THE DIELECTRIC RELAXATION OF CHLOROSTYRENE POLYMERS IN
SOLUTION

by

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ABSTRACT

Dielectric relaxation measurements on samples of unfractionated poly p-chlorostyrene ranging in number average molecular weight from about 5,000 to about 500,000 in solutions of ortho-terphenyl are reported. The critical relaxation time is found to vary with the square root of the polymer molecular weight, in apparent qualitative agreement with the predictions of the Kirkwood-Hammerle theory. A quantitative comparison with the predictions of this theory shows, however, that the actual relaxation process is much slower than that pictured by Kirkwood and Hammerle. In fact, the observed relaxation time for the lowest molecular weight sample of poly p-chlorostyrene agrees quite closely with the time predicted by any of several different theories for the orientation of the molecule as a unit. The times for the higher molecular weight samples are somewhat lower than these predicted orientation times, but are still comparable with them. Furthermore, measurements on polyvinyl bromide solutions have been reported elsewhere in which no dependence of relaxation time on molecular weight has been found. The relaxation times for all the polyvinyl bromides were several orders of magnitude faster than the times predicted for the orientation of the whole molecule. This clearly demonstrates that the relaxation mechanisms in the two polymers are not the same. Since polyvinyl bromide conforms much more closely to the model used by Kirkwood and Hammerle than poly p-chlorostyrene, the agreement of the Kirkwood-Hammerle theory with the observed dependence in poly p-chlorostyrene is simply fortuitous, and in no sense constitutes a validation of this theory.

A mechanism for dielectric relaxation in vinyl halide type polymers which would be independent of molecular weight is proposed, and it is proposed that either this or some similar mechanism is the principal mode of relaxation for polyvinyl bromide solutions, but that this mechanism is rendered inoperative by steric hindrance in poly p-chlorostyrene. Dielectric relaxation in this system is presumed to occur through the orientation of large segments of the chain, a process that could well be, and apparently is, according to our data, molecular weight dependent.

Corroboratory evidence for the stiffness of the poly p-chlorostyrene chain is given by the intrinsic viscosity measurements for this polymer in ortho-terphenyl, and by the effect of temperature on the molecular weight dependence of the relaxation time.

The chain transfer constant of CBr_4 with p-chlorostyrene is determined, and the construction of a simple, lightweight cell for dielectric measurements is described.

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ACKNOWLEDGMENT

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I INTRODUCTION

The behavior of polymer molecules in solution has been a rich source of problems for the investigation of the polymer physical chemist. Since the prediction of the configurations of polymer molecules in solutions is necessarily a statistical problem, considerable progress has been made through the application of the methods of statistical physics to such problems as the dimensions, frictional properties, viscoelastic behavior, and dielectric relaxation of macromolecules in solution. A number of physical models have been developed and various mathematical techniques have been formulated for dealing with such problems; these approaches have met with varying degrees of success.

The behavior of polar polymers in solution under the influence of electric fields has been subject to a considerable amount of such theoretical investigation. Also, measurements of the dielectric relaxation spectra of solutions of many different polymers have been reported since interest in the problems was first aroused, primarily by the early experimental work of Fuoss[1], and the theoretical treatments of Kirkwood and Fuoss[2] in the years around 1940.

It has not yet proved possible, however, to fit the results of the theoretical treatments and of the experimental measurements into a complete understanding of dielectric relaxation processes in polymer solutions. Thus continued interest in this problem has been maintained, with particular emphasis on the question of the effect of polymer molecular weight on the relaxation process.

In this work we have measured the dielectric relaxation of poly p-chlorostyrene in solution. Two principal reasons may be given for our interest in this problem. First, such measurements should provide a check on the quantitative predictions of several of the theories of dielectric relaxation in polymer solutions, and second, the importance of internal barriers to rotation in polymer chains may be estimated to some extent by comparison of the behavior of a sterically hindered polymer like poly p-chlorostyrene with that of polymers which are less sterically hindered.

We shall present, after a discussion of relevant theoretical considerations, our measurements of the dielectric relaxation spectra of solutions of poly p-chlorostyrene, and discuss the significance of these results and their place in the over-all picture of the dielectric behavior of polar polymers in solution.

II THEORY

A. <u>Dielectric Relaxation in Simple Systems</u>

An understanding of the relaxation processes involved
in the dielectric relaxation of systems consisting of
simple, independent dipoles must be gained before corre-
sponding processes are considered in polymers. The theory
may be visualized as follows: If a static electric field
is applied to such a system of simple, independent dipoles
a polarization is acquired by the system which is
proportional to the strength of the field. This polari-
zation is due to a combination of three effects: first, a
displacement of the electrons in the molecule so as to
minimize the local field, second, a distortion of the bond
angles in the molecule (atomic polarization), and third, an
orientation of the permament dipoles in the direction of the
field. The electronic and atomic polarizations, or
"distortion" polarizations, are functions only of the detailed
molecular structure of the molecule in question, and
therefore are constant for any particular substance at
frequencies commonly encountered in dielectric measurements.
The orientation polarization is, for any large assembly of
dipoles, the result of a statistical distribution of
orientations of dipoles about the field vector, and therefore

depends inversely upon the temperature as well as directly upon the magnitude of the dipole moment. It may be shown that[3]

$$P = \frac{4\pi}{3} N(\alpha_o + \mu^2/3kT)$$

where P is the molar polarization

N is the Avogadro's number

α_o is the distortion polarizability

μ is the dipole moment of the molecule

k is the Boltzman's constant

and T is the absolute temperature

The dielectric constant of a medium is defined as the ratio of the capacitance of a capacitor filled with the medium to that of the same capacitor when empty. The dielectric constant may be related to the molar polarization by any of several relationships, the particular choice of which is dictated by the degree of interaction between dipoles. For the case under discussion of simple independent dipoles,

$$P = [(\varepsilon - 1)/3] [M/\rho]$$

where P is the molar polarization

ε is the static dielectric constant

M is the molecular weight

and ρ is the density

Thus it can be seen that the static dielectric constant also is dependent on both distortion and orientation polarization. It may be noted that measurements of P for simple polar gases as functions of temperature agree rather well with the predictions of these equations, and accurate values of both α_o and μ may be determined from such data.

Let us now suppose that, under the influence of a D. C. field, an equilibrium distribution of orientation has been set up about the field vector. If the field is suddenly removed, the polarization does not vanish instantly, but rather decays exponentially due to thermal motion. The time required for the polarization to decrease to $\frac{1}{e}$ th of its initial value after removal of the field is a characteristic time for any given system, and is known as the relaxation time.

If we take a system of simple independent dipoles characterized by a relaxation time τ, and impress upon it an alternating field whose period is long compared to the relaxation time, the equilibrium distribution of dipoles is maintained about the field vector at all times, and no differences between static and low frequency dielectric behavior are noted. The charge displacement in such a system occurs at its maximum rate when the voltage of the applied field is changing most rapidly; that is, at the zeros of voltage. Since the current attains its maximum value when the rate of charge displacement is greatest, the

maxima of the current and the voltage are 90° out of phase. This is a pure capacitive current; there is zero conductance, and no power is dissipated as heat.

If the frequency is increased to the extent that the period is of the order of the relaxation time, the dipoles will be unable to "keep up" completely with the field, and their orientations will lag behind the field vector. This places a component of current in phase with the voltage, and leads to dissipation of power as heat in the medium (dielectric loss). The total polarization is somewhat decreased, since there is less orientation of the dipoles.

If the frequency is increased still more, so that the period of the field is considerably shorter than the relaxation time, the dipoles will be unable to orient at all. The orientation polarization will vanish completely, leaving only the distortion currents, which have no component in phase with the voltage at frequencies commonly encountered in dielectric measurements. The dielectric loss is again reduced to zero, and the dielectric constant is reduced to a value corresponding to the distortion polarization alone.

These observations may be completely described by a generalized complex dielectric constant ε^* introduced by Debye, where

$$\varepsilon^* = \varepsilon' - i\varepsilon''$$

where $\underline{i}$ is $\sqrt{-1}$, ε' is the familiar dielectric constant, and ε'' is the dielectric loss factor. In the notation of the present work, these quantities are defined by:

$$\varepsilon' = C_x/C_o$$

$$\varepsilon'' = G_m/2\pi f C_o$$

where C_o is the capacitance of the empty measuring capacitor

C_x is the capacitance of the same capacitor filled with the unknown medium x

G_m is the conductance of the sample

and f is the frequency of the applied field.

The real part, ε', as has been pointed out, maintains at low frequencies a constant value characteristic of both distortion and orientation polarization, but falls off with increasing frequency until a second constant value characteristic of the distortion polarization alone is reached. The imaginary part ε'' is zero at low frequencies, but rises with increasing frequency until a maximum is reached when the period of the field is exactly equal to 2π times the relaxation time of the dipoles in the system; i.e., when $\tau = 1/2\pi f_m$, where f_m is the frequency at which the maximum in ε'' is reached. Finally ε'' decreases to zero once more at high frequencies. The behavior of ε'

and ε'' as functions of frequency for systems of simple, independent dipoles as shown in Fig. 1.

The components of the complex dielectric constant ε^* may be expressed as functions of τ, the static dielectric constant ε_0, the dielectric constant at very high frequencies ε_∞, and the angular frequency ω by the following equations:[4]

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2 \tau^2} \tag{1}$$

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)\,\omega\tau}{(1 + \omega^2 \tau^2)} \tag{2}$$

Experimental curves for ε' and ε'' for simple systems may often be fitted quite well with equations of this sort.

Theoretical attempts have been made by Debye[3] and others to predict relaxation times for simple polar molecules in viscous media. The model used is the following: the molecules are assumed to be spherical and of radius $\underline{a}$, and the dipoles are taken to be oriented along a diameter of this sphere. The medium is assumed to be homogeneous and structureless and to exhibit the same viscosity η on a molecular scale that it exhibits in bulk flow. This is equivalent to the assumption that the movement of the molecule is governed by Stokes' law. The result of this treatment is

$$\tau = 4\pi a^3 \eta / kT$$

Figure 1.

ε^t and ε'' vs. log f for simple systems of independent dipoles.

ε'

ε"

log f
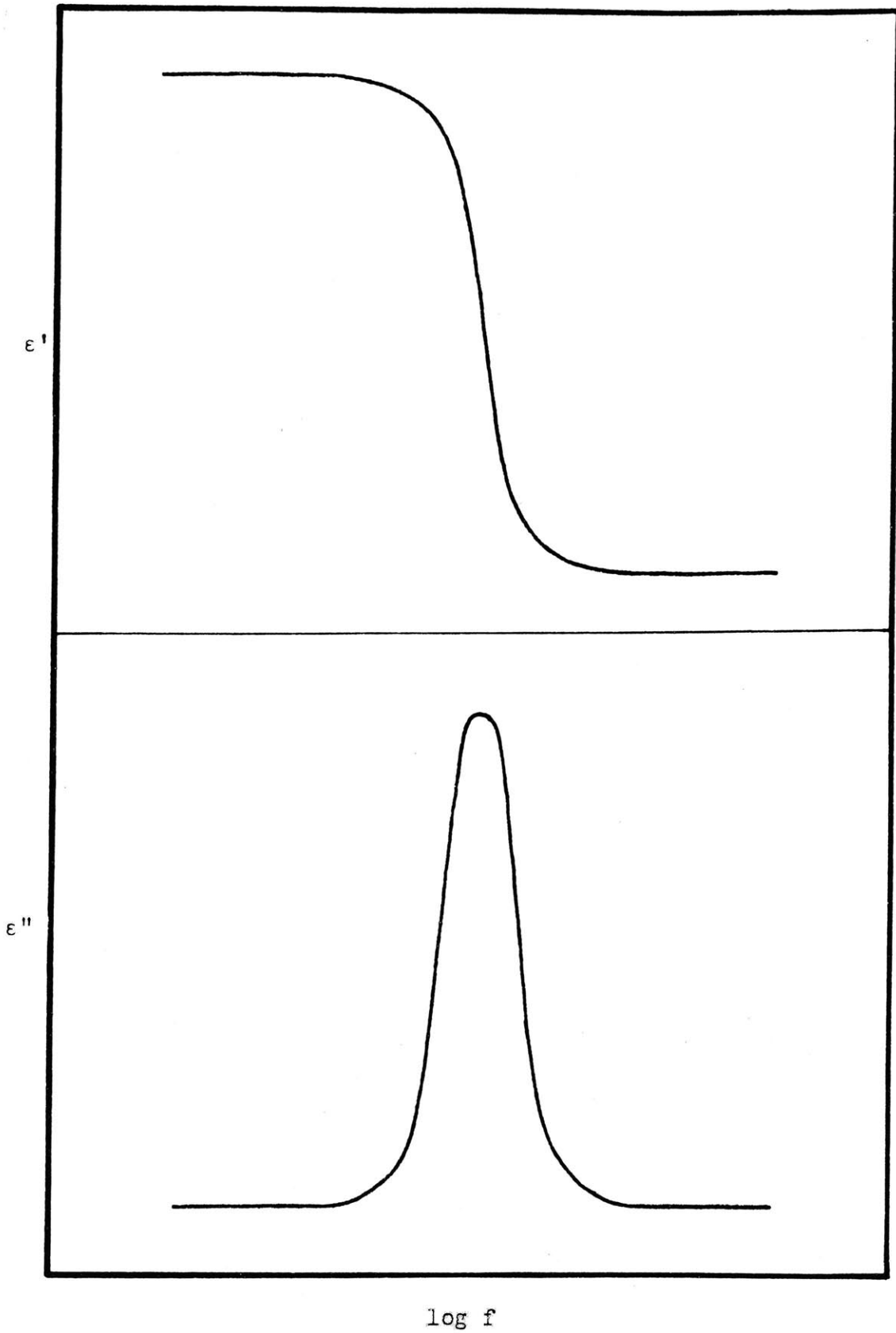
and leads to at least order of magnitude agreement with experiment in many cases in which the assumptions are not too unreasonable.

Dielectric relaxation processes in bulk polar liquids are somewhat more complicated than those just described. The loss peaks found in such systems are, in general, broader and lower than those to be found in simple systems. It is usually impossible to fit experimental ϵ' and ϵ'' data for bulk polar liquids by any such equations as (1) and (2), which involve only a single relaxation time τ. The postulate must then be made that a distribution of relaxation times is required to characterize the relaxation of such systems. Physically, this corresponds to the assertion that the microscopic environment of each dipole is not identical, at any given instant, to the environment of every other dipole in the system because of molecular interactions and statistical fluctuations, and that these environmental differences lead to a number of different relaxation times. If, purely in a formal manner, we take $G(\tau)d\tau$ as the fraction of the total polarization which can be characterized by a relaxation time between τ and $\tau + d\tau$, and $G(\tau)$ is so normalized that $\int_o^\infty G(\tau)d\tau = 1$, then, in analogy with (1) and (2),

$$\epsilon' = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty) \int_o^\infty \frac{1}{1 + \omega^2\tau^2} G(\tau)d\tau \qquad (3)$$

$$\varepsilon'' = (\varepsilon_0 - \varepsilon_\infty) \int_0^\infty \frac{\omega\tau}{1 + \omega^2\tau^2} G(\tau)d\tau \qquad (4)$$

It is common practice to characterize the distribution by a single "critical" relaxation time, about which the other permitted times are grouped. This is usually defined as $\tau_c = 1/2\pi f_m$, which is formally the same as for systems characterized by a single relaxation time.

A much more complete treatment of the dielectric relaxation of simple systems and bulk systems is to be found in an excellent treatise by Böttcher.[4]

B. Dielectric Relaxation in Polymer Solutions

Still further complications arise when our attention is shifted to the dielectric relaxation of polar polymer molecules in solution. As the dipoles are coupled along the chain backbone, they may in no sense be considered independent. In general, the loss peaks found in polymer solutions are broader and lower than those found in simple systems or in most bulk polar liquids, and they occur at much lower frequencies (often in the kilocycle or low megacycle range at temperatures not too far removed from room temperature). Furthermore, a broad distribution of relaxation times is required to characterize the relaxation process, and equations (3) and (4) may be used to fit experimental ε' and ε'' data. In addition to the molecular interactions and statistical fluctuations mentioned

earlier, the distribution of relaxation times in polymeric systems may also be due to the relaxation of segments of 1, 2, 3, ...n monomer units, each of which might be expected to relax with a different characteristic time.

Theoretical work in the dielectric behavior of polymer molecules has been directed primarily toward prediction of $G(\tau)$ and τ_c from the properties of the polymer molecule and the solvent. These problems are extremely difficult to treat theoretically. Investigators in this field have usually either taken reasonably realistic models and made sweeping approximations in the mathematics, or they have taken models of doubtful validity and treated them more or less rigorously. As might be expected, the results of the various theories differ quite widely. A convenient criterion for examination of these theories is the predicted dependence of τ_c upon polymer molecular weight. If this dependence is represented by $\tau_c = KM^p$, values of p are predicted ranging from 0 to 2, depending on the model used and the approximations involved.[2,5,6,7,8]

It should not be assumed, however, that the results of any of these, or any other, calculations based on a single model could describe accurately the dielectric behavior of all polymers in solution. Several types of polar polymers must be recognized in which the dipoles are coupled to the backbone in different ways. In polymers of the polyvinyl halide type, the dipoles are rigidly

attached perpendicular to the chain backbone, and no
orientation of the dipoles is possible without motion of
at least some segment of the chain. There are also polymers,
notably polyvinyl acetate, etc., in which the dipoles are
rather loosely attached on the side chains, and some
orientation is possible independent of chain motion. There
are also polymers in which the dipoles are in the backbone
of the chain itself; these may be coupled in a head to tail
fashion, in such a way that there is a cumulative dipole
moment which increases with increased chain length, or they
may be coupled head to head, so there is no net dipole
moment in the chain. It is no doubt unreasonable to expect
similar dielectric behavior from such diverse systems,
particularly with regard to molecular weight dependence of
relaxation time.

A more reasonable approach would be to consider the
behavior of each type of polymer in the light of whatever
more or less realistic theories and conclusions drawn from
intuitive reasoning are available. Let us consider what
is probably the simplest case to visualize, that of dipoles
in the side chains loosely coupled to the backbone. While
no elegant theory has been proposed for this case, it would
seem that since the relaxation process would be, for the
most part, independent of the motion of the chain as a
whole, it would not be greatly influenced by the chain

length. The relaxation time would, then, be essentially independent of the molecular weight of the polymer. While this simple picture is somewhat clouded by the presence also of dipole components perpendicular to the chain in most polymers which have been investigated, the conclusions seem to be verified by the abundance of data for such polymers as poly methylmethacrylate,[9] polyvinyl acetate, and other similar polymers, in which little or no dependence of τ_c upon molecular weight has been noted.

The case of cumulative dipoles in the chain backbone has been treated by Zimm.[6] He obtains a relaxation time which varies as the product $[\eta]M$, where $[\eta]$ is the intrinsic viscosity of the polymer in the solvent, so that τ_c varies as M^2 for the free-draining polymer molecule, i.e., one in which hydrodynamic interaction between different chain segments through the solvent is negligible; and so that τ_c varies as $M^{3/2}$ when hydrodynamic interaction is extremely important. His picture of the relaxation process is one in which relaxation takes place both by orientation and by stretching of the end-to-end dipole vector.

A strongly molecular weight dependent loss peak has been found in bulk polypropylene oxide by Baur,[10] who attributed it to the relaxation of a parallel component in the backbone of the polymer. Similar peaks have been found in cellulose acetate solutions,[11,12] and these could also be attributed to similar relaxations.

The third case we shall consider is that of the rigidly coupled side chain dipoles. While extensive theoretical investigation has been made of this problem, the physical significance of the results is perhaps the least clear of all. Kirkwood and Fuoss[2] have treated the problem with a model which corresponds essentially to the polyvinyl halides, in which bond lengths and bond angles are kept fixed, but azimuth angles are free to rotate. This model, after the application of some rather drastic assumptions in the mathematical formulation, leads to a dependence of relaxation time upon the first power of the molecular weight.

This same model has been treated again by Kirkwood and Hammerle,[5] with the inclusion of strong hydrodynamic interaction. The result of this calculation, which is subject to the same criticism as the Kirkwood - Fuoss treatment, is a square root dependence of relaxation time upon molecular weight.

It would not be surprising, however, to find the relaxation process in these polymers to be independent of molecular weight if relaxation occurs primarily through the orientation of short segments of the chain.

Until recently, there have been no measurements of polyvinyl halide type polymers in dilute solution which would be appropriate for comparison with these theories.

Measurements have now been reported on polyvinyl bromide in solutions of tetrahydrofuran and in cyclohexanone at temperatures of -15°C and -30°C.[13] No significant dependence of relaxation time on molecular weight was noted. Measurements on poly p-chlorostyrene in solutions of ortho-terphenyl at 40°C to 60°C, reported in the present work, show a dependence of relaxation time on the square root of molecular weight. Since our measurements seem to agree with the predictions of the Kirkwood-Hammerle theory, we must now examine these predictions in somewhat more detail.

Kirkwood and Hammerle obtain as the distribution of relaxation times $G(\tau)$:

$$G(\tau) = \frac{2\tau \, \tau_c}{(\tau + \tau_c)^3}$$

and for the frequency of maximum loss f_m:

$$f_m = \frac{0.044kT}{a^3 \, \eta_o \, n^{1/2}}$$

where k is the Boltzman constant

T is the absolute temperature

a is the "effective bond length" (See below)

η_o is the viscosity of the solvent

and   n is the degree of polymerization.

Since $\tau_c = 1/2\pi f_m$, the predicted dependence of τ_c on $\underline{n}^{1/2}$ is apparent.

The quantity $\underline{a}$ in the above equation requires some further explanation. The mean square end-to-end distance $\overline{\ell^2}$ of a vinyl polymer molecule of degree of polymerization $\underline{n}$, with $2\underline{n}$ identical bonds of length $\underline{a}'$, may be estimated in a rather simple manner. If the assumption is made that all bond angles are completely free to rotate at will in any direction, the problem reduces to a three dimensional random walk calculation of the distance traversed in $2\underline{n}$ random steps of length $\underline{a}'$ each. The result is $\overline{\ell^2} \cong 2n(a')^2$. For a chain of carbon atoms with tetrahedral bond angles, the results are modified to $\overline{\ell^2} \cong 4n(a')^2$. Of course, in any real polymer molecule there are bond angle restrictions, so the steps are not actually random. The actual end-to-end distance is always greater than that predicted by either calculation. The results of this calculation may be made more useful if the actual bond length $\underline{a}'$ is replaced by an "effective bond length" $\underline{a}$, which is defined as the length of the bonds in a hypothetical polymer in which $2\underline{n}$ steps along the carbon chain lead to the observed end-to-end distance ℓ in the actual polymer. Thus $\overline{\ell^2} = 4na^2$, by the definition of $\underline{a}$.

Two difficulties become apparent in the use of the Kirkwood-Hammerle equation. First, the quantity $\underline{a}$ cannot be obtained directly; and second, for a system having a distribution of molecular weights it is not obvious which

average degree of polymerization should be used. We have therefore modified the form of the equation slightly by eliminating both $\underline{a}$ and $\underline{n}$ from explicit appearance by the use of two well-known relationships.

$$\overline{\ell^2} = 4na^2$$

$$[\eta] = \Phi \frac{(\overline{\ell^2})^{3/2}}{M}$$

where $[\eta]$ is the intrinsic viscosity of the polymer
in the solvent used

Φ is a universal parameter.[14]

and   M is the molecular weight of the polymer.
We now obtain:

$$f_m = \frac{0.044kT \; \Phi \; (4)^{3/2}}{\eta_o \; [\eta]M_1}$$

where M_1 is the molecular weight of a monomer unit.

The advantage of this transformation is, of course, that all quantities involved are directly measurable. A comparison of these equations with our measurements will be given in Chapter V.

III EXPERIMENTAL

A. <u>Purification of the Monomer</u>

One hundred grams of p-chlorostyrene was obtained from Monomer-Polymer Laboratories, Borden Co., of Philadelphia, Pennsylvania. To remove the inhibitor, the monomer was washed several times with a dilute aqueous solution of NaOH. The monomer was separated from the aqueous phase, dried for several hours with "Drierite", and distilled at 33.0 - 33.5°C/1 mm Hg. The purified monomer was kept in the refrigerator at 0°C for several days until used for the chain transfer experiments and the full scale polymerizations.

B. Determination of the Chain Transfer Constant of CBr_4 with p-chlorostyrene

While the molecular weight of a polymer produced in a given polymerization may be regulated to some extent by careful choice of initiation rates, it is often simpler to make use of certain reactive compounds called regulators.[15] These compounds readily undergo transfer reactions with growing chains, leading to the termination of the growing chain and the simultaneous initiation of a new chain. In the specific case of CBr_4 as regulator, the reaction is

assumed to proceed as follows:

$$M_x\bullet + Br\text{-}CBr_3 \rightarrow M_xBr + CBr_3\bullet \xrightarrow{M} CBr_3\text{-}M\bullet \xrightarrow{etc.}$$
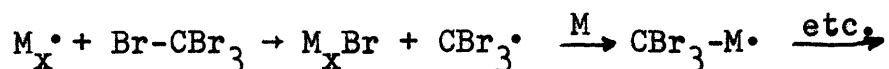
where M refers to a monomer unit, and $M_x\bullet$ a growing

chain of x units.

It may be shown[16] that for a system containing such a

regulator, and in which other transfer reactions with

monomer, polymer and solvent are negligible:

$$\frac{1}{P_n} = \frac{1}{P_o} + C\frac{(S)}{(M)}$$

where P_n is the observed number average degree of

polymerization,

P_o is the degree of polymerization in the

absence of a regulator,

S is the molar concentration of the regulator,

M is the molar concentration of the monomer,

and   C is a constant characteristic of the regulator-

monomer system and the temperature, and is called

the chain transfer of the regulator with the

monomer.

If P_o is made reasonably large, the second term completely

determines the degree of polymerization, and thus the degree

of polymerization may be varied at will over wide ranges

through the simple expedient of changing the regulator

concentration.

It must be noted, however, that since the chain transfer constant is in essence a measure of the relative affinity of the growing chain for the regulator as compared to the monomer, the relative concentrations of regulator and monomer, and thus the degree of polymerization, will change during the course of the polymerization if C differs greatly from unity. Thus the so-called "most probable" molecular weight distribution[17] can be maintained throughout the entire course of a polymerization only if C $\cong$ 1. As the literature value of C for CBr_4 with styrene is 1.36,[18] it was assumed that CBr_4 would also be a reasonable choice for use with p-chlorostyrene, since the transfer constants probably would differ but little for the two systems.

It was then decided to attempt direct measurement of C for CBr_4 with p-chlorostyrene, using essentially the method described by Gregg and Mayo.[19] The following solutions were prepared:

Sample	p-chloro-styrene gms.	Azo-bis isobuty-ronitrile gms.	Benzene ml.	CBr_4 gms.	$\dfrac{(S)}{(M)}$
1	1.9670	1.06×10^{-4}	1.0	0.0107	2.27×10^{-3}
2	1.9670	1.06×10^{-4}	1.0	0.0190	4.04×10^{-3}
3	1.9670	1.06×10^{-4}	1.0	0.0339	7.22×10^{-3}
4	1.9670	1.06×10^{-4}	1.0	0.0499	10.6×10^{-3}

The four samples were then placed in polymerization tubes, frozen in liquid nitrogen and degassed under vacuum, then thawed. This procedure was repeated three times, then the tubes were sealed off under vacuum while still frozen at the completion of the third cycle. The tubes were placed in a Nujol bath at 60°C and allowed to remain 3 days, after which they were opened and the polymer precipitated by pouring into methanol. Conversions of approximately 50 percent were obtained.

The intrinsic viscosities of the four samples were then determined in toluene at 25°C with a Cannon-Ubbelohde dilution viscometer.

In order to determine the degrees of polymerization of these samples, use was made of the somewhat questionable Breitenbach-Forster relationship[20]

$$\log [\eta] = - 3.10 + 0.575 \log P_n$$

where $[\eta]$ is the intrinsic viscosity of poly p-chlorostyrene in liter/gm in toluene at 25°C, and P_n is the number average degree of polymerization.

Further discussion of the use of this equation will be given in the Section "Molecular Weight Determination". It remains, for the present, however, the most reliable published relationship. Results of these determinations

are tabulated below:

Sample	$[\eta]$ liter/g.	P_n
1	0.0260	427
2	0.0173	214
3	0.0114	100
4	0.0074	83.8

From the plot of $1/P_n$ vs. (S)/(M) shown in Fig. 2 the slope C may be taken, and the value 1.1 is obtained. Furthermore, the results of the full scale polymerizations of three of the samples (PPCS Nos. 2, 3, and 4) to be discussed in the next sections comprise a check on this value. From a similar plot in Fig. 3, the result 1.1 is again obtained for C. A much different value of C of 5.2 has been reported,[21] but as two separate checks have given identical values of 1.1, and as our measurements cover a much wider range of P, we must regard our own value as far more reliable.

C.   Polymerization

For the dielectric measurements envisioned in this work, a coverage of a wide range of molecular weights was desirable. It was decided that four samples covering a range of approximately 5,000 - 500,000 in molecular weight

Figure 2.

$\frac{1}{P_n}$ vs. $\frac{(S)}{(M)}$ from C determination data.
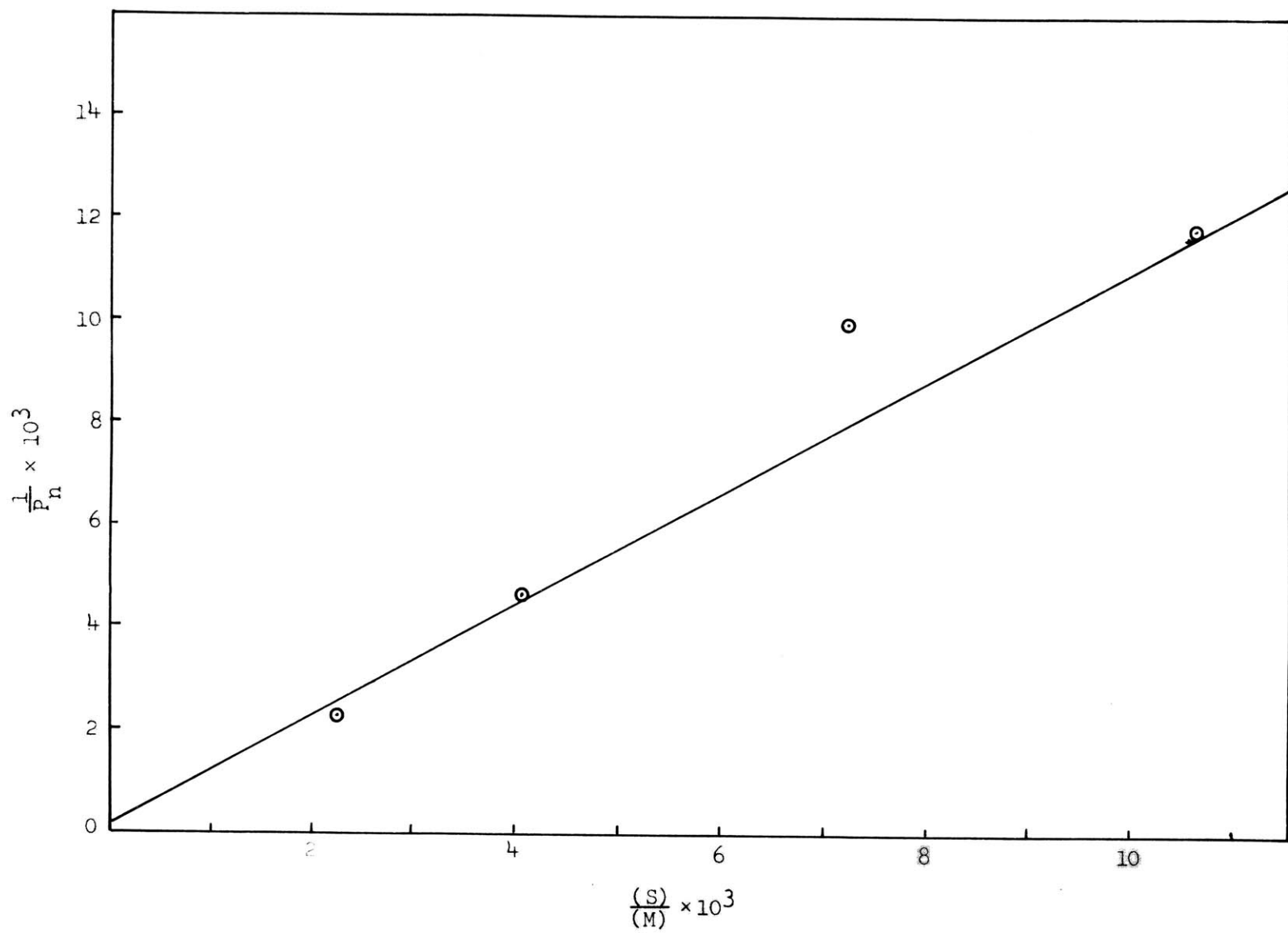
Figure 3.

$\frac{1}{P_n}$ vs. $\frac{(S)}{(M)}$ for PPCS Nos. 2, 3, and 4.
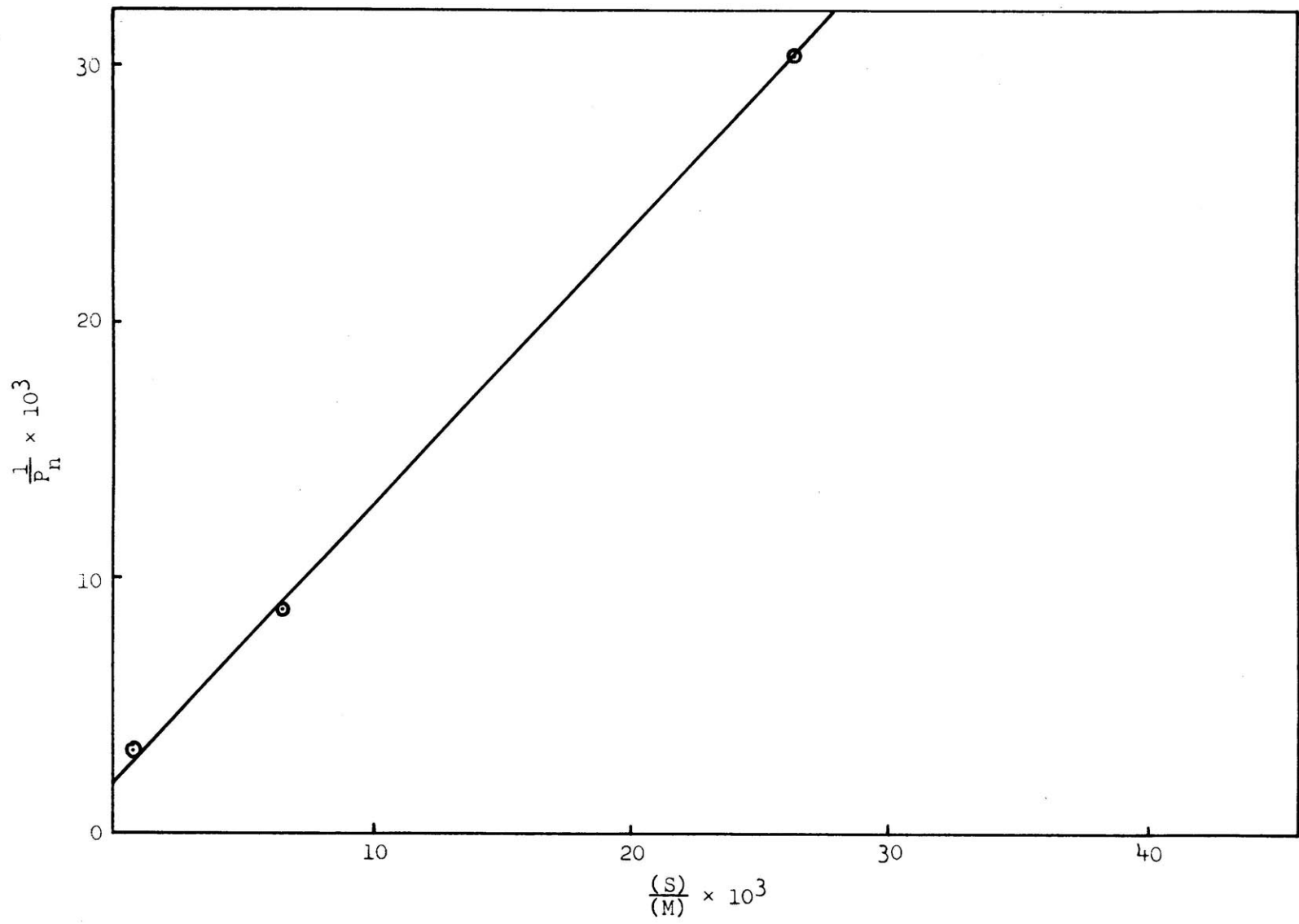
would be sufficient. The following solutions were prepared
accordingly:

Sample	p-chloro-styrene gms.	Benzoyl peroxide gms.	Benzene ml.	CBr$_4$ gms.
PPCS No.1	10.8	0.00204	10.0	0.0000
PPCS No.2	10.7	0.1250	8.0	0.0219
PPCS No.3	10.7	0.1250	8.0	0.1634
PPCS No.4	10.7	0.1250	8.0	0.6857

The solutions were degassed as previously described,
sealed and polymerized in the Nujol bath at 60°C for five
days. The tubes were then opened, the solutions diluted
with about 20 ml. of benzene, and the polymers precipitated
from methanol. For PPCS No.1, a conversion of 40 percent
was found; for the other three samples, conversions were
about 90 percent.

Microanalytical determinations of the chlorine contents
of these polymers were performed by Dr. Stephen Nagy in the
M.I.T. Microanalytical Laboratory, with the following results:

Sample	% Cl
Theoretical	25.58
PPCS No.1	26.49
PPCS No.2	26.37
PPCS No. 3	24.93
PPCS No. 4	26.34

These measurements indicate that no extensive cross linking has taken place through chain transfer with ring chlorine.

D. Molecular Weight Determination

To determine the molecular weights of these polymers, intrinsic viscosities were measured in toluene at $25^{\circ}C$ and the degrees of polymerization calculated with the Breitenbach-Forster relationship, as previously described. The results were:

Sample	$[\eta]$ liters/gm.	P_n	M_n
PPCS No.1	0.085	3750	480,000
PPCS No.2	0.0215	320	41,800
PPCS No.3	0.0121	115	15,900
PPCS No.4	0.00592	32.8	4,450

The validity of the use of the Breitenbach-Forster equation must now be examined in greater detail. In their original work, Breitenbach and Forster prepared by thermal polymerization five samples of poly p-chlorostyrene. The molecular weights of the unfractionated polymers were measured by osmotic pressure determinations in methyl ethyl ketone, and were found to range between 179,000 and 618,000. The intrinsic viscosities of these polymers were then

measured in toluene, and log $[\eta]$ was plotted against log M to determine the parameters $\underline{K}$ and $\underline{a}$ in the Mark-Houwink empirical equation

$$[\eta] = KM^a$$

They obtained as the results:

$$[\eta] = 4.68 \times 10^{-5} (M)^{0.575}$$

where $[\eta]$ is expressed in liters/gm. In terms of degree of polymerization, they obtained

$$\log [\eta] = - 3.10 + 0.575 \log P_n$$

which is the relation used in our calculations.

Unfortunately, the use of unfractionated polymer in osmotic pressure determinations leaves their work open to serious question. Furthermore, even if the Breitenbach-Forster relationship were beyond serious question in the range which they covered, its applicability to our low molecular weight polymers would be somewhat doubtful, as the extrapolation of their equation down to molecular weights as low as 5,000 may not be valid.

Another relationship, $P_n = 6.9 [\eta]^{1.29}$, where $[\eta]$ is measured in cm^3/gm, has also been reported for PPCS in benzene.[21] This was also determined by osmotic pressure measurements on unfractionated polymer, and the molecular weight range covered is less wide than that covered by the

Breitenbach-Forster measurements, so no advantages can be seen for its use over that of Breitenbach and Forster.

A light scattering investigation of two of our samples was undertaken in this laboratory by Mr. A. T. Guertin and Mr. R. E. Bacon. The results they obtained are:

Sample	M_w (light scattering)	M_n (B. F. equation)
PPCS No.2	109,000	41,800
PPCS No.3	44,900	15,900

Since for the "most probable" distribution of chain lengths, $M_w/M_n = 2$,[17] these measurements are in much better agreement than they appear. The fact that the ratio of M_w to M_n in these polymers is about 2.5 indicates that our distribution is somewhat broader than the most probable distribution.

E. The Solvent

Most of the previous dielectric measurements on the poly chlorostyrene systems made in this laboratory have been made in toluene solution. This requires, however, that most measurements be made at temperatures well below $0^{\circ}C$, in order to bring the loss region of the solution within the frequency range which can be covered by the bridge. The difficulties of operating at low temperatures suggested that a more viscous solvent be sought.

Ortho-terphenyl, or ortho diphenyl benzene, had been used as a solvent for dielectric measurements of simple polar molecules by Winslow, Good, and Berghausen.[22] They reported that it was extremely viscous (on the order of one poise), particularly when supercooled, and that it showed no dielectric loss whatever at frequencies up to one megacycle at $0^\circ C$. When preliminary tests indicated (somewhat erroneously, as it developed) that it was also a good solvent for poly p-chlorostyrene, ortho-terphenyl (o-t) was chosen as the solvent for this work.

Ortho-terphenyl is commercially available under the trade name "Santowax-O" from the Organic Chemicals Department of Monsanto Chemical Company, St. Louis, Mo. The material as supplied consists of rather yellowish lumps, but is easily recrystallized from boiling ethanol to yield fine white needles, mp. $56.5^\circ C$.

This material is readily supercooled, if a little care is taken to eliminate dust particles. Filtered samples have been maintained in the liquid state at room temperature for several weeks or longer with no tendency toward crystallization. This ease in supercooling might perhaps be expected from the molecular structure of the compound.

F.   Viscosity Measurements on Ortho-Terphenyl

The viscosity of pure ortho-terphenyl has been measured as a function of temperature in two Ostwald viscometers, a size 200 and a size 400, which were calibrated with glycerol-water mixtures. All measurements were made at flow times long enough that kinetic energy corrections could be assumed negligible. For any simple Newtonian liquid in a viscometer

$$\eta = A\rho t - B\rho/t \cong A\rho t$$

where η is the absolute bulk viscosity of the liquid
in poise

ρ is the density in gm/ml

t is the flow time in seconds

and   A and B are calibration constants.

For the two viscometers used in this work:

Viscometer Size	Number	$\dfrac{A \ \text{(poise)}}{\text{(gm/ml)(sec.)}}$
200	C288	1.223×10^{-3}
400	E477	1.24×10^{-2}

The measured density of liquid ortho-terphenyl at 60°C is 1.064 gm/ml. As a measurement of the temperature dependence of density was not considered worthwhile, we have taken the coefficient of volume expansion to be 10^{-3} deg.$^{-1}$, and have calculated approximate densities for

each temperature. Viscosities were then calculated, and
the data are given in the following table, and appear
plotted in Fig. 4.

Temperature	Viscometer Size	Density g/cc.	Viscosity poise
65°C	No. 200	1.06	0.19
60°C	No. 200	1.064	0.26
55°C	No. 200	1.07	0.37
50°C	No. 200	1.07	0.56
45°C	No. 200	1.08	0.88
45°C	No. 400	1.08	0.88
42.5°C	No. 400	1.08	1.1
40°C	No. 400	1.09	1.5
37.5°C	No. 400	1.09	2.0
35°C	No. 400	1.09	2.7

As may be seen from the plot in Fig. 4, the slope
remains constant from 65°C down to about 45°C, and yields
an activation energy for viscous flow of 15.7 Kcal/mol.
Below 45°, the slope gradually increases until activation
energies of 25 Kcal/mol. or more are observed.

G.   Preparation of Solutions

Solutions were prepared of the four samples of PPCS
in ortho terphenyl on a weight percent basis, since both
polymer and solvent are solids at room temperature.

Figure 4.

Log viscosity of ortho-terphenyl vs. $\frac{1}{T}$.
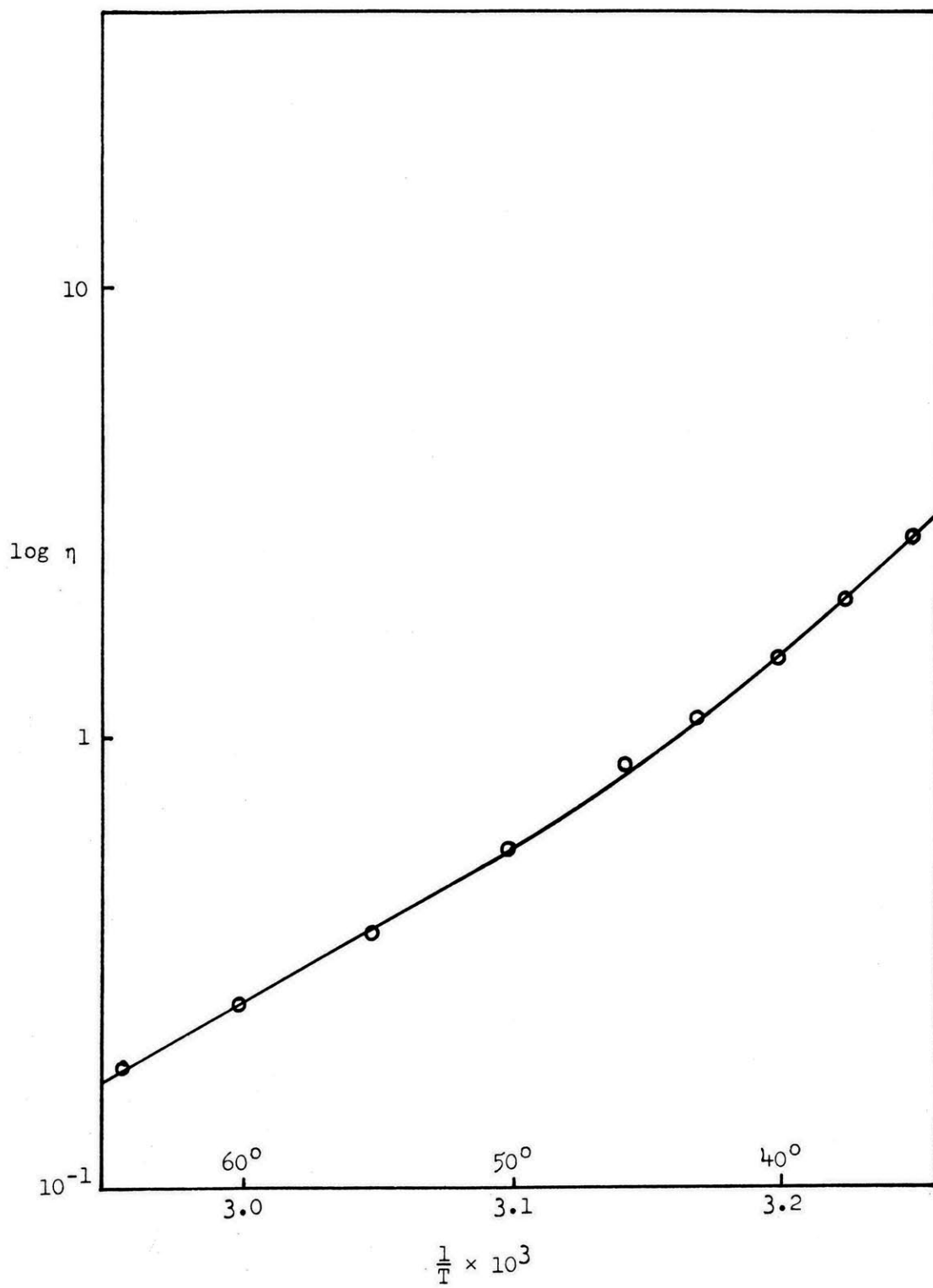
Twenty percent by weight solutions of each polymer sample
were prepared by loosely mixing the two solids, then
heating in the oil bath at 60°C until solution took place.
The highest molecular weight sample, PPCS No. 1, dissolved
very slowly and the solution was extremely viscous. The
process was hastened somewhat by occasional brief heatings
to 100°C in a drying oven. Eventually, however, homogeneous
solutions were achieved in each case at 20 percent concen-
tration.

The solutions of lower concentration used in this work
were in each case prepared by dilution of these more
concentrated solutions. It was found that for the two lower
molecular weight samples, PPCS No. 3 and No. 4, homogeneous
solutions were obtained at all concentrations between
5 percent and 20 percent polymer concentration. Complications
arose with the dilution of solutions of the higher molecular
weight samples, however. It appears that with PPCS No. 1,
and, to a lesser extent with PPCS No. 2, metastable solutions
are formed when attempts are made to prepare 5 - 15 percent
solutions. After several hours, these "solutions" separate
into two liquid phases, a polymer-rich phase and a solvent-
rich phase. The polymer-rich phase is probably about
20 percent polymer, while the solvent rich phase is quite
dilute, certainly less than 5 percent. It happens that the
refractive indices of the two phases are very nearly the

same, and it is extremely difficult to ascertain by visual observation when phase separation takes place.

While it may seem surprising at first glance that the dilution of a solution could lead to phase separation, this phenomenon is easily understandable from a consideration of the theory of liquid-liquid phase behavior in polymer solutions.[23]   A detailed theoretical treatment of this problem will not be attempted here;   suffice it to say that the great difference in size of the polymer and solvent molecules leads to dissymmetry in the partial miscibility curves of two component systems in which one component is a macromolecule. As an illustration, the phase diagrams for three polyisobutylene fractions in di-isobutyl ketone are given in Fig. 5 (after Flory). While the specific temperatures and concentrations shown here are not directly applicable to our system, the analogy is clear.

It appears that the temperatures used in this work ($\sim$ 40-60°C) are above the critical solution temperatures for PPCS No. 3 and No. 4 solutions; therefore complete miscibility is observed. For PPCS No. 1 and No. 2, however, dilutions from 20 percent (which is apparently in the one phase region for all four samples) shift the concentrations into the two phase region. A few more exploratory experiments indicated that the critical solution temperature for PPCS No. 2 solutions is reached around 70°C, but it was not

Figure 5.

Phase diagram for three isobutylene fractions (molecular
weights indicated) in di-isobutyl ketone.

55°

50°   6,000,000

T°C   285,000

45°

40°

35°

20°

                       22,700
15°

10°
    0.00   0.10   0.20

Volume Fraction of Polymer
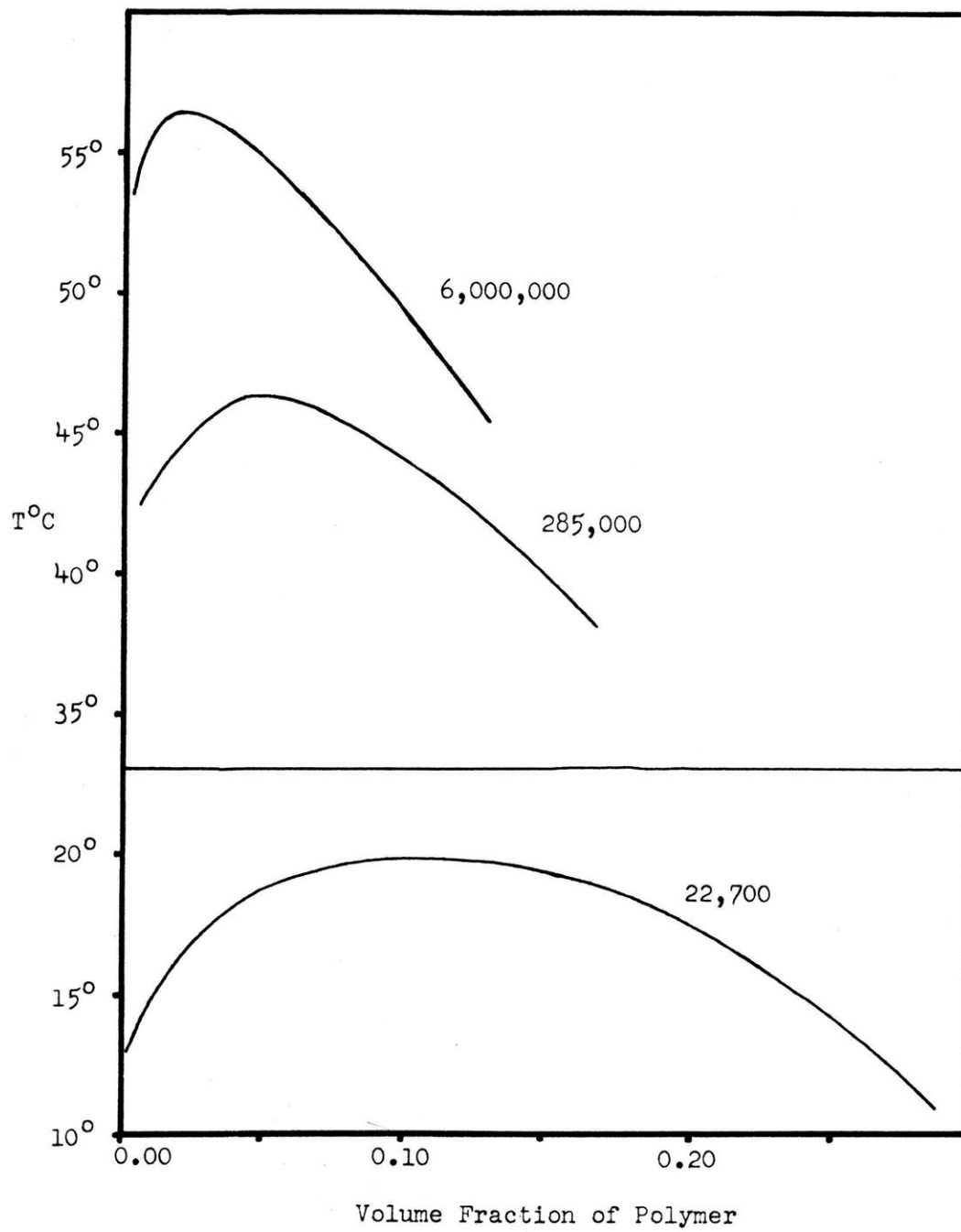
possible to obtain homogeneous solutions of PPCS No. 1 at

10 percent and 15 percent at any temperature up to 120°C.

This observed phase behavior poses considerable problems in

the interpretation of the dielectric measurements; a

consideration of its effects will, however, be reserved

until after the dielectric data have been presented.

H.   Intrinsic Viscosity Measurements in Ortho-Terphenyl

No actual measurements were made on the bulk viscosity

of the 20 percent solutions, partly because of their

extremely high viscosity, and partly because theory indicates

no dependence on the bulk viscosity of the solution, but

only on the "local" viscosity, which in dilute solution should

be simply that of the pure solvent.

The intrinsic viscosities of the PPCS samples in ortho

terphenyl are, however, quantities of considerable theoretical

interest, so measurements have been made of $[\eta]_{o-t}$ for PPCS

Nos. 2, 3, and 4.   PPCS No. 1 proved impossible to measure,

as solutions could not be obtained at any useful concentration

due to phase separation.   The viscosities were measured at

60°C in the previously mentioned size 200 Ostwald viscometer.

The flow time for pure o-terphenyl was 198.6 seconds.

The following values were found for $[\eta]$ in ortho terphenyl,

with the values in toluene given for comparison:

Sample	$[\eta]$ ortho terphenyl	$[\eta]$ toluene cc/g.
PPCS No. 1	---	85.0
PPCS No. 2	12	21.5
PPCS No. 3	9	12.1
PPCS No. 4	6	5.9

It should be noted that while the intrinsic viscosities in the two solvents are about the same for PPCS No. 4, the values in o-terphenyl are considerably lower than those found in toluene for PPCS No. 3 and No. 2, and presumably for No. 1. This is to be expected, for intrinsic viscosities are in general lower in poorer solvents, and this difference becomes more pronounced with increasing molecular weight.

If log $[\eta]_{o-t}$ is plotted against log M_n as in Fig. 6, we find that $[\eta]$ varies as $M_n^{0.31}$. This is a very surprising result, since even in a solvent at its θ temperature, which is the temperature at which the attractive and repulsive interactions between polymer and solvent molecules become equal, $[\eta]$ varies as $M^{1/2}$. As a general rule, polymers do not remain in solution at temperatures very far below the θ temperature for the system, and therefore dependences of $[\eta]$ on M to powers less than 0.5 are seldom observed.

Figure 6.

Log $[\eta]_{o-t}$ vs. log M_n for PPCS Nos. 2, 3, and 4.
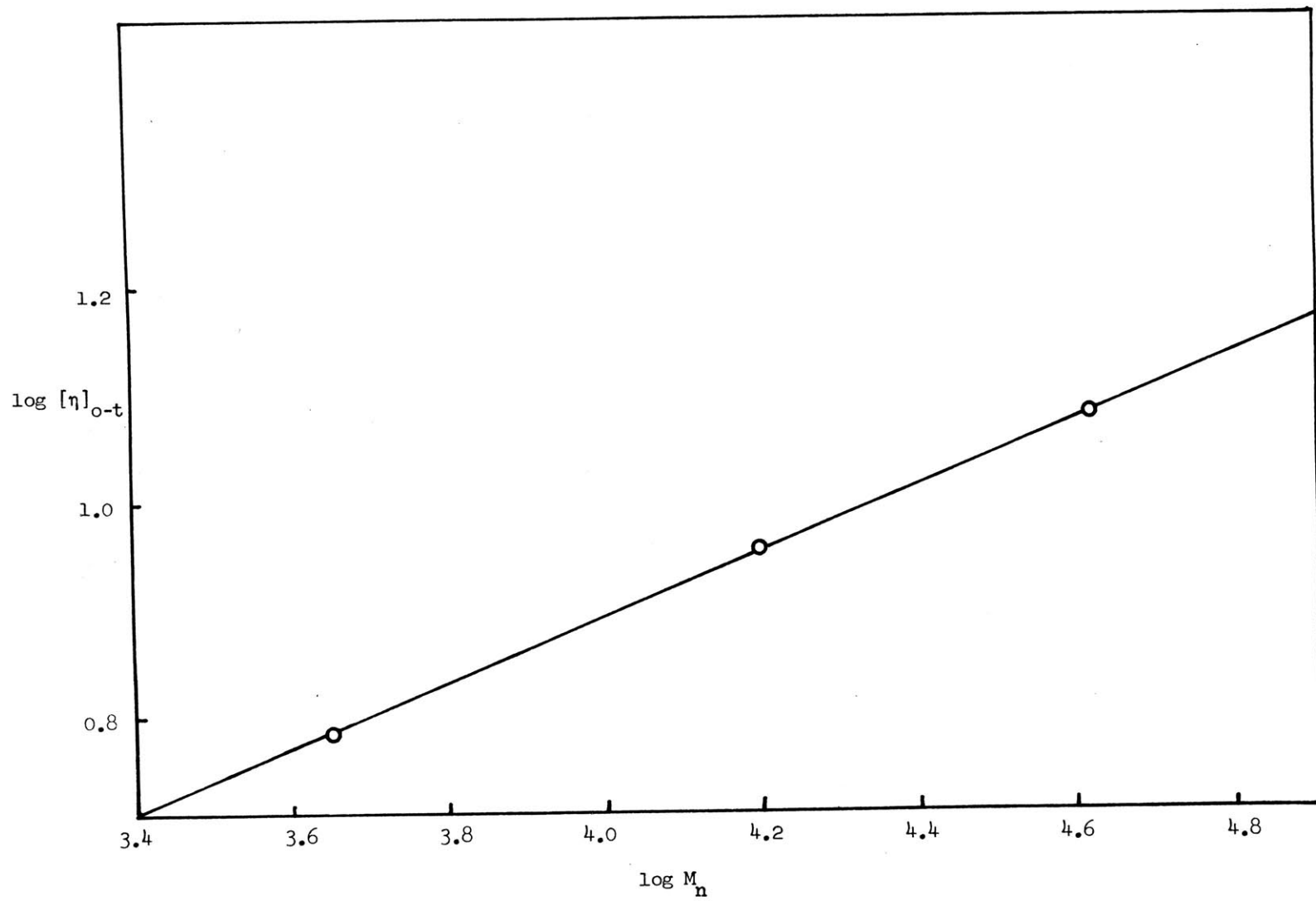
Meyerhoff[24] and Schultz, however, have reported that, for solutions of polystyrene in benzene, polymethylmethacrylate in benzene, and polyisobutylene in di-isopropyl ketone, the slopes of plots of log $[\eta]$ vs. log M decrease noticeably to values less than 0.5 at very low molecular weights ($M_n = 10^3 - 10^4$). Meyerhoff has attributed this to a serious departure from random flight statistics at low M, since the chain is relatively more extended at low M than at high M. Thus our measurements indicate a similar departure from random flight statistics in the poly p-chlorostyrenes in ortho-terphenyl solutions at the three molecular weights investigated. This would indicate that the poly p-chlorostyrene chain is unusually stiff, since the molecular weight range which we investigated includes somewhat higher molecular weights than the range in which such departures were found in other polymer-solvent systems.

IV DIELECTRIC RELAXATION DATA

The real dielectric constant, ε', and the loss factors, ε'', have been measured for solutions of the four samples of poly p-chlorostyrene as functions of frequency, temperature, and concentration. The frequency range covered was from $2 \times 10^2 - 5 \times 10^5$ c.p.s.; the temperature range was $40^{\circ}C - 60^{\circ}C$; and the concentration range was, in most cases, $5 - 20$ percent by weight. These data will now be presented in detail.

PPCS No. 1 - 20 %				

	T = 60°C		T = 55°C	
f(cps.)	ϵ'	ϵ''	ϵ'	ϵ''
2×10^2	2.918	0.000	2.984	0.000
5	2.918	0.000	2.978	0.010
1×10^3	2.912	0.007	2.971	0.021
2	2.912	0.020	2.951	0.042
5	2.893	0.041	2.930	0.074
1×10^4	2.864	0.060	2.910	0.094
2	2.845	0.079	2.863	0.104
5	2.810	0.095	2.802	0.100
1×10^5	2.763	0.098	2.755	0.086
2	2.697	0.080	2.714	0.066
5	---	0.057	2.656	0.039

	T = 50°C		T = 45°C	
f	ϵ'	ϵ''	ϵ'	ϵ''
2×10^2	3.012	0.000	2.971	0.000
5	2.992	0.032	2.924	0.051
1×10^3	2.943	0.058	2.889	0.074
2	2.930	0.079	2.870	0.090
5	2.884	0.098	2.789	0.097
1×10^4	2.837	0.104	2.748	0.088
2	2.789	0.096	2.701	0.076
5	2.729	0.080	2.654	0.051
1×10^5	2.688	0.060	2.634	0.034

PPCS No. 1 - 15%				
	T = 60°C		T = 55°C	
f	ε'	ε''	ε'	ε''
2 × 10²	2.876	0.000	2.903	0.000
5	2.863	0.000	2.876	0.007
1 × 10³	2.863	0.009	2.870	0.021
2	2.856	0.012	2.856	0.036
5	2.850	0.033	2.829	0.053
1 × 10⁴	2.843	0.048	2.796	0.065
2	2.829	0.064	2.783	0.073
5	2.789	0.075	2.735	0.071
1 × 10⁵	2.748	0.070	2.721	0.061
2	2.714	0.058	---	0.042

T = 50°C		
f	ε'	ε''
2 × 10²	2.910	0.000
5	2.897	0.024
1 × 10³	2.870	0.049
2	2.843	0.054
5	2.816	0.070
1 × 10⁴	2.789	0.078
2	2.754	0.069
5	2.701	0.045
1 × 10⁵	2.667	----

PPCS No. 1 - 10 %				
	T = 60°C		T = 55°C	
f (cps.)	ε^{t}	ε''	ε^{t}	ε''
2×10^2	2.863	0.000	2.796	0.000
5	2.863	0.000	2.789	0.005
1×10^3	2.863	0.000	2.789	0.014
2	2.850	0.009	2.775	0.020
5	2.829	0.019	2.761	0.036
1×10^4	2.755	0.034	2.798	0.047
2	2.742	0.042	2.729	0.050
5	2.708	0.050	2.688	0.050
1×10^4	2.708	0.045	2.667	0.040
2	2.694	---	2.641	---

T = 50°C		
f	ε^{t}	ε''
2×10^2	2.829	0.000
5	2.829	0.010
1×10^3	2.816	0.023
2	2.789	0.043
5	2.755	0.049
1×10^4	2.742	0.054
2	2.714	0.049
5	2.694	0.040
1×10^4	2.688	0.028

PPCS No. 2 - 20%				
	T = 60°C		T = 55°C	
f	ε'	ε''	ε'	ε''
2×10^2	2.990	0.000	3.000	0.000
5	2.990	0.000	3.000	0.004
1×10^3	2.990	0.005	3.000	0.009
2	2.990	0.010	2.993	0.022
5	2.980	0.020	2.987	0.044
1×10^4	2.972	0.034	2.959	0.060
2	2.952	0.048	2.925	0.077
5	2.918	0.076	2.871	0.089
1×10^5	2.871	0.088	2.810	0.086
2	2.830	0.086	2.770	0.066
5	2.770	0.060	2.729	---

	T = 50°C		T = 45°C	
f	ε'	ε''	ε'	ε''
2×10^2	3.006	0.000	3.013	0.000
5	3.006	0.018	2.987	0.030
1×10^3	2.987	0.030	2.959	0.058
2	2.972	0.043	2.947	0.072
5	2.946	0.072	2.878	0.086
1×10^4	2.905	0.086	2.830	0.086
2	2.871	0.092	2.796	0.078
5	2.804	0.083	2.742	0.064
1×10^5	2.770	0.066	2.729	0.048
2	2.742	0.046	2.701	---
5	2.716	---	---	---

PPCS No. 2 - 15%				
	T = 60°C		T = 55°C	
f	ϵ'	ϵ''	ϵ'	ϵ''
2×10^2	2.910	0.000	2.910	0.000
5	2.910	0.004	2.917	0.002
1×10^3	2.910	0.009	2.923	0.010
2	2.904	0.014	2.910	0.021
5	2.904	0.022	2.876	0.038
1×10^4	2.889	0.029	2.869	0.050
2	2.876	0.041	2.850	0.059
5	2.856	0.056	2.829	0.066
1×10^5	2.829	0.063	2.796	0.060
2	2.783	0.054	2.762	0.048

	T = 50°C		T = 45°C	
f	ϵ'	ϵ''	ϵ'	ϵ''
2×10^2	2.938	0.000	2.938	0.000
5	2.930	0.010	2.923	0.014
1×10^3	2.917	0.027	2.889	0.034
2	2.889	0.041	2.863	0.052
5	2.863	0.051	2.822	0.066
1×10^4	2.829	0.060	2.796	0.065
2	2.809	0.066	2.768	0.060
5	2.768	0.057	2.735	0.047
1×10^5	2.748	0.046	2.708	0.036

PPCS No. 2 - 10%				
	T = 60°C		T = 55°C	
f	ε'	ε''	ε'	ε''
2×10^2	2.837	0.000	2.816	0.000
5	2.816	0.000	2.802	0.000
1×10^3	2.816	0.000	2.802	0.008
2	2.809	0.006	2.802	0.014
5	2.802	0.008	2.783	0.022
1×10^4	2.809	0.016	2.762	0.028
2	2.802	0.021	2.755	0.031
5	2.789	0.030	2.742	0.034
1×10^5	2.783	0.036	2.729	0.033
2	2.768	0.032	2.714	0.024

	T = 50°C		T = 45°C	
F	ε'	ε''	ε'	ε''
2×10^2	2.775	0.000	2.802	0.000
5	2.796	0.010	2.802	0.010
1×10^3	2.783	0.018	2.775	0.024
2	2.775	0.025	2.762	0.032
5	2.755	0.034	2.735	0.036
1×10^4	2.748	0.039	2.721	0.036
2	2.735	0.040	2.714	0.032
5	2.721	0.036	2.694	0.028
1×10^5	2.701	0.030	2.687	0.022

PPCS No. 2 - 5%				
	T = 60°C		T = 55°C	
f	ε'	ε''	ε'	ε''
2×10^2	2.735	0.000	2.701	0.000
5	2.721	0.000	2.701	0.000
1×10^3	2.708	0.000	2.701	0.000
2	2.708	0.000	2.701	0.004
5	2.708	0.000	2.694	0.010
1×10^4	2.694	0.008	2.681	0.012
2	2.687	0.010	2.694	0.014
5	2.681	0.014	2.681	0.014
1×10^5	2.675	0.012	2.667	0.012
2	2.634	0.006	2.662	0.008

T = 50°C		
f	ε'	ε''
2×10^2	2.721	0.000
5	2.721	0.000
1×10^3	2.714	0.000
2	2.708	0.008
5	2.701	0.016
1×10^4	2.694	0.018
2	2.687	0.020
5	2.681	0.018
1×10^5	2.662	0.014

PPCS No. 3-20%				
	T = 60°C		T = 55°C	
f	ε'	ε''	ε'	ε''
2×10^2	2.950	0.000	2.950	0.000
5	2.950	0.000	2.950	0.000
1×10^3	2.942	0.000	2.950	0.000
2	2.938	0.000	2.950	0.000
5	2.930	0.010	2.940	0.020
1×10^4	2.915	0.026	2.935	0.036
2	2.910	0.038	2.915	0.056
5	2.890	0.062	2.870	0.080
1×10^5	2.855	0.077	2.830	0.090
2	2.815	0.084	2.785	0.084
5	2.770	0.072	2.740	0.060

	T = 50°C		T = 45°C	
f	ε'	ε''	ε'	ε''
2×10^2	2.965	0.000	2.985	0.000
5	2.965	0.000	2.985	0.000
1×10^3	2.965	0.011	2.975	0.022
2	2.960	0.024	2.955	0.040
5	2.955	0.044	2.920	0.064
1×10^4	2.920	0.057	2.890	0.078
2	2.895	0.072	2.860	0.086
5	2.845	0.088	2.800	0.086
1×10^5	2.805	0.090	2.760	0.081
2	2.755	0.076	2.730	0.060
5	2.670	0.042	2.710	---

PPCS No. 3 - 20% (continued)		
T = 40°C		
f	ε'	ε''
2×10^2	2.960	0.000
5	2.945	0.010
1×10^3	2.920	0.030
2	2.890	0.049
5	2.850	0.074
1×10^4	2.810	0.082
2	2.770	0.082
5	2.725	0.070
1×10^5	2.700	0.056
2	2.670	0.036
5	2.635	---

PPCS No. 3 - 15%				
	T = 55°C		T = 50°C	
f	ε'	ε''	ε'	ε''
2×10^2	2.829	0.000	2.897	0.000
5	2.829	0.000	2.889	0.000
1×10^3	2.829	0.000	2.884	0.000
2	2.816	0.000	2.884	0.014
5	2.809	0.014	2.876	0.029
1×10^4	2.802	0.023	2.863	0.036
2	2.802	0.029	2.850	0.045
5	2.783	0.049	2.856	0.058
1×10^5	2.729	0.058	2.837	0.063
2	2.687	0.056	2.721	0.053
5	---	0.032	---	0.029

	T = 45°C		T = 40°C	
f	ε'	ε''	ε'	ε''
2×10^2	2.897	0.000	2.884	0.000
5	2.897	0.000	2.869	0.000
1×10^3	2.890	0.000	2.843	0.020
2	2.876	0.014	2.829	0.039
5	2.856	0.024	2.802	0.056
1×10^4	2.843	0.048	2.768	0.058
2	2.822	0.058	2.748	0.058
5	2.783	0.063	2.719	0.052
1×10^5	2.742	0.058	2.687	0.046
2	2.714	0.046	2.662	0.031

PPCS No. 3 - 10%				
	T = 55°C		T = 50°C	
f	ε'	ε''	ε'	ε''
2×10^2	2.694	0.000	2.714	0.000
5	2.687	0.000	2.714	0.000
1×10^3	2.694	0.000	2.708	0.000
2	2.694	0.000	2.701	0.000
5	2.687	0.000	2.701	0.010
1×10^4	2.687	0.004	2.694	0.018
2	2.681	0.012	2.687	0.024
5	2.675	0.024	2.675	0.034
1×10^5	2.654	0.032	2.657	0.036
2	2.635	0.028	2.650	0.030

T = 45°C		
f	ε'	ε''
2×10^2	2.735	0.000
5	2.729	0.000
1×10^3	2.721	0.000
2	2.714	0.008
5	2.701	0.020
1×10^4	2.694	0.028
2	2.681	0.034
5	2.662	0.037
1×10^5	2.641	0.035
2	2.612	0.026

PPCS No. 4 - 20%				
	T = 55°C		T = 55°C	
f	ϵ'	ϵ''	ϵ'	ϵ''
2×10^2	2.930	0.000	2.940	0.000
5	2.930	0.000	2.940	0.000
1×10^3	2.925	0.000	2.935	0.003
2	2.925	0.006	2.930	0.008
5	2.920	0.012	2.930	0.018
1×10^4	2.910	0.018	2.925	0.030
2	2.905	0.033	2.910	0.051
5	2.880	0.054	2.875	0.072
1×10^5	2.855	0.070	2.835	0.086
2	2.815	0.078	2.790	0.082
5	2.745	0.064	2.690	0.062

	T = 45°C		T = 40°C	
f	ϵ'	ϵ''	ϵ'	ϵ''
2×10^2	2.945	0.000	2.940	0.000
5	2.945	0.000	2.940	0.005
1×10^3	2.945	0.006	2.930	0.020
2	2.945	0.014	2.920	0.034
5	2.940	0.030	2.895	0.056
1×10^4	2.925	0.042	2.865	0.072
2	2.890	0.062	2.830	0.086
5	2.835	0.084	2.770	0.088
1×10^5	2.790	0.086	2.725	0.078
2	2.743	0.074	2.675	0.060
5	2.685	0.050	2.610	0.030

PPCS No. 4 - 15%				
	T = 50°C		T = 45°C	
f	ε'	ε''	ε'	ε''
2×10^2	2.904	0.000	2.910	0.000
5	2.904	0.000	2.917	0.000
1×10^3	2.897	0.000	2.917	0.000
2	2.889	0.004	2.910	0.008
5	2.889	0.012	2.897	0.022
1×10^4	2.897	0.018	2.889	0.030
2	2.884	0.030	2.856	0.044
5	2.863	0.050	2.822	0.062
1×10^5	2.822	0.062	2.748	0.066
2	2.789	0.063	2.742	0.059
5	2.687	0.054	---	---

T = 40°C		
f	ε'	ε''
2×10^2	2.917	0.000
5	2.917	0.000
1×10^3	2.917	0.007
2	2.904	0.020
5	2.884	0.036
1×10^4	2.869	0.048
2	2.850	0.066
5	2.816	0.070
1×10^5	2.762	0.060
2	2.735	0.050

PPCS No. 4 - 10%				
	T = 50°C		T = 45°C	
f	ε'	ε''	ε'	ε''
2×10^2	2.802	0.000	2.822	0.000
5	2.802	0.000	2.816	0.000
1×10^3	2.802	0.000	2.809	0.000
2	2.802	0.000	2.809	0.000
5	2.796	0.000	2.796	0.006
1×10^4	2.796	0.004	2.802	0.017
2	2.783	0.013	2.789	0.026
5	2.775	0.026	2.783	0.036
1×10^5	2.748	0.036	2.768	0.042
2	---	0.036	2.735	0.037

T = 40°C		
f	ε'	ε''
2×10^2	2.843	0.000
5	2.843	0.000
1×10^3	2.837	0.000
2	2.837	0.008
5	2.822	0.018
1×10^4	2.816	0.027
2	2.802	0.038
5	2.783	0.045
1×10^5	2.755	0.043
2	2.729	0.037

V DISCUSSION OF RESULTS

A. Extrapolation to Zero Concentration

The assumptions made in the development of the Kirkwood-
Hammerle theory (and most other theoretical treatments of
the dielectric relaxation of polymers in solution) render
the results applicable only to dilute solutions. It is,
therefore,necessary to investigate the concentration
dependence of the frequencies of maximum loss at each
temperature for each polymer before reaching any conclusions
as to the dependence of relaxation time on molecular weight
in this system.

For PPCS No. 1 and No. 2, the frequencies of maximum
loss seemed to be quite independent of concentration. While
the height of the loss peak was decreased corresponding to
the decrease in concentration, no shift was observed along
the frequency scale.   As an example, the loss peaks for
PPCS No. 2 at 50°C at 5, 10, 15, and 20 percent concentration
PPCS by weight are shown in Fig. 7.

For PPCS Nos. 3 and 4, however, a slight but definite
shift with concentration was noted. The loss peaks for
PPCS No. 3 at 50°C at 10, 15, and 20 percent are shown,
for example, in Fig. 8.   The observed concentration

Figure 7.

ε'' vs. log f for PPCS No. 2 at 50^OC at four concen-
trations.

Figure 8

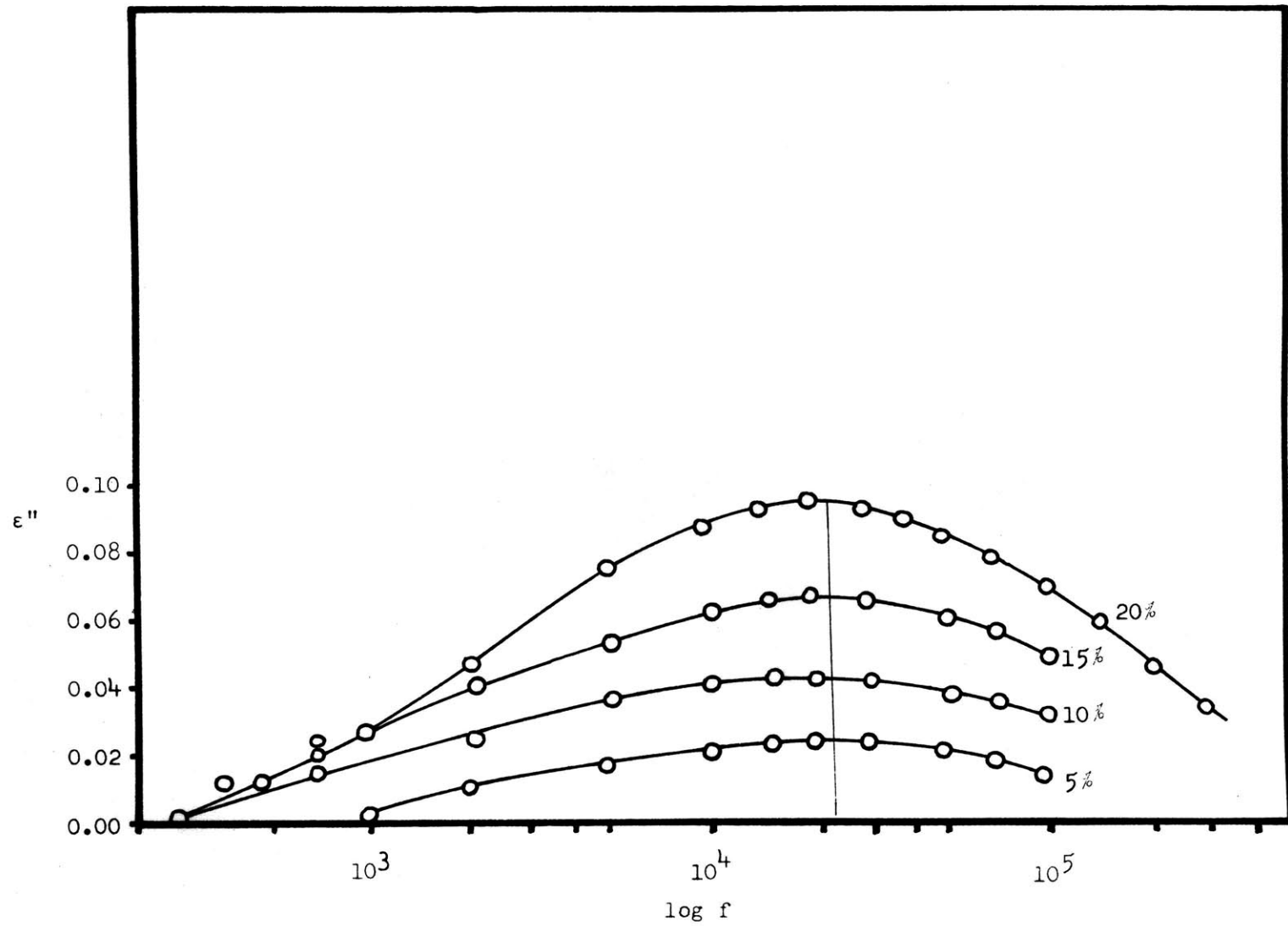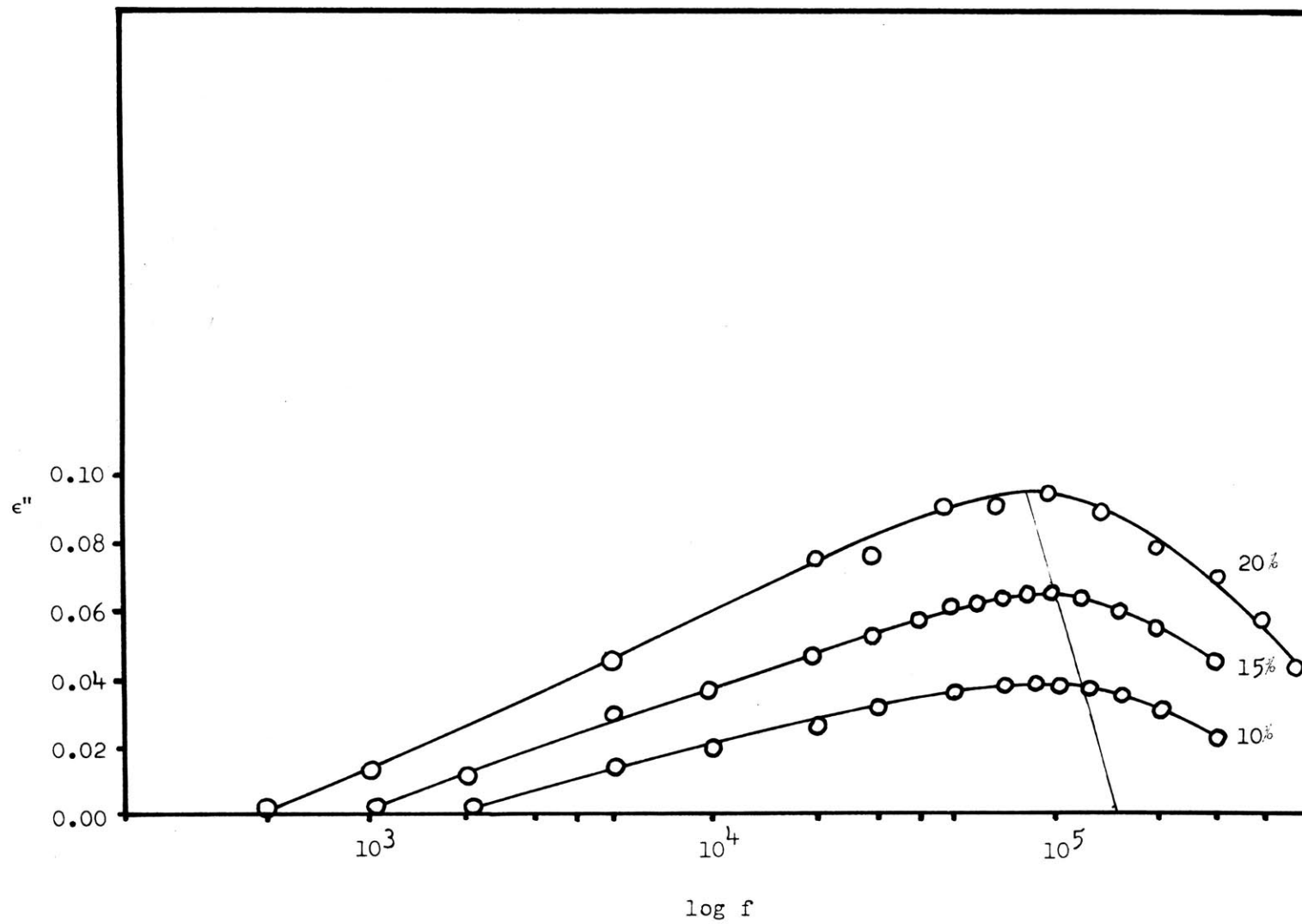ε'' vs. log f for PPCS No. 3 at 50°C at three concentrations.

dependences for PPCS Nos. 3 and 4 at several temperatures
are plotted in Fig. 9. It should be noted that the
dependence is about the same for PPCS No. 3 as for PPCS
No. 4 at any given temperature, and that the dependence
becomes less pronounced at higher temperatures.

This difference in the concentration dependence between
the two lower molecular weight samples and the two higher
molecular weight samples must be explained by a reconsider-
ation of the phase behavior of solutions of PPCS in ortho-
terphenyl. It will be recalled that in the cases of
PPCS Nos. 1 and 2, while homogeneous solutions were formed
at 20 percent by weight concentration, metastable solutions
were produced upon dilution, and separation into two bulk
phases eventually occurred. This did not occur with
PPCS Nos. 3 and 4. It must be concluded, then, that in
all probability the dielectric spectra measured with
solutions of PPCS Nos. 1 and 2 which have been diluted
below 20 percent are those characteristic of the two phase
mixture in which the polymer-rich phase is dispersed
throughout the solvent-rich phase. The environment
experienced by a relaxing polymer molecule is, then,
essentially still that found in a 20 percent solution, even
though the over-all concentration may be much less; thus
it is impossible to observe the actual concentration
dependence in solutions in which phase separation takes
place.

Figure 9

Summary of concentration dependences for PPCS
Nos. 3 and 4.

PPCS No. 4

PPCS No. 3

ε''_{max}

log f_m

69
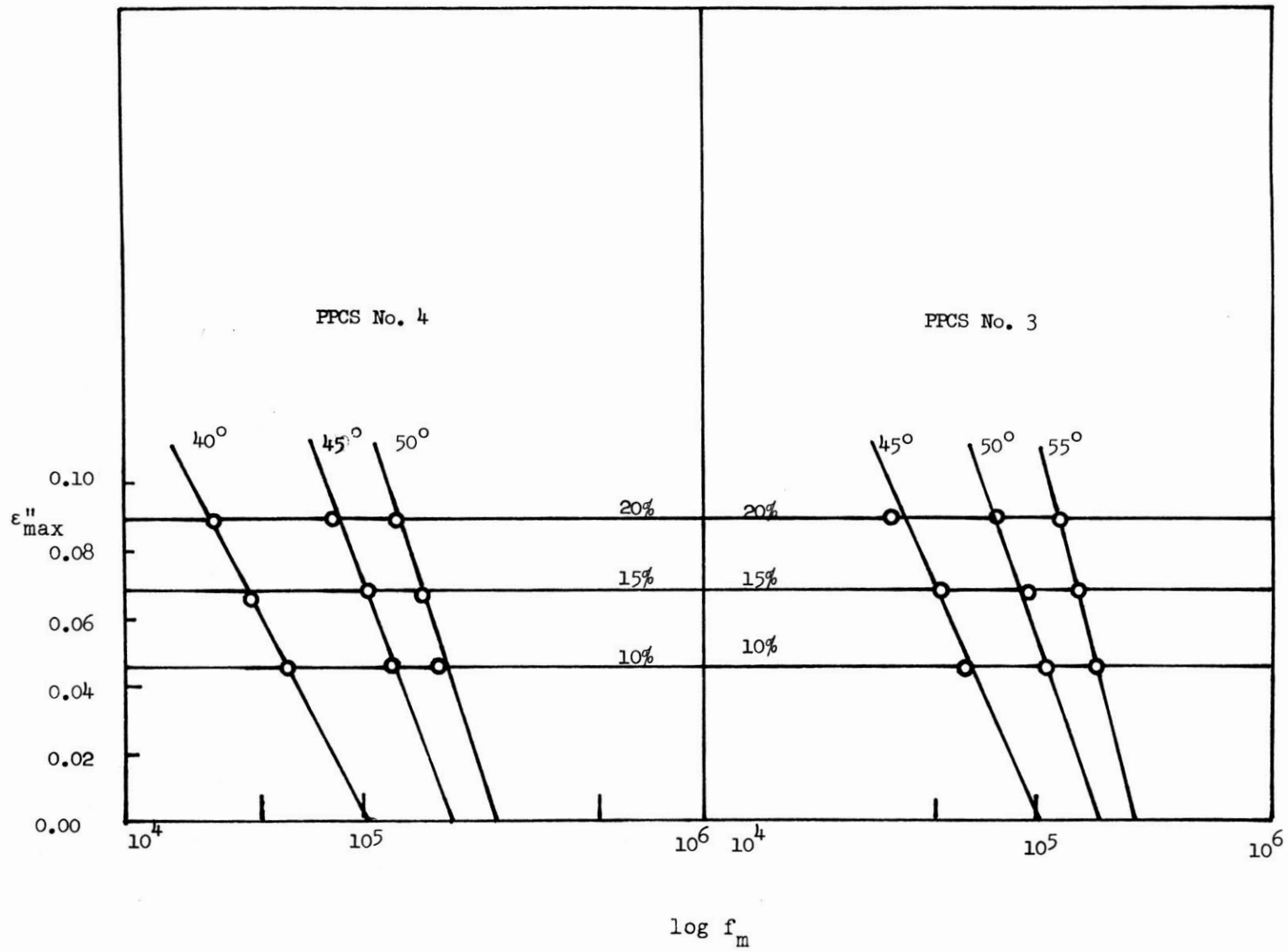
In order to interpret the results of the measurements of PPCS Nos. 1 and 2, an important assumption must be made. We will assume, in the absence of any acceptable alternative, that since the concentration dependence is similar for PPCS Nos. 3 and 4, the same dependence would be observed in Nos. 1 and 2. Since there is essentially no change in the concentration dependence over a three-fold variation in molecular weight between PPCS Nos. 4 and 3, it would be quite surprising to find a great change in the concentration dependence on further change in the molecular weight. The values of f_m for all four PPCS samples have been extrapolated to zero concentration along the curves for the various temperatures as shown in Fig. 9. The results are given in the following table.

CONCENTRATION DEPENDENCE OF PPCS IN SOLUTION						
Sample	T °C	$f_m \times 10^3$				$\tau_c^o \times 10^7$
		20%	15%	10%	0%(extrapolated)	
PPCS No.4	40	35	45	60	100	15.9
	45	80	100	120	180	8.9
	50	120	150	160	250	6.4
	55	200	-	-	350	4.5
	60	350	-	-	640	2.5
PPCS No. 3	40	15	20	-	44	35.4
	45	35	50	60	100	15.9
	50	70	90	100	150	10.6
	55	110	130	140	180	8.9
	60	200	-	-	350	4.5
PPCS No. 2	45	18			42	38
	50	37			79	20
	55	69			110	15
	60	130			210	7.5
PPCS No. 1	45	3.5			11	150
	50	8.8			20	77
	55	22			38	43
	60	44			72	22

We recognize that the validity of this procedure has not been conclusively demonstrated, and in fact that the possibility exists that a marked change in concentration dependence would be found with PPCS Nos. 1 and 2. Therefore,

one would, if he wishes, be justified in disregarding the
measurements on PPCS Nos. 1 and 2. The measurements on
PPCS Nos. 3 and 4 remain, though, and the essential
conclusions of our argument are not altered. We believe,
however, that all these measurements are probably valid,
and they have all been considered in the following
discussions.

B.   Molecular Weight Dependence of Relaxation Time

It is now possible to plot log τ_c^o versus log M to
evaluate the dependence of relaxation time on molecular
weight in solutions of poly p-chlorostyrene in ortho-
terphenyl.   Since we represent the dependence as
$\tau_c = KM^p$, the slope of such a plot should yield directly
the value of p.   Plots of log τ_c^o versus log M are given
at several temperatures in Fig. 10.   The following values
are obtained:

T ^{o}C	p
60	0.48
55	0.48
50	0.54
45	0.62

Two points should be noticed here: first, the values
of p are in the vicinity of 1/2, which is the Kirkwood-
Hammerle prediction; and second, there is a slight but

Figure 10.

Log τ_c^o vs. log M at four temperatures.

Molecular Weight Dependence
Poly p-chlorostyrene
$\log \tau_c^o$ vs. $\log M_n$
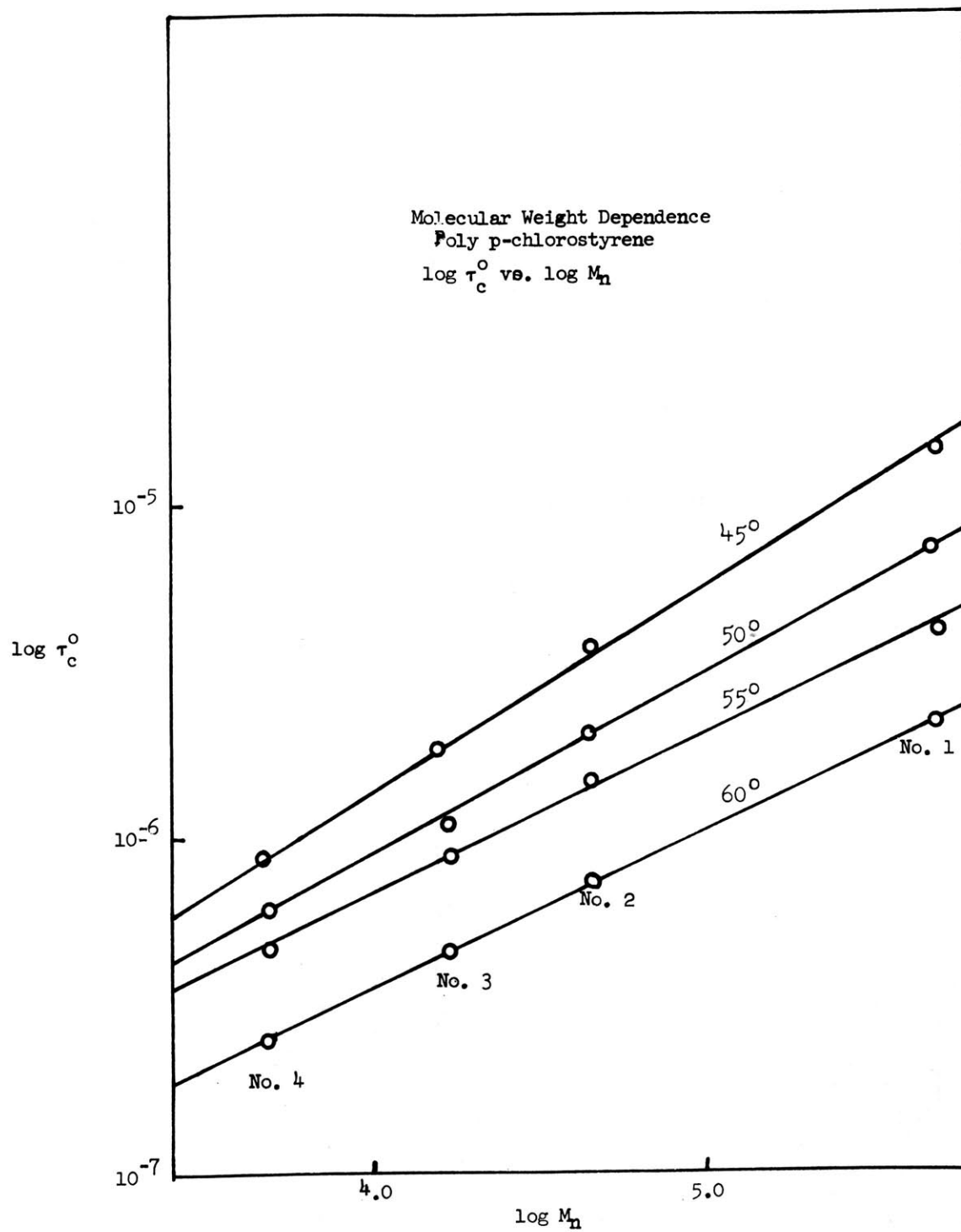
unmistakable increase in p̲ with decreasing temperature. The
consequence of these observations will be discussed in
Section G of this chapter.

C.   Temperature Dependence and Activation Energy

If dielectric relaxation is assumed to be an activation
process, then an activation energy for dielectric relaxation
may be calculated from the slope of a plot of log τ_c^o vs. 1/T.
Such a plot is given for each PPCS sample in Fig. 11, and
the activation energies so obtained are tabulated below,
with the activation energy for viscous flow over the
corresponding temperature range for the solvent.

Sample	Activation Energy for Dielectric Relaxation Kcal.
PPCS No. 1	28.7
PPCS No. 2	23.7
PPCS No. 3	21.2
PPCS No. 4	16.4

Sample	Activation Energy for Viscous Flow Kcal.
Ortho-terphenyl (50-65°C)	15.7

Figure 11.

Log τ_c^o vs. $\frac{1}{T}$ for the four PPCS samples.

Temperature Dependence
Poly p-chlorostyrene
$\log \tau_c^o$ vs. $1/T$
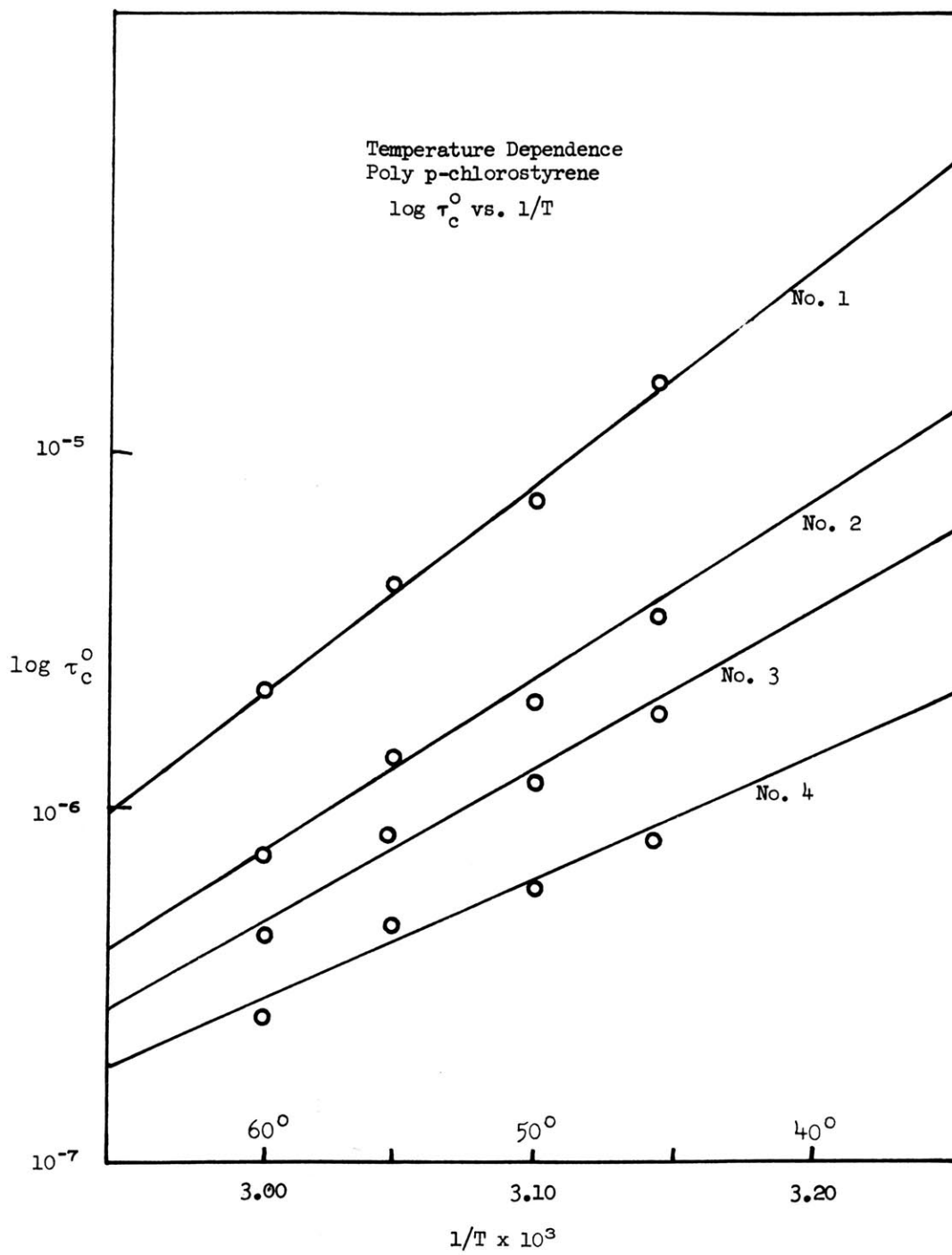
The Kirkwood-Hammerle prediction that the temperature
dependence of the relaxation process is governed by the
viscosity of the pure solvent (neglecting the effects of
the linear factor in T) seems to be realized only for the
lowest molecular weight sample. In each other case, the
temperature dependence is greater than would be predicted
by this theory.

D.   Quantitative Comparison of Measurements with Kirkwood-
Hammerle Theory.

A quantitative comparison of the predictions of the
Kirkwood-Hammerle theory with our measurements may now be
made. The Kirkwood-Hammerle equation for f_m, as modified
for our purposes in an earlier section, gives

$$f_m = \frac{0.044kT \; \Phi \; (4)^{3/2}}{\eta_o[\eta] \; M_1}$$

Using $\Phi = 2.1 \times 10^{23}$ (if $[\eta]$ is expressed in cc./g.),
$\eta_o = 0.56$ poise, and $M_1 = 139$, we may calculate the

values of f_m at, say, $50^\circ C$, with the following results:

Sample	$[\eta]$ o-terphenyl cc/g.	f_m (calculated) cps.	f_m (observed) cps.
PPCS No. 1	-	-	2.0×10^4
PPCS No. 2	12	3.4×10^6	7.9×10^4
PPCS No. 3	9	4.5×10^6	1.5×10^5
PPCS No. 4	6	7.1×10^6	2.5×10^5

It may be seen that the Kirkwood-Hammerle theory does not give quantitative agreement with the observed values. The theoretical predictions of f_m are more than a decade higher than the observed values, and the discrepancy becomes more pronounced with increasing molecular weight. Obviously, the actual relaxation process which occurs in solutions of poly p-chlorostyrene in ortho-terphenyl is much slower than the process envisioned by Kirkwood and Hammerle.

A further test of the theory may be made if we return to the original Kirkwood-Hammerle equation, and estimate the value of $\underline{a}$, the effective bond length, from the observed f_m and the weight average degree of polymerization $\underline{n}$. Let us take, for example, PPCS No. 3 at $50^\circ C$. The weight average molecular weight of this sample is 44,900, and the degree of polymerization if 323; f_m is found to occur at 1.5×10^5 cycles/second.

$$f_m = \frac{0.044kT}{n^{1/2}a^3\, \eta_o}$$

$$a = 11 A^o$$

For comparison, let us calculate a from the intrinsic viscosity data.

$$[\eta] = \frac{\Phi(\overline{\ell^2})^{3/2}}{M}$$

$$[\eta] = 9.0 \text{ cc/g.}$$

$$\Phi = 2.1 \times 10^{23}$$

$$M = 44,900$$

$$\overline{\ell^2} = 1.55 \times 10^{-12} \text{ cm.}^2$$

$$a^2 = \overline{\ell^2}/4n$$

so

$$a = 3.5 \ A^o$$

Similar calculations for PPCS No. 2 also at 50° lead to an a value of 11.6 A^o from the Kirkwood-Hammerle equation, and to an a value of 2.8 A^o from viscosity data. The agreement here is really quite poor. While 2.8-3.5 A^o for a as compared with the actual bond length of 1.5 A^o are quite reasonable values for the effective bond length, as may be seen from Flory's table [25] of calculated and observed $\overline{\ell^2}$ value for a number of polymers, the Kirkwood-Hammerle predictions of about 11 A^o are obviously far too large.

One final investigation of the Kirkwood-Hammerle theory may be made through a comparison of the predicted and observed half-widths of the loss peaks. The width of this peak is determined by the nature of the distribution of relaxation times about the critical value τ_c. Kirkwood and Hammerle give a function $H(x)$, which is a reduced loss curve for a system having their predicted distribution of relaxation times, $G(\tau) = \dfrac{2\tau\tau_c}{(\tau + \tau_c)^3}$. The peak has a maximum of 0.315, and the frequency scale is plotted as $\log \omega/\omega_m$. If we reduce our ε'' data in a similar fashion, we may easily compare the half widths of the predicted and observed loss peaks. This has been done for all peaks at 20 percent concentration, and excellent agreement has been found in each case. The comparison for PPCS No. 2 is shown as an illustration in Fig. 12. However, as is pointed out in Section G, this is not necessarily a triumph for this theory.

E. Dielectric Measurements of Marchal and Kryszewski on Polyvinyl Bromide; Comparison of these Results with Kirkwood-Hammerle Theory.

Let us now consider the results of Marchal and Kryszewski,[13] who, as was mentioned earlier, have measured samples of polyvinyl bromide ranging in molecular weight from 8,500 to 91,300 over a frequency range of 1-32 megacycles/second at -30°C and -15°C, in solutions of

Figure 12.

ε''(reduced) and Kirkwood-Hammerle $H(x)$ vs.

$$\log \frac{\omega}{\omega_{max}} \ .$$

Kirkwood-Hammerle H(x)

- - - - ϵ'' reduced

$\log \omega/\omega_{max}$
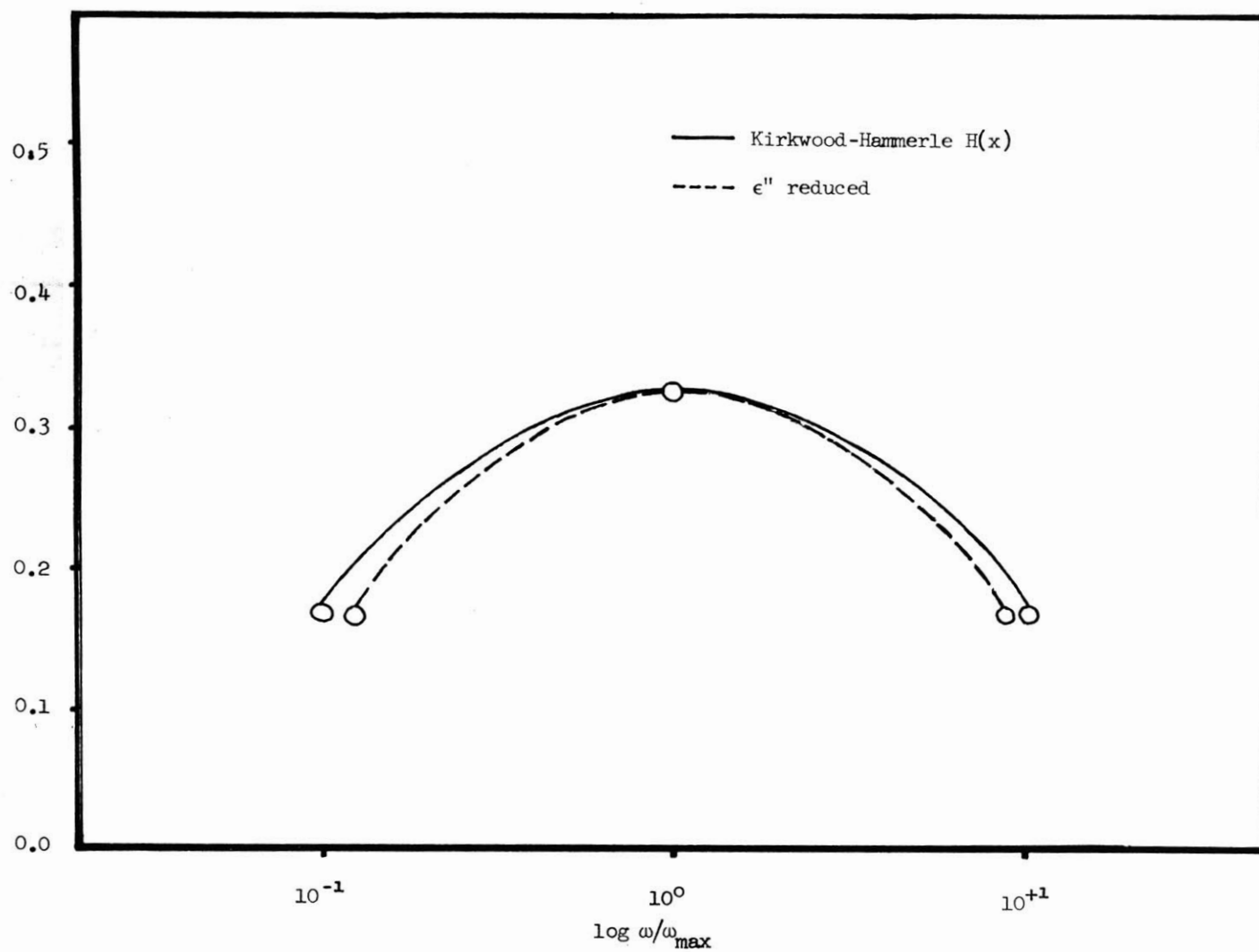
cyclohexanone and of tetrahydrofuran. They report no
dependence of relaxation time on molecular weight. These
measurements flatly contradict the predictions of the
Kirkwood-Hammerle theory. A quantitative comparison of
the predicted and observed relaxation times would be of
interest, however, so we have obtained, from their work
and other sources, the values of the necessary parameters
for this calculation. By extrapolation of viscosity-
temperature data for cyclohexanone given in the International
Critical Tables[28] down to -15°C, we have obtained the
value 0.046 poise, and have decided to make the comparison
in this solvent at this temperature. Values of $[\eta]$ in
cyclohexanone were calculated from the values of $\underline{K}$ and $\underline{a}$
in the Mark-Houwink equation $[\eta] = KM^a$, which have been
determined by Ciferri, Kryszewski, and Weill.[27] The
temperature dependence of $[\eta]$ was neglected, as it should
no doubt be small. Values of f_m were then calculated with
the modified form of the Kirkwood-Hammerle equation.

Polyvinyl Bromide in Cyclohexanone T -15°C					
Sample (their notation)	M_w	$[\eta]$ cc/g.	f_m (theor.) cps.	τ_c (theor.) sec.	τ_c (obs.) sec.
No. 1	91,300	17.4	3.1×10^7	5.3×10^{-9}	6×10^{-9}
No. 11	8,500	4.8	11.0×10^7	1.4×10^{-9}	6×10^{-9}

The relaxation times actually observed are certainly
within an order of magnitude of the predicted times.

The observed times are, however, still slightly longer than those predicted.

Since measurements at two different temperatures are presented in this paper, it is possible to calculate values for the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for dielectric relaxation for polyvinyl bromide in cyclohexanone. The values found for $\Delta H^{\ddagger}$ are around 1000 cal/mol., and for $\Delta S^{\ddagger}$, values of about -16 cal./deg. are observed. Both of these values are somewhat surprising. The $\Delta H^{\ddagger}$ values for dielectric relaxation are smaller than $\Delta H^{\ddagger}$ for viscous flow of the solvent, which is about 3,300 cal./mol., and it is also smaller than $\Delta H^{\ddagger}$ for rotation about C-C bonds in vinyl polymers, which should be somewhere between 3,000 and 6,000 cal./mol. The entropy value is surprising because it is negative; this means that the transition state is more ordered than the normal state of the molecule, and as we have seen from the $\Delta H^{\ddagger}$ values, it is only slightly higher in energy. These observations do not necessarily cast doubt on the validity of these measurements, but the findings are rather unusual. We shall, however, accept these measurements as reliable for the time being, in the absence of any compelling evidence to the contrary, and in the absence of any other published data on comparable systems.

F.   Comparison with the Predictions of the Zimm Theory

As was pointed out earlier, Zimm[6] has treated the problem of the concerted relaxation of all segments of the

polymer molecule, i.e., the orientation of the end-to-end
vector. Specifically, he obtained for the case of over-
whelming hydrodynamic interaction,

$$\tau = \frac{M \, \eta_0 \, [\eta]}{0.586 \; RT(4.04)}$$

and for the free draining case,

$$\tau = \frac{12 \, \eta_0 \, M[\eta]}{\pi^2 \, RT}$$

A similar result differing only slightly in the constant
factors has been derived by Kirkwood and Auer for the
relaxation of rigid rods in solution.[28] The essential
conclusions are, therefore, approximately independent of the
details of the model used in obtaining them.

We have calculated the relaxation times which would be
predicted by the first equation for all the polymer samples
which we have previously considered, since strong hydro-
dynamic interactions seem likely in these systems.   The
results are tabulated along with the observed values
and the values obtained from the Kirkwood-Hammerle
equation in the following table:

Poly p-chlorostyrene in o-terphenyl at 50°C					
Sample	M_n	$[\eta]$ cc./g.	τ_{Zimm} sec.	$\tau_{c_{obs.}}$ sec.	$\tau_{c_{K.H.}}$ sec.
PPCS No.2	41,800	12	9.0×10^{-6}	2.0×10^{-6}	4.7×10^{-8}
PPCS No.3	15,900	9	2.6×10^{-6}	1.1×10^{-6}	3.5×10^{-8}
PPCS No.4	4,450	6	0.48×10^{-6}	0.64×10^{-6}	2.2×10^{-8}

Polyvinyl Bromide in Cyclohexanone at -15°C					
Sample	M_w	$[\eta]$ cc./g.	τ_{Zimm} sec.	$\tau_{c_{obs.}}$ sec.	$\tau_{c_{K.H.}}$ sec.
PVB No. 1	91,300	17.4	1.4×10^{-6}	6×10^{-9}	5.3×10^{-9}
PVB No. 2	8,500	4.8	3.6×10^{-8}	6×10^{-9}	1.4×10^{-9}

As can be seen from the table, the observed relaxation time for PPCS No. 4 and the time predicted by Zimm for orientation of the whole molecule are very nearly the same. Since for PPCS No. 4, the activation energy for dielectric relaxation is the same as the activation energy for viscous flow of the solvent, this correspondence should be maintained over wide ranges of temperature, and strongly indicates that in this sample, relaxation takes place by an orientation of the whole molecule. For the higher molecular weight samples of poly p-chlorostyrene, the observed relaxation times are somewhat shorter, though still much closer to the

Zimm predictions than to the Kirkwood-Hammerle theory. For polyvinyl bromide, on the other hand, the observed relaxation times are several orders of magnitude shorter than those predicted for orientation of the whole molecule.

It would appear that the poly p-chlorostyrene chain is much stiffer than that of polyvinyl bromide. We shall discuss this conclusion in more detail in the next section.

G.   Conclusions

We have now considered all the relevant experimental measurements at our disposal, and have made a number of comparisons of these data with various theoretical predictions. Let us now see what conclusions may be drawn as consequences of these investigations.

The Kirkwood-Hammerle distribution function $G(\tau) = \dfrac{2\tau \ \tau_c}{(\tau + \tau_c)^3}$ seems to give a good description of the actual distribution of relaxation times in the poly p-chlorostyrene - ortho-terphenyl system. The shape of the loss peak is, unfortunately, not strongly "theory sensitive", and a number of rather arbitrary distribution functions of somewhat different form can be used to fit bell-shaped curves of the type found in dielectric loss peaks. The success of the Kirkwood-Hammerle function in fitting the loss peak does not, then, necessarily validate the treatment.

The square root dependence of relaxation time on molecular

weight predicted by the Kirkwood-Hammerle theory, while found in solutions of poly p-chlorostyrene, is not found in solutions of polyvinyl bromide. Now polyvinyl bromide conforms much more closely to the model used by Kirkwood and Hammerle than does poly p-chlorostyrene. The failure of the theory to yield the observed molecular weight dependence in this system no doubt reflects the presence in this treatment of serious errors, which probably lie in the averaging procedure. The square root dependence of τ_c upon M found in poly p-chlorostyrene solutions must, then, not be interpreted as verification of the Kirkwood-Hammerle treatment, but rather as a reflection of some differences in the relaxation mechanisms between the two systems.

These differences may well lie in the internal barriers to rotation found in the two polymers. Polyvinyl bromide, while by no means a completely freely rotating chain, is not nearly so sterically hindered as is poly p-chlorostyrene. (Steric hindrance in poly p-chlorostyrene has been discussed by Debye and Bueche.[29])

A high degree of steric hindrance to internal rotation in any linear polymer has the effect of extending the chain in solution and making it somewhat less flexible on the whole. Also, chain movements of any sort which involve the relaxation of short segments of the chain are much less

energetically favored than in the case of the freely rotating chain. Furthermore, effects due to steric hindrance in general become more pronounced at lower temperatures, since rotation over potential barriers is an activation process. This idea fits well with our observation that the molecular weight dependence of relaxation time becomes somewhat greater at 45°C than at 60°C in solutions of poly p-chlorostyrene. Stiffness of the poly p-chlorostyrene chain is also indicated by the measurements of the intrinsic viscosity of this polymer in ortho-terphenyl.

It does not seem unreasonable, then, to propose that dielectric relaxation in solutions of polyvinyl bromide occurs largely by a mechanism involving reasonably short segments of the chain, a mechanism which either was not considered by Kirkwood and Hammerle, or, more probably, which was drastically under-weighted in their averaging procedure. Such a mechanism could involve the rotation of two or more segments of the chain about fixed points in the chain in perhaps a manner similar to the rotation of a crankshaft:
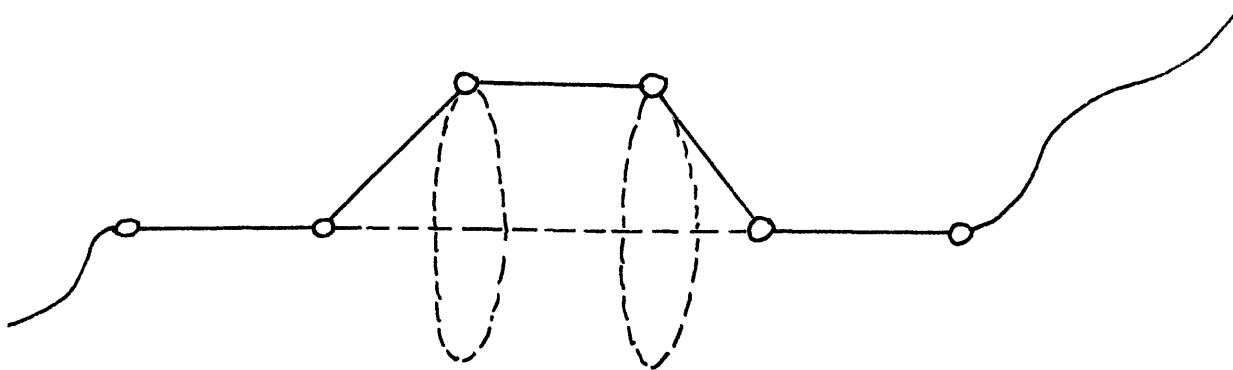
Such a relaxation process would certainly show little of no dependence on chain length. The details of this mechanism are, of course, pure speculation, but it seems clear that some short segment relaxation is involved.

In the case of poly p-chlorostyrene, steric hindrance seems to render the "crankshaft" mechanism inoperative, and dielectric relaxation occurs through orientation of larger units of the chain. This large segment orientation could well be, and apparently is dependent on the chain length. Thus, we propose that the dependence of relaxation times upon molecular weight in solutions of poly p-chlorostyrene is in fact the direct result of steric hindrance, an effect which was not considered by Kirkwood and Hammerle.

Perhaps the most convincing evidence for this point of view is the comparison of the observed relaxation times for poly p-chlorostyrene and polyvinyl bromide with those predicted by the Zimm theory for orientation of the whole molecule. It will be recalled that the lowest molecular weight PPCS sample exhibited a relaxation time in almost perfect agreement with the Zimm theory. For such a short molecule, $(P_n \cong 30)$, this observation could be explained through a high degree of steric hindrance to internal rotation, since the result of such hindrance would be a very stiff molecule which quite possibly would have to orient as a unit. This is not to imply that the molecule is a rigid rod, but rather that it is very difficult to reorient

small segments with respect to one another. For the higher molecular weights, the relaxation times observed are somewhat shorter than, though still comparable with, the Zimm times. These molecules do not orient as a whole, then, but the motion of large segments is clearly involved.

For polyvinyl bromide, in contrast, the observed relaxation times are from one to three orders of magnitude faster than would be predicted by the Zimm theory for orientation of the entire chain. This clearly shows that relaxing segments are not at all of size comparable to the entire chain.

Steric hindrance, then, is without doubt a factor of considerable importance in the determination of the modes of relaxation of polymer molecules. We may not, then, expect any theories based on the simple model of the freely rotating chain to lead to accurate descriptions of the relaxation processes in solutions of sterically hindered polymers.

Much more experimental work will be necessary to develop a complete picture of the relaxation processes in polymer molecules in which there are rigidly coupled dipoles perpendicular to the chain backbone. One experiment which would probably be particularly significant may be suggested here, however. It would be highly desirable to have dielectric measurements of dilute solutions of polymers like

polyethylene oxide or poly-dimethyl siloxane, which have
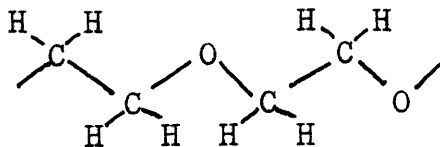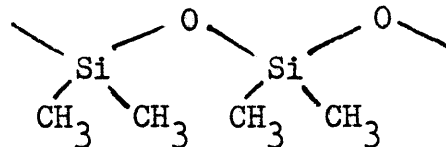
polyethylene oxide   poly dimethyl siloxane

repeating dipoles perpendicular to the chain axis, and in
which there is probably as little steric hindrance to
internal rotation as in any other polymers. Consequently,
either of these polymers would provide one of the closest
practical approaches to the model of the freely rotating
chain with rigid perpendicular dipoles. Comparison of
these measurements with measurements of a sterically
hindered polymer like poly p-chlorostyrene in the same
solvent under essentially the same conditions would
certainly evaluate to a large extent the importance of
steric effects in the relaxation of polymer molecules in
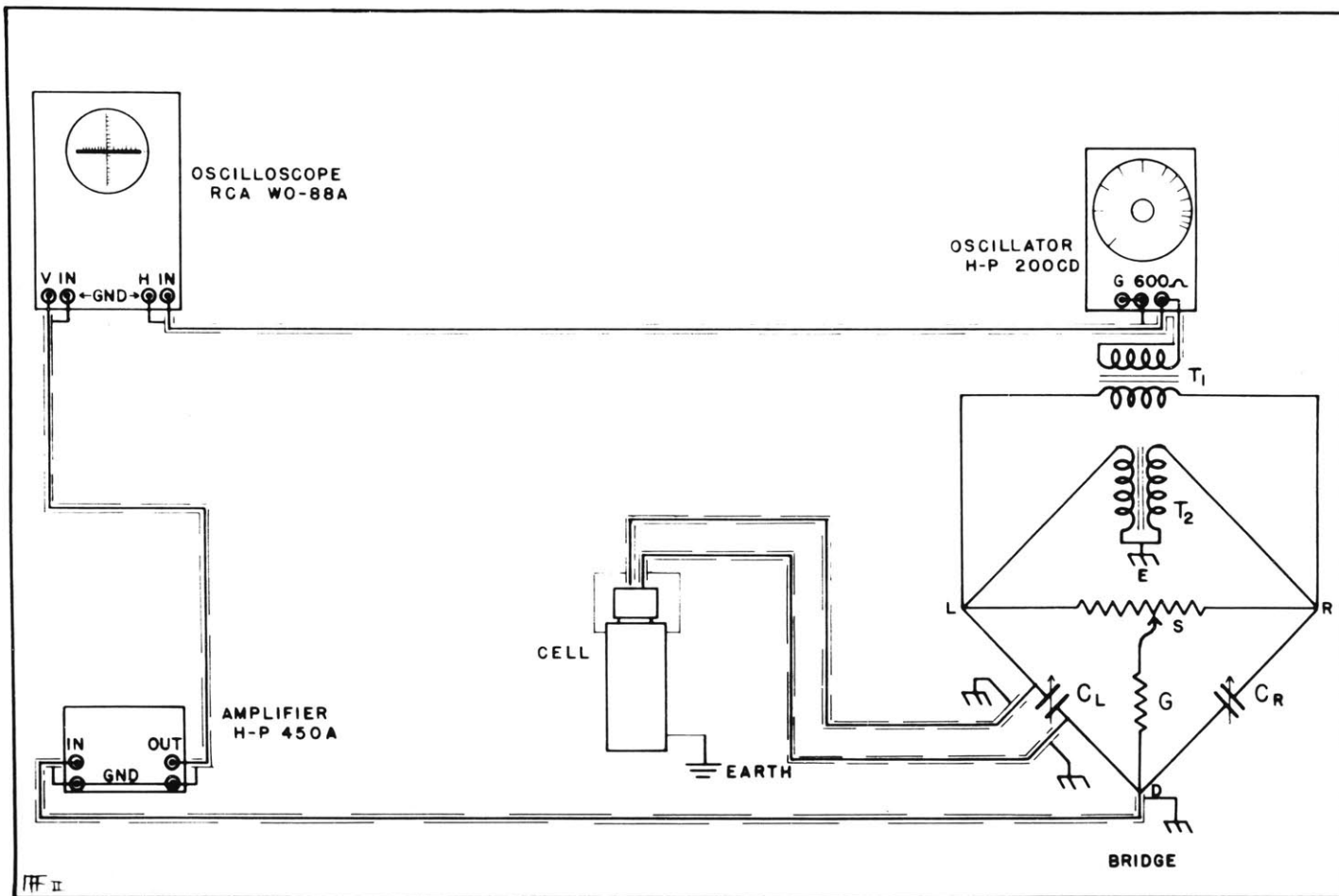solution.

APPENDIX I

THE ELECTRICAL MEASURING SYSTEM

A. General Principles

The measurements of dielectric constant and loss factor
were made on a conductance-capacitance bridge built in this
laboratory by Cleland,[30] following a design of Cole and
Gross.[31] The details of construction and operation of this
instrument have been given by Cleland and others.[32,10]
Since, however, in the present work some modifications have
been made both in the basic design and mode of operation of
the bridge, some reiteration and further comments appear to
be in order.

The Cole-Gross bridge has two features of primary
importance, both of which are readily apparent in the
simplified diagram in Fig. 13. First, a closely coupled
transformer (T_2) with 1-1 turns ratio is used as equal
ratio arms in a Wheatstone bridge circuit. This has the
effect of reflecting any stray voltages or admittances
developed on one side of the circuit over to the other
through the mutual inductance of the coils. Second, a three
terminal wye divider network is connected across the
capacitive arms of the bridge. The variable conductance $\underline{G}$

Figure 13.

The electrical measuring system.

OSCILLOSCOPE
RCA WO-88A

OSCILLATOR
H-P 200CD

V IN ←GND→ H IN

G 600

T_1

T_2

E

L   R
S

AMPLIFIER
H-P 450A

C_L G C_R

IN   OUT
GND

CELL

EARTH

D

BRIDGE

83

in this circuit controls the range of conductance, which
is measured by the position of the center tap (i.e., by
the imbalance between the two sides of the bridge).

Otherwise, the electrical system contains no unusual
features. The signal is introduced from the signal
generator to the bridge through a transformer (T_1). The
output from the bridge at $\underline{D}$ is amplified and put on the
vertical plates of an oscilloscope. The unperturbed
signal from the generator is put directly on the horizontal
plates for comparison. When the bridge is balanced, there
will be no output from the bridge; that is, the signal will
have zero amplitude and will have undergone no shift in
phase. When this condition is obtained, the signal appears
on the scope as a flat horizontal line. If any imbalance
occurs, ellipses of various sizes,shapes and orientations
appear on the scope, depending on the degree of imbalance.

From the equilibrium readings of the standard variable
capacitor C_L (C_R is always maintained at a constant value)
with and without the unknown in the circuit, the capacitance
of the unknown element may be calculated. Similarly, from
the equilibrium settings of the divider circuit with and
without the unknown in the circuit, the conductance of the
unknown may be calculated. The details of these calculations,
as well as certain correction factors which must be applied
to the raw data, will be discussed in Appendix III.

B.   Modifications to the Bridge

Quite early in the course of this research, it became
apparent that the bridge was badly in need of a complete
overhaul. The switches were noisy, the divider contacts
corroded, and many of the soldered connections loose, or
at least shaky. It was impossible to obtain reproducible,
much less meaningful, data from the instrument. Accordingly,
it was decided to clean and rewire the bridge completely.
At the same time, a few modifications were made to eliminate
some unnecessary circuitry and to lead to a simpler and, it
is hoped, more dependable instrument. With the competent
technical assistance of Mr. Marshall Greenspan, a student
in the M.I.T. Electrical Engineering Department, the
following changes were made: First, for stability, general
wiring was done with heavy duty bus bars wherever possible.
Second, the imput selector circuit was eliminated, leaving
only one pair of input terminals on each side of the bridge.
Third, the transformer coil selector circuit, which had
always been a principal source of noise in the past, was
eliminated, and a single transformer mount was provided
inside the bridge housing, thus necessitating manual change
of the coils when desired. (This change, by the way,
constitutes a return to the original design of Cole and
Gross. The coil selector circuit had been incorporated by
Cleland, and in the opinion of the author, constituted an
unsuccessful experiment.) Fourth, a two-conductor shielded

cable was used to convey the signal from the generator to the imput transformer. This allows both the hot lead and the ground lead to enjoy the benefits of shielding, in contrast to the original arrangement, which made the ground connection via the shielding of a single-conductor length of shielded cable. Fifth, the divider reversing switch, another perennial source of trouble, was replaced by a Shallcross 4225-8 switch chosen particularly for its low contact resistance. Sixth, the one-ohm variable resistor was replaced by a duplicate obtained from the Clarostat Co., Dover, N. H. A calibration of this resistor was performed, but the corrections were too small to be significant. Seventh, additional shielding was provided for certain regions inside the bridge housing. Finally, the contacts on the decade resistors in the divider circuit were thoroughly cleaned and coated with a commercial noise suppressor and contact cleaner. The details of the resulting circuit with all modifications incorporated are shown in Fig. 14. This drawing should supersede the one to be found in Cleland's thesis.

In the final analysis, the completed bridge worked quite well, giving quite reproducible and accurate results. The main difficulty noted was a continuing tendency for the contacts of the decade resistors to corrode in spite of the protective agent.

Figure 14.

Schematic Diagram of the Bridge.

THE COLE-GROSS BRIDGE
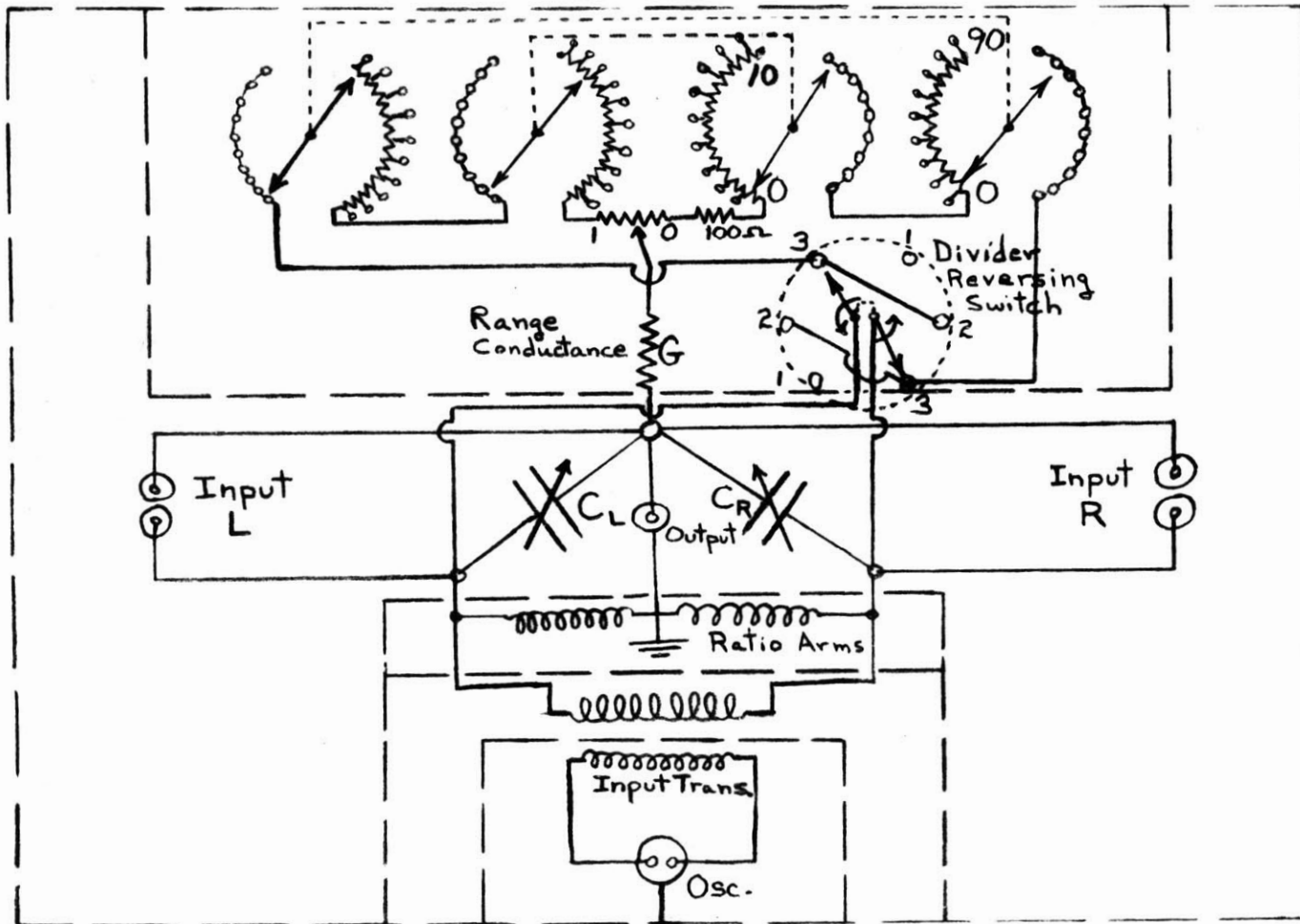
Schematic wiring diagram. Long dashes indicate
shielding, short dashes ganged switches.

MG

APPENDIX II

THE DIELECTRIC CELL

A. <u>Design and Construction.</u>

Since the high-pressure cell[33] used in all previous
measurements in this laboratory is very heavy and incon-
venient to use, it was decided to construct a much lighter
and simpler cell for use exclusively at atmospheric pressure.
Such a cell has been designed by the author and fabricated
from aluminum in the M.I.T. Chemistry Department Machine
Shop. While the basic design of the new cell is much the
same as that of the old cell, i.e., semi-cylindrical
electrodes insulated from the main body of the cell and
supported by electrical rods, the walls are much lighter
and "O" rings are used as the only seals. The cell readily
disassembles for cleaning and loading into three main parts,
as shown in Fig. 15. Further disassembly should be avoided
unless absolutely necessary, as the cell will have to be
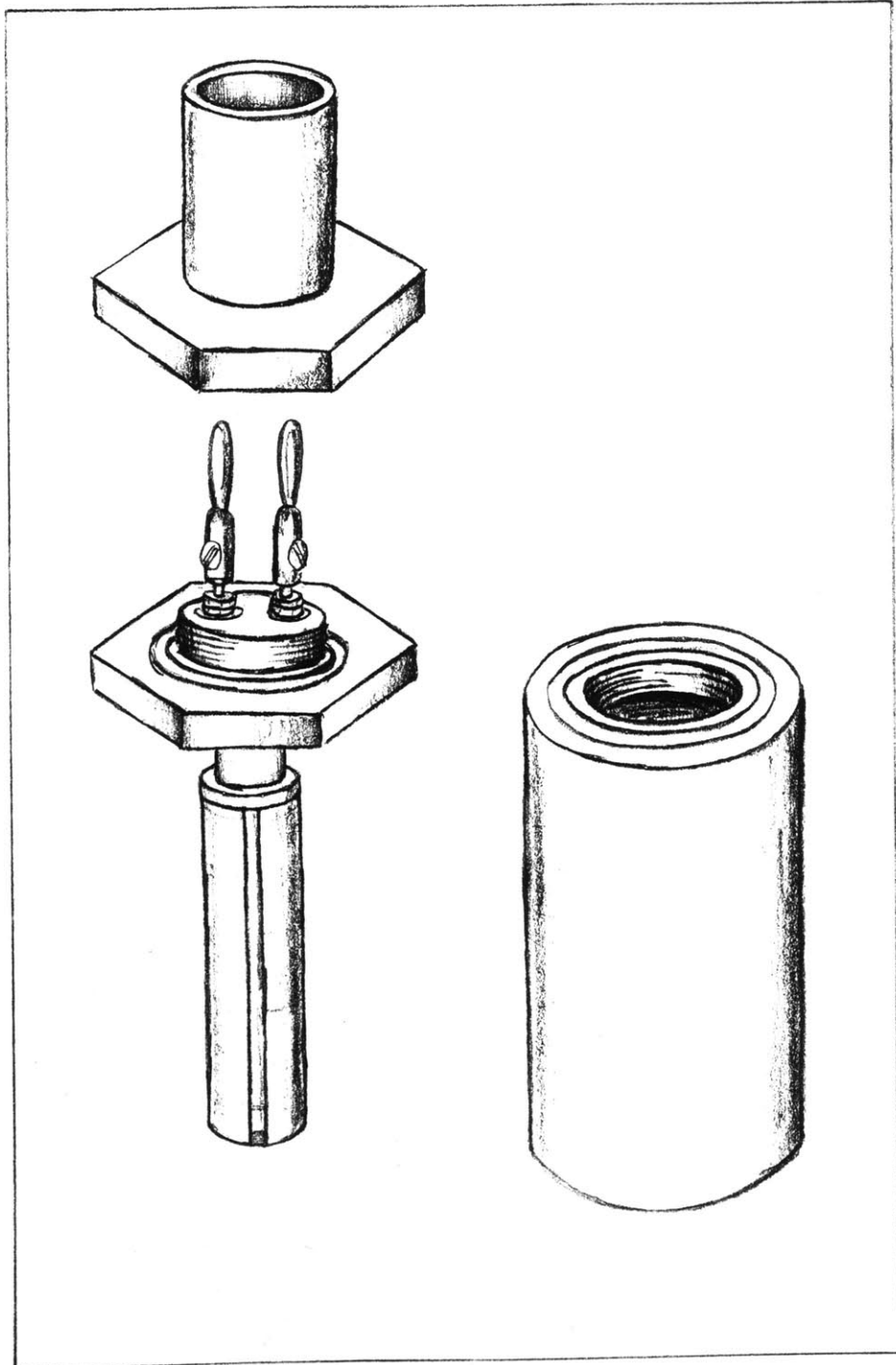completely recalibrated.

The electrodes are supported by steel rods passing
through the middle section of the cell. The rods are
insulated from the grounded aluminum body by lengths of
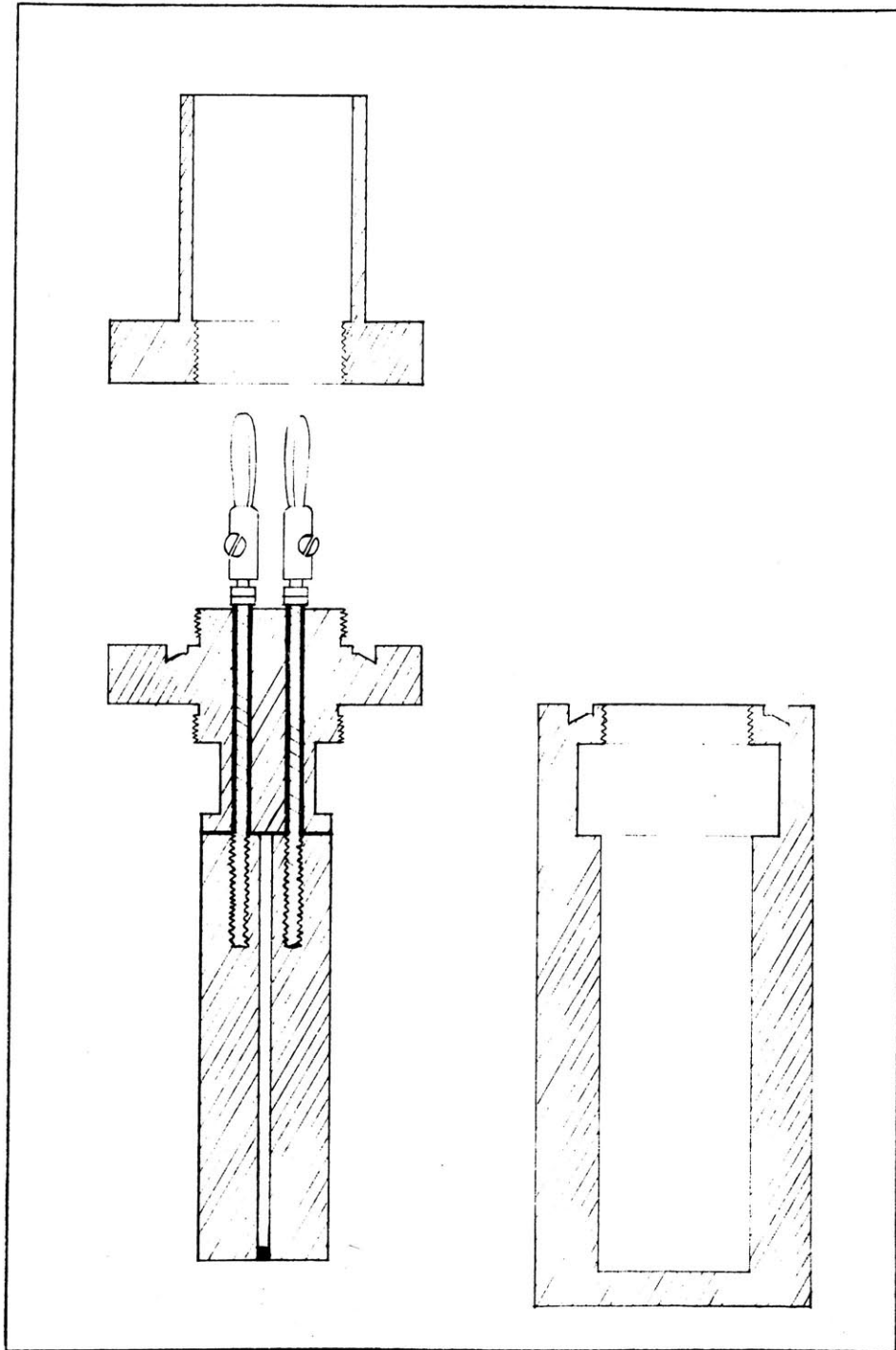Teflon "spaghetti", and are threaded at each end, at the

Figure 15.

The Dielectric cell
  (a) Perspective
  (b) Section

lower ends to receive the electrodes and at the upper ends for banana plugs. The electrodes are insulated by a thin sheet of Teflon through which holes have been drilled for the electrical rods, and the banana plugs are insulated by 5/16 inch O.D. Teflon "O" rings used as washers.

Trapezoidal slots have been provided for a 1-3/8 inch O.D. "O" ring and a 1-7/16 inch O.D. "O" ring to seal the three sections together. (The design submitted by the author called for two identical slots, but through an inexplicable error in the shop, one was made too large; fortunately, "O" rings of this larger size were available.)

The electrodes are 2-7/8 inches long by 3/4 inch wide, and the interelectrode spacing is approximately 0.08 inch. Small glass spacers are cemented between the lower corners of the electrodes with an epoxy resin cement to maintain a constant spacing. The liquid capacity of the cell is 15-20 ml, depending upon whether the temperature will be increased or decreased drastically after loading.

A grounded copper sheet is provided to be placed between the banana plugs. This serves two purposes: first, it negates any stray capacitance between the banana plugs, and second, its contact with the aluminum body of the cell serves as ground connection for the cell.

B   <u>Calibration</u>

Calibration of the cell was effected in the following manner: the capacitance of the empty cell was measured at 3, 4,and 5 kilocycles per second (the region in which the bridge is most sensitive). Then the capacitances were measured at the same frequencies with the cell filled at 25°, first with benzene which had been dried over sodium wire and then with a freshly opened sample of anhydrous diethyl ether. The following values were obtained:

$$C_o = 7.04 \text{ pf. (pf = picofarad = } \mu\mu f)$$

$$C_{benzene} = 15.75 \text{ pf.}$$

$$C_{ether} = 29.12 \text{ pf.}$$

The literature values for the dielectric constants for these liquids are at 25°C:

$$\varepsilon'_{benzene} = 2.274$$

$$\varepsilon'_{ether} = 4.240$$

From this information both the capacitance contributed by the spacers and the capacitance of the remainder of the cell may be calculated. Since the capacitance due to the spacers is a constant quantity occurring in each measurement,

$$\varepsilon'_x = \frac{C_x - C_s}{C_o - C_s}$$

where C_x and C_o are the measured total capacitances of the loaded and empty cell, respectively, C_s is the capacitance due to the spacers, and ε_x' is the dielectric constant of the standard liquid.

Inserting the values for benzene leads to a calculated C_s of 0.23 pf., and the values for diethyl ether lead to a C_s of 0.20 pf. The value 0.21 pf. is chosen as average. Thus 7.04 - 0.21, or 6.83 pf., is the capacitance of the portion of the cell which is actually affected by the presence of a sample in the cell.

Finally, the capacitance C_o of the cell has been measured over a temperature range of $15^{\circ}C$ - $70^{\circ}C$, and no change from the value 7.04 pf. was noted.

APPENDIX III

THE CALCULATION OF DIELECTRIC CONSTANT AND LOSS FACTOR

A. Calculation of ε'

The real part, ε', of the complex dielectric constant, ε^*, is defined as the ratio of the capacitance of the measuring cell containing the substance of interest to the capacitance of the empty cell. It is therefore necessary to determine the absolute value of the capacitance of the cell both empty and filled.

Cleland found that, on the average, 1.000 units of C_L (i.e., one complete revolution of the dial) corresponds to a change in capacitance of 4.62 pf. Therefore, to a first approximation, the difference in capacitance for two settings of C_L is 4.62 $(C_{L_0} - C_L)$. The change in capacitance is, however, only approximately linear with capacitor setting, and small corrections (C_L') have been determined for a number of settings by Cleland, and appear as Fig. 16. These corrections are so defined that the true capacitance of the unknown, C_x, is given by

$$C_x = 4.62(C_{L_0} - C_L)_{corr.} + (C_{L_0}' - C_L')$$

Figure 16.

Capacitor calibration curve (C_L' vs. C_L).
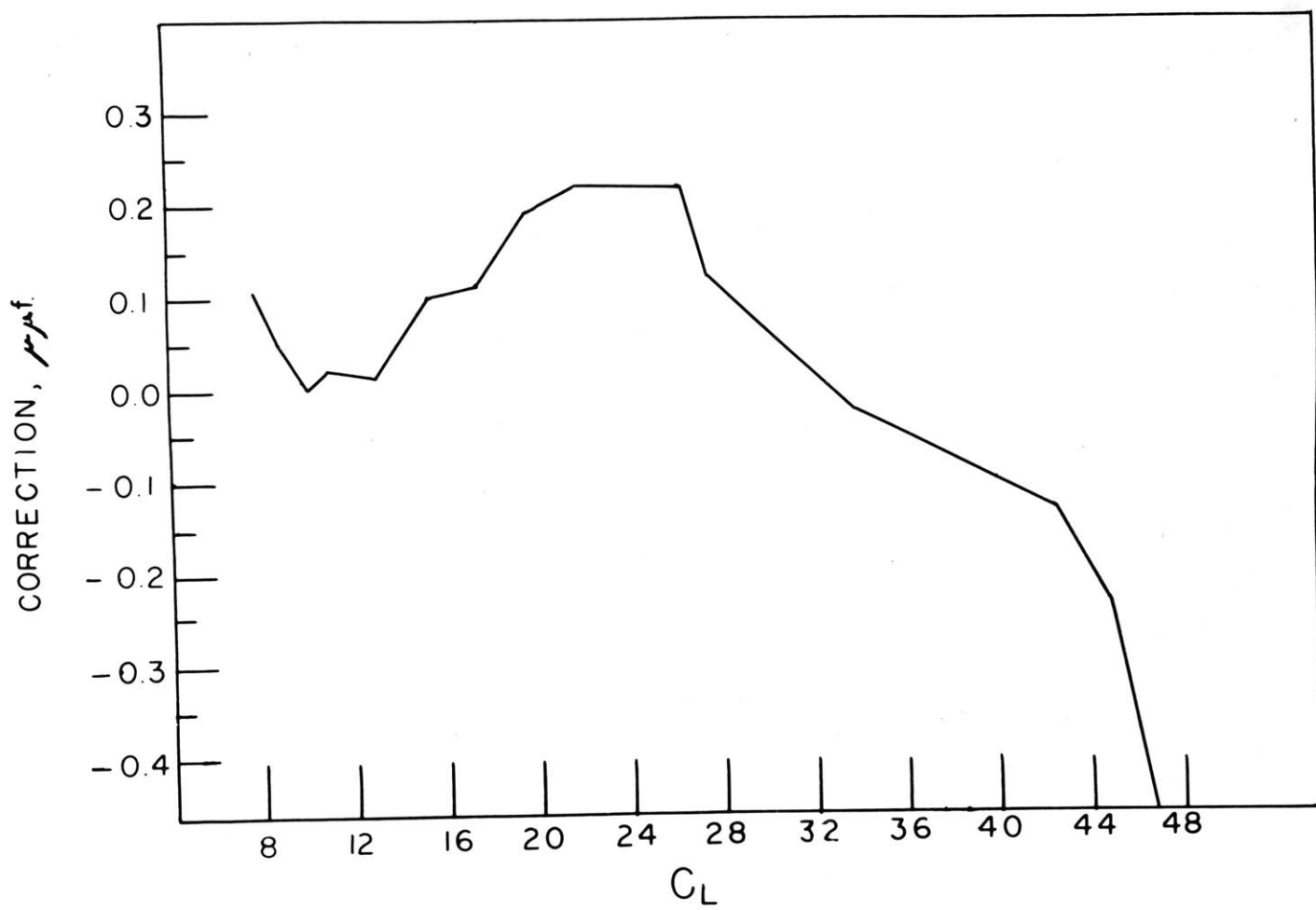
where C_L and C_{L_o} are, respectively, the readings of the left hand capacitor with and without the unknown included in the circuit, as corrected for divider setting according to Fig. 17, and C'_L and C'_{L_o} are the corresponding correction factors taken from Fig. 16 for these settings. It should be noted that the factor 4.62 has been incorporated already in the definition of the correction factors.

The capacitance due to the glass spacers between the electrodes must now be given further consideration. Since the capacitance due to these spacers is constant, it must be subtracted from both the capacitance of the filled cell and the empty cell in the calculation of ε'. As noted earlier, the total capacitance of the empty cell is 7.04 pf., and the capacitance of the spacers is 0.21 pf. The value of ε' is thus given for any unknown liquid by

$$\varepsilon' = \frac{C_x - 0.21}{7.04 - 0.21} = \frac{C_x - 0.21}{6.83}$$

B. Calculation of ε''
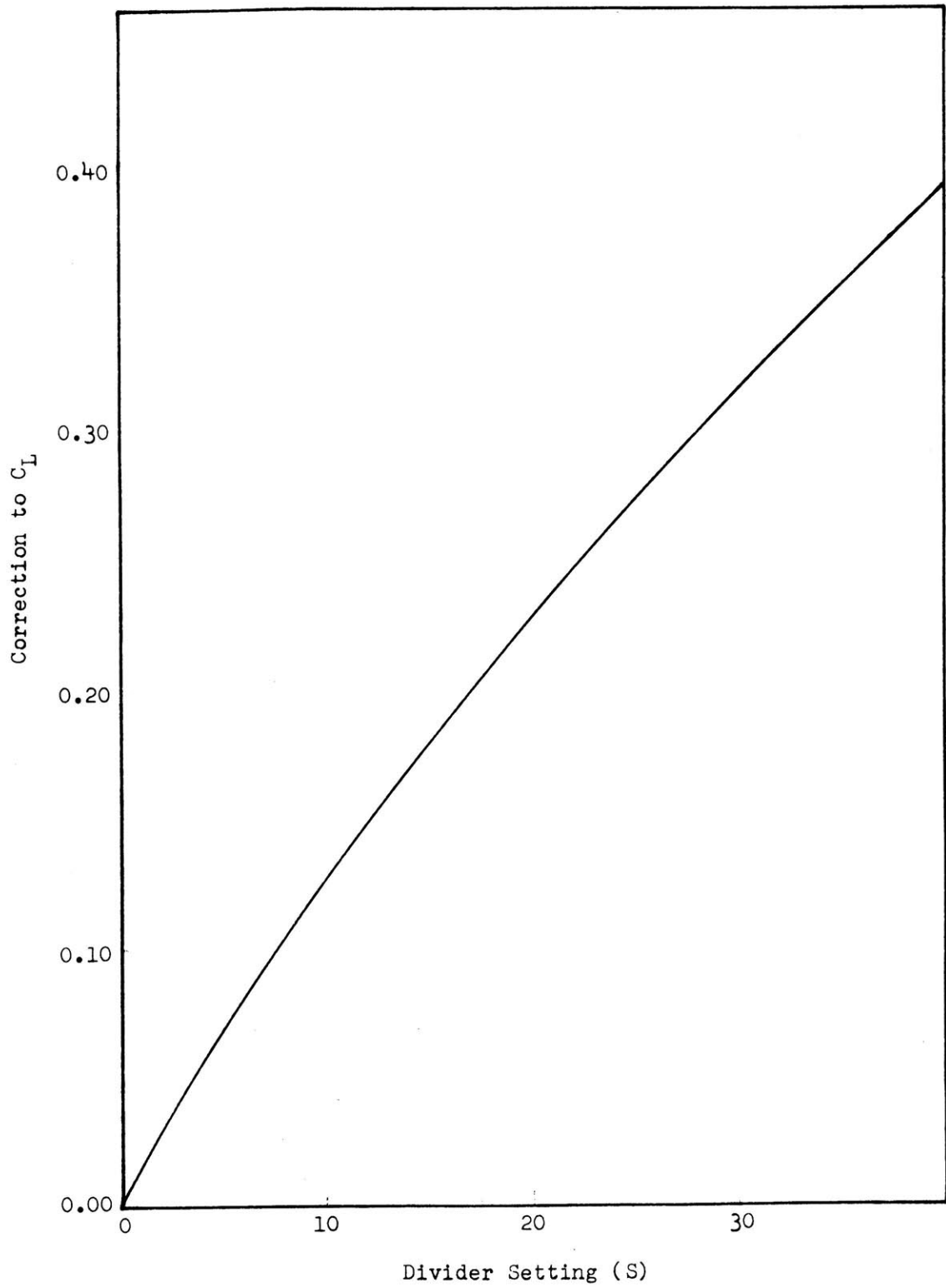
The imaginary part ε'' of the complex dielectric constant is given by

$$\varepsilon'' = \frac{G_m}{2\pi f C_o}$$

where G_m is the conductance of the sample, f is the frequency of measurement, and C_o is the capacitance of the

Figure 17.

Divider Correction to C_L.

empty cell. For the Cole-Gross circuit, the conductance
of the unknown element is given to a first approximation
by[30]

$$G_m = GS/100$$

where G is the setting of the range conductance, and S
is the divider setting. Since, on this instrument, G is
given in micromhos,

$$G_m = (GS/100) \times 10^{-6} = GS \times 10^{-8} \text{ mho.}$$

Two further refinements must now be made. The actual
range conductance at a given frequency is not simply G,
but is the product $Gg(f)$, where $g(f)$ is a correction factor
measured by Cleland, and which is shown in Fig. 18.
Furthermore, samples may often display a residual conductance
at 200 cps. which is not due to the dielectric loss mechanism,
but rather may be due to ionic impurities, moisture, etc.
To avoid confusing this conductance with that due to
dielectric loss, this residual conductance is subtracted
from the total conductance at higher frequencies, leading
to the final conductance equation,

$$G_m = \left[G_g(f)(S-S_0) - G'(S'-S_0') \right] \times 10^{-8} \text{ mho,}$$

where S and S_0 are the divider settings at the frequency
of interest with and without the cell included in the circuit,

Figure 18.

g(f) vs. f for various G values.
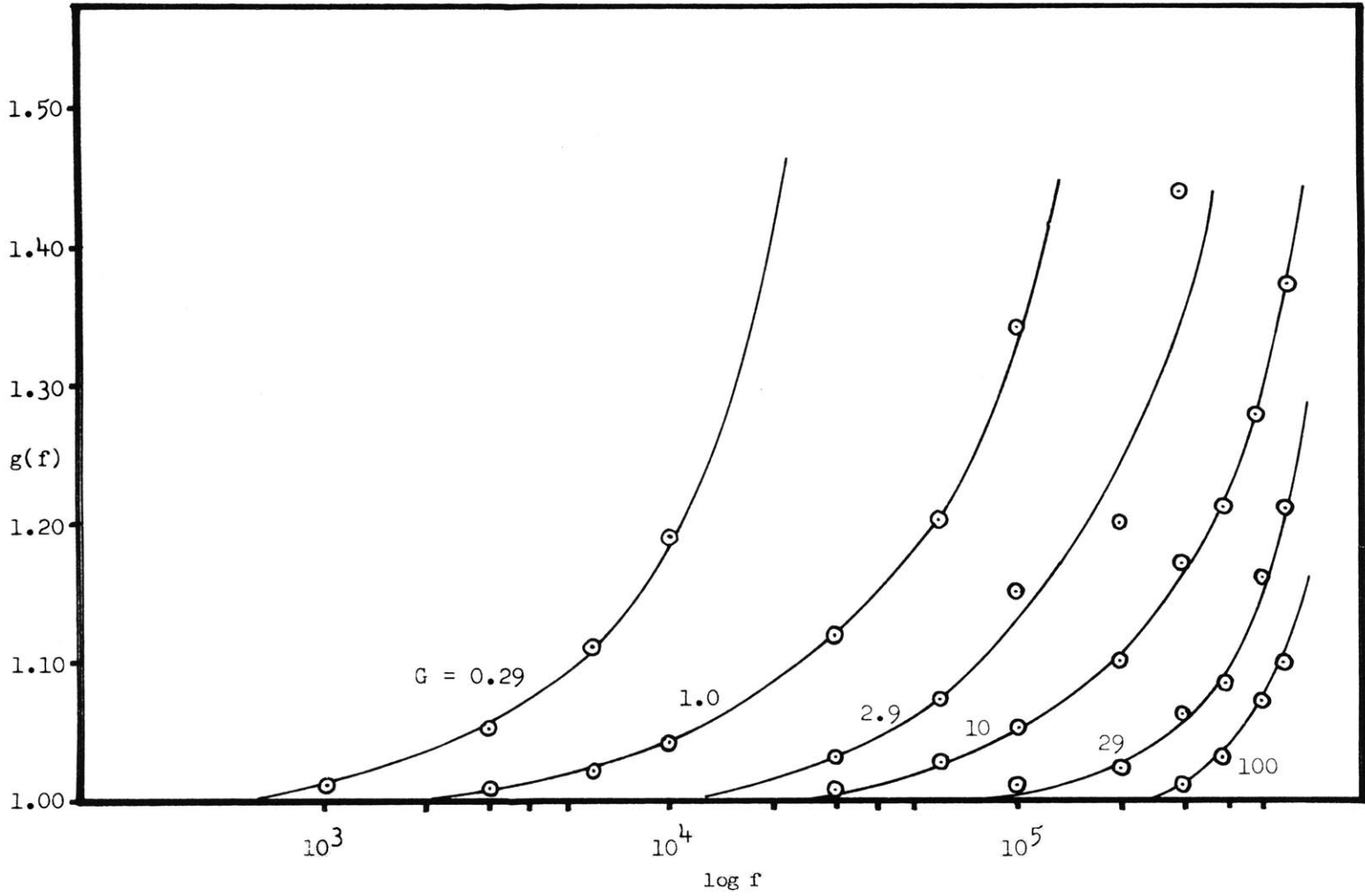
and the primed values refer to the settings at about
200 cps. It is essential, of course, that the temperature
be adjusted to such a value that no actual loss takes place
at 200 cps., and that ε'' should indeed be zero at this
frequency.

Substitution of all values in the ε'' equation now
gives

$$\varepsilon'' = \frac{G_m}{2\pi f C_o} = \frac{\left[Gg(f)(S-S_o) - G'(S'-S'_o) \right]}{(2\pi f)(6.83 \times 10^{-12} \text{farad})} \times 10^{-8}$$

$$\varepsilon'' = \frac{\left[Gg(f)(S-S_o) - G'(S'-S'_o) \right]}{f} \times 2.33 \times 10^2$$

Quite often it will be found that $Gg(f)(S-S_o) \gg G'(S-S'_o)$,
in which case the latter may be completely neglected.

C. Sample Calculations

Two readings from a typical set of data might appear as
follows:

f(cps.)	G	S_o	C_{L_o}	S	C_L
200	0.29	0.45	16.36	0.55	12.20
10,000	1.0	0.50	16.37	15.5	13.00

From the data at 200 cps:

$$C_x = 4.62(16.36 - 12.20)+(0.10 - 0.03)=19.22 + 0.07 = 19.29 \text{ pf.}$$

$$\varepsilon' = \frac{C_x - 0.21}{6.83} = \frac{19.08}{6.83} = 2.79$$

Note that no divider correction to C_L is required because of the small divider setting.

ε'' is presumed to equal zero, since the small difference in S and S_o is ascribed to mechanisms other than dielectric loss. But:

$$G'(S'-S_o') = (0.29)(0.55-0.45) = 0.03 \text{ mho.}$$

For the data at 10,000 cps.:

C_L = 13.00, but the divider correction for S=15.5 is -0.18, so:

$$C_{Lcorr.} = 12.82$$

$$C_{L_o} = 16.37 \text{ (correction negligible)}$$

Therefore:

$$C_x = 4.62(16.37 - 12.82)+(0.10 - 0.03)= 16.40 + 0.07 = 16.47 \text{ pf.}$$

$$\varepsilon' = \frac{16.47 - 0.21}{6.83} = 2.38$$

$$\varepsilon'' = \left[\frac{Gg(f)(S-S_o) - G'(S'-S_o')}{f}\right] \times 2.33 \times 10^2$$

$$\varepsilon'' = \left[\frac{(1.0)(1.04)(15.5 - 0.50) - (0.29)(0.55-0.45)}{10,000}\right] \times 2.33 \times 10^2$$

$$\varepsilon'' = \left[\frac{(15.60 - 0.03)}{10,000}\right] \times 2.33 \times 10^2 = 0.363$$

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BIOGRAPHICAL NOTE

The author was born in Magnolia, Mississippi, on September 12, 1934, and received his early education in the public schools of Magnolia and Starkville, Mississippi. He was graduated from Starkville High School in May of 1952, and entered Mississippi State University in September of that year as a major in chemistry. There he was a member of Sigma Alpha Epsilon social fraternity, Phi Kappa Phi scholastic society, and Omicron Delta Kappa leadership fraternity. In his freshman year he was selected as the outstanding first-year chemistry student, and in his senior year he was awarded the William F. Hand Chemistry Scholarship by the University, and an achievement award by the New Orleans, La., Chapter of the American Institute of Chemists. He was graduated with Special Honors in May of 1956.

In September of 1956 he entered the Massachusetts Institute of Technology as a doctoral candidate in physical chemistry. He served for two years as a teaching assistant, then was awarded a fellowship by the National Science Foundation for the remainder of his graduate study. At M.I.T. he was elected to Phi Lambda Upsilon Chemical Society, and to Sigma Xi; he served as President of the Chemistry Department social organization, the "Icepickers", and as Vice-Chairman

of the M.I.T. Graduate House, and has perhaps come by more of a reputation as a politician than he would savor.

The author has been employed three summers in chemical industry, in Baton Rouge, La., with the Esso Standard Oil Co., and in Kinston, North Carolina, and Buffalo, New York, with the DuPont Company. He has recently been awarded a Post-Doctoral Fellowship by the National Science Foundation for a study of the replication of nucleic acids in bacterial viruses at the California Institute of Technology.