is in the rubbery or solvated state, it is less thrombogenic than when it is in a semicrystalline state, because the molecular units at the blood interface are in a "liquid state" of lower attractive force fields, than the crystalline cells (137). A number of synthetic hydrogels which approximate some of the physical characteristics of tissue have been investigated. They appear to be an especially interesting class of materials (9).

Ionically and covalently bonded heparin

The whole trend for heparinized materials started from the negative charge of the heparin tetramer that can bind via ionic pairing to surfaces which have a positive charge. For this purpose, a fixed nitrogen group of a primary amine reacted on the surface of the polymer is used. A big problem arises from the tendency of ion exchanging of heparin with plasma proteins and it is not surprising to find plasma proteins on the positively charged surfaces (Fig 2-6). Thus work has been done on covalent binding of heparin, because of the more per-
Fig. 2-6: Ion exchange effect on ionically bound heparin on a polymeric surface
manent nature of covalent bonds. Heparin derivatives have been synthesized, which can react with functional groups on polymer surfaces. The most successful of these is heparin/cyanuric chloride adduct (131). Acetal bridges have been used in the previously cited work of Wong and Merrill (256).

However, surfaces with ionically bound heparin generally show greater nonthrombogenicity than those with covalent bonding or cross-linked heparin. This may be in part due to some release of heparin by exchange with proteins from the contacting blood (452).

Therefore, the problem is yet unsolved (382). As already mentioned, the development of blood compatible materials has the very big obstacle of interactions of heparinized surfaces with platelets. The hydrogels, especially in high flow regions, do not perform well and they show a strong tendency to attract platelets with resultant thrombocytopenia (379). This effect can be inhibited by precoating the surfaces with albumin (378).

**Proposed heparinized hydrogels**

Using different reactions, a number of polymers have been heparinized and found to be nonthrombogenic toward human blood by a modified Lee-White test (214). This test primarily reveals activation of the intrinsic plasmocystin and it does not reveal activity toward platelets. The surfaces of many plastics and hydrogels can be made nonthrombogenic by treating them with an inorganic heparin complex system of a soluble metal salt, a solvent,
and heparin (94). The inorganic polymer, entrapped on the surface, reacts with heparin, probably by chelation. The method is very promising but is based on incomplete in vitro and in vivo studies.

Halpern et al (137) have developed heparinized hydrogels from polyacrylamide and its co-polymers. Hoffman et al (152) have developed a new series of biomaterials via irradiation grafting of hydrogels on polyurethane surfaces. Later, they grafted hydroxymethylmethacrylate and N-Vinyl pyrrolidone hydrogels on silicone rubbers and attached heparin to these hydrogels either directly or via an "arm" of 6 carbon atoms (ɛ-amino-caproic acid) (153).

Antithrombogenic cellulose heparinized membranes (45) have also been developed. Of course, the stability and the protein absorption characteristics of heparinized polymer surfaces have been studied by radiosotope labeling tests (99,256).

A classic mistake, repeated innocently by many laboratories, especially when testing ionically coated heparinized surfaces, is the interpretation of indefinite whole blood clotting time, without realizing that heparin can be easily leached out. Loss of heparin from these materials appears to be dependent on the nature of the cationic surface and on the particular protein fraction used (452). For this reason, Eriksson and Lagergren came out with a new process for ensuring that heparin will not leach out (96, 97,210). According to this method, heparinization with a mono-
layer happens in a four-step process.

a) surface cleaning

b) treatment by surfactants

c) heparinization

d) stabilization treatment via formation of a crosslinked net-
work of heparin.

Heparinized PVA-hydrogels

In the initial method of production of PVA-heparin hydrogels "G" (256), the hydrogel was produced by heating a homogeneous water solu-
tion of PVA, sodium heparin, gluteraldehyde and acid catalyst. In con-
trast to other materials, the hematological properties of this material
do not depend on leaching out of free heparin. Improvement of the origi-
nal process was achieved by the so-called "solid state" method, accord-
ing to which heparin can be reacted only on the surface of the PVA hydride-
gel (260). Merrill et al (257) came out of in vivo and in vitro studies
with the following results. Heparinized gels have whole blood clotting
time of 12 hours and if they are pretreated by albumin, the WBCT goes up
to 20 hours. However, the gels having more than 80% water are not pro-
tessable because of their fragility and softness.

From the above discussion it becomes evident that it is necessary to
study thoroughly the substrate and its properties, as well as methods
of reinforcement of it.
F. STATEMENT OF OBJECTIVES

The objectives of this thesis were the following:

1. To synthesize a pure, homogeneous, crosslinked PVA hydrogel via electron-beam and γ-radiation.
2. To study the effects of radiation conditions on the crosslinking density and the processability of the hydrogel.
3. To investigate the effects of the crosslinking density and other parameters on the chemical and mechanical properties of the hydrogel.
4. To develop a mode of reinforcement of the initial weak PVA-hydrogel, without changing the main characteristics of it. This method will be a two-step dehydration-annealing process.
5. To characterize quantitatively the crystallinity of the final hydrogel as a function of its time-temperature history.
6. To study the mechanical behaviour of the crystallized PVA hydrogel (elasticity, tear resistance).

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G. PREVIOUS WORK

Previous study on the PVA-hydrogel has been reported by the Chem. Engineering group at MIT under the direction of Prof. E.W. Merrill.

Preparation of a biomaterial-substrate via chemical crosslinking using different methods, crosslinking agents and composition of reagents has been achieved by Wong (256, 257, 260, 261, 262, 467). Some improvement of his crosslinking method, as well as a thorough analysis of the mechanical properties of these hydrogels has been reported by Silliman (259, 394) and Lee (212). PVA hydrogels with good mechanical properties and up to 75% alcohol units, have been reported (327).

Odian & Leonard (215, 285) have developed and studied PVA membranes crosslinked via radiation in the presence of small amounts of allyl-methacrylate. PVA membranes have been prepared by Markle et al (235) using a dialdehyde crosslinking agent, but without success. PVA membranes have been used for reverse osmosis application and their water and salt permeabilities have been studied by Chen et al (65).

Bray (42, 43) was the first to study the preparation of PVA hydrogels for biomedical uses and Bauer (27, 28) and Peppas (302) did some preliminary work studying the radiation effects and properties of hydrogels of PVA or its copolymers.

PVA membranes via radiation crosslinking have been studied by many Japanese workers (see for example 329) and will be appropriately and extensively referenced in Chapter 3.
CHAPTER 3

HYDROGEL CHEMISTRY

A. PROPERTIES OF PVA

Poly-(Vinyl-alcohol ), from now on designated also as PVA, has the following chemical structure:

\[
\begin{array}{c}
\text{CH}_2 - \text{CH} \\
\mid \\
\text{OH}
\end{array}
\] 

\[n\]

It is a very widely used polymer which was first prepared by W.O.Herrmann and W. Haschne in 1924 (220). After World War II Japanese investigators, under the direction of Ichiro Sakurada, studied extensively its basic properties and applications, especially its fiber and film technology, while at the same time, American and Russian investigators were working on the production and characterization of the material. As results of these extensive studies, reviews on PVA were published, first in Germany by Kainer (171) in 1949, then in Japan (292, 329, 424) by Sakurada and his collaborators, in U.S.S.R. by Ushakov (453) in two volumes, in England by Pritchard (312) and finally by Finch (101). Among these, only Finch's recently published book is easily available to the American readers, but Ushakov's (453) and Sakurada's (329) reviews are the most complete.

The monomer vinyl-alcohol does not exist in a stable form, instead it rearranges to its tautomer acetaldehyde. Thus PVA is commercially produced by polymerization of Vinyl-acetate to Poly-(Vinyl-acetate), from now on designated also as PVAc, and subsequent hydrolysis of this - 108 -
polymer. A typical scheme of production of PVA is shown in Figure 3-1.

\[
CH_2 = CH \rightarrow \text{hydrolysis} \rightarrow \{CH_2 - CH - CH_2 - CH\} \rightarrow \\
\text{OAc} \quad \text{OAc} \quad \text{OAc}
\]

where Ac : CH$_3$ - C -

Figure 3-1: Production of PVA

\[
\leftarrow \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} \rightarrow \text{Isotactic} \\
\text{OH} \quad \text{OH} \quad \text{OH}
\]

\[
\leftarrow \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} \rightarrow \text{Syndiotactic} \\
\text{OH} \quad \text{OH}
\]

\[
\leftarrow \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} \rightarrow \text{Atactic} \\
\text{OH} \quad \text{OH}
\]

Figure 3-2: Stereoregular form of PVA
Polymerization of Vinyl acetate can lead to these different stereo-
regular Polyvinylalcohols, as shown in Figure 3-2, the isotactic, the
syndiotactic, and the atactic forms. Polymerization of vinyl-acetate
can lead to head-to-head structures, containing 1,2-glycol linkages.

\[-(\text{CH}_2-\text{CH}-\text{CH}_2)-\]
\[\text{OH} \quad \text{OH}\]

Commercial polyvinylalcohols are mixtures of the different stereo-
regular types, the atactic being predominant, with about 1-2% head-to-
head structures. Preparation of the PVA with 80% head-to-head structures
can be done by epoxidation of polybutadiene (328).

Poly(vinyl acetate) is not the only polymer that hydrolyses to PVA.
Poly(vinyl trifluoroacetate), poly(vinyl monochloroacetate), poly(vinyl
formate), poly(vinyl t-butyl ether), poly(vinyl benzyl ether) and some-
times poly(vinyl trimethyl silyl ether) have been used as well (101,220).
The stereoregularity of the produced PVA, as well as the chemical and
physical properties are a function of the method of preparation (52,117).

The hydrolysis of PVAC can proceed up to 100%. Commercial PVA comes
in highly hydrolyzed grades (hydrolysis above 98.5%) and partially hydro-
lyzed ones (hydrolysis 80-98.5%)(91). The percentage of acetate groups
in PVA affects its chemical properties, its solubility, and its crystal-
lizability (449,450).

Solubility of PVA in water is a function of the degree of hydro-
lysis and degree of Polymerization. Fig. 3-3 shows the dependence

- 110 -
Fig. 3-3: Dependence of solubility on the percentage of acetate groups (for PVA with DP=1750)
of solubility on the percentage of acetate groups. It must be noted that highly hydrolyzed PVA grades do not easily dissolve in water, unless the temperature is well above 70°C (426). This is common practice in preparing a PVA solution (429). Residual acetate groups are essentially hydrophobic, weakening the intra- and intermolecular hydrogen bonding of adjoining hydroxyl groups (425).

Fully hydrolyzed PVA has a melting point between 210°C - 240°C, and glass transition temperature of 85°C (101). For extensive presentation and discussion of the crystalline and thermal properties of PVA, see Chapter 6.

B. SOLUTION PROPERTIES OF PVA

Aqueous solutions of PVA, rheologically behave as non-Newtonian fluids (370), this nature increasing with PVA molecular weight (371). The intrinsic viscosity of PVA is dependent on the degree of hydrolysis (426). The Mark-Houwink relationship for the intrinsic viscosity of PVA and for 100% hydrolyzed PVA is (24):

\[
[\eta] = 5.95 \times 10^{-4} \times M_w^{0.63}
\]  

(3-1)

where \([\eta]\) is in dI/gra.

The relative viscosity of solution over a range of concentration from 1-25% and temperature 30-80°C, may be expressed in terms of a single function of \(C_2^5 M_w^{-3.4}\), where \(C_2\) is the concentration (wt/wt) (293, 372).
Supermolecular Structures in PVA solution

Aqueous Poly(vinyl alcohol) solutions present many unresolved problems. The literature about the properties of aqueous PVA solutions presents contradictory data and ideas. The lack of clarity on the physicochemical behaviour of PVA-water systems is shown in the fact that one investigator assigned the system to the category of systems with a lower critical miscibility temperature (LCMT), while other investigators assign it to the category with an upper critical miscibility temperature (UCMT) (See Fig. 3-4).

Thus, Dieu (82), judging from viscosity experiments, assigned a theta-temperature of 97°C to the PVA-H₂O system, as well as a negative solution parameter of κ₁=0.173 (enthalpic parameter) and ψ₁=-0.142 (entropic parameter) at 25°C.

This temperature of 97°C corresponds to the LCMT. For definition of theta-temperature and more information on the solution properties of polymers, as well as the definition and relations of χ, κ, ψ parameters, see the extensive analysis in Flory (104). Phase separation occurs when the temperature is increased to LCMT, or decreased to UCMT (79).

Independent studies (307) with viscosity measurements, calculation of the intramolecular expansion factor α and extrapolation, showed that there is a theta-temperature (LCMT) at 102°C, which is in good agreement with other data, previously reported.

Tager et al (418) studied the phase diagrams of the PVA-H₂O
Fig. 3-4: Polymer-solvent system with upper and lower critical miscibility temperatures
system in a wide range of temperatures and they assigned a LCMT of 241°C in a contradiction to Dieu's value of 97°C and Kormanovskaya's value of 80°C (198). They also assigned a UCMT. It was clear that the PVA solubility in water became poorer in the whole range of increasing temperatures and that the turbidity forming in the system as well as the LCMT did not disappear on cooling. They were explained by crosslinking reactions during the separation of the system into phases (418), or by slight gelation due to formation of semicrystalline structures (394). The LCMT was inversely proportional to the molecular weight of PVA (10), so that for higher molecular weight (which favored the formation of these structures), LCMT was lower (almost 231°C).

Klenina (192) presented a diagram (Fig. 3-5) showing the change in supermolecular order in aqueous solutions of PVA. Dilute solutions of PVA undergo marked "retrogradation" in 2-3 days, whereas the turbidity spectra of concentrated solutions (10-15%) do not change substantially in a fairly prolonged time. Retrogradation is the spontaneous precipitation of PVA from water solutions upon standing. It is closely connected with partial crystallization of the precipitate. From the data on the formation and breakdown of supermolecular order in aqueous PVA solutions, the following regions are marked:

i) region 1, where no visual solution of PVA occurs (two layers)

ii) region 2, where macrosolution occurs, but supermolecular order at a colloidal degree of dispersion is present and the formation of this phase kinetically increases with temperature. The
Fig. 3-5: Change of supermolecular order in aqueous solutions of PVA
line between regions 2 and 3 corresponds to the melting points of the supermolecular formations. These melting points correspond to the maximum values of turbidity at each concentration of the solution.

iii) region 3, where the supermolecular order breaks down to the line at temperature of 125-130°C.

iv) region 4, where there is a solution of PVA.

The results once more point out that, because of many factors involved during the preparation (and heat processing) of PVA solutions, complex structures, many times modified by retrogradation, can form under arbitrary methods of preparation of solutions. Thus, the previous history in the thermostatic treatment of a PVA solution is very important.

Of course, this thesis (192) is in contradiction with papers concerning the unique classification of the PVA-water system as a system with a UCMT or with a LCMT. For example, because of the negative values of $\kappa$ and $\psi$ factors (82), the reduction of the second virial coefficient ($247,248,249$) and the heat of solution ($6,252$) measurements, a decrease in the solubility of PVA has been observed in water upon heating. However, we tend to believe that Klenina's data (192) are the most accurate and that PVA-$H_2O$ is a peculiar system with upper and lower miscibility temperatures, complicated by crystallization, the extent of which must surely depend on stereoregular tacticity and that, to a fine degree (e.g., triad, tetrad, pentad sequences). Thus, the method of synthesis is important to a significant extent.

If it is considered that the system PVA-water belongs to sys-
line between regions 2 and 3 corresponds to the melting points of the supermolecular formations. These melting points correspond to the maximum values of turbidity at each concentration of the solution.

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If it is considered that the system PVA-water belongs to sys-
tems with a UCMT, then crystalline characteristics should be assigned to the supermolecular order formed in this temperature. If the system is considered as one with LCMT, then the supermolecular order may be represented as the precipitation of a highly concentrated polymer phase in a colloidal-disperse condition.

The supermolecular structure could simply be nonequilibrated, fluctuating formations, this implying that it is impossible to strictly distinguish single-phase and multiphase systems, when they contain high molecular-weight components, since any particle detectable in such systems could be a "frozen" fluctuation of the same nature as fluctuation of low molecular-weight solutions.

However, the existence of region 3 (192) in the PVA-H₂O solution, where the supermolecular order is broken down, excludes the classical form of a system with a LCMT and points towards a supermolecular organization of paracrystalline nature (298).

Shakhova and Meerson (385) have studied some physicochemical properties of PVA solutions, as well as their partially acetylated products. From studies of the solubility and swelling, it has been shown that a small number of acetyl groups increases the solubility and swelling and an upper critical temperature of mixing is observed. An increase in the number of acetyl groups within the above mentioned range leads to a decrease of the UCMT from 95 °C to 60°C (See Fig. 3-6).

Solutions that were rapidly cooled to a certain specific temperature had a scattering intensity, that gradually increased in scattering.
Fig. 3-6: Change of supermolecular order in aqueous solutions of PVA partially acetylated samples

In some cases this scattering increased over a period of several weeks under isothermal conditions. The increase in light scattering was explained by the formation of particles of a new disperse phase with a refractive index differing by a constant amount from that of the dispersion medium (201). The solutions were cooled from 90°C to 50°C, 40°C, 30°C, 20°C, 0°C. The scattering was significant when the solutions were cooled to 20°C or 0°C, and it was a function of the
concentration of PVA solutions. The kinetics of the formation of the new amorphous phase from metastable solution of PVA differed in a number of respects from these of the formation of a new crystalline phase, especially because of the equilibrium values reacted, and the absence of induction period. It is possible that a relatively stable or even thermodynamically stable equilibrium colloidal dispersed system was formed (187, 188).

A phase diagram for the PVA-water system, constructed from these light scattering measurements (201) showed an UCMT of 75°C (197).

Electron microscope investigations showed that the particles are almost spherical with dimensions up to 1000 Å (198, 199). The dimension of the particles can be calculated using a method developed by Sakurada et al (332). This method uses the "dispersion quotient", which is defined as the ratio of turbidities at two different wavelengths, in relation to the particle size of colloidal dispersion. This method can be used under the assumption of Mie's theory (141, 142). The method was applied in a similar study (154), where turbidity was observed again below 15–20°C. There is a limiting concentration of PVA under which no turbidity is observed. The dispersion quotient depended on the degree of polymerization (e.g., different size of particles was observed with different initial chain length).

The Mie theory can be used when the intensity of the diffused light from the particles exceeds the intensity of the molecular light-diffusion, that the latter may be disregarded. Then the turbidity spectrum τ (λ) of the solution is connected to the particle sizes,
without needing their concentration and their relative refractive
index \( m \) (191).

From similar data it followed that in a certain concentration
range, gels of crystallizable polymers contain structural elements
of supermolecular formations in which a high degree of order in the
arrangement of the macromolecules persists (253).

The supermolecular structures in PVA were observed also in sol-
utions of 2-12\% PVA, thermally processed at temperatures of 80\(^\circ\)C,
90\(^\circ\)C and 100\(^\circ\)C. The critical time of breakdown of supermolecular
particles was 12-15 hours. As expected, the particle size was re-
duced when the temperature of heat-treatment was increased, or the
concentration decreased (191). The shape of the kinetic curves of
the change of the supermolecular order differs significantly in the
region above and below a critical temperature of 130\(^\circ\)C. In contradic-
tion with other investigators, Klenina et al (193) believe that at
these temperatures the dependence of the melting region of the super-
molecular structures is of the same nature as for melting of crys-
talline structures arising during isothermal crystallization of
polymer in the presence of solvent (190).

We consider polymer gels as two-phase systems, where the net-
work of interlacing bundles of macromolecules is formed by polymer
homologs, insoluble under given thermodynamic conditions. It makes
no difference whether these homologs form a continuous phase, inclu-
ding all the system (gel), or if there appear aggregates in the solu-
tion (gel solution) or dense particles of single molecules, tied with
intramolecular bonds (sol). Aging leads later to settling or gelation and change of the gel structure with respect to partial crystallization (126).

The main binding forces in the gelation of PVA may be attributed to hydrogen bonds. This was proven beyond doubt by experiments on the effect of pressure on the sol-gel transformation of this systems (480).

It has been pointed out that statistical structural formations which exist in true polymer solutions may be converted into stable aggregates if the composition of the solvent is changed, forming a disperse phase of a colloidal solution from a true solution. Structural changes are a subsequent stage in the thermodynamic transition of a true solution into a heterogeneous colloidal system. In this transition some of the labile intermolecular bonds become permanent and this leads to separation of a new phase from the solution (125). Two types of bonds "stable" and "labile" are accepted but not characterized.

Dilute aqueous solution of PVA containing precipitants (alcohols) are not homogeneous systems, but they have particles with size of 0.6-0.8μ. The formation of the gel structure is accompanied by a sudden change in the volume of the system. The transition from solution to gel is a phase transition of the first order. X-ray analysis has shown the existence of a crystalline structure (when films are heated above glass transition temperature) and a gel structure (122). The same behaviour was observed with solutions of PVA in ethylene glycol, glycerol, and diethylene glycol.
Upon storing of PVA-solution at 30°C a temporal increase in the scattered light was observed, which may be caused by formation of new microgel particles. No remarkable changes happened by keeping the solution at 0°C, while at 100°C the microgel particles were only partially dispersed. It was suggested that this happens because of a partially crystalline structure of these particles (the rest being amorphous) (248).

The effect of aging on PVA-water systems has been studied by different methods. In concentrated PVA solutions (12-15%), it was found (196) that viscosity increased, and that the amount of viscosity increase was greater, the greater the temperature and the age of solutions. The viscosity increase was attributed to the orientation of the PVA molecules in the solution.

The reversible gelation of concentrated solutions is studied by viscometric measurement and by the measurement of an apparent melting point of the gel (229).

Experiments on the effects of ions on the properties of colloidal solutions of PVA showed decrease of pH with increase of electrolyte (320).

Spectroscopic study of the gel formation in PVA solution was done by forming a complex with Congo red and studying its properties (263).

Zubov and Osipov (478) studied the structures formed in aqueous PVA solutions. The size of the globular supermolecular structures depended upon the concentration of PVA and the cooling temperature. Smaller particles were formed at lower temperatures (476).
Kinetic study of the gelation, in reference to its mechanism and the structure of junctions, as a function of gelling time at temperatures of 30-80°C for different stereoregular PVA has been reported (391).

The observed behaviour of flow birefringence of moderately concentrated PVA-water solutions suggests the existence of gelation or association processes of the polymers during aging in aqueous solutions.

The globular structures with strong chemical intermolecular or intramolecular bonds, depending on the solution concentration were reported also for PVA solutions in anhydrous dimethylformamide (DMF), heated to 145°C and then cooled to temperatures of 70°C, 60°C, 50°C, 30°C, 20°C, and 10°C. (478,479).

Low-viscosity globular solution of PVA produced in anhydrous dimethylformamide by adding small amounts of water, showed a tendency for increase of viscosity with time (477). The variation of viscosity and turbidity was compared to the size of the particles formed, determined by electron microscopy. It was suggested that this kind of increase in viscosity is the result of the redistribution of part of the intra-globular bonds over inter-globular bonds. Globulation of the polymer molecules and gel formation occurred in solution of PVA in DMF. The rate of formation of globules is dependent on temperature and on the composition of the binary mixture. When globular PVA is heated, denaturation occurs as a result of rearrangement of the local intramolecular bonds (479).
It is characteristic that copolymers containing PVA and PVAc do not present the same behaviour of agglomeration. Copolymers with 0-21% PVA do not associate according to light scattering measurements at 25°C, and this was attributed to the formation of intermerar hydrogen bond between neighbored vinylalcohol units (95).

**Importance of phase behaviour of PVA-water systems**

The importance of knowledge of the phase behaviour of PVA-water systems in this thesis can be stated in the following points:

1) **Preparation of Solution**

Supermolecular structures, pregelation, paracrystalline structures, etc. highly depend on the temperature time history of preparation of a PVA solution, so that it is necessary that exactly the same procedure is followed every time a PVA solution is prepared.

2) **Determination of the Molecular Weight**

Because of different conditions in preparation (which resulted in different structures in the "solution") different workers have reported many equations for calculation of the molecular weight of PVA, from viscometric data. None of the reported equations is accurate and in accordance with the manufacturer's value of \( M_w \) (29,82,468,481).

3) **Effects of Structures of PVA Solution, on Crosslinking and Swelling of the Produced Gel**

Consideration must be taken, in analyzing experimental
results, of the effects that the time-temperature history of preparation of the solution can have on crosslinking of PVA. Because of the existence of supermolecular structure, the crosslinking can be treated as an "ideal" one (according to Flory's theory) only approximately, under the assumption that aggregates do not act as already "crosslinked" points and that there is still equal probability of reaction of all the units in the chains of PVA.

**Biological degradation of PVA hydrogels**

It is well known that biological microorganisms grown in polymeric gel can lead to degradation of the polymeric chain. The effects of enzymes and microorganisms on PVA hydrogels have not been studied except in one case (413). In this study by Suzuki et al it was proven that the bacterium *Pseudomonas* 0-3 was found to produce and secrete an inducible enzyme which degraded PVA. Thus, when 0.5% of PVA was added to the culture medium, PVA was almost completely lost from the culture fluid after a week and the concentration of total organic carbon decreased from the initial value of 2700ppm to 300ppm. The mechanism of PVA degradation has not been clarified yet. The optimum pH for enzyme activity was around 7.5 to 8.5 and the optimum temperature 35 to 45°C. Determination of the resistance of these hydrogels to different bacteria has not been done yet, although there is an official ASTM method (20).
C. CHEMICAL REACTIONS OF PVA FOR SYNTHESIS OF HYDROGELS

Poly(vinyl alcohol) undergoes typical chemical reactions of polyhydric alcohols. It can be crosslinked by any difunctional agent that condenses with organic hydroxyl groups. Among different chemical crosslinking agents (102), the following have been used for the production of PVA hydrogels: gluteraldehyde (256), acetaldehyde (182), formaldehyde (287, 288, 369), other monoaldehydes (181, 183), maleic or oxalic acid (49), dimethylurea, glyoxal, trimethylolmelamine, hydrochloric acid (343), polyacrolein, diisocyanates, divinyl sulfate (220), and ceric redox systems (78). Crosslinked PVA gel was formed also during hydrolysis of copolymers of vinyl acetate with glycidyl methacrylate (271).

PVA can be crosslinked by ultraviolet light in the presence of sensitizers (420, 447). It can also be crosslinked by heat or light in the presence of chromium compounds (90).

The use of electron-beam and γ-radiation for the production of PVA hydrogels is now a common practice and it will be studied extensively in the next chapter.
CHAPTER 4

RADIATION EFFECTS ON PVA

Discussion of the effects of ionizing radiation on polymeric materials and their solutions, study of their mechanism and analysis of the results, can be found in books by Chapiro (55), Bovey (40), Charlesby (57), Nikitina (281), Saito (326), and Feng (100), and in review article by Chapiro (54,56), Charlesby (62,63,64), Saito (321,322,323,325), Inokuti (160,161), Dolozel (88), Kat-suura (174), and Collinson (69).

A. EFFECT OF IONIZING RADIATION ON POLYMERS

Types of ionizing radiation

Ionizing radiation covers a whole range of different types of radiations, some of which are of primary source and others of secondary source. Ionizing radiation is electromagnetic radiation of moving particles, which carry enough energy to ionize simple molecules (55) either in air or in water.

In the field of radiation chemistry for macromolecular studies, only a limited number of types of radiation are used, mainly electron beam and γ-radiation.

Artificially accelerated electron beams are available from several machines, which produce them with energy from 0.5 to 20 MeV.

Electron accelerators, such as the commonly used Van de Graaff accelerator, substitute for isotopes emitting β-rays, which are
generally not used in radiation polymer chemistry because of technical problems. The penetration of fast electrons is much smaller than that of γ-rays. Commercially used Van de Graaff accelerators can deliver electrons with energy 2-10 MeV. According to the setting of the accelerator, the dose rate can vary from $10^3$ to $2 \times 10^5$ rads/sec (286). The term "dose" is used to describe the radiation received by a substance placed in a radiation field. The concept of dose implies that energy is transferred from the radiation source to the polymer and dose is therefore expressed in ergs per gram of irradiated polymer or other similar units. One rad corresponds to absorbed energy of 100 ergs per gram of material.

Contemporary dosimetry of ionizing radiation (55,281) uses several physical quantities for the absorbed energy and the description of characteristics of radiation sources.

One roentgen (r) is the quantity of γ-radiation at which the corpuscular emission (electrons), associated with it, produces, in air, ions carrying one electrostatic unit of quantity of electricity of either sign, per 0.00129 gr (1 cm$^3$) of dry air at 760mm Hg. The energy equivalent of a roentgen per unit of mass of air is 83.8 ergs/gr.

One rep-roentgen equivalent physical—measures the quantity of absorbed energy and is equal to the energy equivalent of the roentgen in irradiation in water ($93^{\text{ergs}}$/gr). Thus the relation between rad and rep is:

$$1 \text{ rad} = 1.19 \text{ rep}.$$
A number of typical depth-dose curves for electrons absorbed in water is shown in Figure 4-1.

The γ-rays are emitted by radioactive isotopes and they cover a broad range of energies. Cobalt-60 is the most commonly used source of two monochromatic γ-beams with energies of 1.17 and 1.33MeV (34). Gamma-rays have very high penetrating power and the dose rate can vary between 5-100 rads/sec. The intensity of Co-60 γ-radiation is reduced to 10% of its initial value by passing through 43.2 cm of water or 4.1 cm of lead (55). The half-life of Co-60 is 5.3 years, so that the dose rate should be calculated as a function of time, from the time of installment of a new unit.

Effects of ionizing radiation on macromolecules

Kinetically the absorption of radiation beams by macromolecules, will cause ionization of the polymer species, if the energy absorbed is greater than the ionization potential. Ionization is followed by free radical formation. Hydrogel radicals formed in the previous step can react with polymer radicals and no net effect is observed. This step is called recombination. However, in almost every case polymer free radicals will react to form polymer chains or networks (crosslinking), while other polymer chains may split, forming shorter chains (degradation).

Polymers either crosslink or degrade according to their chemical structure. According to Chapiro (55), polymers that are cross-linked when irradiated include polyethylene, polypropylene, polyst-
Fig. 4-1: Percentage depth dose in water for high energy electrons
yrene, polyacrylates, polyacrylamide, polyvinylchloride, PVA, polyvinylpyrrolidone, polysiloxanes, polyesters, and polyamides. Polymers that are degraded include polyisobutylene, polymethacrylate, polymethacrylamide, polyvinylidene chloride, cellulose and its derivatives and some fluoro-substituted polyethylenes. A number of theories have been advanced in order to account for the fact that some polymers lin crosslink, while others degrade. It seems that large side groups in a long linear chain lead to degradation. It is a rule that among vinyl polymers those

\[ \text{H} \]

with the structure \( \text{CH}_2 - \text{C} \rightarrow \text{n} \) \( \text{R} \) will crosslink, while polymers with the

\[ \text{R} \]

structure \( \text{CH}_2 - \text{C} \rightarrow \text{n} \) \( \text{R} \) will degrade. The steric hindrance presented by a
tetrasubstituted carbon in the chain, is shown by a somewhat higher heat of polymerization, so that a definite correlation exists between the heat of polymerization and the tendency of crosslinking. Thus, the higher the heat of polymerization, the more likely that the polymer will crosslink with irradiation. Shapiro reports (55) that there is a border-line at 16 kcals/mole, and that those polymers that have heat of polymerization higher than 16 kcals/mole crosslink. Both crosslinking and degradation may occur simultaneously and many authors have considered the radiation effects as a kinetic phenomenon, where the rate of crosslinking or degradation predominates (458).

**Gas evolution**

Gas evolution is a common phenomenon during the irradiation
of polymers. A detailed study of the mechanism of the individual irradiation can show how the gas evolution occurs. For example, in many cases hydrogen, formed by two hydrogen radicals, is evolved, which in the case of hydrogels is entrapped in the polymeric materials. The total yield of gases evolved after irradiation of different polymers has been reported, as well as analysis of the gases (173,303).

When bulky pieces of polymer are subjected to irradiation, these effects of gas evolution are less pronounced, since the oxidation process is then diffusion-controlled, and oxidative degradation only becomes noticeable at very low dose-rates, when the rate of diffusion of oxygen into the polymer is higher than the rate of consumption of this gas by the chemical reactions. Not enough attention has been paid to this fact in a number of the earlier studies and this presumably accounts for some of the discrepancies reported in the literature in the behaviour of certain polymers under irradiation.

The effect of Oxygen

A very important factor on the production of crosslinked networks via irradiation is the presence of oxygen during this process. Many polymers normally being crosslinked, degrade if irradiated in air under slow dose rates. A possible explanation of the reason for degradation is the formation of weak peroxidic bonds in the main
polymeric chain. These bonds decompose and cause oxidative degra-
dation of the main chain. Thus, a polymer radical can react in the
following way:

\[
\text{Reaction with oxygen: } \cdot \text{CH} - \text{CH}_2 - + O_2 \rightarrow \cdot \text{CH} \quad \text{CH}_2 - \quad O_2
\]

\[
\text{Decomposition and rearrangement: } \cdot \text{CH} - \text{CH}_2 - \rightarrow \dot{\text{C}} + \cdot \text{CH}_2 - \quad O_2 \quad \text{H}
\]

In many cases breakdown of the material is more rapid in the
presence of oxygen (286,388). Infrared measurements have indicated
that hydroxyl and carbonyl groups are formed. At low dose rates
oxygen can diffuse into the bulk of the polymer quickly enough to
provide sufficient oxygen for peroxide formation. At high dose rates
the oxygen is rapidly used and it cannot be replaced (69).

The degradation and its kinetics have been analyzed by Sakurada
et al (367,368) and Grassie (130).

In the case of polymers that can be affected by oxygen, irra-
diation in vacuo is necessary for the production of a crosslinked
network.

Free radicals produced during irradiation of polymers may be-
come trapped in the irradiated material, especially when the temp-
erature is kept below the glass transition temperature. It was pro-
ven (461) that the life-time of radicals is pretty long \((10^2\text{ to }10^4\text{ sec})\) in solid state and it is not correct to assume a stationary state. If the irradiated polymer is partially crystalline, then the trapped radicals are still more firmly trapped. Nitta et al (282) used area measurements of ESR absorption spectral curves of irradiated polymers to determine the concentrations of induced radicals.

Some aspects of crosslinking

During the process of crosslinking by irradiation, the molecular weight increases (pre-gel reaction), a "sol" extractable (with a good solvent) phase is produced (gel formation), and a crosslinked "gel" phase is formed.

The quantity \(G\), characteristic of the efficiency of radiation energy in initiating on a PVA chain a crosslink, is defined as the number of initiations per 100 electron volts of energy absorbed by the PVA.

Prevednikov et al (310) explained radiation crosslinking of polymers with "hot" H atoms, that react preferably with \(\text{CH}_2\) groups, which then combine with adjacent radicals.

The term endlinking has been proposed for gel formation by main-chain fracture of long chain polymers. After this fracture, the chain can form a network of infinite extent (gel). Two end-groups produced at a fractured site can attach neighboring molecules and react with them (63). The distinction between this process and crosslinking is shown in Figures 4-2 and 4-3. By removal of a side chain
main chain unit

fracture of side chain

crosslinking by side-chain fracture

crosslinking by main-chain fracture

Fig. 4-2: Endlinking and and crosslinking processes on a long chain polymer
Fig. 4-3: Schematic representation of crosslinking and endlinking during irradiation of a polymer.
or hydrogen, a radical is formed in the chain, which can be reacted by a lateral link (crosslinking), or by the fractures of a broken main chain (endlinking). Single main-chain fractures can only produce branching. For network formation, multiple breaks are needed.

The variation of the molecular weight distributions in a polymer after irradiation are described by a series of differential equations (321). The solution of these equations gives the gel point and the average molecular weights. Problems involving cyclization and branching are solved, showing that gel formation is retarded by cyclization. It has been found that for any initial distribution the gel formation occurs only when the ratio of the two probabilities concerning degradation and cross-linking is smaller than 4. The full theoretical discussion of the crosslinking theory is included in Appendix A.

Complicated mechanisms where cyclization and endlinking occur simultaneously are discussed in (322).

The variation of viscosity before and after gelation has been studied (323). G-values of crosslinking and degradation are calculated from the intrinsic viscosity in the period of irradiation. It was shown (160) that the intrinsic viscosity can decrease in certain cases, even if it reaches infinity at the gel point. Such a behaviour of the intrinsic viscosity is possible, only if the initial molecular size distribution is sufficiently broad. The intrinsic viscosity
as a function of radiation dose is shown to behave in a great variety of ways depending on the relative importance of crosslinking and degradation, and in particular, on the shape of the initial distribution (161). The contribution of a branched polymer to the intrinsic viscosity was studied later (174). When impurity hinders crosslinking, all the relations between physical quantities of an irradiated polymer containing impurities, can be reduced to those of a polymer with no impurities, if use is made of a reduced radiation dose instead of the real dose. But this is not the case with the effect of impurities on end-linking (325).

B. EFFECT OF IONIZING RADIATION ON PVA

Danno showed (73) that when PVA is irradiated by ionizing radiations in air, breakdown of main-chain and formation of carbonyl groups takes place.

A possible mechanism is the following:

\[
\begin{align*}
&\text{H} - \text{C} - \text{C} - \text{C} - \text{H} \\
&\text{H} - \text{H} - \text{H} - \text{H} \quad \text{H} - \text{C} - \text{C} - \text{H} \quad \text{H} - \text{H} - \text{H} \\
&\text{H} - \text{C} - \text{C} - \text{C} - \text{H} \quad \text{H} - \text{H} - \text{H} \\
&\text{H} - \text{OH} - \text{H} - \text{OH} \quad \text{H} - \text{OH} - \text{H} - \text{OH}
\end{align*}
\]

- 139 -
The formation of ketonic carbonyl groups and the liberation of hydrogen molecules may be explained as follows:

\[
\begin{align*}
\text{H}_2\text{O}_2 & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{\textbullet} & \quad \text{\textbullet} & \quad \text{\textbullet} & \quad \text{\textbullet} & \quad \text{\textbullet} & \quad \text{\textbullet} \\
\text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{OH} & \quad \text{OH} & \quad \text{H} & \quad \text{OH} & \quad \text{OH}
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{O}_2 & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{\textbullet} & \quad \text{\textbullet} & \quad \text{\textbullet} & \quad \text{\textbullet} & \quad \text{\textbullet} & \quad \text{\textbullet} \\
\text{C} & \quad \text{C} & \quad \text{C} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{OH} & \quad \text{OH} & \quad \text{H} & \quad \text{OH} & \quad \text{OH}
\end{align*}
\]

Danno et al (77) studied the effects of very high dose of γ-rays on solid PVA (higher than 1000 Mgrads), in air and in vacuo at room temperature and low or high temperatures.

Using accurate NMR spectra measurements and based on the changes in methylene's signal produced by the irradiation, Danno et al (76) were able to detect the segmental motions of crosslinked PVA molecules.

Sakurada et al (374) showed that the mechanical properties (especially elongation and tensile-strength) of irradiated PVA films increased or remained almost unchanged.

In another paper Danno (74) showed that irradiated samples subjected to heat treatment showed gel formation and disappearance of
carbonyl groups. The following tentative explanation may be given to the process of forming an intermolecular linkage. According to this, reaction of the carbonyl group with a neighboring molecule to form a ketale linkage occurs.

When PVA is irradiated by γ-rays from Co-60 in air at room temperature, an oxidation reaction occurs. Gamma irradiation causes the formation of double bonds -C =C- at 6.2μ. In view of the reduction of CH₂, the above phenomenon seems to correspond to the occurrence of dehydrated structures (373).

Irradiation of dry PVA powder with γ-rays showed that scission of the main chain predominated, although chain branching reaction could also occur. The C-value for scission was 0.9. It appeared that the γ-irradiation gave rise to one carbonyl and one carboxyl group per mole (341). When irradiated in vacuo the amount of these groups was much smaller (342).

Powder PVA is fractured when subjected to ionizing radiation (150) at room temperature. Their results showed that only some types of bonds can be fractured. Matsumoto and Danno (245) proceeded to an analytical study of these effects. Using temperatures up to 60°C and doses up to 30 Mgrads from Co-60 they studied the concentration of CO and COOH groups. The formation of CO groups increased with radiation dose but was roughly independent of dose rate. The COOH groups were unaffected by irradiation. Crosslinking in PVA was prin-
incipiently 1,2-glycol formed by interaction of COH between the molecules. Reactions of CO and COH are also possible.

PVA on irradiation with γ-rays in the presence of air undergoes degradation with the conversion of the hydroxyl groups to carbonyl groups. After infrared spectra analysis of samples irradiated with different doses, Bhardwaj et al. proposed the following mechanism of degradation:

\[
\begin{align*}
-\text{CH}_2 -\text{CH}^- \rightarrow -\text{CH}_2 -\text{C} - \text{CH}_2 -
\end{align*}
\]

\[
\begin{align*}
\text{H}^- + -\text{CH} - \text{CH}_2 -
\end{align*}
\]

Hirano (148) studied extensively the selective phenomenon of main chain scission in PVA. He studied the effect of irradiation on 1,2-glycol structures and he pointed out that they are more preferable to degradation (149). In another paper Amemiya and Hirano (7) proved that there is a transfer of radiation energy from the head-to-tail structure to the head-to-head one.

When PVA film is heat treated in air or γ-irradiated while be-
PVA samples irradiated with different dose in Co-60, were used to get their NMR spectra and study their structure in detail (111). The ESR spectra and the structure of PVA found that the predominant structure of radicals is of the form \( \cdot \text{C} - \text{O} - \text{C} - \text{H} \) in solid PVA films, PVA is predominantly degraded by random chain-fracture throughout the crystalline and amorphous regions. Effects an amount of endlinking may occur in the amorphous regions. Effects from the results of Sakurada et al. (345) it was concluded that in solid PVA films, PVA is predominantly degraded by random chain-fracture throughout the crystalline and amorphous regions, although an amount of endlinking may occur in the amorphous regions. Effects from the results of Sakurada et al. 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ence between air or vacuum radiation existed. Scavengers of \( I_2, SO_2, NO, H_2S, Cl_2 \), etc. do not change the absorption curve, this meaning that the free radical of PVA is very stable. However, the temperature effect is considerable. When the irradiated samples are heated, the free radicals decay rapidly.

PVA has been protected against radiation by benzalation and benzoylation. The benzoate is found to offer more protection than the benzal derivative (228).

In addition to breakdown of the polymer backbone, a further type of degradation is often observed in which small molecules are eliminated without main-chain scission. A typical example is provided by the initial stage of degradation of PVA, during which elimination of water happens (222).

The effect of acids in gel-formation of PVA induced by \( \gamma \)-rays was studied (278). Tetrahedral anions such as \( ClO_4^- , SO_4^{2-}, PO_4^{3-} \), etc. are helpful to irradiation-induced gel formation, and the coordination of these anions is suitable to produce a preferable alignment of PVA.

One of the least studies on crosslinking of PVA in dry state with \( \beta \)-radiation from accelerator was done by Sakurada et al (363). Most irradiation studies of PVA have used \( \gamma \)-radiation. In the final stage of their studies described, these workers used both \( \gamma \)- and \( \beta \)-irradiation in comparing the effects of heat treatment following irradiation. In another paper (364) they repeated the same experiments on acetylated PVA and they studied the changes in mechanical proper-
ties. Later they presented data on irradiation of PVA at temperatures above the second transition temperature (90°C to 170°C) and below it (50°C to 70°C) (361). Even at high temperatures any difference between Co-60 irradiation and Van de Graaff irradiation on solid PVA is minor up to doses of 10 Mgrads. The changes in the structure of PVA while it was being irradiated at room temperature and heated, were followed by IR analysis. They showed the continuous decrease of -OH and -CH₂ groups (362).

C. IRRADIATION OF POLYMERS IN SOLUTION

Analogous phenomena have been observed during the irradiation of solutions of polymers. Some polymers crosslink, others degrade. Irradiation of a polymer in solution can lead to crosslinking with lower dose than a solid polymer, because of the effects of the radiolysis products on the polymer and because of the lower viscosity in solution which allows free radical diffusion (140).

A typical reaction mechanism is presented. In this mechanism PH is the polymer and SH is the solvent.

**Activation**

\[
\begin{align*}
\text{PH} & \xrightarrow{\text{hv}} \text{PH}^* \\
\text{SH} & \xrightarrow{\text{hv}} \text{SH}^*
\end{align*}
\]

**Free radical formation**

\[
\begin{align*}
\text{PH}^* & \rightarrow \text{P} + \text{H} \\
\text{SH}^* & \rightarrow \text{S} + \text{H}
\end{align*}
\]
Gas evolution

\[ \cdot \cdot \cdot \quad H + H \rightarrow H_2 \]

Recombination

\[ \cdot \cdot \cdot \quad P + H \rightarrow PH \]
\[ \cdot \cdot \cdot \quad S + H \rightarrow SH \]

Energy Transfer

\[ \cdot \cdot \cdot \quad PH + SH^* \rightarrow PH^* + SH \]
\[ \cdot \cdot \cdot \quad PH^* + SH \rightarrow PH + SH^* \]

Radical Transfer

\[ \cdot \cdot \cdot \quad PH + S \rightarrow P + SH \]
\[ \cdot \cdot \cdot \quad P + SH \rightarrow S + PH \]

Cross-linking

\[ \cdot \cdot \cdot \quad P + P \rightarrow P-P \]

Degradation

\[ \cdot \cdot \cdot \quad P_{m+n} \rightarrow P_m + P_n \]

The irradiation of polymers in solution presents a new aspect in that the chemical changes may result either from direct or from indirect effects via the solvent. The direct effect on the polymer molecule is independent of concentration in solution, whereas the indirect effect is dependent upon the concentration \((5)\). The concentration dependence can account for the large effects produced in dilute solution by relatively small radiation doses. Protection against the indirect effect can be altered by additives which can re-
act with the radicals formed in the solvent. The temperature of irradiation can affect the indirect effect.

A number of polymers when irradiated in dilute solutions degrade, but when irradiated in the solid state they crosslink. A dilute polymer solution is one, in which the expanded polymer coils are separated from one another by solvent. Thus, the upper limit of a dilute solution is the concentration where the coils just touch. The size of a polymer coil in solution being a function of its molecular weight, this limit can be easily calculated. For the most of the polymers it is lower than 1%. At some intermediate concentration the polymers change from one pattern of behaviour to another. When the dilute solution is irradiated, its viscosity rises slowly and suddenly a gel structure is formed. This gel may be removed and further swollen in water. If the gel structure is further irradiated, the equilibrium degree of swelling is reduced until the gel exudes the excess water and breaks away from the container wall. Increased radiation causes further shrinking (increased density of crosslinking).

The relation between minimum dose for gelation and polymer concentration is shown in Figure 4-4.

Many polymers in solution undergo simultaneous intermolecular crosslinking and degradation when irradiated. No relation exists between the radiation sensitivity of the solvent and the rate of
Fig. 4-4: Relation between minimum dose of gelation and polymer concentration
crosslinking of dissolved polymers. However, crosslinking seems to be slightly favored in poor solvents. A mechanism was proposed (143) in which the formation of macroradicals and low molecular weight radicals from the solvent by direct action were the primary steps.

Kiran and Rodriguez (189) studied the effects of concentration on the gelation dose, for different degrees of polymerization. Especially interesting is their study on the mechanisms and structures at doses lower than the gelation dose. In unirradiated solutions below their critical concentration, the polymer chains are not overlapping and segmental mobility is high. At low doses, intramolecular linking and chain scission are favored, the former decreasing the segmental mobility. While the viscosity is increasing, intermolecular crosslinks are formed and three-dimensional networks (microgels) appear. However, the distance between such units becomes large with continued radiation and the system becomes diffusion controlled. Finally intramolecular crosslinking (within the intermolecularly linked networks formed in the previous way) and chain scission are favored. Microgel units approach tight units and the solutions display turbidity (See also Figure 4-5).

D. IRRADIATION OF AQUEOUS PVA SOLUTIONS

Aqueous solution of PVA were irradiated with γ-rays from Co-60 and the effects were discussed quantitatively and qualitatively by Danno (75). Carefully fractionated PVA, with acetate groups less
Fig. 4-5: Schematic representations of radiation-induced charges in polymer chains in solutions

- 150 -
than 0.06-0.08% and degrees of polymerization (DP) between 1050 and 2680 were used. The solutions studied were from very dilute up to 10.7% in PVA. The dose rate was 21 rads/sec and the temperature of irradiation approximately 5°C. The critical concentration varies as the initial DP changes. Above the critical concentration insoluble gel is formed. On receiving further radiation the gel shrinks, giving off water. Danno was the first to report the problem of bubbles formation during this irradiation, without suggesting any solution (75). The minimum gelation dose $D_g$ depends on the degree of polymerization and the concentration of the polymer.

Application of Saito's theory (321,322,323) in the case of irradiation of aqueous solutions of PVA by γ-rays and comparison to Danno's data (75) has been done by Saito (324). It is shown that if no impurity is present, the intrinsic viscosity and $M_v$ of irradiated PVA in aqueous solution increase with radiation dose.

Dieu and Desreux (83) studied independently the γ-radiation effects on aqueous solutions of PVA and came to the same conclusions.

In an excellent review Sakurada and Ikada (339) summarized the results of their studies in air and in vacuo. These results will be presented later.

Danno found (72) that although the actual energy used is 10-20 eV, the energy per crosslink to be absorbed by the solution was estimated to be 62 eV, so that only a small fraction of that energy is used for crosslinking. Gamma-ray irradiation of aqueous solutions
of PVA showed that above concentration of 3.7% the molecular weight increases monotonically with the dose. Higher irradiation temperature is sometimes preferable for crosslinking (1,365).

Berkowitch et al (30) studied the effects of γ-rays and electron beam irradiation on PVA solutions. Commercial samples of molecular weight 27,000 - 400,000 with dose rates of 13-215 rads/sec (for γ-rays) or 0.2-1 Mrad/sec (for electron beam irradiation) were used. With electron beam radiation, the gelation dose decreased linearly with the concentration of the polymer until close to a critical value of the concentration. With γ-radiation, the gelation concentration was lower than that of electron-beam radiation.

Other studies on the effects of γ-rays on aqueous solutions were reported by Shinohara et al (393) and Chitani et al (66).

In one of the most interesting reviews on the effects of radiation on PVA (423), a large number of authors studied the effects of γ-rays on aqueous solution of PVA. The gelation was determined at different concentrations of the samples of different degrees of polymerization.

The effect of Co-60 γ-rays on the physical properties of PVA fibers and films irradiated in water has been studied by Sakurada and Mori (344).

PVA films swollen in water show the same behaviour when irradiated with γ-rays in the presence of air (347). Gel formation occurs over a definite radiation dose. For the swollen films, remarkable differences were observed between the irradiation in vacuo and
in air, but for the aqueous solutions of higher concentration there were little difference between both cases.

With decreasing weight fraction, the concentration of radicals H' and 'OH produced by the radiolysis of water is increased, so that crosslinking is promoted. Whether water promotes crosslinking mainly by behaving as a plasticizer or the radicals produced by the radiolysis of water have large influence on crosslinking is still an unanswered question (333).

In the case of irradiation in air, if degradation occurs only because of direct effect on the polymer, it should occur independently of the weight fraction of the polymer. But it does not seem reasonable that the increase in mobility of chain segments may promote degradation. In this case oxygen plays a serious role, influencing degradation remarkably. However, since the amount of oxygen is constant at dry weight fraction range, it seems rather unreasonable that the degradation phenomena can be interpreted by the action of oxygen only. Thus it has been proposed that H\textsubscript{2}O', and HO radicals react forming peroxidic bonds, which then lead to degradation. At the same time by disproportionation, -CH = (OH) - groups are formed, which lead to degradation (128).

At the same time, Sakurada (340) showed that when aqueous solutions were irradiated with γ-rays in air at 25⁰C, scission of the main chain predominated.

Matsumoto (243) continued studies on the effect of oxygen during
γ-irradiation of aqueous PVA solutions. G-values for main chain scission are 0.2-0.6 and become larger at higher dose rate and concentration. Main chain scission occurs predominantly at the 1,2-diol linkages, partially at the other structures.

Ultra-violet and visible-light absorption spectra were used to observe trapped radicals in thick PVA films, which were irradiated with Co-60 γ-rays in air and nitrogen (473). The trapped radicals were very stable but they disappeared entirely when the irradiated films were treated in the temperature range above the glass temperature.

For dilute aqueous solutions of PVA with various degrees of polymerization, exposed to γ-rays in the absence of air, it was found that the gelation dose was inversely proportional to the degree of polymerization of samples used (336).

Below the critical concentration for gel-formation of PVA (which is 0.22%) radiation produced inter-molecular crosslinking, proved by turbidity, viscosity, acetylation, swelling, and X-ray measurements (337,338).

The formation of spherical microgels at doses lower than the gelation dose, was also confirmed by light scattering measurements by Matsumoto (244).

According to all the above information and especially according to Sakurada's and Danno's studies, it is concluded that the mechanism dominating the irradiation of aqueous PVA solutions is the
following:

**Activation**

\[
\begin{align*}
\text{CH}_2 - \text{CH}^- & \quad \text{OH} \quad \rightarrow \quad \text{CH}_2 - \text{CH}^* \quad \text{OH} \\
\text{H}_2\text{O} & \quad \rightarrow \quad \text{HOH}^*
\end{align*}
\]

**Free radical formation**

\[
\begin{align*}
\text{CH}_2 - \text{CH}^* & \quad \text{OH} \quad \rightarrow \quad \text{CH}_2 - \text{C}^* \quad \text{OH} \\
\text{HOH}^* & \quad \rightarrow \quad \text{HO} + \text{H}
\end{align*}
\]

**Gas evolution**

\[
\begin{align*}
\text{H} + \text{H} & \quad \rightarrow \quad \text{H}_2
\end{align*}
\]

**Recombination**

\[
\begin{align*}
\text{CH}_2 - \text{C}^* + \text{H} & \quad \text{OH} \quad \rightarrow \quad \text{CH}_2 - \text{CH}^- \quad \text{OH} \\
\text{HO} + \text{H} & \quad \rightarrow \quad \text{H}_2\text{O}
\end{align*}
\]

**Energy Transfer**

\[
\begin{align*}
\text{CH}_2 - \text{CH}^- + \text{HOH}^* & \quad \text{OH} \quad \rightarrow \quad \text{CH}_2 - \text{CH}^* + \text{H}_2\text{O} \\
\text{CH}_2 - \text{CH}^* + \text{H}_2\text{O} & \quad \text{OH} \quad \rightarrow \quad \text{CH}^- + \text{HOH}^*
\end{align*}
\]
Radical Transfer

\[ -\text{CH}_2 \cdot -\text{CH}^- + \text{OH} \longrightarrow -\text{CH}_2 \cdot -\text{C}^- + \text{H}_2 \text{O} \]

\[ -\text{CH}_2 \cdot -\text{C}^- + \text{H}_2 \text{O} \longrightarrow \text{OH} + -\text{CH}_2 \cdot -\text{CH}^- \]

Crosslinking

\[ -\text{CH}_2 \cdot -\text{C}^- + -\text{CH}_2 \cdot -\text{CH}^- \longrightarrow \text{CH}_2 \cdot -\text{C}^- -\text{CH}_2 \cdot -\text{CH}^- \]

Degradation

\[ -\text{CH}_2 \cdot -\text{CH}^- -\text{CH}^- \longrightarrow -\text{CH}_2 \cdot -\text{C}^- + -\text{CH}_2 \cdot -\text{CH}^- \]

Gas evolution in the case of PVA solution irradiated by $\beta$- or $\gamma$-radiation, has not been discussed but only in one or two publications. Danno (75) admitted that he found some problems with bubble formation and Bray (42) noticed the existence of the problems, proposed the assumption that they were hydrogen bubbles, but he did not solve the problem of production of materials without bubbles.

Only Petrov and Karpov (303) have extensively studied the gas evolution. For PVA they reported that, for dose of $36.5 \times 10^6$ roentgens, the gas yield was 1.81 molecules per 100 eV and that the gas composition was the following with $H_2$ predominating:

- $H_2$ 95.1%,
- $CO$ 4.3%,
- $CH_4$ 0.4%,
- $CO_2$ 0.3% (mole %)
No methods to avoid the gas formation were proposed.

Very often water is a damaging reactant responsible for polymer failure. Water is effective in the cleavage of both primary and secondary bonds. In general terms, chemical agents reacting with primary bonds result in changes in the macromolecular identity of the polymer. Crosslinking, chain scission, addition of attacking agents, or any combination of these, are the final results of primary bond rupture. Thus, crosslinking as that which occurs with the acidolysis of PVA yields intractable products of increased brittleness (124).

\[
\begin{array}{ccc}
\text{\text{-CH -CH-}} & \text{H}^+ & \text{\text{-CH -CH-}} \\
\text{\text{OH}} & & \text{\text{\text{OH}}} \\
\text{\text{OH}} & & \text{\text{\text{H}_2\text{O}}} \\
\text{\text{-CH_2 -CH-}} & & \text{\text{-CH_2 -CH-}}
\end{array}
\]

A full analysis of the effects of electron beam radiation on aqueous PVA solutions was done by Bray and Merrill (42,43), after some preliminary work of Bauer (28). The radiation effects on aqueous solutions of 5%, 10%, 15%, 20%, and 30% at 0°C, 30°C, 60°C, and 85°C under nitrogen and in air were studied as a function of dose. The molecular weight between crosslinks \( M_c \), characterizing the crosslinking density, was calculated from swelling experiments. It was shown that the higher the dose, the higher the crosslinking density.
Also with increase of concentration and temperature the crosslinking density decreases.

Bauer's data (28) are not of high accuracy for three reasons.

1) Use of thick samples (sometimes 5mm), which were not homogeneous in water content and crosslinking density.

11) Existence of entrapped bubbles in the tested hydrogels

111) Wide variations of irradiation temperatures

Bray's data (42) concern mainly the dependence of $M_c$ of hydrogels crosslinked under different irradiation conditions, on the dose and the temperature of irradiation and the concentration of the initial solution. Increasing dose, decreasing temperature, and decreasing initial concentration favored the crosslinking. In electron beam irradiation crosslinking, the presence of oxygen (irradiation under atmospheric conditions) did not affect the crosslinking density.

When PVA partially acetalized with glyoxylic acid was irradiated in air-free aqueous solutions, gelation occurred easily, and with lower critical concentrations, than in the case of pure PVA (334).

Both the rates of degradation and crosslinking for PVA in aqueous solution depended largely upon and were approximately proportional to the amount of vinyl-acetate units in its polymer chain (240).

Radiation induced crosslinking of two soluble polymers was studied by Matsuda et al (241,242). Among other polymer PVA and PVP co-
polymers were the most interesting for applications. The degree of crosslinking in these copolymers was studied by viscosity and solubility measurements. The gelation dose of a mixture of these polymers was proportional to the ratio of polymer dissolved in the solution.

Low dose radiation of PVA in the presence of methanol-water-allyl methacrylate (AMA) mixtures allows crosslinking of the polymers (31).

For the purpose of insolubilizing polymers and making them suitable for biomedical applications, Odian and Leonard (215,285) studied the effect of crosslinking of aqueous PVA solutions in the presence of the same allyl-methacrylate. They reported that the $M_c$ can be calculated as a function of the dose as:

$$M_c = \frac{0.48 \times 10^6}{G_D}$$

(4-1)

where the G value was calculated as 42.

A number of additives have been used for irradiation of deae-rated and aerated aqueous solutions of PVA (335). Among them, methanol, $K_2SO_4$, and NaCl did not have any influence on polymer reactions even at high concentrations. Thiourea, methyl ethyl ketone, ethanol, FeSO$_4$ and CuSO$_4$ were found to modify the rate of crosslinking as well as degradation. Thiourea was the additive which protected polymers against degradation considerably. It was proposed that thiourea
\[ \text{HN} = \text{C(NH}_2\text{)}\text{SH (abbreviated as RSH)} \text{ acts as follows via radical transfer and recombination:} \]

\[ \begin{align*}
\text{P} + \text{RSH} & \rightarrow \text{P} + \text{RS} \\
\text{H} + \text{RSH} & \rightarrow \text{H}_2 + \text{RS} \\
\text{HO} + \text{RSH} & \rightarrow \text{H}_2\text{O} + \text{RS} \\
\text{HO}_2 + \text{RSH} & \rightarrow \text{H}_2\text{O}_2 + \text{RS} \\
\text{P} + \text{RS} & \rightarrow \text{RSH} \\
\text{POO} + \text{RS} & \rightarrow \text{POOSR}
\end{align*} \]

From these reactions, the protective property of thiourea is quite understandable.

Dilute aqueous PVA solutions in the presence of additives were irradiated (γ-rays) and the viscosity was determined. Among the additives urea or NaOH did not vary too much the relative viscosity of PVA solutions after 10 hours of irradiation with dose rate of 13.2 rads/sec (412).

The critical doses of γ-irradiation required for gel formation in aqueous PVA solutions decreased when some additives like HCl, \( \text{H}_2\text{SO}_4 \), \( \text{H}_3\text{PO}_4 \) were added, and increased when NaOH or NH\(_3\) were added (277).

Addition of 5% methyl sulfate to a 5% aqueous solution of PVA inhibits the increase in viscosity with increasing radiation dose. The effect of various acids on the radiolysis of PVA has been briefly reported (228).
Watanabe (462) carried the irradiation experiments, of PVA-insoluble liquid systems. He used CCl₄ as the insoluble liquid. Before irradiation the PVA film was not swollen, but as the dose increased, the liquid molecules entered into PVA and the weight of the film was increased. Thus, here we have to deal with a perfect example of diffusion processes in polymers under irradiation (462).

Aqueous solutions of PVA irradiated with doses of 5-15 Mgrad in the presence of glycerol or isopropanol alcohol showed the formation of highly hydrophilic derivatives of PVA (472) according to the following scheme:

\[
\begin{align*}
\text{OH} & \\
\text{CH}_3-\text{C}-\text{CH}_3 & \\
\text{H} & \quad \text{H} \\
\text{CH}_3 & \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{CH}_2\text{OH} & \\
\text{H} & \quad \text{OH} \\
\text{OH} & \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{OH} \\
\text{CH}_2\text{OH} & \\
\text{OH} & \\
\end{align*}
\]

It is assumed that due to the formation of these derivatives, intermolecular crosslinking of PVA is somewhat restrained, as shown from viscosity measurements.
CHAPTER 5

RUBBER ELASTICITY THEORY

A. DEFINITIONS

Characteristic parameters that define the extent of crosslinking and are used for the evaluation of the mechanical behaviour of polymeric networks, are reported here.

An idealized crosslinked network can be formed by the reaction of \( N \) initial polymer chains of molecular weight \( M_n \). After crosslinking, there is a total of \( v \) crosslinked subunits which form \( v/2 \) crosslinked points. The characterization of the crosslinking density of a network is done by the average molecular weight between two crosslinks, which is designated as \( M_c \) (See Figure 5-1). The theory developed by Flory (104) assumes ideal tetrafunctional crosslinks, e.g., crosslinks where four different chains have combined.

It is obvious that the network will contain some subunits crosslinked at only one end. For this and other defects the theory distinguishes between the total number of subunits \( v \) and the effective one \( v_e \).

The effective number of subunits \( v_e \) can be calculated in terms of the number of perfectly and imperfectly paired chains \( v_o \) and \( v' \) and the functionality of them \( f \). For this purpose it is convenient to consider the formation of the network from the separate \( v_o + v' \) chains to take place in two steps.
Fig. 5-1: Crosslinked network chain.

In the first step chains are combined, forming \( v_0 \)-functional
connections between chain-ends. There are formed \( \frac{2v_o}{f} \) interlinkages
each binding \( 2/f \) linear molecules. The effective number \( v_e \) of these
interlinkages is taken to be equal to the number of them minus the
minimum number \( \frac{v'}{f/2-1} \) required to join the linear molecules into a
single structure. Thus:

\[
v_e = \frac{f}{2} \left( \frac{2v_o}{f} - \frac{v'}{f/2-1} \right)
\]  

(5-1)
or

\[ v_e = v_o \left[ 1 - \left( \frac{v'}{v_o} \right)(\frac{f}{f-2}) \right] \]  \hspace{1cm} (5-2)

Recall that \( \frac{v'}{v_o} = \frac{M_c}{M_n} \) so that the expression becomes

\[ v_e = v_o \left[ 1 - \left( \frac{M_c}{M_n} \right)(\frac{f}{f-2}) \right] \]  \hspace{1cm} (5-3)

B. STUDY OF HYDROGEL NETWORKS

The theoretical study of a hydrogel network has the purpose of revealing the structure and configuration of the chain, by use of the appropriate theoretical models.

The knowledge of the crosslinking density (in other words the effective number of crosslinked subunits \( v_e \) and/or the molecular weight between crosslinks \( M_c \)) is of great importance because of its effect on the mechanical and chemical properties of the produced materials and the behaviour of them upon practical applications.

It is important to have techniques to characterize the structure parameters, such as the cross-link density, the distribution in the length of chains between cross-links, the perfection of the network and the amount of polymeric material not attached to the network. The characterization of the structure of a cross-linked polymer is much more complex because of the many types of networks, in-
cluding regular, highly irregular, tightly or loosely crosslinked and highly imperfect ones with molecules trapped, intramolecular loops, etc. Thus the best that can be done with most networks is to get some kind of an average crosslinking density and the perfection of the network!

Methods of studying network structures include (279, 431):

(i) chemical methods
(ii) swelling methods
(iii) elastic modulus tests
(iv) creep experiments
(v) mechanical damping
(vi) shift in glass transition temperature

In order to analyze the material for its crosslinking density, use of mainly two theories is made, the swelling theory and the rubber elasticity theory.

C. EQUILIBRIUM SWELLING THEORY

If an uncrosslinked polymer is soluble in a liquid, then the same polymer when crosslinked will swell in the liquid.

Three types of data can be obtained from swelling experiments.

(i) the uncrosslinked amount of polymer, the so-called sol fraction.
(ii) the molecular weight of the sol fraction
(iii) the amount of swelling of the gel fraction
Swelling is generally expressed as a swelling ratio $Q$ (by volume)

$$ Q = \frac{\text{Volume of swollen gel}}{\text{Volume of unswollen (relaxed) gel}} $$

(5-4)

For typical vulcanized rubbers $Q$ is of the order of 10 in good solvents and $M_c$ is around 5,000.

As the network is swollen by the absorption of solvent, the chains between the crosslinks assume an elongated configuration, so that a force opposite to the elastic retractive force develops. As swelling proceeds, this force increases, whereas the diluting force decreases. Finally, a state of equilibrium swelling is reached, at which both forces are in equilibrium.

When proceeding to an evaluation of the crosslinking density of a swollen network, we have to consider the existence of the ordinary free energy of mixing $\Delta F_m$ and the elastic free energy $\Delta F_{el}$ consequential to the expansion of the network structure. These two free energies are expressed in terms of thermodynamic and elastic parameters of the system polymer $-\text{H}_2\text{O}$. The full development of the theory and the calculations have been included in Appendix B.

The final expression for the calculation of the molecular weight between crosslinks in a swollen network, where the crosslinks were introduced in the solid state is, according to Flory's theory (104):
\[ \frac{1}{M_c} = \frac{2}{\bar{M}_n} - \frac{\sqrt[3]{v_2, s} (1-u_2, s)+u_2, s+\chi_1 u_2^2, s}{(u_2, s)^{1/3} - \frac{u_2, s}{2}} \]  

(5.5)

where \( u_2, s \) is the equilibrium swollen volume fraction at the swelling temperature, \( v_1 \) and \( \bar{v} \) are the molar volume of solvent and the specific volume of polymer respectively and \( \chi_1 \) is the Flory's chi factor, a polymer-solvent interaction parameter of which more will be said later.

For reasons of simplification and for low degrees of crosslinking (i.e., large \( M_c > 10,000 \)), the swelling ratio \( Q \) already defined is quite high in a good solvent. In this case \( u_2, s^{1/3} \) is considerably greater than \( \frac{u_2, s}{2} \) and we many omit it as a first approximation. (Remember that \( Q = \frac{1}{u_2, s} \)).

Then the previous equation can be simplified to:

\[ Q^{5/3} = \left( \frac{\bar{v}}{v_1} \right) \ast \frac{\bar{M}}{2\bar{M}_C} \ast \left( \frac{\frac{1}{2} - \chi_1}{1 - \frac{\bar{M}}{M}} \right) \]

(5-6)

This equation shows that the swelling of a network depends on the quality of the solvent (chi \([\chi]\) factor) and on the extent of crosslinking \( \frac{M}{M} \) (ratio \( \frac{M}{M} \)).

The above expressions do not apply in the case of a swollen network where the crosslinks have been introduced in the solution state (in the presence of a diluent). In this case the volume fraction of the polymer in the relaxed state, before swelling, \( v_{2,r} \) has to be taken in account, which \( v_{2,r} \) in the first development (Appendix B) was taken as one.

The theory modified for the case of hydrogels has been included in Appendix D. The final expression of the molecular weight between
crosslinks has as follows, according to Bray and Merrill (42):

\[
\frac{1}{M_c} = \frac{2 \ln \left( \frac{1}{u_2, s} \right) + u_2, s + \chi_1 u_2, s}{M_n} - \frac{1}{v_1} \frac{u_2, s}{u_2, r} \left[ \frac{\frac{u_2, s}{u_2, r}}{1/3} - \frac{1}{2} \left( \frac{u_2, s}{u_2, r} \right) \right]
\]

(5-7)

This equation vanishes to the one developed by Flory when \( u_{2, r} = 1 \).

The importance of the \( \chi \) factor

From the above developments, it is evident that the swelling ratio depends on the polymer-solvent interactions. These interactions are expressed in Flory's theory by the chi factor.

The chi(\( \chi \)) factor is defined as:

\[
\chi_1 = \frac{B v_1}{RT}
\]

(5-8)

where \( v_1 \) is the molar volume of the solvent, \( T \) the temperature and \( B \) represents the interaction energy density, characteristic of the solvent-soluble pair, and which \( B \) is given as:

\[
B = \frac{Z \Delta w_{12}}{v'_s}
\]

(5-9)

where \( \Delta w_{12} \) is the change in energy for the formation of an unlike contact pair, \( v'_s \) is the molecular volume of a segment and \( z \) is the total number of segments. \( \Delta w_{12} \) is independent of \( T \), that is, no entropy contribution is contained in \( \Delta w_{12} \). Then \( \chi_1 \) is inversely pro-
portional to $T$.

The chi factor may be related to two more thermodynamic parameters $\kappa$ and $\psi$ under conditions of dilution such that a polymer concentration is around 1 to 5%. In the thermodynamic theory of polymer solutions the heat and entropy of dilution are expressed as:

$$\Delta H_1 = RT\kappa_1 \nu_2^2$$  \hspace{1cm} (5-10)

$$\Delta S_1 = R\psi_1 \nu_2^2$$  \hspace{1cm} (5-11)

where $\nu_2$ is the volume fraction of the solute (polymer), $\kappa_1$ (kappa) factor is the enthalpic parameter and $\psi_1$ (psi) factor is the entropic parameter. Within the limits of Flory's theories (104) validity the $\chi_1$ can be related to $\kappa_1$ and $\psi_1$ via the equation:

$$\chi_1 = \kappa_1 - \psi_1 + \frac{1}{2}$$  \hspace{1cm} (5-12)

Frequently it is preferred to use as a parameter the theta-temperature defined as:

$$\Theta = \frac{\kappa_1 T}{\psi_1}$$  \hspace{1cm} (5-13)

At the temperature $T=\Theta$, $\kappa_1=\psi_1$ and then $\chi_1=0.5$. This is in accordance with the definition of the theta-temperature, because at this temper-
nature the segment-solvent interactions are zero.

D. RUBBER ELASTICITY THEORY

The rubber elasticity theory has been developed in order to explain the data of a standard tensile experiment and to determine the crosslinking density, expressed by the molecular weight between cross-links $M_c$.

The theory of rubber elasticity has been discussed in Appendix C for isothermal deformations of a sample. The following assumptions have been made during the development of this theory.

1. The cross-links have been introduced randomly into the amorphous polymer in the absence of any solvents.

2. Validity of the Gaussian equation for the conformations of the subunits is assured by the assumption that the $n$ subunits of the network are long enough, the crosslinking degree is not excessive and the volume effects negligible.

3. The deformation of the sample occurs at constant volume.

4. The contributions of the effective subunits to the total retractive force are additive.

5. The deformation of the sample is a completely reversible process in the thermodynamic sense.

With these assumptions it can be proven (see Appendix C) that the force per unit initial cross-sectional area is a function of $\alpha = \frac{1}{\alpha^2}$

with $\alpha = \frac{L}{L_0}$.
\[ \tau = RT \left( \frac{\gamma e}{v} \right) \left( \frac{r_i^2}{r_o^2} \right) (\alpha - \frac{1}{\alpha^2}) \]  

(5-14)

Earlier theories, like Flory's first development (113, 114) had considered that the parameter \( \frac{r_i^2}{r_o^2} \) is equal to one.

The same equation can be written in the following way according to Treloar (430).

\[ \tau = RT \left( \frac{\rho}{M_c} \right) \left( 1 - \frac{2M}{M} \right) (\alpha - \frac{1}{\alpha^2}) \]  

(5-15)

In this way it can be applied to the case of crosslinked swollen networks, where the density \( \rho \) is known.

The parameter \( \frac{r_i^2}{r_o^2} \) is called the "front factor" and it enters the expression of the Helmholtz free energy.

The term \( r_i^2 \) is the mean square end-to-end distance for the network subunits in the undeformed isotopic state and \( r_o^2 \) is the corresponding mean-square end-to-end distance for the undeformed subunits in the absence of crosslinks. The term \( r_i^2 \) depends upon the volume of the network, whereas \( r_o^2 \) depends upon the bond length and angles.
temperature and potential hindering rotation.

The above mentioned equation does not apply in the case of hydrogels, where the crosslinks were introduced in the presence of solvent. In that case another expression has been developed by Silliman and Merrill (394). The full analysis of the development of this equation is given in:

\[
\tau = \frac{RTQ^{2/3}}{M_C} \left( 1 - \frac{2M}{M_n} \right) \left( \frac{r_i^2}{r_o^2} \right) (\alpha - \frac{1}{\alpha^2})
\]  

(5-16)

The equation is analogous to an equation derived by Verkhoshina et al (456) for crosslinked swollen polymers and which states that:

\[
M_C = \frac{\rho RT}{\tau_{2,5}^{1/3}} \cdot \left( \frac{r_i^2}{r_o^2} \right) (\alpha - \frac{1}{\alpha^{3/2}})
\]  

(5-17)

In any way, the variation of the above mentioned equations is not significant and either one can be used for the characterization of \( M_C \).

Notable is the problem of unknown functionality of the crosslinks, i.e., values of \( f \) other than 4 by reason of the method of crosslinking with dialdehydes (394).

A further discussion on the thermoelastic properties of networks in swelling equilibrium can be found in (25, 26). Jackson studied the crosslinked PVA networks and their elastic properties and he de-
veloped a network topology theory (167).

In the application of the rubber elasticity theory to the study of swollen cross-linked networks, it should be remembered that factors like finite extensibility of the chains, stress crystallization and the presence of microcrystalline regions violate the basic assumptions of theoretical development and cause non-Gaussian behaviour.

Pines (305) showed that the structural make up of a PVA network is strongly reflected in its time dependent and equilibrium mechanical behaviour. However a direct predictive relation can not be given at this time. The findings point toward a possible occurrence of supramolecular ordering and support the belief that a randomly cross-linked Gaussian network model is often inapplicable. For phase separated and/or structured gels the structure-property relations definitely differ from those based on the Gaussian model.

E. NETWORK STRUCTURE AND DEFECTS

We tried to review the current status of our knowledge of non-crystalline polymer networks. The term "non-crystalline" is preferred to the term "amorphous" because it is the belief of many authors (92) that networks contain somewhat more local ordering or nonhomogeneity than suggested by the common Flory picture of a randomly crosslinked mass of macromolecular chains. At the beginning, it is impossible to give the definition of an ideal network, so that we can treat any real network by reference to this definition. The most acceptable defini-
tion of an ideal network is a collection of Gaussian chains between f-functional junction points (crosslinks).

In non-swollen networks the chains may be (i) in an unstrained state (normal degree of coiling), (ii) in a supercoiled state, (iii) in an expanded state, resulted from a crosslinked network swollen in a mixture of monomers, subsequently polymerized.

Real polymer networks always deviate from the accepted definition of an ideal Gaussian network. Imperfections can come from deviations of the original conditions of crosslinking, from crosslinking of already existing crosslinked networks and from endlinking.

Imperfections are generally

(i) pre-existing order
(ii) network defects
(iii) inhomogeneity
(iv) phase separation

Under the term pre-existing order, there are included many imperfections like crystallites, exhibiting three dimensional order, non-randomly oriented segment sequences, artificially oriented chains and associations of similar groups yielding micellar and globular orders (supermolecular order). Crosslinking has the effect of fixing structural features of the state existing at the moment of reaction.

Extensive experimental support for the existence of equilibrium chain ordering in amorphous polymers, based mainly on electron microscopy, has been presented by Kormanovskaya and coworkers (for example,
Fig. 5-2: Network defects
199,200). On the other hand, it has been always a problem to define the point where an amorphous network starts becoming crystallized (oriented). Because of possible variations of temperature, some non-crystalline networks may contain slightly ordered regions, that cannot be called crystallites, but that are still imperfections.

Clustering (aggregation or association) as a result of dissimilar parts within one chain molecule is well-known especially in the field of biopolymers. Association of various dissimilar parts of chains in solution as well as in bulk can be another reason for pre-existing order.

During aging of solutions, polymolecular micelles, parallel cylinders with ordered chains and sheets are gradually developed, which affect the final network.

Network defects include closed loops, unreacted functionalities, and permanent chain entanglements as shown in Fig. 5-2. Thus, the effect of defects is by no means simple.

Macro- and microsyneresis is the result of another imperfection, e.g., phase separation. Phase separation happens, when the critical value of crosslinking density is exceeded because the amount of the solvent in the gel exceeds the maximum swelling capacity of the gel in the same solvent and under the same conditions.

The final network is a composite one, with imperfections, because crosslinks were introduced at different volumes of the network phase (macrosyneresis). Slow relaxation of the network in comparison
with the rate of establishing local polymer-solvent phase equilibria is one of the reasons for the phenomenon of microsyneresis. In both cases the non-equilibrium states of the network chains are locally stressed. Microsyneresis is expected to occur more in lightly cross-linked networks, whereas macrosyneresis is expected in densely cross-linked networks. In many cases microsyneresis may be accompanied by strong hysteresis effects (supercooling and superheating) and/or the formation of a new phase.
CHAPTER 6

THEORY OF CRYSTALLIZATION OF HYDROGELS

A. CRYSTALLIZATION OF POLYMERS

In the early 1950's it was first proven that many organic polymers can crystallize from dilute solutions as single crystals. Observations of these crystals led to the abandonment of the fringed micelle model in favor of the folded chain one. Several texts survey the crystallization theory and behaviour as well as the molecular structure of single polymeric crystals. Among them Mandelkern (232) is a very good reference for the interested reader. Crystallization of a polymer can happen in three different ways (475).

(i) Crystallization from the melt usually takes the form of spherulites. Spherulites are crystallites formed from a peculiar growth with a preferred chain orientation relative to a center (nucleus). Polarized light reveals that the polymer chains are oriented tangentially around each nucleus, that the area consists of a multitude of crystallites and that spherulites do not exceed 100μ in diameter.

(ii) Crystallization from dilute solutions often yields lamellar single crystals.

(iii) Crystallization of polymer in a polymer-diluent system. This case refers to gels and crosslinked networks and will be discussed later in this section.
Coming back to the crystallization from dilute solutions and the
general features of the crystallinity theory, we must notice that the crys-
tals are about 100 Å thick, while the length of a polymer chain is
often 10,000 Å or longer. The chain direction in lamellae growth
in solution is nearly parallel to the direction of smallest thick-
ness. According to this hypothesis the folded-chain model of crystal
structure was proposed (See Fig. 6-1). The nature of the surface of
single crystals may well be dependent on the crystallization conditions.
Flory has demonstrated that re-entry is the only way of satisfying
the different density requirements of the crystalline and amorphous
regions for bulk or single crystal materials (112).

Many investigators, studying the kinetics of crystallization
have tried to fit the crystallinity-time behaviour of polymers crystal-
lizing from the melt to the Avrami equation (35).

\[ X(t) = 1 - \exp \left( Kt^n \right) \]  \hspace{1cm} (6-1)

where \( X(t) \) is the crystallinity as a function of time and \( K, n \) are
constants. The last constant \( n \), is an integer number whose value
depends on the time dependence of the nucleation rate and on the
growth morphology.

This method of analysis of the results reveals the existence of
two regions in the curve of crystallinity-time. Primary crystalliza-
tion corresponds to radial growth of sherulites, while secondary crys-
Fig. 6-1: Crystallite arrangements
tallization (which is not found in all the crystalline polymers) corresponds to perfection and thickening or new crystallization in the spherulites.

According to the theory of the formation of polymer crystals in the shape of thin lamellae (100-300 A) developed by Hoffman (151), the molecules must be folded, since the molecules have axes perpendicular to the large flat faces of the crystal. Of the possible models for such crystals, the author favors the "regular folding" or "adjacent re-entry fold" model, which has a sharp phase boundary against the liquid or amorphous phase, rather than the "random re-entry fold" model, with a diffuse phase boundary. The older model of a "fringed micelle" also has a diffuse phase boundary. The author supports his model by diffraction measurements and other data. In the crystallization of a whole (non-fractionated) polymer, short chains which cannot fold are rejected from the lamellae and form the amorphous material between lamellae. The critical chain length which can undergo folded-chain crystallization depends on the temperature, i.e., the degree of supercooling, in a reciprocal way. Molecular entanglements do not interfere seriously with folded-chain crystallization. Short chains have no entanglements and long chains are either helped to disentangle themselves by the rejected short chains in the boundary, or, in the high polymer fraction devoid of short chains, the forces of crystallization acting on a point of the chain are sufficient to unfold it. During aging, the lamellae can increase their thickness
2-5 fold, which raises their melting point.

The rate of a primary polymer crystallization process is strongly temperature dependent. The thickness of the lamellae, determined from low angle X-ray scattering, electron microscopy or melting point data, decreases with increasing crystallization undercooling.

The tendency of a polymer to crystallize is enhanced by regularity and polarity. Thus generally linear, isotactic polymers are crystalline while atactic, branched, non-linear polymers are not. However the isotactic form is not always the most crystalline. A classical example is PVA for which more will be discussed later. Polarity favors crystallizability.

The rate of crystallization drops as the molecular weight decreases and on going from linear to space polymers.

B. CRISTALLINE AND THERMAL PROPERTIES OF PVA

The physical properties of Poly(-vinyl alcohol) that have to do with its crystalline structure and its thermal behaviour were not included in the section concerning the physical properties of PVA, but they will be extensively discussed here, because they are very important in the crystallization process that will be discussed in this section. However for more extensive discussion the reader is directed to (451).

Poly(vinyl alcohol) is crystalline and its crystalline melting range is between 220°C - 240°C. Bessonov and Rudakov (32) estimated accurately the melting point as 232°C. Mochizuki (267) found
it as 223°C. According to X-ray diffraction experiments of heat-treated PVA films, a selective unipolar orientation of the crystallites disappeared close to these temperatures (266).

PVA is usually about 20-35% crystalline but with drawing or annealing above \( T_g \) its crystallinity can increase up to 70%. This may increase significantly its mechanical properties.

The glass transition temperature of PVA has been reported at 85°C for dry PVA films. However in the presence of water the glass transition temperature decreases significantly. Glass transition temperatures were determined by Packter and Nerurkar (294) by refractometry using an Abbe refractometer over a wide-temperature range of \( T_g +30^\circ \) to \( T_g -30^\circ \). \( T_g \) was determined as the break in n-T plots. Figure 6-2 shows the glass transition temperature \( T_g \) in PVA-H\(_2\)O systems.

The second-order transition temperatures of swollen PVA films were studied by Sone and Sakurada (407,408). Figure 6-3 shows the variation of the observed \( T_g \) and \( T_g' \) as a function of weight percentage of PVA.

The second order transition points of PVA and its molecular weight dependency were measured by the dilatometry method by Ito (165). A new temperature transition range, near the temperature of -15°C was found besides the well-known transition ranges near 70°C and 130°C.

Single crystals of PVA were first formed by Tsuboi and Mochizuki (434) by isothermal crystallization from their solution.

The crystals belong to the monoclinic system with crystallographic parameters \( a=5.43+0.01\AA, \ c=7.81+0.02\AA, \) and \( \beta=91^\circ \ 30'+15' \). A unit
Fig 6-2: Glass transition temperatures in PVA-H\textsubscript{2}O systems.
Fig 6-3: Second order transition temperatures of PVA in PVA-H₂O systems
cell consists of two monomers (330, 332, 437).

The lamella thickness estimated from the length of the shadow of the electron micrograph is around 100-150Å.

Single crystals of PVA were obtained by the temperature-gradient method from various solvents, such as triethylene glycol, 1,3-butanediol and 1,2-propanediol (268). The single crystals were parallelogramic platelets with a ratio of length to width of about 6. The lamellar thickness of these crystals was 120±10Å.

In a series of later publications Tsuboi & Mochizuki (435-444) studied extensively the ideas of single crystals of PVA. PVA crystals were prepared by isothermal crystallization from 0.3% solution in triethylene glycol (435). The acute angle of the crystals was 55° and the lamella thickness 100-50Å. In addition to the lamellae, modifications of them (twins) are regularly formed (436). The crystal system has a tendency to change from monoclinic to orthorhombic upon electron bombardment. They are fractured by ultrasonic irradiation (438). Upon treating them to 200-220°C particles attached to the longer sides of the crystals disappear (439). The effect of annealing on the morphology of PVA single crystals can be studied by electron microscopy and small angle X-ray. Various kinds of fractionation occur when single crystals form in aqueous solutions. For a number of particles on the edge of the lamellas dissolution was completed at 65°C (440).

Single crystals of PVA prepared from different polymers via hydrolysis had the same structure as above mentioned. Only PVA prepared from
poly-(vinyl-tert-butyl-ether) forms fibrils (441).

Parallel lamellas were obtained from PVA crystallized from solutions in poor solvent at temperatures above 180°C, while spherulitic structures were formed from PVA crystallized in polyhydric alcohols at 130-175°C (442). Birefringence measurements suggest that the molecular chains are, on the average, tangentially oriented (443). Well defined crystals of PVA are also produced by saponification of PVAc at the temperature just below the cloud point of PVA in triethylene glycol (444).

A large part of the experimental material existing in the literature testifies in favor of the ability of PVA to crystallize. An attempt has been made by Bessonov and Rudakov (32) to solve this problem by microscopic studies at high temperatures and investigation of the temperature dependence of the density and the modulus of elasticity.

When crystalline polymers are cooled from a melt they exhibit birefringence patterns visible in the microscope. When heated to the melting point these structures disappear. PVA films studied on an MP-3 polarizing microscope with long focusing objectives and a heated stage, showed no birefringence in the plane of the film (32). When heated to 150-160°C, they showed small birefringence, which disappeared completely at 230°C.

After each heating the light intensity passing through the sample when it was cooled again was less than in the previous cooling. This was explained by the fact that crystallization of PVA becomes difficult as the heat treatment time is increased (32).
Packter and Nerurkar (295) have noticed spherulite growth when crystallizing PVA films from concentrated polyol solutions. The final size of the spherulites increased as the temperature of evaporation increased from 120 to 180°C.

The incipiently crystallized PVA films have a small degree of crystallinity (about 30-35%). In high strength fibers, stretched at 235°C, the density is such that the degree of crystallinity can be almost 70-75%. On the other side, PVA films almost totally amorphous were prepared by a freeze-drying process (164). The crystallinity of these films was 13%.

The amount of crystalline phase in PVA may be increased by oriented tension near the melting point.

The molecular mechanism of transition of PVA from non-oriented to oriented state, has been studied in (381).

As mentioned by Bunn (50,51) the side hydroxyl in PVA is so small in size that it can be interchangeable with the hydrogen atom in the crystalline lattice. Hence, the stereoregularity has little effect on the X-ray pattern of PVA. However, the arrangement of hydrogen bonding in PVA should be different depending on the tacticity of PVA (272).

In a planer zig-zag chain, isotactic configuration favors intramolecular hydrogen bonding, while syndiotactic configuration favors interchain hydrogen bonding. Hence the interchain force in the crystalline part may vary with tactic structure of PVA. Consequently, the cohesion of the crystalline portion in PVA may be dependent on the stereoregula-
rity, although no difference can be observed in X-ray examination.

The increases in melting point and water resistance of essentially syndiotactic PVA seem to provide experimental verification of this view. The experimental result that isotactic PVA shows only very poor crystallinity also indicates the importance of the interchain hydrogen bonding to the crystallization of PVA.

In recent years the stereoregularity of PVA as a function of the method of production has been stressed (71). Also the dependence of crystallizability on the stereoregularity has been the subject of recent literature (139). The isothermal crystallization temperature and the dissolution temperature have been studied and related. The rate of crystallization decreases drastically with an increase in crystallization temperature. The presence of detectable single crystals in the crystallized samples had no effect on the observed dissolution temperature. The crystallinity calculated from the density of the PVA precipitated from dilute solution in triethylene glycol was 42%. Although the overall degree of crystalline perfection of this PVA is low, the linear relationship between $T_s$ (dissolution temperature) and $T_c$ (temperature of crystallization) and the formation of definite shaped single crystals when crystallized from dilute solutions suggests that PVA crystallizes in the same manner as other semicrystalline polymers (185).

The problem of crystallizability of atactic or stereoregular PVA has been widely discussed in a review article by Fujii (117). It is the author's idea, based on much evidence on the literature, that stereoreg-
gular structures do not favor crystallizability. In addition, Fujii (117) reports that the atactic is the most crystallizable form, the syndiotactic is somewhat less crystallizable, whereas the isotactic form does not favor crystallizability.

The crystal structure of atactic PVA has been studied by a number of investigators and the model proposed by Bunn (50) is generally accepted. According to this model PVA is the only polymer, where its atactic form is crystallizable, because the hydroxyl group can easily substitute for the hydrogen group and there is no steric hindrance. It was shown that freeze-dried PVA samples (which are known to be almost 90% amorphous) are predominantly isotactic. Kenney and Willcockson (186) showed that within the range 100-180°C, crystallization proceeded in the order atactic > syndiotactic > isotactic. According to their results, the increased syndiotactic structure did not appear to lead to higher crystallinity. Predominantly isotactic PVA is readily soluble in water when free from crosslinking and heat-treatment is not effective in rendering it water-resistant (103).

It seems also that the increase in crystallinity of PVA caused by the decrease in the polymerization temperature of PVAc is largely attributed to the decrease in the 1,2-glycol content (390). The effects of the 1,2-glycol groups of PVA and the residual acetyl groups, on the crystallizability of PVA films, prepared from PVA solutions has been studied by Yamoura (469).

Highly stereoregular polyvinyl alcohols were prepared and found
to have lower crystallizability than the atactic PVA (411). They also showed higher solubility in water. Other workers (119) studied the water resistance of crystalline PVA samples of different stereoregularity and found the same trend. In earlier experiments Fujii et al (118) had reported the same conclusion, as well as Moritani et al (270).

**Properties of PVA gels**

The gel formation process should not be confused to that of a polymer crystallization. Depending on the solvent nature and the crystallizability of the polymer in it, both crystalline and amorphous PVA gels are formed. They do not differ (in some cases) in their melting point, the energy of bond formation in the network and the equilibrium rigidity. Rogovina et al in a very recent paper reported the heats of gel formation for different solvent-PVA systems as in Table 6-1. (319).

Gelation of aqueous PVA solutions is clearly related to the tacticity of the polymer (127,230). Aqueous solutions of isotactic (predominantly) PVA were stable and no gelation was observed after prolonged standing (117). The mechanism of gelation is apparently associated with the formation of some orders with intermolecular forces, probably hydrogen bonding, that are favored in syndiotactic structures. The apparent melting point of the gels can be calculated from the following equation (229,230):

\[
\log C = \frac{\Delta H}{RT} + K
\]  

\((6-2)\)
<table>
<thead>
<tr>
<th>Diluent</th>
<th>Composition</th>
<th>Concentration</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H$ kcal/mole</th>
</tr>
</thead>
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<td>40-60</td>
<td>5</td>
<td>77</td>
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<td></td>
<td></td>
<td>10</td>
<td>89</td>
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<td>20</td>
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<td></td>
</tr>
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<td>82</td>
<td>13.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>94</td>
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<td></td>
<td></td>
<td>10</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>glycerol-water</td>
<td>80-20</td>
<td>2</td>
<td>96</td>
<td>17.00</td>
</tr>
<tr>
<td></td>
<td></td>
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<tr>
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</tr>
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</tbody>
</table>
where C is the polymer concentration and k is constant. For atactic PVA, $\Delta H = 8.8$ kcal/mole, corresponding to one or two hydrogen bonds.

Study of the melting point and gelation temperatures provides the possibility of ascertaining the nature of the intermolecular interaction from the heats of melting and gelation (122). The bond energy found from $T_{gel}$, equal to 5.72kcal/mole, is not greater than the normal energy of a hydrogen bond, whereas the energy of 18.3kcal/mole calculated from $T_m$ indicates that the junction points of the gel network consist of 2-3 hydrogen bonds. Thus the gel network consists of an amorphous matrix in which crystalline formations are included (123).

A value of $\Delta H = 15.5$ kcals/mole was calculated from gelation in 15% water-glycerine (7:3) solutions of PVA (126). This value indicates that the joints of the gel network are formed by means of at least two hydrogen bonds.

From 8% aqueous PVA solutions gelled at room temperature, $\Delta H$ of 8.8 kcal/mole was obtained, which corresponds to one or two hydrogen bonds (229).

Gels of semicrystalline polymers may exist in various physical states, dependent on the concentration and temperature. Introduction of solvents lowers the melting point and glass transition temperature of the gels without essentially changing the nature of the dependence of the thermodynamic functions on temperature. X-ray diffraction diagrams of PVA and 16% and 20% gels of PVA in a mixture of glycerol (75%) and water (25%)
have been taken (251). They show that in a certain concentration range, gels of crystallizable polymers contain structural elements or supramolecular formations in which a high degree of order in the arrangement of the macromolecules persists.

Gubenkova et al (134) studied the crystallization of PVA from 10% solutions in a mixture of water and glycerol.

In recent papers (208,209) experiments were described showing that gels, formed by PVA swollen in water have a freezing point one or two degrees below zero.

The gelation temperature of other gels has been reported by Maeda et al (230).

Similar results showed that in a region of concentration higher than a certain critical value, PVA acts as being in a plasticized solid, the bond energy being calculated to about 12 kcals/mole (398).

The mechanism of gel formation and the structure of PVA gels from aqueous solutions of them has been studied by Shibatani (389). The formation of junctions can be treated as a binary association of free cross-linking sequences with an activation energy of 13.3 kcals/mole.

Effects of temperature and concentration on the heat of solution of aqueous glycerol gels of PVA have been presented by Meerson (253).

X-ray analysis by Sone et al (399,400) showed that crystallization takes place in PVA gels, because of aging. This phenomenon of retrogradation can be checked by the degree of swelling in water, which
decreases because of aging and it approaches a constant value when the
temperature is constant.

The effect of the temperature on the specific heats of amorphous
and crystallizing polymer gels has been studied by Meerson et al. (254)
and their results confirm that the nature of gel fusion depends on the
phase state of the original polymer, because of the different structures
of the gels.

C. **CRYSTALLIZATION IN POLYMER-DILUENT SYSTEMS**

Crystallization of many polar polymers is associated with strong
kinetic hindrances, on account of which the production of a microscopic
crystalline phase in the form of spherulites or single crystals is
practically impossible. The usual method of crystallization of
difficult to solubilize polymers, consists of crystallizing them in the
presence of a plasticizer, which is a poor solvent for the given polymer.

In the case of PVA and as it was reported in the previous chapter,
it acquires rather compact confirmations in aqueous medium, which do
not promote the formation of extended critical nuclei of crystallization,
and yet, only such crystalline bundles can form crystals. In the
best case, microcrystalline formations may arise. Thus, hindrances of
crystallization of PVA in aqueous solutions may be due to hydrophobic
sites of the PVA chains.

Although PVA has low resistance in water and is completely soluble
in hot water, its resistance to water may be highly improved when films
or fibers from it are subjected to heat treatment. This happens due to the formation of crystallites that normally do not dissolve in water.

As X-ray studies have shown the unit cell for a given crystalline polymer is occupied by a small number of structural units (110). A usual assumption is that the structural units are arranged with perfect regularity in the crystallites so that the configurational entropy may be regarded as zero.

The crystallites are much shorter than the polymer molecules and a single molecule may pass through several crystallites separated by amorphous regions.

The state of an unoriented semicrystalline polymer will be defined by the degree of crystallinity (x) and the average dimension of the crystallite (especially its length \( \xi \)).

Mandelkern (233) posed the problem of the size of crystallites in the chain direction. He found that as the molecular weight increases the size of the crystallites increases too. However despite the wide variation in the crystallite sizes and the relation to the extended chain length, the character and appearance of the crystallites remain essentially unaltered over a molecular weight range.

When a crosslinked polymer, like the PVA network produced via irradiation, is heat-treated, the chains are aligned and they form sites of oriented chains of higher density. These sites are called crystallites and they act as additional crosslinks in distributing the stress applied on a network, not only between the initial crosslinks but also
between the new crystallites. The change because of heat-treatment and the formation of crystallites affect the density and the volume of the network as it will be seen later. Figure 6-4 shows a representation of a crosslinked crystallized network.

The formation of the crystallites in crosslinked polymers depends on the crosslinking density, i.e., the molecular weight between crosslinks $M_c$, and very dense crosslinked polymers do not crystallize under any conditions. Thus an internal relation between the minimum crystallite length $\xi$ and the length between two crosslinks $M_c \times \frac{m}{w}$ (where $w$ is the length of one unit and $m$ is the molecular weight of a unit) controls the formation of crystallites in a network that is heat treated.

Flory (110) has developed the theory of crystallization in high polymers and systems of polymers with diluents. The derivation is quite lengthy and will not be discussed. Some basic points have been included in Appendix F. The theoretical development of crystallization in polymeric networks (crosslinked) with diluents is very complicated and has not been reported.

The heat-treatment introducing crystallinity can be either mild or vigorous and depending on the conditions of drying, the degree of crystallinity and length of crystallites are expected to be different. In the case of crosslinked polymeric networks with a diluent, a slow drying rate process has the purpose of increasing the percentage of the
Fig. 6-4: Structure of a crosslinked semi-crystalline polymer
polymer in the drying system. At the last stage of this process crystallization can start. A fast drying rate process, usually an annealing process can lead to rapid formation of crystallites. Porter (308, 385) has treated mathematically the drying process of a gel as a heat-mass transfer phenomenon. He has developed theoretical models for films and tubings dried. His theory is not applicable in the final stage of drying, during which he should take in account the fast change of the density of the "solid" part of the gel (i.e., the increase of crystallinity). However, his model is of theoretical interest to this thesis because it is the only one to calculate the local strain and the maximum bending stresses on a film being dried in a dish in contact with an inert surface (glass). If the maximum bending stress exceeds the yield stress of the film, then the film will crack. However in most of the cases with PVA hydrogels the gel is "curling" and becomes useless for further applications.

In the development of Porter's (308) theoretical model the diffusivity of water through PVA is of great importance.

Markley (236) found that the steady state diffusivity of water vapor through PVA is highly dependent upon the concentration of water in the polymer. This dependent is of the form

\[ D = D(0)e^{\gamma c} \]  

(6-2)

where \( \gamma \) is a function of temperature increasing as temperature increases.
The change of fine structure of PVA film during heat-treatment was investigated by measuring the change of density and permeability of water vapor by Takahashi and Onozato (419). By the treatment in the temperature range lower than $170^\circ$C, the change of fine structure of the film was mainly due to the compacting of the existent structure. In the temperature range higher than $170^\circ$C, the existent structure was partially decomposed and the segments released were rearranged into a new structure.

The question arising, when PVA films are thermally treated is if chemical crosslinking, perhaps towards etherification occurs. The question might be resolved by measuring the swelling in hydrogen bond-breaking media as concentrated solutions of urea or LiBr. If chemical crosslinking occurs, then the polymers will be insoluble in these solvents. If, however, the insolubility in water is due to crystallinity, then it might be expected that they would be soluble.

Heat-treated PVA films were crystallized using a slow-rate evaporation of ethylene glycol from ethylene glycol-PVA solutions (22). Baranov et al (22) present diffractogram characteristic of the scattering of polarized light from systems containing spherulites.

Mochizuki (265) studied extensively PVA films prepared with the usual drying method and heat-treated under various conditions. Selective uniplanar orientation of the crystallites was observed, as tested by the reflection at about $2\theta=20^\circ$. 

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Features presented by Nomura and Kawai (283) suggest that PVA at relatively high humidities has a structural model such that the crystallites would be embedded in a considerably swollen amorphous matrix without any definite physical interaction with each other so as to form an aggregation of the crystallites, a superstructure.

Haas (136) has shown that humidification of PVA films results in an increase of the ordered regions of PVA at the expense of the amorphous regions and has followed these changes by swelling and x-ray diffraction measurements.

Swelling and solubility characteristics of PVA in water (311) are functions of the previous history of the polymer. Changes are induced by treatment such as humidification or heat-treatment and are interpreted as happening due to secondary bond cross-links from the development of macrocrystalline regions within the gel.

The swelling phenomena of crystalline polymers that consist of continuous compositions of crystalline and non-crystalline regions have been studied (314,315,316) and by hypothesizing that a crystalline region is not affected at all by the solvent and that this region plays the role of crosslinks in a network of a polymer, a thermodynamic theory was derived by Sakurada (350), similar to the one derived by Flory (104) with regard to the swelling of crosslinked networks.

Polymers consist of continuous compositions of both crystalline and non-crystalline regions and no case is found where they are made
of 100% crystalline regions (except in single crystals). Several typical examples to illustrate this fact are PVA, cellulose and its derivatives.

When these crystalline polymers are soaked in an appropriate liquid, a marked phenomenon is observed. A reasonable hypothesis, proved by experimental data, is that the liquid molecules penetrate only the amorphous (non-crystalline) regions and that the crystalline regions remain unaffected by the liquid and they play the role of crosslinks. As the volume of the non-crystalline region increases, the volume of the solid polymer as a whole also increases (swelling). Therefore, the chain-molecules in the non-crystalline region are obliged to be expanded. Thus the force resisting to the expansion of the chain increases. Finally we reach the point of swelling equilibrium. The process of swelling is schematically considered in Figure 6-5.

It is assumed that the length of the chain-molecules is much longer than that of the crystalline regions. Under these hypotheses, the effect of the degree of polymerization on the degree of swelling should be negligible.

The swelling entropy and the development of the thermodynamic aspect of the theory is exactly the same as in the case of crosslinked networks, as analyzed by Flory (104)(See Appendix B for complete derivation).

The corresponding process of swelling of crystalline polymers is
Fig. 6-5: Swollen crystalline polymer
("•" indicates solvent molecules)

represented in Fig. 6-6.

The final equation derived by Sakurada and Nukushina (350, 360) is

\[
Z = \frac{u_2^{1/3}(1-u_2^{2/3}/f)}{u_2^2 [(\frac{1}{2} - x) + \frac{u_2}{3} + \frac{u_2^2}{4} + \cdots]}
\]  

(6.3)
\( v \) chains \( \rightarrow \) unswollen crystalline polymers

\( q \) crystals interlinking of chains (consisting of crystalline and amorphous regions)

\( n \) solvent

(2) molecules

(3) dissolved chains interlinking of chains swollen crystalline polymer

and crystals to crystals

n solvent

(4) molecules

Fig. 6-6: Thermodynamic process for swelling of crystalline polymers

In the above expression \( \chi \) is the chi factor of PVA-H\( \text{O} \) system, \( f \) is the functionality which is generally a very large number (100 or so) and \( v_2 \) is defined as:

\[
v_2 = \frac{1-x}{Q-x} \quad (6-4)
\]

where \( x \) is the percentage of crystalline regions in the unswollen polymer and \( Q \) is the degree of swelling measured in volume of swollen gel per volume of unswollen gel. Finally \( Z \) is defined as:

\[
Z = \frac{V_2}{V_1} = \frac{M}{\rho V_1} \quad (6-5)
\]
where \( \rho \) is the density of the polymer, \( V_1 \) is the molal volume of swelling liquid and \( M_a \) is the average molecular weight in the amorphous region.

The degree of swelling and the solubility of PVA films in water at 30°C were studied, after the relation between density and crystallinity was established. Sakurada et al. (360) found that the swelling ratio is independent of the degree of polymerization and temperature of heat-treatment and that the crystallinity was not changed through swelling. Figure 6-7 shows the degree of swelling as a function of crystallinity. Notice that the degree of swelling is reported here as \( q' = q-1 \) (356) where

\[
q = \frac{\text{weight of swollen film}}{\text{weight of PVA}}
\]

The degree of swelling is originally a function of the heat-treatment as shown in Figure 6-8 (356, 157).

The fact that the crystalline regions remain unchanged during swelling, has been proved by determining the crystallinity before and after swelling (357).

Based on the X-rays analysis Sakurada et al. (357) proved that swelling does not affect the crystalline region of PVA films, at least if they are treated at high temperatures. Some characteristic results are shown in Table 6-2.
Fig. 6-7: Degree of swelling of a partially crystalline polymer

Fig. 6-8: Degree of swelling of partially crystalline polymers as a function of heat-treatment temperature and DP

- 206 -
<table>
<thead>
<tr>
<th>Heat treatment</th>
<th>40</th>
<th>80</th>
<th>120</th>
<th>160</th>
<th>180</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallinity before</td>
<td>28.5</td>
<td>31.6</td>
<td>33.7</td>
<td>38.4</td>
<td>52.3</td>
</tr>
<tr>
<td>x_b (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystallinity after</td>
<td>36.1</td>
<td>34.0</td>
<td>36.0</td>
<td>38.1</td>
<td>51.7</td>
</tr>
<tr>
<td>x_q (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystallinity after swelling calculated</td>
<td>37.2</td>
<td>34.4</td>
<td>35.8</td>
<td>38.9</td>
<td>52.3</td>
</tr>
<tr>
<td>x_q (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solubility</td>
<td>s</td>
<td>0.234</td>
<td>0.082</td>
<td>0.058</td>
<td>0.013</td>
</tr>
<tr>
<td>Swelling ratio</td>
<td>q</td>
<td>5.7</td>
<td>4.6</td>
<td>2.9</td>
<td>1.5</td>
</tr>
</tbody>
</table>

The solubility \( s \) is defined as:

\[
s = \frac{\text{initial wt of dry film} - \text{bone dry wt of film}}{\text{initial wt of dry film}}\tag{6-6}
\]

The term "calculated crystallinity after swelling" refers to the degree of crystallinity after taking in account that a part of the film (especially at low heat-treatment temperatures) is soluble in water.
(solubility s). Thus

$$x_q = \frac{x_b}{1-s}$$  \hspace{1cm} (6-7)

When fairly large amounts of the amorphous regions dissolve during the swelling, stable crystalline regions of high crystallinity appear during drying (358). These crystalline regions are not destroyed by the subsequent swelling process and are the cause of the low degree of swelling of the new samples. The relation between crystallinity and the degree of swelling defers with the drying process, especially in the case of low-temperature heat-treatment. For samples of the same crystallinity, the degree of swelling is arranged in the following order: samples dried at room temperature, in high humidity, and at high temperature (359). The variation of swelling ratio as a function of the crystallinity after swelling for the three different cases is reported in the same paper (359). The degree and the rate of swelling of PVA in aqueous solutions are affected by the existence of certain cations or anions in the solution (465). This difference in the degree of swelling can be as high as 10-15%.

In further studies on the swelling of PVA films were heat-treated at 40°C for 10 minutes, immersed in water at 30°C for the removal of water soluble parts of films and then the extracted films were dried and subjected to heat-treatment at the same as before temperatures for 10 minutes. Extracted films showed lower swelling and higher crystallinity compared to unextracted films heat-treated in the same way (402).
The difference is characteristic especially between 40-120°C. Films prepared from the water soluble and water-insoluble parts of the previous samples and heat-treated under the same conditions showed different swelling and crystallinity (403). This is something to be expected since the soluble parts have lower degrees of polymerization.

In further studies Sakurada and Sone (404) proved that residual acetyl groups in PVA films heat-treated as previously reported change significantly the degree of swelling. Effect of the degree of polymerization was furthermore discussed (405,406).

The gel-sol transition temperatures $T_m$ for the PVA-H$_2$O system over the range of weight fraction 42-92% (PVA) were measured and reported by Packter and Nerurkar (294) as in Figure 6-9. The method used was determination with a Kofler Hot-Stage Microscope (397). Analogous plots have been reported for PVA-glycol systems by Rehage (313).

The effects of a slow drying rate drying process (dehydration) in room temperatures and under different humidity (RH) has been studied by Packter and Nerurkar (294). This is a notable piece of work, because the authors are able to give some approximate expression of the rate of crystallization as a function of the rate of drying. They noted that nucleation and crystal growth in uncrosslinked dried PVA films starts just beyond the sol-gel transition and continues up to the glass transition stage. The degree of crystallinity was calculated from density measurements in water at 25°C. The drying was done at room tempera-
Fig. 6-9: Sol-Gel ($T_{gel} = T_m$) transition temperatures of PVA-water system structure in an atmosphere containing the following drying agents: $K_2Cr_2O_7$, KBr, Ca(NO$_3$)$_2$, MgCl$_2$, SiO$_2$. An induction period $\tau$ was observed below
which the surface area of the micro-crystalline regions is not sufficiently high for a growth surge. This induction period varies from 40-160 hours but it is as high as 560 hours for some drying agents. Kinetically the results were fitted in the Avrami equation and the rate of growth $R_g$ was three times faster than the rate of evaporation $R_e$ (in hr$^{-1}$).

Crystallinities were varying between 30 and 40%, which notably shows that dehydration does not increase significantly the crystallinity. Despite the high degree of crystallinity, crystalline regions were not resolved on microscopic examination. Indeed no significant light scattering was noted. This indicates an average crystallite size well below 1,000Å and a very large number of nuclei. It is noted that this phenomenon is to be expected with polar vinyl polymer films prepared from solutions in good solvents, in which interaction between polar groups on adjacent polymer chains is still very intense.

The data of Packter and Nerurkar (294) are supported by earlier studies of Papkov et al (300), who, by evaporating the water of aqueous solutions of PVA for the preparation of PVA films, found that as the system passed through the stage of gelling, there is a sudden increase of the intensity of the 1141cm$^{-1}$ band, which characterizes the crystallinity. In itself, the crystallization of PVA on the formation of a gel at normal temperatures is not unexpected, because generally fairly high super-saturation of the solution and viscosity below a cer-
tain level are pre-requisites for the crystallization of the polymer. It is thus to be expected that the crystallization rate on gel formation will first rise due to an increase in the super-saturation of the polymer and then it will fall due to an increase in viscosity. This study on the conditions of gel formation and crystallization for different polymeric systems confirms the relations and results obtained for the system PVA-H₂O-precipitant (299).

Imoto (159) prepared PVA films under various polymerization conditions in a temperature range of 30 to 80°C, heat-treated in a range of 120-195°C and swollen in water at 30°C. The degree of swelling becomes greater with decreasing film-forming temperature.

The texture of the heat-treated films depends on the manners of original nucleation and the thermal treatment after the nucleation.

Swollen PVA networks or gels were subjected to stretching and the forces needed in the stepwise stretching processes were measured as a function of gelling time and temperature (391). For the evaluation of the chains per dry unit volume, Flory's equation for swollen fibrous proteins was used. Solutions of 10% PVA in water slightly irradiated at 90°C with electron beam have been used for this study. The tensile force measured as a function of swelling temperature increased initially because of the negative temperature coefficient of the solubility parameter of PVA in water and then it fell rather rapidly.

The reciprocal increments of the number of chains per unit volume were plotted against the reciprocal gelling time, and they gave straight
lines, extrapolation of which to $\frac{1}{t} = 0$ gave the number of junction points at infinite gelling time for various gelling temperatures.

D. METHODS OF EVALUATION OF CRYSTALLINE AND THERMAL PROPERTIES OF PVA

The methods of evaluation of the crystalline properties of PVA are mainly based on the effects that crystallinity has on some of the properties of this polymeric material. The variation of these properties due to the existence of amorphous (non-crystalline) and crystalline phases can be used for the calculation of crystallinity. An apparent degree of crystallinity can be defined on the basis that the solid is composed of an ideal perfectly ordered crystalline phase of volume fraction $u$ and an ideally disordered liquid-like phase, whose properties $(P_c^o)^i$ and $(P_a^o)^i$ are additive. Thus:

$$p^i = u \frac{i}{2} (P_c^o)^i + (1-u) \frac{i}{2} (P_a^o)^i$$ (6-8)

Different methods have been used for the calculation of crystallinity of different polymers (175). In the case of PVA, the following methods have been successfully used, as reported in the literature.

1). Density measurements: use of the principle of additivity of volumes and the densities of 100% crystalline and amorphous PVA, that have already been reported in the literature.

2). Calorimetric methods: they include differential thermal analysis (DTA), differential scanning calorimetry (DSC) and thermogravimetric
analysis (TGA). By an indirect method, the heat of crystallization is compared to the heat of crystallization of 100% crystalline PVA, and the crystallinity is reported.

3). Spectroscopic Methods: Infrared Spectroscopy is mainly used. The intensity of the peak at 1141 cm\(^{-1}\) of the IR spectrum of PVA is dependent on the percentage of crystallinity.

4). X-rays analysis: application of this method on films and fibers of PVA has been widely used.

5). Other methods: they include acoustical methods as the pulse-echo-overlap method, NMR, etc.

1) **Density Measurements**

The use of density measurements for the calculation of the degree of crystallinity is a widely accepted method in the case of materials without imperfections, voids, etc.

This method has been used for dry PVA films (186, 294, 415) for the calculation of the percentages of crystallinity before and after heat-treatment. For this purpose the densities of 100% crystalline and 100% amorphous PVA are needed. Most of the authors use the values that Sakurada *et al.* (357) reported in 1955. These values are \( \rho_c = 1.345\text{gr/cm}^3 \) for the 100% crystalline material and \( \rho_a = 1.269\text{gr/cm}^3 \) for the 100% amorphous PVA. The calculation of these two values (357) was done by plotting the reciprocal density as a function of crystallinity for differ-
ent PVA samples (crystallinities between 20-55%) and different degrees of polymerization (309-4,570). Extrapolation of the straight line to degrees of crystallinity 0 and 100 gave the above mentioned values (See Fig. 6-10).

Fig. 6-10: Density of PVA in semicrystalline PVA samples
The values of degrees of crystallinity used in the above Figure were calculated using an X-ray spectrograph with a Geiger counter (353). Assuming additivity of volumes of the crystalline and non-crystalline regions and denoting by \( \rho_c \), \( \rho_a \), and \( \rho_g \) the densities of 100% crystalline (1.345gr/cm\(^3\)), 100% amorphous (1.269gr/cm\(^3\)) and the examined sample respectively, and by \( X \) the weight percentage of crystalline PVA, we can write the following relation:

\[
\frac{1}{\rho} = \frac{X}{\rho_c} + \frac{1-X}{\rho_g}
\]

(6-9)

In the case of swollen PVA networks (gels) the same equation applies. However in this case we need another equation for the additivity of the volumes of PVA and water. This is an assumption that has been proven reasonable correct, with error less than 1%. Thus denoting by \( \rho_h \) the density of the hydrogel and \( w_{\text{PVA}} \) the weight percentage of PVA in the examined sample, we can write (401)

\[
\frac{1}{\rho_h} = \frac{1-w_{\text{PVA}}}{\rho_{\text{H}_2\text{O}}} + \frac{w_{\text{PVA}}}{\rho_g}
\]

(6-10)

In the above equation \( \rho_{\text{H}_2\text{O}} \) is substituted by the density of the water at the temperature of measurement of the density of the hydrogel \( \rho_h \).

These two equations are used for the evaluation of the density of swollen PVA films. The values of \( \rho_c \), \( \rho_a \), and \( \rho_{\text{H}_2\text{O}} \) are known and the
percentage of PVA in the gel can be found by a thorough drying of the material under vacuum for sufficient time. The accurate estimation of the gel's density is done by displacement of a liquid of known density at a certain temperature and weighing the sample in this liquid and in air, according to the official ASTM method (14).

Using density measurements of heat treated films at very high temperatures Bessonov and Rudakov (32) were able to calculate the degree of crystallinity. Analogous approach was taken by Packter and Nerurkar (294).

Tadakoro et al (415) first noted that the density of PVA films increases when they are dehydrated under certain conditions. They reported the density as a function of water content. It was realized that in PVA films, there can be some empty space (voids) that is filled with water molecules. The apparent volume $V_a$ per gram of polymer in moist state consists of the water percentage $w_{H_2O}$, the net volume of the polymer $v_p$ and the volume of voids $\varepsilon$.

$$V_a = \frac{(1+w_{H_2O})}{\rho} = w_{H_2O} + \frac{v_p}{\rho} + \varepsilon$$  \hspace{1cm} (6-11)

As the water content $w_{H_2O}$ increases, the empty space $\varepsilon$ decreases and it will disappear at last, thereafter the increase in $V_a$ will become equal to the volume of water sorbed and the slope of the line should be 45°.

The problem of voids in PVA samples has been studied extensively
(178). In a later paper Tadokoro et al (416) calculated the crystallinity of PVA films using IR and density measurements.

The density of PVA films as a function of the temperature at which they were quenched, under melting and under crystallization conditions is shown in Figure 6-11 (32).

Fig. 6-11: Density of PVA films as a function of the temperature, at which they were quenched under crystallization conditions(2), and under melting conditions (1).
2). **Calorimetric methods**

The calorimetric methods are indirect methods for calculating the degree of crystallinity of a sample of PVA. The purpose of all the methods is to evaluate the heat of crystallization of the particular PVA sample ΔH^x. Then the degree of crystallinity can be expressed as

\[ x = \frac{\Delta H^x}{\Delta H_c} \] (6-12)

where \( \Delta H_c \) is the heat of fusion in cal · gr⁻¹ of the 100% crystalline phase (86).

Although crystallizability of a polymer is inherently determined by its molecular structure, the degree of crystallinity and the crystallite-size distribution can be considerably different, depending on the previous thermal history of the sample (184).

In the case of several polymers, notably PVC, cellulose, PVA, the calometric methods can not apply, because they decompose before melting. For this reason it is necessary to use a system of the polymer with one of its solvents and apply Flory's theory on the depression of the melting point, in order to calculate the heat of fusion. The same theory is applied in the case of PVA hydrogels (172).

The experimental calorimetric methods used are mainly Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) (231).

In DTA the difference in temperature, ΔT, between a sample and a reference is observed while both are being heated or cooled continuously through
a preselected temperature program. To obtain meaningful data from the
enthalpic effects attending a chemical or physical transformation, it
is required that the thermal characteristics of the sample and reference
cells be alike.

In DSC the temperatures of the sample and reference are maintained
at an equal or fixed differential level during the analysis and the
variation in power required to maintain the level during a transition
is measured.

Melting of high polymers usually takes place over a range of tem-
peratures, since the crystallites surrounded by amorphous regions have
a range of sizes. The melting point is taken by some as the peak tem-
perature, although others postulate that it is the point where the first
crystallite melts (395).

The degree of crystallinity as well as the crystallites size dis-
tribution are dependent on the thermal history of the sample. The
melting characteristics do not seem to be affected by the molecular
weight. However crosslinking affects considerably the melting proper-
ties.

Studies of the effects on the melting of a polymer are of theore-
tical and practical importance permitting a better knowledge of the
nature and magnitude of polymer-diluent interaction.

Flory's expression (104) for the crystalline melting point depres-
sion by the addition of a diluent may be written as follows (85)
\[
\frac{1}{T_m} - \frac{1}{T_0^m} = \left( \frac{R}{\Delta H_c} \right) \left( \frac{V_u}{V_1} \right) \left( u_1 - \chi_1 u_1^2 \right) \tag{6-13}
\]

where

- \( T_m \) is the melting point of the polymer-diluent mixture or gel;
- \( T_0^m \) is the melting point of pure polymer;
- \( V_u \) is the molar volume of the polymer repeating unit;
- \( V_1 \) is the molar volume of the diluent;
- \( u_1 \) is the volume fraction of the diluent;
- \( \chi_1 \) is the chi factor as defined by Flory;
- \( \Delta H* \) is the heat of fusion of the particular sample.

This equation assumes considerable dilution of the amorphous phase so that \( \chi_1 \) is independent of the volume fraction \( u_2 = 1 - u_1 \).

The \( \chi_1 \) factor is expressed at temperature \( T_m \). Usually it is substituted in the expression by the term

\[
\chi_1 = \frac{1}{2} - \psi_1 + \kappa_1 = \frac{1}{2} - \psi_1 + \frac{BV_1}{RT_m} \tag{6-14}
\]

Substitution and rearrangement of the above equation can give \((138)\)

\[
\frac{1}{T_m} - \frac{1}{T_0^m} = \left( \frac{R}{\Delta H_c} \right) \left( \frac{V_u}{V_1} \right) \left( 1 - (\frac{1}{2} - \psi_1)T_m + \frac{BV_1}{T_m} \right) u_1 \tag{6-15}
\]

In some cases the \( \chi \) factor can be substituted \((315)\) by

\[
\chi = \alpha_1 + \beta_1 \frac{1}{T} \tag{6-16}
\]
In the case of crosslinked samples $T_m$ refers to the particular samples with a certain crosslinked density $\rho$, so that the appropriate value has to be calculated and used.

The same equation can also be expressed as

\[
\frac{1}{v_1} - \frac{1}{v_1} \left( \frac{1}{T_m} - \frac{1}{T_0} \right) = \frac{1}{2} - \psi_1 \frac{\psi_0}{T_m} \quad (6-17)
\]

A plot of \((\frac{1}{T_m} - \frac{1}{T_0})/v_1 \times 10^3\) versus \(\frac{v_1}{T_m} \times 10^3\) gives a straight line from which $\Delta H_u$ and the $\chi$ factor can be calculated.

The DSC method has been used to study the effect a diluent like glycerol on the melting of PVA. As reported by Tubbs (448) the melting point of PVA is 228°C. No increase in the melting point of the homo-polymer was observed upon cooling slowly and reheating. However, the rate of heating had a small effect on the melting point. The melting point of PVA was found to decrease with the percentage of glycerol added in a linear relation. Plotting \((\frac{1}{T_m} - \frac{1}{T_0})/v_1 \times 10^3\) versus \(\frac{v_1}{T_m} \times 10^3\) a straight line was gotten. $\Delta H_c$ was obtained as 1.64 kcal/mole and the slope gave the value of $B = -1.9$ cals/cm$^3$ from which the
\( \chi \) factor could be calculated.

The thermodynamic expression relating the melting temperature to the crystal size is (85):

\[
T_m - T_m^0 = \frac{\sigma A}{\Delta S_f}
\]  

(6-18)

where \( \sigma \) is the interfacial free energy in cal/cm\(^2\), \( A \) is the total interfacial area in cm\(^2\)/gr and \( \Delta S_f \) is the entropy of fusion in cal/deg x gr.

The above equation is derived on the assumption that \( \Delta S_f \) and \( \sigma \) are independent of temperature.

The arithmetic value of the \( \chi \) factor that is going to be used for the calculation of the crystallinity, as well as in other calculations (e.g., in the calculation of the crosslinking density via swelling measurements), has always been a problem, since there have not been many data for the \( \chi \) factor of the system PVA-H\(_2\)O. The \( \chi \) factor is a function of temperature and volume fraction of polymer. It can be calculated from osmotic pressure data, swelling data or back calculating from the equation of the melting point depression.

Sakurada et al (348) reported the value of 0.494 at 30\(^\circ\)C (calculated from vapor pressure data) being constant in the concentration range of \( v_2 = 0-0.15 \). However the increase was very large at higher volume fractions. Figure 6-12 includes his data. The \( \chi \) factor is also a function of the degree of polymerization (348) as well as the crosslinking density (454), since it is a function of the local segment concentration (53).
Fig. 6-12: Dependence of the χ factor on the volume fraction of PVA in a PVA-\( \text{H}_2\text{O} \) system.

The freezing point depression of PVA solutions was measured in the concentration range of 5-30% (by volume). Using these data information
concerning the activity of the solvent in the solution can be calculated (176). Using Flory's theory and applying the equation of depression of the freezing point, the $\chi$ factor was calculated. The $\chi$ factor results are plotted against the polymer concentration, expressed as volume fraction and they are compared to Yano's data (470). The unreasonable values of $\chi$ in Yano's results cannot be rationalized unless the existence of crystalline regions and the possible contribution of the entropy of elastic deformation to the activity of solvent are taken into account. Besides Sakurada (338) noticed that their films were of as low as possible degree of crystallization (19%). However the data of Kawai (176) are also questioned, because he used an incorrect PVA density of $\rho=1.337$ gr/cm$^3$.

Takizawa et al (421) data of the interaction parameter $\chi$ as a function of relative vapor pressure and crystallinity of PVA are entirely wrong because he applies Flory's theory in a wrong way using $v_1$ as the volume fraction of the polymer.

The interaction parameters of commercial atactic PVA with different solvents at 267°C (its melting point), using the melting point depression equation, have been calculated as shown in Table 6-3 by Hamada and Nakajima (138).

The $\chi_1$ factor as a function of temperature for different solutions (PVA-H O system, or PVA-H O-Eth. glycol system) has been reported by Sakurada et al (349). For 30°C and $v_2=0.015$ the $\chi$ factor in a PVA-H O system is almost constant and 0.494 (See Fig. 6-13).
TABLE 6-3

THERMODYNAMIC QUANTITIES FOR COMMERCIAL PVA-DILUENT MIXTURES

<table>
<thead>
<tr>
<th>diluent</th>
<th>$\Delta H_{c}^{\text{kcal/mole}}$</th>
<th>$\psi_1$</th>
<th>$\kappa_1 (267^\circ C)$</th>
<th>$\chi_1 (267^\circ C)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>2.47</td>
<td>-0.05</td>
<td>-0.06</td>
<td>0.49</td>
</tr>
<tr>
<td>ethyl-glycol</td>
<td>2</td>
<td>0.50</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>DMF</td>
<td>1.43</td>
<td>0.37</td>
<td>0.06</td>
<td>0.19</td>
</tr>
<tr>
<td>acetamide</td>
<td>1.47</td>
<td>0.10</td>
<td>0</td>
<td>0.40</td>
</tr>
</tbody>
</table>

![Graph](image)

Fig. 6-13: The $\chi$-factor in PVA-water and PVA-ethyl glycol-water systems
3). Spectroscopic Methods

Among the different spectroscopic methods, infrared spectra have been used for qualitative detection of the existence of crystalline regions and quantitative analysis of polymeric materials (70). IR spectra analysis for crystalline regions in PVA films has been widely used (186, 195, 211, 246, 274, 275, 276, 416).

The spectrum of PVA was the subject of much early discussion as Krimm (204) has pointed out.

The typical IR spectrum of PVA is shown in Figure 6-14. The most characteristic bands of PVA and their assignment are analytically shown in Table 6-4 as reported by Krimm (204) in his excellent review on IR of high polymers.

The origin of the 1141 cm\(^{-1}\) band has been the subject of much discussion. It has been reported by many authors (for example 156) that the intensity of this band increases significantly when the sample is heated, treatment which seems to increase the degree of crystallinity. It has been suggested that this band arises from a symmetric C-C stretching mode (414, 415).

It seems that this bond is associated with a structure which is more likely when the chain is in the crystalline state. Krimm (204) suggested that this band is associated with the \(\nu(CO)\) mode of a portion of a chain, where an intramolecular hydrogen bond is formed between two neighboring OH groups that are on the same side of the plane of the carbon chain. In any way he has proven (204) that this band cannot
Fig. 6-14: A typical IR spectrum of oriented PVA
TABLE 6-4

SOME CHARACTERISTIC BANDS OF INFRARED SPECTRUM OF PVA

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>R.I.</th>
<th>Pol.</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>185</td>
<td>v_w</td>
<td></td>
<td>v(OH...O)</td>
</tr>
<tr>
<td>410</td>
<td>w</td>
<td>π</td>
<td>γ_w (CO)</td>
</tr>
<tr>
<td>480</td>
<td>w</td>
<td>σ</td>
<td>δ (CO)</td>
</tr>
<tr>
<td>610</td>
<td>w</td>
<td>σ</td>
<td>γ_w (OH)</td>
</tr>
<tr>
<td>825</td>
<td>v_w</td>
<td>σ_l</td>
<td>γ_w(CH₂)</td>
</tr>
<tr>
<td>915</td>
<td>w</td>
<td>σ_s</td>
<td>v⁺(O)</td>
</tr>
<tr>
<td>1040</td>
<td>v_w</td>
<td>σ_l</td>
<td>v (CC) [O-C-C-O] γ_w (CO) + γ_w(OH)</td>
</tr>
<tr>
<td>1096</td>
<td>s</td>
<td>σ_l</td>
<td>v(CO)</td>
</tr>
<tr>
<td>1141</td>
<td>m</td>
<td>σ_s</td>
<td>v¹(CO)</td>
</tr>
<tr>
<td>1215</td>
<td>v_w</td>
<td>σ</td>
<td>2 × 610</td>
</tr>
<tr>
<td>1320</td>
<td>s</td>
<td>σ</td>
<td>δ(CH⁺OH)</td>
</tr>
<tr>
<td>1430</td>
<td>s</td>
<td>σ</td>
<td>δ(CH₂)</td>
</tr>
<tr>
<td>1446</td>
<td>s</td>
<td>π</td>
<td>γ_w(CH₂)</td>
</tr>
<tr>
<td>2840</td>
<td>v_w</td>
<td>σ</td>
<td>v(CH)</td>
</tr>
<tr>
<td>2910</td>
<td>s</td>
<td>σ''</td>
<td>v_s(CH₂)</td>
</tr>
<tr>
<td>2942</td>
<td>s</td>
<td>σ₄</td>
<td>v(CH₂)</td>
</tr>
<tr>
<td>3340</td>
<td>v_s</td>
<td>σ</td>
<td>v (OH)</td>
</tr>
</tbody>
</table>

π : parallel  δ : bending
σ : perpendicular  v : stretching
be attributed to stretching vibration of \( \nu(C-O-C) \) bonds, formed by de-
hydration and thermal crosslinking as he had initially assumed (205). An-
alogous interpretation was given to the results by Smirnov et al (397).

A large number of papers and reviews have been published on studies
of the structure of PVA by IR spectra (280). The bands at 1141 cm\(^{-1}\)
and 916 cm\(^{-1}\) are sensitive to intermolecular and intramolecular or-
der.

The intensity of the 916 cm\(^{-1}\) band decreases on heat-treatment.
Transition from syndiotactic to the isotactic structure is accompanied
by a diminution in intensity of the absorption band at 1141 cm\(^{-1}\). The
ratio of the bands at 916 cm\(^{-1}\) and 850 cm\(^{-1}\) has been used to determine
the degree of stereoregularity of PVA.

Lebedeva et al (211) confirmed that the 1141 cm\(^{-1}\) band is sensitive
to crystallinity and that the bands 1040, 916, and 825 cm\(^{-1}\) are amorph-
ous-sensitive and are associated with syndiotactic and atactic chain
segments. Study of the heterogeneous, complex microstructure of PVA
films revealed that the crystalline part of the film is mainly made
up by syndiotactic and atactic chain segments, while the amorphous part
consists of isotactic chain segments. Their characteristic results
are included in Table 6-5.

Tadokoro et al (416) noticed that the intensity of the 8.74\(\mu\) (1141cm\(^{-1}\))
band increases as crystallinity increases. They proved that the inten-
sity of this band is not affected by the bound water as long as the
### TABLE 6-5

STEREOREGULARITY AND CRYSTALLINE SENSITIVE BANDS OF THE IR SPECTRUM OF PVA

<table>
<thead>
<tr>
<th>Wave number of band (cm⁻¹)</th>
<th>PVA stereoisomers absorbing</th>
<th>Change in intensity after crystallization</th>
</tr>
</thead>
<tbody>
<tr>
<td>1235</td>
<td>i, s, a</td>
<td>i</td>
</tr>
<tr>
<td>1141</td>
<td>s, a</td>
<td>i</td>
</tr>
<tr>
<td>1124</td>
<td>i</td>
<td>d</td>
</tr>
<tr>
<td>1096</td>
<td>i, s, a</td>
<td>d</td>
</tr>
<tr>
<td>1040</td>
<td>s, a</td>
<td>d</td>
</tr>
<tr>
<td>915</td>
<td>s, a</td>
<td>d</td>
</tr>
<tr>
<td>890</td>
<td>-</td>
<td>i</td>
</tr>
<tr>
<td>850</td>
<td>s, a, i</td>
<td>i</td>
</tr>
<tr>
<td>825</td>
<td>s, a</td>
<td>d</td>
</tr>
</tbody>
</table>

Remarks: i=iso-  s=syndio-  a=atactic/ d=decrease  i=increase

Water content does not exceed several percent.

IR spectra analysis has established, that pyrolysis of oriented and unoriented PVA films is accompanied by dehydration and formation of conjugated double bonds, whose number increases with the duration of the thermal treatment (84).

Upon vigorous drying dehydration of PVA occurs and at the same time
the 1141 cm\(^{-1}\) band disappears (238).

Among the different bands, the 916 cm\(^{-1}\) is sensitive in stereoregularity. There is a close relation between its intensity and the syndiotactic structure of PVA (120). These authors as well as Nagai (274) have noticed a slight decrease of the intensity of this band upon crystallization. This trend is in contrast to the increase of the 1141 cm\(^{-1}\) band and suggests an interaction between these two bands.

The relation between the intensity of the crystalline band at 1141 cm\(^{-1}\) and the angle of taking an X-ray photograph of highly double-oriented PVA specimen has been established by Tadokoro (417).

The intensity of the absorption band of PVA at 8.75\(\mu\) increases with heat-treatment (275,276). The amount of increase is proportional to the density and finally to the crystallinity.

Below 200°C the amount of crystallinity increases with increasing temperature and it shows a maximum at 200°C. The formation of carbonyl groups has been confirmed from the spectra (274).

Tadokoro et al (415) have made the deuteration of the hydroxyl group of PVA in order to clarify the assignment of the 1141 cm\(^{-1}\) band. The band exhibits strong perpendicular dichroism in the case of an elongated sample. The shift of the band with deuteration of the CH or OH group is small. This new experimental fact also supports the theory that the band 1141 cm\(^{-1}\) is mainly due to the stretching vibration of the extended zig-zag chain in the crystalline region.
4). **X-rays analysis**

A traditional way to measure crystallinity in a polymer has been by means of its X-ray diffraction pattern. There is perhaps no other area of polymer study that has had as much controversy as the interpretation of X-ray diffraction patterns. This is mainly because the polymer diffraction patterns are always of "poor quality" and although the "spots" on the pattern are quite sharp, there is a lack of the higher order diffraction found in single crystals (409).

The percentage of crystalline material in a polycrystalline polymer can be determined quantitatively by means of X-rays diffraction methods (206). The method compares the amorphous scattering of a sample to that of a completely amorphous one.

In the aim of many authors to determine the crystallinity of PVA fibers and films in an accurate quantitative way, and to find relations between crystallinity and swelling properties of PVA in water, a method of measurement of different X-ray beams by a Geiger counter was used by Sakurada and his collaborators (360) as first reported by Krimm and Tobolsky (206). The technique was developed by Hermans and Weidinger (144).

Nickel filtered copper radiation was used for the production of the X-rays, which were controlled with voltage regulation of the input to the X-ray machine. The output of the Geiger tube, which was movable in a horizontal plane along a graduated circle was fed into a decimal
ometer or scaler, which gave a direct reading of the number of counts. Corrections for incoherent scattering, for different densities of films, etc., were made (353).

The samples used in a specific study by Sakurada et al. (360) had DP=1500 and they were treated at 80°C, 120°C, 160°C, 200°C, and 225°C for 100 sec - 5 min.

In the case of PVA fibers, the equatorial scans of scattering were reported, as well as the meridional scans up to 2θ=35°, where it is known for PVA that there is no crystalline interference. Since there is no preferred orientation in the amorphous region, the contribution of scattering due to the amorphous region on the equator must be the same as that on the meridian and by subtraction of the latter from the total scattering on the equator, it is easy to find the crystalline scattering on the equator. There was no preferred orientation in the amorphous region (354).

Using now different samples heat-treated at different temperatures (this meaning that they have different crystallinity) they proceeded to the computation of the absolute crystallinity (354).

Let \( i_a \) be the height of the amorphous peak at 2θ=18° on the meridian, \( I_c \) the height of the crystalline peak at 2θ=19° of the hypothetical sample with 100% crystallinity and \( I_a \) the height of the amorphous peak at 2θ=18° of a hypothetical sample whose crystallinity is 0%. Then we can write for the crystallinity \( x \) :

\[-234-\]
\[ i_c = x I_c \]  \hspace{1cm} (6-19) \\
\[ i_a = (1-x) I_a \]  \hspace{1cm} (6-20) \\
\[ i_c = I_c - \frac{I_c}{I_a} i_a \]  \hspace{1cm} (6-21) \\

where \( i_c \) is a relative intensity measure of the crystalline fraction calculated as:

\[ i_c = i_t - i_m \]  \hspace{1cm} (6-22) \\

where \( i_t \) is the height of the peak at about 20=19° measured on the equator and \( i_m \) is the height at the same 20° on the meridian.

A plot of \( i_t \) versus \( i_a \) can lead to the values of \( I_c \) and \( I_a \) so that the crystallinity can be very easily calculated.

The above method can be modified to be used in the case of PVA films (351). A typical example of radical scattering of a PVA film, with its typical peaks is shown in Figure 6-15.

If \( i_t \) is the total intensity of peak \( R_3 \), then the following relation can be written:

\[ i_t = I_c x + I_a (1-x) \]  \hspace{1cm} (6-23) \\

For the second peak \( R_5 \)

\[ i_t' = I_c' x + I_a' (1-x) \]  \hspace{1cm} (6-24)
Assuming $I_c' = vI_c$ (6-25)
we can obtain

$$I_c = \frac{i_t' I_a - i_t I_a'}{(i_t' - I_a') - v(i_t - I_a)}$$ (6-26)

The intensity ratios $v$ of crystalline peaks $R_1/R_3$, $R_2/R_3$, $R_4/R_3$, $R_5/R_3$, and $R_6/R_3$ are constant for different samples. Using the average value of $v$, the mean value of $I_c$ of peak $R_3$ is calculated and the crystallinity is expressed as:

$$x = \frac{i_t - I_a}{I_c - I_a}$$ (6-27)

The final results are of great importance. Crystallinity increases from 30 to 54% as the temperature of heat-treatment increases from 40 to 200°C (355).

The method was successfully used, to correlate the density of the film, as calculated from displacement and weighing in water, to the crystallinity of the film (360). Thus the densities of 100% crystalline and 100% amorphous materials were calculated.

In the case of swollen PVA films the quantitative analysis of the X-ray results is somewhat more complicated, because of the existence of the pattern of water. Quantitative analysis and calculation of the crystalline of swollen film has been reported by Sakurada et al (357)
Fig. 6-15: (a), (b) Radial scattering from a PVA film
and it was needed for the proof that swelling does not change the crystalline regions of PVA films.

The treatment is generally the same as in the previous case (357). Denoting by \( i'_t \) the total intensity of peak \( R_3 \) due to PVA and \( H_2O \), by \( i_t \) the total intensity due to PVA, \( i_w \) the intensity due to \( H_2O \) and \( q' \) the swelling ratio \( (q' = q - 1) \) we can write:

\[
i'_t = \frac{1}{1+q'} i_t + \frac{q'}{1+q'}
\]

(6-28)

or

\[
i_t = q i'_t - (q-1) i_w
\]

(6-29)

Crystallinity is expressed again as

\[
x = \frac{i_t - I_\infty}{I_c - I_\infty}
\]

(6-30)

A typical interference curve of a swollen PVA heat-treated at 40°C and the contribution of PVA in water, in the swollen film are shown in Figure 6-16.

Recently another X-ray analysis method has been used by Kawakami and Miyoshi for the calculation of the crystallinity (177).

Sone (402) prepared films of PVA (DP 1288) by the usual method, heat-treated them at 40, 80, 120, 160, and 200°C and measured the degree of swelling by weight method, by swelling them in water at 30°C.
Neglecting the volume contraction upon swelling (assuming additivity of volumes) he reported the weight degree of swelling $q$ (notice that the swelling ratio reported by him is actually $q' = q - 1$, because he defines it as the weight of liquid absorbed by the weight of unswollen
polymer). In the same table 6-6 the degree of crystallization before swelling as calculated with an X-ray counter is reported. Using the above mentioned equation the Z and $M_a$, molecular weight of non-crystalline chains were calculated.

As it is shown from the table the amorphous region decreases as the temperature of heat-treatment increases, but the magnitude of decrease of the degree of swelling is far greater than is expected from the decrease of the amorphous region.

| TABLE 6-6 |
| DEGREE OF SWELLING q, CRYSTALLINITY x, AND OTHER PROPERTIES OF PVA FILMS (DP=1288) TREATED AT DIFFERENT TEMPERATURES |
| temperature of heat treatment | °C | 40 | 80 | 120 | 160 | 200 |
| degree of swelling | q | 5.7 | 4.6 | 2.9 | 1.5 | 1.2 |
| crystallinity | x | 0.29 | 0.32 | 0.34 | 0.39 | 0.53 |
| average chain length | Z | 546 | 330 | 91.5 | 10.2 | 4.9 |
| molecular weight of chain | $M_a$ | 12800 | 7740 | 2140 | 239 | 115 |

This fact is attributed to the sudden decrease of the average chain length Z in the amorphous region. This cannot be explained by a mere hypothesis that the crystalline region that was developed at low temperatures grown at high temperatures. It is more reasonable that the
crystalline region which can serve as crosslinking points was newly
developed at high temperatures and this resulted in a decrease of Z,
decrease which is far greater in magnitude than the increase of the
crystallinity.

An X-ray method of analysis applied to the characterization of the
process of gel formation and transition in solution was proposed by
Gybenkova et al (133). In the studies of PVA in aqueous glycerine, af-
ter prolonged storage, a high degree of ordering was observed due to
the generation of hydrogen bonds of the mode -OH...HO-. By the pro-
cessing of aqueous PVA solutions the generation of bonds between polymer
molecules was shown, from the reflexes and the diffraction patterns
of gels at 2θ=20°C after ordering. Other relationships between heat-
treatment and the X-ray diagrams of PVA were studied at some length by
Fuchino (116).

Ishikawa and Miyasaka (165) studied the change of dimensions of
the PVA crystallite with temperature.

The difference between the structures of suddenly and slowly cooled
films and fibers was clearly detected by X-ray methods, by Bessonov and
Rudakov (32) and Mochizuki (267).

5). Other Methods

Other methods have also been proposed or applied to the qualitative
detection and quantitative analysis of crystalline regions in polymeric
materials. The acoustical method known under the name "pulse echo over-
The "lap" method (296) can be used in this case. For this purpose the ultrasonic attention in bulk solids is determined. Three interference steps permit the calculation of the reflection coefficient at the transmission line specimen junction and the attenuation coefficient in the specimen (297). The method has been discussed and proposed for the evaluation of crystallinity in PVA samples.

Among other methods, the use of NMR has been of some interest. The NMR curve can be used, under certain conditions for the calculation of the crystallinity. Slichter (396) suggests that a broad and a narrow component of the NMR curve be ascribed to the crystalline and the amorphous regions of the polymer. Measurement of the ratio of the area under the broad curve to the area under the total absorption curve describes the degree of crystallinity. The area under the absorption curve is proportional to the first moment of the derivative of the absorption curve (41).

Experimental estimation of the intrinsic birefringence of crystalline and non-crystalline phases in PVA can be used to calculate the crystallinity (68,147).
CHAPTER 7

THE MECHANICAL BEHAVIOUR OF HIGH POLYMERS

A. GENERALITIES

The term "mechanical behaviour" refers to the characteristic behaviour of polymeric materials upon application of transient or steady mechanical stresses on them. This behaviour depends on the internal structure of the polymeric material, i.e., on the crystalline or amorphous structure, on the orientation or crosslinking, etc., and on the temperature of test relative to $T_g$ or $T_m$. The application of the stress can be uniaxial or biaxial, and according to the direction of the forces, tensile, compressive, or shear. In practical applications it is necessary to know the effects of tensile stresses on a material and especially to determine its rupture point. For the characterization of polymeric materials, certain mechanical tests are used.

Among the mechanical tests employed, tensile strength, creep and tear propagation tests are of great significance in the case of PVA hydrogels. The dynamical properties of the materials are complementary to the equilibrium measurements in elucidating polymer structure, and especially interactions between polymer segments.

1. Tensile Properties of Plastics

The tensile strength tests provide information about the strength
and the maximum elongation attainable from a material. The methods
cover the determination of the tensile properties of plastics in the
form of standard test specimens and when tested under defined con-
ditions of temperature, humidity, and testing machine speed. A
standard experiment records stress-strain curves of one of the three
types shown in Figure 7 - 1.

In many polymers, a yield point is reached, at which an
increase in strain occurs without any increases in stress.

From this kind of test the modulus of elasticity can
be calculated. This term is very important because it is a measure
of the rigidity and the hardness of a polymer. In general the polymeric
materials can be separated in five categories according to their
mechanical behavior. Soft materials have a low modulus and elongation
at break, while hard materials show high modulus. Tough materials
have high elongation and high stress at break and strong materials have
moderate elongation but high yield point. Finally, brittle materials
show low elongation at break. Thus, the five categories are the
following:

i) soft materials

ii) hard materials that are also brittle

iii) soft, tough materials

iv) hard and strong materials

v) hard and tough materials
Fig. 7-1: Typical stress-strain curves of polymers under tensile stresses

A, C & E: U.T.S. and elongation at break

B & D: Tensile strength at yield and elongation at yield
2. Creep Studies

The creep studies provide information on the extension of samples of standard shape as a function of time and the time of rupture of a specimen subjected to constant tensile load under specified environmental conditions.

The results of creep studies of semi-crystalline polymers like PVA hydrogels can be interpreted in terms of Nutting's equation which states that:

\[ J = \psi t^n \]  \hspace{1cm} (7-1)

where \( J \) is the creep compliance, defined as the observed strain per unit of applied stress, \( t \) is the time, and \( \psi \) and \( n \) are constants.

The exponent "n" is a measure of the relative importance of apparent elastic and viscous contributions to the creep behaviour. If \( n \) equals zero, the material is perfectly elastic, while if \( n \) is one, the material acts like a viscous liquid. Thus on a log-log plot of compliance versus time, the Nutting equation gives a straight line with slope \( n \). The equation usually is found to be applicable not over more than four decades of time.

3. Tear Propagation Resistance

The force necessary to propagate a tear in plastic films and thin sheetings or in tubings is of great importance, especially in cases of practical applications where the material is under shear stresses. The tear strength will be different for low extensi-
Fig. 7-2: Tear strength test of high-extensibility films

Fig. 7-3: Tear strength test of low-extensibility films
bility and high extensibility films. It also depends on the thickness of the torn film. Typical stress-strain curves for high and low-extensibility films are shown in Figures 7-2 and 7-3.

The variation of physical properties of high polymers with the temperature is an important characteristic, because the mechanical strength of these materials is a function of the temperature, where they are used. The variation in the condition of a high polymer with temperature can be described by means of a large number of characteristic temperatures, as they have been tabulated by Korschak (203) as in Table 7-1.

B. EFFECTS OF CRYSTALLINITY AND CROSSLINKING ON THE MECHANICAL PROPERTIES OF POLYMERS

Reinforcement of weak polymeric materials is a desirable process for improvement of the mechanical properties of them. This reinforcement can be done by different methods which include crosslinking (network formation), introduction of inert fillers, introduction of crystalline phases, formation of composite materials, etc. In PVA hydrogels the introduction of crosslinks and the formation of a network increase the mechanical properties because the applied stress is redistributed to these points. Introduction of crystalline phases in a hydrogel, as discussed in a previous chapter, leads to orientation of chains in some regions of higher density, so that the material becomes partially crystalline (44). In a semicrystalline polymer, the crystallites act as additional crosslinks for
TABLE 7 - 1

TEMPERATURE CHARACTERISTICS OF HIGH POLYMERS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Brief Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point $T_m$</td>
<td>-First order phase transition</td>
</tr>
<tr>
<td>Softening point $T_s$</td>
<td>-Temperature of deformation under zero load</td>
</tr>
<tr>
<td>Temperature of incipient plastic flow $T_{pl}$</td>
<td>-Temperature of deformation under small load</td>
</tr>
<tr>
<td>Stick point $T_{st}$</td>
<td>-Temperature of adhesion to a hot surface</td>
</tr>
<tr>
<td>Vicat heat resistance temperature $T_{vicat}$</td>
<td>-Temperature of plastic deformation under a load of 5 kg/cm²</td>
</tr>
<tr>
<td>ASTM heat resistance temperatures</td>
<td>-Temperatures of plastic deformation under loads of 18.5 and/or 4.6 kg/cm²</td>
</tr>
<tr>
<td>Martens heat resistance temperature</td>
<td>-Temperatures of plastic deformation under a load of 50 kg/cm²</td>
</tr>
<tr>
<td>Vitrification point $T_{vitr}$</td>
<td>-Second order phase transition</td>
</tr>
<tr>
<td>Embrittlement point $T_{embr}$</td>
<td>-Temperature of loss of resistance to impact loads</td>
</tr>
</tbody>
</table>
further redistribution of the applied stress (4).

Thus, it must be expected that the elastic modulus of a semi-
crystalline, crosslinked polymer will be much higher than the one of an
uncrosslinked polymer. Crystalline polymers are generally "hard".

Crosslinking affects significantly the elongation at break,
because of the restrictions in extensibility of the specimen. Cross-
linked materials are generally more brittle than uncrosslinked ones.
Closely related to the elongation at break is the stress at break.
However, the stress at break is a property depending not only on the
reinforcement of a polymeric material, but also on the orientation,
the internal structure, partial nonhomogeneity, internal voids,
cracks, etc. Depending on the orientation and the contribution
of the crosslinks, crystalline and amorphous regions on the final
structure of a polymeric material, the stress at break can be higher
or lower than of an uncrosslinked polymer.

From the practical standpoint the most important of the mech-
anical properties which may be influenced by crystallization is
the tensile strength. It is known that amorphous hydrogels have
generally lower tensile strengths than crystallizable rubbers.
However the property of tensile strength is notoriously difficult
to represent on a theoretical basis. In the case of hydrogels it
is possible to vary two parameters, the degree of crosslinking and
the crystallinity. Both these parameters are found to exert a mark-
ed effect on tensile strength.
In general, increasing degree of crystallinity increases the tensile strength, the initial modulus, the hardness and the density, whereas it decreases the extensibility, the flexibility, and the toughness.

The introduction of a diluent, to form a gel system of diluent and polymer including crystalline and amorphous structures lowers the elastic modulus and stress at break, of the material.

The tear strength is generally improved by crosslinking and crystallization. However, the final behaviour will definitely depend on the orientation of the crystallites and only in entirely unoriented crystalline materials can a definite value of tear strength be expected.

The rate of creep, as well as the rate of relaxation decrease as the crosslinking density increases. For crystalline materials the stress relaxation rate is proportional to the crystallinity (301).

On the mechanical properties of PVA

The main parameters affecting the mechanical properties of PVA are the molecular weight and degree of hydrolysis (446). There is no other water soluble polymer forming such strong films (8,269). All commercial grades of PVA have excellent film-forming ability. The best results are obtained with fully hydrolyzed high-molecular weight polymer (220). The tensile strength of films increases with the molecular weight and it becomes as high as 18000 psi for fully hydrolyzed PVA samples. Use of good plasticizers can lower the
strength to about 8000 psi for a polymer with 30% glycerol. The elongation at break, of PVA samples can be as high as 500% (11, 221). Although PVA films have good tensile and tear strength, most of their applications rely on the unique combination of water solubility, gas impermeability and high strength (427, 428). Experimental determination of elastic moduli of crystalline regions of PVA have been reported by Sakurada et al. (352). The effects of residual acetyl groups and molecular weight of PVA samples on some of the mechanical properties of its films were studied (445).

The mechanical properties of crosslinked PVA samples have been studied for samples of PVA crosslinked via $S_2Cl_2$ in PhMe solutions at 110°C. (3). Graphs of the elongation, residual elongation and stress at break at 25-250° and of the elasticity modulus at 25°C versus the amount of combined S (i.e., the crosslinking density) have been reported. They showed that crosslinking increases the elasticity modulus and the stress at break, while it decreases the elongation. With roentgenograms they have proved that when the percentage of combined sulfur is lower than 15% then the mechanical properties are due to crosslinks and crystalline areas, while above 15% combined sulfur (where practically all OH groups are substituted) the mechanical properties depend only on the degree of crosslinking (162). Analogous mechanical behavior was noticed on the properties of fibers crosslinked in the same way (163).

Kawakami et al. (179, 180) studied the degree of crystallinity,
the swelling and the mechanical properties of PVA fibers as a function of their heat treatment temperature. This is the only successful effort to correlate the properties to the crystallinity of PVA (see Fig. 7-4 and 7-5).

The effects of crystallinity on the modulus of elasticity of PVA films have been reported by Bessonov and Rudakov (32) and comparison of the properties of amorphous and crystallized samples has been done. It can be seen that because of the increasing temperature and the softening of the sample the elastic modulus decreases (see Figures 7-6 and 7-7).

When freshly formed PVA films and fibers are stretched at a temperature close to the softening point of PVA, the polymer acquires an increased strength and a decreased solubility in water. The degree of crystallinity and the orientation increase during high temperature drawing of the fiber (2). PVA fibers with very high mechanical properties have been studied extensively and their applications are numerous (457).
Fig. 7-4: Degree of crystallinity as a function of heat treatment temperature. Annealing time 45 sec.

Fig. 7-5: Tensile strength and elongation as a function of heat treatment temperature. Annealing time 45 sec.
Fig. 7-6: Logarithm of the modulus of elasticity of PVA as a function of temperature for crystalline (1) and amorphous samples (2)

Fig. 7-7: Logarithm of the ratio of the moduli of elasticity of crystalline ($E_c$) and amorphous ($E_o$) PVA as a function of temperature
CHAPTER 8
EXPERIMENTAL WORK

A. SUMMARY

The main purpose of the experimental work was to study the effects of the conditions of heat-treatment on the crystallinity of the PVA hydrogels. The two stages of the heat-treatment process, i.e., dehydration at room temperature and annealing were studied very carefully, under different conditions. We intended to study the effect of chain-length, as controlled by the crosslinking density, on the crystallinity of the hydrogels. This led to the part concerning the characterization of crosslinked PVA hydrogels, which was done by two different methods, i.e., swelling and tensile properties measurements, on hydrogels prepared by different crosslinking methods. A thorough analysis of some of the PVA solutions, as well as a brief study of the effects of different kinds of radiation on them were other subjects investigated in this thesis.

The characterization of the mechanical behaviour of the crystallized hydrogels was the second part of this thesis, where serious effort was devoted to reveal the effects of conditions of preparation and temperature-time history on the hydrogels.

In summary, the experimental work presented here, includes the following parts:
(i) Cross-linking of PVA in solution: the effect of electron beam and radiation on the network formation

(ii) Spectroscopic study of supermolecular structures in PVA solutions

(iii) Swelling experiments on uncristallized hydrogels, for the characterization of their structure

(iv) Tensile tests on uncrystallized hydrogels

(v) The effects of slow rate dehydration at room temperatures on the crystallinity and the properties of the PVA hydrogels

(vi) Evaluation of swelling ratio and degree of crystallinity of swollen hydrogels and dry PVA films by four independent methods

(vii) Tensile and stress relaxation experiments on swollen PVA hydrogels

(viii) Creep experiments

(ix) Tear strength experiments

B. PREPARATION OF THE CASTING SOLUTIONS

The poly(vinyl alcohol) used in this thesis was supplied by duPont de Nemours (91) and it was Elvanol Grade 73-125G, having the highest commercially available molecular weight. This PVA has less than 0.7% acetyl groups, a maximum of 5% volatiles and 1% ash. It contains traces (below 0.01%) of the following ions: Ca, Mg, Mn, Cu, Ge, Pb, and Si. Na was found in the range of 0.01%-0.1%; it was presumably a residue
of the surfactant of the initial emulsion polymerization of vinyl acetate for the production of PVA (101).

The viscosity of some aqueous solutions at temperatures from 70-160°F is shown in cp in the next table 8-1.

**TABLE 8-1**

**VISCOSITY OF ELVANOL SOLUTIONS IN cp**

<table>
<thead>
<tr>
<th>Elvanol Concentration (%)</th>
<th>T=70°F</th>
<th>100°F</th>
<th>140°F</th>
<th>160°F</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>13</td>
<td>9</td>
<td>4.5</td>
<td>3.2</td>
</tr>
<tr>
<td>4</td>
<td>140</td>
<td>78</td>
<td>38</td>
<td>27</td>
</tr>
<tr>
<td>6</td>
<td>840</td>
<td>500</td>
<td>205</td>
<td>150</td>
</tr>
<tr>
<td>8</td>
<td>3600</td>
<td>2000</td>
<td>800</td>
<td>500</td>
</tr>
</tbody>
</table>

Quantitative IR determination (by Debell and Richardson Labs, Enfield, Conn) showed that the carbonyl groups are less than 0.1%. There was no indication of acetyl, peroxide or carboxylic groups. Determination of the 1,2-glycol groups was done by Burke in his thesis (52). He found that the content was less than 1%.

Data on the molecular weight and molecular weight distribution were supplied by E.I. duPont de Nemours (468). The weight-average degree of polymerization was \( \overline{DP}_w = 4200 \) and the number-average degree of polymerization was \( \overline{DP}_n = 2020 \). These data validate a most probable mole-
cular distribution with

$$\frac{D_{P_w}}{D_{P_n}} = 2.079$$

From the above supplied degree of polymerization, the number-average molecular weight was calculated as

$$\bar{M}_n = 88,880$$

The reader, who will compare the data of this thesis to similar data in Bray's (42), Silliman's (394) and Burke's (52) theses, should have in mind that a different value of $\bar{M}_n$ was used by them, although they used the same commercial PVA. In the first two theses an $\bar{M}_n$ of 100,000 was used, as calculated from viscosity data reported by Beresnyewicz (29). Using Mark-Houwink relationship

$$[\eta] = 5.95 \times 10^{-4} x \bar{M}_u^{0.63}$$

(8-1)

and the intrinsic viscosity in water at 25°C, of $[\eta] = 1.27\text{d}l/\text{g}$ they calculated a value of $\bar{M}_u = 193,000$ and $\bar{M}_n = 100,000$. It must be noted however that the above mentioned relationship has changed since 1959, when this paper was published and the numerical coefficients are not the same for Elvanol 73-125G.

Burke, on the other hand, used a value of $\bar{M}_n = 71,000.$ This value was calculated from Gel Permeation chromatograms of acetylated samples of Elvanol (DeBell and Richardson, Enfield, Conn.) and subsequent calculation of the corresponding $\bar{M}_n$ of the initial PVA. However this value
cannot necessarily be taken as a more reliable one, because of the possible bond-cleavages in the PVA structure during the acetylation. In any case, as it will become clear, the absolute value of $M_n$ need not be known to an accuracy much better than ±20%, especially in view of far more important uncertainties such as chain scission and recombination during irradiation.

Elvanol 73-125G is mostly atactic (above 70%) but stereoregular analysis of it is not available (52).

Since the degree of hydrolysis is higher than 99.3%, it is expected that Elvanol will not dissolve in cold water and that it has to be heated above 80°C to dissolve (101). Since the supermolecular structures formed in PVA solutions are a function of the temperature-time history of the samples, all the prepared samples were dissolved at 90°C for 6 hours. Weighed portions of PVA were placed in Pyrex Petri dishes and degassed in a vacuum desiccator. Degassed (via vigorous boiling) distilled water was added so that the desired weight percentage of PVA was reached. In this study the PVA concentration was mainly 10% or 15%, but other solutions were used in certain cases.

C. SPECTROSCOPIC STUDIES OF THE SUPERMOLECULAR STRUCTURES IN PVA SOLUTIONS.

As reported earlier in this thesis, the temperature-time history of PVA solutions plays an important role in the formation of supermolecular structures in the solution, and the latter phenomenon can change
significantly the behaviour of the final PVA films and hydrogels.

In this study a freezing process of the initial PVA solution has been undertaken for the prevention of bubbles formation during irradiation, as explained in the theory. The study of the supermolecular structures formed during this process was done as follows.

Solutions of 2.5%, 5%, 10%, and 15% PVA were prepared at 90°C for 6 hours and 5ml of them were placed in the cylindrical cells of a Coleman Junior II Spectrophotometer-Model 6/35. The cells (tubes) had an internal diameter of 14mm and an external diameter of 16mm. The tubes were placed in a freezer at -20°C and they were frozen for 45, 60, 75, 105, 120 minutes. After the freezing process, they were placed in room temperature of 23±1°C and they were thawed for long periods of time. During this thawing process the cells were placed in the spectrophotometer and the transmittance of visible light was recorded as a function of thawing time. Wavelengths used were 5000, 6000, 7000, 8000Å.

Denoting by $I_a$ the entrance beam intensity, by $I_b$ the exit beam intensity when the cell is empty, by $I_w$ the exit intensity when the cell is full with distilled water and by $I_s$ the sample intensity, the following terms are defined.

Transmission $= \frac{I_b}{I_a}$

Reference Transmission $= \frac{I_w}{I_a}$

Sample Transmission $= \frac{I_s}{I_a}$

Transmittance $= T = \frac{I_s}{I_w}$
The transmission or the optical density (absorbance) are recorded by the instrument.

According to Lambert-Beer Law:
\[ C = K \log \frac{1}{T} = -K \log T \quad (8-2) \]
where \( C \) is the concentration and \( T \) is the transmittance. Then the optical density is defined as:
\[ D = \log T \quad (8-3) \]
because
\[ C_2 = \frac{C_1 D_2}{D_1} = KD_2 \quad (8-4) \]

D. CROSSLINKING OF AQUEOUS SOLUTIONS OF PVA VIA IRRADIATION

1). Electron beam irradiation

A Van de Graaff accelerator located at the High Voltage Laboratory of the Electrical Engineering Department of M.I.T. (Building N.10) was used. It was operated by Mr. Ken Wright during the runs of this thesis. The characteristics of this accelerator have been reported by Trump et al (132,432,433). In most of the experiments the accelerator delivered 3 MeV electrons at a beam current of 100μA. The electron beam was directed from the source through a window, whose shape is shown in Fig. 8-1 towards the samples that were placed on a conveyor belt. The belt ran with 1.3rpm, i.e., 0.33cm/sec.

Considering the special design of the window, a sample placed in the middle of the belt was irradiated for 7.5cm (i.e. 22.5sec) which is the projected length of the 6.5cm, as shown in Fig. 8-2. A sample placed at distance of 9.5cm from the center of the belt was irradiated
Fig. 8-1: Top view of the "window" of the Van de Graaf Generator at MIT

Fig. 8-2: Side view of the window of the Van de Graaf Generator at MIT
for 21cm (i.e. 63sec), which is the projected length of the 19cm, again as shown in Fig. 8-2. Because of design limitations of the machine a maximum of 5 Mgrads per pass could be delivered. For achievement of higher doses, additional passes of 3 and 2 Mgrads were used. From the above calculations it is obvious that the dose rate varied with the final dose and the position of the samples, as shown in Table 8-2.

**TABLE 8-2**

<table>
<thead>
<tr>
<th>Total dose (Mgrads)</th>
<th>Dose rate (center) rads/sec</th>
<th>Dose rate (9.5cm) rads/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>89,000</td>
<td>31,700</td>
</tr>
<tr>
<td>3</td>
<td>133,000</td>
<td>47,600</td>
</tr>
<tr>
<td>5</td>
<td>222,000</td>
<td>79,400</td>
</tr>
</tbody>
</table>

However this variation of the dose rate did not affect the cross-linking density because all the samples used were of maximum diameter of 5cm, where the dose rate is almost constant (See also Fig. 9-14).

The crosslinking runs were done as follows: weighed portions of PVA were placed in Pyrex-Petri dishes of 50×15mm (with top and bottom) and they were degassed for one day in a vacuum dessicator. After this, they were transferred in model XL7-17 glove bags, that had been purged with nitrogen for about 15 minutes, they were closed tightly, and water which had been degassed with vigorous boiling was added to the dishes until the desired concentration was reached. The used concentrations were mainly 10% and 15%, sometimes also 5% and 20% by weight in PVA.
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The dish bottom was wrapped tightly with Saran Wrap, the cover was put on the top of it and the whole dish was wrapped with more Saran Wrap. About 20 ampules were placed in a large crystallizing dish, covered with Saran Wrap tightly and placed in an oven at 90±0.5°C for 6 hours. Then they were placed back into the nitrogen glove-bag, the Saran Wrap was removed and a thin sheet of 0.25mil film of Mylar (polyethylene terephthalate), which acts as a window for electron beam radiation, was placed and held with a rubber band. The top was placed again and the samples were put in the freezer at -20°C for 60 min, after which they were thawed in room temperature 23±2°C for 6 hours. The thawing was done in the nitrogen glove-bag. Then the samples were transferred for irradiation.

Irradiation was performed at 0°C or 30°C. The samples were immersed in an ice bath (in the case of 0°C irradiation) for 10-15 minutes, or in an glycerol-water bath, preheated to 30°C by heating coils. Irradiation was performed by passing the dishes under the electron beam on the conveyor belt. Check of the temperature was done after each run. The temperature increased 2.5°C per Mgrad (in water). The radiation doses were 5 and 10 Mgrads, sometimes also 3, 8, 13, and 15 Mgrads.

It is well known that electron beam irradiation has very weak penetration and that the effects of it on the irradiated material will vary with depth of irradiation. For this reason all the irradiated samples were thicker that 2.5mm. The reader should notice the effect of this
restriction on some of the final results of this thesis and Bray's thesis (42).

The same radiation process was undertaken for the samples used for the study of the variations of crosslinking density as a function of depth and distance from the center. Films of thickness of 7.5mm and diameter of 15cm were irradiated in the same way and then sliced in three layers of 2.5mm each. The samples were then cut in "rings" of 1.25cm width each. Swelling experiments were performed, as it will be discussed later.

In cases of irradiation in atmosphere, the same procedure was followed except that all the samples were not prepared in glove bags, but in air.

Radiation was performed on the following samples under the following conditions shown in Table 8-3. These samples were prepared for calculation of $M_c$, the crosslinking density $\rho = \frac{M_n}{M_c}$ and the number of crosslinked units $u$.

**Special arrangements for electron beam irradiation**

A series of runs with stationary samples were performed for studying the effect of dose rate on the crosslinking density. The crosslinked solution was always 10% in PVA, irradiated at 30°C with 3 Mgrads. Changing the total beam current, the following dose rates were achieved: 4130, 1652, 826, and 413 rads/sec.

Finally one run with "pauses" was performed. A 10% solution of
TABLE 8-3

CONDITIONS OF IRRADIATION WITH ELECTRON BEAMS

<table>
<thead>
<tr>
<th>C (%)</th>
<th>T (°C)</th>
<th>D (Mgrads)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0</td>
<td>3,5,8,10,13,15</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>3,5,8,10,13,15</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>3,5,8,10,13,15</td>
</tr>
<tr>
<td>20</td>
<td>0</td>
<td>3,5,8,10,13,15</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>3,5,8,10,13,15</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>3,5,8,10,13,15</td>
</tr>
<tr>
<td>15</td>
<td>30</td>
<td>3,5,8,10,13,15</td>
</tr>
<tr>
<td>20</td>
<td>30</td>
<td>3,5,8,10,13,15</td>
</tr>
</tbody>
</table>

PVA was irradiated at 30°C with a total of 3 Mgrads delivered in the following way: Four times 0.25 Mgrads with pauses of 15 minutes, then four times 0.50 Mgrads with pauses of 30 minutes. The belt run with 3.2rpm, i.e. ~0.8cm/sec. Thus the total dose rate in the center was 30800rads/sec and at the sides of the belt 9500rads/sec.

2). γ-Radiation

The γ-Radiation was delivered by the M.I.T.-Cobalt 60 source located (until December 1972) in Building 66. The source had been installed and used for 4 years and 2 months, when the present experiments were performed. The dose rate was appropriately calculated to 3600 rads/minute.
The center radiation chamber was a metallic box of dimensions 22" x 17" x 7" which could be immersed by an automatic mechanism 12 ft. under water, where two cobalt-60 bars were placed. Only the center radiation chamber was used, so that the dose distribution was homogeneous, because of radiation from both sides (87).

Irradiation was done at 0°C and 30°C. When irradiated at 0°C, the samples were immersed in a large ice-water bath which was placed in the radiation chamber. Because of the melting of the ice, the ice-water bath was replaced by another one, every two hours. When irradiated at 30°C, the samples were immersed in a glycerol-water bath, especially designed for this purpose (with control of temperature and stirrer), which was placed in the radiation chamber. All the wires were covered by Polyethylene tubings for prevention of immediate degradation. Because of many technical problems during the control of the temperature, this method was abandoned, after we received some representative experimental measurements.

The samples were prepared in small tubings 13 x 100mm, which were sealed in atmosphere or under vacuum, according to the experiments. Sealing under vacuum was done in an equipment prepared by Mr. Stan Mitchell and located in Room 12-120. The sealed tubings were transferred to the Co-60 source and irradiated immediately with the appropriate dose. The irradiated samples are included in Table 8-4.
<table>
<thead>
<tr>
<th>$C_c$ (%)</th>
<th>$T_c$ (°C)</th>
<th>$D_c$ (Mgrads)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0</td>
<td>3, 5, 8, 10, 15</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>3, 5, 8, 10, 15</td>
</tr>
<tr>
<td>20</td>
<td>0</td>
<td>3, 5, 8, 10, 15</td>
</tr>
<tr>
<td>25</td>
<td>0</td>
<td>3, 5, 8, 10, 15</td>
</tr>
<tr>
<td>15</td>
<td>30</td>
<td>5, 8, 10, 15</td>
</tr>
<tr>
<td>20</td>
<td>30</td>
<td>5, 8, 10, 15</td>
</tr>
<tr>
<td>25</td>
<td>30</td>
<td>5, 8, 10, 15</td>
</tr>
</tbody>
</table>

Preparation of hydrogels in the form of long tubings

For biomedical and hematological experiments long tubings from PVA solutions were prepared as follows. Solutions of 10% and 15% PVA were sucked (using a vacuum pump) in the space between two concentric glass tubings with teflon stoppers at their ends. The dimensions inside/outside diameter were 6/13 and 5/17 in mm. The tubings were frozen at -20°C for 60 min, thawed at room temperature for 6 hours and brought for irradiation. After irradiation they were removed from the glass tubing and soaked in water at 30°C. The following samples were made (See Table 8-5).
TABLE 8-5

CONDITIONS OF IRRADIATION OF TUBINGS WITH ELECTRON BEAMS

<table>
<thead>
<tr>
<th>$C_c$ (%)</th>
<th>$T_c$ ($^\circ$C)</th>
<th>$D_c$ (Mgrads)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>30</td>
<td>3</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>8</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>15</td>
</tr>
</tbody>
</table>

The dose delivered was the total of two doses delivered in both sides.

E. SWELLING EXPERIMENTS

The samples after irradiation were allowed to equilibrate at 30$^\circ$C for one hour and then the measurements necessary to perform the swelling calculations were taken. As discussed earlier, Bray (42) has developed an expression the necessary information includes the volume fraction of polymer in the relaxed state (immediately after irradiation) $v_{2,r}$ and the volume fraction after the sample was swollen in water at 30$^\circ$C, $v_{2,s}$.

In this thesis, whose purpose, as far as the irradiation part is concerned, was not to repeat Bray's experiments, but only to complete them, by verifying the data that are needed in this work and calculating selective values of $M_c$, we will report data on $M_c$, swelling ratio, percentage of PVA and percentage of water in swollen and relaxed gels. The term "relaxed" gels means gel immediately after irradiation.
The volume of the polymer gel after irradiation was determined by weighing the gel in air and in water at 30°C according to ASTM (14)

\[ V_r = \frac{W_{a,r} - W_{w,r}}{\rho_w} \quad (8-5) \]

where \( V_r \) = relaxed volume of sample
\( W_{a,r} \) = weight of sample in air
\( W_{w,r} \) = weight of sample in water
\( \rho_w \) = density of water at 30°C = 0.996 gr/cm\(^3\)

The samples were then placed in water overnight at 90°C. This was done to release any crystallization that may have existed in the hydrogel and of course to extract the sol fraction. The sol fraction was at maximum 1.35% and it was neglected.

Then the samples were placed in distilled water at 30°C and they were swollen until they reached a constant weight (thermodynamic swelling equilibrium). This usually happened after 4-5 days. The swollen volume \( V_s \) was determined in the same way (14)

\[ V_s = \frac{W_{a,s} - W_{w,s}}{\rho_w} \quad (8-6) \]

The samples were always kept in distilled water, where formalin was added for the prevention of biodegradable degradation (413).

For the calculation of the bone dry weight of the gel, i.e., the weight of PVA, the samples were dried at 100°C for 48 hours in a vacuum desiccator. The weights of the samples were determined and the volume
calculated using a density of 1.269 gr/cm$^3$.

$$V_p = \frac{W_p}{\rho_p}$$  \hspace{1cm} (8-7)

where $V_p$ = volume of dried polymer  
$W_p$ = weight of dry polymer  
$\rho_p$ = bulk density of PVA (1.269 gr/cm$^3$)

From these experiments the following values can be obtained

i) The relaxed volume fraction of polymer

$$\nu_{2,r} = \frac{V_2}{V_p}$$  \hspace{1cm} (8-8)

ii) The swollen volume fraction of polymer

$$\nu_{2,s} = \frac{V_2}{V_s}$$  \hspace{1cm} (8-9)

iii) The weight percentage of PVA in the swollen hydrogel

$$\text{PVA}_\% = \frac{W_{PVA}}{W_{a,s}} = \frac{W_p}{W_{a,s}}$$  \hspace{1cm} (8-10)

iv) The swelling ratio (weight)

$$q = \frac{W_{a,s}}{W_p} = \frac{1}{\nu_{2,s}}$$  \hspace{1cm} (8-11)

v) The swelling ratio (volume)

$$Q = \frac{V_s}{V_p} = \frac{1}{\nu_{2,s}}$$  \hspace{1cm} (8-12)
Determination of swelling properties of hydrogels at different temperatures was done by placing them in water at the desired temperature of swelling in an oven, until constant weight was reached.

F. DETERMINATION OF THE ELASTIC BEHAVIOUR OF THE HYDROGELS

Irradiation was done by the previously mentioned procedure at temperatures 0°C and 30°C, on solution of 10 and 15%. The dose delivered was 3,5,8,10 and 15 Mgrads. The only difference was that the samples were prepared in 150 x 20mm Petri dishes.

After irradiation and swelling at 30°C as described before, the samples were cut with an ASTM dumbbell die and tensile experiments were performed.

The full description of the tests performed is reported in Ch.8-I.

G. CRYSTALLIZATION PROCEDURE

The crystallization was done in a two-stage procedure.

1) Dehydration

The hydrogels were produced via radiation crosslinking as it was described previously. The samples immediately after irradiation were taken in a dust free environment where they were dehydrated by a slow drying rate process at 23±2°C and RH 40% for 24 hours.

This is the general dehydration procedure undertaken for all the samples used for determination of the crystallinity and study of the mechanical properties.

Other experiments had the intention of revealing the effect of
dehydration conditions on the crystallinity of the samples. Five drying media and two kinds of films of different crosslinking density were used. The films were cut in rectangular pieces (thickness ~1mm) and hung in the appropriate dessicators.

The two samples used were

a) $M_c = 5715$ (15%, 30°C, 5Mgrads)
b) $M_c = 4770$ (10%, 30°C, 5Mgrads)

The temperature was 25±1°C. The drying media used were SiO₂, Ca(NO₃)₂, MgCl₂, KBr and K₂Cr₂O₇. After dehydration, swelling experiments were performed.

2). Annealing

The second stage of the process is the annealing procedure. Annealing is the process of heating a sample at temperatures above the Tg with subsequent slow cooling. Quenching is the process where the heating above the Tg is followed by a very fast cooling.

After dehydration the samples were placed in an oven at temperatures of 90, 105, 120 and 135°C for 5 min, 10 min, 15 min, 20 min, 30 min, 60 min 90 min, and 120 min. Other samples were placed in the oven at 165, 175, 185, 195°C for significantly shorter periods of time.

With this procedure the whole process of crystallization has occurred. Figure 8-4 shows the complete process.

The samples tested in this thesis are shown in Table 8-6. As it is evident a series of casted uncrosslinked PVA films (no irradiation)
Fig. 8-4: Preparation and Drying Procedure of PVA hydrogels
have been dried under the same conditions for reasons of comparison.

TABLE 8-6
CONDITIONS OF EXPERIMENTS OF THIS THESIS

<table>
<thead>
<tr>
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<th>Drying Conditions</th>
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<td>no crosslinking</td>
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<td>30</td>
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H. EVALUATION OF CRYSTALLINITY IN HEAT-TREATED FILMS

1). Crystallinity indirectly evaluated by Swelling Experiments

As already discussed, the swelling ratio, the percentage of $H_2O$ in the swollen hydrogel and similar terms, are a means of interpretation of the degree of crystallinity.

The samples, that had undertaken the whole drying process, were swollen in water at 30°C and the volume of the swollen after crystalli-
zation hydrogel \( V_{s,c} \) was determined by immersing and weighing the samples in air and water.

\[
V_{s,c} = \frac{W_{a,c} - W_W}{\rho_W} 
\]

(8-13)

where \( W_{a,c} \) = weight in air after crystallization

\( W_W \) = weight in water at 30°C

\( \rho_W \) = density of water at 30°C (0.996)

The samples were then placed in a vacuum desiccator at 100°C for 48 hours and the bone dry weight was calculated. The volume of the dry polymer was calculated as:

\[
V_p = \frac{W_p}{\rho_p} 
\]

(8-14)

where \( V_p \) = volume of dried polymer

\( W_p \) = weight of dry polymer

\( \rho_p \) = density of PVA = 1.269 gr/cm³

The following terms can be measured and evaluated by the data already gotten.

(i) The swollen volume fraction of polymer after crystallization

\[
u_{2,sc} = \frac{V_p}{V_{s,c}} 
\]

(8-15)

(ii) The weight percentage of \( H_2O \) in the swollen hydrogel.

\[
PVA\% = \frac{W_{PVA}}{W_{a,sc}} = \frac{W_p}{W_{a,c}} 
\]

(9-16)
(iii) The swelling ratio (weight)

\[ q = \frac{W_{sc}}{W_P} = \frac{1}{W_{PVA}} \quad (8-17) \]

(iv) The swelling ratio (volume)

\[ Q = \frac{V_{sc}}{V_P} = \frac{1}{u_{2,sc}} \quad (8-18) \]

Effect of swelling temperature on the crystallinity

The PVA samples after dehydration and annealing were placed in distilled water at 5°C and they were swollen to constant weight. The swelling ratio and the percentage of water were reported. The same samples were then placed in water at 30°C and they were swollen to constant weight. The swelling ratio was again calculated. The same procedure was then followed for the swelling of the same samples at 45, 60, 75°C.

2) Crystallinity via density methods

The swollen heat-treated PVA hydrogels, after having equilibrated in water at 30°C to constant weight, were weighed in air and in water at 30°C. The density of the hydrogel \( \rho_h \) was calculated as:

\[ \rho_h = \frac{W_a \times \rho_w}{W_a - W_w} \quad (8-19) \]

where \( W_a \) = weight in air

\( W_w \) = weight in water of density \( \rho_w \) (0.996 gr/cm\(^3\))
The density was calculated using the relations referred in the theoretical part.

\[
\frac{1}{\rho_h} = \frac{W_{\text{PVA}}}{\rho_g} + \frac{1-W_{\text{PVA}}}{\rho_w} \quad (8-20)
\]

\[
\frac{1}{\rho_g} = \frac{x}{\rho_c} + \frac{1-x}{\rho_a} \quad (8-21)
\]

which combine to the general equation

\[
\frac{1}{\rho_h} = W_{\text{PVA}} \left( \frac{x}{\rho_c} + \frac{1-x}{\rho_a} \right) + \frac{1-W_{\text{PVA}}}{\rho_w} \quad (8-22)
\]

Finally

\[
x = \frac{\frac{1}{\rho_h} - \frac{1-W_{\text{PVA}}}{\rho_w} - \frac{W_{\text{PVA}}}{\rho_a}}{\left( \frac{1}{\rho_c} = \frac{1}{\rho_a} \right) W_{\text{PVA}}} \quad (8-23)
\]

where \( \rho_h \) = density of the swollen hydrogel after crystallization

\( \rho_a \) = density of 100% amorphous PVA = 1.260 gr/cm\(^3\)

\( \rho_c \) = density of 100% crystalline PVA = 1.345 gr/cm\(^3\)

\( W_{\text{PVA}} \) = percentage of PVA in swollen hydrogel

\( x \) = crystallinity (%) defined as the ratio of crystalline PVA to the total PVA (weight)

\( \rho_w \) = density of water at 30°C = 0.996 gr/cm\(^3\)

Substituting the arithmetical values, the final relation is:

\[
x = 18.8732 - 23.9501 \times \frac{\frac{1}{\rho_n} - \frac{1-W_{\text{PVA}}}{0.996}}{W_{\text{PVA}}} \quad (8-24)
\]
3) **Differential Scanning Calorimetry**

The instrument used is a Perkin-Elmer Differential Scanning Calorimeter DSC-1. A block diagram of the instrument system is shown in Fig. 8-5. The system consists of two separate control loops, one for average temperature control, the second for differential temperature control (291,463). In the average temperature loop, a programmer provides an electrical signal which is proportional to the desired temperature on the sample and reference holders. The programmer temperature information is also relayed to the recorder temperature marker pen and appears as the abscissa scale marking. At the average temperature amplifier, the programmer signal is compared with the average signal from platinum resistance thermometers permanently embedded in the sample and reference holders. In this way, the average temperature of the holders is made to follow the command from the programmer.

In the differential temperature control loop, signal representing the sample and reference temperatures measured by the platinum thermometers are fed to a circuit which determines whether the reference or sample temperature is greater. The differential temperature amplifier output will then correct any temperature difference between them (463).

The operator, using front-panel controls, raises the average temperature of the sample holders to a desired initial temperature, selects one of eight temperature program rates (0.625°C/min. up to 80°C/min.) and programs the desired change in average temperature of the sample holders. When a transition such as melting, boiling, dehydration, or
crystallization occurs in the sample material, an endothermic or exothermic reaction occurs. The change in power required to maintain the sample holder at the same temperature as the reference holder during the transition is the differential power and is recorded as a peak. The peaks indicate the total energy transfer to or from the sample.

The DSC-1 was calibrated with indium for the high temperatures (melting temperature 155°C at 5°C/min.) and with palmitic acid (61°C at 5°C/min.). Since the $T_m$ of the gels was expected to be around room temperature, we used the lower temperatures cell, which covers the range of -100°C to 400°C.

The hydrogel to be analyzed was cut with a round die of internal diameter 6mm, and this disk (which weighed always between 8-15mg) was placed in the pan, covered with an aluminum disk and pressed in the sample pan crimper supplied with the instrument, so that it made a pellet including the sample. The pellet was placed on the right-hand sample holder, while an empty pan with cover was placed on the left-hand sample holder. The low-temperature cover was placed on the top of the sample holders and it was twisted to lock it in place. Dry nitrogen passing through a trap with drying medium was purged for about 15 minutes, before coolant was introduced.

Then the temperature was set at 273°C, but this point, when using the low-temperature cover, represents a temperature of 173°C, i.e., -100°C. The low-temperature cover is nothing more than a dewar flask,
where one or two fillings of liquid nitrogen were needed until the average temperature (green) light showed that the temperature of the sample holder came into control at -100°C. Then the lid of the low-temperature cover was placed in position and the run was started. When the run was complete (at about 250°C) the temperature was lowered manually back to -100°C (the instrument being off) and another experiment was started.

A typical run of one of the hydrogels is shown in Fig. 8-6. The thermogram is characterized by two peaks the first (A) of which is the one referring to the melting of the crystallites of the hydrogel, produced during the mild dehydration-annealing process, while the second peak (B) refers to the melting of PVA.

Because of the existence of humidity in the sample holders (although careful drying of the cover and purging with nitrogen were done before each experiment), attenuations of the form $A_\perp$ could be recorded on the thermogram. In some samples the existence of "water bubbles" (sign of partial non-homogenicity) was detected by the peak of water at 0°C and 100°C. These samples were discarded.

There are many ways of calculating the $T_m$ (melting point) of the examined gels. In Fig. 8-7 there are shown some of these ways. Among them the first method is used by most of the authors and has been used in this thesis, too (395).

The geometry of the sample affects the peak shape (455). As shown
Fig. 8-7: Methods of determining $T_m$ and calculating the area under a DSC peak
in Fig. 8-8 the peak is sharper in the case of a flat sample than in
the case of a granular one (24).

Experiments were done on the effects of the scanning speed on the
shift of the melting point of the examined hydrogels as well as on the
reproducibility of the results. The melting point of the calculated
polyvinylalcohol was calculated from the second peaks (B) of the typi-
cal thermographs as the one shown in Fig. 8-6.

The effect of the scanning speed on the melting point of a sample
is shown in Fig. 8-9.

4) **Infrared Spectroscopy**

IR spectra analysis was done for the quantitative determination
of the crystallinity of the dry PVA films.

The method of crosslinking was exactly the same as reported above.
The samples were casted as very thin films. For accurate quantitative
data with IR spectra the films must have thickness between 10-40 microns.
The thickness is measured using a Dial Comparator, which could meas-
ure with accuracy ±0.05 mil.

Microscope slides 3×1 inch were treated with an 1% Siliclad solu-
tion for about 10 seconds, so that the films would not stick on the sur-
face of the glasses. A drop of 10% or 15% PVA solution was placed on
one of the microscope slides and another microscope slide was put on
top, separated at the ends by two small square glasses 20ml thick.
Films casted in this way, were irradiated at 3,5 and 10 Mgrads at 0°C
and 30°C, using the same technique as before.
Area 9.2
Sample 6.3 mg Bi

Fig. 8-8: Effect of sample geometry on peak shape of DSC thermogram
Fig. 8-9: Effect of scanning speed on the melting point as calculated from DSC
The same procedure of dehydration and annealing was followed and finally the samples were ready for testing. Table 8-7 includes the samples tested.

An IR spectrophotometer Perkin Elmer 237 was used. The frequency of the light varied between 2000 and 650 cm\(^{-1}\) (5-16 microns).

A typical IR spectrum of a heat-treated PVA film is shown in Fig. 8-10.

The intensity of the 1141 cm\(^{-1}\) band was recorded as a function of temperature-time history. The basis for determining the per cent crystallinity in PVA from IR spectra is this crystalline sensitive band (8.7\(\mu\)). A straight line was drawn along the portion of the spectrum between 9 and 9.2 microns, extended far enough to intercept a vertical line through the peak of the 8.7\(\mu\). The vertical distance \(d\) between the 8.7 peak and the intercept was determined. Then the vertical distance \(c\) between the 7.1 peak and the base line was determined. Knowing that the percent of crystallinity is proportional to the intensity of the peak at 8.7\(\mu\), a relation of the following form can be established.

\[
x(\%) = A' \left( \frac{d}{c} \right) - B'
\]  

(8-25)

The coefficients \(A'\) and \(B'\) can be calculated by an appropriate calibration. The method has been successfully used for uncrosslinked films (186).
Fig. 8-10: Typical IR spectrum of PVA
TABLE 8-7

PREPARATION CONDITIONS OF PVA FILM USED FOR ANALYSIS WITH IR-SPECTROSCOPY

<table>
<thead>
<tr>
<th>Conditions of irradiation</th>
<th>Conditions of drying</th>
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<td>( T_c ) (°C)</td>
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I. CHARACTERIZATION OF THE MECHANICAL BEHAVIOUR OF THE CRYSTALLIZED HYDROGELS

1. Tensile Experiments

A table model Instron testing instrument (Instron Corporation, Canton, Massachusetts) was used to perform both Tensile and Elastic Modulus Measurements. The samples have a dumbbell shape and they are cut by an ASTM certified die. The dimensions and the set-up of the tensile experiment are shown in Fig. 8-11.

One of the advantages of the dumbbell shaped samples is that ultimate fracture happens in the center of the sample and is not affected by the stress concentration at the jaws. In order to prevent slippage
Fig. 8-11: Tensile experiment set-up
of the sample in the jaws as well as breakage at the jaws, serrated plastic grip faces were glued on the jaws, so that the friction between them and the sample prevented any possible slippage. Since only hydrogels were tested, the whole set-up of the grips, jaws, etc. was immersed in a water-bath supplied with a control-heater.

All the tensile experiments at 30°C and at higher temperatures were done by setting the appropriate temperature (Some tensile experiments of specimens swollen at 5°C were done by transferring the sample from the jar kept at 5°C to the water-bath at room temperature and performing the run at this temperature. The error was considered). The method used is the official ASTM method (12).

The Instrom is first calibrated and the gage length indicator on the Instrom panel is set to zero, when the jaws just touch. Thus, the indicator reads the initial gage length when the sample is clamped. A 2000gms load cell was used for the required tension in the tensile strength experiments. For obviously "weak" specimens the sensitive 200gr. load cell was used. In the regular runs with the 2000grs. the strip chart recorder read 20gms per smallest division of the chart paper. The rate of extension used was 1 in/min. On the horizontal axis (elongation axis) the smallest division was 0.05 inches.

The preparation of the samples used for the mechanical tests was done in the way reported previously. All the films used were irradiated with electron-beam irradiation in Petri dishes of 150×20mm. The drying process was done in these dishes, so that the one surface was always
in contact with the inert glass surface. This was done in order to prevent any curling due to possible internal stress formation. The thickness of the final film was controlled by casting a calculated volume of solution, so that the final thickness was between 20 and 25mil. The reader should notice that because of the final swelling which depends on the percentage of crystallinity introduced during the drying process, an accurate prediction of the thickness was not possible. However, volume of 40-45mil of PVA 10% solution was enough for a final film of 20-25mil thickness.

The swollen samples were cut with the dumbbell shape die.

During irradiation of the 15cm on dishes with the casted films, the direction of the conveyor belt was noted on the sample. When cutting the dumbbell samples with the ASTM die, only two samples were cut from each film, along the direction already noted, whereas the rest of the film was discarded. In this way the film was homogeneous as far as crosslinking was concerned.

The thickness of the samples was measured in five different points along its length using a model Dial Comparator, which could measure the thickness with accuracy ±0.05mil. The average of the five measurements was reported as the average thickness, if the deviation from the average value was not more than ±10%, otherwise the sample was discarded.

The samples were immediately transferred to the water-bath of the Instron (kept at the same temperature with the swelling temperature of
the samples, temperature which for almost all runs was 30°C) and gripped on the jaws. The initial gage length was recorded, and the run was performed until the sample was ruptured. If the ultimate failure did not happen in the middle of the sample, it was discarded. One to four specimens were tested at each crosslinking and heat-treatment combination.

A typical stress-strain diagram, as gotten after the tensile experiment is shown in Fig. 8-12. Table 8-8 includes the materials tested.

Some of the term characterizing the mechanical behaviour of the hydrogels can be calculated from Fig. 4-12, as follows:

(i) The initial modulus $E_i$ under extension rate of 1 in/min

$$E_i = \frac{\tau}{\varepsilon}$$

It is the ratio of the stress ($\tau$) to corresponding strain ($\varepsilon$) at strain zero. The (tensile) stress $\tau$ is defined as the ratio of the tensile load to the unit area of minimum original cross-section (denoting by $t$ the thickness and having in mind the dimensions of the die used for cutting the samples, the cross-section is $0.25 \times t$ in$^2$). The strain $\varepsilon$ is defined as the change in length per unit of original length.

(ii) The secant modulus

It is the ratio of stress to corresponding strain at any specified point on the stress-strain curve.

(a) The secant modulus at 10%, $E_{10}$

It is the ratio of stress to strain at 10% elongation
Fig. 8-12: Typical tensile experiment stress-strain curve
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<thead>
<tr>
<th>Conditions of irradiation</th>
<th>Conditions of drying</th>
<th>Mechanical Test</th>
</tr>
</thead>
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<td>$C_c$ (%)</td>
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<td>$D_c$ (Mgrads)</td>
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<td>5</td>
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</tbody>
</table>

e=tensile properties  
c=creep experiments  
t=tear pr. strength
(b) The secant modulus at 100%, \( E_{100} \)

It is the ratio of stress to strain at 100% elongation

(iii) The ultimate tensile strength (UTS)

It is the maximum tensile stress sustained by a specimen during a tension test and it is expressed as the force at break per initial cross-section

\[
E_i = \frac{F_u}{A_o}
\]

(iv) The elongation at break

It is the maximum increase in length produced in the gage length of the test specimen by a load, at the point of break.

(v) The proportional limit

It is the greatest stress which a material is capable of sustaining without any deviation from proportionality of stress to strain (Hooke's Law).

2. Creep experiments

A constant load creep experiment has been performed for most of the crosslinked crystallized hydrogels. All the runs were done in water and because of the different buoyancy forces on the loads and the different cross-sections of the samples (due to uneven thickness for the reasons discussed in part 8-I-1) constant stress experiments could not be done.

In a creep run, as the specimen creeps, the length increases and
the cross-section decreases, so that the actual stress increases. If the results are to be treated on a theoretical basis, creep experiments at constant stress should be performed. However, in the case of linear polymers creep experiments can be performed at constant load.

The method used is the official ASTM method (13,18). A rigid horizontal aluminum rod of 0.5 in. in diameter was supported about 1-1/2 ft. above a wooden base. Three dumbbell shaped specimens could be suspended from the rod at any time. A 6 inches long piano wire hook was hung from the rod and connected to the upper part of the specimen by means of a lucite clamp made of two 1 x 0.5 x 0.125 inch lucite pieces. Brass wignuts were used to tighten the clamp. The lower part of the specimen was also clamped in the same way. The whole system was immersed in a 2ft. x 3.5 inch glass cylinder filled with distilled water. Three cylinders were used, so that three runs could be done at the same time.

Weights of 500gms, 200gms, 100gms were used as loads. Two dots were made on the surface of the hydrogel, symmetrically along its length and at distance of approximately 0.5cm. The dots were made using two drops of a 10% solution of albumin, which was then stained with two drops of amido-black. The Creep experiment set up is shown in Fig. 8-13.

The samples were prepared, swollen, cut, and their average thickness measured as in the case of tensile experiments. Then they were clamped on the clamps and the distance between the two dots was measured,
Fig. 8-13 Creep experiment set-up
using a cathetometer, in the absence of load (the weight of the lower clamp - around 12gms - was not enough to cause any elongation). The load to be applied, already in the cylinder and hanging from another steel wire, was raised with a system of counter-weights passing over the horizontal aluminum rod and the hook of the weight touched the hook of the lower clamp of the specimen. Then the load (using again the mechanism of counterweights) was left to suspend freely and elongation started. Readings were taken at the following intervals: 1,3,6, 9,12,18,24,30 minutes, 1,2,3,5,10,20,30 hours. A cathetometer was used for the readings. The cathetometer could measure differences as low as 0.005cm. in length. At the end of the 30 hours creep period, the weight was again removed and recovery of the sample was followed in the same fashion. One or two samples were tested at each crosslinking and heat-treatment combination.

From the data gotten, the following important mechanical properties could be calculated:

(i) The Creep Compliance (J)

It is defined as the ratio of the strain corresponding to a certain creep stress at any time. Thus it is the reciprocal of the creep modulus.

\[ J = \frac{\varepsilon}{\tau} \]

(ii) The instantaneous strain

It is the strain occurring immediately upon loading a creep
specimen (for practical purposes after one minute).

(iii) The instantaneous recovery

It is the strain occurring immediately upon unloading a specimen (for practical purposes defined after one minute of unloading).

(iv) The permanent elongation after recovery

It is defined as the elongation of the specimen, after a long time recovering (usually the specimen's final length is bigger than its initial one).

3. Stress-Strain Quasi-equilibrium experiments

Stress-strain experiments were performed on some of the hydrogels. A horizontal aluminum rod was supported about 1-1/4 ft. above a wooden base. A one inch long spring was suspended from the rod and it was connected with a stop-ring and a piano wire one foot long to the upper clamp of the specimen. The lower clamp was permanently supported by a hook and a lower rubber stopper on the wooden base. The whole system was immersed in a glass cylinder 1ft. x 2in. filled with distilled water. Three such cylinders were used, so that three specimens could be studied at the same time. The whole system is shown in Fig. 8-14.

At first the springs used, which were supplied by PIC Design Corp, Rockaway, N.Y., and had the model numbers AZ-26, A2-30, and AZ-48 were calibrated. The specimens were produced, swollen, cut, stained, and measured as in the case of creep experiments. Then they were clamped on the clamps of the systems, and the spring was suspended from the upper horizontal aluminum rod. Turning the upper screw connected di-
Fig. 8-14: Stress-strain quasi equilibrium tests set-up
rectly to the spring, the spring was elongated, changing the load applied. After 20 minutes, the elongation of the specimen and the spring were reported. The twenty minutes time was considered as longer than the relaxation time of PVA hydrogels. Unfortunately, no values have been reported on this relaxation time and this was judged by comparison to the corresponding relaxation time of silicone rubbers (which is 5 minutes). After each cycle, the elongation of the spring was changed and the new elongation after 20 minutes was reported. The elongations were measured using a cathetometer. The method used was the official ASTM method (19). From the results the elastic modulus was measured.

4) Tear Strength and Tear Propagation Experiments

The method covers the determination of the force necessary to propagate a tear in plastic films (318). For the experiments the same Instron, used for the tensile properties is used, as it is modified with its bath.

The samples were made in exactly the same way as previously. The specimens were cut from these films in strips of 3\text{in.} long by 1\text{in.} wide and they had a clean longitudinal slit of 2\text{in.} cut with a sharp razor blade (Fig. 8-15). The thickness of the specimens was measured below the slit, and the average of three values was reported.

The one tongue of the specimen was secured in one grip and the other on the other grip of the constant-rate-of-grip separation testing machine, using an initial grip separation of 50\text{mm}(2\text{in.}). The major axis of the specimen was aligned so that it was on the same imaginary line
rectly to the spring, the spring was elongated, changing the load applied. After 20 minutes, the elongation of the specimen and the spring were reported. The twenty minutes time was considered as longer than the relaxation time of PVA hydrogels. Unfortunately, no values have been reported on this relaxation time and this was judged by comparison to the corresponding relaxation time of silicone rubbers (which is 5 minutes). After each cycle, the elongation of the spring was changed and the new elongation after 20 minutes was reported. The elongations were measured using a cathetometer. The method used was the official ASTM method (19). From the results the elastic modulus was measured.

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The one tongue of the specimen was secured in one grip and the other on the other grip of the constant-rate-of-grip separation testing machine, using an initial grip separation of 50mm(2 in). The major axis of the specimen was aligned so that it was on the same imaginary line.
Fig. 8-15: Sample for Tear Propagation Experiments

Fig. 8-16: Tear strength test set-up
joining the centers of the grips. The grip separation rate used was 1 in/min (See Fig. 8-16).

Specimens cut from the same film but with different "direction" of their long axis, were studied.

The load was recorded as a function of time. Two typical graphs for highly extensible film as well as low-extensible films have been presented in Figures 7-2 and 7-3. For PVA films almost all the diagrams were of the type of "low extensibility" as shown in Fig. 8-17. The method used is the official ASTM method (15,16,17).
Fig. 8-17: Typical tear-strength test stress-strain curve for a PVA hydrogel
CHAPTER 9

RESULTS AND DISCUSSION

The results of this thesis are presented in three sections; the first section includes studies concerning the characterization of crosslinked PVA networks and their mechanical properties.

The second section includes the investigation of the method of reinforcement of these networks via crystallization, as well as the quantitative analysis of the effect of the temperature-time history of the samples on their physical properties (swelling ratio, crystallinity, etc.).

The third section deals with the determination of the mechanical behavior of these crystallized samples, and particularly their behavior upon tensile forces, creep and tearing.

A. TURBIDITY STUDIES OF PVA SOLUTIONS

PVA solutions, prepared by dissolving PVA in distilled water at 90° for 6 hours, were subjected to a freezing-thawing process, after which gelation had occurred and turbidity had appeared.

Turbidimetric study of the gels using visible light of wave-lengths between 5000 and 8000 Å has been performed. Data of the transmittance and/or optical density as a function of PVA concentration in the solution, time for freezing and time of thawing are reported in Fig. 9-1, 9-2, 9-3 and 9-4.
Fig. 9-1: Transmittance of visible light (\(\lambda=5000\text{Å}\)) through 10% PVA solutions, after freezing at \(-20^\circ\text{C}\) and thawing at \(25^\circ\text{C}\), versus time of thawing.
Fig. 9-2: Transmittance of visible light ($\lambda=5000\,\text{Å}$) through PVA solutions, after freezing at $-20^\circ\text{C}$ for 60 minutes and thawing at $25^\circ\text{C}$, versus time of thawing.
Fig. 9-3: Transmittance of visible light of varying wavelength, through 15% PVA solutions, after freezing at -20°C for 60 minutes and thawing at 25°C, versus time of thawing.
Fig. 9-4: Transmittance of visible light of varying wavelength through 10% PVA solutions, after freezing at -20°C for 60 minutes and thawing at 25°C, versus time of thawing.
A method for determining the parameters of the supermolecular particles in polymer solutions is used here. This method was suggested by Klenin et al. (191) and has been applied to PVA particles with the assumption that they behave as small spheres. The assumption has not been yet evaluated. Calculation of the parameters of the particles produced via the cooling-thawing process, has never been reported.

In this investigation plots of log D versus log λ were used (where D is the optical density of the solution and λ the wavelength of the light) giving straight lines over a range of A between 5000 Å and 7000 Å. The slope n of this line is a complex function of the sizes and the relative refractive index m. For PVA-H₂O systems m max ~ 1.12. Apparently it is theoretically possible to find a way of determining m, but in the first stage of a study of the supermolecular particles, there is no great need for this. The function of m has been tabulated (141). Using this value, the term α can be calculated from the same figures (141), where α is defined as

\[ \alpha = \frac{2\pi r}{\lambda} \]  \hspace{1cm} (9-1)

where λ is the wavelength and r is the average radius. This radius is determined in this way. A typical calculation of turbidimetric properties of a PVA solution is shown in Appendix G.

The sizes of the supermolecular particles and the turbidity of
PVA solutions undergo major changes during this freezing-thawing process. Figure 9-5, and 9-6 show the variation of the average radius of the particles with the time of thawing. Figure 9-5 shows that in the first stage of thawing process, the sizes of the supermolecular particles increased with time which would naturally be connected with gelling of the particles. As the thawing treatment continues, $\bar{r}_w$ is reduced to a certain limiting value which then remains constant up to fifteen hours of heat treatment. Evidently the second stage of the change in the particles is connected with the breakdown of previously swollen particles.

The data given above lead us to suppose that the formation of PVA gels in aqueous PVA solutions may be accompanied by a partial crystallization of the polymer, which also explains the progressive clouding of the gel. This process of partial crystallization takes place at room temperature although till now it was assumed that PVA would crystallize only at high temperatures.

Matsuo and Inagati (248, 249) suggested a hypothetical scheme of the structure of supermolecular particles in aqueous solutions of PVA envisaging a conjunction of the paracrystalline (region of very dense crystalline structures) and amorphous regions. This scheme was proposed by the authors without any experimental evidence. It is all the more remarkable that the proposed model is justified by our experiments. Absorption of the solvent by amorphous segments (during the first 2-5 hours of thawing process) with subsequent dissolution of these regions
Fig. 9-5: Average radius of supermolecular particles, versus thawing time: Freezing time 105 min. Solution 5% PVA

Fig. 9-6: Average radius of supermolecular particles, versus thawing time: Freezing time 60 min.
causing breakdown of the particles. Only very dense regions (the para-crystalline) do not break down during prolonged thawing process. The particles formed are bigger for more concentrated solution. This difference can be as high as 10%.

B. ELECTRON-BEAM RADIATION EFFECTS ON PVA SOLUTIONS

1. Evaluation of the Crosslinking Density

A measure of the crosslinking density of an irradiated sample is the average molecular weight between crosslinks \( M_c \). Evaluation of \( M_c \) has been done by swelling experiments in water. The effects of electron beam irradiation on PVA solutions on a function of temperature and dose of irradiation and concentration of solution have been studied.

The equation used for the evaluation of the molecular weight between crosslinks \( M_c \), is the one developed by Bray and Merrill (43).

\[
\frac{1}{M_c} = \frac{2}{M_n} - \frac{\bar{\nu}}{v_1} \left[ \ln (1 - \nu_{2,s}) + \nu_{2,s} + \chi_1 \nu_{2,s}^2 \right] \frac{1}{1/3} \left\{ \nu_{2,r} \left[ \frac{\nu_{2,s}}{v_2,r} \right] - \frac{1}{2} \left( \frac{\nu_{2,s}}{v_2,r} \right)^2 \right\}
\]

(9-2)

where

\( \nu_{2,r} \) = relaxed volume fraction of polymer (immediately after irradiation)
\[ v_{2,s} \] = swollen volume fraction of polymer (after swelling)

\[ \chi \] = Flory's PVA water interaction factor and \( 30^\circ C = 0.494 \)

\[ \bar{\upsilon} \] = specific volume of polymer = 0.788 cm\(^3\)/gr \hspace{1cm} (348)

\[ V_1 \] = molar volume of solvent = 18 cm\(^3\)/mole

\[ M_n \] = 88,880

The complete derivation of this relation has been included in Appendix D.

The numerator of it, represents the contribution of the free energy of mixing, while the denominator represents the contribution of the elastic refractive force of the network. This equation is different to the one developed by Flory in that it takes in account the fact that the crosslinks were introduced in solution and not in the solid state \((v_{2,r} \neq 1)\).

2. Variation of Crosslinking Density with Radiation Conditions.

The crosslinking density (expressed as \( M_c \)) of PVA hydrogels was studied by irradiating 5%, 10%, 15% and 20%, PVA solutions at 0\(^\circ\)C and 30\(^\circ\)C by delivering doses of 3, 5, 8, 10, 13 and 15 Mgrads.

It is not the purpose of this thesis to repeat the data reported in Bray's thesis (42) but rather to increase the reliability of data in the following respects by improvement of the method, for the different errors that had been made in the first place. These include:

(i) The calculation of \( M_c \) from "thick" films (thicker than 3mm) that, because of the poor penetration
of electron beams, did not have uniform crosslinking density. The variations of crosslinking density with depth, will be discussed later.

(ii) The existence of visible bubbles in some of the samples. As a result, the reported relaxed and swollen volume fractions of PVA (calculated from density measurements) were not correct.

(iii) Macrosyneresis phenomena. Bray (42) proposed that at very high doses (above 10 Mgrads) the value of $M_c$ did not decrease in a consistent way. It is, however, obvious from the derivation of the equation, that it is inapplicable to cases of very dense crosslinking that result in removal of water from the hydrogel (macro crosyneresis phenomenon), so that the evaluation of $M_c$ cannot be done with the above-mentioned relation. Please notice also, that the $M_n$ used is 88,880 instead of 100,000 in Bray's (42) calculations.

For all these reasons the experiments and the evaluation have been repeated for the samples that were needed in the rest of this thesis. Fig. 9-7, 9-8, 9-9, 9-10 and 9-11 show the behavior of crosslinking density as a function of dose and temperature of irradiation and concentration of PVA solution.
Fig. 9-7: $M_c$ as a function of Dose for samples irradiated at 0°C.
Fig. 9-8: $M_c$ as a function of dose for samples irradiated at 30°C.
Fig. 9-9: $M_c$ as a function of dose for irradiated 5% PVA solutions
Fig. 9-10: $M_c$ as a function for irradiated 10% PVA solutions
Fig. 9-11: $M_c$ as a function for irradiated 15% PVA solutions
Among these samples, 12 different conditions of irradiation are of particular interest because, they will be used in the rest of this thesis. They are included in Table 9-1. Calculation of \( M_c \) of typical samples via swelling methods has been included in Appendix H.

For these samples the term \( M_c, \rho \) and \( u \) have been calculated and reported. \( M_c \) is the average molecular weight between crosslinks, \( \rho \) is the crosslinking density, i.e. the ratio of the number average molecular weight \( M_n \) to the average molecular weight between crosslinks \( M_c \) (thus expressing the average number of crosslinks formed on an initial polymer chain) and \( u \) is the number of monomer units between two crosslinks, i.e., the ratio \( \frac{M_c}{44} \) where 44 is the molecular weight of a "monomer unit".

As the dose increases the crosslinking density increases, finally reaching an almost constant value, at about 15-20 Mgrads. Above this does the phenomenon of macrosyneresis occurs and the apparent crosslinking density seems to decrease again. As explained above, the equation becomes increasingly less applicable by means of loss of water by syneresis.

Plotting \( \rho \) versus dose we can get a linear relationship (as shown in Figure 9-12). This behavior is expected and it is consistent to Danno's equation \((73)\) which states that:

\[
\rho = k' \left( D_c - D' \right) 
\]

\[(9-3)\]
### TABLE 9-1

SAMPLES USED IN THIS THESIS, CONDITION OF IRRADIATION AND CROSSLINKING PARAMETERS

<table>
<thead>
<tr>
<th>Conditions of Irradiation</th>
<th>( c_c ) (%)</th>
<th>( T_c ) (°C)</th>
<th>( D_c ) (Mgrads)</th>
<th>( M_c )</th>
<th>( \rho )</th>
<th>( u )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
<td>0</td>
<td>3</td>
<td>7650</td>
<td>11.6</td>
<td>174</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0</td>
<td>5</td>
<td>3765</td>
<td>23.6</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0</td>
<td>10</td>
<td>1495</td>
<td>59.4</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>30</td>
<td>3</td>
<td>9370</td>
<td>9.5</td>
<td>213</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>30</td>
<td>5</td>
<td>4770</td>
<td>18.6</td>
<td>108</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>30</td>
<td>10</td>
<td>1395</td>
<td>63.7</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0</td>
<td>3</td>
<td>8420</td>
<td>10.6</td>
<td>191</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0</td>
<td>5</td>
<td>3960</td>
<td>22.4</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0</td>
<td>10</td>
<td>1790</td>
<td>49.6</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>30</td>
<td>3</td>
<td>9850</td>
<td>9.0</td>
<td>224</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>30</td>
<td>5</td>
<td>5715</td>
<td>15.5</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>30</td>
<td>10</td>
<td>2190</td>
<td>40.6</td>
<td>50</td>
</tr>
</tbody>
</table>
Fig. 9-12: Crosslinking density $\rho$ as a function of dose for samples irradiated at 30°C
where $D'_c$ is the gelation dose, depending on the percentage of the PVA solution.

The molecular weight between crosslinks $M_c$ varies in the region tested between 10,000 and 1,000. Hydrogels with $M_c$ between 3,500 and 6,000 are considered as moderately crosslinked materials and can be used for further applications. This range corresponds to about 80-135 monomer units per chain or 25-15 crosslinks per chain. Hydrogels with $M_c$ above 10,000 are in no way workable, because they are very weak, sometimes very "sticky" too, because of still uncrosslinked sol fraction. Hydrogels with $M_c$ less than 2,000 are very brittle and they are easily shattered upon application of tensile stress.

Increase of the PVA content in the solution as well as the temperature of irradiation lead towards lower crosslinking density. The explanation of these phenomena is not the purpose of this thesis, as it has already been discussed by Bray (42).

The absorption of the charged particles in electron beam irradiation is a function of the depth of the irradiated solution. In the case of the Van de Graaff generator used for the irradiation of this thesis the percentage depth dose has been calculated as a function of the depth of PVA solution (shown as curve 2 in Fig. 9-13) and compared to the experimental curve (corrected for the density of the hydrogel) reported for electrons with 3 MeV (shown as curve 1 in Fig. 9-13).

The crosslinking density of irradiated sampler is a function
Fig. 9-13: Dose delivered by Van de Graaff generator as a function of depth of hydrogel

Curve (1) Theoretical (3MeV)
Curve (2) Experimental
of depth of irradiation when the samples are irradiated with electron beams. $M_c$ of different thin layer of hydrogels varies widely. In Figure 9-14 and 9-15 the $M_c$ and crosslinking density $\rho$, as well as the polymer volume fraction after swelling, $\nu_2$, have been reported for 15% PVA irradiated at 30ºC with 8 Mgrads, as a function of thickness and distance from the center of the electron beam.

The crosslinking density of three different "layers" as well as the average $M_c$ of the whole film are reported in Table 9-2. The values included are average ones, for films of diameter 5 cm. irradiated in the center of the electron beam. The error when a "thick film" is used for calculation of the crosslinking density can be as high as 15%. Indeed, our results and Bray's results have a difference of 15% but in many cases as high as 25-30% especially in the low doses of irradiation.

The author can attribute these differences, among other reasons to the formation of visible gas bubbles in the hydrogel, as it will be discussed in some detail.

Among the products of radiolysis of water, hydrogen and hydroxy-radicals are formed, as well as $HO_2^-$, etc. (89). Some of the possible reactions with the polymer chains and with other radicals are the following:

- **Hydrogen Formation**
  \[ H^+ + H^+ \rightarrow H_2 \]  

- **Radical Transfer**
  \[ H^+ + PH \rightarrow P^+ + H_2 \]

  \[ OH + PH \rightarrow P^+ + H_2O \]

- **Crosslinking**
  \[ P^+ + P^+ \rightarrow PP \]
Fig. 9-14: Variation of $M_c$ with thickness of samples:

Sample 15%, 30°C, 8 Mgrads
Curve (1) Depth 0-0.25 cm.
Curve (2) Depth 0.25-0.50 cm.
Curve (3) Depth 0.50-0.75 cm.
Curve (4) Depth 0-0.75 cm.
Fig. 9-15: Variation of polymer volume fraction after swelling, with thickness of irradiated samples: Sample 15%, 30°C, 8 Mrads

Curve (1) Depth 0-0.25 cm.
Curve (2) Depth 0.25 - 0.50 cm.
Curve (3) Depth 0.50 - 0.75 cm.
Curve (4) Depth 0-0.75 cm.
TABLE 9-2

EFFECT OF THICKNESS OF FILM ON THE CROSSLINKING DENSITY

<table>
<thead>
<tr>
<th>Layer</th>
<th>( M_c )</th>
<th>Error in ( M_c )*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-0.25 cm.</td>
<td>2800</td>
<td>12.5%</td>
</tr>
<tr>
<td>0.25 - 0.50 cm.</td>
<td>3100</td>
<td>3 %</td>
</tr>
<tr>
<td>0.50 - 0.75 cm.</td>
<td>4300</td>
<td>35 %</td>
</tr>
<tr>
<td>Average/Total</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0. - 0.75 cm.</td>
<td>3200</td>
<td>---</td>
</tr>
</tbody>
</table>

* It refers to the error, if the average value (3,200) is used instead of the correct one.
Degradation \[ P_{m+n}^* \rightarrow P_m^* + P_n^* \] (5)

Thus during the irradiation of PVA solution gas is formed which mainly consists of hydrogen, as it has been already reported by Petrov and Karpov (303).

This has been observed in the first irradiations of this thesis. It is clear now that the formation of the gas bubbles is a diffusion rate limited phenomenon, depending mainly on the diffusion coefficient of hydrogen through very viscous PVA solutions. During electron beam irradiation the actual process of crosslinking does not last more than 20 seconds and the gelation dose (where the solution becomes a gel and any diffusion of gases becomes impossible) is only a fraction of the total dose used. This leads to the conclusion that because of the very fast dose rate, the hydrogen cannot diffuse and it is entrapped in the gel. For this reason, the effect of dose rate has been studied, as it will be reported later. Qualitatively the gas formation seemed to be higher in the more dilute solutions. One would expect that the gas formation would be favored by high viscosity (concentrated solution), which prevents the mobility and diffusion of the bubbles. This, however, is not the case here, where we are dealing with a very fast crosslinking phenomenon, where the effects of viscosity cannot be of significant value. However, the higher rate of gas formation in the more dilute solution can be explained, if we consider the ratio of water to polymer in the initial solution.
<table>
<thead>
<tr>
<th>PVA solution %</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>moles $H_2O$</td>
<td>47</td>
<td>22</td>
<td>14</td>
<td>10</td>
</tr>
<tr>
<td>molc- monomer</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Thus the higher the water percentage, the higher the production of radiolysis products of $H_2O$, which leads to a higher formation of hydrogen bubbles.

During swelling the hydrogen bubbles are eventually filled by water and the hydrogel does not behave as a homogeneous material. During subsequent dehydration the structures may collapse because of the existence of these irregular "cave" like vacuoles in the structure.

The problem was not solved by Bray. We proposed a freezing-thawing process, which would finally lead to a gel with weak hydrogen bonds between the monomer units of the macromolecules. During irradiation of these "gelled" PVA samples, gas bubbles are not formed, prevented by the immobility and the solid-like state of the material.

However, the process introduces the problem of the change in swelling of the final material, because of the possible existence of some oriented phases (these may include microcrystallites, but the whole phenomenon is still discussed, as the literature clearly shows). For this purpose an increase of the temperature of swelling has been proposed for "meeting out" all the possibly formed oriented states, so that all the hydrogels after this treatment, are in the amorphous state. (This statement can be questioned. Sakurada (348) has observed via...
x-ray diffraction patterns that even under extremely careful conditions of preparation, a PVA hydrogel cannot have less than 12% crystallinity.

In electron-beam irradiation, the effect of oxygen is negligible - within experimental error - as, among others, Bray has quantitatively indicated (See 42, Fig. 8-16).

However, this is not the case with varying the dose rate. Electron-beam irradiation can be delivered in some cases by modification of the Van de Graaff generator characteristics. In our studies, we investigate the effect of dose rate from 400 rads/sec up to 80,000 rads/sec. The results are shown in Fig. 9-16.

Because of the absence of oxygen, the sole phenomenon studied in this series of experiments, is the competition of crosslinking and degradation reactions in the PVA solution, as well as the diffusion rate of the gas bubbles formed in it. Because of the slow rate of dose, the hydrogen molecules diffuse out without forming bubbles by supersaturation and nucleation even in the case of hydrogel prepared without any pretreatment (freezing-thawing)(135). At the same time the crosslinking density increase, suggesting that the degradation reaction predominates only at high dose rates. This can be explained by reference to the direct and indirect phenomena of effects of radiation on PVA solutions. At high dose rates, the rate of chain scission due to the direct radiation phenomenon is very high and the probability of the formation of shorter chains is higher. At lower dose rates (and always under absence of oxygen), the indirect phenomenon predominates and crosslinking occurs.
The data compared, have been obtained from application of the same "technique" of irradiation. Director comparison of quantitative cross-linking affects of doses delivered and dose-rates used, cannot always be done because of different parameters used for the production of the electron beams (current, voltage, etc.). Thus although a qualitative comparison of electron beam and γ-irradiation data can be done, the values of $M_c$ via γ-radiation cannot be included in Fig. 9-16 and Table 9-3.

In any way, the variation of the crosslinking density with dose rate is not that important (maximum 10%) to be considered as a very significant parameter.

Further evidence of the fact that degradation is favored by fast dose-rates is a series of irradiation of 5%, 10% and 15% PVA solutions at 30°C with dose 3 Mgrads, delivered in short times with pauses of 30 minutes between two irradiations. (See experimental part). Table 9-4 shows the crosslinking density and $M_c$ of these terms, if irradiation was done continuously. The method used delivers the dose of 3 Mgrads in 6 equal time intervals with pauses of 30 minutes in between. The dose rate during the irradiation was 35000 rads/sec. As it is shown, almost half the crosslinking density is achieved by this method. This can be explained by the assumption that direct radiation effect produces chain scission, which during the pause leads to stabilization of lower molecular weight products. These, in turn, irradiated for a second time, again by high dose-rate irradiation, lead to
**Fig. 9-16**: Crossing density as a function of dose rate of electron beam irradiation: Samples: 10%, 30°C, 3 Mgrads

<table>
<thead>
<tr>
<th>Dose Rate (D)</th>
<th>log D</th>
<th>$M_C$</th>
<th>$\rho = \frac{M_n}{M_C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>133,330</td>
<td>5.13</td>
<td>9,370</td>
<td>9.49</td>
</tr>
<tr>
<td>4,130</td>
<td>3.62</td>
<td>8,287</td>
<td>10.72</td>
</tr>
<tr>
<td>1,652</td>
<td>3.22</td>
<td>8,230</td>
<td>10.80</td>
</tr>
<tr>
<td>826</td>
<td>2.92</td>
<td>8,184</td>
<td>10.86</td>
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<tr>
<td>413</td>
<td>2.57</td>
<td>8,180</td>
<td>10.86</td>
</tr>
</tbody>
</table>
TABLE 9-4

EFFECT OF RADIATION DERIVED WITH "PAUSES", ON THE CROSSLINKING CHARACTERISTICS OF FILMS

<table>
<thead>
<tr>
<th>Conditions</th>
<th>C_c (%)</th>
<th>T_c (°C)</th>
<th>D_c (Mgrads)</th>
<th>M_c</th>
<th>( \rho )</th>
<th>M_c Continuous</th>
<th>( \rho ) Continuous</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
<td>30</td>
<td>3</td>
<td>8451</td>
<td>10.52</td>
<td>3860</td>
<td>23.03</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>30</td>
<td>3</td>
<td>13610</td>
<td>6.53</td>
<td>9370</td>
<td>9.49</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>30</td>
<td>3</td>
<td>18827</td>
<td>4.72</td>
<td>9850</td>
<td>9.02</td>
</tr>
</tbody>
</table>

- 338 -
more degradation than crosslinking etc. It must be noted that visible bubble formation was not observed during this process. Evidently, the gas formed diffuses through the gel, during the first irradiation pause.

C. GAMMA-RADIATION EFFECTS ON PVA SOLUTION

Gamma-radiation was proposed as an alternative to electron beams for solving the problem of bubble formation and for achieving a higher crosslinking density.

Gamma radiation under atmospheric conditions is known not to give a crosslinked material, because of the oxygen that continuously diffuses through the solution and slowly forms peroxidic bonds that are very weak and are subjected to degradation.

Thus the effect of $\gamma$-irradiation was studied only in samples irradiated in vacuo or sealed under nitrogen. A significant increase of crosslinking density was observed as shown in Fig. 9-17.

As mentioned before in the case of slow dose rate electron beam irradiation, crosslinking predominates, provided that oxygen is excluded. Gamma-irradiation used here had a dose rate of 60 rads/sec., so that the phenomena of very high crosslinking can be explained in the same way as in slow dose rate electron-beam irradiation.

Using Danno's (75) equation relating the gelation dose ($D'$) the degree of polymerization (DP) and the concentration of polymer (C)
Fig. 9-17: $M_c$ as a function of dose for samples irradiated at 0°C with γ-rays.
\[(D') \ (DP) = 5.1 \times 10^8 + 1.37 \times 10^8 \cdot C \] (9-4)

we can calculate that for irradiation of a 15% PVA solution, the
gelation dose is approximately 0.26 Mgrad. This dose can be delivered
by the Cobalt-60 source used in this thesis in one hour and twelve
minutes. Only above this gelation dose the material is in the gel form.
It is assumed that this time is sufficient for the bubbles to diffuse
through the solution. Thus \(\gamma\)-irradiated PVA hydrogels do not show any
visible bubbles.

A comparison of the data of crosslinking densities of electron-
beam and \(\gamma\)-rays irradiated hydrogels is shown in Fig. 9-18 and Table 9-5.
As it can be seen, the ratio of crosslinking densities of \(\gamma\)- and electron-
beam irradiated samples, decreases with increasing dose up to 13 Mgrads.
Above this dose, syneresis phenomenon occurred in some samples and it was
difficult to judge and make any conclusions from the data.

Table 9-6 includes the final results of this study, of the
effects of different kinds of radiations, dose rates and radiation conditions
on PVA solutions.

Clearly, gamma irradiation is preferred for more crosslinked
materials. However, technical difficulties (very small chambers) as well
as very long time of irradiation are disadvantages of this method of
irradiation. In the rest of this thesis, electron-beam irradiation was
used as the only method of crosslinking. In any event, it is clear that
the final result in terms of crosslinking polymer chain is substantially
<table>
<thead>
<tr>
<th>Conditions of irradiation</th>
<th>electron</th>
<th>beam</th>
<th>γ-radiation</th>
<th>( \frac{\rho(\gamma)}{\rho(e)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cc Tc Dc</td>
<td>Mc</td>
<td>( \rho )</td>
<td>Mγ</td>
<td>( \rho )</td>
</tr>
<tr>
<td>10 0 3</td>
<td>3612</td>
<td>24.6</td>
<td>7650</td>
<td>11.6</td>
</tr>
<tr>
<td>10 0 5</td>
<td>3970</td>
<td>22.4</td>
<td>3765</td>
<td>23.6</td>
</tr>
<tr>
<td>10 0 8</td>
<td>1876</td>
<td>47.4</td>
<td>1990</td>
<td>44.7</td>
</tr>
<tr>
<td>10 0 10</td>
<td>1826</td>
<td>48.7</td>
<td>1495</td>
<td>59.4</td>
</tr>
<tr>
<td>15 0 3</td>
<td>4777</td>
<td>18.6</td>
<td>8420</td>
<td>10.6</td>
</tr>
<tr>
<td>15 0 5</td>
<td>2995</td>
<td>29.7</td>
<td>3960</td>
<td>22.4</td>
</tr>
<tr>
<td>15 0 8</td>
<td>2869</td>
<td>31.0</td>
<td>2190</td>
<td>40.6</td>
</tr>
<tr>
<td>15 0 10</td>
<td>2958</td>
<td>30.1</td>
<td>1790</td>
<td>49.6</td>
</tr>
</tbody>
</table>
Fig. 9-18: Effect of dose on the ratio of crosslinking densities of gamma and electron beam irradiated samples under identical conditions.
### TABLE 9-6

**COMPARISON AND RESULTS OF ELECTRON-BEAM AND \( \gamma \)-RAYS INDUCED CROSSLINKING**

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Electron-Beam</th>
<th>( \gamma )-rays</th>
</tr>
</thead>
<tbody>
<tr>
<td>In air</td>
<td>x-linking</td>
<td>Degradation</td>
</tr>
<tr>
<td></td>
<td>( H_2 ) bubbles formation</td>
<td></td>
</tr>
<tr>
<td>In nitrogen</td>
<td>x-linking (same ( M_c ))</td>
<td>x-linking (lower ( M_c ) than electron-beam)</td>
</tr>
<tr>
<td></td>
<td>( H_2 ) bubbles formation</td>
<td>No bubbles</td>
</tr>
<tr>
<td>Prefreezing</td>
<td>x-linking (almost same ( M_c ))</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>No bubbles</td>
<td></td>
</tr>
<tr>
<td>In vacuo</td>
<td>---</td>
<td>x-linking (lower ( M_c ))</td>
</tr>
<tr>
<td></td>
<td></td>
<td>technical difficulties.</td>
</tr>
</tbody>
</table>
independent of the source of irradiation, provided of course, that secondary effects (oxygen from air, hydrogen super-saturation) are eliminated or taken into account.

D. EVALUATION OF $M_c$ FROM TENSILE MEASUREMENTS

Tensile experiments on crosslinked uncocrystallized PVA hydrogels have been performed for two purposes. The first is to evaluate the crosslinking density and the second is to study the mechanical properties of hydrogels.

The mechanical properties have been studies on selected, electron-beam radiation crosslinked, and at 30°C swollen, PVA hydrogels. Table 9-7 includes the condition of irradiation, $M_c$ as calculated from swelling experiments, the initial modulus of elasticity, the ultimate tensile strength, the elongation at break and the polymer volume fraction $v_2$.

The initial modulus, ultimate tensile strength and elongation at break as a function of $M_c$ have been plotted in Figure 9-19, 9-20, 9-21. The initial modulus, characterizing the rigidity of the hydrogels, increases as the $M_c$ decreases, i.e., as the number of crosslinks increases. This increase
<table>
<thead>
<tr>
<th>C&lt;sub&gt;c&lt;/sub&gt; (%)</th>
<th>T(°C)</th>
<th>D&lt;sub&gt;c&lt;/sub&gt; (Mgrads)</th>
<th>M&lt;sub&gt;c&lt;/sub&gt; (swell. exp.)</th>
<th>ρ = M&lt;sub&gt;n&lt;/sub&gt; / M&lt;sub&gt;c&lt;/sub&gt;</th>
<th>Vol. fr. polym. ν&lt;sub&gt;2&lt;/sub&gt;</th>
<th>Initial Modulus E&lt;sub&gt;i&lt;/sub&gt; (psi)</th>
<th>UTS (psi)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0</td>
<td>3</td>
<td>7650</td>
<td>11.6</td>
<td>0.066</td>
<td>4.6</td>
<td>2.6</td>
<td>84.1</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>5</td>
<td>3765</td>
<td>23.6</td>
<td>0.084</td>
<td>11.8</td>
<td>4.0</td>
<td>40.8</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>8</td>
<td>1990</td>
<td>44.7</td>
<td>0.106</td>
<td>20.8</td>
<td>2.3</td>
<td>11.7</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>10</td>
<td>1495</td>
<td>59.4</td>
<td>0.125</td>
<td>31.7</td>
<td>3.8</td>
<td>13.6</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>15</td>
<td>950</td>
<td>93.6</td>
<td>0.128</td>
<td>49.4</td>
<td>4.0</td>
<td>9.3</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>10</td>
<td>1395</td>
<td>63.7</td>
<td>0.114</td>
<td>19.3</td>
<td>2.4</td>
<td>13.8</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>10</td>
<td>1790</td>
<td>49.7</td>
<td>0.129</td>
<td>30.7</td>
<td>4.3</td>
<td>15.5</td>
</tr>
</tbody>
</table>
Fig. 9-19: Initial modulus of uncrystallized PVA hydrogels as a function of $M_c$. 
Fig. 9-20: Ultimate tensile strength of uncry stallized PVA hydrogels as a function of $M_c$
Fig. 9-21: Elongation at break of uncrystallized PVA hydrogels as a function of $M_c$
seems to be linear as it can be seen from Fig. 9-22 where the modulus is plotted versus the number of crosslinks per initial polymer chain. This means that even with 100 crosslinks per chain, the crosslinking is not very dense and the structure is quite simple. The corresponding number of monomer units between two crosslinks is about 20.

The ultimate tensile strength has similar behavior upon crosslinking, i.e., it is higher for higher degrees of crosslinking. This can be easily explained, since the stress is redistributed in a bigger number of crosslinks (points of reinforcement).

Elongation at break of crosslinked materials, is always restricted by the number of crosslinks and very dense crosslinked materials have very low extensibility. This is the case with PVA hydrogels too, where the elongation at break increases with $M_c$, i.e., it decreases with increase of crosslinking density.

In general the modulus of moderately crosslinked hydrogels ($M_c$ 3500-6000) is 10-15 psi, the UTS is 3 psi and the elongation 40-60%.

The initial modulus, the ultimate tensile strength and the elongation at break are also related to the polymer volume fraction of the hydrogel. The modulus and UTS increase with increasing polymer volume fraction, whereas the elongation decreases. The corresponding plots
Fig. 9-22: Initial modulus of uncrystallized PVA hydrogels as a function of crosslinking density $\rho$. 

INITIAL MODULUS $E_i$ (psi) vs CROSSLINKING DENSITY $\rho$
are shown in Fig. 9-23, 9-24 and 9-25.

The tensile experiments have been also used for the determination of \( M_c \). This method was the relation between \( M_c \) and tensile stress as it was developed by Flory. For a complete derivation of the relation see Appendix E. The equation contains the volume swelling ratio \( Q \) and as such it is used for swollen hydrogels as:

\[
\tau = RT Q^{-1/3} \left( \frac{\nu_e}{\nu} \right) \frac{\tau_i}{\tau_o} \left( \alpha - \frac{1}{a} \right) \quad (9-5)
\]

or by substituting

\[
\frac{\nu_e}{\nu} = \frac{C_{2,i}}{M_c} \left( 1 - \frac{2M}{M_c} \right) \quad (9-6)
\]

as:

\[
\tau = RT \frac{C_{2,i}}{M_c} \cdot \frac{1}{Q^{1/3}} \cdot (1 - \frac{2M}{M_n})(\alpha - \frac{1}{a}) \quad (9-7)
\]

where

- \( \tau \) is the tensile stress
- \( T \) is the temperature
- \( C_{2,i} = \frac{\nu_{2,i}}{\nu} = \frac{\text{volume fraction of polymer in relaxed state}}{\text{molar volume of polymer}} \)
- \( Q \) is the volumetric swelling ratio
- \( \alpha = \frac{\rho}{\rho_o} \)
are shown in Fig. 9-23, 9-24 and 9-25.

The tensile experiments have been also used for the determination of $M_c$. This method was the relation between $M_c$ and tensile stress as it was developed by Flory. For a complete derivation of the relation see Appendix E. The equation contains the volume swelling ratio $Q$ and as such it is used for swollen hydrogels as:

$$\tau = RT \frac{1}{3} \left( \frac{v}{v'} \right) \left( \frac{r_i}{r_o} \right)^2 \left( a - \frac{1}{a^2} \right)$$  \hspace{1cm} (9-5)$$

or by substituting

$$\frac{v}{v} = \frac{C_{2,i}}{M_c} \left( 1 - \frac{2M_c}{M_c} \right)$$  \hspace{1cm} (9-6)$$

as:

$$\tau = RT \frac{C_{2,i}}{M_c} \cdot \frac{1}{Q^{1/3}} \cdot \left( 1 - \frac{2M_c}{M_n} \right) \left( a - \frac{1}{a^2} \right)$$  \hspace{1cm} (9-7)$$

where

- $\tau$ is the tensile stress
- $T$ is the temperature
- $C_{2,i}$ is the volume fraction of the polymer in relaxed state
- $\frac{v}{v'}$ is the molar volume of polymer
- $Q$ is the volumetric swelling ratio
- $a = \frac{b}{b_o}$
Fig. 9-23: Initial modulus of uncrystallized PVA hydrogels as a function of polymer volume fraction $u_2$

Fig. 9-24: Ultimate tensile strength of uncrystallized PVA hydrogels as a function of polymer volume fraction $u_2$
Fig. 9-25: Elongation at break of uncrystallized PVA hydrogels as a function of polymer volume fraction $v_2$
For this purpose some swelling characteristics for the tested hydrogels have been taken and reported in Table 9-8 and Fig. 9-26. The swelling ratio increases with decreasing crosslinking density, whereas the polymer volume fraction decreases at the same time. This is to be expected since less crosslinked materials can be thermodynamically expanded more freely than highly crosslinked ones.

From the above stated equation, we note that the tensile stress is directly proportional to the term \( a - \frac{1}{\alpha^2} \) and that from this relation, \( M_c \) can be calculated in an independent way. This linear relationship holds for values up to \( \alpha = 3 \). In the case of swollen PVA hydrogels, the elongation at break is much lower so that we should expect that the above relation holds for the whole range of the test. This is true. Fig. 9-27 shows plots of the tensile stress \( \tau \) (in psi) as a function of the term \( a - \frac{1}{\alpha^2} \).

The experimental points for five tested samples (irradiation of 10% solution at 0°C with different doses) fit on straight lines, as shown in Fig. 9-27. The tensile stress at 10% elongation varies with \( M_c \) and/or crosslinking density in similar way as the initial modulus, as it can be seen in Fig. 9-28 and 9-29.
<table>
<thead>
<tr>
<th>Radiation Conditions</th>
<th>M&lt;sub&gt;Swell. Exp.&lt;/sub&gt;</th>
<th>Water in Swollen gel(%)</th>
<th>0&lt;sub&gt;2,r&lt;/sub&gt;</th>
<th>0&lt;sub&gt;2,s&lt;/sub&gt;</th>
<th>Volume Swelling Ratio</th>
<th>C&lt;sub&gt;2,i&lt;/sub&gt; = ( \frac{v_2^r}{V} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 0 3</td>
<td>7650</td>
<td>93</td>
<td>0.179</td>
<td>0.066</td>
<td>2.720</td>
<td>0.227</td>
</tr>
<tr>
<td>10 0 5</td>
<td>3765</td>
<td>90</td>
<td>0.098</td>
<td>0.084</td>
<td>1.174</td>
<td>0.124</td>
</tr>
<tr>
<td>10 0 8</td>
<td>1990</td>
<td>87</td>
<td>0.119</td>
<td>0.106</td>
<td>1.129</td>
<td>0.151</td>
</tr>
<tr>
<td>10 0 10</td>
<td>1495</td>
<td>86</td>
<td>0.141</td>
<td>0.125</td>
<td>1.124</td>
<td>0.179</td>
</tr>
<tr>
<td>10 0 15</td>
<td>950</td>
<td>83</td>
<td>0.143</td>
<td>0.128</td>
<td>1.116</td>
<td>0.181</td>
</tr>
<tr>
<td>10 30 10</td>
<td>1395</td>
<td>87</td>
<td>0.164</td>
<td>0.114</td>
<td>1.451</td>
<td>0.208</td>
</tr>
<tr>
<td>15 0 10</td>
<td>1790</td>
<td>86</td>
<td>0.141</td>
<td>0.129</td>
<td>1.096</td>
<td>0.179</td>
</tr>
</tbody>
</table>
Fig. 9-26: Dependence of the swelling ratio $Q$ and the polymer volume fraction on $M_c$
Fig. 9-27: Tensile stress $\tau$ of uncrystallized PVA hydrogels as a function of the extension factor $\alpha - \frac{1}{\alpha^2}$ for various crosslinking.
Fig. 9-28: Tensile stress at 10% elongation $\tau_{10}$ for uncrysallized PVA hydrogels as a function of $M_c$. 
Fig. 9-29: Tensile stress at 10% elongation $\tau_{10}$ as a function of crosslinking density $\rho$
It has been stated in literature that the thermodynamic swelling experiments give generally more reliable results of $M_c$ than the tensile experiments, because in the latter case, entanglements and other defects of the chains affect the mechanical properties, the stress and finally the calculated values of $M_c$. Using the values of $M_c$ obtained from swelling experiments, a hypothetical value of the tensile stress $\tau_{\text{calc}}$ can be calculated and compared to the observed (experimental) tensile stress $\tau_{\text{obs}}$ for the same sample. Fig. 9-30 shows the ratio $\frac{\tau_{\text{obs}}}{\tau_{\text{calc}}}$ as a function of the elongation $(\alpha - 1) \times 100$. This ratio is lower than one and it decreases with increasing crosslinking density. Deviations in the values of $\tau$ from theory probably originate largely from oversimplified treatment of the network structure. Entanglements tend to enhance the restraints imposed on the chains when the polymer is elongated. Their percent effect should be greater for low degrees of crosslinking, hence the observed $\tau$'s are higher at low degrees of crosslinking.

Intra-molecular crosslinks, yielding short-circuit structures contributing nothing to the elastic reaction of the network, should become increasingly important at higher degrees of crosslinking. Such waste of 'effective' crosslinks may account for the low values of $\tau$ for higher crosslinking.

The ratio $\frac{\tau_{\text{obs}}}{\tau_{\text{calc}}}$ is almost constant for moderate elongations up to 50% ($\alpha = 1.5$) and for moderate crosslinking densities.
Fig. 9-30: Dependence of the ratio of experimental tensile stress $\tau_{\text{obs}}$ to the theoretical one $\tau_{\text{calc}}$ on the elongation and the degree of crosslinking of various PVA hydrogels.
The molecular weight between crosslinks \( M_c \) as calculated from swelling experiments is finally compared to the \( M_c \) from swelling experiments as shown in Fig. 9-31 and Fig. 9-32. Calculation of \( M_c \) of typical samples via tensile-tests is shown in Appendix I. The latter is 2 to 3 times less than the former. Thus, a swelling experiment on a PVA crosslinked network will generally show double crosslinking than a tensile experiment. The ratio of number of crosslinks as calculated from swelling experiments to the number of crosslinks as calculated from tensile tests is almost a linear function of the effective number of crosslinks.

The explanation of the two different values of \( M_c \) can be given by the same reasoning that we used to explain the difference in \( \tau_{\text{obs}} \) and \( \tau_{\text{calc}} \). The value calculated from tensile experiments includes also entanglements, loops and other defects that may be present in the network and tend to enhance the restraints imposed on the chains when the polymer is elongated. During elongation many of these pseudo-crosslinks as well as other defects do not exist anymore, because of the stress applied and they act only as parts of polymer chains, hence the \( M_c \) from tensile experiments is lower than the correct one.

Also, according to Flory (485) it is recently becoming clear that in the swelling experiment, the \( \chi \) factor, herein assumed constant should be allowed to vary with \( v_2 \), volume fraction of polymers, as determined from uncrosslinked solutions; i.e. \( \chi_1 \) should be regarded as both empirical and variable. While with such additional experiments,
Fig. 9-31: $M_c$ calculated via tensile experiments versus $M_c$ calculated via swelling experiments

Fig. 9-32: Ratio of $M_c$ calculated via tensile experiments to $M_c$ calculated via swelling experiments versus $M_c$ via swelling experiments
Fig. 9-33: Ratio of the crosslinking densities $\rho$ as calculated via tensile and swelling experiments versus the crosslinking density $\rho$ via swelling experiments.
greater accord between \( M_c \) - tensile and \( M_c \) - swelling should be obtainable, the nature of the conclusions drawn herein regarding the fundamental polymer network, or its utilization, would be unchanged.

E. DEHYDRATION EXPERIMENTS

The dehydration experiments have the purpose of removing most of the water from the hydrogels and of starting the crystallization of PVA in the last stages of the evaporation of water. By the term "dehydration" in this thesis we mean the process of slow evaporation of water and drying of a PVA hydrogel at room temperatures. This procedure is affected by different parameters.

From considerations of thermodynamics, heat and mass transfer, the drying process will depend, among other factors, on the rate of drying, the diffusivity of water through the polymer and its variation with depth, the polymer temperature, the ambient air temperature the partial pressure of water vapor in ambient air etc. For these reasons, dehydration experiments with different drying agents have been undertaken, to show the effect of drying rate on the crystallization, since several processes occur at once, e.g. collapse at the polymer gel, nucleation of crystallites, possibly growth of the same and transport of water.

Figure 9-34 and 9-35 shows the weight percent of polymer in the hydrogels for different drying media. All drying temperatures were 25±1 °C.
Fig. 9-34: Polymer weight % in hydrogel as a function of time of drying for different drying agents. Temperature 25 ± 1°C
1, 2, 3, 4, 5; $M_c = 5715 - 1'$, 4'; $M_c = 4770$
Fig. 9-35: Polymer weight % in hydrogel as a function of time of drying for different drying agents. Temperature 25 ± 1°C. 1,3,4,5: $M_c = 5715 - 1', 4': M_c = 4770$
The effects of the crosslinking density, the relative humidity and temperature of drying in air without any drying agents have been extensively studied. Some of the results have been presented in Fig. 9-36 to 9-38. They show clearly the effects of these parameters on the drying rate of the material. Higher crosslinking density (lower M_c) means lower initial water percentage which favors the case of drying (see Fig. 9-36). Lower relative humidity and higher temperature increase the drying rate as would be expected. The initial drying rate is approximately a logarithmic function of gas-phase humidity. The nature of the experimental drying rates plots are qualitatively very similar to the theoretical plots of Porter's paper (385). The dependence and the conclusion are also the same.

From the experimental data shown in Fig. 9-35, the crystallinity degree can be calculated as a function of time of drying as shown in Fig. 9-39. There is an induction time of crystallization $\bar{t}$ of 10-118 hours, depending on the drying rate. Below this time, no crystallites can be formed mainly because of the presence of water in the film. The crystallinity can rise up to 70% in some cases and after very vigorous drying for up to 600 hours. However, generally the crystallinity is not more than 35%.

The initiation of crystallization is a function of water percent in the polymer and this can be seen in Fig. 9-40 where crystallinity is introduced only when the film has above 77-84% PVA.
Fig. 9-36: Drying rate as a function of drying time for two different $M_c$. Drying temperature 45°C, RH 25%
Fig. 9-37: Drying rate as a function of drying time for different drying temperatures:
Relative humidity RH 25%
Fig. 9-38: Drying rate as a function of drying time for different relative humidity conditions: Drying temperature 25°C
Fig. 9-39: Degree of crystallinity of slowly dehydrated PVA hydrogels as a function of drying time, for different drying agents: Temperature 25±1°C.

1, 2, 4, 5: $M_c = 5715 - 1': M_c = 4770$
Fig. 9-40: Degree of crystallinity of slowly dehydrated PAV hydrogels as a function of polymer weight fraction for different drying agents. Temperature 25 ± 1°C. 1,3,4,5: M_c = 5715 - 3',4': M_c = 4770
The plot as well as the next one (Fig. 9-41) prove that dehydration for 24 hours in most cases does not introduce any crystallization and that the main procedure that introduces crystallization is the annealing stage and not the dehydration stage, the former being at a much higher temperature than the latter.

From the above results, a necessary condition for the crystallization of PVA at room temperature is the formation of a gel. The crystallization of PVA *per se* on the formation of a gel at normal temperature is not unexpected in view of the fact that, prerequisite for the crystallization of the polymer are:

a) high supersaturation of the solution, which determines the high rate of crystallization

b) viscosity remaining below a certain level, which gives the macro-molecules the requires mobility.

On the evaporation of an aqueous solution of PVA, the system is for a short period at the stage of high supersaturation. Crystallization cannot proceed sufficiently because of rapid evaporation of water, which brings the PVA to the glass state and reduces the crystallization rate almost to zero. As a result, a film of very low degree of crystallinity is formed.

At elevated temperatures the viscosity falls rapidly and crystallization becomes possible even in the absence of water. The crystallinity of PVA increases even more rapidly at temperatures around the melting point.
Fig. 9-41: Phase diagram of crystalline PVA, amorphous PVA and water at any time \( t \), during a dehydration process at 25\(^\circ\)C and RH 38%
F. ANNEALING EXPERIMENTS

The annealing procedure, following the dehydration stage, is the one that introduces the crystallites in a PVA hydrogel and strengthens the material. The crystallization process can be observed either by determination of the degree of crystallinity or by determination of the water percentage of the hydrogel after swelling (hence the swelling ratio). As reported in the theory, since only amorphous region are swollen, the swelling ratio will be different for different degrees of crystallinity.

Report of the water percent of hydrogels as a function of annealing conditions has a great practical value in the case of biomedical application where the reader is interested in this value rather than the degree of crystallinity.

Figure 9-42 shows the polymer percentage of PVA hydrogels as a function of annealing time for different drying conditions. The reader should have in mind that the actual temperature of the hydrogel during a drying process is not the temperature of the oven where the drying process is done, but substantially less. For more on this subject, see Appendix J. The polymer weight percent of heat-treated PVA hydrogels increases significantly with temperature of annealing and can be as high as 50% in some cases, although the original hydrogel had only 8-10% PVA (for 10% initial solutions) and the original dehydrated (at room temperature) film (crystallinity 10-15%) did not have more than 18-20% PVA. Many other data on other conditions are available, but are
Fig. 9-42: PVA weight percent as a function of annealing temperature for various degrees of crosslinking. Annealing time 30 min.
Fig. 9-43: PVA weight percent as a function of crosslinking density for different annealing conditions. Annealing time 30 min.
not presented here. Of more value and interest are the results of PVA weight percent as a function of crosslinking density. In Figs. 9-43 to 9-46 data on the variation of the PVA in the swollen hydrogels are reported for four different annealing times (30,60,90,120 min) and four annealing temperatures (90,105,120,135°C) as well as two initial PVA solution concentrations (10% and 15% per weight). The time of annealing does not seem to affect significantly the crystallinity of the material, obviously because the crystallites are formed in a shorter period of time. However, the temperature of annealing affects the crystallinity as judged for the polymer percent of the hydrogels and samples heat treated at 90°C and/or 135°C for the same time can have a polymer content of ~30% and ~50% respectively upon reswelling in water.

As far as the crosslinking density is concerned, very high degrees of crosslinking do not favor crystallinity because a critical minimum length is necessary for a crystallite to form. Thus, very low degrees of crystallinity, i.e. very low equilibrium polymer percent in the gel, are reported for \( \rho = \frac{M}{N_c} > 40 \). As the crosslinking density decreases, the polymer weight percent (hence the degree of crystallinity) increases because of the more favorable chain length for formation of crystallites and because of the absence of defects closely related to very densely crosslinked materials (like loops, entanglements, etc.) which prevent the "easy" formation of crystallites.
Fig. 9-44: PVA weight percent as a function of crosslinking density for different annealing conditions. Annealing time 60 min.
Fig. 9-44: PVA weight percent as a function of crosslinking density for different annealing conditions. Annealing time 60 min.
Fig. 9-45: PVA weight percent as a function of crosslinking density for different annealing conditions. Annealing time 90 min.
Fig. 9-46: PVA weight percent as a function of crosslinking density for different annealing conditions. Annealing time 120 min.
For the same reason the formation of crystallites is easier in the 10% solutions than in the 15% ones, because in the latter chain entanglements prevent sufficient chain mobility for orientation to form crystalline regions.

The increase of the polymer weight percent with decreasing crosslinking density is characteristic for all the samples annealed for short times (30-60 minutes) and low temperatures (90-105°C). As temperatures increase, the curves PVA wt % vs ρ reach a maximum and then the PVA decreases as ρ decreases. This phenomenon, which seems sufficiently complicated, can be explained if we consider that as temperature increases, the material becomes more crystalline and the crystallites act as additional crosslinks. The swelling stress is absorbed by both "kinds of crosslinks" and the crystallites can be melted or plasticized if the stress gets sufficiently high. Thus the crosslinks act to protect and maintain these crystalline regions so that, if ρ gets very low, the crystallites will be dissolved and the PVA weight percent will be lower.

The crystallites formed by these annealing processes are not stable at very high temperatures and as a result of an increase of the temperature of swelling, they melt out and the water percent of the swollen hydrogel is gradually increasing. In Fig. 9-47 and 9-48 two plots of samples dried and tested for swelling at different temperatures are presented. The highly crosslinked crystallized hydrogels have a
Fig. 9-47: "Melting Out" of crystallites of semi-crystalline swollen PVA hydrogels upon increase of swelling temperature initial PVA solution: 15%. (The arrows determine the melting regions)
Fig. 9-48: "Melting Out" of crystallites of semi-crystalline swollen PVA hydrogels upon increase of swelling temperature. Initial PVA solution: 10%. (The arrows determine the melting regions.)
higher percent of water (lower crystallinity) and as the temperature increases, the crystallites melt out and the swelling behavior finally approaches the behavior of amorphous PVA networks (lines 1, 2, 3 in Figures 9-47 and 9-48).

Because of the wide variety of crystallites and their different sizes, a "melting area" is observed instead of a distinctive change in the volume at a certain temperature.

Figures 9-49 and 9-50 show the melting points of the crystallites for different $M_c$. Smaller crystallites melt at lower temperatures and since highly crosslinked materials and concentrated solutions do not favor the formation of crystallites, it is expected that lower melting points will be observed in samples prepared from 15% PVA solutions, very densely crosslinked ($M_c < 4000$). This is, indeed, the case as it is shown in Fig. 9-49. However, the variations are not significant ($T_m$ varies between 15 and 25°C) mainly because the method is not that sensitive. The temperature $T_m$ at which all the crystallites have melted is also a function of $M_c$ and initial percent of solution (Fig. 9-50). There does not seem to be any difference between 10% and 15% solutions and the behavior of the crystallites formed in them, and they melt at the same temperature.

The variation of the water percent as a function of swelling temperature is reported for PVA samples ($M_c = 5715$) dried at 90°C without previous dehydration for 1-6 hours (Fig. 9-51). The melting of the crystallites starts at higher temperatures for the shortly heat-
Fig. 9-49: Initial melting point $T_m$ as a function of $M_c$

Fig. 9-50: Final melting point $T'_m$ as a function of $M_c$
Fig. 9-51: "Melting Out" of crystallites of semi-crystalline swollen PVA hydrogels upon increase of swelling temperature, for various heat treated samples. $M_c = 5715$. Drying temperature 90°C
treated samples. This is not explained by the size of the crystallites, but by the number of them.

Repeated cycles of drying-swelling processes increase the crystallinity as judged by the water percent in the hydrogel. Figure 9-52 shows the effect of a second or third drying cycle on the crystallinity.

Vigorous annealing conditions increase the polymer weight percent in the hydrogel up to 65%, provided that care has been taken so that no decomposition (or either bond formation occurs) for very short periods of time of annealing and temperatures of 165-195°C the polymer percent is above 50% while the initial PVA film before annealing had an equilibrium swelling PVA wt % of 18-20%. (Fig. 9-53).

As in the case of mild annealing conditions, the dependence of PVA weight percent on the crosslinking density is of the same form (Fig. 9-54).

In many practical applications the effect of short-time increases of temperature is of great importance. Unfortunately in PVA hydrogels, even very short (one hour) exposure of the sample in high temperatures (90°C) will lead to melting out of the crystallites (degree of crystallinity decreasing from 70% to 55%) and immediate change of its mechanical properties (see Fig. 9-55).
Fig. 9-52: "Melting Out" of crystallites of semi-crystalline swollen PVA hydrogels upon increase of swelling temperature, for repeated drying cycles. $M_c=5715$. Drying temperature 90°C. Drying time 3 hrs.
Fig. 9-53: PVA weight percent as a function of annealing time and temperature. $M_c = 4770$ (High temperature)
Fig. 9-54: PVA weight percent as a function of crosslinking density for different annealing conditions. Annealing time 10 mins. (High temperatures)
Fig. 9-55: Dependence of crystallinity on time of swelling. Sample: $M_x=4770$.
Drying conditions 90°C 5 hrs. Swelling temperature 90°C
The degree of crystallinity can be calculated from the above data using density measurements. (See also Appendix K). Fig. 9-56 to 9-58 show the variation of the weight percent degree of crystallinity as a function of annealing time. The degree of crystallinity refers to the percentage of the PVA that is crystalline. It varies with time and temperature of annealing and usually it is not higher than 50%. These values are reasonable, since similar values have been reported for other polymer-diluent systems. The degree of crystallinity of the dehydrated polymer is only 12-15% so that, it is the annealing process that introduces the crystallites. Kinetically the degree of crystallinity increases with time of annealing, depending also on the crosslinking density (Fig. 9-56).

The variation of the degree of crystallinity with crosslinking is shown in Fig. 9-59. The degree of crystallinity shows the same behavior as the polymer weight percent in the hydrogel (see Fig. 9-43). A maximum in the value of crystallinity is shown for most of the curves, which is explained by the same reasoning as in the case of Fig. 9-43.

The degree of crystallinity varies between 30-60% depending on the thermal history of the sample. Recalling that the PVA weight percentage is between 30% and 50%, we conclude that the crystalline phase in the final PVA hydrogel is not more than 9-30%, yet it is responsible for the highly reinforced materials and the high modulus and ultimate properties.
Fig. 9-56: Degree of crystallinity as a function of annealing time for different $M_c$. Annealing Temperature 90°C. Initial Solution: 10%
Fig. 9-57: Degree of crystallinity as a function of annealing time for different annealing temperatures. \( M_c = 1495 \)
Fig. 9-58: Degree of crystallinity as a function of annealing temperature for different $M_c$. Annealing Time 30 min. Initial Solution 10%
Fig. 9-59: Degree of crystallinity as a function of $M_c$ for different annealing conditions. Annealing time 30°C
It is a common observation, made on a great variety of gel growth systems, that the crystals become increasingly scarce and more perfect with increasing distance from the gel interface.

The number of crystals growing diminishes with increasing distance from the gel surface. In these regions, the diffusion gradients are different from those near the surface and this is believed to be the principal explanation of the observed crystal distribution. However, there is a contributory cause arising from gel aging. Crystals which nucleate in the lower regions obviously nucleate in an older gel. The existence of such a contribution has been substantiated by systematic experiments on gels after varying amounts of pre-aging.

The crystals which grow at substantial depths in the gel grow more slowly than those near the top because of the smaller concentration gradients. There is every reason to believe that the rate of solute arrival, affects the perfection of the nuclei formed. Slow diffusion should lead to more perfect nuclei which, because of their higher energy content, should be less likely to reach critical size.

Scanning electron microscope analysis of semi-crystalline PVA hydrogels, shows evidence of absence of "holes" in the structure of the material. Pictures 9-1 and 9-2 show two pictures of the edge of a specimen under magnification of 100 and 500.
Picture 1. Electron Micrograph of Semi-Crystalline PVA Sample.

Magnification 100
Picture 1. Electron Micrograph of Semi-Crystalline PVA Sample.

Magnification 100
Picture 2. Electron Micrograph of Semi-Crystalline PVA Sample.
Magnification 500
Picture 2. Electron Micrograph of Semi-Crystalline PVA Sample.
Magnification 500
The method used for staining was the one reported by Arnold et al (484). After reaction with a 3% solution of gluteraldehyde, the material was stained with 1% osmium tetroxide (OsO₄) solution for three days and the water was extracted by solvent-solvent extraction with three subsequent solutions of 50% alcohol, 95% and 100% ethyl alcohol. Finally, the alcohol was extracted with propylene oxide.

Under the scanning electron microscope it can be seen that the hydrogel is homogeneous, as far as vacuoles and "holes" in the structure are concerned.

G. EVALUATION OF CRYSTALLINITY VIA DIFFERENTIAL SCANNING CALORIMETRY

The method of differential scanning Calorimetry was used in order to verify some of the results of crystallinity presented in the previous section and reveal some of the thermodynamic properties of crosslinked PVA and PVA hydrogels.

Different samples of Mₐ between 1495 and 9370 from two different initial solution concentrates 10% and 15% in PVA, heat treated at different conditions, were studied. They were compared to the uncrosslinked crystalline PVA films prepared in the same way. For the test a DSC-1 model was used and the thermograms were used to calculate the melting point of crosslinked PVA, the "melting point of the hydrogels", the heat of fusion of the 100% crystalline crosslinked PVA and the degree of crystallinity.
For the purpose of elimination of errors because of different testing conditions all the samples were tested with a scanning speed at 5°C/min. It was found that the scanning speed affects greatly the melting point and that it shifts the whole curve of melting. Repeated cycles of melting of the PVA did not show significant change of the melting point of PVA. For more information on the preliminary characterization of the instrument and the choice of scanning speed etc., see Appendix L.

In the rest of this discussion, the point where the recorded line of a thermogram starts deviating from the baseline, will be considered as the "melting point", as it has already been explained in the experimental part of this thesis. (395).

The melting point of Elvanol 73-125G used in three experiments has been reported as 218-219°C. The melting point is a function of crosslinking density (482) and Mandelkern has shown that the depression of the melting point is higher, the higher the degree of crosslinking is (232). Using the melting peak of PVA in the DSC - thermogram (Peak B in Figure 8-6) we were able to calculate the melting points (see Table 9-9) and melting point depressions of crosslinked PVA networks (Figure 9-60).
<table>
<thead>
<tr>
<th>Solution</th>
<th>$M_c$</th>
<th>$\frac{M_n}{M_c}$</th>
<th>$T_m$</th>
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<td>59.45</td>
<td>208.6</td>
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<td>3765</td>
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<td>4770</td>
<td>18.63</td>
<td>210</td>
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<tr>
<td></td>
<td>9370</td>
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</tr>
<tr>
<td></td>
<td>$\infty$</td>
<td>1.00</td>
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<tr>
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<td>200</td>
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<td>5715</td>
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</tr>
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<td>8420</td>
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<td>211</td>
</tr>
<tr>
<td></td>
<td>$\infty$</td>
<td>1.00</td>
<td>216.5</td>
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</table>
Fig. 9-60: Melting point depression because of crosslinking in PVA crosslinked networks
Thermograms for six samples (different PVA weight percent) of light different crosslinking densities were obtained and the $T_m$ of these gels was calculated. The equation

$$\left(\frac{1}{T_m} - \frac{1}{T_0}\right) / \nu_1 = \left(\frac{RV_u}{\Delta H_u V_n}\right) \left(1 - \frac{B / V_{1/1}}{RT_m}\right)$$  \hspace{1cm} (9-8)$$

was used for plotting the data. In this equation $V_u$ is the molar volume of the polymer repeating unit, $V_1$ is the molar volume of the solvent, $\nu_1 = 1 - \nu_2$ is the solvent volume fraction, $B$ is the interaction energy between polymer and solvent and $\Delta H_u$ is the heat of fusion of the 100% crystalline polymer.

Plot of $\left(\frac{1}{T_m} - \frac{1}{T_0}\right) / \nu_1$ versus $\nu_1 / T_m$ should give straight lines. Using the intercepts of these plots ($\frac{RV_u}{\Delta H_u V_1}$) the term $\Delta H_u$ could be calculated. Then using the slope of the lines, the term $B$ could be calculated. Figure 9-61 and 9-62 show the plots for different crosslinked hydrogels and for two different initial solution concentrations. Table 9-10 gives the results of $\Delta H_u$ and $B$. Typical calculations of these parameters are shown in Appendix M.

In Figure 9-63 the variation of $\Delta H_u$ with crosslinking density has been presented. The results are indeed very puzzling and further consideration and discussion has to be devoted to this subject. The values of $\Delta H_u$ vary with crosslinking density between 0.58 and 1.46
Fig. 9-61: Application of Flory's theory for the calculation of $\Delta H_u$ from DSC data. Initial PVA solution 10%
Fig. 9-62: Application of Flory's theory for the calculation of $\Delta H_u$ from DSC data. Initial PVA solution 15\%
<table>
<thead>
<tr>
<th>Initial Concentration</th>
<th>$M_c$</th>
<th>$\rho = \frac{n}{M_c}$</th>
<th>$\Delta H_u$ (cals/mole)</th>
<th>$B$ (cals/cm$^3$)</th>
</tr>
</thead>
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<td>24.18</td>
</tr>
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<tr>
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<td>580</td>
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<td>40.55</td>
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<tr>
<td></td>
<td>2190</td>
<td>40.58</td>
<td>1044</td>
<td>25.17</td>
</tr>
</tbody>
</table>
Fig. 9-63: Heats of fusions of 100% crystalline PVA for different degrees of crosslinking $\rho$
kcals/mole. These values, although very different, are not unreasonable. Finch (101) reports deviation of $\Delta H_u$ between 0.56 and 247 k cals/mole depending on the method of calculation. The value of 0.56 k cals/mole has been reported when the Flory equation is applied to the melting points of randomly reacetylated, PVA. Using glycerol as the diluent the heat of fusion of PVA was found to be 1.64 k cal/mole. In any case, the experimental values of this thesis are within the range of acceptability. What seems unreasonable or at least puzzling, however, is the fact that $\Delta H_u$ decreases as the crosslinking density decreases. One would expect that at higher degrees of crosslinking, the crystallites turn to be more imperfect and the $\Delta H_u$ is less than in lower degrees of crosslinking. It is known, however, that Elvanol used in this thesis is a mixture of different stereoregular forms of PVA with the atactic form being the predominant one. Finch notes (101) that the effects of tacticity on the heat of fusion and melting entropy of PVA have not been reported. Furthermore, he notes that hydrogen bonding of the hydroxyl side groups on the polymer could affect the melting process. Mandelkern (232) on the other side refers to the melting point, $T_m$ of the isotropic network and expresses it as:

$$\frac{1}{T_m} = \frac{\Delta S^0 + \Delta S^0_X + \Delta S^0_{ex}}{\Delta H}$$

(9-9)
where $\Delta S^o$ is the entropy of fusion of the pure uncrosslinked polymer, $\Delta S^o_X$ is the alteration of the chain configurational entropy in the reference state, which alteration results from the presence of the crosslinks and $\Delta S_{eq}$ is the entropy change that occurs in going from the reference state to the real isotropic state. Mandelkern states that the melting temperature depressed even if $\Delta H$ is unaffected by the presence of crosslinks. Flory (483) notes that, to the extent that the formation of crosslinks does not interfere directly with crystallization at the units involved in crosslinks, both $\Delta H$ and $\Delta S^o$ may be taken to be independent of the degree of crosslinking. This seems a reasonable assumption for fibrous proteins. In other polymers, crosslinked units are likely to be excluded from crystalline regions by their steric requirements with the result that the entropy of fusion is increased and the melting point is depressed. Generally, upon depression of $T_m$, the term $\frac{\Delta S}{\Delta H}$ should increase, which can happen when $\Delta H$ decreases, or when both $\Delta S$ and $\Delta H$ increase with $\Delta S > \Delta H$. If, however, we accept the assumption that $\Delta H$ remains unaffected by the presence of crosslinks, then the data of the different samples can be replotted as in Figure 9-64 and a straight line can be drawn through them. This line gives $\Delta H_u = 1.05$ kcal/mole and $B = 24.90$ cal/cm$^3$.

The calculation of the heat of fusion of the particular samples $\Delta H^*$ was done by measuring the area and converting it to kcals/mole. In this way the crystallinity was calculated for some representative PVA hydrogel samples. Table 9-11 includes the degree of crystallinity of
Fig. 9-64: Application of Flory's theory for the calculation of $\Delta H_u$ from DSC data
<table>
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<th>$M_c$</th>
<th>Annealing Conditions</th>
<th>Crystallinity from DSC</th>
<th>Crystallinity From Density</th>
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<td>90 90</td>
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<td></td>
<td>90 60</td>
<td>43.10</td>
<td>44.85</td>
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</table>
these samples in comparison to the degree of crystallinity as calculated from density measurements.

The data are quite satisfactory and the variation of the two arithmetic values in most of the cases is not more than ±5%. However, it is the authors' opinion, that the density measurements lead to more reliable data, than the DSC measurements because in the latter case, errors in drawing the "baseline" of the thermogram may lead to false calculation of $\Delta H^*$ and subsequently of the degree of crystallinity.

The $\chi$ Factor

The problem of the $\chi$ factor of PVA-H$_2$O systems although discussed in three publications (348, 176, 470) has not been solved. In this thesis and in the calculation of crosslinking densities, the value of 0.494 at 30°C and $v_2 = 0 \div 0.15$ has been used as reported by Sakurada (348). However, extensive tests have been done to elucidate the behavior of the chi factor as a function of polymer volume fraction and temperature. For this purpose swelling experiments on PVA hydrogels with $M_c$ 2190, 5715 and 8420 were performed and the polymer volume fraction was calculated. Applying the equation

\[
\ln(1-v_{2,s}^2) + v_{2,s}^2 + x_1 v_{2,s}^2 = \frac{v_1}{\nu M_c} - \left(1 - \frac{2M_c}{M_n}\right) v_{2,r}^2
\]

\[
\left[\frac{v_{2,s}}{v_{2,r}}\right]^{1/3} - \frac{1}{2} \left(\frac{v_{2,s}}{v_{2,r}}\right)
\]

(9-10)
derived from Flory's theory when \( \mu_1 - \mu_0 = 0 \), we can evaluate \( \chi_1 \) for different \( \nu_2 \) and temperatures. Lines 1, 2, 3 on Figure 9-47 shows the original data of swelling. The results of the \( \chi \) factor and its dependence on the temperature and volume fraction are shown in Figure 9-65, 9-66 and 9-67. Calculations of the \( \chi \) factor are included in Appendix N.

The data of \( \chi \) factor versus \( \nu_2 \) can fit on straight lines for different temperatures. A somewhat significant derivation is noticed at high \( \nu_2 \) (above 0.10). The plots are in agreement with similar data of Flory (104) in other polymer-diluent systems. The values of \( \chi \) factors vary between 0.45 and 0.51. Throughout this thesis the value of 0.494 at 30°C was used as reported by Sakurada et al. (348). This value, according to the data presented here, is valid for \( \nu_2 = 0.13 \), but for lower volume fractions somewhat lower values of \( \chi \) must be used. The value of \( \chi \) factor at 30°C in the range of \( \nu_2 = 0.04 - 0.14 \) varies between 0.475 - 0.495. Provided that this value is used for the calculation of crosslinking densities, the assumption of constant value of \( \chi \), for \( \nu_2 = 0.15 \), as Sakurada et al. proposed (348) can be equally good and valid.

### H. EVALUATION OF CRYSTALLINITY VIA IR SPECTROSCOPY

Evaluation of the crystallinity via IR spectroscopy was done in order to verify the results of the previously mentioned methods. The
Fig. 9-65: Dependence of the $\chi$ factor of PVA - $H_2O$ systems on the polymer volume fraction $v_2$ and the temperature of the system
Fig. 9-66: Dependence of the $\chi$ factor of PVA-H$_2$O systems on the polymer volume fraction $v_2$ and the temperature of the system
Fig. 9-67: Dependence of the $\chi$ factor of PVA-H$_2$O systems on the polymer volume fraction $v_2$ and the temperature of the system.
method is concerned with the relation of the intensity of the peak at 1141 cm$^{-1}$ to the crystalline weight percent of PVA. IR Spectroscopy can be done only on dry samples, so that this is a method to check the truth of the theory of swelling in semi-crystalline polymers (i.e. that swelling occurs only in the amorphous regions and it does not affect the crystalline sections).

A series of samples crosslinked with electron beam irradiation and with $M_c = 4770$ ($\rho = 18.63$) were annealed at different temperatures and the IR spectrum was recorded. Using the intensities of the peaks at 1141 cm$^{-1}$ and 1425 cm$^{-1}$ as shown in Figure 8-10, the following equation was derived (For derivation, see Appendix 0).

\[
\text{Crystallinity \%} = 26.7 + 102.6 \left[ \left( \frac{d}{c} \right) - 0.36 \right] \quad [9-11]
\]

Table 9-12 includes the results calculated by this method as well as the corresponding crystallinity as calculated from density measurements after swelling. The arithmetic values of the crystallinites are surprisingly close. The difference is higher when the crystallinity increases, probably because of slight etherification, although those samples (e.g. Sample annealed at 120°C for 90°Cmin) do not show any evidence of CO groups (See Figure 8-10).
TABLE 9-12

CRYSTALLINITY OF CERTAIN PVA HYDROGELS AS JUDGED FOR IR SPECTROSCOPY

<table>
<thead>
<tr>
<th>Annealing Conditions</th>
<th>T(%)</th>
<th>t (min)</th>
<th>d/c</th>
<th>Crystallinity From IR</th>
<th>Crystallinity From Density</th>
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<td></td>
<td>90</td>
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<td>90</td>
<td>0.730</td>
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</table>
I. TENSILE EXPERIMENTS

Tensile experiments were performed on most of the crystallized and swollen samples and the initial modulus, the ultimate tensile strength and the elongation are reported and plotted for different annealing conditions. Some of the experiments were performed by Demetriou (80).

Preliminary experiments on the effect of the swelling ratio and the thickness of the final hydrogels, on the mechanical properties of the materials, show that that initial modulus, the ultimate tensile strength and the elongation are functions of the thickness of the hydrogels. The experimental results for a sample of $M_c = 8420$ annealed at $90^\circ\text{C}$ for 60 minutes are plotted in Fig. 9-68. These data clearly show that the idea of a "sandwich" model of crystalline material may be correct. According to this model, crystallinity is introduced in "layers" and films dried at the same condition will swell and show different properties if they have different thickness. Figure 9-69 shows that the swelling ratio is indeed a function of the thickness (for films dried under the same conditions). In this way, Fig. 9-70 is constructed, which shows the effect of the swelling ratio on the mechanical properties. An increase in the swelling ratio means increase of the water percent of the hydrogel (lower crystallinity) and thus the modulus will be lower. The lower overall crystallinity of these films (which, however, have been treated under the same conditions of
Fig. 9-68: Dependence of the initial modulus of crystallized PVA hydrogels on the thickness of the tested samples. $M_c=8420$
Annealing conditions 90°C, 60 min.

Fig. 9-69: Dependence of the swelling ratio of crystallized PVA hydrogels on the thickness of the tested samples. $M_c=8420$
Annealing conditions 90°C, 60 min.
Fig. 9-70: Dependence of the initial modulus of crystallized PVA hydrogels on the swelling ratio. $M_c = 8420$. Annealing Conditions 90°C, 60 min.
temperature and time) shows the importance of the thickness of the samples as well as the way of drying (one or two "surfaces" of drying) of the films.

The mechanical properties are a strong function of the crystalline percent of the hydrogels. It has been proved by experiments reported in previous sections that increase of the swelling temperature would cause a significant change of the degree of crystallinity of a hydrogel, and that at about 70-75°C all the crystallites have "melted out".

The mechanical properties of crystallized hydrogels as a function of the swelling temperature have been studied for some selected samples of PVA hydrogels, and plotted in Fig. 9-71 and 9-72. The initial modulus of crosslinked crystallized hydrogels decreases by two or three orders of magnitude as the temperature increases from 30°C to 70°C. During this rise of the temperature, the crystallites are "melted out" and the material has finally moduli of 5-10 psi which are of the same order of magnitude as the moduli of noncrystallized hydrogels swollen at 30°C (as reported in previous section of this chapter).

The mechanical behavior is a function of crosslinking and increasing crosslinking shifts the curves towards higher values of moduli at higher temperatures, as well as towards the formation of a "plateau" as predicted by the theory. The shape of the curves of modulus versus temperature as well as the orders of magnitude, clearly
Fig. 9-71: Effect of the swelling temperature on the initial modulus of crystallized PVA hydrogels. Annealing conditions 105°C, 60 min.
Fig. 9-72: Effect of the swelling temperature on the initial modulus of crystallized PVA hydrogels. Annealing time 60 min., $M_c = 9370$
show that some of the five classical viscoelastic region as defined by Tobolsky (422) can be recognized in the mechanical behavior of these materials. At low temperatures a crystalline region (a "plateau" with almost constant values of moduli for 10-15 degrees) is shown, followed by a region of very rapid decrease of the moduli, which region can be considered as a transition region. This region is followed by the rubbery and the amorphous regions (which correspond to the noncrystalline crosslinked hydrogels). If it were not for the crosslinks, the last region would be a "liquid flow region" where the modulus decreases significantly and the material becomes very weak. This is the case of an uncrosslinked sample which above 50-55°C dissolved in water.

However, in crosslinked materials, this last region is presented by a plateau which is more distinctive, the higher the degree of crosslinking. The shift of the curves because of higher crystallinity in the initial hydrogel is shown in Fig. 9-72 where comparison is made of two samples \( M_c = 9370 \) annealed for 60 minutes at 90°C and 105°C.

Similar behavior is shown by the Ultimate Tensile Strength and the elongation. They are functions of both the annealing and the swelling temperatures (Fig. 9-73 and 9-74). It must be stressed once more, as shown in these figures, that the high values of the mechanical properties are a function of crystallinity and the temperature of the environment and that the material cannot be used above 50°C.
Fig. 9-73: Ultimate tensile strength as a function of swelling and annealing temperatures. $M_c = 9370$, annealing time 60 min.

Fig. 9-74: Elongation at break as a function of swelling and annealing temperatures. $M_c = 9370$, annealing time 60 min.
In Fig. 9-75 to 9-78 the Ultimate Tensile Strength and the elongation are plotted as functions of crosslinking density of the initial material and swelling temperature.

These terms show a maximum with crosslinking density for any swelling temperature. This is exactly the same behavior as in the case of the dependence of the degree of crystallinity on the crosslinking density, or discussed earlier.

The behavior of the elongation as a function of swelling temperature can be explained using Fig. 9-79. This figure is the schematic representation of the stress-strain for different swelling temperatures and it resembles the failure envelope enclosing curves at constant strain rates.

In this section, the results obtained from the stress-strain tests will be presented and discussed. It must be recalled that these experiments were done on crystallized (via different heat-treatment conditions) hydrogels, of different degrees of crosslinking. Thus the main parameters studied were:

(i) annealing temperature
(ii) annealing time
(iii) crosslinking density
(iv) percent PVA in initial solution
**Fig. 9-75:** Ultimate tensile strength as a function of crosslinking density $\rho$ for different swelling temperatures. Annealing conditions $105^\circ\text{C}$, 60 minutes. Samples 15% PVA

**Fig. 9-76:** Ultimate tensile strength as a function of crosslinking density $\rho$ for different swelling temperatures. Annealing conditions $105^\circ\text{C}$, 60 minutes. Samples 10% PVA

- 432 -
Fig. 9-77: Elongation at break as a function of crosslinking density $\rho$ for different swelling temperatures. Annealing conditions 105°C, 60 minutes. Samples 15% PVA

Fig. 9-78: Elongation at break as a function of crosslinking density $\rho$ for different swelling temperatures. Annealing conditions 105°C, 60 minutes. Samples 10% PVA
Fig. 9-79: Stress-strain curves of samples swollen at various temperatures. $M_c = 9370$. Conditions of heat treatment 90°C, 60 min.
The initial modulus (Fig. 9-80 to 9-84), the ultimate tensile strength (Fig. 9-85 to 9-89) and the elongation at break (Fig. 9-90 to 9-93) were studied as functions of the above parameters. Typical calculation of these parameters are shown in Appendix P. The same tests were repeated for uncrosslinked PVA films, so that valuables comparisons could be made. As previously explained, mild annealing conditions (temperatures < 150°C) lead to tough, workable materials with significantly high extensibility, while annealing at temperatures above 160°C leads to materials with very high modulus of elasticity.

The initial modulus increases with increasing time of annealing. This is attributed to the increase of crystallinity of the samples. It can also be observed that under mild annealing conditions the modulus curves level off, showing an almost constant value of crystallinity, which is correct, having in mind the previous diagrams of the variation of crystallinity with annealing time. The values of moduli vary between 200-1500 psi depending on the crosslinking and annealing conditions, while the corresponding values of the noncrystalline materials are very low, that is between 5 and 25 psi. This comparison clearly shows the effects of crystallization on the mechanical properties. The initial modulus increases with increasing temperatures of annealing as well. The results can only be used to make a general conclusion. Two or three samples were tested at each drying condition and the results that did not vary more than 5% were reported. The thickness was kept
Fig. 9-80: Dependence of initial modulus on the annealing conditions. $M_c = 3765$ (10% PVA solution)

Fig. 9-81: Dependence of initial modulus on the annealing conditions. $M_c = 4770$ (10% PVA solution)
Fig. 9-82: Dependence of initial modulus on the annealing conditions. Uncrosslinked samples.
**Fig. 9-83:** Dependence of initial modulus on the annealing conditions. $M_c = 8420$ (15% PVA solution)

**Fig. 9-84:** Dependence of initial modulus on the annealing conditions. $M_c = 5715$ (15% PVA solution)
Fig. 9-85: Dependence of ultimate tensile strength on the annealing conditions $M_c = 9370$ (10% PVA solution)

Fig. 9-86: Dependence of ultimate tensile strength on the annealing conditions $M_c = 4770$ (10% PVA solution)
Fig. 9-87: Dependence of ultimate tensile strength on the annealing conditions $M_c = 3765$ (10% PVA solution)

Fig. 9-88: Dependence of ultimate tensile strength on the annealing conditions, Uncrosslinked samples
Fig. 9-89: Dependence of ultimate tensile strength on the annealing conditions $M_c = 8420$ (15% PVA solution)

Fig. 9-90: Dependence of elongation at break on the annealing conditions $M_c = 8420$ (15% PVA solution)
Fig. 9-91: Dependence of elongation at break on the annealing conditions $M_c = 3765$ (10% PVA solution)

Fig. 9-92: Dependence of elongation at break on the annealing conditions $M_c = 4770$ (10% PVA solution)

Fig. 9-93: Dependence of elongation at break on the annealing conditions $M_c = 9370$ (10% PVA solution)
strictly close to 20 mils. Very low $M_c$ (high degree of crosslinking) introduces very high tension in the network; indeed the internal tension can readily, with composition of slight external stress, lead to catastrophic failure through rapid crack propagation.

The ultimate tensile strength and the elongation at break show the same behavior as the initial modulus. The first has values between 500 and 1500 psi, whereas the uncrystallized materials have values of 20-40 psi. The elongation at break varies between 120% and 500%, whereas the uncrystallized materials do not show values higher than 100%.

In any event, the mechanical behavior of the hydrogels is a definite function of the crystallinity of the materials. As shown in Figure 9-94, the initial modulus can be plotted as a function of the weight fraction of the crystalline PVA in the total PVA of the hydrogel. The relation is, of course, complicated by dependence of the modulus additionally on the variation of the swelling ratio of the hydrogel (i.e. the water percent of the samples). If, however, the same data are plotted against the crystalline PVA weight percent of the hydrogel (crystalline PVA, in the PVA plus water system) then a better fitting of the curve is succeeded (see Fig. 9-95). The relation is well represented by a single nearly linear relationship for crystallinities 10-25%, levelling off at higher percentages of
Fig. 9-94: Initial modulus of crystallized PVA hydrogels as a function of degree of crystallinity.

Fig. 9-95: Initial modulus of crystallized PVA hydrogels as a function of the crystalline polymer weight percent in the hydrogel.
crystallinity. Analogous behavior is observed for the ultimate tensile strength and the elongation at break (See Fig. 9-96 and Fig. 9-97) for the same parameter. The modulus is plotted against the crystallinity for two different crosslinking densities. For the same degree of crystallinity the modulus is higher for the more densely crosslinked material. This is one of the most significant conclusions of this thesis. Even after introduction of the crystallites in the crosslinked material, the crosslinks continue to play an important role in "receiving" a part of the stresses applied on the system and they tend to behave in the same way as the crystallites redistributing the tensile stress almost equally between the crystallites and the crosslinks.

The higher the crosslink density, the higher one would expect the modulus to be, if there were no crystallites as has already been developed in preceding discussion. The data clearly shows that the presence of crystallites, which drastically improves tensile tear strength, does not overwhelm the inherent state properties of the crosslinked network.

Annealing under vigorous conditions (temperatures above 150°C) is done for very short periods of time (up to 15 minutes). The serious problem of decomposition is faced here. Evidence of internal dehydration is a yellowish color of the hydrogel film. Films showing this color were not tested. Even in cases of very short annealing times, decomposition cannot be avoided. The initial modulus and the ultimate tensile strength are significantly higher and the values vary between
Fig. 9-96: Ultimate tensile strength of crystallized PVA hydrogels as a function of degree of crystallinity $M_c = 4770$.

Fig. 9-97: Ultimate tensile strength of crystallized PVA hydrogels as a function of the crystalline polymer weight percent in the hydrogel.
1000 and 3500 psi (for $E_i$) and 700 and 1500 psi (for UTS). (See Fig. 9-98 and 9-99). The elongation at break is significantly lower (200-250%) than in the case of mild annealing condition (temperatures below 150°C) and no correlation between elongation and annealing history could be developed. This, among other reasons, can be attributed to the decomposition of the material, which leads to unpredictable "weak" bonds in the material, so that the elongation is not related to the actual structure of the hydrogel, but to the number of newly formed bonds.

The effect of crosslinking density on the initial modulus, the ultimate tensile strength and the elongation at break, is shown in Fig. 9-100, 9-101 and 9-102.

As it has been already explained, a critical length of chain is needed before a crystallite can be formed, with larger crystallites arising from larger segments. Thus larger crystallites and higher tendency to crystallize, should be expected as the crosslinking density decreases. As the crystallinity affects directly the mechanical properties, lower crosslinking densities should lead to higher moduli, strengths at break and elongations as it has been obtained in the tensile tests. However, when the stress gets sufficiently high and in the case of low crosslinking, the crystallites can be "melted" - plasticized -
Fig. 9-98: Initial modulus as a function of annealing time (a) and temperature (b) (High temperatures)
Fig. 9-99: Ultimate tensile strength as a function of annealing time (a) and temperature (b) (High temperatures)
Fig. 9-100: Dependence of the initial modulus on the crosslinking density. Annealing time 60 min.
Fig. 9-101: Dependence of the ultimate tensile strength on the crosslinking density.
Annealing time 60 min.
Fig. 9-102: Dependence of the elongation at break on the crosslinking density.
Annealing time 60 min.
and then crosslinks act to protect and maintain the crystalline region so that if the crosslinking density gets too low, the crystallites will be dissolved and the mechanical properties will be lower.

It must be noticed that the mechanical properties depend on the initial concentration of the solution (10% or 15%) and that the higher the initial solution concentration, the higher the mechanical properties such as the tensile modulus.

It has to be noticed that in some cases the number of samples tested was not more than three, so that only speculations can be drawn, but in general the trend of the mechanical behavior of the hydrogels is as discussed above.

J. CREEP EXPERIMENTS

Creep experiments were performed to study the viscoelastic properties of PVA hydrogels in a different prospective Figures 9-103 to 9-109 contain some of the results of those studies. Fig. 9-103 shows a typical plot of strain $\varepsilon = \frac{\Delta l}{l_0}$ as a function of time of creep for a crystalline sample ($M_c = 3765$, annealing conditions 90°C 60 minutes, stress 175 psi).

The measured elongation is 121% after 30 hours. The plot shows an instantaneous elongation immediately upon application of load, followed by a test rate of creep region, where the rate gradually decreased to a constant rate up to 30 hours, when the load was removed.
Fig. 9-103: Typical creep data. Strain versus time elapsed Sample: $M_c = 3765$.

Annealing conditions 90°C, 60 min. Stress $\tau = 175$ psi
The recovery was studied in the same way.

Previous creep experiments on PVA hydrogels have not been reported, but it is well known that hydrogels in general elongate until the rate of creep reaches a near zero value.

All the creep experiments were done under constant load and not constant stress. This was unavoidable, first because of small variation in the initial thickness of the swollen tested films (this variation came from different swelling ratio upon different heat-treatment history) and second because of the different buoyancy forces of the different loads used (recall that all the experiments were done in water).

The molecular interpretation for long time creep behavior observed in PVA hydrogels, crystallized by an annealing process, can be explained in terms of the fringed micelle model. Creep happens first in the amorphous region between crystallites, until a critical elongation is reached at which the stress becomes equal to the yield stress of the weakest crystallities. At this point, the second creep process starts and the crystallites deform in the order of their strength. The strongest crystallites keep the material from rupturing, and the high strains imposed on each specimen result in small permanent deformation, after a period of fifteen hours from the start of the recovery period.
This could also be interpreted as melting out and partial recrystallization in the direction of relieving the stress.

Fig. 9-104 and 9-109 show the characteristic creep recovery curves of two samples ($M_c = 3765$, annealing condition $90^\circ$C, 30 and 90 min) subjected to three consecutive creep cycles. The creep cycle lasted thirty hours and the recovery cycle fifteen hours.

The strain after 30 hours (Figure 9-110) was 170% but dropped to 96% after a second test and remained almost constant after the third cycle (94%).

On the other hand, the permanent strain after recovery decreased from 51.4% to 4% and finally became almost zero (i.e., there was no more permanent deformation). (Fig. 9-111).

This supports an interpretation of crystallite melting out and rearrangement which formally ceases if the total stress be kept at a fixed level, despite the number of cycles.

**Stress-Strain Experiments**

Stress-strain experiments under quasi-equilibrium conditions were performed in selected PVA samples for the purpose of revealing the behavior of the crystallites in the PVA-network structure. Increasing stress was applied on the specimen and the elongation after twenty minutes was recorded. Fig. 9-112 represents a plot of the tensile
Fig. 9-104: Strain versus the elapsed. Same: $M_c = 3765$. Annealing conditions 90°C, 30 min. Stress $\tau = 155.7$ psi
Fig. 9-105: Strain versus time elapsed. Sample: $M_c = 3765$. Annealing conditions $90^\circ C$, 30 min. Stress $\tau = 155.7$ psi. Second creep cycle
Fig. 9-106: Strain versus time elapsed. Sample: $M_c = 3765$. Annealing conditions 90°C, 30 min. Stress $\tau = 155.7$ psi. Third creep cycle.
Fig. 9-107: Strain versus time elapsed. Sample: M = 3765. Annealing conditions 90°C, 90 min. Stress τ = 231 psi.
Fig. 9-108: Strain versus time elapsed. Sample: $M_c = 3765$. Annealing conditions 90°C, 90 min. Stress $\tau = 231$ psi. Second creep cycle.
Fig. 9-109: Strain versus time elapsed. Sample: $M_c = 3765$. Annealing conditions 90°C, 90 min. Stress $\tau = 231$ psi. Third creep cycle
Fig. 9-110: Strain after the creep cycle (30 hrs.) as a function of number of cycles.

Fig. 9-111: Strain after the recovery cycle (15 hrs.) as a function of number of cycles.
stress $\tau$ of six semi-crystalline PVA hydrogels as a function of the extension parameter ($\alpha = \frac{1}{a^2}$). The experimental points, except for slight deviations, fell on a straight line. According to the rubber elasticity theory the relationship of $\tau$ and ($\alpha - \frac{1}{a^2}$) is linear for an ideal rubber network. Although Gaussian statistics apply only up to $\alpha = 3.0$, the linear relationship could apply even at $\alpha = 5.0$ for samples of low crystallinity. Typical calculations of the parameters, are shown in Appendix R.

The results prove that the crystallites introduced act mostly as regular crosslinks. The strong resemblance between the observed behavior of semi-crystalline PVA hydrogels and crosslinked amorphous PVA hydrogels deserves further attention from the experimental as well as theoretical points of view. Deviations from the theory of rubber elasticity originate from the difficulty of performing force-dehydration measurements under equilibrium conditions. The behavior of crosslinked networks undergoing deformation is non-equilibrium conditions has been shown to follow the equation:

$$\frac{\tau}{(\alpha - \frac{1}{a^2})} = 2C_1 + 2C_2 \frac{(1/\alpha)}{\alpha}$$  \hspace{1cm} (9-12)

where $C_1$ and $C_2$ are parameters depending on the creep time. The slight variation in the lines of Fig. 9-112 could not be predicted. Therefore, these affects were not solely responsible for the small deviations reported.
Fig 9-112: Stress-strain quasi equilibrium tests
Samples 1: $M_c = 8420$ (15%) - ann. cond. 90°C, 90 min. - $x' = 21.0$
2: $M_c = 4770$ (10%) - ann. cond. 90°C, 120 min. - $x' = 18.6$
3. $M_c = 4770$ (10%) - ann. cond. 90°C, 90 min. - $x' = 15.9$
4. $M_c = 4770$ (10%) - ann. cond. 90°C, 60 min. - $x' = 14.2$
5. $M_c = 8420$ (15%) - ann. cond. 90°C, 30 min. - $x' = 12.6$
6. $M_c = 4770$ (10%) - ann. cond. 90°C, 30 min. - $x' = 9.3$
A comparison of the stress-extension behavior of two samples subjected to tensile and stress-strain quasi-equilibrium experiments shows that because of the non-equilibrium conditions, (Line 1 of Fig. 9-113) the modulus of elasticity is different if calculated by the two different experiments. A modulus of 3.75 times higher is calculated if non-equilibrium tensile experiments are used. Significant deviations from the straight line 1 are shown in the same plot. The decrease of the modulus in a quasi-equilibrium experiment can be attributed to the melting of some of the crystallites that were initially present in the hydrogel, acting as crosslinks. Thus, after enough relaxation, the film has a different structure and it is more amorphous than the initial film. This evidence is supported by the results of reported cycles of creep-recovery experiments, as they have been discussed earlier.

The stress at 10% elongation, during stress-strain quasi-equilibrium experiments of the samples mentioned in Fig. 9-114 is plotted against the crystalline PVA weight percent in the hydrogel. Since the stress is directly proportional to the modulus, it can be seen that the modulus increases very sharply with crystallinity. This behavior is somewhat different than the behavior of the modulus of elasticity from tensile experiments. A possible explanation is that during the quasi-equilibrium experiment, some crystallites melt out so that the stress must be distributed in less number of crystallites and crosslinking points.
Fig. 9-113: Stress versus extension factor \((a - \frac{1}{a^2})\) for two types of stress-strain tests. Annealing conditions 90°C, 30 min.

\[ M_c = 8420 \]
Fig. 9-114: Stress at elongation 10% versus crystalline PVA weight % in the hydrogel
Application of Nutting's Equation

Nutting's equation gives a simple characterization of the viscoelastic properties of crystalline PVA hydrogels, for the whole range of deformation considered. Previous work has not been done on the application of this equation to PVA hydrogels. The usefulness of a Nutting analysis relies on the facility to compare the data in terms of concentration, heat-treatment history and applied stress.

The creep compliance \( J \), defined as the observed strain per unit of applied stress, in proportional to \( t^n \), where \( t \) is the time and \( n \) is assumed to be constant at a given temperature. Typical calculation of the creep parameters are included in Appendix Q.

Plots of \( \ln J \) versus \( t \) are shown in Fig. 9-115 to 9-118. As it can be seen the experimental points fit fairly well on straight lines, the slopes of which correspond to different values of "\( n \)".

Theoretically, the upper limit of \( n \) is one for materials which act like viscous liquids and the lower limit is zero for perfectly elastic materials. Fig. 9-115 shows that \( n \) is independent of stress within the range of stresses used in these experiments. Two identical PVA samples of \( M_c = 3765 \) were subjected to the same heat-treatment conditions (90°C - 90 minutes) but the creep experiments were done under stresses of 230 and 370 psi. The two lines \( \ln J \) vs \( t \) were parallel.
Fig. 9-115: $\ln J$ versus time $M_c = 3765$. Annealing conditions $90^\circ C$, 90 min.
Fig. 9-116: $\ln J$ versus time. $M_0 = 3765$. Annealing time 60 minutes.
Fig. 9-118: \( \ln J \) versus time. Annealing Conditions: 900°C, 30 min.
It must be expected that this behavior holds only for small stresses and strains (linear viscoelastic behavior). It can be noted that for the sample tested and presented in Fig. 9-115, the UTS is 1600 psi and the creep stresses were 230 and 370 respectively, that is only 14% and 23% of the strength at break. At large stresses these effects lead to non linear viscoelastic behavior.

In Fig. 9-116 to 9-118, the effects of different parameters on the exponent "n" are studied. Some of the results shown here indicate that the exponent "n" has higher values when the temperature of annealing, the time of annealing and the $M_c$ increase. This is one more evidence that this term is in direct relation to the degree of crystallinity of hydrogels tested. The value "n" was analytically tested for samples of different crosslinking density, annealed at different temperatures for the same time of 60 minutes. It must be recalled that although the stress was not the same (because of the reasons explained above) for all the samples tested, the arithmetic value of "n" does not change with stress in the range of the stresses used here (up to 20% of UTS). The arithmetic values are shown in Table 9-13.

Figure 9-119 includes some plots of n as a function of crosslinking density $\rho = \frac{M_n}{M_c}$. The curves show a peak at a certain crosslinking density. The explanation is the same as in the case of the tensile properties tested.
### Table 9-13

ARITHMETIC VALUES OF "n" OF NUTTINGS'S EQUATION $J = \psi t^n$ WHERE $t$ IS HOURS AND $J$ IS PSI

<table>
<thead>
<tr>
<th>$M_c$</th>
<th>$\rho = \frac{M_n}{M_c}$</th>
<th>Annealing Conditions</th>
<th>$n$</th>
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<td>3765</td>
<td>23.61</td>
<td></td>
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<td>23.61</td>
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<td>0.1220</td>
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<td>18.63</td>
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<td>-</td>
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<tr>
<td>$\infty$</td>
<td>-</td>
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<td>0.1122</td>
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Fig. 9-119: Exponent "n" of Nutting's equation as a function of crosslinking density ρ. Annealing time 60 min.
In conclusion, semicrystalline PVA hydrogels have extraordinary creep properties. They show very low creep tendency at long times, a large short-time compliance and a significant creep recovery, all typical signs of three dimensional network behavior.

K. TEAR PROPAGATION EXPERIMENTS

In the hydrogel field, interest has largely centered on the process of tearing, that is, the propagation of a cut or crack already existing in the material, because when a hydrogel parts under excessive forces in a practical application, it usually fails owing to the development of a tear.

In the tear propagation experiments, the load (in gms) was recorded and reported as a function of different parameters concerning the temperature time history of the hydrogels. Because of variations of the thickness of some samples, experiments were performed to study the relation of load to thickness. This was found (Fig. 9-120) to be linear above a certain thickness. Typical calculation of tear strength are reported in Appendix S.
Fig. 9-120: Tear load dependence on the thickness of tested samples.

$M_c = \text{8420}$. Annealing condition 90°C, 30 min.
Since most of the samples had thickness around 20 mil, the results are comparable. In Figures 9-121 and 9-122, the load necessary to tear a simple (as described in the experimental part) divided by the thickness of the sample was plotted against the annealing time for different temperature conditions and crosslinking densities. Increasing crystallinity increases the tear strength, because the crystallites act as additional crosslinks reinforcing the hydrogel. For the same reasons, increasing $M_c$ favors the formation of large and more crystallites and increases the tear strength. Typical values of tear strength are between 2 and 4 grams per mil thickness of semicrystalline PVA hydrogels, whereas uncrosslinked crystallized materials have values below 2 gm/mil and crosslinked noncrystalline PVA hydrogels have very low (almost zero) values.

The somewhat different values of uncrosslinked crystallized PVA films from 10% to 15% solution, can be attributed to the different drying rate, that produces different sizes of crystallites in the two cases.

The effect of the crosslinking density on the tear strength is shown in Fig. 9-123. The behavior of the same trend as in the study of other mechanical properties previously discussed. The tear strength increases with decreasing crosslinking and shows a maximum, after which it gradually decreases.
Fig. 9-121: Dependence of tear strength on the annealing conditions.
Initial solution 10% in PVA

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>M_c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>105</td>
</tr>
<tr>
<td>2</td>
<td>105</td>
</tr>
<tr>
<td>3</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>90</td>
</tr>
</tbody>
</table>

Fig. 9-122: Dependence of tear strength on the annealing conditions
Initial solution 15% in PVA
Fig. 9-123: Dependence of tear strength on the crosslinking density $\rho$
CHAPTER 10
CONCLUSIONS

A. CROSSLINKING OF PVA SOLUTIONS

Poly (vinyl alcohol) solutions of concentrations 10% and 15% were crosslinked via electron beam and γ-radiation of 0°C and 30°C in air and under nitrogen to form transparent hydrogels of varying crosslinking densities and properties. Gamma radiation favored crosslinking, leading to more dense networks than electron beam radiation, for the same dose delivered. The effect of oxygen was significant in γ-radiation, where degradation was finally achieved. In electron beam irradiation no effect of oxygen on crosslinking was observed. The final crosslinking density depended on the dose rate as well. Bubble formation was a problem during electron beam irradiation, because of the slow rate of diffusion of gases as compared to the rate of crosslinking, and it was overcome by a freezing - thawing process.

Crosslinked PVA hydrogels with crosslinking density between 10 and 25 crosslinks per polymer unit ($M_c = 3500 \div 8000$) were weak, easy to shatter, and non-extensible materials. The initial moduli of these swollen hydrogels varied between 10 - 70 psi (increasing with decreasing $M_c$), the strength at break varied between 1 - 10 psi (again increasing with decreasing $M_c$) and the elongation at break was not more than 100% (increasing with increasing $M_c$). These hydrogels had polymer volume fraction of 5 - 15%. Application of the rubber elasticity the-
ory for an independent calculation of $M_c$ and comparison to the $M_c$'s calculated via swelling experiments was done and the differences of the two values were discussed.

These hydrogels could not be used for practical applications unless reinforced in some way.

Reinforcement of PVA hydrogels by induction of partial crystallization was accomplished by a two stage drying process. The first stage was a dehydration state, where almost all the water was evaporated and crystallinity increased to 15-20%, while the polymer volume fraction after swelling reached 25-30%. The second stage was an annealing stage, which was mainly responsible for the reinforcement of the material. The swollen hydrogels after annealing had polymer volume fractions between 30 and 60% and crystallinity widely varying between 30 and 65%, depending on the temperature-time history of the specimen. The annealing temperatures were in the range of 90-200°C and the annealing periods of time were between 5 minutes and 2 hours. The crystallized hydrogels had initial moduli of up to 1500 psi (increasing almost linearly with increasing crystalline polymer weight percent in the gel), ultimate tensile strengths up to 2500 psi (also increasing with degree of crystallinity) and elongation at break as high as 600%. These materials showed very high tear resistance. In practical applications they could be used in water up to 40°C without significant alteration of their properties.
The crystallites acted as additional crosslinks redistributing the stress equally among them. The physical and mechanical properties were functions of the initial crosslinking density and they showed a maximum at a certain arithmetic value of $M_c$.

The materials are proposed to be used, after heparinization as potential nonthrombogenic biomaterials.
CHAPTER 11

RECOMMENDATIONS

1. The crystallized and uncry stal lized materials developed in this thesis need to have their dynamic mechanical properties tested, for purposes of detection of their behaviour under repeated deformations, as well as characterization, by another method, of their crosslinking density, since the storage modulus is related to the effective number of crosslinks. This can be the subject of an M.S. thesis.

2. An extensive study of the heparinization reaction on the developed hydrogels is the physical sequence of this thesis. The prospective investigator will face many interesting problems. Some of the questions to be answered will include:

   1). Is the rate of heparinization on crystalline and amorphous PVA the same? Is the heparinization uniform?

   11). If heparinization is done on the uncry stall ized hydrogel, does heparin diffuse in the network?

   111). If heparinization is done on the uncry stall ized hydrogel using a bifunctional crosslinking agent, as some investigators have proposed, what will the effect of secondary crosslinking be, on the final drying-cry stall ization process? Is the material still workable?

3. Investigation of the in vitro properties of heparinized radia-
tion-crosslinked, crystallized PVA hydrogels needs to be done. This will include WBCT tests on different substrates as well as a thorough quantitative study of the elution of heparin from the PVA surface, due to blood flow. Comparison of in vitro tests of these materials to similar tests of heparinized chemically-crosslinked hydrogels will give valuable information for further development of the system. A model device for testing the hematological properties of these hydrogels has to be designed, taking in consideration fluid mechanics features as well as technical requirements of production and casting of the PVA hydrogel. This work could fit within the scope of an Sc.D. thesis.

4. Extensive study of the in vivo properties of these hydrogels will be the last stage of this investigation.

5. It is the opinion of the author, that use of crosslinked copolymers of PVA with less number of hydroxyl groups can be a method of overcoming the problem of high secondary crosslinking during heparinization and brittleness after subsequent drying. An M.S. thesis could study model materials from copolymers of PVA with another polymer. Investigation of vinyl-pyrrolidone- Poly(vinyl alcohol) copolymers for biomedical applications has been of interest to the author and Merrill (302) and the prospective study should follow the results already obtained. Partial acetylation of PVA hydrogels could lead towards PVA-PVAc copolymers with less hydrogel groups than the original PVA.
APPENDIX A

ON THE THEORY OF CROSSLINKING

It is usually assumed that crosslinks are produced randomly by radiations and that the number of cross-links is proportional to the radiation dose. This proportionality is a reasonable assumption, as long as the number of crosslinks is sufficiently small in comparison to the total number of structural units so that the probability that radiation attacks the crosslinks is negligible (207).

A statistical theory of crosslinking was first given by Flory (106, 107, 108, 109). Charlesby's theory (58, 59, 60, 61) is preferable to this of Flory, because he solved by probability theorem the problem of crosslinked polymers, which have an initial arbitrary molecular size distribution. However, even this theory is not satisfactory because it needs different theories to consider solubility and molecular weights. The last theory proposed by Saito (321, 322, 323) starts with a basic equation for the change in molecular size distribution of polymers due to crosslinking.

Different molecular size distributions have been developed by different workers for characterization of dispersed molecular weight systems.

The random distribution (57) is governed by equation.

\[ w(p) = \frac{p}{u^2} \exp \left( - \frac{p}{u} \right) \]  

(A-1)
Other distributions used (326) are the general Schulz-Zimm distribution, the Tung distribution and the Wesslau distribution.

It is extended to the complicated problems of simultaneous crosslinking and degradation endlinking, copolymers, etc.

1. Crosslinking

The following assumptions have been made (321)

(i) Crosslinks are produced in random

(ii) Every structural units crosslinks with the same probability

(iii) The number of crosslinks is small in comparison to the total number of structural units

(iv) Intramolecular linkings are negligible.

Denoting \( p \) the degree of polymerization, \( X \) the total number of crosslinks, \( x \) the density of crosslinks and \( N \) the total number of structural units, then

\[
x = \frac{X}{N} \quad \text{(A-2)}
\]

The change in the weight fraction of molecules having \( p \) structural units, with respect to the density of crosslinking is given by the following equation (321).

\[
\frac{1}{p} \frac{\partial w(p, x)}{\partial x} = -2w(p, x) \int_0^\infty w(\ell, x) d\ell + \int_0^p w(\ell, x) w(p-\ell, x) d\ell \quad \text{(A-3)}
\]

The equation says that the rate of increase of the number of
molecules having \( p \) structural units equals the rate with which the molecules of \( p \) structural units crosslink and the rate with which the molecules of \( p \) structural units are produced by crosslinking of molecules of \( \lambda \) units with molecules of \( p - \lambda \) units.

2. Degradation

The following assumptions are made (321)

(i) All polymer molecules are linear

(ii) Every structural unit is fractured with equal probability

(iii) The average molecular weight is large.

(iv) The total number of main chain scissions is much smaller than the total number of structural units.

Denoting by \( y \) the density of main chain scissions (number of main chain scissions per structural unit), the basic equation which expresses the change in molecular size distribution is

\[
\frac{3w(p,y)}{\partial y} = -pw(p,y) + 2p \int_{\frac{p}{l}}^{\infty} \frac{w(l,y)}{l} \, dl \quad (A-4)
\]

The solution of this equation is (321)

\[
w(p,y) = [w(p,0) + py \int_{\frac{p}{l}}^{\infty} \frac{(2+y\lambda-yp)}{\lambda} w(l,0) \, dl] \exp \left( -py \right) \quad (A-5)
\]
Using the expression
\[ f_j(y) = \int_0^\infty p^{j-1} w(p,y) dp \]  \hspace{1cm} (A-6)

(This expression is called the jth moment of molecular size distribution. For a full definition of it see (321)), and the solution of the previous equation we can express the number-average degree of polymerization without crosslinking as

\[ \frac{\bar{P}_n}{\bar{P}} = \frac{1}{u} + y \]  \hspace{1cm} (A-7)

independent of any initial molecular size distribution.

The weight-average degree of polymerization is calculated as

\[ \bar{P}_w(y) = 2 \sum_{k=0}^{\infty} \frac{(-y)^k}{(k+2)!} f_{k+2}(0) \]  \hspace{1cm} (A-8)

which is independent of the initial molecular size distribution.

3. Molecular Weights

In the case of irradiation of polymers, where crosslinking and main chain scission occur simultaneously the number average degree of polymerization is given as:

\[ \frac{1}{\bar{P}_n(x,y)} = \frac{1}{u} + y - x \]  \hspace{1cm} (A-9)
where $u$ is the initial number average degree of polymerization. Thus

$$M_n = P_n(x,y)w$$  \hspace{1cm} (A-10)

where $w$ is the molecular weight of a structural unit. The weight average degree of polymerization is:

$$\frac{1}{P_w(x,y)} = \frac{1}{2u} + \frac{Y}{2} - 2x$$  \hspace{1cm} (A-11)

Since $x$ and $y$ are proportional to radiation dose, the plot of

$$\frac{1}{P_w(x,y)}$$

vs. radiation dose is linear.

4. Gelation

Gel point is called the instant when an incipient insoluble in any solvent part grows in the polymer substance, during irradiation.

The general crosslinking equation can be solved with a given initial value $w(p,0)$ and if we put:

$$f_n(x) = \int_0^\infty p^{n-1} w(p,x)dp$$  \hspace{1cm} (A-12)

Then the equation gives:

$$\frac{df_n}{dk} = -2f_{n+1} + \sum_{k=0}^{h} \binom{n}{k} f_{k+1} f_{n-k+1}$$  \hspace{1cm} (A-13)

For $n = 0$ and 2, we get:
\[
\frac{df_1}{dk} = -f_1^2 = -1 \quad \text{and} \quad \frac{df_2}{dk} = 2f_2^2
\]

\((f_1 = 1\ \text{according to definition}).\)

These two give

\[
f_2(x) = \frac{f_2(0)}{1 - 2xf_2(0)} \quad (A-14)
\]

Thus the density of crosslinking at the gel point is:

\[
x_g = \frac{1}{2f_2(0)} = \frac{1}{2P_w(0)} \quad (A-15)
\]

or

\[
x = \frac{N}{2P_w(0)} \quad (A-16)
\]

When crosslinking and degradation occur simultaneously then the density of crosslinks at the gel point is larger than when no degradation occurs.

In the case of a random initial distribution (Charlesby, 57)

with

\[
w(p) = \frac{p^a}{u^2} \exp\left(-\frac{p}{u}\right) \quad (A-17)
\]

then

\[
x_g = \frac{v}{4} + \frac{1}{2P_w(0)} \quad (A-18)
\]
Because of crosslinking in the post-gel-point structures the basic equation of crosslinking is rewritten as:

\[
\frac{1}{p} \frac{\partial w(p,x)}{\partial x} = -2w(p,x) + \int_{0}^{p} w(l,x)w(p-l,x)dl \tag{A-19}
\]

where \(w(p,x)\) is the weight fraction of molecules contained in the sol part and having \(p\) structural units.

A general solution of this equation, using the Laplace transform, is:

\[
f(\zeta,x) = F\{\zeta + 2x[1-f(\zeta,x)]\} \tag{A-20}
\]

Since

\[
1-g = \int_{0}^{\infty} w(p,x) \, dp = f(0,x) \tag{A-21}
\]

where \(g\) is the gel fraction we get

\[
s = 1-g = f(0,x) = F(0+2x[1-f(0,x)]) = F(2gx) \tag{A-22}
\]

Finally

\[
s = \int_{0}^{\infty} w(p,0) \, e^{-2p(1-s)x} \, dp \tag{A-23}
\]

For an initial random distribution, it gives

\[
s + \sqrt{s} = \frac{1}{xp(0)} \tag{A-24}
\]

which is the Charlesby-Pinner relationship (64).
In the case of simultaneous crosslinking and degradation.

\[ s + \sqrt{s} = \frac{v}{2x} + \frac{1}{\frac{x}{w}(0)} \]  

(A-25)

Thus a plot of \( s + \sqrt{s} \) vs. reciprocal of radiation dose gives a straight line. From the intersection of this line with the ordinate \( \left( \frac{v}{2x} \right) \), the ratio of crosslinks and main chain scissions is calculated \( \frac{v}{x} \). In many papers this ratio is also referred to as \( \frac{p}{q} \).

5. Molecular Weight Distribution

The change in molecular size distribution due to crosslinking has been calculated for different initial distributions.

In the case of polymers with initial random size distribution the weight fraction distribution of a crosslinked polymer is:

\[ w(p,x) = \frac{p}{u^2} e^{-\frac{(2x+1)p}{u^2}} \sum_{k=0}^{\infty} \frac{2^k}{(k+1)!(2k+1)!} \]

\[ (\frac{p}{u})^{3k}(ux)^k \]  

(A=26)

6. Intrinsic Viscosity

Intrinsic viscosity depends on the molecular weight of polymer \( M \), the number of branches \( b \) and the ratio \( g_b \) of the radius of gyration of molecules with \( b \) branches, as shown below

\[ [\eta] = K g_b^\gamma M^\alpha \]  

(A-27)
where \( g_b^v = \frac{R^2(b)}{R^2(Q)} \) and \( k, \alpha \) and \( v \) are constants.

For a polymer that undergoes both crosslinking and degradation the intrinsic viscosity is given as

\[
[n] = Kw^\alpha \sum_{b=0}^\infty g_b^v \int_0^\infty p^{\alpha} w_b(p, x, y) dp \tag{A-28}
\]

Katsuura (174) has calculated the intrinsic viscosity of a polymer with initial random molecular size distribution, and earlier in collaboration with Inokuti (161) they calculated it for an initial Schulz-Zimm molecular size distribution.

7. Effects of Impurities

Impurities or additives change the density of crosslinks, either promoting crosslinking or hindering it. The second case is applicable generally for impurities in PVA.

Denoting by \( k \) the ratio of the rate coefficient of a reaction between a radial and an impurity molecule to that of the crosslinking reaction and by \( m \) the ratio of the number of impurities to the total number of structural units, then the probability of crosslinking between a radial and a structural unit is \( \frac{1}{1+km} \). Also

\[
c_{x_l} = \frac{c_x}{1+km} \tag{A-29}
\]

where \( x_l \) is the true density and \( x \) the virtual density of crosslinks. Thus the equation becomes (325)
\[
\frac{\partial w(p,x)}{\partial x} = \frac{P}{1+km} \left[ -2w(p,x) + \int_0^P w(\ell,x) w(p-\ell,x) d\ell \right] \quad (A-30)
\]

Since
\[
dm = -\frac{km}{(1+km)} \, dx = -km \, dx_p \quad (A-31)
\]

we get
\[
x' = x_e + m(0)(1-e^{-kx_e}) \quad (A-32)
\]

This equation can be written as
\[
D = D_e + \frac{m(0)}{c} (1-e^{-kcD_e}) \quad (A-33)
\]

where \( c \) is a proportionality coefficient between dose and density of crosslinks. When the initial amount of impurity is known, the constants \( k \) and \( c \) are obtained easily and from the last of them the yield of crosslinks can be calculated as:

\[
G(X) = 0.96 \cdot \frac{c}{w} \quad (A-34)
\]

where \( w \) is the molecular weight of the structural unit (44 for PVA) and the unit of radiation is 1 Mgrad.

In the case of impurities promoting crosslinking (no such additive is known for PVA) analogous analysis has been done and the final expression is
\[
D_e = D + \frac{m(0)}{c} (1-e^{-kcD_e}) \quad (A-35)
\]
8. Endlinking Associated with Main Chain Scission

Charlesby (63) has showed that endlinking is a very probable reaction in irradiated polymers. Saito developed (322) an expression analogous to Eq. (A-3) of the Appendix, for the case of endlinking.

Finally for polymer substances having an initial random molecular size distribution, when crosslinking, endlinking and degradation occur simultaneously the number and weight average degrees of polymerization are given as:

\[ P_n(y,z) = \frac{u}{1+uy-uz} \]  \hspace{1cm} (A-36)

\[ P_w(y,z) = \frac{2u}{1+uy-2uz} \]  \hspace{1cm} (A-37)

where 2 refers to the density of endlinks.
APPENDIX B

STATISTICAL MECHANICS OF SWELLING OF NETWORK STRUCTURES

The theory of swelling of network structures was developed by Flory (104, 111).

When a three-dimensional polymer network is immersed in a solvent, it absorbs this solvent by a swelling process. Swelling continues till an equilibrium is reached, at which the diluting force and the elastic retractive force are in balance.

For this process, the free energy change $\Delta F$ can be considered as consisting of two components, the ordinary free energy of mixing $\Delta F_m$ and the elastic free energy $\Delta F_{e\lambda}$.

$$\Delta F = \Delta F_m + \Delta F_{e\lambda} \quad \text{(B-1)}$$

The free energy of mixing can be expressed in terms of the polymer molecules and their properties as:

$$\Delta F_m = kT(n_1 \ln n_1 + \chi n_1 n_2) \quad \text{(B-2)}$$

The elastic free energy $\Delta F_{e\lambda}$ can be calculated as (104)

$$\Delta F_{e\lambda} = \frac{k T v e}{2} (3a_s^2 - 3 - 4n a_s^3) \quad \text{(B-3)}$$

(See also Appendix D).
The chemical potential of the solvent in the swollen gel is given as:

\[ \mu_1 - \mu_0 = \frac{\partial F}{\partial n_1} + \left( \frac{\partial F}{\partial \alpha_s} \right) \left( \frac{\partial \alpha_s}{\partial n_1} \right) \]  

(B-4)

The term \( \frac{\partial \alpha_s}{\partial n_1} \) is evaluated from the definition of \( \alpha_s \) as:

\[ \alpha_s^{3} = \frac{1}{v_2} = \frac{v_o + n_1 v_1}{v_o} \]  

(B-5)

Thus

\[ \frac{\partial \alpha_s}{\partial n_1} \frac{v_1}{3 \alpha_s^2 v_o} \]  

(B-6)

Thus we finally obtain

\[ \mu_1 - \mu_0 = RT \left[ \ln(1-v_2) + v_2 + x_{1,2} v_2^2 + v_1 \left( \frac{v_e}{v_o} \right) \left( v_2 - \frac{v_o}{2} \right) \right] \]  

(B-7)

When swelling equilibrium has been reached then the chemical potential is zero. Thus we get

\[ -[\ln(1-v_2) + v_2 + x_{1,2} v_2^2] = v_1 \left( \frac{v_e}{v_o} \right) \left( v_2 - \frac{v_2, s}{2} \right) \]  

(B-8)

The entropy of swelling of a network and expressions for the swelling parameters derived therefrom, are derived here. Corrected relationships for the partial metal-free energy of dilution, swelling equilibrium and influence of deformation on swelling equilibrium are developed.
For this purpose let us consider the following cycle of a swelling process.

\[ \text{vchains} \xrightarrow{(1)} \text{unswollen network} \]

interlinking of chains

\[ \xrightarrow{(2)} +n \text{ solvent molecules} \]

\[ \xrightarrow{(4)} +n \text{ solvent molecules} \]

\[ \xrightarrow{(3)} \text{dissolved chains} \xrightarrow{\text{interlinking of chains}} \text{swollen network} \]

The entropy change associated with process (4), or \( \Delta S_s \), is:

\[ \Delta S_s = S_2 + S_3 - S_1 \]  \hspace{1cm} (B-9)

In the development and evaluation of the swelling entropy we will use a polyfunctionally connected network of functionality \( f \).

For the calculation of \( S_1 \) we make use of the Boltzmann relation. The probability that a chain-end is surrounded by \( f-1 \) other chain-ends, each in a volume element \( \Delta r \), can be written as:

\[ \left( \frac{2\pi\Delta r}{V} \right)^{f-1} \]  \hspace{1cm} (B-10)

The probability that a second such group is formed is:
Finally the probability for the $\frac{2v}{f}$ group to be formed is:

$$\begin{align*}
\left(\frac{2v}{f}\right)^{f-1} \left(\frac{v}{V}\right)^{2v(f-1)} \frac{\Delta t}{f}
\end{align*}$$

where $V$ is the volume of the system.

Introducing Stirlings approximation, we get

$$S_1 = \left[2kv \frac{(f-1)}{f}\right] \ln(\frac{2v\Delta t}{V})$$

The entropy change during process (2) is expressed as:

$$S_2 = -k[n \ln(1-v) + n v_2]$$

Process (3) includes dilation of the most probable chain displacement length distribution, followed by joining of the chain-ends to reproduce an equivalent network structure.

Thus $S_3$ includes the entropy during the process of joining the ends of chains precisely as in process (1) except that the volume $V$ is replaced by the swollen volume $V'$ where $V'/V = Q = \frac{1}{v_2,s}$. In the evaluation we have to include also the elastic entropy evaluated by Flory as
\[ S_{el} = -\frac{3}{2}kv(u_2^{-3/2} - 1) - kV \ln u_2 \]  \hspace{1cm} (B-15)

Thus
\[ S_3 = S_1' + S_{el} = [2kv \left(\frac{f-1}{f}\right) \ln(\frac{2v}{Vf}) + S_{el} ] \hspace{1cm} (B-16) \]

Substitution of the expressions for \( S_1, S_2, S_3 \) and rearrangement gives the following expression for \( \Delta S_s \):
\[ \Delta S_s = -k[n \ln(1-u_2) + \frac{3v}{2}(u_2^{-2/3} - 1) + \frac{2v}{f} \ln u_2] \hspace{1cm} (B-17) \]

Using this expression for the entropy of swelling and recalling (see also text in Chapter 5) that the heat of mixing is given by Van Laar's form,
\[ \Delta H_x = kT \chi n u_2 \]  \hspace{1cm} (B-18)

we can evaluate the modal free energy of dilution of an elastically undeformed (\( \alpha = 1 \)) network as:
\[ \Delta \overline{F} = RT[n \ln(1-u_2) + u_2(s(1 - \frac{2}{Z}) + u_2^{1/3}/Z + \chi u_2^2)] \hspace{1cm} (B-19) \]

The parameter \( Z \) introduced here is the ratio of the volume of a chain to the volume of a solvent molecule defined as:
\[ Z = \frac{n u_2}{v(1 - u_2)} = \frac{M_c}{\rho V_1} \]  \hspace{1cm} (B-20)

At equilibrium swelling \( \Delta \overline{F} = 0 \) giving
\[ Z = \frac{\frac{2u_2}{x} - u_2^{1/3}}{[\ln(1-u_2) + u_2 + xu_2^2]} \]  
\hspace{1cm} (B-21)

An easier way of calculating has been developed by series expansion giving:

\[ Z = \frac{M_c}{\rho V_1} = \frac{u_2^{1/3} (1-2u_2^{2/3}/x)}{u_2^2 [(1/2 - x) + u_2/3 + u_2^2/4 + \cdots]} \]  
\hspace{1cm} (B-22)

For large swelling volumes we can get

\[ u_2^{5/3} = \frac{1}{2} \frac{5/3}{Z(1-2x)} = \frac{2\rho V_1}{M_c (1-2x)} \]  
\hspace{1cm} (B-23)

The above derivation can be repeated in the case that the crosslinked were introduced in the presence of solvent; when \( u_{2,r} \) is not any more one. Then we can get:

\[ \Delta F_1 = RT [\ln(1-u_2) + u_2 (1 - \frac{2}{2x}) + (u_{2,r})^{2/3} (u_2)^{1/3} / Z + x u_2^2] \]  
\hspace{1cm} (B-24)
APPENDIX C

RUBBER ELASTICITY THEORY

In this appendix we are going to deal with the basic ideas and development of the Rubber elasticity theory as it stands today. The basic references used include Flory (104), Meares (250) and Treloar (430).

When a crosslinked network acting as an elastomer, is stretched, it reaches an equilibrium strain, whereas the stress remains constant. The rubber elasticity theory explains such equilibrium states treating them thermodynamically.

For the system of a sample of length L, where a linear force \( f \) is applied, the work done by it, is

\[
dW = - fdL + PdV
\]  \hspace{1cm} (C-1)

where \( dL \) is a small extension, and \( dV \) is the increase of volume.

Thus the first thermodynamic law can be written as:

\[
dE = TdS - fdL + PdV
\]  \hspace{1cm} (C-2)

The free energy is defined as

\[
A = E - TS
\]  \hspace{1cm} (C-3)
Differentiating and substituting we get

\[ dA = -PdV + f\dot{L} - SdT \]  

(C-4)

Finally

\[ f = -\left(\frac{\partial A}{\partial L}\right)_{T,V} \]  

(C-5)

The assumption of constant volume in isothermal deformations is a reasonable one, at least for amorphous polymers.

For the correlation of the applied force and the free energy we need a way of calculating the free energy from the characteristics of the network, to which the stress has been applied (67). For this purpose consider a \( x, y, z \) rectangular coordinate system and a subunit having its one end at the origin of the system and the other end at a distance \( r_i \), with coordinates \((x_i, y_i, z_i)\). After a deformation, the subunit will get a new position at which the end of it will be at a distance \( r \) and its new coordinates will be \((x, y, z)\). The deformations on the three axis are \( \delta x, \delta y, \delta z \) and they are defined as:

\[ \delta x = \frac{x}{x_i}, \quad \delta y = \frac{y}{y_i}, \quad \delta z = \frac{z}{z_i} \]  

(C-6)

Thus the network consists of \( \nu_e \) active subunits of \( r_i^2 \) mean square length in the unstrained state and \( r^2 \) mean square length in the deformed state and:

\[ \frac{1}{3} (\alpha_x^2 + \alpha_y^2 + \alpha_z^2) r_i^2 \]  

(C-7)
For an isothermal process $\Delta A = -W$ so that

$$W = -3\ v\ e^{\frac{KT}{r_0}}\ \int \frac{r_1^{1/2}}{r_0^{1/2}}\ dr = -\Delta A_{e\ell} \quad (C-8)$$

From (C-7) and (C-9) we get:

$$\Delta A_{e\ell} = \nu\ e^{\frac{KT}{2}}\ \frac{r_i^2}{r_0^2} (\frac{\alpha^2}{\alpha_x} + \alpha_y^2 + \alpha_z^2 - 3) \quad (C-9)$$

If we consider now an elongation at one direction then

$$\alpha = \frac{L}{L_0} = \alpha_x$$

and since $\alpha_x\alpha_y\alpha_z = 1$

we get

$$\alpha_y = \alpha_z = \alpha^{-1/2}$$

Thus

$$\Delta A_{e\ell} = \nu\ e^{\frac{KT}{2}}\ \frac{r_i^2}{r_0^2} (\alpha^2 - \frac{2}{\alpha} - 3) \quad (C-10)$$

From Eq. (C-5)

$$f = -\left(\frac{\partial A}{\partial L}\right)_{T,V} = -\frac{1}{L_0} \left(\frac{\partial A}{\partial \alpha}\right)_{T,V} \quad (C-11)$$

From Eq. (C-11) and (C-10) we get

$$f = \frac{\nu\ e^{\frac{KT}{L_0}}}{r_0^2} (\frac{r_i^2}{r_0^2})(\alpha - \frac{1}{\alpha}) \quad (C-12)$$

- 506 -
From (C-12) using also the equation $L_0 = \frac{v}{A_0}$ we get

$$\frac{f}{A_0} = \tau = RT \left( \frac{v}{v_0} \right) \frac{r_i^2}{r_0^2} \left( \alpha - \frac{1}{a^2} \right)$$  \hspace{1cm} (C-13)
APPENDIX D

EQUILIBRIUM SWELLING THEORY APPLIED TO HYDROGELS

Bray (42) developed an equation for calculating the molecular weight between crosslinks ($M_c$) in terms of easily measurable quantities. This equation differs to that developed by Flory (104) in that it takes into account that the crosslinks were introduced in the swollen state (irradiation of a PVA solution) and not in the solid state (irradiation of solid PVA and then swelling).

Let us denote by $v_{2,r}$ the relaxed volume fraction (volume fraction immediately after radiation) and by $v_{2,s}$ the swollen one (volume fraction after equilibrium swelling in water at a certain temperature).

The change of free energy is composed of a mixing and an elastic refractive term, so that

$$\Delta F = \Delta F_{\text{mix}} + \Delta F_{\text{el}}$$

(D-1)

The standard relationship for $\Delta F_{\text{mix}}$ of a polymer and solvent is (104)

$$\Delta F_{\text{mix}} = kT[n_1 \ln v_1 + n_2 \ln v_2 + \chi_{12} n_1 v_2]$$

(D-3)
where $n_1, n_2$ are the moles of solvent and polymer

$\nu_1, \nu_2$ are the corresponding volume fractions

$k$ is the Boltzmann constant

$T$ is the temperature

$\chi_1$ is the polymer-solvent interaction parameter

For a crosslinked system with no separate polymer chains $n_2 = 0$

$$\Delta F_{\text{mix}} = kT \left[ n_1 \ln \nu_1 + n_2 \ln \nu_2 + \chi_1 n_1 \nu_2 \right] \quad (D-3)$$

On the other hand $\Delta F_{el}$ is calculated as:

$$\Delta F_{el} = \Delta H_{el} - T \Delta S_{el} \quad (D-4)$$

with

$$\Delta H_{el} = 0.$$ 

Denoting as $\alpha = \left( \frac{V}{V_0} \right)^{1/3}$

The contribution to the deformation from a relaxed state (where

$\alpha x, \alpha y, \alpha z$ are the three-dimensional constituents of it) with $V_0$

being the volume in the relaxed state, we can express, using statistical

mechanics, the elastic contribution to entropy.

$$S_e = C - \frac{k \nu}{2} [\alpha x^2 + \alpha y^2 + \alpha z^2 - 3 - \ln(\alpha x \alpha y \alpha z)] \quad (D-5)$$

- 509 -
and

\[ \Delta S_{\text{el}} = S_{\text{swelled}} - S_{\text{relaxed}} \]  \hspace{1cm} (D-6)

Assuming that the material is isotropic

\[ \alpha = \alpha_x = \alpha_y = \alpha_z \]  \hspace{1cm} (D-7)

and recalling that at relaxed state \( \alpha = 1 \) and at swelled state \( \alpha = \frac{V}{V_r} \) we can get.

\[ \Delta S_{\text{el}} = -\frac{3k\nu}{2} \left[ \alpha_s^2 - 1 - \ln \alpha_s \right] \]  \hspace{1cm} (D-8)

or

\[ \Delta \mu_{\text{el}} = \frac{3kT\nu}{2} \left[ \alpha_s^2 - 1 - \ln \alpha_s \right] \]  \hspace{1cm} (D-9)

At the final equilibrium the chemical potential of the solvent in the gel equals the chemical potential of solvent in the bulk.

\[ \mu_{1} - \mu_{0} = 0 \]  \hspace{1cm} (D-10)

But

\[ \mu_{1} - \mu_{0} = \frac{\Delta F}{\partial n_1} = \frac{\Delta F_{\text{mix}}}{\partial n_1} + \frac{\Delta F_{\text{el}}}{\partial n_1} \]  \hspace{1cm} (D-11)

Thus finally

\[ \frac{\Delta F_{\text{mix}}}{\partial n_1} + \frac{\Delta F_{\text{el}}}{\partial n_1} = 0. \]  \hspace{1cm} (D-12)

- 510 -
From the previous derivation and Eq. (D-2)

\[
\frac{\partial \Delta F_{\text{mix}}}{\partial n_1} = kT[\ln(1-v_2,s) + v_2,s + \chi_1 v_2^2,s]
\]  
(D-13)

Also

\[
\frac{\partial \Delta F_{\text{el}}}{\partial n_1} = \frac{3kTv}{2} \left(2\alpha - \frac{1}{\alpha}\right) \frac{\partial \alpha}{\partial n_1}
\]  
(D-14)

Since

\[
\alpha^3 = \frac{V_s}{V} = \frac{V}{V} \left(\frac{p n_1 V}{V} \right) = \frac{V_{2,r}}{V_{2,s}}
\]  
(D-15)

\[
\frac{\partial \alpha}{\partial n_1} = \frac{V_{1,r}}{V_{1,s}} \cdot \frac{1}{3\alpha^2}
\]  
(D-16)

Substituting and rearranging

\[
\frac{\partial \Delta F_{\text{el}}}{\partial n_1} = kT \nu_e \frac{V_{1,r}}{V_{2,s}} \left[\frac{v_2^2}{V_{2,s}}\right]^{1/3} - \frac{1}{2} \left(\frac{v_2^2}{V_{2,s}}\right)
\]  
(D-17)

But

\[
\nu_e = \nu \left(1 - \frac{2M}{M_n}\right)
\]  
(D-18)

and

\[
\nu = \frac{V_p}{\bar{v} M_c}
\]  
(D-18)

where \(\bar{v}\) = specific volume of polymer.
Then finally

\[
\frac{\Delta F_{el}}{d n_1} = \frac{kT}{v} \left( \frac{1}{M_c} - \frac{2}{M_n} \right) u_{2,r} \left[ \frac{u_{2,s}}{u_{2,r}} \right]^{1/3} - \frac{1}{2} \left( \frac{u_{2,s}}{u_{2,r}} \right)
\]  

(D-20)

From Eqs. (D-12), (D-13), (D-20) we get

\[
kT[\ln(1-u_{2,s})+u_{2,s} + \chi_1 u_{2,s}^2] + \frac{kT}{v} \left( \frac{1}{M_c} - \frac{2}{M_n} \right) u_{2,r}
\]

\[
\left[ \frac{u_{2,s}}{u_{2,r}} \right]^{1/3} - \frac{1}{2} \left( \frac{u_{2,s}}{u_{2,r}} \right) = 0
\]  

(D-21)

Finally

\[
\frac{1}{M_c} = \frac{2}{M_n} - \frac{\frac{u_{2,r}}{v_1} \left[ \ln(1-u_{2,s}) + u_{2,s} + \chi_1 u_{2,s}^2 \right]^{1/3}}{u_{2,r} \left( \frac{u_{2,s}}{u_{2,r}} \right) - \frac{1}{2} \left( \frac{u_{2,s}}{u_{2,r}} \right)}
\]  

(D-22)

Analogous expression has been derived by Flory (104) but he uses

\[u_{2,r} = 1, \text{ i.e., that crosslinks are introduced in the solid state.}\]
APPENDIX E

RUBBER ELASTICITY THEORY MODIFIED FOR HYDROGELS

Silliman (394) has developed an equation for the calculation of the molecular weight between crosslinks \( M_c \), using the Rubber elasticity theory as developed by Flory (104) but taking in account that the crosslinks were introduced in the gel phase (starting from a solution).

From the derivation of the rubber elasticity theory, the change of the Helmholtz free energy of a network is given as:

\[
\Delta A_{el} = \frac{V e^{kT}}{2} \left( \frac{r_1^2}{r_0^2} \right) (\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) \quad (E-1)
\]

where \( \alpha_x, \alpha_y, \alpha_z \) represent the three dimensional changes due to combination of swelling and deformation.

Thus

\[
\alpha_x \alpha_y \alpha_z = \frac{V_s}{V_i} \quad (E-2)
\]

The network formed at volume \( V_i \) and volume fraction polymer \( \nu_{2,i} \) is subsequently swollen by the diluent to a volume \( V_s \). For the deformation due to elongation the constant volume assumption is used. Thus
\[ \frac{u_{2,s}}{u_{2,i}} = \frac{V_i}{V_s} \]  \hspace{1cm} (E-3)

and \( V_s \) = constant.

Define the swelling ratio

\[ Q = \frac{V_s}{V_i} \]  \hspace{1cm} (E-4)

Then

\[ \alpha_x \alpha_y \alpha_z = Q \]  \hspace{1cm} (E-5)

For a simple elongation in the direction of the \( x \)-axis we can write

\[ \alpha = \frac{L_{f,s}}{L_{o,s}} \]  \hspace{1cm} (E-6)

For isotropic swelling:

\[ \frac{L_{o,s}}{L_o} = \left( \frac{V_s}{V_i} \right)^{1/3} = Q^{1/3} \]  \hspace{1cm} (E-7)

Then

\[ \alpha_x = \alpha Q^{1/3} \]  \hspace{1cm} (E-8)

and

\[ \alpha_y = \alpha_z = \frac{Q^{1/3}}{\alpha^{1/2}} \]  \hspace{1cm} (E-9)

Substituting (E-8) and (E-9) in (E-9) in (E-1) we get:

\[ \Delta_A_{el} = \frac{kT \nu e Q^{2/3}}{2} \left( \frac{r_1^2}{r_0^2} \right) \left( \alpha^2 + \frac{2}{\alpha} - \frac{3}{Q^{2/3}} \right) \]  \hspace{1cm} (E-10)

- 514 -
The elastic retractive force for the swollen network is

\[ f = \frac{1}{L_{o,s}} \left( \frac{\partial A}{\partial a} \right)_{T,V} \quad \text{(E-11)} \]

From (E-10) and (E-11) we get:

\[ f = \frac{kT \nu Q^{2/3}}{L_{o,s}} \left( \frac{r_i^2}{r_o^2} \right) (a - \frac{1}{a^2}) \quad \text{(E-12)} \]

where \( Q \) is constant.

Since

\[ L_{o,s} = \frac{V_s}{A_{o,s}} \]

and

\[ \tau = \frac{f}{A_{o,s}} \]

we get

\[ \tau = kT Q^{2/3} \left( \frac{\nu}{V_s} \right) \left( \frac{r_i^2}{r_o^2} \right) (a - \frac{1}{a^2}). \quad \text{(E-13)} \]
APPENDIX F

FLORY'S THEORY OF CRYSTALLIZATION OF

HIGH POLYMERS IN THE PRESENCE OF DILUENTS

Flory's (110) theory of crystallization of polymers is briefly described here. For a complete analysis the reader should refer to the original paper. Flory uses the following definitions.

\[ d = \text{total number of structural units in a polymer molecule} \]
\[ z = \text{number of segments per structural unit} \]
\[ d' = zd = \text{number of segments per molecule} \]
\[ z_s = \text{ratio of molar volume of solvent to the volume of a segment} \]
\[ n = \text{number of solvent molecules} \]
\[ n' = z_s n = \text{number of sequences occupied by solvent molecules} \]
\[ N = \text{number of polymer molecules} \]
\[ v = \text{number of crystallites} \]
\[ \sigma = \text{number of chains "participating" in the formation of a crystallite.} \]
\[ m = v\sigma = \text{total number of crystalline chains} \]
\[ \zeta = \text{average length of crystallite in number of units} \]
\( \zeta' = z \zeta = \text{average length of crystallite in number of segments} \)

\( m_\zeta = \text{total number of crystalline units} \)

\[
\upsilon_1 = \frac{n'}{n'+d'N} = \text{volume fraction of solvent} \quad \text{(F-1)}
\]

\[
\upsilon_2 = \frac{d'N}{n'+d'N} = \text{volume fraction of polymer} \quad \text{(F-2)}
\]

\[
x = 1- \frac{dN - \zeta m}{dN} = \text{degree of crystallinity} \quad \text{(F-3)}
\]

\( \gamma = \text{coordination number of a pseudo-lattice attributed to a liquid polymer} \)

The entropy difference between the totally liquid solution and the semicrystalline mixture, this difference being also referred as the entropy of fusion \( \Delta S^{\text{f}} \) is:

\[
\Delta S^\text{f} \zeta m k z \ln \left( \frac{\gamma - 1}{e} \right) - k((n+N)\ln\left[\frac{(n'+d'N-\zeta m)}{(n'+d'N)}\right] + m \ln\left[\frac{\ln(\gamma - 1)d'N}{z e (n'+d'N)}\right] + m \ln \left( \frac{d-\zeta+1}{d} \right) \quad \text{(F-4)}
\]

Then he denotes

\[
S_u = k z \ln \left( \frac{\gamma - 1}{e} \right) \quad \text{(F-5)}
\]

and

\[
D = \frac{(\gamma - 1)}{z e} \quad \text{(F-6)}
\]
By redefinition of \( n, N, m \) and \( s_u \) to represent molar quantities the above relation can be written as:

\[
\frac{\Delta S_f}{dN} = x s_u - R \left( \frac{z}{z_S} \right) \left( \frac{1-u_2}{v_2} \right) + \frac{1}{d} \ln(1-xu_2) - \frac{X}{\zeta} \cdot [\ln(u_2D) + \ln(d - \zeta + 1)] \quad (F-7)
\]

The free energy change accompanying the fusion process is given by

\[
\Delta F_f = \Delta H_f - T\Delta S_f \quad (F-8)
\]

The heat of fusion consists of the heat of fusion referring to the melting of the crystallites and the heat of mixing. Expression of it and substitution gives

\[
\frac{\Delta F_f}{dN} = x(h_u - Ts_u) + RT \left( \frac{z}{z_S} \right) \left( \frac{1-u_2}{v_2} \right) + \frac{1}{d} \ln(1-xu_2) + \frac{X}{\zeta} \cdot [\ln(u_2D) + \ln(d - \zeta + 1)]
\]

\[
\quad + \frac{\chi(1-u_2)^2x}{[1-u_2+u_2(1-x)]^2} \quad (F-9)
\]

where \( \chi \) is the chi factor and

\[
D = \frac{(\gamma - 1)}{z e^{1 + h_e/RT}} \quad (F-10)
\]

The equilibrium crystallite length \( \zeta_e \) can be calculated by maximizing

\[
\Delta F_f
\]

\[
- u_2D = \frac{\zeta_e}{(d - \zeta_e + 1)} + \ln \frac{(d - \zeta_e + 1)}{d} \quad (F-11)
\]

- 518 -
or

\[ -v_2D = \frac{1}{d} + \frac{1}{2} \left( \frac{\xi c}{d} \right)^2 + \frac{2}{3} \left( \frac{\xi c}{d} \right)^3 + \cdots \]  

(F-12)

For heterogeneous polymers with most probable distribution, the conclusion is that the first crystals formed from the heterogeneous polymer will be extremely long at equilibrium.

The equilibrium degree of crystallinity can be calculated again by differentiation

\[ \frac{1}{T_m^0} - \frac{1}{T_m} = \left( \frac{R}{h_u} \right) \left\{ \frac{z}{s} \frac{(1-v_2)}{1-xv_2} + \frac{v_2}{d} \frac{1}{d-\xi+1} - \chi \left( \frac{1-v_2}{1-xv_2} \right) \right\} + \]

\[ + \frac{1}{h_u} \frac{\xi c}{x dN} \left( \frac{\partial F}{\partial \xi} \right) (1-x) \]  

(F-13)

where

\[ \frac{h_u}{s_u} = \frac{T_m^0}{T_m} \]
APPENDIX G

SAMPLE CALCULATION OF TURBIDIMETRIC PROPERTIES OF PVA SOLUTIONS

Calculations are presented for a sample undergone freezing process at -20°C for 105 minutes and then thawed at 30°C for long periods of time. The initial PVA solution had concentration of 5% by weight, and the spectrophotometric-turbidimetric studies were done with visible light of 5000-7000 Å.

RAW DATA

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<th>λ = 5000 A</th>
<th></th>
<th>λ = 6000 A</th>
<th></th>
<th>λ = 7000 A</th>
</tr>
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<tbody>
<tr>
<td>t</td>
<td>D</td>
<td>t</td>
<td>D</td>
<td>t</td>
<td>D</td>
</tr>
<tr>
<td>1 h 08'</td>
<td>0.240</td>
<td>1 h 06'</td>
<td>0.198</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1 h 47'</td>
<td>0.158</td>
<td>1 h 51'</td>
<td>0.102</td>
<td>1 h 56'</td>
<td>0.076</td>
</tr>
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<td>2 h 16'</td>
<td>0.146</td>
<td>2 h 17'</td>
<td>0.100</td>
<td>2 h 19'</td>
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<td>0.167</td>
<td>3 h 08'</td>
<td>0.108</td>
<td>3 h 12'</td>
<td>0.078</td>
</tr>
<tr>
<td>11 h 00'</td>
<td>0.177</td>
<td>10 h 58'</td>
<td>0.135</td>
<td>10 h 53'</td>
<td>0.107</td>
</tr>
</tbody>
</table>

D = Optical Density = - \log T  \quad T = Transmittance
\lambda = Wavelength  \quad t = Time of thawing

CALCULATIONS

Plot log D versus time (See Fig. G-1) Get values of log D at t = 1,2,3,5,7,10 hrs, so that comparison can be made.
<table>
<thead>
<tr>
<th>Time (Hrs.)</th>
<th>$\lambda$=5000 Å</th>
<th>$\lambda$=6000 Å</th>
<th>$\lambda$=7000 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>-0.64</td>
<td>-0.73</td>
</tr>
<tr>
<td>2</td>
<td>-0.82</td>
<td>-0.99</td>
<td>-1.12</td>
</tr>
<tr>
<td>3</td>
<td>-0.78</td>
<td>-0.98</td>
<td>-1.10</td>
</tr>
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<td>5</td>
<td>-0.76</td>
<td>-0.99</td>
<td>-1.06</td>
</tr>
<tr>
<td>7</td>
<td>-0.76</td>
<td>-0.91</td>
<td>-1.02</td>
</tr>
<tr>
<td>10</td>
<td>-0.745</td>
<td>-0.87</td>
<td>-0.97</td>
</tr>
</tbody>
</table>

| $\log \lambda$=0.700 | $\log \lambda$=0.779 | $\log \lambda$=0.846 |

Then, log D is plotted versus $\log \lambda$ and the slopes $n$ are calculated. Using these slopes from (141) the corresponding values of $\alpha$ are calculated, for $m = 1.12$ (191). Average radius $r_w^2 = \frac{\alpha \lambda}{2\pi}$.

$\lambda = 5500$ Å.

Processed Data

<table>
<thead>
<tr>
<th>Time (Hrs.)</th>
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<th>$\alpha$</th>
<th>$r_w(\mu)$</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
<td>3</td>
<td>-2.47</td>
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</tr>
<tr>
<td>5</td>
<td>-2.10</td>
<td>25.4</td>
<td>2.22</td>
</tr>
<tr>
<td>7</td>
<td>-1.81</td>
<td>24.7</td>
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<tr>
<td>10</td>
<td>-1.55</td>
<td>22.8</td>
<td>1.99</td>
</tr>
</tbody>
</table>
Fig. G-1: Effect of the thawing time on the optical density

Fig. G-2: LogD versus logλ for different thawing times
APPENDIX H

SAMPLE CALCULATION OF \( M_c \) VIA SWELLING METHODS

Calculations are presented for sample Code Number 10003, tested after equilibrium swelling at 30°C. Radiation conditions: Van de Graaff generator, 10%, 0°C, 3 Mgrads.

Raw Data

Temperature 30°C. Water density 0.996 gr/cm\(^3\).

\[ V_R = \text{Volume of relaxed gel} = \frac{W_a - W_w}{\rho_w} = 11.575 \text{ cm}^3 \]

\[ V_s = \text{Volume of swollen gel} = \frac{W_a - W_w}{\rho_w} = 31.489 \text{ cm}^3 \]

\[ V_p = \text{Volume of polymer} = \frac{W_p}{\rho_{PVA}} = \frac{W_p}{1.269} = 2.072 \text{ cm}^3 \]

\[ M_n = 88,880 \]

\( \chi \) = 0.494 at 30°C and \( v_2 = 0 \div 0.15 \)

\( \nu \) = specific volume of polymer = 0.788 cm\(^3\)/g m

\( V_1 \) = molar volume of solvent = 18 cm\(^3\)/mole

Calculations

\( v_{2,r} \) = volume fraction of polymer in relaxed gel = \( \frac{V_p}{V_R} = \frac{2.072}{11.575} = 0.179 \)

\( v_{2,s} \) = volume fraction of polymer in swollen gel = \( \frac{V_p}{V_s} = \frac{2.072}{31.489} = 0.0658 \)

swelling ratio \( q = \frac{V_s}{V_R} = \frac{v_{2,r}}{v_{2,s}} = 2.720 \)

- 523 -
\[
\frac{1}{M_c} = 2 \frac{v}{M_n} \left[ \frac{v}{1 - v} \ln(1 - v) + v \chi v^2 \right]^{-1/3} \\
\{u_2, r \left[ \frac{u_2}{v_2} \right] - \frac{1}{2} \left( \frac{u_2}{v_2} \right)^2 \}
\]

\[M_c = 7650\]

\[\rho = \text{Crosslinking Density} = \frac{M_n}{M_c} = \frac{88,880}{7,650} = 11.62 \text{ crosslinks per polymer chain number of monomer units} = \frac{c}{M} = \frac{7650}{44} = 174 \text{ units between two crosslinks.}\]
APPENDIX I

SAMPLE CALCULATION OF \( M_c \) VIA TENSILE-TEST DATA

Calculations are presented for sample Code Number 10003, tested after equilibrium swelling at 30°C. Radiation Conditions: Van de Graaff generator, 10%, 0°C, 3 Mgrads.

**Raw Data**

Temperature 30°C

Other preliminary data: See Appendix H

Thickness = 0.0840 in

Area = \( A_o \) = 0.0210 in\(^2\)

\( L_o \) = initial gage length = 3.90 cm.

**Data Readings**

<table>
<thead>
<tr>
<th>Datum No</th>
<th>Load (gms)</th>
<th>( \Delta L )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>0.60</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>1.00</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>1.45</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>1.95</td>
</tr>
</tbody>
</table>

**Calculations**

(a) Stress \( \tau \)

\[
\tau = \frac{\text{Load}}{A_o}
\]

(b) Elongation at break

\[
\epsilon' = \frac{\Delta L \text{ at break}}{L_o}
\]
(c) Elongation \( \alpha \)

\[
\alpha = \frac{l}{l_0} = \frac{\Delta l + l_0}{l_0} = 1 + \varepsilon
\]

Processed Data

<table>
<thead>
<tr>
<th>Datum No.</th>
<th>( \tau ) (psi)</th>
<th>( \alpha )</th>
<th>( \alpha - \frac{1}{\alpha^2} )</th>
<th>( \alpha - 1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.048</td>
<td>1.155</td>
<td>0.405</td>
<td>0.155</td>
</tr>
<tr>
<td>2</td>
<td>1.571</td>
<td>1.256</td>
<td>0.622</td>
<td>0.256</td>
</tr>
<tr>
<td>3</td>
<td>2.095</td>
<td>1.364</td>
<td>0.827</td>
<td>0.364</td>
</tr>
<tr>
<td>4</td>
<td>2.619</td>
<td>1.508</td>
<td>1.068</td>
<td>0.508</td>
</tr>
</tbody>
</table>

Calculations

Stress \( \tau \)

\[
\tau = \frac{RT \cdot C_{2,i}}{M_c} \left( \frac{1}{Q^{1/3}} \right) (1 - \frac{2M_c}{M_n}) (\alpha - \frac{1}{\alpha^2})
\]

\( Q = \) Swelling ratio = 2.720 \( Q^{-1/3} = 0.7164 \)

\( C_{2,i} = \frac{\nu_{2,i}}{\frac{\varepsilon}{\nu}} \) \( \frac{gR}{cm^3} = \frac{\nu_{2,i}R}{\frac{\varepsilon}{0.788}} = \frac{0.179}{0.788} = 0.227 \)

\( T = 303 \text{ °K} = 30\text{°C} \)

\( R = 82 \text{ atm cm}^3 \text{ mol}^{-1} \text{ °K}^{-1} = 1205.07 \text{ psi cm}^3 \text{ mol}^{-1} \text{ °K}^{-1} \)

Term \( R \cdot C_{2,i} \cdot Q^{-1/3} = 136.3 \)
### Processed Data

<table>
<thead>
<tr>
<th>Data No.</th>
<th>( \tau_{\text{obs}} ) (psi)</th>
<th>( \tau_{\text{calc}} ) (psi)</th>
<th>( \tau_{\text{obs}} / \tau_{\text{calc}} )</th>
<th>( \tau_{\text{obs}} / a - \frac{1}{a^2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.048</td>
<td>2.608</td>
<td>0.402</td>
<td>2.59</td>
</tr>
<tr>
<td>2</td>
<td>1.571</td>
<td>4.006</td>
<td>0.392</td>
<td>2.53</td>
</tr>
<tr>
<td>3</td>
<td>2.095</td>
<td>5.326</td>
<td>0.393</td>
<td>2.53</td>
</tr>
<tr>
<td>4</td>
<td>2.619</td>
<td>6.278</td>
<td>0.381</td>
<td>2.45</td>
</tr>
</tbody>
</table>

In a plot of \( \tau \) versus \( a - \frac{1}{a^2} \), the data points can fit to a straight line with slope \( \tau_{\text{obs}} / a - \frac{1}{a^2} = 2.55 \pm 0.04 \)

Back calculation gives \( M_c = 15,297 \).

\[
\frac{M_c \text{ (tensile)}}{M_c \text{ (swelling)}} = \frac{15,297}{7,650} = 2.00
\]
APPENDIX J

A NOTE ON THE DRYING CONDITIONS OF PVA HYDROGELS

The temperature of a PVA hydrogel being dried in an oven under well characterized drying conditions, is not the same with the temperature of the oven, but only after a long period of time. For determination of the variation of the temperature of a hydrogel as a function of time of drying, thermocouples were introduced in PVA hydrogels being dried and the variation of the temperature was recorded. (Figures J-1 and J-2).
Fig. J-1: Variation of the temperature of a hydrogel dried in an oven at 90°C.
Fig. J-2: Variation of the temperature of a hydrogel dried in an oven at 120°C
APPENDIX K

SAMPLE CALCULATION OF CRYSTALLINITY VIA DENSITY METHODS

Calculations are presented for sample Code Number 15003/90-1/2, tested after equilibrium swelling at 30°C:

Annealing Conditions 90°C 30 minutes. Crosslinking density

\[ \rho = \frac{M_n}{M_c} = 10.56, \quad M_c = 8420. \]

Raw Data

Temperature 30°C  Water density = 0.996 gr/cm³

\[ W_a = \text{Weight of swollen PVA in air} = 0.3907 \text{ gm.} \]

\[ W_w = \text{Weight of swollen PVA in water} = 0.0382 \text{ gm.} \]

\[ W_p = \text{Weight of PVA dried at 100°C for 48 hours under vacuum} = 0.1668 \text{ gm.} \]

Calculations

(a) Hydrogel density, \( \rho_n \)

\[ \rho_n = \frac{W_a}{W_a - W_w} \rho_w = \frac{0.3907}{0.3907 - 0.0382} \cdot 0.996 = 1.1039 \text{ gr/cm}^3 \]

(b) Swelling ratio \( q(\text{weight}) \)

\[ q = \frac{\text{weight of hydrogel}}{\text{weight of PVA}} = \frac{W_a}{W_p} = \frac{0.3907}{0.1668} = 2.3423 \]

(c) Polymer weight percent in hydrogel

\[ \text{PVA \%} = \frac{W_p}{W_a} = \frac{0.1668}{0.3907} = \frac{1}{q} = 0.4269 = 42.69\% \]

- 531 -
(d) Water weight percent in hydrogel

\[ \text{H}_2\text{O} \% = 1 - \text{(PVA\%)} = 1 - 0.4269 = 0.5731 = 57.31\% \]

(e) Crystallinity \( X \)

\[ X = 18.87324 - 23.95014 + \frac{1 - \text{(H}_2\text{O})}{\frac{\rho}{n} - 0.996} \]

\[ X = 0.3325 \text{ or } 33.25\%. \]
APPENDIX L

DIFFERENTIAL SCANNING CALORIMETRY CHARACTERISTICS

Experiments of the effect of scanning speed of DSC-1 and the repetition of cycles of heating-cooling process are reported here.

1. **Effect of scanning speed**

The effects of scanning speeds of 5-80 °C/min on the shift of the melting peak of PVA (peak B in typical thermogram Figure 8-6) are reported here of crosslinked, crystallized samples (\(M_c = 8420, x = 47.63\%, PVA = 48.52\%\) wt.)

<table>
<thead>
<tr>
<th>Scanning speed (°C/min)</th>
<th>(T_m) °C(heating)</th>
<th>(T'_m) °C(cooling)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>213</td>
<td>190</td>
</tr>
<tr>
<td>10</td>
<td>211</td>
<td>185</td>
</tr>
<tr>
<td>20</td>
<td>198</td>
<td>179</td>
</tr>
<tr>
<td>40</td>
<td>192</td>
<td>178.5</td>
</tr>
<tr>
<td>80</td>
<td>192</td>
<td>170.3</td>
</tr>
</tbody>
</table>

\(T'_m\) temperatures are always 20-25°C lower than \(T_m\) because of hysteresis phenomena during cooling.

The scanning speed chosen for all the experiments is 5°C/min.
2. **Effect of repeated heating-cooling cycles**

The effect of heating-cooling cycles on the $T_m$ and $T'_m$ of crosslinked, crystallized samples ($M_c = 8420$, $\alpha = 47.63\%$, $\text{PVA} = 48.52\%$ wt.) is reported here. The scanning speed is $20^\circ\text{C/minute}$. The temperature was raised up to $250^\circ\text{C}$ and then it was lowered using the same scanning speed.

<table>
<thead>
<tr>
<th>Heating-cooling cycles</th>
<th>$T_m^\circ\text{C(heating)}$</th>
<th>$T'_m^\circ\text{C(cooling)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>197.2</td>
<td>186</td>
</tr>
<tr>
<td>2</td>
<td>197.3</td>
<td>186.2</td>
</tr>
<tr>
<td>3</td>
<td>196.2</td>
<td>186.5</td>
</tr>
<tr>
<td>4</td>
<td>195</td>
<td>188.3</td>
</tr>
</tbody>
</table>

$T_m$ and $T'_m$ do not change significantly with these repeated cycles.
APPENDIX M

SAMPLE CALCULATION OF CRYSTALLINITY FROM DSC TESTS

Calculations are presented for samples Code Numbers 100010, tested after equilibrium swelling at 30°C: Crosslinking density

\[ \rho = \frac{M_c}{M^n} = 59.45, \quad M_c = 1495. \]

Annealing Conditions (T°C, time, hrs.)

\[ 90, \quad 1/2 - 105, \quad 1 - 120, \quad 1/2 - 135, \quad 1 1/2 \]

RAW DATA

Scanning Speed 5°C/min Range 8

Chart Speed 12 in/hr

\[ T_m^o = 208.6°C = 481.6^oK \]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ann. Conditions</th>
<th>PVA %</th>
<th>Weight (mg)</th>
<th>T_m (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>90 1/2</td>
<td>20.77</td>
<td>8.0</td>
<td>47.5</td>
</tr>
<tr>
<td>2</td>
<td>105 1</td>
<td>24.73</td>
<td>4.9</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>120 1/2</td>
<td>31.23</td>
<td>12.2</td>
<td>42</td>
</tr>
<tr>
<td>4</td>
<td>135 1 1/2</td>
<td>45.67</td>
<td>7.3</td>
<td>48</td>
</tr>
</tbody>
</table>

CALCULATIONS

\[ \left( \frac{1}{T_m} - \frac{1}{T_m^o} \right) / \nu_1 = \frac{R \nu u}{\Delta H \nu_1} \left( 1 - \frac{B V \nu_1}{RT_m} \right) \]
\[ V_u = 0.788 \text{ cm}^3/\text{gr} = 34.67 \text{ cm}^3/\text{mole}. \]

\[ V_1 = 18 \text{ cm}^3/\text{mole} \]

\[ R = 1.98 \text{ cals/mol \degree K} \]

Data are plotted as \( \frac{\frac{1}{T_m} - \frac{1}{T_0}}{\frac{1}{T_m}} \times 10^3/\sqrt{u} \) versus \( \frac{\frac{1}{T_m}}{10^3} \) and the intercept and the slope are calculated:

**Processed Data**

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \frac{\frac{1}{T_m} - \frac{1}{T_0}}{\frac{1}{T_m}} \times 10^3/\sqrt{u} )</th>
<th>( \frac{\frac{1}{T_m}}{10^3} \times 10^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.260</td>
<td>2.586</td>
</tr>
<tr>
<td>2</td>
<td>1.409</td>
<td>2.538</td>
</tr>
<tr>
<td>3</td>
<td>1.492</td>
<td>2.338</td>
</tr>
<tr>
<td>4</td>
<td>1.727</td>
<td>1.874</td>
</tr>
</tbody>
</table>

\[ \Delta H_u = \frac{3.852}{\text{intercept}} \text{ (cal/mole)} \]

\[ B = - \frac{\text{slope}}{\text{intercept}} \times \frac{1}{g} \text{ (cal/cm}^3) \]

From plot: intercept = 2.64 slope = - 0.510. Thus

\[ \Delta H_u = 1459.3 \text{ cals/mole} \approx 1.46 \text{ k cal/mole} \]

\[ B = 21.46 \text{ cals/cm}^3 \]
$\Delta H^*$ is calculated for the individual samples from the thermogram.

Degree of crystallinity $x = \frac{\Delta H^*}{\Delta H_u}$. 
APPENDIX N

SAMPLE CALCULATION OF $\chi$ FACTOR OF A PVA SOLUTION

Calculations are presented for sample code number 15003, tested after swelling equilibrium at 5, 10, 20, 30, 40, 50, 60, 70, 80 and 90°C: Crosslinking density $\rho = \frac{M}{M_c}$, $M_c = 8420$

RAW DATA

<table>
<thead>
<tr>
<th>Datum No.</th>
<th>Temperature (°C)</th>
<th>Weight % PVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>6.00</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>6.25</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>6.75</td>
</tr>
<tr>
<td>4</td>
<td>30</td>
<td>7.75</td>
</tr>
<tr>
<td>5</td>
<td>40</td>
<td>8.20</td>
</tr>
<tr>
<td>6</td>
<td>45</td>
<td>8.45</td>
</tr>
<tr>
<td>7</td>
<td>50</td>
<td>8.80</td>
</tr>
<tr>
<td>8</td>
<td>60</td>
<td>9.50</td>
</tr>
<tr>
<td>9</td>
<td>70</td>
<td>10.15</td>
</tr>
<tr>
<td>10</td>
<td>75</td>
<td>10.90</td>
</tr>
<tr>
<td>11</td>
<td>80</td>
<td>11.00</td>
</tr>
<tr>
<td>12</td>
<td>90</td>
<td>11.50</td>
</tr>
</tbody>
</table>
CALCULATIONS:

Volume fraction \( u_{2,s} = \frac{P/1.269}{P/1.269 + (1-\rho)/\rho_w} \)

where \( \rho = \text{weight \% PVA} \) and \( \rho_w = \text{density of water at } t = T \)

Calculation of \( \chi \) factor from following equation:

\[
- \left[ \ln (1-u_{2,s}) + u_{2,s} + \chi \frac{u_{2,s}}{\bar{v}} \right] = \frac{V_1}{\bar{M}_c} \left( 1 - \frac{2M_c}{M_n} \right) u_{2,r} \left[ \frac{u_{2,s}}{u_{2,r}} \right]^{1/3}
- \frac{1}{2} \left( \frac{u_{2,s}}{u_{2,r}} \right)
\]

where \( M_c = 8420 \) \( \quad \bar{v} = 0.788 \text{ cm}^3/\text{gr} \)

\( V_1 = 18 \text{ cm}^3/\text{mole} \) \( \quad u_{2,r} = 0.1273 \)
## PROCESSED DATA

<table>
<thead>
<tr>
<th>Datum No.</th>
<th>Temperature (°C)</th>
<th>( p_w )</th>
<th>( u_{2,s} )</th>
<th>( X )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>0.99999</td>
<td>0.0479</td>
<td>0.4514</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>0.99973</td>
<td>0.0499</td>
<td>0.4570</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>0.99823</td>
<td>0.0539</td>
<td>0.4633</td>
</tr>
<tr>
<td>4</td>
<td>30</td>
<td>0.99568</td>
<td>0.0618</td>
<td>0.4818</td>
</tr>
<tr>
<td>5</td>
<td>40</td>
<td>0.99225</td>
<td>0.0653</td>
<td>0.4872</td>
</tr>
<tr>
<td>6</td>
<td>45</td>
<td>0.99025</td>
<td>0.0672</td>
<td>0.4898</td>
</tr>
<tr>
<td>7</td>
<td>50</td>
<td>0.98807</td>
<td>0.0699</td>
<td>0.4934</td>
</tr>
<tr>
<td>8</td>
<td>60</td>
<td>0.98324</td>
<td>0.0752</td>
<td>0.4997</td>
</tr>
<tr>
<td>9</td>
<td>70</td>
<td>0.97781</td>
<td>0.0801</td>
<td>0.5047</td>
</tr>
<tr>
<td>10</td>
<td>75</td>
<td>0.97489</td>
<td>0.0859</td>
<td>0.5101</td>
</tr>
<tr>
<td>11</td>
<td>80</td>
<td>0.97183</td>
<td>0.0865</td>
<td>0.5107</td>
</tr>
<tr>
<td>12</td>
<td>90</td>
<td>0.96534</td>
<td>0.0899</td>
<td>0.5135</td>
</tr>
</tbody>
</table>
APPENDIX O

SAMPLE CALCULATION OF CRYSTALLINITY VIA IR SPECTROSCOPY

Calculations are presented of a series of samples with
general code number 10305 annealed at different temperatures for
different periods of time and analyzed for IR spectra, immediately
after their heat treatment. Crosslinking density \( p = 18.63 \)
\( (M_c = 4770) \).

RAW DATA

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Annealing Conditions</th>
<th>d</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T(°C)   t (min)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>90       30</td>
<td>0.29</td>
<td>0.72</td>
</tr>
<tr>
<td>2</td>
<td>90       60</td>
<td>0.38</td>
<td>0.75</td>
</tr>
<tr>
<td>3</td>
<td>90       90</td>
<td>0.47</td>
<td>0.78</td>
</tr>
<tr>
<td>4</td>
<td>105      30</td>
<td>0.39</td>
<td>0.76</td>
</tr>
<tr>
<td>5</td>
<td>105      60</td>
<td>0.40</td>
<td>0.75</td>
</tr>
<tr>
<td>6</td>
<td>105      90</td>
<td>0.46</td>
<td>0.75</td>
</tr>
<tr>
<td>7</td>
<td>120      30</td>
<td>0.49</td>
<td>0.805</td>
</tr>
<tr>
<td>8</td>
<td>120      60</td>
<td>0.48</td>
<td>0.78</td>
</tr>
<tr>
<td>9</td>
<td>120      90</td>
<td>0.54</td>
<td>0.74</td>
</tr>
</tbody>
</table>
CALCULATIONS:

The ratio of \( \frac{d}{c} \) is calculated where:

- \( d \) intensity of peak at 1141 cm\(^{-1}\)
- \( c \) intensity of peak at 1425 cm\(^{-1}\)

The crystallinity x% of the samples as calculated from density measurement is plotted versus the ratio \( \frac{d}{c} \). (See Fig. 0-1)

Using least square method, the following equation is derived:

\[
\text{Crystallinity \%} = 26.7 \div 102.6 \left[ \left( \frac{d}{c} \right) - 0.36 \right]
\]

This equation is used for the final calculation of the crystallinity.
<table>
<thead>
<tr>
<th>Sample No.</th>
<th>$d_0$</th>
<th>Crystallinity from Density Measurement (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.403</td>
<td>30.04</td>
</tr>
<tr>
<td>2</td>
<td>0.507</td>
<td>42.53</td>
</tr>
<tr>
<td>3</td>
<td>0.602</td>
<td>50.84</td>
</tr>
<tr>
<td>4</td>
<td>0.513</td>
<td>43.15</td>
</tr>
<tr>
<td>5</td>
<td>0.533</td>
<td>45.01</td>
</tr>
<tr>
<td>6</td>
<td>0.613</td>
<td>56.10</td>
</tr>
<tr>
<td>7</td>
<td>0.609</td>
<td>50.84</td>
</tr>
<tr>
<td>8</td>
<td>0.615</td>
<td>52.42</td>
</tr>
<tr>
<td>9</td>
<td>0.730</td>
<td>64.68</td>
</tr>
</tbody>
</table>
Fig. 0-1: Calculation of crystallinity from IR data
APPENDIX P

SAMPLE CALCULATION OF TENSILE-EXPERIMENT DATA

Calculation are presented for sample number 41a, tested after equilibrium swelling at 30°C; Annealing condition 90°C for 60 minutes. Crosslinking density $\rho = \frac{M_n}{M_c} = 9.49$, $M_c = 9370$

RAW DATA

Temperature 30°C Thickness = 0.018 in

$A_0 =$ Area = 0.0045 in$^2$

$L_0 =$ Initial gage length as determined by the grip distance before application of any stress = 2.19 cm.

$\Delta l =$ Change in sample length

DATA READINGS

<table>
<thead>
<tr>
<th>Datum No.</th>
<th>$\Delta l$</th>
<th>Load (gms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.21</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>0.47</td>
<td>200</td>
</tr>
<tr>
<td>3</td>
<td>1.56</td>
<td>400</td>
</tr>
<tr>
<td>4</td>
<td>2.81</td>
<td>600</td>
</tr>
<tr>
<td>5</td>
<td>3.66</td>
<td>800</td>
</tr>
<tr>
<td>6</td>
<td>4.32</td>
<td>1000</td>
</tr>
<tr>
<td>7</td>
<td>4.86</td>
<td>1200</td>
</tr>
<tr>
<td>8</td>
<td>5.31</td>
<td>1400</td>
</tr>
<tr>
<td>9</td>
<td>5.70</td>
<td>1600</td>
</tr>
<tr>
<td>10</td>
<td>6.01</td>
<td>1800</td>
</tr>
<tr>
<td>11</td>
<td>6.31</td>
<td>2000</td>
</tr>
<tr>
<td>12</td>
<td>6.67</td>
<td>2250</td>
</tr>
</tbody>
</table>
CALCULATIONS

a. Stress $\tau$

$$\tau = \frac{\text{Proportionality load}}{\text{Area}} = \frac{0.22/0.453}{0.0045} = 107.91 \text{ psi}$$

b. Strain $\varepsilon$

$$\varepsilon = \frac{\text{Proportional $\Delta l$}}{l_0} = \frac{0.50}{2.19} = 0.2283$$

c. Initial modulus $E_i$

$$E_i = \frac{\tau}{\varepsilon} = \frac{107.91}{0.2283} = 472.67 \text{ psi}$$

d. Ultimate tensile strength UTS

$$\text{UTS} = \frac{\text{Ultimate Load}}{\text{Area}} = \frac{2.250/0.453}{0.0045} = 1103.7 \text{ psi}$$

e. Elongation at break $\varepsilon'$

$$\varepsilon' = \frac{\Delta l \text{ at break}}{l_0} = \frac{6.67}{2.19} = 3.046 \text{ or } 304.6 \%$$
APPENDIX Q

SAMPLE CALCULATION OF CREEP EXPERIMENTS DATA

Calculation are presented for sample number 37b, tested after equilibrium swelling at 30°C: Annealing conditions 90°C, 60 minutes. Crosslinking density \( \rho = \frac{M}{M_c} = 23.61, M_c = 3765 \)

RAW DATA

Temperature 30°C Thickness = 0.0218 in

\[ A_0 = \text{Area} = 0.00545 \text{ in}^2 \]

\[ L_0 = \text{initial gage length as determined by distance between gage marks on specimen} = 0.585 \text{ cm} \]

Load = Weight + Grips - Buoyancy force = 500 + 17.9 - 85 = 432 \text{ gr} = 0.954 \text{ lbs}

\( \Delta l = \text{change in sample length} \)

\( t = \text{elapsed time} \)
<table>
<thead>
<tr>
<th>Datum No.</th>
<th>t</th>
<th>( \Delta l )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Creep</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>7 min</td>
<td>0.626</td>
</tr>
<tr>
<td>2</td>
<td>18</td>
<td>0.674</td>
</tr>
<tr>
<td>3</td>
<td>31</td>
<td>0.682</td>
</tr>
<tr>
<td>4</td>
<td>1 hr</td>
<td>0.729</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>0.761</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>0.761</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>0.780</td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td>0.817</td>
</tr>
<tr>
<td>9</td>
<td>20</td>
<td>0.858</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>0.860</td>
</tr>
<tr>
<td>Recovery</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>0 min</td>
<td>0.240</td>
</tr>
<tr>
<td>12</td>
<td>3</td>
<td>0.200</td>
</tr>
<tr>
<td>13</td>
<td>12</td>
<td>0.200</td>
</tr>
<tr>
<td>14</td>
<td>18</td>
<td>0.200</td>
</tr>
<tr>
<td>15</td>
<td>24</td>
<td>0.195</td>
</tr>
<tr>
<td>16</td>
<td>30</td>
<td>0.180</td>
</tr>
<tr>
<td>17</td>
<td>1 hr</td>
<td>0.180</td>
</tr>
<tr>
<td>18</td>
<td>2</td>
<td>0.165</td>
</tr>
<tr>
<td>19</td>
<td>3</td>
<td>0.150</td>
</tr>
<tr>
<td>20</td>
<td>5</td>
<td>0.145</td>
</tr>
<tr>
<td>21</td>
<td>15</td>
<td>0.135</td>
</tr>
</tbody>
</table>
CALCULATIONS

a. Stress $\tau$

\[ \tau = \frac{\text{Load}/A_0}{0.00545} = 0.954/0.00545 \text{ lb/in}^2 = 175 \text{ psi} \]

\[ = 1.206 \times 10^{-7} \text{ dynes/cm}^2 \]

b. Strain $\varepsilon$

\[ \varepsilon = \frac{\Delta l}{l_0} \]

c. Creep Compliance $J$

\[ J = \varepsilon/\tau \]

PROCESSED DATA

<table>
<thead>
<tr>
<th>Datum No.</th>
<th>$\varepsilon$ (in/in)</th>
<th>$J \times 10^7$ (cm$^2$/dynes)</th>
<th>$&amp; J_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Creep</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.070</td>
<td>0.887</td>
<td>-16.238</td>
</tr>
<tr>
<td>2</td>
<td>1.153</td>
<td>0.956</td>
<td>-16.163</td>
</tr>
<tr>
<td>3</td>
<td>1.166</td>
<td>0.966</td>
<td>-16.152</td>
</tr>
<tr>
<td>4</td>
<td>1.246</td>
<td>1.034</td>
<td>-16.083</td>
</tr>
<tr>
<td>5</td>
<td>1.301</td>
<td>1.079</td>
<td>-16.042</td>
</tr>
<tr>
<td>6</td>
<td>1.301</td>
<td>1.079</td>
<td>-16.042</td>
</tr>
<tr>
<td>7</td>
<td>1.333</td>
<td>1.105</td>
<td>-16.018</td>
</tr>
<tr>
<td>8</td>
<td>1.397</td>
<td>1.158</td>
<td>-15.971</td>
</tr>
<tr>
<td>9</td>
<td>1.466</td>
<td>1.216</td>
<td>-15.922</td>
</tr>
<tr>
<td>10</td>
<td>1.470</td>
<td>1.219</td>
<td>-15.920</td>
</tr>
<tr>
<td>Recovery</td>
<td>$\varepsilon$ (in/in)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>----------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>0.410</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>0.342</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>0.342</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>0.342</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>0.333</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>0.308</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>0.308</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>0.282</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>0.256</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.248</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>0.231</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Nutting's equation:

$$J = \psi t^n$$

For this particular specimen Fig. 9-103 shows the strain as a function of time. On the other hand $\ln J$ versus $\ln t$ was plotted and the resulting slope was, by least squares $0.0575 \pm 0.0013$. 

- 550 -
APPENDIX R

SAMPLE CALCULATION OF STRESS-STRAIN DATA

Calculation are presented for sample number 63d, tested after equilibrium swelling. Annealing condition 90°C, 30 minutes.

Crosslinking density \( \rho = \frac{M_n}{M_c} = 18.63 \), \( M_c = 4770 \)

RAW DATA

Thickness = 0.0404 in \( A_0 \) = Area = 0.01010 in\(^2\)

<table>
<thead>
<tr>
<th>Datum No.</th>
<th>Sample Length</th>
<th>Spring Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( h' = 51.69 ) cm</td>
<td>87.625 cm</td>
</tr>
<tr>
<td></td>
<td>( h = 50.29 )</td>
<td>87.195</td>
</tr>
<tr>
<td>2</td>
<td>52.675</td>
<td>90.28</td>
</tr>
<tr>
<td></td>
<td>50.81</td>
<td>90.755</td>
</tr>
<tr>
<td>3</td>
<td>53.185</td>
<td>90.355</td>
</tr>
<tr>
<td></td>
<td>51.105</td>
<td>89.830</td>
</tr>
<tr>
<td>4</td>
<td>54.345</td>
<td>94.28</td>
</tr>
<tr>
<td></td>
<td>51.775</td>
<td>93.685</td>
</tr>
</tbody>
</table>
CALCULATION:

A. Elongation

\[ \alpha = \frac{L}{L_0} \quad L_0 = 0.45 \, \text{cm} \]

\[ \phi(\alpha) = \alpha - \frac{1}{\alpha^2} \]

B. Stress

Spring force \[ f = k \Delta s + f_0 \]
where \( s = \) spring length, cm
\( k = \) spring constant
\( f_0 = \) force required to begin spring elongation

C. Calibration Data for Spring A-48-1

\[ k = 1181 \quad f_0 = 42 \]

Equilibrium tension \( \tau_0 = \frac{f}{A_0} \)

\[ \Delta s = s - s_0 = s - 0.25 \, \text{cm}. \]
**PROCESSED DATA:**

<table>
<thead>
<tr>
<th>Datum No.</th>
<th>L (cm)</th>
<th>Δs (cm)</th>
<th>f (gr)</th>
<th>τ₀ (psi)</th>
<th>α</th>
<th>α - (\frac{1}{a^2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.40</td>
<td>0.180</td>
<td>254.6</td>
<td>55.6</td>
<td>3.11</td>
<td>3.01</td>
</tr>
<tr>
<td>2</td>
<td>1.865</td>
<td>0.225</td>
<td>307.7</td>
<td>67.3</td>
<td>4.15</td>
<td>4.09</td>
</tr>
<tr>
<td>3</td>
<td>2.080</td>
<td>0.275</td>
<td>367.9</td>
<td>80.4</td>
<td>4.62</td>
<td>4.57</td>
</tr>
<tr>
<td>4</td>
<td>2.570</td>
<td>0.345</td>
<td>449.5</td>
<td>98.2</td>
<td>5.71</td>
<td>5.68</td>
</tr>
</tbody>
</table>

These data are plotted as τ versus φ (α) as in Fig. 9-112
APPENDIX S

SAMPLE CALCULATION OF TEAR STRENGTH-EXPERIMENT DATA

Calculations are presented for sample number 5lc, tested after swelling at 30°C, annealing conditions 90°C 30 minutes

Crosslinking density \( \rho = \frac{M_n}{M_c} = 15.55, \ M_c = 5715 \)

RAW DATA

Temperature \( 30°C \)

Thickness \( = 0.0253 \) in

Load \( = 46 \) gms

CALCULATION

Tear Strength \( = \frac{\text{Load}}{\text{Thickness}} = \frac{46}{0.0253} = 1818 \) gms/in of thickness
APPENDIX T

SOME HEMATOLOGICAL TESTS OF PVA HYDROGELS

Hematological experiments and discussion are presented on certain crystalline PVA hydrogels after heat-treatment and swelling at 30°C (466).

The materials tested are tubings of external diameter 17 mm and internal diameter 7 mm, irradiated with 5 and 10 Mgrads at 0°C. Two types of PVA tubings were produced with $M_c$ 3765 and 1790. All tubings were dried in a dust-free room at 24±1°C and RH 32±0.5% for 24 hours. The degree of crystallinity after dehydration was 14.18%. All tubings were annealed at different temperatures for different times. Crystallinity was calculated via density measurements.

The whole blood clotting time was reported as recorded using the Lee-White Clotting Test (257). The results are shown in the next table.

RESULTS
a. Standard: Glass 5 minutes - Siliconized tube 11 minutes
b. $M_c = 3765$

Annealing Conditions

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>t(min)</th>
<th>Water %</th>
<th>Degree of Crystallinity (%)</th>
<th>WBCT (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>dehydration</td>
<td>82.24</td>
<td>14.18</td>
</tr>
<tr>
<td>90</td>
<td>30</td>
<td>75.16</td>
<td>25.97</td>
<td>17.5</td>
</tr>
<tr>
<td>90</td>
<td>60</td>
<td>68.18</td>
<td>28.16</td>
<td>16</td>
</tr>
<tr>
<td>105</td>
<td>30</td>
<td>61.44</td>
<td>41.73</td>
<td>11</td>
</tr>
</tbody>
</table>

c. $M_c = 1790$

|     |       |        |                     |            |            |
|-----|-------|--------|---------------------|------------|
| 90  | 30    | 71.85  | 31.55               | 18.5       |
| 90  | 60    | 68.66  | 39.06               | 17.5       |
| 90  | 90    | 64.89  | 45.91               | 16.5       |
| 105 | 30    | 63.42  | 39.06               | 15         |
| 105 | 60    | 53.82  | 58.60               | 15         |
| 120 | 30    | 56.82  | 55.91               | 14         |

**DISCUSSION**

_PVA per se_ is not a biomaterial, or at least it is not much better than other nonheparinized polymers. The WBCT shows a trend of dependence on the degree of crystallinity. Although, within the experimental error of the method, the results cannot be considered of absolute value, it can be concluded that increasing degree of crystallinity does not favor the thromboresistance properties. Besides it seems that the WBCT does not depend only on the degree of crystallinity, but also on the size of the crystallites.
APPENDIX U

PRELIMINARY OBSERVATIONS OF HEPARINIZATION OF CRYSTALLINE PVA HYDROGELS

Heparinization of PVA hydrogels in the form of tubings has been done and qualitative observations are reported here.

The method used is a variation of Wong's method (260) of a two stage heparinization. In the first stage equal volumes of solution of 10% heparin and 5% gluteraldehyde are mixed and sulphuric acid is added up to pH = 5.5. This solution is immediately poured in the tubings and reacts for 60 minutes at 85°C. The second stage of quenching with 80% ethanol lasts for 30 minutes. At the end, the tubings are continuously rinsed with distilled water and they are stained for one minute in a 0.01% solution of toluidene blue. Heparinized materials show a purple color in constrast to the blue color of non-heparinized surfaces.

Uncrystallized hydrogels are easily and homogeneously heparinized. Crystallized hydrogels cannot be subjected to a homogeneous heparinization, as it is evident from "bands" "lines" and "spots" of heparin on the surface of the hydrogels. There is a slight evidence of preferable rate of reaction of heparin to the non-crystalline sites of PVA than to the crystalline ones. This suggests a process of (i) heparinization and (ii) dehydration.
In subsequent experiments this sequence of preparation of heparinized films was tried. Because of secondary crosslinking, due to the existence of gluteraldehyde and sulphuric acid in an acidic solution, the PVA hydrogels became so brittle (high crosslinking) that they shattered upon application of slight stresses during dehydration.

Detection of the elution of heparin from the surface of heparinized uncry stallized PVA hydrogels can be done, using $^{35}$S labelled heparin. Data kindly supplied by P.S.L. Wong of the Biomedical Engineering Laboratory show that the final heparin (in $\mu g/cm^2$) after heparinization of a PVA hydrogel ($M_c = 4770$) with $pH = 4$ and heparin elution at 9% NaCl solution was:

<table>
<thead>
<tr>
<th>Time of elution (hrs)</th>
<th>Final Heparin (mg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>13.8</td>
</tr>
<tr>
<td>4</td>
<td>7.2</td>
</tr>
<tr>
<td>8</td>
<td>4.8</td>
</tr>
<tr>
<td>12</td>
<td>3.6</td>
</tr>
<tr>
<td>16</td>
<td>3.4</td>
</tr>
<tr>
<td>20</td>
<td>3.3</td>
</tr>
<tr>
<td>50</td>
<td>3.1</td>
</tr>
<tr>
<td>100</td>
<td>3.1</td>
</tr>
</tbody>
</table>
However, it is realized now that heparin can diffuse through the whole hydrogel and that it does not stay bound only on the surface of the hydrogel.
APPENDIX V

LOCATION OF ORIGINAL DATA AND ANALYTICAL DEVICES USED IN THIS THESIS

a. The original data of this thesis as well as the calculations and computer programs are in the possession of Professor Edward W. Merrill, Building 12, Room 108, M.I.T.

b. Xeroxed copies of the references mentioned in this thesis, as well as translation of the German, Russian and Japanese articles are in the possession and can be obtained from the author, Building 12, Room 170, M.I.T.

c. The following analytical instruments and devices have been used.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Van de Graaff Generator</td>
<td>M.I.T. Building N-10</td>
</tr>
<tr>
<td>(ii) Cobalt-60 (not in existence now)</td>
<td>M.I.T. Building 66</td>
</tr>
<tr>
<td>System for sealing under vacuum</td>
<td>Chem. Eng. Dept., Room 12-127</td>
</tr>
<tr>
<td>(iii) DSC-1</td>
<td>Chem. Eng. Dept., Room 12-038</td>
</tr>
<tr>
<td>DSC-1B</td>
<td>Mater. Science Dept., Room 4-007</td>
</tr>
<tr>
<td>(iv) IR-Spectrophotometer</td>
<td>Chem. Dept., Room 18-050</td>
</tr>
<tr>
<td>Coleman, Mod.6-35, Spect.</td>
<td>Chem. Eng. Dept., Room 12-170</td>
</tr>
<tr>
<td>(v) Insotron (tensile tests)</td>
<td>Chem. Eng. Dept., Room 12-032</td>
</tr>
<tr>
<td>Creep and Stress Relaxation systems</td>
<td>Chem. Eng. Dept., Room 12-172</td>
</tr>
</tbody>
</table>
d. All the tested samples are in the possession of the Director of the Polymer Laboratory, Building 12, Room 170, M.I.T.
APPENDIX W

NOMENCLATURE*

A
A_0
A', B'
B
C
C_c
C_1, C_2
c_2,i
c_d
D
D_c
D'_c
\bar{DP}_n
\bar{DP}_w
E_i
E_{10}
E_{100}

Interface area
Cross-sectional area (in tensile experiments)
Constants
Interaction energy
Polymer concentration in a gel
Concentration of irradiated solution
Constants
Concentration of polymer (= u_2,r/V)
Intensities of peaks of IR
Optical Density
Dose of radiation
Dose of gelation
Degree of polymerization (number average)
Degree of polymerization (weight average)
Initial modulus of elasticity (=\tau/\varepsilon)
Secant modulus (10%) (Modulus at 10% elongation)
Secant modulus (100%) (Modulus at 100% elongation)

* Nomenclature includes letters used only in the text and the discussion, but not in the Appendices
f  Functionality
F_n  Load at break
G  Value of irradiated samples
I  Intensity of visible light
I_a  Intensity of light before entrance in a sample
I_b  Intensity of light after exit from an empty sample holder
I_w  Intensity of light after exit from a sample with water
I_s  Intensity of light after exit from a sample with gel
I  Intensity of x-rays
I_a  Height of the amorphous peak at \(2\theta=18^\circ\) of a hypothetical amorphous sample
I_c  Height of the crystalline peak at \(2\theta=19^\circ\) of a hypothetical crystalline sample (100%)
i_a  Height of amorphous peak at \(2\theta=18^\circ\)
i_c  Relative intensity measure of the crystalline fraction
i_m  Height of peak at \(2\theta=19^\circ\) measured on the meridian
i_t  Height of peak at \(2\theta=19^\circ\) measured at the equator
J  Creep compliance \((=\varepsilon/\tau)\)
k, K  Constants of different equation (in general)
\(l_0\)  Initial length of a sample
\(l\)  Length of a sample at any time
m  Molecular weight of a "molecular unit"
$M_2$  Average molecular weight in amorphous region

$M_c$  Average molecular weight between crosslinks

$M_n$  Number average molecular weight

$M_u$  Viscosity average molecular weight

$M_w$  Weight average molecular weight

$n$  Exponent of Nutting's equation

$P_s, P_c, P_a$  Properties (in general) of semi-crystalline, crystalline and amorphous polymers

$q$  Swelling ratio (weight) $(= w_a/w_p = 1/w_{pva})$

$q'$  Swelling ratio defined as $(w_a - w)/w_p = q - 1$

$Q$  Swelling ratio (volume) $(= V_s/V_p = 1/u_{2,s})$

$r_i, r_o$  Mean square end-to-end distance of a polymer chain

$R$  Crystalline peak's intensity (X-rays)

$RH$  Relative humidity

$s$  Solubility

$t$  Time

$\bar{t}$  Induction time of crystallization

$T$  Temperature (in general)

$\tau$  Transmittance (in spectroscopy)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_c$</td>
<td>Temperature of irradiation of a sample</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>$T'_g$</td>
<td>Other second-order transition temperature</td>
</tr>
<tr>
<td>$T_m, T'_m$</td>
<td>Melting point of a hydrogel</td>
</tr>
<tr>
<td>$T_m^0$</td>
<td>Melting point of a polymer network without diluent</td>
</tr>
<tr>
<td>$u$</td>
<td>Number of monomer units between crosslinks</td>
</tr>
<tr>
<td>UTS</td>
<td>Ultimate Tensile Strength</td>
</tr>
<tr>
<td>$v_1$</td>
<td>Solvent volume fraction in a polymer-solvent system</td>
</tr>
<tr>
<td>$v_2$</td>
<td>Polymer volume fraction in a polymer-solvent system</td>
</tr>
<tr>
<td>$v_{2,r}$</td>
<td>Polymer volume fraction of a relaxed gel (after irradiation)</td>
</tr>
<tr>
<td>$v_{2,s}$</td>
<td>Polymer volume fraction of a swollen gel</td>
</tr>
<tr>
<td>$\bar{v}$</td>
<td>Specific volume of polymer</td>
</tr>
<tr>
<td>$V_1$</td>
<td>Molar volume of solvent</td>
</tr>
<tr>
<td>$V_a$</td>
<td>Apparent volume of polymer</td>
</tr>
<tr>
<td>$V_P$</td>
<td>Volume of polymer</td>
</tr>
<tr>
<td>$V_R$</td>
<td>Volume of relaxed polymer</td>
</tr>
<tr>
<td>$V_s$</td>
<td>Volume of swollen polymer</td>
</tr>
<tr>
<td>$V_s'$</td>
<td>Molecular volume of a segment</td>
</tr>
</tbody>
</table>
\( V_u \)  
Molar volume of a polymer repeating unit

\( w \)  
Length of a "molecular unit"

\( w_{PVA} \)  
Weight percent of PVA in a hydrogel

\( w_{H_2O} \)  
Weight percent of H\(_2\)O in a hydrogel

\( W_a \)  
Weight of a sample in air

\( W_w \)  
Weight of a sample in water

\( X, x \)  
Degree of crystallinity

\( x_b \)  
Crystallinity before swelling

\( x_g \)  
Crystallinity after swelling

\( z \)  
Total number of segments

\( Z \)  
Polymer chain length

**GREEK LETTERS**

\( \alpha \)  
\( l/l_0 = 1 + \varepsilon \)

\( \alpha_l, \beta_l \)  
Factor used in the expression of \( \chi \) as a function of \( T \)

\( \Delta H^f \)  
Heat of fusion (calculated)

\( \Delta H_c \)  
Heat of fusion of 100% crystalline material

\( \Delta l \)  
Increase of the length of a polymer upon application of tensile stress
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>$\Delta s_f$</td>
<td>Entropy of fusion</td>
</tr>
<tr>
<td>$\Delta T$</td>
<td>Depression of melting point</td>
</tr>
<tr>
<td>$\Delta w_{12}$</td>
<td>Change in energy for the formation of an unlike contact pair</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Strain ($= \Delta l/l_0$)</td>
</tr>
<tr>
<td>$\xi$</td>
<td>Volume of voids in a polymer</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>Critical length of a crystalline</td>
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<tr>
<td>$[\eta]$</td>
<td>Intrinsic viscosity</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Angle (x-rays)</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Theta temperature</td>
</tr>
<tr>
<td>$\kappa_1$</td>
<td>Enthalpic parameter</td>
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<tr>
<td>$\mu$</td>
<td>Chemical potential</td>
</tr>
<tr>
<td>$v$</td>
<td>Ratio of two crystalline peaks</td>
</tr>
<tr>
<td>$v_e$</td>
<td>Effective number of crosslinks</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density of polymer</td>
</tr>
<tr>
<td>$\rho_a$</td>
<td>Density of amorphous polymer</td>
</tr>
<tr>
<td>$\rho_c$</td>
<td>Density of crystalline polymer</td>
</tr>
<tr>
<td>$\rho_g$</td>
<td>Density of semicrystalline polymer</td>
</tr>
<tr>
<td>$\rho_h$</td>
<td>Density of hydrogel</td>
</tr>
<tr>
<td>$\rho_w$</td>
<td>Density of water</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Crosslinking density of a network ($=\frac{M_n}{M_c}$)</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Interfacial free energy</td>
</tr>
</tbody>
</table>
\( \tau \)  
Stress

\( \chi \)  
Chi factor (Interaction parameter of polymer-solvent molecules)

\( \psi \)  
Constant of Nutting's equation

\( \psi_1 \)  
Enthalpic parameter
APPENDIX X

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Nagoya Kogyo Gijutsu Shikensko Hokoku
Repts. Governm Ind. Res. Instit, Nagoya

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Oyo Butsuri
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Sen-i-Gakkaishi

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ADDENDUM


BIOGRAPHICAL NOTE

Nikolaos A. Peppas, son of Mr. Athanassios N. Peppas and Mrs. Aliki P. Rousopoulos, was born in Athens, Greece, in August, 1948. After graduation from the 10th Public Lyceum of Athens, he took the advanced national examinations (Academic diploma - Ακαδημαϊκό Απολυτήριον) and he entered the Chemical Engineering Department of the National Technical University of Athens (Ethnikon Metsovon Polytechnion - Εθνικό Πανεπιστήμιο Πολυτεχνείου) in September 1966. He received the Diploma in Chemical Engineering in June 1971, graduating first in his class, with the Cryssoverghion Award. At N.T.U., he had the opportunity to work with Prof. G. N. Valkanas, who introduced him to the field of polymers and technology of plastics. His Dipl. Eng. thesis was on "The Production of Certain Thermoresistant Polybenzylenes".

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The author is a member of Sigma Xi, AIChe, American Chemical Society, Division of Polymers of ACS, the Technical Chamber of Greece, the Greek Chemical Engineers Association and the Greek Chemists Association.

He held positions in Shell Netherland Refinery (Pernis, Rotterdam, Netherlands) and BESO, Industry of Food Products (Patras, Greece).

Upon graduation the author will return to Greece for a six-month term of military service in the Greek Army.

His interests include teaching and research in the fields of Thermodynamics, Polymers, Biomedical Engineering and Organic Chemical Technology.

OTHER PUBLICATIONS:


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OTHER PUBLICATIONS:


- N.A. Peppas and G. N. Valkanas "Polycondensation of Chloromethylated Derivatives of O-, m- and p-xylene in Highly Ionizing Systems"
Chemika Chronika, New Series (submitted for publication).
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<td>Fig. 6-9 Ordinate is T(°C)</td>
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<td>Eq. 6-9 ( \frac{x}{\rho} + \frac{1-x}{\rho} )</td>
<td>( \frac{x}{\rho_c} + \frac{1-x}{\rho_a} )</td>
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