INVESTIGATION OF THE ANALOGIES BETWEEN
VISCOMETRIC AND LINEAR VISCOELASTIC PROPERTIES
OF POLYSTYRENE FLUIDS

by

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KENJI YASUDA

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ment of the degree of Doctor of Philosophy

ABSTRACT

In studying the flows in the polymer processing operations
which are central to many industries, it is essential to know the
steady shear flow properties of polymeric liquids but direct measure-
ments are difficult. Analogies between viscometric or steady shear
flow properties (steady shear viscosity, \( \eta \), and primary normal stress
difference, \( N_1 \)) and the more easily measured linear viscoelastic
properties (dynamic viscosity, \( \eta' \), and dynamic storage modulus, \( G' \))
can be used to advantage in this regard.

Such analogies were studied for concentrated solutions of
polystyrene (narrow and broad molecular weight linear polymers and
narrow distribution star-branched polymers) in 1-Chloronaphthalene
and other non-volatile solvents. Wide ranges of concentration and
molecular weight were used.

Viscometric properties were measured in the cone and plate
mode using the Rheometrics Mechanical Spectrometer and the Instron
rotary rheometer. Linear viscoelastic properties were measured in
the eccentric rotating disc mode and cone and plate forced oscilla-
tion mode with the Mechanical Spectrometer. Analogies were studied
by comparing master curves of linear viscoelastic properties to those
of viscometric properties; these master curves were obtained using
time-temperature superposition to extend the effective frequency or
shear rate range of the data.

There were deviations from analogies both for viscous (\( \eta, \eta' \))
and elastic (\( N_1, G' \)) properties, particularly at high shear rates
or frequencies (\( \eta > \eta', N_1 > 2G' \)). The Cox-Merz rule, and empiricism
which suggests the following:

\[ \eta = |\eta^*| \equiv (\eta')^2 + (G'/\omega)^2 \]
was applicable for most of our linear and star branched samples with narrow distribution. The Cox-Merz rule failed to fit data of a very high molecular weight and concentration (cM=6x10^5) solution for which \( n < |n^*| \) and solutions with broad molecular weight distribution for which \( n > |n^*| \) at high shear rates.

Rheological parameters (power law slopes, \( d, d' \), curve fitting parameters, \( a, a' \), critical shear rate/frequency, \( \gamma_0, \omega_0 \) zero shear rate viscosity \( \eta_0 \)) were obtained from master curves by curve fittings with modified Carreau equations. These parameters were used to study the relationship between viscometric properties and linear viscoelastic properties quantitatively. \( \gamma_0 \) and \( \omega_0 \) were equal for narrow distribution polystyrene but \( \gamma_0 = 1.7 \omega_0 \) for broad distribution. Correlations between power law slopes were obtained so that \( n(\dot{\gamma}) \) could be estimated up to high shear rates from \( n'(\omega) \).

Parameters of elastic properties were also studied. The effect of concentration, molecular weight, and star branching on these parameters were mostly consistent with the literature. The zero shear rate viscosity \( \eta_0 \) of star branched polystyrene was the same as \( \eta_0 \) of linear polymer of same molecular size (taking branching into account), but steady shear compliance \( J_e^0 \) was higher for star branched polymer solutions.

Linear viscoelastic properties were reduced into the discrete spectrum from which any linear properties can be derived. Modified rubber-like liquid model was used to fit viscometric properties with a strain dependent damping function \( h(\gamma) \) combined with the discrete spectrum. With the single exponential approximation for \( h(\gamma) \), viscometric properties were sufficiently well predicted for broad distribution polystyrene but narrow distribution polymers show large errors. A double exponential form for \( h(\gamma) \) was sufficient to fit high shear rate properties.

As a result of this study the analogies between steady viscometric properties and linear viscoelastic properties were examined over wide range of \( c, M \) and branching. The deviations were correlated to linear viscoelastic properties. The modified rubber-like liquid was a convenient model for describing the deviations.

Thesis Supervisors

Robert E. Cohen, Associate Professor of Chemical Engineering
Robert C. Armstrong, Assistant Professor of Chemical Engineering
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who has given us unlimited supply of encouragement and warmth to weather the tragedy my family and I had to come through during the period of our stay at M. I. T.

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Born Nov. 11, 1947 in Japan. Graduated from University of Tokyo, Faculty of Engineering, Department of Synthetic Chemistry with Bachelor of Engineering, in March 1970 and graduated from The Graduate School, University of Tokyo, in March 1972 with Master of Engineering. B. E. Thesis was 'Reaction of Carbanion, Abnormal Addition of Cumyl-K to Benzophenone' which was presented at the national meeting of Chem. Soc. Japan in August 1970. M. S. Thesis was 'Reaction of Carbanion: Reactions between -Methylstyrene oligomers or cumyl-K and aromatic ketones'. Part of the research was presented at the national meeting of Chem. Soc. Japan in 1976. Attended M. I. T. since 1975 and received M. S. Ch. E. from M. I. T. in June 1977. M. S. thesis was titled 'Investigations of the analogies between linear viscoelastic and viscometric properties of polystyrene'. Research Chemist/Engineer with Oji Paper Col., Tokyo, Japan since 1972 and co-inventor of several patents granted to his employer in the fields of synthetic papers and pressure sensitive copying papers, including USP3919450.
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CHAPTER I. INTRODUCTION

1. Motivation

Polymer processing operations are important in many industries and there is a strong need to model the flows of polymeric liquids in polymer processing operations (1)(2). But polymer melts and polymer solutions used in the processing are viscoelastic and behave quite differently from Newtonian liquids within a flow system. In order to study the shear flows involved in polymer processing operations it is necessary to know steady shear flow properties of the fluid over a wide range of processing conditions including shear rates.

Direct measurement of steady shear flow properties from steady shear flow experiments is difficult and time consuming over the range of shear rates for which data are needed for modeling polymer flows in industrial processes (3). The reasons for this are industrial processing of polymers usually contains both very high and very low shear rate flow of polymer melts or polymer solutions, and because at high shear rates polymers may degrade, heat generation changes material properties heterogeneously, and shear flow becomes unstable and results in shear fracture, while at low shear rate, high sensitivity is required and measurement takes a long time to reach equilibrium.

On the other hand linear viscoelastic material functions as functions of frequency can be measured much more easily in small
amplitude oscillatory experiments over a wide range of frequency. Such measurements are possible from $10^{-2}$ rad/s to $10^2$ rad/s (4)(5) with conventional equipment and with special high frequency instruments, frequencies of $10^3 - 10^6$ rad/s are also attainable (3)(6).

There are analogies between the frequency dependence of linear viscoelastic properties and the shear rate dependence of steady shear flow properties. In view of the discussion presented above such analogies represent a significant opportunity in the search for understanding of polymer processing operations. If modelling, analysis and control could be based on the more easily obtained linear viscoelastic properties, significant advances would be made. Thus a detailed investigation of these rheological analogies is warranted.

In order to describe the analogies it is first necessary to define the material functions of steady shear flow and linear viscoelasticity (7). For a steady shear flow as shown in Fig. 1-1,

$$v_1 = \dot{\gamma} x_2$$
$$v_2 = 0$$
$$v_3 = 0$$

If the fluid is Newtonian we know from Newton's law of viscosity that, in this flow

$$\tau_{21} = -\mu \frac{dv_1}{dx_2} \quad \text{[1-1]}$$

and all other $\tau_{ij} = 0$. 
Fig. 1-1  Steady Shear Flow between Two Plates

However, for polymeric liquids which are non-Newtonian we do not have a constitutive equation which tells us all the steady shear flow properties exactly.

Stress and rate of strain tensor notation will first be defined, then various material functions will be defined using this notation. Most of the symbols and notations in this study follow those of "Dynamics of Polymeric Liquids" (7).

For a flow unit shown in Fig. 1-2, components of a stress tensor are shown in eq. 1-2

$$\tau_{ij} = \begin{pmatrix} \tau_{11} & \tau_{12} & \tau_{13} \\ \tau_{21} & \tau_{22} & \tau_{23} \\ \tau_{31} & \tau_{32} & \tau_{33} \end{pmatrix}$$

[1-2]

For shear flows the nine stress tensor components reduce to four from symmetry arguments.

$$\tau_{ij} = \begin{pmatrix} \tau_{11} & \tau_{12} & 0 \\ \tau_{21} & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{pmatrix}$$

[1-3]

The rate of strain tensor $\dot{\gamma}$ is defined by eq. 1-4

$$\dot{\gamma} = \nabla \gamma + (\nabla \gamma)^\top$$

[1-4]
Fig. 1-2 The Components of Stress Tensor (2)
the magnitude of $\dot{\gamma}$ is the shear rate $\dot{\gamma}$ in a shear flow. In a steady simple shear flow,

$$v_1 = \dot{\gamma}x_2$$
$$\dot{\gamma} \text{ constant}$$

$$v_2 = v_3 = 0$$

as shown in eq. 1-6, 1-7, and 1-8, three material functions can determine a stress tensor (in eq. 1-3) completely. They are steady shear viscosity ($\eta$), primary normal stress difference ($N_1$) or primary normal stress difference coefficient ($\psi_1$), and secondary normal stress difference ($N_2$) or secondary normal stress difference coefficient ($\psi_2$).

$$\tau_{12} = \tau_{21} = -\eta(\dot{\gamma}) \cdot \dot{\gamma}$$

$$\tau_{11} - \tau_{22} = -\psi_1(\dot{\gamma}) \cdot \dot{\gamma}^2 = -N_1(\dot{\gamma})$$

$$\tau_{22} - \tau_{33} = -\psi_2(\dot{\gamma}) \cdot \dot{\gamma}^2 = -N_2(\dot{\gamma})$$

Note only normal stress differences can be normal stresses for an incompressible fluid. In experiments $p + \bar{\pi}$ rather than $\bar{\pi}$ is obtained. Pressure ($p$) cannot be measured experimentally if incompressible fluid (density constant) is assumed (7). Therefore, it is impossible to know $\tau_{ii}$ but it is only possible to take differences like $\tau_{11} - \tau_{22}$.
Linear viscoelastic material functions can be measured in small amplitude forced oscillation shear flow experiments:

\[ \gamma_1 = x_2 \cdot \dot{\gamma} \]
\[ \dot{\gamma} = \dot{\gamma}_0 \omega \cos \omega t \]
\[ \tau_{21} = -\gamma_0 [G' \sin \omega t + G'' \cos \omega t] = \tau_{21}^0 \sin (\omega t + \delta) \]

\[ \delta \] phase angle

Dynamic storage modulus and loss modulus are linear material functions.

\[ G'_{(\omega)} = -\frac{\tau_{21}^0}{\gamma} \cos \delta \] \hspace{1cm} [1-11]

\[ G''_{(\omega)} = -\frac{\tau_{21}^0}{\gamma} \sin \delta \] \hspace{1cm} [1-12]

Sometimes it is more convenient to work with

\[ n'(\omega) = \frac{G'(\omega)}{\omega} \] \hspace{1cm} [1-13]

\[ n''(\omega) = \frac{G''(\omega)}{\omega} \] \hspace{1cm} [1-14]

complex viscosity

\[ n^* = n' - i n'' \]

\[ |n^*| = \sqrt{(n')^2 + (n'')^2} \] \hspace{1cm} [1-15]
G" (or \( \eta' \)) represent viscous behavior of the polymer and G' (or \( \eta'' \)) describes the elastic behavior. For Newtonian fluid, \( \eta' = \mu \) and \( \eta'' = 0 \).

These linear viscoelastic material functions of a particular polymeric liquid can ultimately be reduced into a single function called linear viscoelastic spectrum (5) which can generate any of the linear viscoelastic material functions.

\[ G(t) = \text{relaxation modulus} \]

\[ H(\tau) = \text{relaxation spectrum} \text{ is commonly used as the linear spectrum.} \]

They will be explained further in Sec. 3 (c) of this chapter.

A simple analogy between the shear rate dependent viscometric properties and the frequency dependent linear viscoelastic properties (See Figure 1-3 and eq. 1-15-1-17) was found experimentally by Pao (8) and Buche (9) decades ago.

![Graph](image)

**Fig. 1-3** The Simple Analogy
\[ \eta'(\gamma) = \eta'(\omega) \bigg|_{\omega=\gamma} \quad [1-15] \]

\[ \psi'(\gamma) = \frac{2}{\omega^2} \cdot G'(\omega) \bigg|_{\omega=\gamma} \quad [1-16] \]

or

\[ N'(\gamma) = 2G'(\omega) \bigg|_{\omega=\gamma} \quad [1-17] \]

However detailed experimental observations did not show an exact analogy. At high shear rates where applications of this theorem could have importance, the deviation becomes large. The shear viscosity is as much as ten times larger than dynamic viscosity. Only at low shear rates do these two material properties become equal experimentally and, as we will show later, theoretically.

Cox and Merz (10) proposed an empirical correction to this phenomenon. The Cox-Merz rule gives the following analogy:

\[ \eta'(\gamma) = \left| \eta'(\omega) \right| \bigg|_{\omega=\gamma} \quad [1-18] \]

where \[ \left| \eta'(\omega) \right| = \sqrt{(n')^2 + (n'')^2} \quad [1-19] \]

Although somewhat better than the simple analogy of Figure 1-1, there have been some experimental evidence that the Cox-Merz rule does not always apply (11).

The first object of this study is to establish an experimental data base to correlate the deviations from the analogies to polymer molecular parameters and other experimental parameters. The failure or the success of the Cox-Merz rule will also be studied using this data base.
The experimental correlations will supply practical information to estimate viscometric properties from linear viscoelastic properties. Currently some part of the polymer related industry uses Cox-Merz rule to compute steady shear viscosity from linear viscoelastic data easily available from highly automated instruments like the Rheometrics V.E. tester (12). This study will supply a more quantitative way to compute steady shear viscosity and normal stress differences from the same kind of data.

The second objective is to evaluate theoretical models to predict non-Newtonian properties. Theory has not produced definitive constitutive equations in polymer rheology corresponding the Newton's law in Newtonian flow. The constitutive equations describe the relationship between stress tensor and deformation, which is expressed by strain tensor or rate of strain tensor. Some constitutive equations are formulated from molecular theories, some from continuum mechanics and others from empirical model building. But not many of them have successfully predicted both the linear viscoelastic and the viscometric properties simultaneously.

It is not too difficult to fit linear viscoelastic properties with an appropriate model. However viscometric properties and time dependent non-linear properties become difficult to fit. This problem has not been obvious until recently because the error of experimental data sometimes exceeded the error from the model prediction.

Because the analogy is the relation between two different groups
of material functions, the evaluation of constitutive equations based on their ability to predict the analogy is important. One way to evaluate constitutive equations is to fit non-linear parameters of the models from data of the deviations from the analogies. We have particular interest in a constitutive equation called the Goddard corotational memory integral expansion (13). The Goddard expansion is a very general expression of the constitutive equation for rheologically simple fluid. It is an expansion in memory integrals (7). The expansion is of particular interest to us because the first term of the expansion predicts the simple analogy as shown in eq. 1-15 and eq. 1-16 and higher order terms describe deviations from the simple analogy. Because the deviations experimentally observed are not large, we felt that one extra term may be satisfactory.

2. Problem Description and Background
   a. Phenomenological analogies

   The rheological analogies have been observed between linear viscoelastic properties and viscometric properties for non-Newtonian liquids. (Most of non-Newtonian liquids experimentally studied are polymeric liquids.)
Fig. 1-4 Simple phenomenological analogies

When plotted on double logarithmic scale, \( \eta(\dot{\gamma}) \) and \( \eta'(\omega) \) have similar shapes. \( \psi_1(\dot{\gamma}) \) and \( 2G'/\omega^2 \) also have similar shapes. At low shear rate and low frequencies, \( \eta \) and \( \eta' \) approach the same constant value \( \eta_0 \) which is called a zero shear rate viscosity while \( \psi_1 \) and \( 2G'/\omega^2 \) approach constant value called zero shear primary normal stress difference coefficient. 

\[
\eta(\dot{\gamma}) \bigg|_{\dot{\gamma} \to 0} = \eta'(\omega) \bigg|_{\omega \to 0} = \eta_0 \quad [1-20]
\]

\[
\psi_1(\dot{\gamma}) \bigg|_{\dot{\gamma} \to 0} = \left( \frac{2G'(\omega)}{\omega^2} \right) \bigg|_{\omega \to 0} = \psi_1^0 \quad [1-21]
\]

Above a certain shear rate or frequency which is characteristic of the material all of the material functions start to decrease, and the deviations from the analogies begin to appear. Generally \( \eta' \) decreases faster than \( \eta \) and \( \psi_1 \) decreases faster than \( 2G'/\omega^2 \) with increasing shear rate and frequency. Although there is not enough data to confirm the deviation on the elastic side, \( \eta > \eta' \) is almost always in this region.
As shown in Fig. 1-5, some researchers claimed (14) this deviation appears in the form of horizontal shift of the curve, while others attributed to the difference in slope or shape of the curves because they observed \( \eta \) and \( \eta' \) started decreasing at about the same \( \dot{\gamma} \) and \( \omega \) (11).

Cox and Merz proposed an empiricism of eq. 1-18 instead of a simple analogy (10).

Qualitatively, the contribution of \( \eta'' \), which is a measure of the elasticity of the material, makes up the difference between \( \eta \) and \( \eta' \). However, theoretical models proposed to justify the Cox-Merz rule (15)(16) have been incorrect (17)(18). The Cox-Merz rule offers no help in understanding the difference between \( \psi_1 \) and \( 2G'/\omega^2 \).

But within experimental results the Cox-Merz rule has shown good agreement with a few apparent failures as we will show in the later section.

When the shear rate or the frequency become still higher, the deviations become more complicated. \( \eta' \) approaches constant value called infinite viscosity: \( \eta'_\infty \) which depends on concentration, monomer unit, and solvent viscosity and is independent of polymer
structure or molecular weight (5).

The decrease in the power law slope of \( \eta' \) starts from a moderately high frequency. While steady shear viscosity has a straight line power law region for over a few decades on a double logarithmic scale, dynamic viscosity has essentially an S-shape curve and this is never a true straight line.*

![Graph showing shear viscosity over a range of frequencies](image)

---

b. Practical application of polymer rheology in general and the analogy in particular

Processing polymeric material in the liquid state, polymer melt or a solution, is an important part in many industrial operations. Thermoplastic polymers are easily fabricated through the molten state by using injection molding, blow molding, or film extrusion technique into designed shapes.

*In principle, \( \eta \) also has constant value \( \eta_\infty \) but measurements at \( \dot{\gamma} \) high enough to observe \( \eta_\infty \) have been experimentally impossible.
These processes contain high shear rate flows, elongational flows, and low shear rate flows. Under these circumstances, polymer melts behave as non-Newtonian and viscoelastic fluids. Shear viscosity varies by more than 2 or 3 orders of magnitude depending on the range of shear rate. Also the normal stresses increase rapidly with increasing shear rate and cause abnormal phenomena like the extrudate swell at the exit of a die.

In order to design or analyze the model of a polymer flow in the process, or to design polymeric materials to be used in the processing, one has to know the non-Newtonian material properties over the shear rate range this polymer actually encounters during the processing. Viscometric properties govern the steady shear flow which is dominant in many parts of the process.

In industrial operations, shear rates often reach as high as $10^2 - 10^4 \text{ s}^{-1}$, a regime of flow which is hard to attain in laboratory experiments. But experimental measurement of viscometric properties over such range of shear rate is very difficult because of reasons explained previously.

Using the rheological analogy, these viscometric material functions can be estimated from linear viscoelastic properties. As mentioned earlier, linear viscoelastic properties can be easily measured fast and accurately over a sufficiently wide range of frequency at a quality control level laboratory using a dynamic instrument.

Also if one knows both viscometric and linear viscoelastic
properties, one can compute time dependent properties like stress overshooting assuming some constitutive equations because both linear and non-linear properties are already known.

**Table 1-1**

Example of Industrial Processes of Polymer Flows Affected by Non-Newtonian Properties

<table>
<thead>
<tr>
<th>Non-Newtonian Property</th>
<th>Process Affected by the Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shear Rate Dependent</td>
<td>Extrusion</td>
</tr>
<tr>
<td>Viscosity</td>
<td>Paper or Film Coating by Melts or Solutions</td>
</tr>
<tr>
<td></td>
<td>Injection Molding</td>
</tr>
<tr>
<td>Primary Normal Stress Difference</td>
<td>Extrusion - Die Swell Effect</td>
</tr>
<tr>
<td></td>
<td>Injection Molding</td>
</tr>
<tr>
<td></td>
<td>Paper Coating</td>
</tr>
<tr>
<td>Elongational Properties</td>
<td>Melt Spinning</td>
</tr>
<tr>
<td></td>
<td>Film Blowing</td>
</tr>
</tbody>
</table>
3. Previous Work
   a. History of Phenomenological Analogy

   As shown in Fig. 1-7, the simple analogies between viscometric functions and linear viscoelastic properties were first proposed by Buech (15) and Pao (8). Exact measurement revealed that there are deviations from the simple analogy. The three different empiricisms proposed for the deviation are summarized in Fig. 1-7. They are different in the following way: shift of \( \dot{\gamma} \) and \( \omega \) predicts \( \eta \) and \( \eta' \) have the same shape and \( \eta \) is shifted to higher shear rate than \( \eta' \) with the shift factor = C. Slope difference model tells that both \( \eta \) and \( \eta' \) begin decreasing at the same shear rate/frequency but \( \eta' \) decreases at a greater slope than \( \eta \). The Cox-Merz rule predicts \( \eta \) is equal to \( |\eta'| \) (Eq. 1-18) which is larger than \( \eta' \) due to the contribution of \( \eta'' \) which is an elastic property.

   b. Review of Experimental Data to Check Simple Analogy and the Cox-Merz Rule

   Among experimental data that have appeared in the literature only those containing both linear viscoelastic and viscometric properties of the same sample fluids were chosen to check the analogies.

   Table 1-2 shows the result of this check of the viscous analogy. The analogy was evaluated at shear rates below the critical shear rate (Newtonian region) and above the critical shear rate (the power law region).
Fig. 1-7 Historical Overview of the Phenomenological Analogies

Simple Analogy
Buech and Pao

\[ \eta' (\dot{\gamma} \prime) = \eta' (\omega = \dot{\gamma} \prime) \]

\[ \eta = | \eta' (\dot{\gamma} = \dot{\gamma} \prime) | \]

Cox and Kierz

Shift of \( \eta \) and \( \eta' \)

\[ \eta (\dot{\gamma} \prime) = \eta' (\omega = c \dot{\gamma} \prime) \]

Slope Difference

\[ \eta \sim \dot{\gamma}^{-m} \]
\[ \eta' \sim \omega^{-sm} \]

at high \( \dot{\gamma} \) and \( \omega \)
## Table 1-2

**Elastic Properties**

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Sample Description</th>
<th>n =</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Undiluted Polystyrene 1</td>
<td>n =</td>
<td>19</td>
</tr>
<tr>
<td>2</td>
<td>Styron 666 190°C</td>
<td>n =</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>Styron 686 200°C</td>
<td>n =</td>
<td>21</td>
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<tr>
<td>4</td>
<td>LDPE 06002 190°C</td>
<td>n =</td>
<td>22</td>
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<tr>
<td>5</td>
<td><strong>D</strong></td>
<td>n =</td>
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**Viscous Properties**

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<td>Styron 686 200°C</td>
<td>n =</td>
<td>21</td>
</tr>
<tr>
<td>4</td>
<td>LDPE 06002 190°C</td>
<td>n =</td>
<td>22</td>
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<tr>
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<td>n =</td>
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<td><strong>D</strong></td>
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**Literature**

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<td>n =</td>
<td>19</td>
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<td>Styron 666 190°C</td>
<td>n =</td>
<td>20</td>
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<td>Styron 686 200°C</td>
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<td>4</td>
<td>LDPE 06002 190°C</td>
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<td>22</td>
</tr>
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<td>5</td>
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<td><strong>D</strong></td>
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*Note: The table entries are placeholders for the actual data from the literature.*
**Table 1-2 (Cont.)**

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<th>Samples</th>
<th>Literature</th>
<th>VISCOS PROPERTIES</th>
<th>ELASTIC PROPERTIES</th>
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<td><strong>Comparison</strong></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td><em>η</em> ↔ <em>η</em>' ↔ <em>η</em>'</td>
<td><em>η</em> ↔ <em>η</em>' ↔ <em>η</em>'</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>Low γ***</td>
<td>High γ</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Constant η₀</td>
<td>Power Law Region</td>
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<td>III. Undiluted Polypropylene</td>
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<td>12</td>
<td>PP-A</td>
<td>25</td>
<td><em>η</em> =</td>
<td><em>η</em></td>
</tr>
<tr>
<td>13</td>
<td>PP-B</td>
<td>25</td>
<td><em>η</em>' =</td>
<td><em>η</em></td>
</tr>
<tr>
<td>14</td>
<td>PP</td>
<td>12</td>
<td><em>η</em> =</td>
<td><em>η</em></td>
</tr>
<tr>
<td>15</td>
<td>PP filled with glass beads</td>
<td>12</td>
<td><em>η</em> &gt;</td>
<td><em>η</em></td>
</tr>
<tr>
<td>16</td>
<td>E115</td>
<td>21</td>
<td><em>η</em> =</td>
<td><em>η</em></td>
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<tr>
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<td>Poly(1-Olefin)melts</td>
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<td>EMA</td>
<td>27</td>
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<td>EMA</td>
<td>27</td>
<td><em>η</em> =</td>
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<tr>
<td>20</td>
<td>EMA-Na, EMA-Ca</td>
<td>27</td>
<td><em>η</em> =</td>
<td><em>η</em></td>
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<td>V. PST Solutions</td>
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<tr>
<td>21</td>
<td>860,000/PCB 0.071 g/ml</td>
<td>28</td>
<td><em>η</em> =</td>
<td><em>η</em></td>
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</table>
Table 1-2 (Cont.)

<table>
<thead>
<tr>
<th>Sample #</th>
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<td>Comparison</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>$\eta \rightarrow \eta^* \rightarrow</td>
<td>$N_{1/2} \rightarrow G' at</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\eta^* \rightarrow</td>
<td>$N_{1/2} \rightarrow G' at</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>low $\dot{\gamma}$**</td>
<td>low $\dot{\gamma}$</td>
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<td></td>
<td></td>
<td></td>
<td>(Constant $\eta_0$)</td>
<td>(Constant $\psi_1$)</td>
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<td></td>
<td></td>
<td></td>
<td>Region)</td>
<td>Region)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>$n =</td>
<td>\eta^*</td>
</tr>
<tr>
<td>22</td>
<td>3.1M/DEP 0.166 g/ml</td>
<td>29</td>
<td>$n =</td>
<td>\eta^*</td>
</tr>
<tr>
<td>23</td>
<td>5.53M/DEP 0.139 g/ml</td>
<td>29</td>
<td>$n =</td>
<td>\eta^*</td>
</tr>
<tr>
<td>24</td>
<td>3.1M/DEP 0.221 g/ml</td>
<td>29</td>
<td>$n =</td>
<td>\eta^*</td>
</tr>
<tr>
<td>25</td>
<td>5.55M/DEP 0.221 g/ml</td>
<td>29</td>
<td>$n =</td>
<td>\eta^*</td>
</tr>
<tr>
<td>26</td>
<td>1.8M/TCP 8wt%</td>
<td>30</td>
<td>$n =</td>
<td>\eta^*</td>
</tr>
<tr>
<td>27</td>
<td>1.8M/TCP 12wt%</td>
<td>30</td>
<td>$n =</td>
<td>\eta^*</td>
</tr>
</tbody>
</table>

* for example at low $\dot{\gamma}$: $n = \eta^* = \eta$

** all three viscosities must be same as $\dot{\gamma}$ and $\omega$ approaches zero. This is the check of experimental accuracy and consistency

*** These properties must be same if there is no abnormal phenomena

**** abnormal phenomena
The Cox-Merz rule proved to be a fair empiricism for most of the data reviewed in this section. The only systematic deviation from the Cox-Merz rule was found for samples of large values of the product of c (concentration g/ml) and M (molecular weight) for solutions of polystyrene in diethylphthalate (cM \( \geq 7 \times 10^5 \)) and in tricresylphosphate (cM \( \geq 2 \times 10^5 \)). For both systems the deviation appeared as \( |\eta^*| > \eta \). No other apparent cause has been found for the failures of the Cox-Merz rule which are mostly \( |\eta^*| < \eta \) at high shear rates.

Not much data were available to check the analogy between \( \psi_1 \) and \( 2G'/\omega^2 \) and in most of the existing data, relatively narrow ranges were covered. We could not conclude in general that either \( \psi_1 = 2G'/\omega^2 \) at high shear rate or \( \psi_1 > \frac{2G'}{\omega^2} \) as in the case of the viscous part of the analogy from the information.

It has been an established fact from experimental observations and theoretical considerations that \( \psi_1 = \frac{2G'}{\omega^2} \) at low frequencies and shear rates. But we also found a few examples in the literature (21) (24)(25) where this rule was apparently violated with no abnormality on the analogy of viscosities. It is very likely that this abnormality was due to some experimental errors rather than a real phenomenon because the measurement of normal stress is by far more difficult compared to the steady shear viscosity measurement.

From this literature review, it is evident that there is not enough data available to study how polymer structures affect the deviations from the analogies even with well studied materials such as polystyrene solutions or polyethylene melts.

It is surprising that no study could be found of the analogies
of anionically synthesized narrow molecular weight distribution polystyrene in molten state.

Onogi et al. studied the analogy with (20) five radical polymerized polystyrene and fractioned samples with narrow molecular weight distribution in molten state. The data shows good agreement with the Cox-Merz rule but lacks elastic property data.

Other information available about these narrow distribution polystyrenes is the indirect comparison made by Graessley (11). He compared the dynamic viscosity and the complex viscosity curves of polystyrene melts of $\overline{M_w}=215,000$ and $\overline{M_w}=581,000$ to the steady shear viscosity of polystyrene melt of $\overline{M_w}=411,000$. $\eta'$ of $\overline{M_w}=215,000$ is almost equal to $\eta$ of $\overline{M_w}=411,000$, which suggested that $\eta^* \eta = \eta'$ at high shear rate. The Cox-Merz rule failed.

One reason for the lack of this kind of data can be that narrow distribution polymers are expensive but more important is the problem with the instrument. As the temperature dependence of the viscosity of polystyrene melt is very large, temperature control of the rheometer must be $\pm 0.5^\circ C$ or less for satisfactory measurements. However temperature control of existing rotary rheometers with air ovens cannot be better than $\pm 1^\circ C$ due to temperature fluctuations and temperature gradients because the metal plate, the cone and the drive shaft work as heat sinks (appendix-6). Also it is more difficult to measure the high shear rate properties of polystyrene melt than those of polyethylene melt because polystyrene melts have a lower surface tension than polyethylene melt and are more susceptible to shear fracture (31). It is also surprising that there has been no published
study of the analogies of star branched polymers either in the form of melts or solutions.

C. Previous Theoretical Work on the Analogies

In this section, the prediction of the analogies from representative constitutive equations are reviewed. First models are divided into two categories: 1) differential models and 2) integral models. In Table 1-3 the material functions expressed by these models, along with the prediction of the rheological analogies, are listed.

From this review theoretical models are classified based on their ability to predict the analogies and the deviations from the simple and qualitative analogies into the following categories:

1) Models which have no ability to predict any type of the analogies,
   The Oldroyd-Walters-Fredrickson model
   The Lodge rubber-like liquid model

2) A model which predicts exact analogies
   The Goddard-Miller model

3) Models which predict horizontal shifts as the deviations from the analogies
   The Oldroyd 3-constant model
   The Spriggs model
   The Phan Thien model
   The Segalman-Johnson model
4) Models that can accommodate any deviations by incorporation of arbitrary parameters and/or spectra.

The Bird-Carreau model
The Wagner model
The Tanner-Simmons model
The Shroff-Shida model
The Carreau B model

It is important to note that only the Goddard expansion states the deviation from the analogies systematically, using the higher order non-linear kernel functions. In the Goddard expansion the deviations are expressed in terms of kernel functions, $G_{III}$, $G_{IV}$, inside triple integrals and with still higher order kernels. $G_{III}$ and $G_{IV}$ can be computed from the deviations from the analogies.

$$n(\gamma) - n'(\omega) \mid_{\omega=\gamma} = \gamma^2 \int\int\int_0^\infty [2G_{III} \cos \gamma s \cos \gamma (s'-s'')]$$

$$+ G_{IV} \cos \gamma (s''-s'+s')] ds''ds'ds + \ldots \quad [1-22]$$
### Table 1-3 (a) Prediction of Material Functions and Analogies by Constitutive Equations

#### I. DIFFERENTIAL MODEL

<table>
<thead>
<tr>
<th>Model</th>
<th>Ref.</th>
<th>Constitutive Equation</th>
<th>Viscometric Properties</th>
<th>Linear Viscoelastic Properties</th>
<th>Analogies</th>
</tr>
</thead>
<tbody>
<tr>
<td>White Metzner</td>
<td>33</td>
<td>( 1 + \frac{2}{3}\lambda(1))</td>
<td>( \eta = n(\gamma) ) Adjustable ( \psi_2 = 0 )</td>
<td>( \eta' = \frac{n_0}{1+(\lambda\omega)^2} )</td>
<td>no simple analogy</td>
</tr>
<tr>
<td>Tanner</td>
<td>34</td>
<td>( 1 + \lambda\beta(1))</td>
<td>( \eta = n(\gamma) : \text{adjustable} ) ( \psi_2 = 0 )</td>
<td>( \eta'' = \frac{n_0\lambda\omega}{1+(\lambda\omega)^2} )</td>
<td>same as above no simple analogy</td>
</tr>
<tr>
<td>Oldroyd</td>
<td>35</td>
<td>( 1 + \frac{2}{3}\lambda(1))</td>
<td>( \eta = n(\gamma) )</td>
<td>( \eta' = \frac{1+\lambda_1\lambda_2\omega^2}{n_0} )</td>
<td>( \eta(\gamma) = \eta' \left( \frac{T}{3}\omega \right) )</td>
</tr>
<tr>
<td>Oldroyd</td>
<td>36</td>
<td>( 1 + \frac{2}{3}\lambda(1))</td>
<td>( \eta = n(\gamma) )</td>
<td>( \eta'' = \frac{(\lambda_1-\lambda_2)}{n_0} )</td>
<td>( \frac{T}{3} ) shift factor</td>
</tr>
</tbody>
</table>

\( n_0, \lambda_1, \lambda_2 \) are constants.
Table 1-3(a) Cont.

<table>
<thead>
<tr>
<th>Model</th>
<th>Constitutive Equation</th>
<th>Viscometric Properties</th>
<th>Linear Viscoelastic Properties</th>
<th>Analogies</th>
</tr>
</thead>
<tbody>
<tr>
<td>4. Oldroyd</td>
<td>( \gamma \cdot ) constant ( \dot{\gamma} )</td>
<td>[ \psi_2 = - \frac{\psi_1}{\eta_0 \lambda_1} \left( \frac{\mu_1}{\lambda_1} \frac{n}{\lambda_1} - \frac{\mu_2}{\lambda_1} \right) ]</td>
<td>[ \eta' = \frac{\eta_0}{Z(a)} \sum \frac{n^a}{n} \frac{2\alpha c^2 \lambda}{\lambda} ]</td>
<td>[ n(\dot{\gamma}) = n'(c \cdot \gamma) ]</td>
</tr>
<tr>
<td>5. Spriggs</td>
<td>( \bar{\xi} = \sum_{k=1}^{n} \bar{\xi}_k )</td>
<td>[ n'' = \frac{\eta_0}{Z(a)} \frac{1}{n} 2\alpha c^2 \lambda \gamma ]</td>
<td>[ \psi_1 = \frac{2n_0 \lambda}{Z(a)} \frac{n^a}{n} \frac{1}{2\alpha c^2 \lambda \gamma} ]</td>
<td>[ C^2 \psi_1 = \frac{C^2}{2} \psi_1(\dot{\gamma}) = G'(c \cdot \gamma) ]</td>
</tr>
<tr>
<td>( \lambda_k = \lambda/\alpha ) ( \eta_k = \eta_0 \lambda_k / \Sigma \lambda_k )</td>
<td>[ \psi_2 = \frac{n_0 \lambda}{Z(a)} \frac{1}{n} 2\alpha c^2 \lambda \gamma ]</td>
<td>[ \eta''_0 = \frac{\eta_0 \lambda}{Z(a)} \frac{1}{n} 2\alpha c^2 \lambda \gamma ]</td>
<td>[ C : \text{shift factor} ]</td>
<td></td>
</tr>
</tbody>
</table>

6. Phan-Thien  | \( \bar{\xi} = \sum_{k=1}^{n} \bar{\xi}_k'(1) \) | \[ n'' = \frac{\eta_0}{Z(a)} \frac{1}{n} 2\alpha c^2 \lambda \gamma \] | \[ \psi_1 = \frac{2\varepsilon}{1+\varepsilon(2-\varepsilon)\lambda_1 \gamma} \] | \[ n''(\omega) = \frac{n''(\omega)}{\varepsilon(2-\varepsilon)} + O(\varepsilon) \] |
| 38            | \( \lambda_1 \frac{D}{D} \bar{\xi}'(1) + \gamma \left( \text{tr} \bar{A}(1) \right) \right) | \[ n' = \frac{\varepsilon}{1+c(2-\varepsilon) \lambda_1 \gamma} \] | \[ \psi_2 = \frac{n}{2} \psi_1 \] | \[ n'(\omega) = \frac{n'(\omega)}{\varepsilon(2-\varepsilon)} + O(\varepsilon) \] |
| \( \bar{\xi}'(1) = G_1 \lambda_1 \bar{D} \) | \[ \psi_1 = \frac{2\varepsilon}{1+c(2-\varepsilon) \lambda_1 \gamma} \] | \[ \psi_2 = \frac{n}{2} \psi_1 \] | \[ \xi = 1 - \psi_2 = -\frac{1}{2} \psi_1 \] | \[ \xi = 1 - \psi_2 = -\frac{1}{2} \psi_1 \] and no shift |
**Table 1-3(a) Cont.**

<table>
<thead>
<tr>
<th>Model</th>
<th>Ref</th>
<th>Constitutive Equation</th>
<th>Viscometric Properties</th>
<th>Linear Viscoelastic Properties</th>
<th>Analogies</th>
</tr>
</thead>
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<td>INTEGRAL MODELS</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>7. Oldroyd-</td>
<td>39</td>
<td>[ I = \int_{-\infty}^{t} G(t-t') \zeta_o(t') dt' ]</td>
<td>( \eta = \eta_o, \psi_1 = \psi_1^0, \psi_2 = 0 )</td>
<td>( n' = \int G(s) \cos \omega ds )</td>
<td>no simple analogy</td>
</tr>
<tr>
<td>Walters-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fredrickson</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>8. Lodge's</td>
<td>40</td>
<td>[ I = \int_{-\infty}^{t} \mu(t-t') \zeta_o(t') dt' ]</td>
<td>same as above</td>
<td>( n'' = \int G(s) \sin \omega ds )</td>
<td></td>
</tr>
<tr>
<td>Rubber-like Liquid</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9. Bird Carreau</td>
<td>40</td>
<td>[ I = \int_{-\infty}^{t} \mu(t-t', \pi_o(t')) ]</td>
<td>( \eta = \frac{\nu}{k} \frac{\eta_k}{1 + (\lambda_k^*(2)\omega)^2} )</td>
<td>( n' = \int \frac{\eta_k}{k} \frac{\eta_k(2)}{1 + (\lambda_k(2)\omega)^2} )</td>
<td>deviations from simple analogy by ( \alpha_1 \leftrightarrow \beta_1 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( [(1 + \frac{\nu}{2})\zeta_o(t') - (\frac{\nu}{2})\pi_o(t')] dt' )</td>
<td>( \psi_1 = 2 \sum \frac{\eta_{k} \lambda_k(2)}{k} \frac{\eta_k(2)}{1 + (\lambda_k(2)\omega)^2} )</td>
<td>( n'' = \int \frac{\eta_k}{k} \frac{\eta_k(2)}{1 + (\lambda_k(2)\omega)^2} )</td>
<td></td>
</tr>
<tr>
<td>10. Tanner-Simmons</td>
<td>41</td>
<td>[ I = \int_{t-t_R}^{t} \mu(t-t') [(1 + \frac{\nu}{2})\zeta_o(t')] dt' ]</td>
<td>( \eta = kT \sum {1 - [1 + (\frac{\beta}{\lambda \zeta}] e^{-\frac{\beta}{\chi \lambda \zeta}] } )</td>
<td>( n' = \int \frac{\eta_{j}}{j} \frac{\eta_j}{1 + (\lambda_j \omega)^2} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \psi_1 = kT \sum \eta_j \lambda_j \left[2 - 2e^{2(\frac{\beta}{\lambda \zeta})} - \frac{\beta}{\lambda \zeta} \right] )</td>
<td>( \psi_2 = 0 )</td>
<td>( n'' = \int \frac{\eta_j}{j} \frac{\eta_j}{1 + (\lambda_j \omega)^2} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( t_R = t_R(III) ) rupture time</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Model</td>
<td>Ref</td>
<td>Constitutive Equation</td>
<td>Viscometric Properties</td>
<td>Linear Viscoelastic Properties</td>
<td>Analogies</td>
</tr>
<tr>
<td>-----------------------</td>
<td>-----</td>
<td>---------------------------------------------------------------------------------------</td>
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</tr>
<tr>
<td>11. Carreau-B</td>
<td>42</td>
<td>$\dot{\gamma} = \int_{t'=t}^{t} \frac{1}{2} c(t' - t')^{\alpha} \left[ \tau(t') \right] dt$</td>
<td>$\eta = \frac{1}{\dot{\gamma}} \left[ \frac{2(\alpha - 1)}{\alpha} \right]$</td>
<td>$\eta' = \frac{1}{\dot{\gamma}'} \left[ \frac{2(\alpha - 1)}{\alpha} \right]$</td>
<td>$n(\dot{\gamma}) = n' \left[ \frac{\dot{\gamma}}{\dot{\gamma}'} \right]$ when slope of $\eta = \text{slope of } \eta'$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\frac{\psi'_{1}}{\psi} = \frac{(1 + 2\alpha) \dot{\gamma}^{2} - 1}{(2a + 1)(2\alpha + 1) / 3}$</td>
<td>$\frac{\psi''}{\psi} = \frac{1}{(2a + 1)(2\alpha + 1) / 3}$</td>
<td>$\frac{\eta}{\eta_{0}} = \frac{1}{Z(a) - 1} \sum_{i=1}^{\infty} \frac{p^a + (2\alpha \omega)^2}{p^a}$</td>
<td>$\dot{\gamma} \rightarrow \log \gamma$ (power law von $\gamma$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$Z(a)$ is the Riemann zeta function</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12. Wagner</td>
<td>43</td>
<td>$\dot{\gamma} = \int_{0}^{t} \nu(t) \dot{\gamma}(t) \dot{\gamma}(t) \frac{a_1}{a_0} dt$</td>
<td>$n(\dot{\gamma}) = \frac{a_1 \dot{\gamma}^{2}}{(1 + a_0 \dot{\gamma})^2}$</td>
<td>$n'(\omega) = \frac{a_1 \omega^{2}}{(1 + \omega \dot{\gamma})^2}$</td>
<td>deviation by $\dot{\gamma}$ (if $h = e^{-h}\dot{\gamma}$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$(t-t') \nu(t-t') \dot{\gamma}(t-t')$</td>
<td>$\psi_1(\dot{\gamma}) = \frac{2 a_1 \dot{\gamma}^{3}}{(1 + a_0 \dot{\gamma})^3}$</td>
<td>$\psi''(\omega) = \frac{2 a_1 \omega^{3}}{(1 + \omega \dot{\gamma})^3}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\beta(t-t')h(\dot{\gamma})$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13. Schroff-</td>
<td>44</td>
<td>same as 9</td>
<td>$\eta = \int H(\tau, \dot{\gamma})d\tau$</td>
<td>$n''(\omega) = \frac{1}{\omega^{2}} \int H(\tau) \frac{\omega^{2}}{1+\omega \dot{\gamma}} d\tau$</td>
<td>deviation is implied by $H(\tau, \dot{\gamma})$ or $h(\alpha), g(\alpha)$</td>
</tr>
<tr>
<td>Shida</td>
<td></td>
<td>$H(\tau, \dot{\gamma}) = H(\tau) h(\theta) g(\theta) \dot{\gamma}^{2}$</td>
<td>$\psi_1 = \int H(\tau, \dot{\gamma}) \dot{\gamma}^{2} d\tau$</td>
<td>$\psi_1 = \int H(\tau) \frac{\omega^{2}}{1+\omega \dot{\gamma}} d\tau$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\theta = (\dot{\gamma}/2)\tau$</td>
<td>$\psi_1 = \int H(\tau, \dot{\gamma}) \dot{\gamma}^{2} d\tau$</td>
<td>$\psi_1 = \int H(\tau) \frac{\omega^{2}}{1+\omega \dot{\gamma}} d\tau$</td>
<td></td>
</tr>
<tr>
<td>14. Goddard-</td>
<td>45</td>
<td>$\dot{\gamma} = -\int_{0}^{t} G(t-t') \frac{a_1}{a_0} dt'$</td>
<td>$n = \int G(s) \cos \dot{\gamma} ds$</td>
<td>$n''(\omega) = \int G(s) \sin \omega ds$</td>
<td>$n = n''(\dot{\gamma})$</td>
</tr>
<tr>
<td>Miller</td>
<td></td>
<td>$\dot{\gamma} = -\int_{0}^{t} G(t-t') \frac{a_1}{a_0} dt'$</td>
<td>$\psi_1 = \frac{2}{\dot{\gamma}} \int G(s) \sin \dot{\gamma} ds$</td>
<td>$\psi_2 = -\frac{1}{\dot{\gamma}} \int G(s) \sin \dot{\gamma} ds$</td>
<td>$\psi_1 = n''(\dot{\gamma})$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$n'' = \int G(s) \cos \omega ds$</td>
<td>$\psi_2 = -\frac{1}{\dot{\gamma}} \int G(s) \sin \dot{\gamma} ds$</td>
<td></td>
</tr>
<tr>
<td>Model</td>
<td>Ref</td>
<td>Constitutive Equation</td>
<td>Linear Viscoelastic Properties</td>
<td>Analogies</td>
<td></td>
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<tr>
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</tr>
<tr>
<td>15. Goddard</td>
<td>7.46</td>
<td>( \chi = - \int G_1(t-t') e^t' dt' + \frac{1}{2} \int G_{II}(t-t', t-t'') dt'' dt' + \frac{1}{2} \int \int [2G_{IV}(t-t', t-t'', t-t''') dt'' dt'''] dt'''' dt''' dt' + \cdots )</td>
<td>( n' = \int G_1(s) \cos \omega ds )</td>
<td>1st term as above simple analogy</td>
<td></td>
</tr>
<tr>
<td>Expansion</td>
<td></td>
<td></td>
<td>( n'' = \int G_1(s) \sin \omega ds )</td>
<td>2nd, 3rd..., term for deviations</td>
<td></td>
</tr>
<tr>
<td>Models</td>
<td>Analogy</td>
<td>Power Law Slopes $m,m'$</td>
<td>Critical Shear Rate $\dot{\gamma}_0$</td>
<td>Critical Frequency $\omega_0$</td>
<td></td>
</tr>
<tr>
<td>---------------------</td>
<td>---------------------------------------</td>
<td>-------------------------</td>
<td>-------------------------------------</td>
<td>-------------------------------</td>
<td></td>
</tr>
<tr>
<td>3. Oldroyd 3-Constant</td>
<td>Horizontal ((\dot{\gamma}-\omega) axial) shift</td>
<td>No power law zone</td>
<td>$\sqrt[3]{0.3}$</td>
<td>$\sqrt[3]{0.2}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\sqrt{0.8\lambda_1^2-\lambda_1\lambda_2}$</td>
<td>$\sqrt{0.8\lambda_1^2-\lambda_1\lambda_2}$</td>
<td></td>
</tr>
<tr>
<td>4. Oldroyd 8-Constant</td>
<td>Deviation by parameters</td>
<td>No power law zone</td>
<td>$\sqrt[3]{0.27}\sqrt{-\lambda_1\lambda_2+0.8}$</td>
<td>$\lambda_1^2 u_0 (-u_2+0.8u_1)$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$-\frac{3}{2}(-u_2+0.8u_1)-u_1$</td>
<td>$\frac{1}{2}(-u_2+0.8u_1+u_2+0.8u_1)$</td>
<td></td>
</tr>
<tr>
<td>5. Spriggs</td>
<td>Horizontal Shift by spectrum and $C$</td>
<td></td>
<td>$\dot{\gamma}_0 = C\omega_0$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. Pham-Thien</td>
<td>Horizontal Shift $n,n'$ same slope</td>
<td></td>
<td>$\dot{\gamma}_0 = (\sqrt[3]{2-5}) \omega_0$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9. Bird-Carreau</td>
<td>slope difference by $\lambda_1,\lambda_2$ and $m = \frac{a_1-1}{a_1}$</td>
<td></td>
<td>$\dot{\gamma}_0 = \frac{1}{2a_1\lambda_1^{1-\alpha_1}} \left[ \frac{1-\alpha_1}{2a_1} \pi (\zeta \alpha_1-1) \frac{a_2}{\alpha_2} \right]^{\frac{1}{1-\alpha_1}}$</td>
<td>$\omega_c = \frac{1}{2a_1\lambda_2^{1-\alpha_1}} \left[ \frac{1+2\alpha_2-\alpha_1}{2a_2} \pi (\xi \alpha_1-1) \frac{a_2}{\alpha_2} \right]^{\frac{1}{1-\alpha_1}}$</td>
<td></td>
</tr>
<tr>
<td>10. Tanner-Simmons</td>
<td>Deviation implied in complicated expressions</td>
<td>$m \neq m'$</td>
<td>$\dot{\gamma}_0 \neq \omega_0$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14. Goddard-Miller</td>
<td>exact analogy</td>
<td>$m = m'$</td>
<td>$\dot{\gamma}_0 = \omega_0$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
\[ \frac{\dot{\gamma}}{2} \psi_1(\dot{\gamma}) \mid_{\omega=\dot{\gamma}} = \gamma^2 \int_0^\infty \left[ 2G_{III} \sin \gamma s \cos \gamma (s'-s) \right] ds'' ds' ds + \ldots \quad [1-23] \]

Attempts to get \( G_{III} \) and \( G_{IV} \) mathematically (by truncating higher order integrals) from the data of the deviations are described in a later section.

The Goddard expansion is useful as a theoretical framework. For example, recently it has been suggested that the long chain branching of polymer molecules such as polyethylene changes the processibility of the film blowing operation significantly without changing the shear flow properties such as \( \eta, \eta', \) or \( G' \) but drastically changing extensional viscosities: \( \overline{\eta}. \)

According to the Goddard expansion, \( \eta' \) and \( G' \) depend on \( G_I \) only. And \( \psi_1 \) depend on \( G_I, G_{III} \) and \( G_{IV} \) while \( \psi_2 \) depends on \( G_I, G_{II}, G_{III} \) and \( G_{IV} \), \( \overline{\eta} \) depends on \( G_I \) and \( G_{II} \).

Therefore, if the long chain branching actually changes the elongational viscosity without changing the steady shear viscosity and the dynamic viscosity, it can be predicted from the Goddard expansion that \( \psi_2 \) must be changed by the long chain branching.

d. Review of the Effect of Polymer Structure on Rheological Properties

The flow properties of a Newtonian fluid depend on the chemical structure of each molecule. However the flow properties of polymeric
liquids depend, not only on the unit structures, but on other macro-
molecular structural factors such as molecular weight, molecular
weight distribution and the long chain branching density.

It would be very interesting to know the effect of these
polymeric structures on the rheological analogies, because the
effect of these structural factors may work differently on the linear
viscoelastic properties and on the viscometric properties. These
rheological properties have been studied for various polymer melts
and solutions of different structures because the relationship be-
tween the polymer structure and the processibility which largely
depends on the viscometric properties has a significant industrial
application.

Table 1-4 lists studies of the effect of the structure on the
flow properties. Very few projects have been performed to study
the relation between the viscometric and the linear viscoelastic
properties in the context of the polymer structure, like the long
chain branching density, by taking both the dynamic measurement
and the steady shear flow measurements of the same sample liquid.

Schroff and Shida examined the Cox-Merz rule for polyethylene
melts of various long chain densities and found that the rule
failed at the high branching density (47). Their experiments
were based on commercial polyethylene samples with rather compli-
cated structure as shown in Fig. 1-8 compared to star shaped
polymers or comb shaped polymers studied elsewhere which are
anionically synthesized and have narrow molecular weight distribution.
Table 1-4
The Effect of the Structure on Viscometric
and Linear Viscoelastic Properties of Polymers

<table>
<thead>
<tr>
<th>Reference</th>
<th>Author</th>
<th>Material</th>
<th>Properties Measured</th>
<th>Structural Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>51</td>
<td>Onegi et al.</td>
<td>polystyrene melt</td>
<td>$G'(\omega)$, $G''(\omega)$, $\eta_0$</td>
<td>linear and star, MW, MWD</td>
</tr>
<tr>
<td>52</td>
<td>Graessley et al.</td>
<td>polystyrene melt</td>
<td>$\eta(\dot{\gamma})$, $\alpha_T$</td>
<td>linear and star MWD</td>
</tr>
<tr>
<td>53</td>
<td>Ferry et al.</td>
<td>polystyrene solution</td>
<td>$G'(\omega)$, $G''(\omega)$, $\eta_\infty$</td>
<td>star, comb and linear</td>
</tr>
<tr>
<td>54</td>
<td>Onogi et al.</td>
<td>polystyrene solution</td>
<td>$G'(\omega)$, $G''(\omega)$, $\alpha_T$</td>
<td>random branching</td>
</tr>
<tr>
<td>55</td>
<td>Nagasawa et al.</td>
<td>polystyrene dilute solution</td>
<td>$[\eta]_D$</td>
<td>comb</td>
</tr>
<tr>
<td>56</td>
<td>Nagasawa et al.</td>
<td>polystyrene melt</td>
<td>$E(t)$, $\alpha_T$</td>
<td>comb, MWD</td>
</tr>
<tr>
<td>57</td>
<td>Ferry et al.</td>
<td>polystyrene dilute solution</td>
<td>$[G'']_R$, $[G']_R$</td>
<td>star and linear</td>
</tr>
<tr>
<td>58, 59</td>
<td>Utracki et al.</td>
<td>polystyrene solution</td>
<td>$\eta(\dot{\gamma})$, $\psi_1(\dot{\gamma})$, $\eta_0$</td>
<td>linear and star MN</td>
</tr>
<tr>
<td>47</td>
<td>Schrott et al.</td>
<td>polyethylene melt</td>
<td>$\eta(\dot{\gamma})$, $\eta'(\omega)$, $G'(\omega)$, $\eta^*$</td>
<td>LCB</td>
</tr>
<tr>
<td>60</td>
<td>Mendelson</td>
<td>polyethylene melt (HDPE, LDPE)</td>
<td>$\eta(\dot{\gamma})$, $\eta'(\omega)$, $\eta^*$</td>
<td>LCB, MW**</td>
</tr>
<tr>
<td>61, 62</td>
<td>Mendelson et al.</td>
<td>polyethylene melt (HDPE, LDPE)</td>
<td>$\eta(\dot{\gamma})$</td>
<td>MW, MWD, LCB</td>
</tr>
<tr>
<td>48</td>
<td>Boghetich et al.</td>
<td>polyethylene melt</td>
<td>$\eta(\dot{\gamma})$</td>
<td>LCB</td>
</tr>
<tr>
<td>63</td>
<td>Wild et al.</td>
<td>LDPE melt</td>
<td>$\eta(\dot{\gamma})$, $\eta_0$, die swell</td>
<td>MW, MWD, LCB</td>
</tr>
<tr>
<td>64</td>
<td>Combs et al.</td>
<td>polyolephine melt</td>
<td>MI, MF, MS</td>
<td>MWD, SCB</td>
</tr>
</tbody>
</table>

**range of $\eta(\dot{\gamma})$ is too narrow to check the Cox-Merz rule**
Table 1-4
The Effect of the Structure on Viscometric and Linear Viscoelastic Properties of Polymers

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<thead>
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<td>$G'(\omega), G''(\omega), \eta_0$</td>
<td>linear and star, MW, MWD</td>
</tr>
<tr>
<td>52</td>
<td>Graessley et al.</td>
<td>polystyrene melt</td>
<td>$\eta(\dot{\gamma}), a_T$</td>
<td>linear and star MWD</td>
</tr>
<tr>
<td>53</td>
<td>Ferry et al.</td>
<td>polystyrene solution</td>
<td>$G'(\omega), G''(\omega), \eta'_\omega$</td>
<td>star, comb and linear</td>
</tr>
<tr>
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<td>Onogi et al.</td>
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<td>random branching</td>
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<tr>
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<td>Nagasawa et al.</td>
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<td>$[\eta]_o$</td>
<td>comb</td>
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<td>$E(t), a_T$</td>
<td>comb, MWD</td>
</tr>
<tr>
<td>57</td>
<td>Ferry et al.</td>
<td>polystyrene dilute solution</td>
<td>$[G^n]_R [G'']_R$</td>
<td>star and linear</td>
</tr>
<tr>
<td>58, 59</td>
<td>Utracki et al.</td>
<td>polystyrene solution</td>
<td>$\eta(\dot{\gamma}), \psi(\dot{\gamma}) \eta_0$</td>
<td>linear and star MW</td>
</tr>
<tr>
<td>47</td>
<td>Schrott et al.</td>
<td>polyethylene melt</td>
<td>$\eta(\dot{\gamma}), \eta'(\omega), G'(\omega), \eta^*$</td>
<td>LCB</td>
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<td>Mendelson</td>
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<td>61, 62</td>
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<td>Wild et al.</td>
<td>LDPE melt</td>
<td>$\eta(\dot{\gamma}), \eta_0$, die swell</td>
<td>MW, MWD, LCE</td>
</tr>
<tr>
<td>64</td>
<td>Combs et al.</td>
<td>polyolephine melt</td>
<td>$\eta(\dot{\gamma}), \eta_0$, die swell</td>
<td>MWD, SCB</td>
</tr>
</tbody>
</table>

**range of \(\eta(\dot{\gamma})\) is too narrow to check the Cox-Merz rule**
<table>
<thead>
<tr>
<th>Reference</th>
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<th>Material</th>
<th>Properties Measured</th>
<th>Structural Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>65</td>
<td>Mieras</td>
<td>SBR, bulk and oil extended</td>
<td>η(\dot{\gamma}), G'(ω)</td>
<td>linear and star</td>
</tr>
<tr>
<td>66, 67</td>
<td>Kraus et al.</td>
<td>polybutadiene</td>
<td>η(\dot{\gamma}), η₀</td>
<td>star, MW</td>
</tr>
<tr>
<td>68</td>
<td>Graessley et al.</td>
<td>polyisoprene solution</td>
<td>η(\dot{\gamma}), ψ₁(\dot{\gamma})</td>
<td>linear and star</td>
</tr>
<tr>
<td>69</td>
<td>Leblanc</td>
<td>polybutadiene-styrene block copolymer melt</td>
<td>η(\dot{\gamma}), ψ₁(\dot{\gamma}), α₁</td>
<td>star</td>
</tr>
<tr>
<td>70</td>
<td>Ferry et al.</td>
<td>polybutadiene dilute</td>
<td>[G''] [G']</td>
<td>star</td>
</tr>
<tr>
<td>71</td>
<td>Kurata et al.</td>
<td>polystyrene-butadiene block copolymer (SBS) solution</td>
<td>α₁ and concentration dependence, viscosity growth and decay at small \dot{\gamma}</td>
<td>star</td>
</tr>
</tbody>
</table>

NOTE:  
MW Molecular weight  
MWD Molecular weight distribution  
LCB Long chain branching  
SCB Short chain branching
It would be difficult to analyze the data from commercial polyethylene theoretically to get a quantitative relationship between the deviations from the analogies or the deviations from the Cox-Merz rule and the long chain density. The deviations might be due to other structural factors which changed simultaneously with increasing long chain branching density.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{H} \\
\text{CH}_2 & \quad \text{H} \\
\text{CH} & \quad \text{CH}_3
\end{align*}
\]

Fig. 1-8 The Composite Structure of Polyethylene (48)

Notice that there is a complete lack of studies that contain both the viscometric and the linear viscoelastic properties with star shaped polymers or comb shaped polymers. One of the original objectives for synthesizing these tailor structured polymers with a great difficulty was to check the effect of structure (especially the long chain branching) on flow properties of polymer melts and solutions.

As shown in Table 1-4 linear viscoelastic properties of these star shaped polymers and comb shaped polymers have been extensively
studied. The viscomeric properties, namely the steady shear viscosity and primary normal stress difference have been measured for some of the samples but none of these publications contain the linear viscoelastic data of the same sample.

The synthesis of the star shaped polystyrene, polybutadiene, and polyisoprene, with well defined structure and the narrow distribution of the molecular weight and the branching density, has been accomplished by anionic polymerization and some of the results appear in table 1-3 (49).

Professor Paul Rempp of C.N.R.S., Strasbourg generously supplied us with samples of such narrow distribution star shaped polystyrene which made this project possible (50).

Long chain branching shrinks the size of the polymer molecule at the random coil state. Zimm and Stockmayer (72) and Zimm and Kilb (73) theoretically calculated the effect of the long chain branching to the molecular size from the bead-spring model. For f-branched equal arm length star shaped polymer, the following expression was obtained.

\[ g = \frac{3f-2}{f^2} \]  \hspace{1cm} [1-24]

where \( g = \frac{<s^2>}{<s'^2>1} \) : branched/linear polymer ratio of mean square, radius of gyration (same MW)  \hspace{1cm} [1-25]

The relaxation time spectra have been computed for the star
shaped polymers in the infinite dilution (74)(75). Star shaped polymers show non-uniform distribution of the relaxation time, compared to the monotonous decreasing distribution for linear polymers as shown in Fig. 1-9. The longest relaxation time (which dominates the flow behavior) is shorter for the branched polymers.

Most of the dilute solution linear viscoelastic properties of star shaped polymers have been explained quantitatively by the molecular size shrinkage and the change of the relaxation time spectrum.

![Diagram of relaxation spectra](Fig. 9. Relaxation spectra of linear, 8-arm star, and 8-branch comb polymers with $N_s = 5$ and $k^* = 0.25.$ (74))
Kraus et al. (66)(67), and Graessley et al. (68) have observed that star shaped polybutadiene solutions and polyisoprene solutions of large cM value have abnormally high zero shear viscosities. Both zero shear viscosities and steady state shear compliances become larger than expected from g, M, and c, as shown in the Fig. 1-10. The $M^{3.4}$ power dependence (76) of zero shear viscosity which is applicable for most of the polymeric liquids in the high cM region does not apply for these star shaped polymer solutions of large cM value. This phenomenon is called the "enhancement effect".
4. Strategy

Fig. 1-11 gives an overview of the strategy for this project. The strategy was based on the following considerations. The sample was polystyrene because of the reasons listed below.

1) Polystyrene is by far the most studied material in polymer science. There is a great accumulation of rheological data.
2) Linear polymers of narrow molecular weight distribution are commercially available. As mentioned above, Prof. P. Rempp of C.N.R.S., Strasbourg, has supplied us with samples of star shaped polystyrene with narrow molecular weight and branching density distributions (50).
3) Polystyrene is relatively stable during measurements even at high temperatures as it lacks reactive sites such as carbon-carbon double bonds.
Fig. 1-11 Strategy for the Investigation of the Analogies between Viscous and Linear Viscoelastic Properties

**SAMPLE**
- **POLYMER**
  - **PSPoly**
  - **Narrow Distb.**
  - **Broad Distb.**
  - **Linear**
  - **Star**

**FORM**
- **Undiluted**
- **Solution**
- **Concentrated**
- **Dilute**

**MEASUREMENT**
- Dynamic Measurement
- Viscometric Measurement
- **ERD** (Cone and Plate Oscillatory)
- **RMS**
  - Cone and Plate
  - Parallel Plate

**ANALYSIS**
- Dynamic Data
- Viscometric Data
  - Structure, c, n Dependence
  - Analogy

**THEORETICAL STUDY**
- Wagner Model
- Goddard Expansion

**CONCLUSION**
- Information obtained
4) It is one of the commodity plastics that has wide industrial applications.

In many of the industrial processes undiluted polystyrene melts are used. Therefore a polymer melt was our first choice for the form of the samples. However we encountered various problems as listed below.

1) Thermal degradation of the polystyrene melts, although not significant for a short time, makes repeated use of sample questionable. Therefore, more than 20 g of polymer is required for each sample which is hard to obtain for well characterized polymers.

2) Temperature control of the rotary rheometers is not good enough to work with such temperature sensitive materials as polystyrene melts. The temperature fluctuation is ± 1°C at best and there is also a large temperature gradient of a few degrees within the sample liquid which is explained further in the appendix 6.

3) Preliminary work on polystyrene melt showed that the time-temperature superposition principle is not directly applicable for the steady shear properties possibly due to large systematic error in the measurement. This is explained in chapter 4 in detail.

As a result, concentrated solutions which have large polymer chain-chain interactions similar to melts were chosen as the form
of the sample. The concentrations are between 0.088 and 0.62 g/ml so that c[n] is greater than or equal to 10 for all but one of the solutions examined.

We were not primarily interested in the dilute solution properties because they have been extensively studied (77)(57), because we do not have a particularly good facility for studying high frequency phenomena, and because we would obtain no information about the chain-chain interaction which dominates the polymer flow behavior in the molten state or in a concentrated solution which are the ordinary forms in industrial processes.

Planning of experimental measurements depends in part on our laboratory facility. We chose the Rheometrics Mechanical Spectrometer as our main research tool because it is a versatile and reliable instrument. We also had access to the following instruments.

The Instron 3250 rotary rheometer by the courtesy of Instron Corporation and Drs. M. Hauber and L. Frost.

The Rheometrics Mechanical Spectrometer with forced oscillatory measurement capability, by the courtesy of Rheometrics, Inc.

The Instron 3211 capillary rheometer by the courtesy of Prof. C. Rha of the Department of Nutrition and Food Science, M.I.T.
The Monsanto capillary rheometer by the courtesy of Prof. N. Suh of the Department of Mechanical Engineering, M.I.T.

Most of the linear viscoelastic data came from the eccentric rotary disc (ERD) mode (see Chap. 2) of our Mechanical Spectrometer. The cone and plate oscillatory measurements are used to double check the accuracy of ERD measurements and to supplement some high frequency data. Steady shear measurements are performed with our Mechanical Spectrometer with the cone and plate mode. Capillary rheometers are used to acquire more reliable steady shear viscosity data at high shear rates. The parallel plate mode with our Mechanical Spectrometer was used to obtain \( \psi_1 - \psi_2 \) and to double check steady shear viscosity.

All measurements with solution samples were performed over the temperature range from -5°C to 40°C except for the case of capillary measurements at 25°C only. Then data are reduced into master curves with 25°C as a reference temperature using the time-temperature superposition technique (5). These master curves are used for the study of analogies because they have much wider ranges of frequency and shear rate compared to the curves at single temperatures.

The deviations from the analogies computed from these data will be combined with constitutive equations for theoretical interpretations and for the evaluation of the models. The Wagner model and the Goddard expansion are chosen for the theoretical investigation.
As explained before, the Goddard expansion was chosen because of its capability to predict the analogies and the deviations from them systematically and the capability to predict various non-Newtonian properties. The Wagner model can predict a wide range of properties with relatively simple computations. Its ability to predict non-Newtonian properties accurately has been proven (43) for molten polymers.
CHAPTER II. EXPERIMENTS

In this chapter materials, instruments and rheological measurements used to obtain linear viscoelastic properties and viscoemtric properties are described.

1. Samples

Samples for measurements are concentrated solutions of polystyrene in non-volatile solvents as well as undiluted polystyrene in molten state. Polystyrene, non-volatile solvents and polystyrene solutions are described in detail.

a. Polystyrene.

All of the polystyrene samples used in the experiments are amorphous. Physical properties of amorphous polystyrene found in the literature (78) are listed below.

Density: \( \rho = 1.04 \sim 1.065 \) (1.05 is used for calculation)

Glass Transition Temperature: \( T_g = 100^\circ C \)

Intrinsic Viscosity: \( [\eta] = 7.81 \times 10^{-3} M^{-0.754} \) \[2-1\]

The constants in the Mark-Houwink-Sakurada equation (79) are measured with the dilute solutions of linear narrow distribution polystyrene samples in 1-chloronaphthalene. Complete data can be found in Appendix 2-5.

Polystyrene samples used in this study are listed in Table 2-1 along with their physical properties.
### Table 2-1

List of Polystyrene Samples

<table>
<thead>
<tr>
<th>Sample #</th>
<th>$\overline{M}_W$</th>
<th>$\overline{M}_W/\overline{M}_n$</th>
<th>$f$</th>
<th>$(\overline{M}_W)_b$</th>
<th>$g$</th>
<th>$g\overline{M}_W$</th>
<th>$g_2$</th>
<th>$[\eta]^{35}_{1-CN}$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14 b</td>
<td>$2 \times 10^6$</td>
<td>$&lt;1.30$</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>440</td>
</tr>
<tr>
<td>3 b</td>
<td>$3.9 \times 10^5$</td>
<td>$&lt;1.10$</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>125</td>
</tr>
<tr>
<td>4 b</td>
<td>$1.1 \times 10^5$</td>
<td>$&lt;1.06$</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>7 b</td>
<td>$3.7 \times 10^4$</td>
<td></td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>22</td>
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<tr>
<td>41220</td>
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<td>$&lt;1.06$</td>
<td>2</td>
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<td></td>
<td></td>
<td></td>
<td>16</td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stylon</td>
<td>$3.69 \times 10^5$</td>
<td>$3.45$</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2)</td>
</tr>
<tr>
<td>Star</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HA31</td>
<td>$7.9 \times 10^5$</td>
<td>$1.25$</td>
<td>8</td>
<td>$1.05 \times 10^5$</td>
<td>0.344</td>
<td>$2.72 \times 10^5$</td>
<td>0.219</td>
<td></td>
<td>98*</td>
</tr>
<tr>
<td>HA29</td>
<td>$6.05 \times 10^5$</td>
<td>$1.18$</td>
<td>7</td>
<td>$8.8 \times 10^4$</td>
<td>0.388</td>
<td>$2.35 \times 10^5$</td>
<td>0.252</td>
<td></td>
<td>88*</td>
</tr>
<tr>
<td>HA26</td>
<td>$2.06 \times 10^5$</td>
<td>$1.05$</td>
<td>8</td>
<td>$3.2 \times 10^4$</td>
<td>0.344</td>
<td>$7.08 \times 10^4$</td>
<td>0.277</td>
<td></td>
<td>35*</td>
</tr>
<tr>
<td>HA27</td>
<td>$1.25 \times 10^5$</td>
<td>$1.12$</td>
<td>6.4</td>
<td>$1.56 \times 10^4$</td>
<td>0.420</td>
<td>$5.25 \times 10^4$</td>
<td>0.219</td>
<td></td>
<td>28*</td>
</tr>
</tbody>
</table>

1) Pressure Chemical Co.

2) Dow Chemical Co.

3) These star-shaped polystyrenes were generously supplied to us by Prof. P. Rámpf of CNRS, Strasbourg.

The Polymerization Conditions are:

- Overall conc.: 10%
- Solvent: benzene -THF 1/1
- Temperature: -30° to -35°
- Initiator: s. BuLi
- Amount of DVB used: 4 moles/living end (except for HA 30: 10 moles/living end)
- Fractionation is used to separate unlinked precursor. Remaining amount always less than 3%. (49)
b. Solvents

Non-volatile solvents with high boiling points were used to avoid the change of solution composition during the measurement with rheometers. Table 2-2 lists all the solvents used to prepare solutions along with their physical properties.

Solvent viscosities were measured with the Mechanical Spectrometer by the parallel plate steady shear flow at temperatures ranging from \(-5^\circ \text{C}\) to \(25^\circ \text{C}\). Subsequently the activation energies of each solvents were obtained from the temperature dependence of viscosities with the Arrhenius plot, \(\log \eta_0 \text{ vs } 1/T\) as shown in Fig. 2-1.

DBP, KMC-A and 1-CN have melting points well below \(-5^\circ \text{C}\), the lowest temperature used in the rheological measurements. But DMP has m.p. 0 to \(2^\circ \text{C}\).

c. Solutions

The sample solutions were prepared by the following method. Polystyrene powders or pellets were dried under vacuum for several days at room temperature. Solvents were used directly from the bottle without further purification. Weighted polymer and solvent were mixed into a glass bottle and closed tightly with a cap. The bottle was left at room temperature for a long period ranging from two weeks to several months until the polymer powders or pellets were completely dissolved. Occasionally the bottle was turned upside down to stirr the contents. Other means of mixing were not practical as viscosity was high and diffusion of solvent into polymer
Table 2-2
List of Solvents Used to Prepare Polystyrene Solutions

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Abbreviation</th>
<th>mp(°C)</th>
<th>bp(°C)</th>
<th>ρ</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Chloronaphthalene</td>
<td>1-CN</td>
<td>-20</td>
<td>258.8</td>
<td>1.194</td>
<td>Eastman</td>
</tr>
<tr>
<td>Alleynaphthalene (mixture)</td>
<td>KMC-A</td>
<td>-30</td>
<td>285-304</td>
<td>0.96</td>
<td>Kureha Chemical</td>
</tr>
<tr>
<td>Dibutylphthalate</td>
<td>DBP</td>
<td>-35</td>
<td>340</td>
<td>1.047</td>
<td>Eastman</td>
</tr>
<tr>
<td>Dimethylphthalate</td>
<td>DMP</td>
<td>0-2</td>
<td>283.8</td>
<td>1.191</td>
<td>Eastman</td>
</tr>
</tbody>
</table>

\[
\frac{\eta_0 (P-S)}{\eta_0 (25°C)} \quad \frac{\eta_0 (-5°C)}{\eta_0 (5°C)} \quad \frac{\eta_0 (15°C)}{E_a (-5-25°C)}
\]

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Listed</th>
<th>ρ</th>
<th>measured</th>
<th>measured</th>
<th>measured</th>
<th>measured</th>
<th>measured</th>
<th>measured</th>
<th>E_a (-5-25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-CN</td>
<td>0.028</td>
<td>(30°C)</td>
<td>0.030</td>
<td>0.050</td>
<td>0.042</td>
<td>0.031</td>
<td>2.78</td>
<td>Kcal/mol</td>
<td></td>
</tr>
<tr>
<td>KMC-A</td>
<td>0.07</td>
<td></td>
<td>0.092</td>
<td>0.044</td>
<td>0.027</td>
<td>0.015</td>
<td>7.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DBP</td>
<td>0.16</td>
<td></td>
<td>0.59</td>
<td>0.032</td>
<td>0.023</td>
<td>9.44</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMP</td>
<td>0.13</td>
<td></td>
<td>0.90</td>
<td>0.036</td>
<td>0.020</td>
<td>5.86</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Physical properties from Beilstein, Merck and Aldrick catalog*
Fig. 2-1 Temperature Dependence of Solvent Viscosity

\[ \log \eta_s \]

- DMP
- DBP
- KMC-A
- 1-CN

\[ \frac{1}{T} \]

3.3 3.4 3.5 3.6 3.7
particle takes a very long time. After the polymer was dissolved, total weight of the vessel was checked and significant loss of solvent was seldom observed.

Table 2-3 lists the solutions used for rheological measurements. The highest concentrations for each polymer are close to the practical upper limit of concentration. Beyond these concentrations viscosity increases drastically and solutions could not be obtained by mixing solvent and solution at room temperature as we did in this study.

A3 and B1 are designed to have identical $\bar{M}_w$ and A3 and B1 have very close $c[\eta]$. $\bar{M}_w$ and $c[\eta]$ are often used to indicate the extent of polymer chain-chain interaction. $c[\eta]$ is called a chain overlap parameter and $\bar{M}_w$ is known to correlate the behavior of highly concentrated solutions.

d. Undiluted Polystyrene Samples

Samples for polymer melts measurements were injection molded into disks by Mini Max Molder Model CS-183. (Custom Scientific Instruments, Inc., Whippany, N.J.)

According to the manufacturer this equipment minimizes the thermal degradation of plastics during the sample molding by shortening the melting cycle and because of its small capacity. For our polystyrene, temperature was 190° C and each cycle to mold the specimen was 3-5 minutes. The specimen has the diameter of 25 mm and thickness of 2.5 mm.
<table>
<thead>
<tr>
<th>Sample #</th>
<th>$M_w$</th>
<th>$c$ (g/mL)</th>
<th>$\nu$ (cP)</th>
<th>$\gamma$</th>
<th>$c_{\nu}^M$</th>
<th>$c_{\gamma}^{\gamma}$</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>$2 \times 10^6$</td>
<td>0.30</td>
<td>28.6</td>
<td>26.0</td>
<td>$6 \times 10^5$</td>
<td>132</td>
<td>1-CN</td>
</tr>
<tr>
<td>A2</td>
<td>$2 \times 10^6$</td>
<td>0.15</td>
<td>14.3</td>
<td>12.0</td>
<td>$3.0 \times 10^5$</td>
<td>66</td>
<td>1-CN</td>
</tr>
<tr>
<td>A3</td>
<td>$2 \times 10^6$</td>
<td>0.082</td>
<td>8.38</td>
<td>7.45</td>
<td>$1.76 \times 10^5$</td>
<td>34.7</td>
<td>1-CN</td>
</tr>
<tr>
<td>B1</td>
<td>$3.9 \times 10^5$</td>
<td>0.45</td>
<td>42.9</td>
<td>39.7</td>
<td>$1.76 \times 10^5$</td>
<td>56.3</td>
<td>1-CN</td>
</tr>
<tr>
<td>B2</td>
<td>$3.9 \times 10^5$</td>
<td>0.30</td>
<td>28.6</td>
<td>26.0</td>
<td>$1.17 \times 10^5$</td>
<td>37.5</td>
<td>1-CN</td>
</tr>
<tr>
<td>B3</td>
<td>$3.9 \times 10^5$</td>
<td>0.344</td>
<td>32.8</td>
<td>30</td>
<td>$1.34 \times 10^5$</td>
<td>43</td>
<td>DMP</td>
</tr>
<tr>
<td>C1</td>
<td>$1.1 \times 10^5$</td>
<td>0.52</td>
<td>49.5</td>
<td>46.3</td>
<td>$5.72 \times 10^4$</td>
<td>26</td>
<td>1-CN</td>
</tr>
<tr>
<td>C2</td>
<td>$1.1 \times 10^5$</td>
<td>0.45</td>
<td>42.9</td>
<td>39.7</td>
<td>$4.95 \times 10^4$</td>
<td>22.5</td>
<td>1-CN</td>
</tr>
<tr>
<td>C3</td>
<td>$1.1 \times 10^5$</td>
<td>0.344</td>
<td>32.8</td>
<td>30</td>
<td>$3.78 \times 10^4$</td>
<td>17.2</td>
<td>1-CN</td>
</tr>
<tr>
<td>D1</td>
<td>$3.7 \times 10^4$</td>
<td>0.62</td>
<td>59.0</td>
<td>55.9</td>
<td>$2.29 \times 10^4$</td>
<td>13.6</td>
<td>1-CN</td>
</tr>
<tr>
<td>D2</td>
<td>$3.7 \times 10^4$</td>
<td>0.45</td>
<td>42.9</td>
<td>39.7</td>
<td>$1.67 \times 10^4$</td>
<td>9.9</td>
<td>1-CN</td>
</tr>
<tr>
<td>D3</td>
<td>$3.7 \times 10^4$</td>
<td>0.344</td>
<td>32.8</td>
<td>30</td>
<td>$1.27 \times 10^4$</td>
<td>7.6</td>
<td>DMP</td>
</tr>
<tr>
<td>E1</td>
<td>$1.75 \times 10^4$</td>
<td>0.62</td>
<td>59.0</td>
<td>55.9</td>
<td>$1.09 \times 10^4$</td>
<td>9.9</td>
<td>1-CN</td>
</tr>
<tr>
<td>E2</td>
<td>$1.75 \times 10^4$</td>
<td>0.45</td>
<td>42.9</td>
<td>39.7</td>
<td>$7.88 \times 10^3$</td>
<td>7.2</td>
<td>1-CN</td>
</tr>
</tbody>
</table>

**Star Branched Polystyrene Solutions**

<table>
<thead>
<tr>
<th>Sample #</th>
<th>$\bar{M}_w$ (g/mol)</th>
<th>$c$ (g/mL)</th>
<th>$\nu$ (cP)</th>
<th>$\gamma$</th>
<th>$c_{\nu}^M$</th>
<th>$c_{\gamma}^{\gamma}$</th>
<th>Solvent</th>
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</thead>
<tbody>
<tr>
<td>F1</td>
<td>$2.72 \times 10^5$</td>
<td>0.45</td>
<td>42.9</td>
<td>35.7</td>
<td>$1.22 \times 10^5$</td>
<td>44.0</td>
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</tr>
<tr>
<td>F2</td>
<td>$2.72 \times 10^5$</td>
<td>0.30</td>
<td>28.6</td>
<td>26.0</td>
<td>$8.16 \times 10^4$</td>
<td>26.3</td>
<td>1-CN</td>
</tr>
<tr>
<td>G1</td>
<td>$2.35 \times 10^5$</td>
<td>0.45</td>
<td>42.9</td>
<td>35.7</td>
<td>$1.06 \times 10^5$</td>
<td>35.4</td>
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<tr>
<td>H1</td>
<td>$7.08 \times 10^4$</td>
<td>0.45</td>
<td>42.9</td>
<td>35.7</td>
<td>$3.19 \times 10^4$</td>
<td>15.9</td>
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<tr>
<td>J1</td>
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<td>35.7</td>
<td>$2.36 \times 10^4$</td>
<td>12.7</td>
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</table>

**Footnote:** $\rho = 1.05$ assumed and additivity of volume is assumed to compute values of $c_{\nu}, c_{\gamma}$. 

---

"63"
Table 2-3 (Cont.)

<table>
<thead>
<tr>
<th>Sample #</th>
<th>$M_w$</th>
<th>$c_{g/ml}$</th>
<th>volume %</th>
<th>weight %</th>
<th>$cP_w$</th>
<th>$c[c^2]$</th>
<th>Solvent</th>
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<td>Styron</td>
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<tr>
<td>K1</td>
<td>3.69x10^5</td>
<td>0.473</td>
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<td>41.2</td>
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<td>1-CN</td>
</tr>
<tr>
<td>K2</td>
<td>3.69x10^5</td>
<td>0.42</td>
<td>40</td>
<td>37.0</td>
<td>1.55x10^5</td>
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<td>1-CN</td>
</tr>
<tr>
<td>K3</td>
<td>3.69x10^5</td>
<td>0.368</td>
<td>35</td>
<td>32.1</td>
<td>1.36x10^5</td>
<td></td>
<td>1-CN</td>
</tr>
<tr>
<td>K4</td>
<td>3.69x10^5</td>
<td>0.315</td>
<td>30</td>
<td>27.5</td>
<td>1.16x10^5</td>
<td></td>
<td>DMP</td>
</tr>
<tr>
<td>K5</td>
<td>3.69x10^5</td>
<td>0.368</td>
<td>35</td>
<td>32.1</td>
<td>1.36x10^5</td>
<td></td>
<td>DMP</td>
</tr>
<tr>
<td>K6</td>
<td>3.69x10^5</td>
<td>0.263</td>
<td>25</td>
<td>22.7</td>
<td>9.71x10^4</td>
<td></td>
<td>DBP</td>
</tr>
<tr>
<td>K7</td>
<td>3.66x10^5</td>
<td>0.315</td>
<td>30</td>
<td>30.1</td>
<td>1.16x10^5</td>
<td></td>
<td>KHGA</td>
</tr>
<tr>
<td>K8</td>
<td>3.69x10^5</td>
<td>0.315</td>
<td>30</td>
<td>31.9</td>
<td>1.16x10^5</td>
<td></td>
<td>C-10</td>
</tr>
</tbody>
</table>

Undiluted Polystyrene Used for Rheological Measurements

| Styron | 3.69x10^5 | 1.05 | 100 | 100 | None |
| Linear | 1.1x10^5  | 1.05 | 100 | 100 | None |
2. Measurement of the Rheological Properties
   a. Objective

   The objective of our shear flow experiments is to acquire "master
curves" of each viscoelastic functions and viscometric functions of
each sample over the widest possible range of shear rate and frequency.

   \begin{table}[h]
   \centering
   \caption{Shear Flow Properties}
   \begin{tabular}{ll}
   \hline
   Viscometric Properties & Linear Viscoelastic Properties \\
   \hline
   \( \eta(\dot{\gamma}) \) & \( \eta'(\omega) \) \\
   \( \psi_1(\dot{\gamma}) \) & \( G'(\omega) \) \\
   \( \psi_2(\dot{\gamma}) \) & \\
   \hline
   \end{tabular}
   \end{table}

   The next two sections show the theory, operation and data reduction
of various steady shear flow experiments and small amplitude dynamic
flow experiments.

   Double check of data from different shear flows and instruments
are used whenever possible. For example, steady shear viscosities
from cone and plate mode, parallel plate mode and a capillary rheo-
meter were compared to each other. Dynamic viscosities and dynamic
moduli from ERD mode and from cone and plate forced oscillation were
compared to each other. The same mode of measurements with the
Mechanical Spectrometer and with the Instron Rotary Rheometer 3250
were compared to each other.
b. Steady shear flow experiments to measure viscometric functions.

b-1) Cone and plate steady shear flow (C + P)

In this mode of shear flow sample fluid is exposed to a shear flow between a cone and a plate, both concentric and the same diameter (3)(7).

Fig. 2-2 shows the geometry of cone and plate flow. In this geometry, shear rate: \( \dot{\gamma} \) is constant throughout the gap between a cone and a plate.

In the case of the Mechanical Spectrometer or Instron 3250 Rheometer, the upper fixture is a cone which rotates at a constant angular velocity (W), while the lower fixture is a stationary plate directly connected to the torque and normal force transducer (4).

Theoretically, the top of the cone should touch the center of the plate, but for experimental convenience, the top of the cone is flattened by 50\( \mu \) in case of RMS as shown in Fig. 2-2. Measured forces are interpreted using the following formulas.

\[
\eta(\dot{\gamma}) = \frac{\tau_{12}}{\dot{\gamma}} = \frac{3J}{2\pi R^3 \dot{\gamma}} \quad [2-2]
\]

\[
\psi_1(\dot{\gamma}) = \frac{\tau_{11} - \tau_{22}}{\dot{\gamma}^2} = \frac{2F_z}{\pi R^2 \dot{\gamma}^2} \quad [2-3]
\]

\( \dot{\gamma} = W/\dot{\theta}_0 \)

In addition to these principal equations, 1) negative normal
force effect due to the inertia and 2) gap correction due to the thermal expansion of experimental fixtures, were taken into consideration. Details can be found in the appendix - 6. The limit of shear rate for the measurement and the reliability of data are also explained in the appendix - 6.

Fig. 2-2 Cone and Plate Geometry

b-2) Parallel plate steady shear flow (PP) (3)(7)

Another type of steady shear flow experiment with a rotary rheometer is the flow between two concentric parallel disks.

The upper plate is rotating while the lower plate is fixed. The result is the shear flow of sample fluid filled between these plates where shear rate varies. Shear rate is highest at the rim and zero in the center.

Therefore, the equations are more complex. Mathematical interpretation can be done either by differential equations [2-4], [2-5] or integral equations, [2-8][2-9] to obtain $\eta(\dot{\gamma})$ and $\psi_1(\dot{\gamma}) - \psi_2(\dot{\gamma})$ from torque and normal force measurements (7).
Table 2-4 summarizes major advantages and disadvantages between the parallel plot mode and the cone and plate mode.

\[ \eta(\dot{\gamma}_R) = \left\{ \frac{1}{2\pi R^3} \right\} \left\{ 3 + \frac{d\ln(1/2\pi R^3)}{d\ln \dot{\gamma}_R} \right\} \] \hspace{2cm} [2-4]

\[ \psi_1(\dot{\gamma}_R) - \psi_2(\dot{\gamma}_R) = \frac{Fz/\pi R^2}{\dot{\gamma}_R^2} \left\{ 2 + \frac{d\ln(Fz/\pi R^2)}{d\ln \dot{\gamma}_R} \right\} \] \hspace{2cm} [2-5]

\[ \dot{\gamma}_R = \frac{W_0 R}{H} \] \hspace{2cm} [2-6]

\[ \psi_2(\dot{\gamma}_R) = \frac{\tau_{22} - \tau_{33}}{\dot{\gamma}_R^2} \] \hspace{2cm} [2-7]

\( H \) = separation between plates
\( m \) = rate of shear at the rim of disk \( \text{sec}^{-1} \)
R, \( W_0 \), , Fz are the same as A.

Or from integral equation,

\[ = 2\pi \frac{R^3}{3} \int_{\dot{\gamma}_R}^{\dot{\gamma}_R} \eta(\dot{\gamma})\dot{\gamma}^3 \, d\dot{\gamma} \] \hspace{2cm} [2-8]

\[ z = \frac{\pi R^2}{2} \int_{\dot{\gamma}_R}^{\dot{\gamma}_R} (\psi_1(\dot{\gamma}) - \psi_2(\dot{\gamma}))\dot{\gamma}^3 \, d\dot{\gamma} \] \hspace{2cm} [2-9]
Combined with data of $\psi_1(\dot{\gamma})$ from the cone and plate mode, $\psi_2(\dot{\gamma})$ can be calculated.

As the shear rate can be increased by decreasing the gap ($H$) even at the same rotational speed, this mode is mechanically capable of much higher shear rates than the cone and plate mode.

![Parallel Plate Geometry](image)

**Fig. 2-3** Parallel Plate Geometry

Tanner has shown that Eq. 2-11 can be solved by iteration to give a solution for the viscosity which avoid differentiation of data thus avoiding the error from random scattering of data points (80).

b-3) Capillary flow

A capillary flow rheometer has a long capillary through which sample liquid flows in one direction. The volume flow rate of the fluid and the pressure drop over the length of the capillary are measured.
The flow situation and the mathematical interpretation of data are similar to those of the parallel plate rotational flow. Either a differential equation [2-10] or an integral equation [2-11] may be used.

\[ \dot{\gamma}_R = \frac{Q}{\pi R^3} (3 + \frac{d\ln(Q/\pi R^3)}{d\ln \tau_R}) \quad [2-10] \]

\[ \frac{Q}{\pi R^3} = \frac{1}{\tau_R^3} \int_0^{\tau_R} \dot{\gamma}_R \tau^2 \, d\tau \quad [2-11] \]

\( n(\dot{\gamma}_R) = \tau_R / \dot{\gamma}_R \)

\( Q = \) volume flow rate

Fig. 2-4 Capillary Flow

Pressure Drop = \( P_0 - P_L \)
In the vicinity of the entrance or the exit, the flow is not completely at steady state and an experimental end correction is necessary. If \( Q \) is constant, Eq. 2-12 can be used.

\[
P_0 - P_L = 2\tau_R (L/R + e) \quad [2-12]
= 4\tau_R (L/D + e)
\]
e: end correction factor

Most polymeric liquids have end correction factors less than 10. Therefore, this end correction may be negligible for capillaries of very large \( L/R \).

The advantage of the capillary rheometer is that there is no free surface within the shear flow zone. The shear fracture of the sample can be minimized and a high shear rate steady flow is possible. (see Appendix 6) The normal stress difference is very difficult
to measure with a capillary rheometer. If a slit die is used instead of a capillary, normal force can be measured (21). But we did not have such a rheometer with a slit die capable of these measurements with small amount (5 ml) of sample solutions.

c. Small amplitude dynamic measurement of linear viscoelastic properties.

c-1) Eccentric rotating disk flow (ERD) (3)(7)(81)

Between the upper disk and the lower disk which are rotating at the same angular velocity to the same direction while the centers of the rotation are offset for small amounts, sample fluid is exposed to small amplitude sinusoidal oscillation.

In practice, the lower plate is supported on a very low friction air bearing and driven by the force (shear stress) transmitted through the sample fluid from the upper plate which is connected to the motor.

X- and Y- directional steady forces (Y is the offset direction) are observed at the lower plate. With the use of equations [2-15] ~ [2-20] the linear viscoelastic properties are obtained. The frequency of the oscillation is equal to the angular velocity of two plates.

\[
F_y = y\text{-directional force, offset direction} \, \text{N} \\
F_x = x\text{-directional force, perpendicular to offset direction} \, \text{N} \\
H = \text{separation between disks} \, \text{m} \\
R = \text{radius of disks} \, \text{m} \\
w = \text{angular velocity rad/s}
\]
Fig. 2-5. Eccentric Rotating Disk Mode

The working formulas are:

\[ G' = \frac{F_y}{\pi R^2 Y_0} \] [2-15]
\[ G'' = \frac{F_x}{\pi R^2 Y_0} \] [2-16]
\[ Y_0 = \frac{a}{H} \] [2-17]
\[ \gamma = \frac{a}{H} \sin \omega t \] [2-18]
\[ \omega = w \] [2-19]
\[ \dot{Y}_0 = Y_0 \cdot \omega \] [2-20]

When the offset ratio \((a/H)\), which is the strain amplitude of the oscillation, becomes larger, these viscoelastic properties start to depend on the strain amplitude and become non-linear properties.
According to experimental observations (81) these properties are linear and not affected by the strain amplitude when it is smaller than 25%. We used 5% or 10% of \( \alpha/H \) in our experiments.

Both the upper and lower disks can be tilted by large \( x \)-directional or \( y \)-directional forces. Necessary corrections are made according to the method of Macosko and Davis (81) with the experimentally measured compliance value of the instrument. (see appendix 6 for details).

c-2) Forced oscillation of cone and plate flow

The linear viscoelastic properties of polymeric liquids can also be obtained from the forced sinusoidal oscillation of the cone and plate geometry (3)(5). The experimental set up is exactly the same as the cone and plate steady shear flow experiment (Fig. 2-2).

The upper cone is driven in sinusoidal motion at a small amplitude and at the lower disk the sinusoidal shear stress is measured as a function of the frequency. Then linear viscoelastic properties such as the dynamic viscosity and the dynamic storage modulus are computed according to equations [2-21] - [2-26].

\[
\begin{align*}
\text{Shear rate} & \quad \dot{\gamma} = \gamma_0 \cos \omega t \\
\text{Shear stress} & \quad \tau = \tau_0 \sin (\omega t + \delta) \\
\gamma_0 & = \omega \gamma_0
\end{align*}
\]
75

Dynamic Storage Modulus

\[ G' = \frac{T_0}{T_0} \cos \delta \]  [2-23]

Loss Modulus

\[ G'' = \frac{T_0}{T_0} \sin \delta \]  [2-24]

Dynamic Viscosity

\[ \eta' = \frac{G''}{\omega} \]  [2-25]

Amplitude of Complex Viscosity

\[ |\eta'| = \sqrt{(\eta')^2 + (G' / \omega)^2} \]  [2-26]

\( \delta \) : phase angle

This mode is used to double check the results of ERD. A comparison between ERD and this mode is given in Table 2-5.

**Table 2-5** Comparison between ERD and Cone and Plate Oscillatory Measurement of Linear Viscoelastic Properties

<table>
<thead>
<tr>
<th>ERD</th>
<th>Cone and Plate Oscillation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steady Force Measurement</td>
<td>Sinusoidal Signal Measurement and Phase Angle Analysis</td>
</tr>
<tr>
<td>Steady Motion</td>
<td>Sinusoidal Drive</td>
</tr>
</tbody>
</table>
3. Instruments used for the shear flow experiments

In this section, the principles and the operation of instruments used for the steady shear flow and the dynamic shear flow experiments are described.

a. Rheometrics Mechanical Spectrometer (RMS) (4)

This is currently the standard rotary rheometer. The Mechanical Spectrometer is a versatile rotary rheometer capable of: 1) cone and plate steady flow, 2) parallel plate steady flow, 3) ERD and, 4) with an optional position control loop and a phase generator/phase analyser*, which we do not have yet, cone and plate oscillatory

*Solatron 1170 Frequency Response Analyser/Generator is commonly used with the Mechanical Spectrometer.
flow of viscoelastic fluids. Table 2-6 shows the details.

A variety of transitional flow experiments are also possible. Torque control loop allows creep experiments and constrained recoil. The performance specification of this instrument is in Table 2-7 along with that of the Instron rotary rheometer. As shown in Fig. 2-6, the steady shear flow deformation takes place between an upper fixture (a cone or a disk) and a lower fixture (a disk). The upper fixture is driven at designated speeds by a servomotor and the lower disk is connected to a force transducer which measures x-, y- and z-directional forces and torque.

The temperature of the experiment is controlled by a forced air convection environmental chamber with a liquid nitrogen hook up for measurement below room temperature. Actual limit of the shear rate or the frequency maybe different from the mechanical limit of the rotation because of errors and flow irregularities. They are described in detail in Appendix-6.

b. Instron Rotary Rheometer Model 3250 (IRR) (82)

This instrument works on the same principle as the Weissenberg Rheogoniometer and the Rheometrics Mechanical Spectrometer, but was most recently developed. We were able to use this rheometer by the courtesy of Instron Corporation and Dr. M. Hauber.

Major differences of this rheometer from RMS are the use of the digitally controlled drive, the capability of low angular velocity and the adjustment of parallelness between the upper and the lower
<table>
<thead>
<tr>
<th>Name of Mode</th>
<th>A) Cone and Plate (C&amp;P)</th>
<th>B) Cone and Plate Oscillatory</th>
<th>C) Pararell Plate (PrPl)</th>
<th>D) Eccentric Rotating Disk (ERD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper Fixture</td>
<td>Cone</td>
<td>Cone</td>
<td>Plate</td>
<td>Plate</td>
</tr>
<tr>
<td></td>
<td>;rotating at</td>
<td>;rotating at</td>
<td>;rotating at</td>
<td>rotating at</td>
</tr>
<tr>
<td></td>
<td>constant speed</td>
<td>sinusoidal oscillation</td>
<td>constant speed</td>
<td>constant speed</td>
</tr>
<tr>
<td>Lower fixture</td>
<td>Plate</td>
<td>Plate</td>
<td>Plate</td>
<td>Plate</td>
</tr>
<tr>
<td></td>
<td>;stationary</td>
<td>;stationary</td>
<td>;stationary</td>
<td>;rotating at the same speed as</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>upper plate</td>
</tr>
<tr>
<td>Center of both Disks</td>
<td>Concentric</td>
<td>Concentric</td>
<td>Concentric</td>
<td>Eccentric</td>
</tr>
<tr>
<td>Force measurement</td>
<td>Torque, ( F_z )</td>
<td>Torque, ( F_z )</td>
<td>Torque, ( F_z )</td>
<td>( F_x, F_y )</td>
</tr>
</tbody>
</table>

![Diagram A](image1.png)

![Diagram B](image2.png)

![Diagram C](image3.png)

![Diagram D](image4.png)
fixtures. Detailed comparison between RMS and IRR is in Table 2-7.

From these advantages, we used IRR for the low shear rate steady shear flow experiments coupled with a sensitive transducer to obtain the zero shear viscosity and the zero shear normal stress difference coefficient.

Table 2-7 Performance Specification of RMS and IRR

<table>
<thead>
<tr>
<th></th>
<th>Rheometrics Mechanical Spectrometer (RMS)</th>
<th>Instron Rotary Rheometer 3250 (IRR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotational Speed</td>
<td>$10^{-3}$ - 200 rad/s</td>
<td>$10^{-6}$ - 100 rad/s*</td>
</tr>
<tr>
<td>Speed Control</td>
<td>Analog</td>
<td>Digital</td>
</tr>
<tr>
<td>ERD Frequency</td>
<td>$(10^{-3})$ - 200 rad/s</td>
<td>$(10^{-6})$ - 100 rad/s</td>
</tr>
<tr>
<td>Temperature Measurement</td>
<td>Thermocouple in contact with plate/cone</td>
<td>Thermocouple imbedded in plate with hook-up. Temperature measurement impossible with ERD.</td>
</tr>
<tr>
<td>Temperature Control</td>
<td>Forced Convection -120° C - 320° C</td>
<td>Radiant Heating r.t. - 400° C (cooling below r.t. is very difficult)</td>
</tr>
<tr>
<td>Unit</td>
<td>Conventional Metric</td>
<td>SI</td>
</tr>
<tr>
<td>Air Bearing</td>
<td>Lower</td>
<td>Upper and Lower (ERD only)</td>
</tr>
</tbody>
</table>
Forced measurement with standard transducer
Torque

F\textsubscript{z}  

F\textsubscript{x}, F\textsubscript{y}  

Force measurements with Sensitive Transducer Torque

F\textsubscript{z}  

F\textsubscript{x}, F\textsubscript{y}  

Transducer Capability

Single transducer measures all forces \((X, Y, Z, T)\)

Rheometrics Mechanical Spectrometry (RMS)  

Instron Rotary Rheometer 3250 (IRR)  

\(200-10^5 \text{ g.cm Full Scale}\)  

\(5 \times 10^{-2} - 2 \text{N}\)

\((500-2 \times 10^4 \text{ g.cm}) \text{ Full Scale}\)

\(2-100 \text{ N}\)

\((200-10^4 \text{ g}) \text{ Full Scale}\)

\(2-100 \text{ N}\)

\((200-10^4 \text{ g}) \text{ Full Scale}\)

\(0.2-100 \text{ g.cm Full Scale}\)  

\(5 \times 10^{-4} - 2 \times 10^{-2} \text{Nm}\)

\((5-200 \text{ g.cm})\)

\(2 \times 10^{-2} - 1 \text{N}(2-100g)\)

\(-\)

\(-\)

*The nominal speed is an average value. Due to digitally controlled position control, movement of the fixture is not steady but, as shown in Fig. 2-8, stepwise motion. As of Aug., 1978, velocities below \(10^{-3} \text{ rad/s}\) were very questionable. Technological improvement may have been made but \(10^{-6} \text{ rad/s}\) appears impossible without fundamental redesigning. For further detail, see Appendix - 7.*
**actual limit is $10^3$ g, the air bearing has been broken down with large x- or y- force.**

c. Instron Capillary Rheometer 3211 (83)

Among two types of capillary rheometers available for us, the Instron Capillary Rheometer was chosen because of several advantages over the Monsanto Capillary Rheometer (see Appendix-7) (84).

Polymeric fluid is filled in a barrel and the fluid is pressed by a plunger from the top of the barrel and flows through the capillary die at the bottom at a flow rate determined by the speed of the plunger (Fig. 2-8).

The shear rate at the capillary is changed by the speed of the plunger and the choice of the capillary. The plunger speed is variable from 0.06 to 20 cm/min with a standard set of gears and can be changed from 0.02 to 40 cm/min by changing the combination of the gears.
The force required to drive the plunger (roughly) equals to the wall shear stress at the capillary. This force is measured with a load cell of maximum capacity of 2000 kg (force).

As the force and the shear rate ranges of this rheometer are primarily suitable for polymer melts of relatively long relaxation time, special small diameter long capillaries are designed to allow high shear rate flow at the same plunger speed range and to result in larger force (Fig. 2-9) for the same wall shear stress.

Entrance angle was 90° to minimize the entrance effect with smooth entrance of the fluid. L/R ratios are 424 for capillary #1 and 247 for capillary #2. As ordinary end correction factors are 2 to 10, it is safe to neglect them compared to the usual experimental
Fig. 2-9 Capillaries for Instron 3211 Capillary Rheometer
error of 5% or more.

The actual lower limit of the shear rate is often higher than the mechanical limit. The friction between the plunger and the wall is one of the errors causing the limitation.

Figure 2-10 shows the overview of this instrument.

Fig. 2-10 Instron Capillary Rheometer Model 3211 (83)
CHAPTER III. RESULTS OF EXPERIMENTS

In this chapter the results of the experiments outlined in the proceeding chapter are presented. First the steady shear flow experiments are discussed and small amplitude oscillatory experiments are discussed next.

1. Steady shear flow properties

Steady shear viscosity is constant at low shear rates and starts decreasing above a certain shear rate. At high shear rate zone, the plot of steady shear viscosity vs. shear rate on double logarithmic scale appears as a straight line. This region is called the power law zone because equation 3-1 fits the relationship.

\[ \eta = K \dot{\gamma}^{-m} \]  \[3-1\]

Similarly \( \psi_1 \) has a constant value at low shear rate and decreases at high shear rate as shear rate increases. But the slope is steeper than the shear viscosity curve.

Both \( \eta \) and \( \psi_1 \) decrease as temperature increases as shown in figures in this section. At the same time critical shear rate above which \( \eta \) and \( \psi_1 \) begin decreasing from their constant value increases. In other words, in the double logarithmic plot curve of \( \eta(\dot{\gamma}) \) or \( \psi_1(\dot{\gamma}) \) at higher temperature is shifted to the lower right direction.

Figures 3-1 ~ 3-7 show representative data from steady shear flow
experiments of the cone-and-plate mode with the Rheometrics Mechanical Spectrometer. The entire set of data appears in Appendix 2 in the reduced variables only.

Six different temperatures, from -5\(^\circ\) C to 40\(^\circ\) C, were used in the measurements in order to make use of the time-temperature superposition principle. A forced convection environmental chamber was used to control the temperature with liquid nitrogen as a coolent.

Data were taken over the widest possible range of shear rate. The lower limit of shear rate was determined by the minimum rotational speed of 10\(^{-3}\) rad/s which results 10\(^{-2}\)S\(^{-1}\) for the smaller cone (diameter =25 mm, cone angle = 0.1 rad) and 2.5 x 10\(^{-2}\)S\(^{-1}\) for the larger cone (diameter = 72mm, cone angle = 0.04 rad). When the viscosity is low, the shear stress becomes too small to be measured by the force transducer and limits the lowest possible shear rate. The upper limit of shear rate was usually determined by the flow instability which appears at high shear rate. We could seldom use the highest rotational velocity of the instrument for steady shear flow because of the instability. Figure 3-1 shows the typical representation of shear fracture which is a primary source of flow instability.
Fig. 3-1 Schematic of shear fracture observed in a parallel-plate rheometer. (Basically same for a cone and plate mode, Fig. 4.14 of ref. 3). These instabilities of shear flows are discussed in detail in Appendix-6.

Table 3-1 lists figures in this section.

Table 3-1 Representative plots of cone and plate steady shear flow data

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \eta(\dot{\gamma}) )</th>
<th>( \psi_1(\dot{\gamma}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2</td>
<td>Fig. 3-2</td>
<td>Fig. 3-3</td>
</tr>
<tr>
<td>F1</td>
<td>Fig. 3-4</td>
<td>Fig. 3-5</td>
</tr>
<tr>
<td>K2</td>
<td>Fig. 3-6</td>
<td>Fig. 3-7</td>
</tr>
</tbody>
</table>

*See Table 2-3 for complete description of each sample.
Fig. 3-2  Steady Shear Viscosity from Cone and Plate Mode
Sample: (A2) Narrow distribution polystyrene  $M_w = 2,000,000$
0.15 g/ml in 1-Ch

-5 C  5 C  15 C  25 C  35 C  40 C
Fig. 3-3 Primary Normal Stress Difference Coefficient from Cone and Plate Mode
Sample: (A2) Narrow distribution polystyrene $M_w = 2,000,000$
0.15 g/ml in 1-CN

$F(s) (N \times s) = R_5$
Fig. 3-4  Steady Shear Viscosity from Cone and Plate Mode

Sample:  (F1) Star branched polystyrene (HA31)
0.45 g/ml in 1-CN
Fig. 3-5 Primary Normal Stress Difference Coefficient from Cone and Plate Mode

Sample: (P1) Star branched polystyrene (HA31)
0.45 g/ml in 1-CN
Fig. 3-6: Steady Shear Viscosity from Cone and Plate Mode

Sample: (X2) Commercial polystyrene STYRON with broad molecular weight distribution 0.42 g/mL in 1-CN

Shear Viscosity (Pa·s)

Shear Rate (sec⁻¹)
Fig. 3-7 Primary Normal Stress Difference Coefficient
from Cone and Plate Measurements
Sample: (K1) Commercial polystyrene STYRON with broad
molecular weight distribution 0.42 g/dl in 1-CN
Fig. 3-8 and Fig. 3-9 show results from the cone and plate steady shear flow measurements using the Instron rotary rheometer 3250 with its most sensitive transducer. These experiments were performed at Instron Corporation, Canton, MA. The differences between these data and those obtained on the Mechanical Spectrometer at M.I.T. are as following:

1) Lower shear rates were attainable on the Instron apparatus, \(10^{-4} \text{s}^{-1}\) compared to \(10^{-2} \text{s}^{-1}\) on the Mechanical Spectrometer.

2) Higher sensitivity was obtained on the Instron apparatus \(2 \times 10^{-4} \text{Nm or 2g.cm full scale compared to 200 g.cm full scale of our Mechanical Spectrometer.}\)

For further comparison between the Instron 3250 and the Mechanical Spectrometer, see Chap. 2 and Appendix-7.

Figures 3-9-3-14 show some of the results obtained in steady shear flow of sample solutions between parallel plots using the Mechanical Spectrometer. All conditions are similar to the cone and plate flow except there is an additional variable, the gap between two disks.

Experimentally, it is found that the observed viscosity curves are independent of the gap when the gap is larger than 1 \(-1.5 \text{ mm}\) for both large plates (\(R = 36 \text{ mm}\)) and small plates (\(R = 12.5 \text{ mm}\)). Because in the parallel plate mode the shear rate varies across the gap, viscosity and normal stress difference were computed using the
Fig. 3-8 Steady Shear Viscosity from IRR and from RMS
with Cone and Plate Mode
Fig. 3-9  Primary Normal Stress Difference from Cone and Plate Mode of IRR and RMS
appropriate differential equations (eq. 2-4 and eq. 2-5) using a linear regression method. The computer program is in Appendix 4.

The data from the parallel plate mode are usually as good as from the cone and plate mode. The upper and lower limits of shear rate are almost the same. Higher shear rate is possible with smaller gap of parallel plate geometry without apparent shear fracture up to a certain limit. As mentioned before, if the gap was smaller than 1mm different values of $\eta$ and $\psi_1-\psi_2$ were obtained with the varying gap*. This phenomenon is due to the edge effect or irregularity of flows. Table 3-2 lists figures in this section.

Table 3-2 Representative data from parallel plate mode experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\eta(\dot{\gamma})$</th>
<th>$\psi_1(\dot{\gamma})-\psi_2(\dot{\gamma})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2</td>
<td>Fig. 3-10</td>
<td>Fig. 3-11</td>
</tr>
<tr>
<td>FI</td>
<td>Fig. 3-12</td>
<td>Fig. 3-13</td>
</tr>
<tr>
<td>KI</td>
<td>Fig. 3-14</td>
<td>Fig. 3-15</td>
</tr>
</tbody>
</table>

*In appendix 6, effect of gap width to normal force measurement is shown in Fig. A6-1 and A6-2. If shear rate is high and normal force is large, these errors appear less significant than small normal force at low shear rate. For sample C1 $\eta_0$ measured with gap = 1mm is 10-30% larger than $\eta_0$ measured with gap = 2mm over temperature range of -5°C to 40°C.
Fig. 3-11 $\Psi_1 - \Psi_2$ from Parallel Plate Mode

Sample: (A2) Narrow distribution polystyrene $M_w = 2,000,000$

0.15 cP/ml in 1-CN
Fig. 2-12 Steady Shear Viscosity from Parallel Plate Mode

Sample: (F1) Star branched polystyrene (MA31)
0.45 g/ml in 1-CN
Fig. 3-13 $\Psi_1 - \Psi_2$ from Parallel Plate Mode
Sample: (P1) Star branched polystyrene (HA31)
0.45 g/ml in 1-CN
Fig. J-14 Steady Shear Viscosity from Parallel Plate Mode 3
Sample: (K2) Commercial polystyrene STYRON with broad
molecular weight distribution 0.42 g/ml in 1-CN
Fig. 3-15 $\Psi_1 - \Psi_2$ from Parallel Plate Mode

Sample: (K2) Commercial polystyrene STYRON with broad molecular weight distribution 0.42 g/ml in 1-CN

$\Psi_1 - \Psi_2$ (Pa.s$^2$)

SHEAR RATE (S$^{-1}$)
Fig. 3-16 shows shear rate dependent viscosity measured with the Instron 3211 Capillary Rheometer. Compared to the Mechanical Spectrometer, much higher shear rate measurement was possible without apparent flow instability. Surface irregularity similar to 'the melt fracture' was observed for extrudates at high shear rates (in the power law zone) with high viscosity samples.

Temperature lower than room temperature was practically impossible. Only 25°F (± 0.5°F) was used.

As explained in Chapter 2, two capillaries with the same diameter and different length, therefore different L/D ratio, were used but no significant end correction was found. For further details of error estimation, see Appendix-6. As will be shown in Chapter 4, $\eta(\dot{\gamma})$ from the cone and plate flow and the capillary flow agree within experimental scatter.

2. Linear viscoelastic properties from dynamic measurements

Both dynamic viscosity ($\eta'$) and complex viscosity ($|\eta^*|$) have constant value at low frequency which is equal to zero shear rate viscosity. $\eta'$ and $|\eta^*|$ begin decreasing above certain frequency with increasing frequency. Dynamic storage modulus ($G'$) increases as frequency increases, but with decreasing slope. If $2G'/\omega^2$ is plotted instead of $G'$, the curve appears analogous to $\psi_1$ vs. $\dot{\gamma}$ and constant at low frequency and decreases at slope close to -2 in the high frequency range with increasing frequency.
Fig. 3-16  Steady Shear Viscosity of Polystyrene Solutions
Sample A1, A2, A3 measured by Instron Capillary Rheometer

\[ \eta_0 \quad \text{Pa·s} \]

Shear Rate (s\(^{-1}\))

100  
1000
Fig. 3-17~3-22 show representative data from the eccentric rotating disk (ERD) measurement with the Mechanical Spectrometer*. The same sample solutions as used for steady shear flow experiments were used for dynamic measurements. Six different temperatures from -5° C to 40° C were used, again to allow an effectively wider range of frequency coverage after application of time-temperature superposition.

The upper limit of frequency is caused by catastrophic flight of sample droplets from the gap between the plates due to the large centrifugal force. The lower limit of frequency was usually caused by the low signal/noise ratio. Low frequency measurements take a longer time and background noise, as well as secondary flows like gravitational flow, cause larger noise during the measurement. The result is shown in Fig. 3-19 as large apparent scatters of data at lower end of frequency. Table 3-3 lists figures in this section.

| Sample | \( n'(\omega) \), \(|n^*(\omega)|\) | \( G'(\omega) \) |
|--------|-----------------|---------------|
| A2     | Fig. 3-17       | Fig. 3-18     |
| F1     | Fig. 3-19       | Fig. 3-20     |
| K2     | Fig. 3-21       | Fig. 3-22     |

*Rest of data will be found in Appendix 2 in the reduced variables.
Fig. 3-18 Dynamic Storage Modulus from ERD Mode
Sample: (A2) Narrow molecular weight distribution
polystyrene $M_w = 2,000,000$ 0.15 g/ml in 1-CN

$G' (Pa)$
Fig. 3-19 Dynamic Viscosity and Complex Viscosity from ERD Mode

Sample: (P1) Star branched polystyrene (HA31)
0.45 g/ml in 1-CN
Fig. 3-21 Dynamic Viscosity and Complex Viscosity from ERD Mode
Sample: (K2) Commercial polystyrene STYRON with broad molecular weight distribution 0.42 g/ml in 1-CN
Fig. 3-22 Dynamic Storage Modulus
from ERD Mode
Sample: (X2) Commercial polystyrene STYRON with broad
molecular weight distribution 0.42 g/ml in 1-CN
Dynamic properties obtained from the cone and plate forced oscillation with the Mechanical Spectrometer equipped with a frequency analyzer/generator at Rheometrics, Inc., Union, NJ are recorded in this section.

Table 3-4 lists representative data and the rest is in Appendix 2-1 in the form of reduced variables.

**Table 3-4**

| Sample | $n'(\omega)$, $|n^*(\omega)|$ | $G'(\omega)$ |
|--------|-----------------------------|-------------|
| A2     | Fig. 3-23                   | Fig. 3-24   |
| F1     | Fig. 3-25                   | Fig. 3-26   |
| K2     | Fig. 3-27                   | Fig. 3-28   |

The upper limit of frequency of the measurement is an instrumental limit 100 rad/s. The limit of the phase analyser's ability to determine the phase angle difference between stress and strain from small sinusoidal signal with background noise caused the lower limit of frequency. With the cone and plate oscillation, higher frequency measurement was possible compared to the ERD mode. It was especially effective for low viscosity samples which would have flown away by centrifugal force if ERD had been used. The lower limit of measurement is about the same as the ERD mode. Detailed theoretical comparison between ERD and cone and plate oscillation has been give in Chapter 2.
Fig. 3-23 Complex Viscosity and Dynamic Viscosity from Cone and Plate Oscillatory Mode
Sample: (A2) Narrow Distribution Polystyrene
M_w = 2,000,000 0.15 g/ml in 1-CN
Fig. 3-24  Dynamic Storage Modulus and Dynamic Loss
Modulus from Cone and Plate Oscillatory Mode
Sample:  (A2) Narrow molecular weight distribution
polystyrene $M_w = 2,000,000$  0.15 g/ml in 1-CN
Fig. 3-25 Dynamic Storage Modulus and Dynamic Loss Modulus from Cone and Plate Forced Oscillation
Sampler:  (P1) Star branched polystyrene (HA31)
0.45 g/ml in 1-CN
Fig. 3-27 Dynamic Viscosity and Complex Viscosity from Cone and Plate Oscillatory Mode
Sample: K2 Commercial polystyrene STYRON with broad molecular weight distribution 0.42 g/ml in 1-CN
Fig. 3-28 Dynamic Storage Modulus and Dynamic Loss Modulus from Cone and Plate Forced Oscillation Sample: Commercial polystyrene S1000N with broad molecular weight distribution 0.42 g/ml in 1-CN

$G'$

$G''$

$C_0$ (rad/s)

$10^2$

$10^3$

$10^4$
3. Rheological properties of polystyrene melts

Figure 3-29 shows steady shear viscosity and Fig. 3-30, primary normal stress difference coefficient. Fig. 3-31 shows dynamic viscosity and complex viscosity data of polystyrene melts. Sample polymer is broad distribution commercial polystyrene. Fig. 3-32 shows dynamic storage modulus. These linear viscoelastic properties were measured by the ERD mode. Steady shear viscosity was measured by the cone and plate mode.
Fig. 3-29 Linear Viscoelastic Properties: Reduced Dynamic Viscosity and Reduced Complex Viscosity from ERD Mode

Sample: Undiluted STYRO; broad molecular weight distribution polystyrene Standard temperature = 200°C
Fig. 3-30 Dynamic Storage Modulus from ERD Mode
Sample: Undiluted commercial polystyrene, STYRON
with broad molecular weight distribution
Fig. 3-31  Steady Shear Viscosity from Cone and Plate Mode
Sample: Undiluted commercial polystyrene STYRON with broad distribution
Fig. 3-32 Primary Normal Stress from Cone and Plate Measurement of STYHII melts
CHAPTER IV. TEMPERATURE DEPENDENCE AND CONCENTRATION

DEPENDENCE OF ZERO SHEAR RATE VISCOSITY

1. Temperature dependence of zero shear rate viscosity

Zero shear rate viscosities $\eta_0$, were obtained both from the steady shear viscosities and the dynamic viscosities.

$$\eta(\gamma)_{\gamma \to 0} = \eta'(\omega)_{\omega \to 0} = \eta_0$$  \hspace{1cm} [4-1]

Table 4-1 shows $\eta_0$ for all of sample solutions. Zero shear rate viscosities of polymeric fluids are temperature dependent and decrease with increasing temperature. The temperature dependence of the zero shear rate viscosity can be expressed by an Arrhenius equation with an apparent energy of flow, $E_a$, over moderate temperature range (p. 544 of ref. 5) (p. 274 of ref. 76). $E_a$ is known to increase with increasing concentration (5)

$$\eta_0 = A \exp \left( \frac{E_a}{RT} \right)$$  \hspace{1cm} [4-2]

$R = 1.986$ cal/mol°K

$$E_a = -R \frac{d \ln \eta_0}{d(T/T)}$$  \hspace{1cm} [4-3]
Table 4-1

Zero Shear Viscosity of Polystyrene Solutions

<table>
<thead>
<tr>
<th>Sample #</th>
<th>-5°C</th>
<th>5°C</th>
<th>10°C</th>
<th>15°C</th>
<th>25°C</th>
<th>35°C</th>
<th>40°C</th>
<th>50°C</th>
<th>Mw x 10^3</th>
<th>Cg/ml</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear Narrow Distribution Polystyrene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>A1</td>
<td>7,000</td>
<td>3,500</td>
<td>2,300</td>
<td>1,400</td>
<td>1,040</td>
<td>28,000</td>
<td>20,000</td>
<td>2,000</td>
<td>0.30</td>
<td>1-CN</td>
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</tr>
<tr>
<td>A2</td>
<td>320</td>
<td>263</td>
<td>130</td>
<td>90</td>
<td>67</td>
<td>58</td>
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</tr>
<tr>
<td>B1</td>
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<td>75,000</td>
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<td>4,000</td>
<td>3,600</td>
<td>390</td>
<td>0.45</td>
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<td></td>
<td></td>
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<tr>
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<td>495</td>
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<td>135</td>
<td>77</td>
<td>67</td>
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<td>264</td>
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<td>0.52</td>
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<tr>
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<td>61</td>
<td>110</td>
<td>0.45</td>
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</tr>
<tr>
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<td>517</td>
<td>37</td>
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<tr>
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<td>4.9</td>
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<td>Star Branched Polystyrene</td>
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<td></td>
<td></td>
<td></td>
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</tr>
<tr>
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<td>1,850</td>
<td>750</td>
<td>560</td>
<td>HA31</td>
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<td>168</td>
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<td>33</td>
<td>19</td>
<td>15</td>
<td>HA31</td>
<td>0.30</td>
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</tr>
<tr>
<td>G1</td>
<td>35,500</td>
<td>8,700</td>
<td>2,550</td>
<td>1,050</td>
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<td>345</td>
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<td>14</td>
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<td>5.5</td>
<td>HA27</td>
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<tr>
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<td>550</td>
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<td>67</td>
<td>29.5</td>
<td>19.8</td>
<td>HA26</td>
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</table>

*See Table 2-1 for description
<table>
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<tr>
<th>Sample #</th>
<th>-5°C</th>
<th>5°C</th>
<th>10°C</th>
<th>15°C</th>
<th>25°C</th>
<th>35°C</th>
<th>40°C</th>
<th>50°C</th>
<th>Polymer #</th>
<th>Cg/ml</th>
<th>Solvent</th>
</tr>
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<tbody>
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</tr>
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<td>2,950</td>
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<td>340</td>
<td>208</td>
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<td>103</td>
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<td>255</td>
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<td>120</td>
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<td>27</td>
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<tr>
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<td>12,500</td>
<td>4,900</td>
<td>2,400</td>
<td>810</td>
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<td>1,800</td>
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<td>124</td>
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<td>Styron</td>
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<td>DBP</td>
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</tbody>
</table>
Fig. 4-1  Temperature Dependence of Zero Shear Viscosity
Sample: Undiluted Commercial Polystyrene (TYPICAL)

\[ \eta_0 \text{(Pa·s)} \]

-10^2
-10^4
-10^6

\[ \frac{1}{T} \]

2.0x10^{-3}  2.5x10^{-3}

O from G+P
O from ETD
In this chapter temperature dependence and concentration dependence of zero shear rate viscosity of polystyrene solutions are discussed. Based on the temperature dependence of zero shear rate viscosity, time-temperature superposition technique is applied to obtain master curves of viscometric properties and linear viscoelastic properties at standard temperature. $E_a$ for each sample solution over the experimental temperature range (-5 to 40°C) was calculated by the linear regression method. Table 4-2 lists the results. Some errors may exist as the temperature control of the mechanical spectrometer is not very good ($\pm 1^\circ C$ at best).

Figure 4-1 shows a graphical method for obtaining $E_a$. Sample was undiluted broad distribution polystyrene. The slope apparently is not constant over the entire range of the measurement. $E_a$ depends on the temperature range chosen. Table 4-3 shows the results.

Table 4-3 Activation energy of undiluted broad distribution polystyrene (STYRON)

<table>
<thead>
<tr>
<th>Temperature Range</th>
<th>$E_a$</th>
</tr>
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<tbody>
<tr>
<td>140 - 250°C</td>
<td>34.5 kcal/mol</td>
</tr>
<tr>
<td>140 - 150°C</td>
<td>46.2 kcal/mol</td>
</tr>
<tr>
<td>200 - 250°C</td>
<td>26.9 kcal/mol</td>
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Table 4-2
Apparent Activation Energy of Polystyrene Solutions

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_w$</th>
<th>C</th>
<th>Solvent</th>
<th>$E_a$ Kcal/mol</th>
<th>InA</th>
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<td>Linear Polystyrene</td>
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<tr>
<td>A1</td>
<td>2,000,000</td>
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<td>1-CN</td>
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<td>-1.39</td>
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<tr>
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<td>-5.82</td>
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<td>1-CN</td>
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<td>1-CN</td>
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<td>1-CN</td>
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<td>22.26</td>
<td>-32.38</td>
</tr>
<tr>
<td>D1</td>
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<td>1-CN</td>
<td>32.93</td>
<td>-47.04</td>
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<tr>
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<td>0.45</td>
<td>1-CN</td>
<td>18.71</td>
<td>-28.71</td>
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<tr>
<td>E1</td>
<td>17,500</td>
<td>0.62</td>
<td>1-CN</td>
<td>35.82</td>
<td>-55.03</td>
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<td>E2</td>
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<td>0.45</td>
<td>1-CN</td>
<td>18.34</td>
<td>-29.61</td>
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<tr>
<td>F1</td>
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<td>0.45</td>
<td>1-CN</td>
<td>18.36</td>
<td>-23.40</td>
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<tr>
<td>F2</td>
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<td>0.30</td>
<td>1-CN</td>
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<td>-19.50</td>
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<td>1-CN</td>
<td>17.12</td>
<td>-21.88</td>
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<td>Commercial Polystyrene (Styron)</td>
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<td>17.42</td>
<td>-21.00</td>
</tr>
<tr>
<td>K2</td>
<td>0.42</td>
<td></td>
<td>1-CN</td>
<td>14.48</td>
<td>-17.73</td>
</tr>
<tr>
<td>K3</td>
<td>0.368</td>
<td></td>
<td>1-CN</td>
<td>13.85</td>
<td>-18.06</td>
</tr>
<tr>
<td>K4</td>
<td>0.315</td>
<td></td>
<td>1-CN</td>
<td>12.11</td>
<td>-16.31</td>
</tr>
<tr>
<td>K5</td>
<td>0.368</td>
<td></td>
<td>DMP</td>
<td>18.16</td>
<td>-22.97</td>
</tr>
<tr>
<td>Sample #</td>
<td>$\overline{M_w}$</td>
<td>C</td>
<td>Solvent</td>
<td>$\xi$ Kcal/mol</td>
<td>$\ln\Lambda$</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------</td>
<td>-----</td>
<td>---------</td>
<td>-----------------</td>
<td>------------</td>
</tr>
<tr>
<td>K7</td>
<td>0.315</td>
<td></td>
<td>DBP</td>
<td>16.22</td>
<td>-21.34</td>
</tr>
<tr>
<td>K8</td>
<td>0.315</td>
<td></td>
<td>KMC</td>
<td>19.25</td>
<td>-26.49</td>
</tr>
</tbody>
</table>

* $r^2 = \frac{(\Sigma xy - \Sigma x \Sigma y/n)^2}{\Sigma (\Sigma x^2 - (\Sigma x)^2/n) (\Sigma y^2 - (\Sigma y)^2/n)}$

$r^2$ (coefficient of determination) was $0.995 - 0.96$ (73)

1 Kcal = $4.19 \times 10^3$ J
Fig. 4-2 Activation Energy of flow for Polystyrene Solutions in 1-CN and other solvents

Symbols

Linear: $A \bar{M}_w = 2,000,000$
$B \bar{M}_w = 390,000$
$C \bar{M}_w = 110,000$
$D \bar{M}_w = 37,000$
$E \bar{M}_w = 17,500$

Star: $F$ HA31
$G$ HA29
$H$ HA25
$J$ HA27

Styron: $K$ in 1-CN
DMP
DBP
KMC-A

$E_a$ (kcal/mol)

$c$ (g/ml)

0.1 0.2 0.3 0.4 0.5 0.6
Figure 4-2 shows the concentration dependence of $E_a$. As has previously been shown (5) $E_a$ is larger for solutions of higher concentration. The effect of molecular weight appears to be modest. Solutions of lower molecular weight polymers appear to have higher $E_a$ but error or scattering of data made this observation less significant.

Some researchers have observed abnormally high activation energy for branched polyethylene melts (86) but others observed no change in temperature dependence of $\eta_0$ of star and linear polystyrene melts (52). In regard to this point, the present results (Figure 4-2) indicate that star branched polystyrene solutions have the same order of activation energy as linear polystyrene solutions.

2. Time-temperature superposition

a. Objective

As was shown in the figures in Chapter 3 (Fig. 3-1-3-29) curves of shear rate dependent viscometric properties and curves of frequency dependent linear viscoelastic properties are temperature dependent but have similar shape for each property. It is possible to superpose curves at different temperatures into a single curve at a reference temperature for each property and for each sample using shift factors based on the time-temperature superposition principle (5) as shown in Fig. 4-3.

The time-temperature superposition principle is derived from linear viscoelasticity theory but there have been some experiments
Fig. 4-3 Time-Temperature Superposition Technique
(5) for which the same superposition was applicable even to non-Newtonian steady shear flow properties.

In this chapter the superposition technique is used to get a wider range of effective shear rate or frequency than is possible at a single temperature. By this technique we could get almost the entire range of linear viscoelastic functions from the terminal zone ($\eta' + \eta_0$) through the transition zone to the plateau zone.

Theoretical basis and criteria of applicability of the superposition are first discussed. Then experimental check of the applicability was performed using both viscometric properties and linear viscoelastic properties shown in Chapter 3.

When the superpositions appear good and certain criteria satisfied, superposed curves are used as master curves at the selected reference temperature. When superposition is good, the master curve correctly represents the material property at the reference temperature over the entire range of reduced frequency or shear rates obtained. Properties at various other temperatures can then be obtained merely by shifting the entire master curve by the shift factor.

b. Theoretical basis of the time-temperature superposition (5)

Theoretical basis of the time-temperature superposition is in the molecular theory of linear viscoelasticity. In the theories for dilute solutions of flexible polymer molecules based on the bead-spring model, the contribution of the solute (polymer) to the storage shear modulus ($G'$) or loss modulus ($G''$) is proportional to $nkT$ or
cRT/M as in equations,

\[
G'(\omega) = nkT \sum_{p=1}^{N} \frac{\omega^{2\tau_p^2}}{1 + \omega^{2\tau_p^2}} \quad [4-5]
\]

\[
G'(\omega) = \omega\eta_s + nkT \sum_{p=1}^{N} \frac{\omega\tau_p}{1 + \omega^{2\tau_p^2}} \quad [4-6]
\]

(equation 19, 20 in chapter 9 of reference 5)

\(k\): Boltzmann's constant

\(n\): number of molecules per ml

\(\tau_p\): relaxation time of element

\(N\): number of submolecules in a molecule

\(c\): concentration g/ml

\(M\): molecular weight

Each term is associated with a relaxation time \(\tau_p\) which is proportional to

\[
\frac{(n-n_S)M}{cRT}
\]

For example, from the Rouse theory the relaxation time spectrum is given by

\[
\tau_p = \frac{\delta(n-n_S)}{\pi^2 p^2 nkT} \quad [4-7]
\]

and from the Zimm theory,

\[
\tau_k = \frac{1.71(n-n_S)}{\lambda_k nkT} \quad [4-8]
\]
Thus temperature dependence of these relaxation times enters in four variables which are \( n, n_s, T, c(\text{or } n) \) and can be expressed by a shift factor \( a_T \).

\[
\frac{[\tau_p]_T}{[\tau_p]_{T_0}} = a_T = \frac{[(n_0 - n_s)c]_T T_0}{[(\eta - n_s)c]_{T_0} T} \tag{4-9}
\]

In equation 4-8, \( a_T \) is constant for all values of \( p \) which means that all relaxation times are affected equally by changes in temperature. This further insures that various sets of isothermal data for the linear viscoelastic functions (which depend on the relaxation spectrum) will be superposable on the log t or log \( \omega \) axis.

In many publications, a linear viscoelastic property of polymer melts and solutions which satisfied the criterion \( [a_T = a_T(T \text{ only})]; \text{same for all } p \) is termed thermorheologically simple. If different parts of the relaxation spectrum are affected differently by changes of temperature (the value of \( a_T \) depends on the value of \( p \)) the superposition of isothermal segments of linear viscoelastic data will not be observed; such materials (87) are termed thermorheologically complex.

\( a_T \) for undiluted polymers have the following form (5)

\[
a_T = \frac{(n_0)_T}{(n_0)'_T} \frac{T_{0p}}{T_{0p}} \tag{4-10}
\]
Table 4-4 lists reduced variables based on the time-temperature principle. When the principle is applicable, a single master curve for each property is obtained.

Table 4-4 Reduced Variables in the Time-Temperature Superposition

<table>
<thead>
<tr>
<th>Linear Viscoelastic Properties</th>
<th>Reduced Variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \omega )</td>
<td>( \omega \cdot a_T )</td>
</tr>
<tr>
<td>( G' )</td>
<td>( G' T_0 \rho_0 / T_\rho )</td>
</tr>
<tr>
<td>( G'' )</td>
<td>( G'' T_0 \rho_0 / T_\rho )</td>
</tr>
<tr>
<td>( \eta' )</td>
<td>( \eta' \cdot (\eta_0 T_0) / (\eta_0)_T )</td>
</tr>
</tbody>
</table>

\( a_T \) from equation 4-9

There is no molecular theory for undiluted polymers that justifies the use of the time-temperature superposition. Dilute solution theory which has been used in this chapter may be extended into concentrated solutions and undiluted polymers provided \( M < M_c \) or \( cM < M_c \), where \( M_c \) is a critical molecular weight. If \( M > M_c \) or \( cM > M_c \), chain-chain interaction plays an important role and many rheological properties behave differently (11). Therefore, in the high molecular weight region the applicability of the time-temperature superposition has no firm theoretical basis and should be tested for each material.

Experimentally linear viscoelastic properties of some polymers have been successfully superposed by \( a_T \) as in Table 4-4 but for some
others, these reduced variables were not applicable (5). Whether linear viscoelastic properties of particular polymer melts or solutions can be superposed or not can be shown only experimentally.

The applicability of time-temperature superposition technique for viscometric properties is a different problem. Experimentally, Gruer (88) and Mendelson (60) found this technique is applicable to viscometric properties.

Theoretically same time constants enter linear viscoelastic properties and viscometric properties at least in some of the constitutive equations shown in Table 1-3. For example, according to Spriggs model,

\[ n' = \frac{n_0}{Z(\alpha)} \sum_{p=1}^{n} \frac{p^{-\alpha}}{1+\omega^2 \tau_1^2 \frac{2}{\zeta}} \]  \hspace{1cm} [4-11]

\[ n = \frac{n_0}{Z(\alpha)} \sum_{p=1}^{n} \frac{p^{-\alpha}}{1+\gamma^2 \tau_1^2 \frac{2}{\zeta}} \]  \hspace{1cm} [4-12]

\[ \frac{c^2 \gamma^2}{2} \psi_1(\dot{\gamma}) = G'(\omega = c \dot{\gamma}) \]  \hspace{1cm} [4-13]

Therefore it is possible that the temperature dependence of viscometric properties is described by similar reduced variables as used for linear viscoelastic properties with the same shift factors as shown in Table 4-5.
Table 4-5 Reduced Variables for Viscometric Properties

<table>
<thead>
<tr>
<th>Viscometric Properties</th>
<th>Reduced Variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\dot{\gamma}$</td>
<td>$\dot{\gamma} \cdot a_T$</td>
</tr>
<tr>
<td>$n$</td>
<td>$n \cdot \frac{(n_0)_{T_0}}{(n_0)_T}$</td>
</tr>
<tr>
<td>$N_1$</td>
<td>$N_1 \cdot \frac{T_0 \rho_0}{T_0}$</td>
</tr>
<tr>
<td>$\psi_1$</td>
<td>$\psi_1 \cdot \frac{T_0 \rho_0}{T_0} \cdot \frac{1}{a_T^2}$</td>
</tr>
</tbody>
</table>

$a_T$ from equation 4-19

There are three criteria for the applicability of the time-temperature superposition technique. These can be checked experimentally. (P. 302 of 5)

1) Exact matching of the shapes of overlapping regions of adjacent curves (see Fig. 4-3).
2) Same values of $a_T$ superpose all the material functions.
3) Temperature dependence of $a_T$ must have a reasonable form.

c. Application of time-temperature superposition to experimental data of polystyrene solutions

The criterion 2) can be satisfied by using the same shift
factors $a_T$ from zero shear viscosity at each temperature for all linear viscoelastic functions and viscometric functions. This automatically satisfied criterion 3) because the zero shear viscosity has been interpreted by the activation energy as detailed in a previous section of this chapter. By superposing all reduced functions of each temperature of measurement into a reference temperature, criterion 1) was experimentally checked.

Table 4-6 lists figures of reduced material functions that can be found in this section. The rest of the master curves are in Appendix 2-1. The reference temperature is 25° C and shift factors are all computed from zero shear rate viscosity.

Figure 4-8, for a linear polystyrene solution (A2) and figure 4-20, for a STYRON solution (K2) show good superpositions of steady shear properties.

On the other hand, figure 4-15 for a star branched polystyrene solution (F1) is not as good a superposition. However judging from the more accurate data of capillary rheometer of higher shear rate, the failure of superposition is probably not a real phenomenon but a result of experimental error caused by flow instabilities. A detailed discussion of the error is given in appendix 6.

The check of superposition for the steady shear properties from the parallel plate mode shows similar results, good superposition for linear polymers and apparently poor superposition for star-branched polystyrene. Data from parallel plate mode with star
Table 4.6 Master Curves from Time-Temperature Superposition

<table>
<thead>
<tr>
<th>Sample</th>
<th>A2</th>
<th>F1</th>
<th>K2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Properties</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( n',</td>
<td>n^*</td>
<td>) from sinusoidal oscillation of cone and plate mode</td>
<td>Fig. 4-4</td>
</tr>
<tr>
<td>( n',</td>
<td>n^*</td>
<td>) from eccentric rotating disc, ERD mode</td>
<td>Fig. 4-6</td>
</tr>
<tr>
<td>( G',G'' ) from sinusoidal oscillation of cone and plate mode</td>
<td>Fig. 4-5</td>
<td>Fig. 4-12</td>
<td>-</td>
</tr>
<tr>
<td>( G',G'' ) from ERD mode</td>
<td>Fig. 4-7</td>
<td>Fig. 4-14</td>
<td>Fig. 4-19</td>
</tr>
<tr>
<td>( n, N_{1/2} ) from cone and plate mode</td>
<td>Fig. 4-8</td>
<td>Fig. 4-15</td>
<td>Fig. 4-20</td>
</tr>
<tr>
<td>( n ) from parallel plate mode</td>
<td>Fig. 4-9</td>
<td>Fig. 4-16</td>
<td>Fig. 4-21</td>
</tr>
<tr>
<td>( \psi_1-\psi_2 ) from parallel plate mode</td>
<td>Fig. 4-10</td>
<td>Fig. 4-17</td>
<td>Fig. 4-22</td>
</tr>
</tbody>
</table>
Fig. 4-4  Linear Viscoelastic Properties; Reduced Dynamic Viscosity and Reduced Complex Viscosity from ERD Mode

Sample: (A2) Narrow Molecular Weight Distribution
Polystyrene, $M_w = 2,000,000$  0.15 g/ml in 1-CN

Reference Temperature = 25°C
Fig. 4-5 Linear Viscoelastic Properties: Reduced Dynamic Storage Modulus and Reduced Dynamic Loss Modulus from ERD Mode

Sample: (A2) Narrow distribution polystyrene $M_w = 2,000,000$

0.15 g/ml in 1-CN
Fig. 4-6 Linear Viscoelastic Properties; Reduced Dynamic Viscosity and Reduced Complex Viscosity from Cone and Plate Oscillatory Mode. Reference Temperature = 25°C
Sample: (A2') Narrow Distribution Polystyrene
\( M_w = 2,000,000 \) 0.15 g/ml in 1-CN
Fig. 4-7. Linear Viscoelastic Properties: Reduced Dynamic Storage Modulus and Reduced Dynamic Loss Modulus from Cone and Plate Oscillatory Mode Reference Temperature = 25°C
Sample: (A2) Narrow Distribution Polystyrene
M_w = 2,000,000 0.15 g/ml in 1-CN

\[ G' \quad G'' \quad \omega' \quad \omega'' \quad \eta \]

\( 10^2 \quad 10^4 \quad 10^6 \quad 10^8 \quad 10^{10} \)
Fig. 4-9 Reduced Steady Shear Viscosity from Parallel.

Plate Mode  Reference Temperature = 25 C
Sample: (A2) Narrow Distribution Polystyrene
$M_w = 2,000,000$ 0.15 g/ml in 1-CN

$\\eta/\eta_0$ vs. $\gamma \cdot a_T$ (s$^{-1}$)
Fig. 4-10 Reduced $\Psi_1 - \Psi_2$ from Parallel Plate Mode

Reference Temperature = 25°C

Sample: (A2) Narrow Distribution Polystyrene
$M_w = 2,000,000$ 0.15 g/ml in 1-CN
Fig. 4-11  Linear Viscoelastic Properties: Reduced Dynamic Viscosity and Reduced Complex Viscosity from Cone and Plate Oscillatory Mode
Sample: (P1) Star shaped polystyrene (HA 31) 0.45 g/ml
in 1-CN
Reference Temperature = 25°C
Fig. 4.12 Linear Viscoelastic Properties: Reduced Dynamic Storage Modulus and Reduced Dynamic Loss Modulus from Cone and Plate Forced Oscillation Sample: (F1) Star shaped polystyrene (H401) 0.45 g/ml in 1-CN Reference Temperature = 25°C
Fig. 4-13 Linear Viscoelastic Properties; Reduced Dynamic Viscosity and Reduced Complex Viscosity from ERD Mode
Sample: (21) Star-shaped polystyrene (HA31) 0.45 g/ml
in 1-ON Reference Temperature = 25°C
Fig. 4-14 Linear Viscoelastic Properties; Reduced Dynamic Storage Modulus and Reduced Dynamic Loss Modulus from ERD Mode

Sample: (F1) Star shaped polystyrene (HA31) 0.45 g/ml
in 1-CN     Reference Temperature = 25 C

\(\omega \cdot \alpha_T \ (S^{-1})\)
Fig. 4-15 Reduced Steady Shear Viscosity and Reduced Normal Stress Difference from Cone and Plate Mode.

Sample: (P1) Star-shaped polystyrene (HA31) 0.45 g/ml in 1-CN Reference Temperature = 25°C
Fig. 4-18 Linear Viscoelastic Properties: Reduced Dynamic Viscosity and Reduced Complex Viscosity from ERD Mode

Sample: (K2) Commercial polystyrene STYRON with broad molecular weight distribution 0.42 g/ml in 1-CN

Reference Temperature = 250
FIG. 4-19 Linear Viscoelastic Properties: Reduced Dynamic Storage Modulus and Reduced Dynamic Loss Modulus from EPR Mole. Reference temperature = 25°C
Sample: (K1) Commercial polystyrene S6800M with broad molecular weight distribution 0.42 g/ml in 1-DN

\[ G^*_T \text{ (N/m²)} \]

\[ 10^3 \]

\[ 10^4 \]

\[ 10^5 \]

\[ 10^6 \]

\[ 10^7 \]

\[ 10^8 \]
Fig. 4-20 Reduced Stedy Shear Viscosity and Reduced Normal Stress Difference from Cone and Plate Mode

Sample: \( X_2 \) Commercial polystyrene STYRON with broad molecular weight distribution 0.42 g/ml in 1-CN

Reference Temperature = 25 C

\[ \dot{\gamma} \cdot \Delta T \left( S^{-1} \right) \]
Fig. 4-21 Reduced Steady Shear Viscosity from Parallel
Plate Mode  Reference Temperature = 25°C
Sample: (X2) Commercial polystyrene STYRON with broad
molecular weight distribution 0.42 g/ml in 1-CN
Fig. 4-22: Reduced $\Psi_1 - \Psi_2$ from Parallel Plate Mode
Reference Temperature = 25°C
Sample: (K2) Commercial polystyrene STYRON with broad molecular weight distribution 0.42 g/ml in 1-CN

$\log \left( \Psi_1 - \Psi_2 \right)_{\text{red}}$

$\log \gamma \cdot \Delta \tau (s^{-1})$

$10^2$

$10^0$

$10^{-1}$

$10^{-2}$

$10^{-3}$

Symbols:
- $+$: -5°C
- $\times$: 5°C
- $\triangledown$: 15°C
- $\triangle$: 25°C
- $\triangledown$: 35°C
- $\Delta$: 40°C
polystyrene (Fl) shows poorer superposition than data from cone and plate mode. But it should be noted that the scatter is random. Reduced viscosities at around critical shear rate are in the following order in Fig. 4-16.

\[ \eta_0 \text{ at } 25^\circ C > -5^\circ C > 5^\circ C > 35^\circ C > 15^\circ C > 40^\circ C \]

It is concluded that the time-temperature superposition technique is applicable for all of our polystyrene solutions even for the viscometric properties such as steady shear viscosity and normal stress difference.

d. The time-temperature superposition for polymer melt samples

The same time-temperature superposition technique as for polymer solutions was successfully applied to the linear viscoelastic data from undiluted broad distribution polystyrene samples with 200° C as a standard temperature.

Figure 4-23 shows the complex viscosity and the dynamic viscosity master curves. Figure 4-24 shows the storage modulus and the loss modulus master curve. The shift factors based on the zero shear rate viscosities are used.

However, the same shift factors do not appear to be applicable to the steady shear properties. Figure 4-25 shows an unsuccessful attempt to superpose the shear viscosity curves using the same shift factors based on the zero shear rate viscosity.
Fig. 4-23 Linear Viscoelastic Properties; Reduced Dynamic Viscosity and Reduced Complex Viscosity from ERD Mode

Sample: Undiluted STYRON; broad molecular weight distribution polystyrene Reference temperature = 200 °C

+ 140°C
× 160°C
△ 180°C
▼ 200°C
▽ 210°C
△ 220°C
△ 250°C
Fig. 4.24 Linear Viscoelastic Properties; Reduced Dynamic Storage Modulus and Reduced Dynamic Loss Modulus from ERD Mode
Sample: Undiluted STYRON; broad molecular weight distribution polystyrene Reference temperature = 200.0
Fig. 4-25 Reduced Steady Shear Viscosity from Cone and Plate Mode

Sample: Undiluted STYRENE, broad molecular weight distribution polyethylene
Reference temperature = 200°C
There is a systematic horizontal deviation in Figure 4-25. Notice that, different from random deviation in Figure 4-16 for a star branched polystyrene solution, reduced steady shear viscosity is higher for a lower temperature at around critical shear rate.

\[ \eta \text{ at } 160^\circ C > 180^\circ C > 200^\circ C > 220^\circ C > 240^\circ C \]

Empirical shift factors \( \alpha_T' \) which are different from the shift factors \( \alpha_T \) from the zero shear viscosity were used to get a graphical superposition. Table 4-7 and Fig. 4-26 show the difference between these shift factors \( \alpha_T \) and \( \alpha_T' \) along with the shift factors computed from the WLF equation (Eq. 4-14). WLF equation is an empiricism which fit a wide variety of polymers successfully with two empirical constants \( C_1^0 \) and \( C_2^0 \).

\[
\log \alpha_T = \frac{-C_1^0 (T-T_0)}{C_2^0 + (T-T_0)} \quad [4-14]
\]

Values of \( C_1^0 \) and \( C_2^0 \) are taken from literature (p. 316 of 5), \( C_1^o = 13.3 \) and \( C_2^o = 47.3 \) (89). Reference temperature was taken to be \( 373^\circ K \): Tg. \( \alpha_T \) computed from Eq. 4-14 and these constants are shown in Fig. 4-26.

Similar failure of the time-temperature superposition based on \( \eta \) has been reported by Graessley for narrow distribution polystyrene melts as shown in Fig. 4-27 (52). They suggested that
Fig. 4-26 Shift Factors ($a_T$) for the Time-Temperature Superposition
Sample: Undiluted Commercial Polystyrene
STYRON Reference Temperature = 200°C
Table 4-7
Shift Factors for Time-Temperature Superposition of Undiluted Polystyrene (Styron)

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>(\eta_0^{(C+P)}) Pa.s</th>
<th>(a_T) from Superposition of C+P data</th>
<th>(\eta_0) (ERD) Pa.s</th>
<th>(a_T) from WLF eq.</th>
</tr>
</thead>
<tbody>
<tr>
<td>140</td>
<td>(6.2 \times 10^5)</td>
<td>16.4</td>
<td>9.05 \times 10^6</td>
<td>871</td>
</tr>
<tr>
<td>160</td>
<td>(5.3 \times 10^3)</td>
<td>3.07</td>
<td>5 \times 10^5</td>
<td>32.8</td>
</tr>
<tr>
<td>180</td>
<td>(8.4 \times 10^4)</td>
<td>2.02</td>
<td>6 \times 10^4</td>
<td>3.78</td>
</tr>
<tr>
<td>200</td>
<td>(1.8 \times 10^4)</td>
<td>1.00</td>
<td>1.65 \times 10^4</td>
<td>4.68</td>
</tr>
<tr>
<td>220</td>
<td>(5.3 \times 10^3)</td>
<td>0.282</td>
<td>4.97 \times 10^3</td>
<td>0.31</td>
</tr>
<tr>
<td>240</td>
<td>(1.9 \times 10^3)</td>
<td>0.0922</td>
<td>1.8 \times 10^3</td>
<td>0.102</td>
</tr>
<tr>
<td>250</td>
<td>(1.06 \times 10^3)</td>
<td>0.0589</td>
<td></td>
<td>0.083</td>
</tr>
</tbody>
</table>

*reference temperature 200° C
anomaly occurs when temperature is close to $T_g$ or below 190° C. Graessley's publication (52) lacks linear viscoelastic data of samples. Authors stated that it was generally supposed the same $a_T$ is applicable to both $\eta$ and linear viscoelastic properties because the characteristic time constant $\tau_0$ ($\tau_0 = 1/\dot{\gamma}_0$) is assumed to be proportional to $\tau_R$, the longest relaxation time of the Rouse molecular theory

$$\tau_R = \frac{\gamma M}{\pi^2 \rho}$

in a number of molecular theories (90). Therefore they claimed that anomaly could be observed for linear viscoelasticity of polystyrene melts.

Fig. 4-27 Systematic Failure of Time-Temperature Superposition Technique (52). Sample: Narrow Distribution Linear Polystyrene Melts.

(Δ) 165°C; (○) 173°C; (●) 175°C; (□) 179°C; (■) 193°C; (△) 217°C.
However studies of linear viscoelastic properties of narrow distribution polystyrene melts showed that the time-temperature superposition is fully applicable (91)(92). Also we measured both viscoelastic functions and steady shear functions (Figs. 4-23, 4-24 and 4-25) but this abnormality existed only for the steady shear properties. Also it has been observed that time-temperature superposition is applicable to concentrated solutions of polystyrene (93). The reasons why undiluted polystyrene shows the failure of time-temperature superposition whereas solutions of polystyrene are successfully superposed by $a_T$ are not known. However, we suspect the following causes:

1) Flow Instability

The steady shear flow of polymeric liquids are known to become unsteady at high shear rates. This is especially evident when an open edge geometry like the cone and plate flow is used. The shear fracture starts from the free surface and decreases the observed shear stress. (This source of error is explained in detail in Appendix 6).

Even when steady stress is observed it does not necessarily mean steady shear flow exists as prescribed. Polystyrene melt is less stable against shear fracture than polyethylene melt because it has less surface tension. Surface tension is considered to hold sample fluid within the gap against the shear fracture (31).

Experiments of more stable shear flow using enclosed geometrics such as a capillary rheometer or a slit die rheometer along with a
cone and plate rheometer for low shear rate are necessary to determine whether time-temperature superposition is applicable to polystyrene melts. Currently few such rheometers capable of accurate measurement with small amount of sample polymer (~5g) exist. We sent three samples of narrow distribution polystyrene to Mr. F.N. Cogswell of ICI plastics division. Only one of them ($\bar{M}_w = 110,000$) was possible to be measured by their small capacity capillary rheometer. One sample ($\bar{M}_w = 390,000$) was too viscous to flow while another ($\bar{M}_w = 37,000$) had too low viscosity to be measured (94).

2) Errors by Temperature Variation

Polystyrene melts have unusually large activation energy of viscous flow and thus their viscosity is very sensitive to the temperature variation.

Due to the design limitation of current rotational rheometers with air ovens, there is inevitably some temperature fluctuation and large temperature gradient within the sample fluid*. The gradient becomes larger as measurement temperature differs more from room temperature which may result in systematic errors depending on measurement temperature. (For details, see appendix 6).

*errors from temperature fluctuation and gradient are in the order of $\pm 2^\circ$ C at 200$^\circ$ C and larger at higher temperature
3) Real Difference of Shift Factors

If the difference in shift factors are real, the deviation from the analogies includes a temperature dependent \( \dot{\gamma} - \omega \) axial shift between \( \eta(\dot{\gamma}) \) and \( \eta'(\omega) \). This would be a very interesting finding but in order to reach that conclusion, additional polymer melt shear flow experiments free from errors cited in 1) and 2) must be performed. We did not have the capability to do that kind of measurement.
3. Concentration Dependence of Zero Shear Rate Viscosity

a. Objective - Concentration dependence of zero shear rate viscosity of star and linear polystyrene solutions are studied. Star branching of polymers has an interesting effect on the zero shear rate viscosity \( \eta_0 \) - concentration \( c \) - molecular weight relationship of a polymer solution. At low \( cM \), the zero shear rate viscosity of a star polymer solution is lower than that of a linear polymer solution of the same molecular weight because the radius of gyration (size of the polymer chain) is smaller. This can be corrected by \( g \) of eq. 1-25. However when \( cM \) is large, star branched polymers have a higher zero shear rate viscosity than the linear polymer of same \( c \) and \( M \).

Fig. 4-28 shows the different molecular weight dependence of \( \eta_0 \) for linear polymer solutions and star branched polymer solutions. The increase in slope of the log \( \eta_0 \) vs log \( cM \) curve at high \( \overline{M}_w \) is called the enhancement effect. This phenomena was observed for undiluted polybutadiene (66), polybutadiene extended by Aroclor or naphthalenic oil (67) and polyisoprene solution in tetrade cane (68). But for polystyrene melts \( \eta_0 \) of star branched polymers are much lower than \( \eta_0 \) of linear polymers up to \( cM_w = 10^6 \) (51).

In order to study this enhancement effect in polymer solutions, it is necessary to establish \( \eta_0 - c - \overline{M}_w \) relationship for the particular polymer-solvent combination.

For polyisoprene solutions in tetrade cance the plot of \( \frac{\eta_0}{c^{1.5}} \) vs. \( cM \) gives a unified curve for linear polymers and another unified curve
Fig. 4-28 Enhancement Effect of Star Branching on Zero Shear Viscosity
for star branched polymers of same extent of branching (68).

The $\eta_0 - c - \overline{M}_w$ relationship for polyisoprene solution is expressed by eq. 4-15 or eq. 4-16.

$$\eta_0 = K c^5 M^{3.4} \quad [4-15]$$

$$\frac{\eta_0}{c^{1.5}} = K c M^{3.4} \quad [4-16]$$

We found that these equations did not give unified curve for polystyrene solutions in 1-CN. We examined various ways of $\eta_0 - c - \overline{M}_w$ correlation previously used by others. They are the Martin equation, the Simha correlation, and the power law correlation.

The concentration of a polymer solution is usually classified into three categories based on the chain overlap parameter $= c[\eta]$ (p. 239 and p. 518 of 5).

1) Dilute Solution $c[\eta] < 1$

The intermolecular force on chain-chain interaction is small for this type of solution and physical properties are usually slight modification of infinite dilution properties.

2) Moderately concentrated solution $1 < c[\eta] < 10$

Intermediate range between 1) and 2)

3) Concentrated solution $10 < c[\eta]$

Polymer chain-chain interaction becomes dominant and its flow properties cannot be explained from the dilute solution properties only.
When the molecular weight is sufficiently large \((cM > M_c)\), the 3.4 power dependence of \(\eta_0\) on \(\bar{M}_W\) appears in concentration regimes 2) and 3). All but one (solution E2) of our samples are concentrated solutions (in category 3).

b. Molecular weight dependence

Fig. 4-29 shows the molecular weight dependence of \(\eta_0\) at constant concentrations. Linear polystyrene solutions of \(c = 0.30, 0.45\) and 0.52 g/ml are used. Within experimental scatter, the 3.4 power rule is applicable as expressed in eq. 4-15.

\[
\eta_0 = F(c) \times M^{3.4} \tag{4-17}
\]

if \(cM > M_c\)

c. Techniques to correlate \(\eta_0 - c - \bar{M}_W\) relationship

Several techniques are tried in this section to know \(F(c)\) in eq. 4-17.

As mentioned before, all but one of our solutions are concentrated solutions. In order to study the \(\eta_0 - c - \bar{M}_W\) relationship for both concentrated and moderately concentrated solutions, Ferry et al.'s data on polystyrene solutions in Aroclor (53) were used along with our data.
Fig. 4.29 Molecular Weight Dependence of Zero Shear Viscosity: Linear Narrow Distribution Polystyrene Solutions in 1-CN

\[ \eta_o \]

\( c = 0.52 \text{ g/ml} \)

\( c = 0.45 \)

\( c = 0.30 \)

slopes = 3.4
(C-1) Power Correlation

\( \eta_0 \) vs \( M_W^{\tilde{M}} \) was plotted in order to see if eq. 4-18 is applicable to the data

\[ \eta_0 = (cM_W)^x \cdot K' \quad [4-18] \]

As shown in Fig. 4-30 for polystyrene/Aroclor and in Fig. 4-31 for polystyrene/1-CN solutions, eq. 4-18 did not fit experimental data and there are systematic shifts depending on \( M_W^{\tilde{M}} \).

Onogi et al. have shown that \( \eta_0 \) of concentrated polystyrene solutions (c=4 ~ 20 wt%, M = 2x10^5 ~ 2x10^6) in toluene and in decalin can be correlated by a power law type equation (95).

\[ \eta_0 = K(c \rho)^\alpha M^\beta \quad [4-19] \]

\( \alpha = 4.7 \) and \( \beta/\alpha = 0.72 \) for toluene solutions and \( \alpha = 5.6 \), \( \beta/\alpha = 0.60 \) for decalin solutions.

From eq. 4-15 which described \( M_W^{\tilde{M}} \) dependence of sample solutions, following equations were derived (95).

\[ \eta_0 = K' M^{3.4} C^x \quad [4-20] \]

or

\[ \eta_0 = K' \left(C M^x \right)^{\frac{3.4}{x}} \quad [4-21] \]

\( \log \eta_0 = \log K' + 3.4 \log M + x \log C \quad [4-22] \)
Fig. 4-30  Power Correlation between $\eta_0$ and $c \cdot \overline{M}_w$
or $c \cdot g \cdot \overline{M}_w$  Sample: Polystyrene in Aroclor

\[ \eta_0 \]

\[ 10^3 \]

\[ (\text{Pa} \cdot \text{s}) \]

\[ 10^2 \]

\[ 10 \]

\[ c \cdot g \cdot \overline{M}_w \]

\[ 10^4 \]

\[ 10^5 \]
Fig. 4-31  Power Correlation between $\eta_0$ and $c_{w}$ and $c_{w}$ Sample: Polystyrene in 1-CN

*Uncorrected total $M_{w}$ for star polystyrene  
other symbols same as

Fig. 4-2
Therefore in the plot of log $n_o$ vs log $c$, the slope is $x$. Fig. 4-32 shows the plot for polystyrene/Aroclor solution. Most of the solutions have slopes between one and two but none has a constant slope.

Fig. 4-33 shows the plot of log $n_o$ vs log $c$ for polystyrene/1-CN solution. Concentrations are some ten times larger than polystyrene/Aroclor solutions and the slopes are much steeper. The value of $x$ (slope) is larger for solutions of large $c$ even when $cM$ is smaller.

It has been suggested that eq. 4-20 fits $n_o = c - \tilde{M}_w$ relationship with the following parameters which depend on $cM$ and solvent.

$$n_o = K'(cM^y)^z \quad [4-23]$$

1) For a good solvent system

$$y = 0.625 \sim 0.68$$
$$z = 5.4 \sim 5 \quad cM > M_c$$
$$z = 1.6 \sim 1.47 \quad cM < M_c$$

2) For a poor solvent system

$$y = 0.5$$
$$z = 6.8 \quad cM > M_c$$
$$z = 2 \quad cM < M_c$$

Fig. 4-34 show the application of these methods of reduced variables to polystyrene/Aroclor solutions. 3) $n_o$ vs $cM^{0.5}$ appears to result the best superposition even though Aroclor is believed to
Fig. 4-32 The Plot of $\log \eta_0$ vs. $\log c$ to check Power Correlation
Sample: Polystyrene in Aroclor

Other symbols same as Fig. 4-30
Fig. 4.33 Plot of $\log \eta_o$ vs. $\log c$ to check the Power Correlation eq. 4.18
Sample: Polystyrene in 1-C3.
Fig. 4-34 Plot of $\gamma_0$ vs. $cm^x$ to check the applicability of Eq. 4-23. Sample: Polystyrene in Aroclor.
be a good solvent of polystyrene. It should be noted that star branched polymers followed some master curve when corrected for the size shrinkage by $g$ of eq. 1-25.

Fig. 4-35 shows the plot of $\eta_0$ vs $cM^{0.5}$ for polystyrene/1-CN solutions. The superposition is modestly good for polymers of $\bar{M}_w \geq 110,000$. Star branched polymers show the same relationship if corrected by $g$. (All star branched polymer used here have $\bar{M}_w$ and $g \bar{M}_w$ larger than 110,000). However data of broad distribution polystyrene lie on a different curve. For a narrow distribution polymer $\bar{M}_w$, $M_n$ and other means of averaging have supposedly the same value. But for a broad distribution polymer appropriate way of averaging is required for each physical property. $\bar{M}_w$ is too large for correlating viscosity. Other means of averaging such as viscosity average $\bar{M}_v$, which can be computed from $[\eta]$ and usually is smaller than $\bar{M}_w$, could be more suitable.

In eq. 4-23 $\eta_0$ is proportional to the power of $CM^{0.5}$ or $C^2M$ for polystyren/1-CN solutions. The following equations are derived.

$$\eta_0 = K' (c^2\bar{M}_w)^{3.4} \quad [4-24]$$

$$\frac{\eta_0}{c^{3.4}} = K' (c\bar{M}_w)^{3.4} \quad [4-25]$$

Therefore the plot of $\frac{\eta_0}{c^{3.4}}$ vs $c\bar{M}_w$ is expected to give a unified curve of the $\eta_0 - c - \bar{M}_w$ relationship. The result of such a plot appears in Fig. 4-36 which is a modest success. Low molecular weight,
Fig. 4-35 Plot of $\eta_0$ vs. $c^{0.5}$ or $c(\omega^0.5)$ to check the Applicability of eq. 4-24
Sample: Polystyrene in 1-1.

Symbols

Linear: A $F_w=2,000,000$
B 390,000
C 110,000
D 37,000
E 17,500

Star: F # HA31
G HA29
H HA26
J HA27

Styron: K in 1-CN
Fig. 4-36 Plot of \( \frac{\eta_0}{c^{3.5}} \) vs. \( \frac{c}{c_{w}} \)

to get a Unified Curve of
\( \eta_0 - c - c_{w} \) Relationship
Sample: Polystyrene in 1-CN

slope = 3.4
high concentration solution (B1 and C1) did not obey these equations which may be the result of relatively high $T_g$ for these solutions.

2) Other correlation techniques

Other correlations known to fit the $c - M - \eta_0$ relationship of moderately concentrated solutions are the Martin equation and the Simha correlation (96).

The Martin equation results in a plot of $\log \left( \frac{\eta_0}{cM^a} \right)$ vs $cM^a$ where $a$ is from the Mark-Hauwink-Sakurada equation. The Simha correlation results in a plot of $\frac{\eta_0}{cM^a}$ vs $\log c - \log \gamma$ where $\gamma$ is an empirical shift factor.

Neither technique was applicable to our data from polystyrene/1-CN solutions. It is reasonable from the fact that all of the solutions are highly concentrated. Details may be found in appendix 2-6.

3) Empirical correlation

We found that the plot of $\log \left( \frac{\eta_0}{cM^{0.75}} \right)$ vs $c$ or $\log \left( \frac{\eta_0}{cM^{0.75}} \right)$ vs $c$ for each molecular weight as shown in Fig. 4-37 resulted in straight lines with same slopes for all of our sample solutions. By using empirical shift factor $\gamma'$ on the semi-logarithmic scale, one unified straight line as shown in Fig. 4-38 was obtained.

$$\log \left( \frac{\eta_0}{cM^{0.75}} \right) = (c + \gamma') k_1 + k_2 \quad [4-26]$$
Fig. 4-37 Plot of \( \log \left( \frac{\eta_s}{e^{-0.75} \cdot \eta_s} \right) \) vs. c
Fig. 4-38 Unified Curve from Fig. 4-37 by Graphical Superposition with Shift Factors $\gamma'$
Sample: Polystyrene in 1-CN

\[ \frac{\eta}{cM^{0.75}} \]

\[ c + \gamma' \]
Fig. 4-39 shows the molecular weight dependence of $\gamma'$. Linear polystyrene solutions of $M_w = 110,000$ is used as standard ($\gamma' = 1$). The relationship between $\gamma'$ and $M_w$ can be expressed by the following equations:

$$\gamma' = k_3 \log M_w + k_5 \quad \text{for } M_w > 110,000 \quad [4-27]$$

$$\gamma' = k_4 \log M_w + k_6 \quad [4-28]$$

$k_3 = 0.288 \quad k_5 = 5.17$

$k_4 = 0.106 \quad k_6 = 5.02$

For linear polystyrene solutions in 1-CN.

From eq. 4-26, 4-27, and 4-28, the following simple $n_0 - c - M_w$ relationship was postulated*.

$$n_0 = c(K_1)^c M_w^y \cdot K_2 \quad [4-29]$$

$y = 3.4 \quad \text{for } cM_w > M_c$

$y = 1 \quad \text{for } cM_w < M_c$

From Fig. 4-38, $K_2 = 0.085$ and $K_1 = 6.31 \times 10^{11}$. If eq. 4-29 is applicable to our data the reduced variables are,

$$\frac{n_0}{cK_1^c} \quad \text{vs} \quad M_w$$

*This is not a simple mathematical rearrangement from eq. 4-26, 4-27, and 4-28, but a postulation that simple expression of eq. 4-29 can exist.
Fig. 4-39 Shift Factors for Graphical Superposition in Fig. 4-38 and Their $\bar{U}_w$ Dependence
Fig. 4-40 show this plot on double logarithmic scale. A unified curve of $\eta_0 - c - \bar{M}_w$ relationship was obtained. The slopes are $y$ in eq. 4-36.

Notice there is no enhancement effect for star branched poly-styrene solutions if $g \bar{M}_w$ is used instead of $\bar{M}_w$ in this plot.

Fig. 4-41 shows the plot of $\frac{\eta_0}{K_1 c}$ vs $c \bar{M}_w$ for comparison. As is clear from eq. 4-29, this is good only when $y$ is close to 1 at low molecular weight where the correlation is even better than in Fig. 4-41.

d. Discussion

A similar effect to the $\eta_0 - c - \bar{M}_w$ relationship as the enhancement by star branching is observed for polymer solutions in a poor or a $\Theta$ solvent than for a good solvent because the size of the chain is smaller. But at higher concentrations, (above 15-30% (96)), the $\Theta$ solvent solution has larger $\eta_0$ as shown in Figure 4-42.

Gandhi et al. speculated that this enhancement effect by poor solvents on $\eta_0$ may be due to the effect of $T_g^*$. $T_g^*$ of polymer solutions depend on whether solvent and concentration. $T_g^*$ is higher for a poor solvent solution and lower for a good solvent solution. In Fig. 4-44, $T_g^*$ for a good solution is far below the measurement temperature. $T_g^*$ for a poor solution is far below when $c^X M^Y$ is small but close to the measurement temperature when concentration is high and $c^X M^Y$ is large.
Fig. 4-40 A Master Curve of $\eta_0 - \bar{M}_w - c$ Relationship by the plot of $\frac{\eta_0}{cK_1}$ vs. $\bar{M}_w$.
Fig. 4-41 Another Master Curve of \( \frac{\eta_o}{\kappa_1^c} \) vs. c\( \kappa_1^c \)
by the plot of \( \frac{\eta_o}{\kappa_1^c} \) vs. c\( \kappa_1^c \)
From intrinsic viscosity measurement (Appendix 2-5) 1-CN behaves as a good solvent of polystyrene at 35° C. But the study of the concentrated polystyrene solutions in 1-CN (correlated by cM^{0.5}) suggests that they might be $\Theta$-solvent solutions. In analyzing the data this may be considered. On the other hand it may be natural that concentrated solution behave closer the $\Theta$-solvent, because in concentrated solution polymer chain is surrounded by other polymer chains which have similar solubility to a $\Theta$-solvent.

In conclusion, it has been found that:

1) No conventional correlative technique to obtain $\eta_0 - c - M_w$ relationship was totally successful.

2) The best correlation was obtained by eq. 4-29

$$\eta_0 = c(K_1)^c M_w^y \cdot k_2$$  [4-29]

$K_1 = 6.31 \times 10^{11}$

$K_2 = 0.085$
Fig. 4-42 (a) Plots of Reduced Steady Shear Viscosity and Reduced Normal Stress Difference Coefficient for 2% solutions of Narrow Distribution Polystyrene of Various Molecular Weights (97)

- (O) ø 1.02 x 10^6; (O) ø 1.52 x 10^6
- (O) ø 1.14 x 10^6; (O) ø 0.91 x 10^6
- (O) ø 1.06 x 10^6; (O) ø 2.73 x 10^6

(in weight per cent): (O) ø 7.6%; (O) ø 3.5%; (O) ø 1.6%; (O) ø 0.571; (O) ø 0.116

Fig. 4-42 (b) Reduced Steady Shear Viscosity and Reduced Normal Stress Difference Coefficient vs. Shear Rate for Solutions of Various Concentrations of a Narrow Distribution Polystyrene with $\overline{M}_w = 1.82 \times 10^6$ (97)
Fig. 4-43 'Enhancement' Effect on the $\eta_o - c - \overline{M}_w$ Relationship by a Poor Solvent compared to a Good Solvent
\[ y = 3.4 \quad c\bar{M}_W > Mc \quad \text{and} \]
\[ y = 1.0 \quad c\bar{M}_W < Mc \]

Unified curve of \( \eta_o - c \cdot \bar{M}_W \) was obtained. No enhancement effect on \( \eta_o \) by star branching was observed if \( g \bar{M}_w \) is used for star branched polystyrene instead of \( \bar{M}_w \).

4. Discussion of temperature dependence and concentration dependence of rheological properties

The temperature dependence of rheological properties is accounted for by the time-temperature superposition. Reduced variables of concentration dependence, on the other hand, do not lead to unified master curves because shapes of the curves depend on concentration and molecular weight.

Super master curves which include all \( c, \bar{M}_W, \) and \( T \) dependences of \( \eta(\dot{\gamma}) \) or \( \eta'(\omega) \) were only meant to be the limiting value when \( cM \) or \( c[\eta] \) is very large (\( c[\eta] > 100 \) for our samples). Many measurements of \( \eta(\dot{\gamma}) \) for polymer solutions reported in the literature are restricted to high \( \bar{M}_W \) and low \( c \); thus this limitation may sometimes be overlooked. When measurements were performed for wide range of \( c \) and \( M \), as in the case of Endo et al. (97), the superposed curves show the difference at high shear rate clearly in Fig. 4-43. It is also clear from this figure that steady shear flow measurements with a cone and a plate rheometer were possible at higher shear rate when \( M \) is larger or \( c \) is smaller.
CHAPTER V. PHENOMENOLOGICAL STUDY
OF THE DEVIATIONS FROM THE ANALOGIES

1. Introduction

In this chapter master curves of linear viscoelastic and visco-
metric properties for each sample solution are used to check the
analogies between them. The evaluation is done in two ways:

1) Graphically - overall shapes of the master curves of the
viscometric properties on double logarithmic scale are compared to
those of the linear viscoelastic properties as shown below.

The simple analogies:
\[ \eta(\dot{\gamma}) = \eta'(\omega) \text{ at } \dot{\gamma} = \omega \]
\[ \frac{N_1(\dot{\gamma})}{2} = G'(\omega) \]

Cox-Merz rule:
\[ \eta(\dot{\gamma}) = |\eta^*(\omega)| \text{ at } \dot{\gamma} = \omega \]

2) Obtain rheological parameters from each master curves then
compare these parameters.

A modified Carreau viscosity equation is used to fit viscosity
master curves to obtain the critical shear rate, \( \dot{\gamma}_0 \), critical frequency
\( \omega_0 \) and power law slopes \( d \) and \( d' \). The dependence of these parameters
such as molecular weight, concentration, branching functionality for
star branched polymers and polydispersity index will be discussed in
Chapter 6.
2. Graphical Evaluation of the Analogies

Representative results of the comparison between overall shape of master curves of viscometric properties and that of linear viscoelastic properties are shown in Fig. 5-1, 5-2, and 5-3.

The comparison for the rest of the sample will be found in Appendix 2-2. Simple analogies are studied for $\eta(\dot{\gamma})$ vs $\eta'(\omega)$ and $N_1(\dot{\gamma})/2$ vs $G'(\omega)$. The Cox-Merz rule ($\eta(\dot{\gamma}) = |\eta^*(\omega)|$) was also studied graphically using these figures.

In Fig. 5-1, for sample A2 (narrow distribution linear polystyrene solution) the Cox-Merz rule accurately describes the data over the entire range of the two master curves. The dynamic viscosity is much smaller than the steady shear viscosity at high shear rates. Normal stress difference ($N_1/2$) is larger than storage modulus at high shear rates.

For sample F1 in Fig. 5-2 (star-branched polystyrene solution) the Cox-Merz rule is also in good agreement except at larger values of $\dot{\gamma}$ or $\omega$. Dynamic viscosity is well below the $\eta$ and $|\eta^*|$ curves at a high shear rate/frequency.

In Fig. 5-2, the difference between $N_1/2$ and $G'$ at a high shear rate/frequency could not be observed because the steady shear flow in the cone and plate mode became unstable at high shear rate. We could obtain viscosity but not normal stress difference from high shear rate capillary measurement.

In Fig. 5-3 for sample K2 (broad distribution polystyrene solution)
Fig. 5-1 Comparison between the Viscous Properties and the Linear Viscoelastic Properties; reduced to Standard Temperature = 25°C

Sample: (A2) Narrow Distribution Polystyrene

\( M_w = 2,000,000 \) 0.15 g/ml in 1-CN
Fig. 5-3 Comparison between the Viscometric Properties and the Linear Viscoelastic Properties; reduced to Standard temperature = 25°C
Sample: (K2) Commercial polystyrene STYRON with broad molecular weight distribution 0.42 g/ml in 1-CN
<table>
<thead>
<tr>
<th>Samples**</th>
<th>Low $\dot{\gamma}$ (Newtonian Zone)</th>
<th>High $\dot{\gamma}$ (Power Law Zone)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>$n =</td>
<td>n^*</td>
</tr>
<tr>
<td>A2</td>
<td>$n =</td>
<td>n^*</td>
</tr>
<tr>
<td>A3</td>
<td>$n =</td>
<td>n^*</td>
</tr>
<tr>
<td>B1</td>
<td>$n =</td>
<td>n^*</td>
</tr>
<tr>
<td>B2</td>
<td>$n =</td>
<td>n^*</td>
</tr>
<tr>
<td>C1</td>
<td>$n =</td>
<td>n^*</td>
</tr>
<tr>
<td>C2</td>
<td>$n =</td>
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</tr>
<tr>
<td>K4</td>
<td>$n =</td>
<td>n^*</td>
</tr>
</tbody>
</table>

** Table 5-1: Graphical Check of Analogies of Polystyrene Solutions: Viscous Properties **
| Samples ** | \( n = |n^*| = n' \) | \( n > |n^*| > n' \) |
|----------|-----------------|-----------------|
| K5       |                 |                 |
| K6       |                 |                 |
| K7       |                 |                 |
| K8       |                 |                 |

** See Table 2-3 of Chapter 2 for description of sample solutions

* high shear rate data not available
Table 5-2
Graphical Evaluation of Analogies of Polystyrene Solutions: Elastic Properties

<table>
<thead>
<tr>
<th>Samples **</th>
<th>Low $\dot{\gamma}$ ($\psi_1$ vs $\frac{2G'}{\omega^2}$)</th>
<th>High $\dot{\gamma}$ ($N_{1/2}$ vs $G'$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>$N_{1/2} = G'$</td>
<td>*</td>
</tr>
<tr>
<td>A2</td>
<td>$N_{1/2} = G'$</td>
<td>$N_{1/2} &gt; G'$</td>
</tr>
<tr>
<td>A3</td>
<td>$N_{1/2} = G'$</td>
<td>$N_{1/2} &gt; G'$</td>
</tr>
<tr>
<td>B1</td>
<td>$N_{1/2} = G'$</td>
<td></td>
</tr>
<tr>
<td>B2</td>
<td>$N_{1/2} = G'$</td>
<td>*</td>
</tr>
<tr>
<td>C1</td>
<td>$N_{1/2} = G'$</td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>$N_{1/2} = G'$</td>
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</tr>
<tr>
<td>D2</td>
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<td></td>
</tr>
<tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>E2</td>
<td>$N_{1/2} = G'$</td>
<td>*</td>
</tr>
<tr>
<td>F1</td>
<td>$N_{1/2} = G'$</td>
<td>*</td>
</tr>
<tr>
<td>F2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G1</td>
<td>$N_{1/2} = G'$</td>
<td>$N_{1/2} &gt; G'$</td>
</tr>
<tr>
<td>H1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>J1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K1</td>
<td>$N_{1/2} = G'$</td>
<td>$N_{1/2} &gt; G'$</td>
</tr>
<tr>
<td>K2</td>
<td>$N_{1/2} = G'$</td>
<td>$N_{1/2} &gt; G'$</td>
</tr>
<tr>
<td>Samples **</td>
<td>Low $\dot{\gamma}$ ($\psi_1$ vs $\frac{2G'}{\omega^2}$)</td>
<td>High $\dot{\gamma}$ ($N_{1/2}$ vs $G'$)</td>
</tr>
<tr>
<td>------------</td>
<td>---------------------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>K3</td>
<td>$N_{1/2} = G'$</td>
<td>$N_{1/2} &gt; G'$</td>
</tr>
<tr>
<td>K4</td>
<td>$N_{1/2} = G'$</td>
<td>$N_{1/2} &gt; G'$</td>
</tr>
<tr>
<td>K5</td>
<td>$N_{1/2} = G'$</td>
<td>$N_{1/2} &gt; G'$</td>
</tr>
<tr>
<td>K6</td>
<td>$N_{1/2} = G'$</td>
<td>$N_{1/2} &gt; G'$</td>
</tr>
<tr>
<td>K7</td>
<td>$N_{1/2} = G'$</td>
<td>$N_{1/2} &gt; G'$</td>
</tr>
<tr>
<td>K8</td>
<td>$N_{1/2} = G'$</td>
<td>$N_{1/2} &gt; G'$</td>
</tr>
</tbody>
</table>

*Experimental scattering jig or measurement impossible due to flow instability*

**See Table 2-3 for description of sample solutions**
\( \eta > |\eta^*| > \eta' \) at high shear rates/frequencies. So there is a little deviation from the Cox-Merz rule. On the elastic part of the analogy \( N_{1/2} \) is slightly higher than \( G' \) at moderate shear rates/frequencies.

Throughout the comparison in Fig. 5-1, 5-2, and 5-3, all of the master curves showed exact analogy at low shear rate as they must.

This is, \( \eta(\dot{\gamma})|_{\dot{\gamma} \to 0} = \eta'(\omega)|_{\omega \to 0} = \eta_0 \) \[5-1\]

\[ \psi_1(\dot{\gamma})|_{\dot{\gamma} \to 0} = \frac{N_1(\dot{\gamma})}{\dot{\gamma}^2|_{\dot{\gamma} \to 0}} = \frac{2G'(\omega)}{\omega^2|_{\omega \to 0}} = \psi_1^0 \] \[5-2\]

The comparison between \( \eta \), and \( |\eta^*| \) and \( \eta' \) for all samples are summarized in Table 5-1 and the comparisons between \( N_{1/2} \) and \( G' \) are in Table 5-2. The comparisons were done at low shear rates where all the samples show the exact analogy and at high shear rates where various deviations from the analogies are shown.

Although there are some exceptions like in Fig. 5-3, most samples obeyed the Cox-Merz rule within experimental error. It is possible to draw a misleading conclusion about the applicability of the Cox-Merz rule if one uses the data from the cone and plate steady shear flow only. As shown in Fig. 5-2 even when cone and plate data suggested \( |\eta^*| > \eta \), more reliable data from capillary flow showed that \( \eta = |\eta^*| \). This error is due to the shear fracture at high shear rate which decreases the observed steady shear viscosity.

As briefly mentioned in Chapter 1, one of the significances of this study is the high shear rate data of viscometric properties of polymer solutions with wide variety of concentration and molecular weight.
As is detailed in the Appendix 6, it is usually only with polymer solutions with special conditions (high molecular weight and low concentration) that one can observe the power law zone with cone and plate mode or parallel plate mode (68), without significant shear fracture starting at the open surface at the edge. In actual measurement as shown in Fig. 5-4, this shear fracture which develops with time and results in decreasing force measurements is coupled with the stress overshooting phenomena. There is no convenient way to separate these two contributions to obtain real steady measurement.

![Diagram showing stress vs. time]

*Fig. 5-4 Combined Effect of Stress Overshoot and Shear Fracture to Time Dependent Stress for Sudden Start of Steady Shear Flow*

*Experimental investigations of apparent stress overshoot are not conclusive. Recently Walters et al. (98) have shown experimentally that stress overshoot actually exists as well as that significant shear fracture occurs in high shear flow.*
Therefore, the use of the capillary rheometer is essential for high shear rate viscosity measurement. We wish to emphasize that there is no warranty for the automatic extensions of rheological properties of samples with very high molecular weight and low concentration or observations with these samples to low molecular weight and high concentration solutions or low molecular weight polymer melts simply based on \( cM \) or \( c[n] \) values. There are few industrial polymer fabrication processes which use low concentration high molecular weight polymer solutions. The majority of the polymers have low to moderate molecular weight and are used in the form of melts or in high concentration solutions. To describe the rheology of these materials a wide range of \( c, M \) values must be covered as has been done here.

Two types of exceptions to the Cox-Merz rule were found from our experiments.

1. A1 (\( \bar{M}_w = 2,000,000, c = 0.30 \)) where \( cM \) is \( 6 \times 10^5 \) and \( |\eta^*| > \eta > \eta' \) at high shear rate. Osaki et al. [27] found similar abnormality in their sample of narrow distribution polystyrene solutions in diethylphthalate when \( cM \geq 6.6 \times 10^5 \).

2. C1 (\( \bar{M}_w = 110,000, c = 0.52 \)), C2 (\( \bar{M}_w = 110,000, c = 0.45 \)) and all but one (K1) of the broad distribution polystyrene solutions deviates from the Cox-Merz rule slightly.

\[ \eta > |\eta^*| > \eta \]

\( |\eta^*| \) is smaller than \( \eta \) by 20-50% at high shear rate/frequency. See
Fig. 5-3 for K2. Similar deviations were found by Harris for a narrow distribution polystyrene solution in PCB with $cM = 6 \times 10^4$ with high solvent viscosity (high M and low c) (11).

It is interesting to find that all the solutions of star branched polystyrene also show good agreement with the Cox-Merz rule although viscometric properties of star branched polystyrene solutions showed large experimental scattering.

In some cases, at very high shear rates, $|\eta^*(\omega)|$ starts to separate downwards from $\eta(\dot{\gamma})$ which is still a straight line of power law zone. Whereas $\eta(\dot{\gamma})$ has a straight line of the power law region over a few decades of shear rate while $|\eta^*(\omega)|$ is slightly S-shaped and $\eta'(\omega)$ is strongly S-Shaped. (See Fig. 5-2)

Although we found a few exceptions to the automatic application of the Cox-Merz rule, it is a good approximation for narrow distribution polystyrene solutions of both linear and star branched structure if $cM < 6 \times 10^5$. For these solutions errors in application of the Cox-Merz rule do not exceed experimental error.

For the analogy between elastic properties, $N_1/2$ is higher than $G'$ at high shear rates/frequencies whenever measurement is possible. The samples and ranges of shear rate of normal stress measurements were very limited because of shear fracture as mentioned before. Note that the effect of shear fracture would be to reduce the experimental value of $N_1$; thus, because shear fracture is present in our high shear rate experiments, the observed difference between $N_1/2$ and $G'$ (Figs. 5-1, 5-3) could be smaller than the true material behavior.
A rheometer with a slit die and very sensitive transducers should, in principle, be able to measure normal stress difference of these polymer solutions at very high shear rate without severe shear fracture. The measurements of normal stress difference with a slit die has been performed with molten commercial polymers (53). But the simple check of the analogy (at $\dot{\gamma} = \omega + \alpha$) in Table 1-2 of these data in the literature revealed that the accuracy of the measurements were not very good.

3. Study of the Rheological Analogy with Parameters of Linear Viscoelastic Functions and Viscometric Functions

A more quantitative way than graphical comparison to investigate the deviation from analogy is to use linear viscoelastic and non-Newtonian parameters. They are $\eta_0$ (zero shear rate viscosity), $\dot{\gamma}_0$ (critical shear rate), $\omega_0$ (critical frequency) and $d$ and $d'$ (power law slopes of $\eta(\dot{\gamma})$ and $\eta'(\omega)$). All of these parameters are determined by fitting experimental data with a modified Carreau equation. The deviation from the analogy can be expressed by the differences between these parameters.

There are two typical types of the deviation from the analogy of viscosities as shown in Fig. 5-5. The critical shear rates, $\dot{\gamma}_0$, is the shear rate at which steady shear viscosity starts decreasing from its zero shear rate value. Likewise the critical frequency, $\omega_0$, is the frequency at which dynamic viscosity starts decreasing from its zero frequency value. One way to get critical shear rate and critical
a) Horizontal Shift

b) Different Slope

Fig. 5-5 Two types of Deviations from the Exact Analogy between Dynamic Viscosity and Steady Shear Viscosity

\[ \frac{\omega_0}{\dot{\gamma}_0} = \frac{\omega_c}{\dot{\gamma}_c} \] (a) \[ \omega_c \neq \dot{\gamma}_c \] (b)

Fig. 5-6 Graphical Determination of Critical Shear Rate (\( \dot{\gamma}_0, \dot{\gamma}_c \)) and Critical Frequency (\( \omega_0, \omega_c \))

\( \dot{\gamma}_c \) and \( \omega_c \) based on zero shear viscosity while \( \dot{\gamma}_0 \) and \( \omega_0 \) based on power law slope
frequency is to take the $\dot{\gamma}$ value at which $\eta$ becomes 80% of zero shear rate viscosity value (11).

$$\eta(\dot{\gamma} = \dot{\gamma}_c) = 0.8\eta (\dot{\gamma} \to 0) \quad [5-3]$$

$$\eta'(\omega = \omega_c) = 0.8\eta (\omega \to 0) \quad [5-4]$$

where $\dot{\gamma}_c$ is critical shear rate based on the 0.8 criterion and $\omega_c$ is critical frequency similarly defined. Graessley said that the factor 0.8 had been used to obtain $\dot{\gamma}_c$ and $\omega_c$ from experimental data successfully. (P. 131 of 11)

However the use of the factor 0.8 to obtain $\dot{\gamma}_c$ and $\omega_c$ involves a systematic error of the type shown in Figure 5-6. If the critical shear rate, $\dot{\gamma}_0$, is equal to critical frequency, $\omega_0$, as shown in Figure 5-6b, $\dot{\gamma}_c$ and $\omega_c$ obtained cannot equal owing to the different slopes of the $\eta(\dot{\gamma})$ and $\eta'(\omega)$ curves.

If the Cox-Merz rule is exactly valid at around critical shear rate/frequency, in principle, one can obtain $\omega_c$ from complex viscosity

$$|\eta^* (\omega = \omega_c)| = 0.8|\eta^* (\omega \to 0)| \quad [5-5]$$

The value $\omega_c$ obtained from Equation 5-5 is free of error due to the
different slopes.

However, another problem for this method is the experimental scatter of $\eta$, $\eta'$ and $|\eta^*|$ which is significant at around the critical shear rate frequency.

Fig. 5-7 Total Shape of the Dynamic Viscosity Curve and Curve Fit by the Modified Carreau Viscosity Equation

$\eta_0$

slope = -d

Modified Carreau Equation

$\eta_\infty + \eta_s$

$\eta_\infty$ : infinite dynamic viscosity, $\eta_s$ : solvent viscosity
Rather than using such an arbitrary scheme, we used the Carreau viscosity equations modified to fit a broad change from zero shear viscosity to power law slope by introducing curve fitting parameters (a and a') which are equations 5-7 and 5-8 [we fit total shape of viscosity functions graphically on double logarithmic scale].

\[ \eta(\dot{\gamma}) = \eta_o \left(1 + (\lambda \dot{\gamma})^a\right) \frac{d}{\dot{a}} \]  
\[ \eta'(\omega) = \eta_o \left(1 + (\lambda' \omega)^{a'}\right) \frac{d}{\dot{a'}} \]  

[5-6]  
[5-7]

Relaxation time \( \lambda = 1/\gamma_o \)  
constants are, \( \lambda' = 1/\omega_o \)  
Carreau viscosity equation (7)

As \( \eta'(\omega) \) has a S-shape curve, only data up to maximum power law slope (max. \( \dot{\omega} \)) was fitted as shown in Fig. 5-7. It was not possible to get straight line power law slope by simply taking \( \eta' - (\eta'_\infty + \eta_s) \) instead of \( \eta' \) as both \( \eta'_\infty \) and \( \eta_s \) are much smaller than \( \eta' \) even at these high \( \omega \) (see later section).

* The Carreau equation fit of \( \eta' \) contains errors at high frequency behavior. As a result the linear viscoelastic spectrum is distorted at short times. Details are in Chapter 7. Here it is used to obtain particular parameters \( \dot{d}' \) and \( \omega_o \).

** If one uses \( \eta' - (\eta'_\infty + \eta_s) \) instead of \( \eta' \) and applies a least squares fit, \( \omega_o \) and \( \dot{d}' \) obtained are subject to significant errors. The details are given in Chapter 7.
Figure 5-8 shows the fit of $\eta(\dot{\gamma})$ of sample A2 with the modified Carreau equation [5-7]. If $a = 2$ as is the case for the original Carreau equation, a large error of about 20-30% exists at around $\dot{\gamma}_o$: critical shear rate. But if $a$ is taken as an adjustable parameter which is the case of equation 5-6, a good fit over the entire range of shear rate was obtained.

Figure 5-9 shows the fit of $\eta'(\omega)$ of sample C1 with equation 5-7. As explained earlier with Figure 5-7, at high frequency, actual $\eta'$ is larger than the value from equation 5-7. This large error at high frequency could be observed only for high concentration, low molecular weight samples.

Tables 5-3 and 5-4 list parameters for each sample solutions obtained through this curve fitting technique. We can start systematic and quantitative evaluation of the analogies using these parameters rather than using the entire curves. In addition, traditional correlation of these parameters to polymer structures such as $M_w$, $c$, $f$ (for star) will be studied in the next chapter.

1) Correlation between the critical shear rate $\dot{\gamma}_c$ and the critical frequency $\omega_0$

For the exact analogy $\dot{\gamma}_o = \omega_0$ whereas some constitutive equations predict $\dot{\gamma}_o = \omega_0 \cdot c$ with other parameters being the same. In this latter case, a horizontal shift of viscosity curve is the only factor accounting for the deviation from the analogy between $\eta(\dot{\gamma})$ and $\eta'(\omega)$.

Figure 5-11 shows plot of $1/\dot{\gamma}_o$ vs $1/\omega_0$ for all of sample solutions including linear and star branched polymers with narrow and broad
Fig. 5-8 Viscosity Curve Fitted by the Modified Carreau Equation Sample: A2

Fig. 5-9 Carreau Equation Fitting of Dynamic Viscosity Curve Sample: C1
molecular weight distribution. It is seen that \( \dot{\gamma}_0 = \omega_0 \) for most of the linear and star-branched polystyrene solutions with narrow molecular weight distribution for over four decades of time scale. Three samples have \( \dot{\gamma}_0 \) smaller than \( \omega_0 \). This is probably mostly due to experimental error because these solutions have extremely large critical shear rate and no power law slope data was available even from the capillary rheometer. We had to estimate \( \dot{\gamma}_0 \) only from the transition zone between power law zone and constant viscosity zone. It is not surprising such extent of errors are found in the estimate.

Commercial polystyrene with a broad molecular weight distribution \((\overline{M}_w/\overline{M}_n = 3.45)\) has \( \dot{\gamma}_0 \) larger than but proportional to \( \omega_0 \). On the average \( \dot{\gamma}_0 = 1.7 \omega_0 \) for Styron.

As a conclusion, the horizontal (\( \dot{\gamma} \) and \( \omega \)-axis) shift of \( \eta'(\omega) \) curve from \( \eta(\dot{\gamma}) \) curve appears not to be the basic phenomenon causing the deviation from the analogy between \( \eta \) and \( \eta' \). The shift of \( \dot{\gamma}_0 \) from \( \omega_0 \) is due to broad molecular weight distribution.

2) Correlation between power law slopes

For narrow distribution polymers, both linear and star-branched, the comparison between \( d \) and \( d' \) in Figure 5-12 shows that most of the data points are correlated by equation 5-8.

\[
d = d' + 0.259 \pm 0.053^* \tag{5-8}
\]

*Average and standard deviation assuming \( d \) vs \( d' \) has slope = 1.
Table 5-3(a)

Viscometric Parameters for Use in Modified Carreau Equation (Eq. 5-7) at 25° C (reference temperature)

<table>
<thead>
<tr>
<th>Sample #</th>
<th>$\bar{M}_w$</th>
<th>C$_g$/ml</th>
<th>$\eta_0$ Pa·s</th>
<th>$\dot{\gamma}_o$ (s$^{-1}$)</th>
<th>$\lambda$(s)</th>
<th>d</th>
<th>a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear and Narrow Distribution Polystyrene in 1-CN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A1</td>
<td>$2 \times 10^6$</td>
<td>0.30</td>
<td>73,000</td>
<td>$4.55 \times 10^{-2}$</td>
<td>22.0</td>
<td>0.861</td>
<td></td>
</tr>
<tr>
<td>A2</td>
<td>$2 \times 10^6$</td>
<td>0.15</td>
<td>1,400</td>
<td>$6.25 \times 10^{-1}$</td>
<td>1.60</td>
<td>0.800</td>
<td>1.25</td>
</tr>
<tr>
<td>A3</td>
<td>$2 \times 10^6$</td>
<td>0.088</td>
<td>90</td>
<td>2.64</td>
<td>$3.79 \times 10^{-1}$</td>
<td>0.735</td>
<td>0.98</td>
</tr>
<tr>
<td>B1</td>
<td>$3.9 \times 10^5$</td>
<td>0.45</td>
<td>8.080</td>
<td>$9.02 \times 10^{-1}$</td>
<td>1.109</td>
<td>0.696</td>
<td>2</td>
</tr>
<tr>
<td>B2</td>
<td>$3.9 \times 10^5$</td>
<td>0.30</td>
<td>135</td>
<td>27.7</td>
<td>$3.61 \times 10^{-2}$</td>
<td>0.695</td>
<td>2</td>
</tr>
<tr>
<td>C1</td>
<td>$1.1 \times 10^5$</td>
<td>0.52</td>
<td>1.180</td>
<td>10.8</td>
<td>$9.24 \times 10^{-2}$</td>
<td>0.559</td>
<td>2</td>
</tr>
<tr>
<td>C2</td>
<td>$1.1 \times 10^5$</td>
<td>0.45</td>
<td>166</td>
<td>57.8</td>
<td>$1.73 \times 10^{-2}$</td>
<td>0.462</td>
<td>2</td>
</tr>
<tr>
<td>D1</td>
<td>$3.7 \times 10^4$</td>
<td>0.62</td>
<td>3.930</td>
<td>10</td>
<td>$10^{-1}$</td>
<td>0.783</td>
<td>2*</td>
</tr>
<tr>
<td>D2</td>
<td>$3.7 \times 10^4$</td>
<td>0.45</td>
<td>15</td>
<td>$1.65 \times 10^3$</td>
<td>$6.06 \times 10^3$</td>
<td>2*</td>
<td></td>
</tr>
<tr>
<td>E1</td>
<td>$1.75 \times 10^4$</td>
<td>0.62</td>
<td>680</td>
<td>25.4</td>
<td>$3.93 \times 10^{-2}$</td>
<td>2*</td>
<td></td>
</tr>
<tr>
<td>E2</td>
<td>$1.75 \times 10^4$</td>
<td>0.45</td>
<td>4.03</td>
<td>$5 \times 10^3$</td>
<td>$2.0 \times 10^{-4}$</td>
<td>2*</td>
<td></td>
</tr>
<tr>
<td>Undiluted Linear Narrow Distribution Polystyrene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melt** 190°C</td>
<td>$1.1 \times 10^5$</td>
<td>1.06</td>
<td>2.33-2.5×10</td>
<td>$4.0-4.3 \times 10^{-2}$</td>
<td>0.82-0.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Star Branched Polystyrene in 1-CN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F1</td>
<td>HA31</td>
<td>0.45</td>
<td>1,850</td>
<td>3.72</td>
<td>$2.69 \times 10^{-1}$</td>
<td>0.676</td>
<td>2*</td>
</tr>
<tr>
<td>F2</td>
<td>HA31</td>
<td>0.30</td>
<td>33</td>
<td>97.1</td>
<td>$1.03 \times 10^{-2}$</td>
<td>0.639</td>
<td>1.53</td>
</tr>
<tr>
<td>Sample #</td>
<td>Cg/ml</td>
<td>η₀ ρ₀ S</td>
<td>˙γ₀ (s⁻¹)</td>
<td>λ(s)</td>
<td>d</td>
<td>a</td>
<td>g Mₘ</td>
</tr>
<tr>
<td>----------</td>
<td>-------</td>
<td>---------</td>
<td>-----------</td>
<td>------</td>
<td>---</td>
<td>---</td>
<td>-----</td>
</tr>
<tr>
<td>G1</td>
<td>0.45</td>
<td>1,050</td>
<td>11.3</td>
<td>8.86x10⁻²</td>
<td>0.668</td>
<td>2*</td>
<td>235,000</td>
</tr>
<tr>
<td>H1</td>
<td>0.45</td>
<td>67</td>
<td>1.15x10²</td>
<td>8.70x10⁻³</td>
<td>0.510</td>
<td>2*</td>
<td>70,800</td>
</tr>
<tr>
<td>J1</td>
<td>0.45</td>
<td>14</td>
<td>10³</td>
<td>10⁻³</td>
<td>0.447</td>
<td>2*</td>
<td>52,500</td>
</tr>
</tbody>
</table>

* estimate

** measured at ICI by Mr. Cogswell with a capillary rheometer
<table>
<thead>
<tr>
<th>Sample #</th>
<th>$\eta$ (cP)</th>
<th>$\omega_0$ (s^{-1})</th>
<th>$\lambda'$ (s)</th>
<th>$d'$</th>
<th>$a'$</th>
<th>$\bar{c}_w$</th>
<th>$c_{w}'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>132</td>
<td>3.51x10^{-2}</td>
<td>28.5</td>
<td>1.075</td>
<td>6x10^5</td>
<td>1.60x10^4</td>
<td></td>
</tr>
<tr>
<td>A2</td>
<td>66</td>
<td>4.20x10^{-1}</td>
<td>2.38</td>
<td>0.997</td>
<td>1.25</td>
<td>3</td>
<td>7.98x10^3</td>
</tr>
<tr>
<td>A3</td>
<td>34.7</td>
<td>2.56</td>
<td>0.391</td>
<td>0.930</td>
<td>0.997</td>
<td>1.76</td>
<td>4.68</td>
</tr>
<tr>
<td>B1</td>
<td>56.3</td>
<td>8.85x10^{-1}</td>
<td>1.13</td>
<td>1.018</td>
<td>1.91</td>
<td>1.76</td>
<td>7.02</td>
</tr>
<tr>
<td>B2</td>
<td>37.5</td>
<td>24.8</td>
<td>4.3x10^{-2}</td>
<td>0.973</td>
<td>2</td>
<td>1.17</td>
<td>4.68</td>
</tr>
<tr>
<td>C1</td>
<td>26</td>
<td>10.6</td>
<td>9.43x10^{-2}</td>
<td>0.826</td>
<td>2</td>
<td>5.72x10^4</td>
<td>3.14</td>
</tr>
<tr>
<td>C2</td>
<td>22.5</td>
<td>55.3</td>
<td>1.81x10^{-2}</td>
<td>0.813</td>
<td>2.5</td>
<td>4.95</td>
<td>2.72</td>
</tr>
<tr>
<td>D1</td>
<td>13.6</td>
<td>7.04</td>
<td>0.142</td>
<td>0.366</td>
<td>(2)</td>
<td>2.29</td>
<td>1.65</td>
</tr>
<tr>
<td>D2</td>
<td>9.9</td>
<td>2.22x10^3</td>
<td>4.50x10^{-4}</td>
<td></td>
<td></td>
<td>1.67</td>
<td>1.20</td>
</tr>
<tr>
<td>E1</td>
<td>9.9</td>
<td>1.98x10^2</td>
<td>5.05x10^{-3}</td>
<td>0.279</td>
<td></td>
<td>1.09</td>
<td>9.43x10^2</td>
</tr>
<tr>
<td>E2</td>
<td>7.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7.88x10^3</td>
<td>6.85</td>
</tr>
<tr>
<td>F1</td>
<td>44.0</td>
<td>4.51</td>
<td>0.222</td>
<td>0.939</td>
<td>2.7</td>
<td>1.22x10^5</td>
<td>5.36x10^3</td>
</tr>
<tr>
<td>F2</td>
<td>26.3</td>
<td>1.05x10^2</td>
<td>9.52x10^{-3}</td>
<td>0.848</td>
<td></td>
<td>8.15x10^4</td>
<td>3.57</td>
</tr>
<tr>
<td>G1</td>
<td>39.4</td>
<td>8.62</td>
<td>0.116</td>
<td>0.958</td>
<td></td>
<td>1.06x10^5</td>
<td>4.80</td>
</tr>
<tr>
<td>H1</td>
<td>15.9</td>
<td>2.34x10^2</td>
<td>4.27x10^{-3}</td>
<td>0.724</td>
<td></td>
<td>3.19x10^4</td>
<td>1.95</td>
</tr>
<tr>
<td>J1</td>
<td>12.7</td>
<td>2.06x10^3</td>
<td>4.85x10^{-4}</td>
<td>0.754</td>
<td></td>
<td>2.36x10^4</td>
<td>1.56</td>
</tr>
</tbody>
</table>

Table 5-3(b)
Linear Viscoelastic Parameters for Use in Modified Carreau Equation (at 25^o C)

$$c_{w}' = c_{g_{w}}(g_{w})^{0.75}$$
Table 5-4(a)

Viscometric Parameters for Use in Modified Carreau Equation (Eq. 5-7)

<table>
<thead>
<tr>
<th>#</th>
<th>Sample</th>
<th>$\bar{M}_w$</th>
<th>C_{g/ml}</th>
<th>$\eta_0$ Pa·s</th>
<th>$\dot{\gamma}_0$ (s^{-1})</th>
<th>$\lambda (s)$</th>
<th>d</th>
<th>a</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>Styron in 1-CN</td>
<td>369,000</td>
<td>0.473</td>
<td>4089</td>
<td>1.0</td>
<td>1.0</td>
<td>0.614</td>
<td>1.21</td>
</tr>
<tr>
<td>K2</td>
<td>(Mn = 107,000)</td>
<td></td>
<td>0.42</td>
<td>800</td>
<td>3.36</td>
<td>2.98 x 10^{-1}</td>
<td>0.602</td>
<td>1.01</td>
</tr>
<tr>
<td>K3</td>
<td></td>
<td></td>
<td>0.368</td>
<td>200</td>
<td>10.4</td>
<td>9.64 x 10^{-2}</td>
<td>0.586</td>
<td>1.23</td>
</tr>
<tr>
<td>K4</td>
<td></td>
<td></td>
<td>0.315</td>
<td>58</td>
<td>35.7</td>
<td>2.80 x 10^{-2}</td>
<td>0.550</td>
<td>0.90</td>
</tr>
<tr>
<td>K5</td>
<td>Styron in DMP</td>
<td></td>
<td>0.368</td>
<td>2400</td>
<td>6.41 x 10^{-1}</td>
<td>1.56</td>
<td>0.522</td>
<td></td>
</tr>
<tr>
<td>K6</td>
<td></td>
<td></td>
<td>0.263</td>
<td>88</td>
<td>12.7</td>
<td>7.85 x 10^{-2}</td>
<td>0.444</td>
<td></td>
</tr>
<tr>
<td>K7</td>
<td>Styron in DBP</td>
<td></td>
<td>0.315</td>
<td>410</td>
<td>2.60</td>
<td>3.84 x 10^{-1}</td>
<td>0.422</td>
<td>1.2</td>
</tr>
<tr>
<td>K8</td>
<td>Styron in KMC</td>
<td></td>
<td>0.315</td>
<td>375</td>
<td>2.07</td>
<td>4.83 x 10^{-1}</td>
<td>0.352</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 5-4(b)

Linear Viscoelastic Parameters for Use in Modified Carreau Equation (Eq. 5-8)

<table>
<thead>
<tr>
<th>#</th>
<th>Sample</th>
<th>$\bar{M}_w$</th>
<th>C_{g/ml}</th>
<th>$\omega_0$ (s^{-1})</th>
<th>$\lambda'(s)$</th>
<th>d'</th>
<th>a'</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>Styron in 1-CN</td>
<td>369,000</td>
<td>0.473</td>
<td>0.752</td>
<td>1.329</td>
<td>0.75</td>
<td>0.90</td>
</tr>
<tr>
<td>K2</td>
<td></td>
<td></td>
<td>0.42</td>
<td>1.94</td>
<td>0.515</td>
<td>0.71</td>
<td>1.12</td>
</tr>
<tr>
<td>K3</td>
<td></td>
<td></td>
<td>0.368</td>
<td>7.30</td>
<td>0.137</td>
<td>0.72</td>
<td>1.14</td>
</tr>
<tr>
<td>K4</td>
<td></td>
<td></td>
<td>0.315</td>
<td>17.5</td>
<td>5.73 x 10^{-2}</td>
<td>0.68</td>
<td>1.16</td>
</tr>
<tr>
<td>K5</td>
<td>Styron in DMP</td>
<td></td>
<td>0.368</td>
<td></td>
<td></td>
<td>0.69</td>
<td></td>
</tr>
<tr>
<td>K6</td>
<td></td>
<td></td>
<td>0.263</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K7</td>
<td>Styron in DBP</td>
<td></td>
<td>0.315</td>
<td>2.5</td>
<td>0.400</td>
<td>0.67</td>
<td>1.00</td>
</tr>
<tr>
<td>K8</td>
<td>Styron in KMC</td>
<td></td>
<td>0.315</td>
<td>3.15</td>
<td>0.317</td>
<td>0.70</td>
<td>1.16</td>
</tr>
<tr>
<td></td>
<td>Styron Melt at 200° C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.88</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 5-10  The Correlation between Critical Shear Rate and Critical Frequency of Polystyrene Solutions
Fig. 5-11 The Correlation between Power Law Slopes of Dynamic Viscosity and Steady Shear Viscosity of Narrow Distribution Polystyrene Solutions
For broad distribution polystyrene similar relationship was obtained in Figure 5-13 for solutions in a good solvent (1-CN) and undiluted polymer.

\[ d = d' - 0.127 \pm 0.013^* \]  

[5-9]

This relationship is significantly different from that of narrow distribution polymers of equation 5-8. The correlation of 5-9 does not apply to solutions in solvents other than 1-CN which is a good and moderately polar solvent. Other solvents are non-polar and poor solvent KMC-A and polar and poor solvent DBP and DMP. The correlation for the solutions of these solvents may be expressed as follows. But not enough data points were taken to provide information in these equations.

\[ d = d' - 0.35 \quad \text{KMC} \]
\[ d = d' - 0.17 \quad \text{DMP} \]
\[ d = d' - 0.25 \quad \text{pBP} \]

The result of the above comparison can be summarized as follows: For narrow distribution polystyrene solutions, the deviation from the analogy between \( n \) and \( n' \) appears in the form of different power law slope with same critical shear rate/frequency.

*Average and standard deviation assuming \( d \) vs \( d' \) has slope = 1.*
Fig. 5-12 The Correlation between Power Law Slopes of Dynamic Viscosity and Steady Shear Viscosity of Broad Distribution Polystyrene Solutions
Only for samples with broad molecular weight distribution is the critical shear rate different from and larger than the critical frequency.

If one has total shape of dynamic viscosity vs frequency curve, which now can be obtained in a very short time with an automated instrument, one can estimate steady shear viscosity from three parameters \((\eta_0', \lambda', d')\)

\[
\eta' = \eta_0 \left(1 + (\lambda' \omega)^2\right)^{\frac{d'}{2}} \quad [5-10]
\]

\[
\eta = \eta_0 \left(1 + (\lambda' \dot{\gamma})^2\right)^{\frac{d}{2}} \quad [5-11]
\]

\[
d = d' - 0.259 + 0.05 \quad [5-8]
\]

This is a good approximation at least for our polystyrene solutions, better than the Cox-Merz model. Equation 5-11 gives better approximation than the Cox-Merz at high shear rate and at around critical shear rate where the Cox-Merz rule fails to be exact as mentioned earlier.

Then for broad distribution a slight modification is necessary.

\[
\eta' = \eta_0 \left[1 + (\lambda' \omega)^a\right] \frac{d'}{a} \quad [5-12]
\]

\[
\eta = \eta_0 \left[1 + \left(\frac{\lambda' \dot{\gamma}}{1.7}\right)^a\right] \frac{d' - 0.13}{a} \quad [5-13]
\]
Equation 5-12 and 5-13 are good for our particular samples of commercial polystyrene (Styron) in good solvents or melts.

For narrow distribution polystyrene polymers for broad distribution as shown in equations 5-12 and 5-13 a is close to 2, same as the original Carreau viscosity equation.

The measurement of normal stress difference at high shear rate was very difficult. For a few samples with which measurements were possible, data were fitted graphically by the Carreau-type equations, equations 5-14 and 5-16 as shown in Figure 5-14. G' or $2G'/\omega^2$ was also fitted by Equation 5-15.

![Carreau Equation-type Fitting of Elasticity Functions](image)

\[ \psi_1 = \psi_1^0 \left(1 + \left(\lambda_e Y\right)^b\right)^{m-2} \frac{b}{m-2} \]  

[5-14]
\[ G' = 2 \cdot \omega^2 \cdot \psi_1^0 \left(1 + (\lambda_e \omega)^b_1 \right) \frac{m'-2}{b_1} \]  
\[ N_1 = 2 \cdot \psi_1^0 \cdot \dot{\gamma}^2 \left(1 + (\lambda_e \dot{\gamma})^b \right) \frac{m-2}{b} \]  
\[ \lambda_e = 1/\gamma_e \quad \lambda_e' = 1/\omega_e \]

\( \dot{\gamma}_e \): critical shear rate for \( \psi_1(\dot{\gamma}) \)

\( \omega_e \): critical frequency for \( G'(\omega) \)

\( \lambda_e \): time constant of elastic properties

\( \lambda_e' \): time constant of elastic properties

As shown in Figure 5-15 \( \dot{\gamma}_e \): critical shear rate of \( \psi_1 \) or \( N_1 \) is close to \( \dot{\gamma}_e \): critical shear rate of \( \eta \). Similarly \( \omega_e \): critical frequency of \( G'(\eta) \) is close to \( \omega_0 \): critical frequency of \( \eta' \) (or \( G'' \)). All four critical shear rate/frequency parameters are within factor of 2 for narrow distribution polystyrene. Compared to the accuracy of measurement, it is possible \( \dot{\gamma}_0, \dot{\gamma}_e, \omega_0 \) and \( \omega_e \) are equal for a polystyrene solution with narrow molecular weight distribution.

Figure 5-17 shows the correlation between \( m \): power law slope of \( N_1/2 \) vs \( m' \): power law slope of \( G' \). The slope \( m \) increases as \( m' \) increases.

Figure 5-18 shows the correlation between \( m \) vs \( d \): power law slope of \( \eta \). The slope \( m \) decreases as \( d \) increases. Broad distribution polystyrene has somewhat larger \( m \) than narrow distribution polystyrene.
Fig. 5-14 Correlation between Critical Shear Rates $\gamma_\varepsilon$ (from $\Psi_1$) and $\gamma_\alpha$ (from $\Psi$)

Fig. 5-15 Correlation between Critical Frequencies $\Omega_\varepsilon$ (from $G'$) and $\omega_\alpha$ (from $\eta_\alpha'$)
Fig. 5-17 Correlation between Power Law parameters of \( n \) and \( m \).
These correlations between m, m', and d seem significant and interesting. But it should be noted that m, and γ e contain certain amount of errors. Therefore, further discussion is not appropriate until more accurate high shear rate data of N₁ become available.

Also, curve fitting of G' at plateau zone with a straight line power law zone is an approximation and not 100% quantitative. m' for some of the sample solutions (B1 in Figure A2-8, for example) are even negative.

As a summary, for the "elastic" analogy, the best approach for estimating the normal stress difference from linear viscoelastic data of G' is use of Equations 5-14 and 5-15 with parameters λ e = λ 'e b = b' and m = m' + x (x ≈ 0.4 in Figure 5-16). Whereas for the "viscous" analogy, Equations 5-17 ~ 5-13 provide a more quantitative means for estimating n from n' data.
CHAPTER VI. EFFECT OF POLYMER STRUCTURE
AND CONCENTRATION ON THE LINEAR VISCOELASTIC
AND NON-NEWTONIAN PROPERTIES

Effect of concentration, molecular weight, and star-branching
to the rheological parameters obtained in Chapter V is studied in
this chapter. The parameters considered are as follows:

Viscosity Parameters

- critical shear rate, \( \dot{\gamma}_0 \), critical frequency, \( \omega_0 \), power law
- slope of \( n, d \), power law slope of \( n', d' \). (\( \eta_0 \) already studied
  in Chapter IV)

Elasticity Parameters

- zero shear rate limiting values of \( \psi_1 \) and \( 2G'/\omega^2 \), \( \psi_1^0 \), \( (\frac{2G'}{\omega^2})_0 \)

Not enough data are available to justify conclusion regarding
critical shear rate of \( \psi_1, \dot{\gamma}_e \), critical frequency for \( G', \omega_e \), and
power law slopes of \( \psi_1 \) and \( G' \), \( m \) and \( m' \).

1. Concentration and molecular weight dependence of the critical
shear rate \( \dot{\gamma}_0 \) and the critical frequency \( \omega_0 \)

The following equation was derived by Graessly from the modified
Rouse theory (P. 545 of ref. 5)
\[
\frac{1}{\tau \eta} = \frac{Ac}{\eta_0 M} + \frac{Bc^2}{\eta_0} \tag{6-1}
\]

where \( A = \frac{\pi^2 RT}{G} \)

\( B = \frac{A}{\rho^2 M_c} \)

\( \tau \eta \approx 1/y_0 \)

\( \rho_2 = \text{density of solute (polymer)} \)

\( M_c = \text{critical molecular weight for effect of "chain-chain interaction" of } \eta_0. \)

Therefore, \( \dot{y}_0 \), can be described as in equation 6-2

\[
\dot{y}_0 \approx \frac{\pi^2 RT}{6} \left( \frac{c}{\eta_0 M} + \frac{c^2}{\rho_2 \eta_0 M_c} \right) \tag{6-2}
\]

Applicability of equation 6-2 will be tested as following. Equation 6-2 can be derived into two asymptotic forms shown in equation 6-3 and equation 6-8 which appears later in this section. When \( c M \) is smaller than \( M_c \), equation 6-2 may be simplified into equation 6-3.

\[
\dot{y}_0 \approx \frac{\pi^2 RT C}{6 \eta_0 M} \tag{6-3}
\]

Applicability of equation 6-3 may be checked by the use of reduced variable \( \beta_0 \) which is defined in equation 6-4. The reduced critical shear rate: \( \beta_0 \) is derived from equation 6-3.

\[
\beta_0 = \dot{y}_0 \frac{\eta_0 M}{CRT} \tag{6-4}
\]
If equation 6-3 is applicable or the modified Rouse theory is good at low values of cM, \( \beta_0 \) is expected to have a constant value which is in the order of \( \Pi^2/6 \). Similarly for dynamic viscosity, \( \eta'(\omega) \)

\[
\beta_0' = \omega_0 \frac{\eta_0 M}{CRT} \tag{6-5}
\]

In general, reduced shear rate: \( \beta \) and reduced frequency: \( \beta' \) as shown in equation 6-6 and equation 6-7 can be used to obtain master curves of \( \eta(\dot{\gamma}) \) and \( \eta'(\omega) \) from data with different molecular weight \( (\bar{M}_w)^* \) and concentration if such master curves exist.

\[
\beta = \frac{\eta_0 M}{CRT} \cdot \dot{\gamma} \tag{6-6}
\]

\[
\beta' = \frac{\eta_0 M}{CRT} \cdot \omega \tag{6-7}
\]

Tables 6-1, 6-2 list \( \beta_0 \) and \( \beta_0' \) computed from our data with equation 6-4 and equation 6-5. Figure 6-1 shows the plot of \( \beta_0 \) vs \( c\bar{M}_w \) and figure 6-2 shows the plot of \( \beta_0' \) vs \( c\bar{M}_w \). Note that \( g \cdot \bar{M}_w \) is used for star-branched polymers instead of \( \bar{M}_w \) which indicates that relaxation time is correlated to size corrected by \( g \) rather than \( \bar{M}_w \). \( g \): size correction factor for branching

*For narrow molecular weight distribution polymers, all average molecular weights are close to each other. \( \bar{M}_w \) is used instead of \( M \).
Table 6-1
Parameters of Elastic Properties from Viscometric Properties

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\dot{\gamma}_0 \eta_0 J_e^o$</th>
<th>$\beta_0$</th>
<th>$\psi_1^o$ (Pa·s²)</th>
<th>$J_e^o$ (Pa⁻¹)</th>
<th>$J_e^R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>1.56</td>
<td>8.94</td>
<td>5 x 10⁶</td>
<td>4.59 x 10⁻⁴</td>
<td>1.74 x 10⁻¹</td>
</tr>
<tr>
<td>A2</td>
<td>1.57</td>
<td>4.83</td>
<td>7 x 10³</td>
<td>1.79 x 10⁻³</td>
<td>3.33 x 10⁻¹</td>
</tr>
<tr>
<td>A3</td>
<td>1.76</td>
<td>2.18</td>
<td>1.2 x 10²</td>
<td>7.41 x 10⁻³</td>
<td>8.09 x 10⁻¹</td>
</tr>
<tr>
<td>B1</td>
<td>0.667</td>
<td>2.55</td>
<td>9.2 x 10³</td>
<td>9.15 x 10⁻⁵</td>
<td>2.62 x 10⁻¹</td>
</tr>
<tr>
<td>B2</td>
<td>0.789</td>
<td>1.96</td>
<td>7.7</td>
<td>2.11 x 10⁻⁴</td>
<td>4.03 x 10⁻¹</td>
</tr>
<tr>
<td>C1</td>
<td>0.303</td>
<td>1.09</td>
<td>1.1 x 10²</td>
<td>3.95 x 10⁻⁵</td>
<td>4.63 x 10⁻¹</td>
</tr>
<tr>
<td>C2</td>
<td>0.609</td>
<td>0.95</td>
<td>3.5</td>
<td>6.35 x 10⁻⁵</td>
<td>6.44 x 10⁻¹</td>
</tr>
<tr>
<td>D1</td>
<td>0.444</td>
<td>0.95</td>
<td>3.5 x 10²</td>
<td>1.13 x 10⁻⁵</td>
<td>4.70 x 10⁻¹</td>
</tr>
<tr>
<td>D2</td>
<td>0.257</td>
<td>0.823</td>
<td>7.5 x 10⁻³</td>
<td>1.04 x 10⁻⁵</td>
<td>3.14 x 10⁻¹</td>
</tr>
<tr>
<td>E1</td>
<td>0.216</td>
<td>0.20</td>
<td>25</td>
<td>1.25 x 10⁻⁵</td>
<td>1.10 x 10⁰</td>
</tr>
<tr>
<td>E2</td>
<td>0.147</td>
<td>0.32</td>
<td>2 x 10⁻²</td>
<td>7.30 x 10⁻⁶</td>
<td>4.66 x 10⁻¹</td>
</tr>
<tr>
<td>F1</td>
<td>0.695</td>
<td>1.68</td>
<td>6.3 x 10²</td>
<td>1.31 x 10⁻⁴</td>
<td>6.50 x 10⁻¹</td>
</tr>
<tr>
<td>F2</td>
<td>0.420</td>
<td>1.17</td>
<td>4.2 x 10⁻¹</td>
<td>1.31 x 10⁻⁴</td>
<td>5.62 x 10⁻¹</td>
</tr>
<tr>
<td>G1</td>
<td>1.31</td>
<td>1.27</td>
<td>2.2 x 10²</td>
<td>1.10 x 10⁻⁴</td>
<td>8.03 x 10⁻¹</td>
</tr>
<tr>
<td>H1</td>
<td>0.292</td>
<td>0.66</td>
<td>3.4 x 10⁻¹</td>
<td>3.79 x 10⁻⁵</td>
<td>9.05 x 10⁻¹</td>
</tr>
<tr>
<td>J1</td>
<td>0.375</td>
<td>0.49</td>
<td>1.05 x 10⁻²</td>
<td>2.68 x 10⁻¹</td>
<td>8.95 x 10⁻¹</td>
</tr>
<tr>
<td>K1</td>
<td></td>
<td></td>
<td>3 x 10⁴</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K2</td>
<td>9.54 x 10⁻¹</td>
<td>886</td>
<td>6.92 x 10⁻⁴</td>
<td>1.953</td>
<td></td>
</tr>
<tr>
<td>K3</td>
<td>8.43 x 10⁻¹</td>
<td>32.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K4</td>
<td>9.80 x 10⁻¹</td>
<td>4.3</td>
<td>6.39 x 10⁻⁴</td>
<td>1.353</td>
<td></td>
</tr>
<tr>
<td>K5</td>
<td>6.23 x 10⁻¹</td>
<td>3.6 x 10³</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K6</td>
<td>6.33 x 10⁻¹</td>
<td>14.2</td>
<td>9.17 x 10⁻⁴</td>
<td>1.621</td>
<td></td>
</tr>
<tr>
<td>K7</td>
<td>5.04 x 10⁻¹</td>
<td>380</td>
<td>1.13 x 10⁻³</td>
<td>2.392</td>
<td></td>
</tr>
<tr>
<td>K8</td>
<td>3.67 x 10⁻¹</td>
<td>290</td>
<td>1.03 x 10⁻³</td>
<td>2.181</td>
<td></td>
</tr>
</tbody>
</table>

*See Table 2-3 for description*
Table 6-2
Parameters of Elastic Properties from Linear Viscoelastic Properties

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\beta_0$</th>
<th>$\frac{2G'}{\omega^2}$ (Pa·s²)</th>
<th>$J_e^0$ (Pa⁻¹)</th>
<th>$J_e^R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>6.90</td>
<td>1.32x10^2</td>
<td>8.15x10⁻³</td>
<td>8.91x10⁻¹</td>
</tr>
<tr>
<td>A2</td>
<td>3.17</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A3</td>
<td>2.12</td>
<td>1.32x10^2</td>
<td>8.15x10⁻³</td>
<td>8.91x10⁻¹</td>
</tr>
<tr>
<td>B1</td>
<td>2.50</td>
<td>8.7x10³</td>
<td>8.65x10⁻⁵</td>
<td>2.48x10⁻¹</td>
</tr>
<tr>
<td>B2</td>
<td>1.76</td>
<td>5.1</td>
<td>1.40x10⁻⁴</td>
<td>2.68x10⁻¹</td>
</tr>
<tr>
<td>C1</td>
<td>1.07</td>
<td>1.05x10²</td>
<td>3.77x10⁻⁵</td>
<td>4.41x10⁻¹</td>
</tr>
<tr>
<td>C2</td>
<td>0.907</td>
<td>2.2</td>
<td>1.00x10⁻⁵</td>
<td>4.07x10⁻¹</td>
</tr>
<tr>
<td>D1</td>
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<td>5x10²</td>
<td>1.62x10⁻⁵</td>
<td>6.72x10⁻¹</td>
</tr>
<tr>
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<td>7.5x10⁻³</td>
<td>1.04x10⁻⁵</td>
<td>3.12x10⁻¹</td>
</tr>
<tr>
<td>E1</td>
<td>1.54</td>
<td>10</td>
<td>5.0x10⁻⁶</td>
<td>4.39x10⁻¹</td>
</tr>
<tr>
<td>E2</td>
<td></td>
<td>2.6x10⁻³</td>
<td>9.5x10⁻⁷</td>
<td>6.06x10⁻²</td>
</tr>
<tr>
<td>F1</td>
<td>2.03</td>
<td>4.3x10²</td>
<td>1.37x10⁻⁴</td>
<td>8.84x10⁻²</td>
</tr>
<tr>
<td>F2</td>
<td>1.27</td>
<td>4.6x10⁻¹</td>
<td>1.25x10⁻⁴</td>
<td>5.37x10⁻²</td>
</tr>
<tr>
<td>G1</td>
<td>1.91</td>
<td>1.7x10²</td>
<td>8.5x10⁻⁵</td>
<td>6.22x10⁻²</td>
</tr>
<tr>
<td>H1</td>
<td>0.997</td>
<td>2.4x10⁻¹</td>
<td>2.67x10⁻⁵</td>
<td>6.38x10⁻²</td>
</tr>
<tr>
<td>J1</td>
<td>1.36</td>
<td>4.0x10⁻³</td>
<td>9.69x10⁻⁶</td>
<td>3.23x10⁻²</td>
</tr>
<tr>
<td>K1</td>
<td>9.69x10⁻¹</td>
<td>&gt;10⁴</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K2</td>
<td>6.89x10⁻¹</td>
<td>834</td>
<td>6.52x10⁻⁴</td>
<td>1.840</td>
</tr>
<tr>
<td>K3</td>
<td>5.91x10⁻¹</td>
<td>63.5</td>
<td>7.94x10⁻⁴</td>
<td></td>
</tr>
<tr>
<td>K4</td>
<td>4.80x10⁻¹</td>
<td>6.5</td>
<td>9.66x10⁻⁴</td>
<td>2.045</td>
</tr>
<tr>
<td>K7</td>
<td>4.85x10⁻¹</td>
<td>316</td>
<td>9.40x10⁻⁴</td>
<td>1.990</td>
</tr>
<tr>
<td>K8</td>
<td>5.59x10⁻¹</td>
<td>320</td>
<td>1.14x10⁻³</td>
<td>2.413</td>
</tr>
</tbody>
</table>

* for description see Table 2-3
Table 6-3

Reduced Critical Shear Rates $\dot{\gamma}_o^R$ and $\omega_o^R$

<table>
<thead>
<tr>
<th>Sample #</th>
<th>$\dot{\gamma}_o^R$</th>
<th>$\omega_o^R$</th>
<th>$\bar{cM}_w^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.605</td>
<td>0.467</td>
<td>$6 \times 10^5$</td>
</tr>
<tr>
<td>A2</td>
<td>0.638</td>
<td>0.429</td>
<td>3</td>
</tr>
<tr>
<td>A3</td>
<td>0.503</td>
<td>0.488</td>
<td>1.76</td>
</tr>
<tr>
<td>B1</td>
<td>0.590</td>
<td>0.579</td>
<td>1.76</td>
</tr>
<tr>
<td>B2</td>
<td>0.681</td>
<td>0.610</td>
<td>1.17</td>
</tr>
<tr>
<td>C1</td>
<td>0.773</td>
<td>0.759</td>
<td>$5.72 \times 10^4$</td>
</tr>
<tr>
<td>C2</td>
<td>0.777</td>
<td>0.743</td>
<td>4.95</td>
</tr>
<tr>
<td>D1</td>
<td>1.68</td>
<td>1.18</td>
<td>2.29</td>
</tr>
<tr>
<td>D2</td>
<td>2.00</td>
<td>2.70</td>
<td>1.69</td>
</tr>
<tr>
<td>E1</td>
<td>0.737</td>
<td>5.74</td>
<td>1.09</td>
</tr>
<tr>
<td>E2</td>
<td>1.63</td>
<td></td>
<td>$7.88 \times 10^3$</td>
</tr>
<tr>
<td>F1</td>
<td>0.557</td>
<td>0.678</td>
<td>$1.22 \times 10^5$</td>
</tr>
<tr>
<td>F2</td>
<td>0.584</td>
<td>0.631</td>
<td>$8.15 \times 10^4$</td>
</tr>
<tr>
<td>G1</td>
<td>0.961</td>
<td>0.733</td>
<td>$1.06 \times 10^5$</td>
</tr>
<tr>
<td>H1</td>
<td>0.624</td>
<td>1.27</td>
<td>$3.10 \times 10^4$</td>
</tr>
<tr>
<td>J1</td>
<td>1.13</td>
<td>2.34</td>
<td>$2.36 \times 10^4$</td>
</tr>
<tr>
<td>K1</td>
<td>0.300</td>
<td>0.225</td>
<td>$1.75 \times 10^5$</td>
</tr>
<tr>
<td>K2</td>
<td>0.250</td>
<td>0.144</td>
<td>1.55</td>
</tr>
<tr>
<td>K3</td>
<td>0.252</td>
<td>0.177</td>
<td>1.36</td>
</tr>
<tr>
<td>K4</td>
<td>0.342</td>
<td>0.168</td>
<td>1.16</td>
</tr>
</tbody>
</table>
In chapter V, it was shown that $\dot{\gamma}_0 = \omega_0$ for narrow distribution polystyrene solutions. From the comparison between Figure 6-1 and Figure 6-2, similar conclusion was obtained.

$$\beta_0 = \beta_0' \text{ for all values of } c\bar{M}_w$$

for broad distribution polystyrene solution,

$$\beta_0 > \beta_0'$$

In the region $c\bar{M}_w < 10^{4.5}$ the plot of $\beta_0$ vs $c\bar{M}_w$ is scattered due to experimental error and we could not check the applicability of equation 6-3. But the plot of $\beta_0'$ vs $c\bar{M}_w$ shows $\beta_0'$ has a constant value (~1) as expected from the modified Rouse theory.

In the region $c\bar{M}_w > 10^{4.5}$ both $\beta_0$ and $\beta_0'$ increase in the double logarithmic scale at a slope close to 1 up to the highest $c\bar{M}_w$ of our sample solutions.

Previous knowledge of $\bar{M}_w$ dependence of $\beta_0$ and $\beta_0'$ is consistent with this observation (P. 134 of ref. 11).

If $cM > M_c$, then in equation 6-2, $c/\eta_0M$ becomes negligible compared to $c^2/\rho^2\eta_0M_c$ and equation 6-2 may be simplified into equation 6-8.

$$\dot{\gamma}_0 = \frac{\pi^2}{6} \left( \frac{RT}{\rho_2M_c} \right) \frac{c^2}{\eta_0} \quad \text{[6-2]} \quad \text{(*)}$$

$M_c$, the critical molecular weight is 38,000 from literature (P. 409 of ref. 5) and equation 6-9 leads $\dot{\gamma}_0^R = \dot{\gamma}_0 \frac{\eta_0}{c^2} x 1.64 x 10^{-5}$
\[ \dot{\gamma}_o^R = \dot{\gamma}_o \left( \frac{\rho S M_c}{RT} \right) \left( \frac{n_o}{c^2} \right) \]  \[ 6-9 \]

\[ \omega_o^R = \omega_o \left( \frac{\rho S M_c}{RT} \right) \left( \frac{n_o}{c^2} \right) \]  \[ 6-10 \]

If equation 6-8 is applicable both \( \dot{\gamma}_o^R \) and \( \omega_o^R \) are expected to have a constant value \( \pi^2/6 \) at large \( cM \).

\( \dot{\gamma}_o^R \) and \( \omega_o^R \) computed from our sample solutions are listed in Table 6-3. Figure 6-3 shows the plot of \( \dot{\gamma}_o^R \) vs \( cM_W \) (or \( cgM_W \)) while Figure 6-4 shows the plot of \( \omega_o^R \) vs \( cM_W \) (or \( cgM_W \)). Both \( \dot{\gamma}_o^R \) and \( \omega_o^R \) have constant value (\( \approx 0.6 \)) in the range of \( cM > M_c \) as expected from equation 6-8.

In all four plots shown in Figure 6-1 – Figure 6-4, star-branching had no effect on critical shear rate or critical frequency if molecular size is corrected by the size correction factor, \( g \). Therefore, the effect of star-branching on critical shear rate/frequency in the concentrated solutions is the same as in the dilute solutions in which \( g \) is known to be applicable (see Chapter 1, section 3-d).

From the above observation universal set of reduced critical shear rate and critical frequency can be in the form of equation 6-11 and equation 6-12. Although no examination was performed at around \( cM \sim M_c \)

\[ \text{Reduced } \dot{\gamma}_o = \frac{\dot{\gamma}_o}{RT} \left( \frac{c}{n_o M} + \frac{c^2}{\rho^2 n_o M c} \right) \]  \[ 6-11 \]

\[ \text{Reduced } \omega = \frac{\omega}{RT} \left( \frac{c}{n_o M} + \frac{c^2}{\rho^2 n_o M c} \right) \]  \[ 6-12 \]
However even with the use of these reduced variables, it is not possible to get a "super-master curve" including concentration and molecular weight as well as time-temperature superposition because power law slopes also depend on concentration and molecular weight.

2. Concentration and molecular weight dependence of power law slopes: d and d'

It is well known that power law slope of $\eta(\dot{\gamma})$ depends on concentration and molecular weight of polymer solutions (see Figure 4-42). Ashare has proposed an empirical correlation for narrow distribution linear polystyrene in Arochloc

$$\alpha_1 = 1 + 15 c \log (M/120,000) \quad [6-13]$$

where power law slope: $d = (1-\alpha_1)/\alpha_1 \quad [6-14]$  

It also has been shown that the power law slope parameter, d, can be correlated to $c[\eta]$, the coil overlap parameter (P. 132 of ref. 11).

As has been shown in chapter 5, d and d' are closely related. Here we examine both d vs $c[\eta]$ and d' vs $c[\eta]^*$ correlations. Figure 6-5 shows the plot of d vs $c[\eta]$; Figure 6-7 shows the plot of d' vs $c[\eta]$; and Figure 6-76 shows the plot of d vs log ($c[\eta]$). In the

*The value of [\eta] in 1-CN appears in Table 2-1.
Fig. 6.5 The Correlation of Power Law Slope to the Coll Overlap Parameter $\alpha$ (T)

Fig. 6.6 The Correlation of Power Law Slope of $\tau$ to the Coll Overlap Parameter on Semi-Logarithmic scale
Fig. 6-7 The Correlation of Power Law Slope of \( L \) to the Coin Overlap Parameter \( c(\eta) \)
Table 6-4

Power Law Slope Parameters of Polystyrene *

Solutions in Aroclor by Ashare (99)

<table>
<thead>
<tr>
<th>(c_{g/ml})</th>
<th>(\bar{M}_w)</th>
<th>(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0856</td>
<td>1,800,000</td>
<td>0.56</td>
</tr>
<tr>
<td>0.0331</td>
<td>1,800,000</td>
<td>0.38</td>
</tr>
<tr>
<td>0.0133</td>
<td>1,800,000</td>
<td>0.29</td>
</tr>
<tr>
<td>0.0976</td>
<td>860,000</td>
<td>0.67</td>
</tr>
<tr>
<td>0.0656</td>
<td>860,000</td>
<td>0.47</td>
</tr>
<tr>
<td>0.0331</td>
<td>860,000</td>
<td>0.37</td>
</tr>
<tr>
<td>0.0976</td>
<td>411,000</td>
<td>0.44</td>
</tr>
<tr>
<td>0.0656</td>
<td>411,000</td>
<td>0.38</td>
</tr>
</tbody>
</table>

*Linear and narrow molecular weight distribution*
plot of $d$ vs $c[\eta]$ Ashare's data of narrow distribution polystyrene solutions in Aroclor (Table 6-4) were used to supplement moderate $c[\eta]$ zone along with our data of highly concentrated solutions (Table 6-3).

As shown in Figure 6-5 the plot of $d$ vs $c[\eta]$ shows a good correlation over the entire range of $c[\eta]$ although there is some scatter. No effect of star-branching is observed as molecular size is corrected by $g$ for $[\eta]$.

According to Graessley's deviation of molecular theory, the limiting value of power law slope at high $c[\eta]$ is

$$d = \frac{9}{11} = 0.8181$$

and according to the modified version of Graessley's theory (P. 546 of 2) $d = 1.0$.

As the range of $c[\eta]$ we could cover was only from 4 to 100, we are not sure if some constant value had already been reached or not from Figure 6-5 and 6-6. However from Figure 6-6 it appears that $d$ has not approached a limiting value even at $c[\eta] = 100$ and that values of $d$ in excess of 0.82 are quite possible. Physical limit of $d$ is 1 because shear stress must not decrease with increasing shear rate for a steady shear flow.

There is also a good correlation between log $d'$ and $c[\eta]$ as shown in Figure 6-7. It is found that $d'$ approaches its limiting value faster than $d$ with increasing $c[\eta]$.
3. Concentration and molecular weight dependence of the steady state shear compliance

The steady state shear compliance \( J_e^o \) can be computed either from linear viscoelastic properties or from steady shear properties.

\[
J_e^o = \frac{\psi_1^0}{2 \cdot \eta_0} \quad [6-15]
\]

\[
J_e^o = \frac{G'}{\omega^2 \cdot \eta_0} \quad [6-16]
\]

\( J_e^o \) is used rather than \( \psi_1^0 \) because it has more convenient relationship to theoretical models as will be shown in this section.

From the Rouse theory the following relationship has been obtained (11)(68).

\[
J_e^o = \frac{2M}{cRT} \quad [6-17]
\]

From equation 6-17, reduced steady shear compliance, \( J_e^R \), was defined for linear polymer.

\[
J_e^R = J_e^o \cdot \frac{cRT}{M} \quad [6-18]
\]

For star-branched polymers, with the Rouse theory as extended by Han (11),

\[
J_e^o = \frac{2}{3} \cdot g_2 \frac{M}{cRT} \quad [6-19]
\]
\[ g_2 = \frac{15f-14}{(3f-2)^2} \]  \[ \text{[6-20]} \]

Reduced steady shear complaince for star-branched polymer is

\[ J_e^R = J_e^0 \cdot \frac{cRT}{M} \cdot \frac{1}{g^2} \]  \[ \text{[6-21]} \]

It has been observed that equation 6-17 and equation 6-19 fit data from infinite dilution (57) to low concentration solutions (58,59) for linear and star-branched polystyrene. But for star-branched polystyrene melts (51) and comb shaped polystyrene melts, \( J_e^0 \) is almost 10 times larger than that of linear polymer counterparts due to the so called enhancement effect ( ) of long chain branching. The enhancement effect of branching is the fact that steady shear compliance \( J_e^0 \) or zero shear viscosity \( \eta_0 \) of polymer melts or solutions with long chain branching has value larger than expected from its linear polymer counterpart after molecular size is corrected by g or \( g_2 \). This enhancement effect has been observed only when molecular weight (or \( cM_w \)) is larger than some critical value.

It is interesting that no apparent enhancement effect was observed for zero shear viscosity of star branched polystyrene solutions in this study or melts studied by Onogi et al. (51) up to the \( cM \) value of \( 1 \times 10^6 \).

Graessley et al. observed enhancement effects of star-branching both on \( \eta_0 \) and \( J_e^0 \) in polyisoprene solutions in tetradecane (68).
They mentioned that the enhancement effect on zero shear viscosity was much larger for polyisoprene than for polystyrene. But the enhancement effect on \( J_e^0 \), steady shear compliance is larger for polystyrene melts which is on the order of 10 or more than for polyisoprene which is on the order of 1 to 6.

They found no correlation between the enhancement on \( J_e^0 \) and the enhancement on \( \eta_0 \) of polyisoprene (68). Our data in Figure 6-8 and Figure 6-9 show a slight enhancement effect of star-branching on steady shear compliance. On the average values of \( J_e^R \) of star-branched polymers are 50-75% larger than \( J_e^R \) of linear polymers after molecular size is corrected by the size correction factor \( g_2 \). It is often the case that enhancement effects on \( \eta_0 \) or \( J_e^0 \) might be attributed to polydispersity of molecular weight or the presence of a small amount of extremely high molecular weight species.\(^*\)

However, the star-branched polystyrene samples used in our study have small \( M_w/M_n \) and the molecular weight distribution is as narrow as for the linear polystyrene samples (see Table 2-1) Therefore, the observed enhancement must be due to the star-branching itself.

These larger steady shear compliances for star-branched poly-

\(^*\)If small amount of chain-chain cross linking has occurred during the synthesis of star-branched polymers or on the shelf, the presence of such gels or extremely high molecular weight chains will affect \( J_e^0 \) more than their weight proportion.
styrene solutions are consistent with the observation during the experiment that star-branched polystyrene solutions showed more shear fracture. According to Hutton (31) the flow stability which is the resistance to shear fracture starting at the free surface edge of a cone and plate rheometer or parallel plate rheometer is correlated to the ratio of surface tension to normal stress.

\[(N_1)_c = n' \Gamma / R \theta \quad \text{(for cone and plate flow)} \quad [6-20] \]

\(\Gamma\) surface tension

\((N_1)_c\) critical normal stress above which shear fracture becomes apparent

\(n'\) empirical factor

\(R\) radius of cone

\(\theta\) cone angle

Because all other parameters in this equation are the same for both star-branched and linear polystyrene, \((N_1)_c\) determines at what \(\dot{\gamma}\) shear fracture occurs. Therefore, if \(N_1\) is larger for star-branched polymer shear fracture starts at a smaller shear rate.

This is not a perfect argument because \(J_e^0\) is a linear viscoelastic property while \(N_1\) is a non-linear shear rate dependent property. It is possible that \(J_e^0\) is large enough for star branched polymers so that \(N_1\) exceeds \((N_1)_c\) when \(\dot{\gamma}\) is still small and \(\psi_1\) is close to \(\psi_1^0\).
4. Infinite viscosity - high frequency limiting value of \( \eta' \)

It has been observed that the dynamic viscosity approaches a limiting value called the infinite frequency viscosity, \( \eta'_\infty \) at high frequency as shown in Figure 6-10

\[
\lim_{\omega \to \infty} \eta' = \eta'_\infty + \eta_S \tag{6-23}
\]

A similar limiting value (\( \eta_\infty \)) is expected for the steady shear viscosity but no experimental observation has ever been done because it is extremely difficult to achieve a steady shear flow at sufficiently high shear rates (3).

Ferry et al. have shown experimentally that infinite frequency viscosity depends only on \( C \) and the structure of the monomer units (86). For polystyrene

\[
\log \frac{\eta'_\infty}{\eta_S} = 6.0 \cdot c \tag{6-24}
\]

Equation 6-24 is good for star-branched, comb branched and linear polystyrene solutions. \( \eta'_\infty \) for our samples were computed from Equation 6-22 and listed in Table 6-4.

Many of the dynamic viscosity curves in this study show a decrease of slope from maximum at the short straight line power law slope but at the upper limit of frequency \( \eta' \) is not yet constant. The lowest observed values of \( \eta' \) are still much higher than \( \eta'_\infty \) calculated as can be seen from Table 6-5

\[ \eta_o >> \eta'_\infty >> \eta_S \]

for most of our sample solutions.
Table 6-5
Infinite Viscosity and Zero Shear Viscosity of Polystyrene
Solutions (at 25° C, Reference Temperature)

<table>
<thead>
<tr>
<th>Sample</th>
<th>C g/ml</th>
<th>$\eta_\infty$ Pa·S</th>
<th>$\eta_0$ Pa·S</th>
<th>$\eta_S$ Pa·S</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.30</td>
<td>0.19</td>
<td>73,000</td>
<td>3x10^{-3}</td>
</tr>
<tr>
<td>A2</td>
<td>0.15</td>
<td>0.024</td>
<td>1,400</td>
<td>3x10^{-3}</td>
</tr>
<tr>
<td>A3</td>
<td>0.088</td>
<td>0.010</td>
<td>90</td>
<td>3x10^{-3}</td>
</tr>
<tr>
<td>B1</td>
<td>0.45</td>
<td>1.50</td>
<td>8,080</td>
<td>3x10^{-3}</td>
</tr>
<tr>
<td>B2</td>
<td>0.30</td>
<td>0.19</td>
<td>135</td>
<td>3x10^{-3}</td>
</tr>
<tr>
<td>C1</td>
<td>0.52</td>
<td>3.95</td>
<td>1,180</td>
<td>3x10^{-3}</td>
</tr>
<tr>
<td>C2</td>
<td>0.45</td>
<td>1.50</td>
<td>166</td>
<td>3x10^{-3}</td>
</tr>
<tr>
<td>D1</td>
<td>0.62</td>
<td>15.7</td>
<td>3,930</td>
<td>3x10^{-3}</td>
</tr>
<tr>
<td>D2</td>
<td>0.45</td>
<td>1.50</td>
<td>15</td>
<td>3x10^{-3}</td>
</tr>
<tr>
<td>E1</td>
<td>0.62</td>
<td>15.7</td>
<td>680</td>
<td>3x10^{-3}</td>
</tr>
<tr>
<td>E2</td>
<td>0.45</td>
<td>1.50</td>
<td>4.03</td>
<td>3x10^{-3}</td>
</tr>
<tr>
<td>F1</td>
<td>0.45</td>
<td>1.50</td>
<td>1,850</td>
<td>3x10^{-3}</td>
</tr>
<tr>
<td>F2</td>
<td>0.30</td>
<td>0.19</td>
<td>33</td>
<td>3x10^{-3}</td>
</tr>
<tr>
<td>G1</td>
<td>0.45</td>
<td>1.50</td>
<td>1,050</td>
<td>3x10^{-3}</td>
</tr>
<tr>
<td>H1</td>
<td>0.45</td>
<td>1.50</td>
<td></td>
<td>3x10^{-3}</td>
</tr>
<tr>
<td>J1</td>
<td>0.45</td>
<td>1.50</td>
<td></td>
<td>3x10^{-3}</td>
</tr>
<tr>
<td>K1</td>
<td>0.473</td>
<td>2.07</td>
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<td>3x10^{-3}</td>
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CHAPTER VII. THEORETICAL STUDY-LINEAR VISCOELASTICITY

1. Objective

It is well established that all linear viscoelastic properties can be derived from the linear viscoelastic spectra of the material. The objective of this chapter is the opposite, i.e. to obtain the spectra from experimental data of linear viscoelastic properties. A complete review of methods for estimating spectra from linear viscoelastic properties data is given by Ferry (5).

Various forms of mathematical expressions for the linear viscoelastic spectra are considered. Then experimental data of linear viscoelasticity (dynamic viscosity and dynamic storage modulus) are used to obtain these linear spectra.

The linear spectra thus obtained are used as the basis of non-linear memory functions to be studied in the next chapter.

2. Expressions of the linear viscoelastic spectrum (5)

Polymeric liquids behave viscoelastically under deformations. In the limit of an infinitesimal deformation, linear viscoelastic properties which are strain independent, are observed; that is, in very small deformation flows, the stress is linearly proportional to the strain.

All the linear viscoelastic properties, such as the dynamic storage modulus and the dynamic viscosity are interrelated and can be derived from each other.
The simplest model of the linear viscoelasticity is the single Maxwell element which is composed of a spring connected to a dashpot as shown in Fig. 7-1.

![Figure 7-1](image)

The spring has pure rigidity, $G$, while the dashpot has pure viscosity, $\eta$. Then a relaxation time is defined as $\tau = \frac{\eta}{G}$.

The linear viscoelastic properties of this model are based on these parameters as follows:

**Relaxation Modulus:**

$$G(t) = G e^{-t/\tau} \quad [7-1]$$

**Dynamic Storage Modulus:**

$$G'(\omega) = G \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \quad [7-2]$$

**Dynamic Loss Modulus:**

$$G''(\omega) = G \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad [7-3]$$

**Dynamic Viscosity:**

$$\eta'(\omega) = \frac{G''}{\omega} = G \frac{\tau}{1 + \omega^2 \tau^2} \quad [7-4]$$
However a real polymeric liquid has a distribution of the relaxation time rather than a single time constant. The Maxwell model cannot predict the linear viscoelastic properties exactly.

There are two approaches to introduce the distribution of relaxation times into this Maxwell model. One is the use of a discrete viscoelastic spectrum with the model of parallel Maxwell elements as shown in Fig. 7-2.

```
\begin{center}
\begin{tikzpicture}
\node (spring) [shape = rectangle] at (0,0) {Spring};
\node (dashpot) [shape = rectangle] at (0,-1) {Dashpot};
\draw [->] (spring) -- (dashpot);
\end{tikzpicture}
\end{center}
```

*Fig. 7-2 Generalized Maxwell Model*

Another is to use a continuous relaxation spectrum with integrals. (cf Eq. 7-8)

Based on a discrete spectrum of relaxation times \( \tau_i (i = 1, \ldots, n) \), the linear viscoelastic properties are expressed as sums of the Maxwell model expressions.
\[ G(t) = \sum_{i=1}^{n} G_i e^{-t/\tau_i} \quad [7-5] \]
\[ = \sum_{i=1}^{n} a_i \frac{\tau_i}{e^{t/\tau_i}} \]
\[ a_i = \frac{G_i}{\tau_i} \]
\[ G'(\omega) = \sum_{i=1}^{n} G_i \frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2} \quad [7-6] \]
\[ G''(\omega) = \sum_{i=1}^{n} G_i \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2} \quad [7-7] \]

This model has been shown to approximate the linear viscoelastic properties of polymeric liquids sufficiently well with a limited number of \( G_i \) (or \( a_i \)). However, the model can be criticized because the values of \( a_i(\tau_i) \) or \( G_i(\tau_i) \) have no direct physical significance as the choices of \( \tau_i \) are arbitrary.

These problems can be eliminated by using continuous spectra.

There are three popular forms of the continuous spectra which are:

- \( M(t) \) or \( \mu(t) \) : memory function
- \( G(t) \) : relaxation modulus
- \( H(\tau) \) : relaxation spectrum

They are interrelated as shown in eq. 7-8 ~ 7-10.

\[ G(t) = \int_{0}^{\infty} M(t) dt \quad [7-8] \]
\[ G(t) = \int_{0}^{\infty} H(\tau) \frac{e^{-t/\tau}}{\tau} d\tau \quad [7-9] \]

(p. 300 of ref. 7)
\[ G'(\omega) = \int_{\infty}^{\infty} H(\tau) \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \, d\ln\tau \quad [7-10] \]

\[ G''(\omega) = \int_{\infty}^{\infty} H(\tau) \frac{\omega \tau}{1 + \omega^2 \tau^2} \, d\ln\tau \quad [7-11] \]

These equations may be derived from the generalized Maxwell model in Fig. 7-2 with infinite number of elements. Relaxation spectrum \( H(\tau) \) has often been used as a basic expression of the linear viscoelasticity and compared to the relaxation times predicted from bead-spring models.

A dual approach involving \( L(\tau) \), the retardation spectrum, and the compliance material function can be found in the review contained in Ferry's book (5).

The relaxation modulus \( G(t) \) and the memory function \( M(t) \) will be used throughout this study because it is mathematically simpler to use in the Goddard expansion and in Wagner's model.

In principle, a continuous spectrum such as the relaxation modulus or the relaxation spectrum is a unique solution from the experimental linear viscoelastic data because no arbitrary choice of time constants are involved as is the case with the discrete spectrum. In practice some estimate of the spectrum is required as \( t \to 0 \) and \( t \to \infty \), however, and so this approach is not without difficulties of its own. Also, in practical applications, the difference between the discrete spectrum and the continuous spectrum is not straightforward. A number of approximations are required to compute the relaxation spectrum from the dynamic viscosity or the dynamic
storage modulus. In these computations, as well as in the measurement, limited number of data points over the time scale are taken. Also the direct result of computations of $G$ or $H$ from different linear viscoelastic properties may not agree exactly. Then repeated iterations and modifications of data are required.

Therefore, use of the discrete spectrum to reduce our linear viscoelastic data can be justified as long as the resulting spectrum predicts other linear viscoelastic properties accurately.

3. The continuous spectrum

The relaxation modulus can be computed from dynamic viscosity and dynamic storage modulus with eq. 7-14 and eq. 7-15 and dynamic viscosity and dynamic storage modulus can be derived from the relaxation modulus with eq. 7-12 and eq. 7-13 by one of the following methods of integration.

i) Analytical integrations of equation 7-14 and 7-15 with special choices of mathematical forms for $\eta'$ and $\eta''$ based on models to obtain $G(s)$.

ii) Numerical integrations of eq. 7-14 and 7-15 with experimental data of $\eta'$ and $\eta''$ to obtain $G(s)$.

\[
\eta'(\omega) = \int_0^\infty G(s) \cos \omega s \, ds \quad [7-12]
\]

\[
\eta''(\omega) = \frac{G'(\omega)}{\omega} = \int_0^\infty G(s) \sin \omega s \, ds \quad [7-13]
\]
Then from the Fourier inversion the following relationship are obtained.

\[ G(s) = \frac{2}{\pi} \int_0^\infty n'(\omega) \cos \omega s \, d\omega \quad [7-14] \]

\[ G(s) = \frac{2}{\pi} \int_0^\infty n''(\omega) \sin \omega s \, d\omega \quad [7-15] \]

a. Analytical Solutions with Empirical and Theoretical Expressions of Linear Viscoelastic Properties

a-1) The Carreau viscosity equation

If \( n'(\omega) \) is given by the Carreau viscosity equation

\[ n'(\omega) = n_0 (1 + \lambda^2 \omega^2)^{-\frac{1}{2}} \quad [7-16] \]

then this integration can analytically be solved to result in eq. [7-17] (7)

\[ G(s) = \left(\frac{2n_0}{\pi \lambda}\right) \left(\frac{2\lambda}{s}\right)^\frac{n}{2} \frac{1}{\Gamma(\frac{1-n}{2})} K_{\frac{n}{2}} \left(\frac{s}{\lambda}\right) \quad [7-17] \]

\( K_{\frac{n}{2}} \) is a modified Bessel function of the second kind.

We could not find an exact solution of \( K_{\frac{n}{2}} \) when \( n \) is not an integer. Asymptotic values are as follows when \( s/\lambda \ll 1 \), from

\* See next page for footnote for eq. [7-16].
Fitting of \( \eta' \) by eq. 7-16 is described in detail in Chap. 4. There is no evidence that

\[
\frac{\eta' - \eta'_\infty}{\eta'_0 - \eta'_\infty} = \left(1 + \lambda^2 \omega^2 \right)^{\frac{n-1}{2}}
\]  

[7-22]

gives better description of \( \eta'(\omega) \) than eq. 7-16. The reasons are as follows:

1. Experimental determination of \( \eta'_\infty \) was not possible.
2. Calculated values of \( \eta'_\infty \) from Ferry's equation (eq. 6-22) are much smaller than minimum values of \( \eta' \) at high \( \omega \).
3. Eq. 7-22 predicts much sharper change from power law zone to \( \eta'_\infty \) than experimental data (eq. 7-22 with theoretical values of \( \eta'_\infty \)).
4. Eq. 7-22 predicts a long power zone while experimental data show very short zone of straight line.

As a consequence, regression based on eq. 7-22 (see Fig. 7-3) will result \( \eta, \lambda, \) and \( \eta'_\infty \) which are different from an experimental power law parameter, a critical frequency parameter and infinite viscosity. Use of eq. 7-22 with theoretical value of \( \eta'_\infty \) (from c only) is expected to be better than eq. 7-16 but difference is small except very high \( \omega \) properties.

Figure 7-3
Fig. 7-3 Curve Fitting of Dynamic Viscosity vs. Frequency by eq. 7-15 and eq. 7-23
9.6.2 and 9.6.10 of ref. (103)

\[ K \left( \frac{s}{\lambda} \right) = \frac{n}{Z} \frac{\pi^{\frac{n}{2}}}{\sin\left(\frac{n}{2}\pi\right)} \left( \frac{s}{2\lambda} \right)^{\frac{n}{2}} \sum_{k=0}^{\infty} \frac{(-\frac{s^2}{2})^k}{k! \Gamma(k+1-\frac{n}{2})} \]

\[ - \left( \frac{s}{2\lambda} \right)^{\frac{n}{2}} \sum_{k=0}^{\infty} \frac{(-\frac{s^2}{4\lambda^2})^k}{k! \Gamma(kH+\frac{n}{2})} \]  

[7-18]

when \( s, \lambda \ll 1 \), from 9.7.2 of ref. (103)

\[ K \left( \frac{s}{\lambda} \right) = \frac{\pi \lambda}{2s} e^{-\frac{s}{\lambda}} \left[ 1 + \frac{(n^2-1)\lambda}{8s} + \frac{(n^2-1)(n^2-9)\lambda^2}{2! 8s^2} \right. \]

\[ + \frac{(n^2-1)(n^2-9)(n^2-25)\lambda^3}{3! 8s^3} + ... \]  

[7-19]

Both equation result in \( K \to \infty \) as \( s \to 0 \). Fig. 7-4 shows the overall figures of \( G(s) \) computed from these two asymptotic values. 

Eq. 7-19 has little value as \( G(s) \) approaches to zero very fast as \( s/\lambda > 1 \). Eq. 7-18 shows that \( G(s) \) increases almost linearly as \( s \) decreases on the double logarithmic scale. This is different from \( G(s) \) observed from step strain experiments and \( G(s) \) computed with a discrete spectrum. The deficiency of the Carreau equation at short time scale is associated with its inability to fit high frequency properties (see discussion in section 3 of chapter 5).

In some experimental data, the power law slope \( d' \) is -1.

Then eq. 7-18 becomes
Fig. 7-4 Linear Relaxation Modulus

\[ G(s) \] from Carreau Kernel

\[ G(s) \text{ for } s > \lambda \]

\[ G(s) \text{ for } s < \lambda \]

\[ G(s) \text{ estimated at } s \sim \lambda \]

\[ s < \lambda \quad (G < 0) \]

\[ s > \lambda \]

\[ \log s \]
$$G(s) = \left( \frac{2n}{\sqrt{\pi}} \lambda \right) \frac{\kappa}{\Gamma(1/2)}$$  \hspace{1cm} [7-20]$$

$K_0(s/\lambda)$ is available in IBM 1130 scientific subroutine package; and Eq. 7-20 has the same undesirable behavior as eq. 7-18 at high frequency.

Analytical expressions for $G'(\omega)$ or $\eta''(\omega)$ can, in principle, be obtained by eq. 7-13 but it was not performed analytically as several of our attempts failed.

$$G'(\omega) = \left( \frac{2n}{\sqrt{\pi}} \lambda \right) \frac{n'}{(\lambda^2)\Gamma(1-n)} \int_0^\infty \kappa - \frac{n}{2} \frac{(s/\lambda)^n}{(\lambda/2)^n} ds$$  \hspace{1cm} [7-21]$$

a-2) The Segalman kernel function

Segalman proposed the following kernel function as an empirical model of the relaxation modulus (7).

$$G(s) = \frac{\eta_0}{\lambda \Gamma(1-n)} \left( \frac{\lambda}{s} \right)^n e^{-s/\lambda}$$  \hspace{1cm} [7-23]$$

The analytical integration of this kernel function for arbitrary values of $\eta$ and $\lambda/s$ is possible and results in the following expressions for the linear viscoelastic properties.

$$\eta'(\omega) = \eta_0 \left( 1 + \omega^2 \lambda^2 \right)^{-1/2} \cdot \cos \left[ (1-n)\tan^{-1}\omega \lambda \right]$$  \hspace{1cm} [7-24]$$

$$G'(\omega) = \eta_0 \left( 1 + \omega^2 \lambda^2 \right)^{-1/2} \cdot \omega \cdot \sin \left[ (1-n)\tan^{-1}\omega \lambda \right]$$  \hspace{1cm} [7-25]$$
Notice that the expression for the dynamic viscosity is the product of the Carreau viscosity equation and a cosine function. The value of this cosine function changes as shown below.

\[
\cos \left( (1-n) \tan^{-1} (\lambda \omega) \right) \bigg|_{\omega \to \infty} = \cos \left( (1-n) \frac{\pi}{2} \right)
\]

\[
\cos \left( (1-n) \tan^{-1} (\lambda \omega) \right) \bigg|_{\omega = 0} = \cos[0] = 1
\]

and

\[
\cos \left( (1-n) \frac{\pi}{2} \right) \bigg|_{n = 0} = 0
\]

\[
\cos \left( (1-n) \frac{\pi}{2} \right) \bigg|_{n = 1} = 1
\]

The Segalman viscosity equation [7-24] becomes equal to the Carreau viscosity equation [7-16] only when \( \omega = 0 \), which is zero shear viscosity or when \( n = 1 \), which is a Newtonian fluid. Viscosity is constant under these conditions.

In contrast, for a non-Newtonian liquid at the power law region, where \( \omega \) is large and \( n \) is smaller than 1 and close to zero, the Segalman equation results in a lower viscosity than the Carreau equation predicts as shown in Fig. 7-5. As just discussed, a strange hump around the critical frequency (\( \omega_0 = 1/\lambda \)) is another drawback of the Segalman model. Furthermore, this model cannot be used when \( n \) is negative, which has been observed in several experiments. Figure 7-6 shows relaxation modulus \( G(s) \) from Carreau and Segalman equation. The difference is evident at small \( s \) which corresponds to large frequency.
Figure 7-5

![Dynamic Viscosity Curves](chart)

Fig. 7-5 Dynamic Viscosity Curves from the Carreau kernel and from the Segalman kernel; parameters are from experimental value of A2 solution.

b. Numerical Integration

The relaxation modulus $G(s)$ was computed from $\eta'(\omega)$ and $G'(\omega)$ using eq. 7-14 and eq. 7-15 by numerical integration. Values of $G(s)$ computed from $\eta'(\omega)$ and $G'(\omega)$ agreed fairly well. One of the computation programs is in appendix 4.
Equation [7-14] can be numerically integrated as shown below

\[
\int_{0}^{\infty} \eta'(\omega) \cos \omega s \, d\omega = \sum_{i=1}^{n} \eta'(\omega_i) \cos \omega_i s (\omega_i - \omega_{i-1})
\]

\[
= \sum_{k=1}^{m} \cos^k \omega_k s \left( \sum_{i=1}^{n} (-1)^{i+1} \eta'(\omega_k + ia) \right) \cdot a
\]

\[
\omega_k = \pi k / s m
\]

Figure 7-6 shows the relaxation modulus, G(s) computed from \(\eta'(\omega)\) and \(G'(\omega)\). Both agree over the entire range. It has thus been shown that numerical invasion of the eq. 7-12 to compute the relaxation modulus is possible. No further attempts of numerical integration have been made because

1) G(s) can be computed more easily from the discrete spectrum.
2) The validity of the discrete spectrum has been proved experimentally as will be shown in the next chapter.
3) The error from the numerical computation grows as integrations are repeated. At least two numerical integrations are necessary, first to compute G(s) from \(\eta'(\omega)\) then to compute \(\eta'(\omega)\) again from G(s) to check the result.

Figure 7-7 shows the effect of curve fitting parameter, a, in eq. 5-8 (modified Carreau viscosity equation) which adjusts broad
Fig. 7-6  Linear Relaxation Modulus from
Analytical Solutions (Carreau and Segalman models)  
and Numerical Solutions of eq. 7-26

\[ G(s) \]: Analytical Solution of Carrau  
Kernel (n=0)

\[ \dot{G}(s) \]: Numerical Solution from \( \eta' \)

\[ G(s) \]: Numerical Solution from \( G' \)

\[ G(s) \]: Segalman Kernel

\( 10^{-2} \)  \( 10^{-1} \)  \( 10^0 \)
change from Newtonian zone to power law zone on $\eta' - \omega$ curve.

As shown in Fig. 7-7 "a" is smaller than 2 (1.25) and $G(s)$ decreases slowly as time increases compared to sharp decreases for $a=2$ which is an analytical solution of eq. 7-20.

4. The discrete spectrum

The discrete spectrum $a_i(\tau_i)$ was obtained by solving a set of simultaneous equations for each linear viscoelastic property curve (104) at $n$ data points.

$$\eta'(\omega_j) = \sum_{i=1}^{n} \frac{a_i \tau_i^2}{1 + \omega_j \tau_i^2} \quad [7-27]$$

$(j = 1, 2, \ldots n)$

or

$$G'(\omega_j) = \sum_{i=1}^{n} \frac{a_i \tau_i^3 \omega_j}{1 + \omega_j \tau_i^2} \quad [7-28]$$

$(j = 1, 2, \ldots n)$

Both sets of the simultaneous equations were solved by the Gauss-Seidel iterative method. There are some physical requirements for the solution as listed below

1) $a_i \geq 0$

2) $\eta'(\omega \rightarrow 0) = \sum_{i=1}^{n} a_i \tau_i^2$

3) The discrete spectrum from the dynamic viscosity must agree with the spectrum from the dynamic storage modulus.
Fig. 7-7  Linear Relaxation Modulus $G(s)$ computed from Dynamic Viscosity of Sample A2 by Numerical Integration Eq. 7-26 and by Analytical Solution Eq. 7-17 with $a=2$, $n=0$
Note:
\[
\frac{2}{\omega^2} G'(\omega \rightarrow 0) = \psi_0 = \sum_{i=1}^{n} a_i \tau_i^3
\]
is not required because experimental accuracy is inadequate.

In most of the cases, the simple algebraic solutions of these simultaneous equations [7-27] or [7-28] did not satisfy any of these physical requirements probably due to the sensitivity to the small values of \( G' \) and \( G'' \) (=\( n' / \omega \)) at lower frequencies where experimental measurement is not as accurate as at higher frequencies.

Then the constraints 1) to 3) are included in each step of iteration. As a result the iteration did not converge completely but converged to a satisfactory solution which is within experimental error. All of the physical constraints are automatically satisfied.

Data points are taken from equal spacing on the logarithmic scale over the entire range of frequency of the measurement. Time constants \( \tau_i \) are those at same interval at points \( \tau_i = 1/\omega_i \).

First time constants were taken to be spaced at decade intervals. The resulting discrete spectra did not give satisfactory prediction of linear viscoelastic properties, especially for narrow molecular weight distribution polymers for which the change from the plateau zone to the terminal zone is sharp. If the time constants were spaced every half decade the result was satisfactory.

Table 7-1 shows the discrete spectra computed from such solution of the equations [7-27] and [7-28].
Table 7-1a

RELAXATION MODULUS FROM DISCRETE SPECTRA

<table>
<thead>
<tr>
<th>Sample A2</th>
<th>G(s) from $\eta'$</th>
<th>G(s) from $G'$</th>
<th>s</th>
<th>$a_1\tau_1$ from $\eta'$</th>
<th>$a_1\tau_1$ from $G'$</th>
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</table>
Table 7-1c

RELAXATION MODULUS FROM DISCRETE SPECTRA

<table>
<thead>
<tr>
<th>Sample K2</th>
<th>G(s) from ( \eta' )</th>
<th>G(s) from ( G' )</th>
<th>s</th>
<th>( a_{1-i} ) from ( \eta' )</th>
<th>( a_{1-i} ) from ( G' )</th>
<th>( \bar{i} )</th>
</tr>
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<td>1.06E 00</td>
<td>1.32E 00</td>
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<td>1.11E 02</td>
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<td>1.33E 03</td>
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<td>1.87E 04</td>
<td>5.79E 03</td>
<td>1.00E-03</td>
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</table>
Fig. 7-8  Linear relaxation modulus: $G(s)$

- $\times$ from $G'$
- $+$ from $G''$

Fig. Discrete linear viscoelastic spectrum: $a_1 \tau_1$

- $\triangle$ from $G'$
- $+$ from $G''$

Sample: (A2) Narrow distribution polystyrene $M_w = 2,000,000$

$C=15$ g/ml in 1-CN
Fig. 7-9  Linear relaxation modulus: \( G(\omega) \)

- \( \times \) from \( G' \)
- \( + \) from \( G'' \)

Sample: (F1) Star-shaped polystyrene (HA31) 0.45 g/ml in 1-CN  Standard temperature = 25 °C

Fig.  Discrete linear viscoelastic spectrum: \( a_1 \tau_1 \)

- \( \Delta \) from \( G' \)
- \( + \) from \( G'' \)
Fig. 7-10  Linear relaxation modulus: $G(s)$

$\times$ from $G'$
$\div$ from $G''$

Fig.  Discrete linear viscoelastic spectrum: $a_i \tau_i$

$\triangle$ from $G'$
$\div$ from $G''$

Sample: (K2) Commercial polystyrene STYRON with broad molecular weight distribution 0.42 g/ml in 1-CN
Fig. 7-6(b), 7-7(b) and 7-8(b) show the discrete linear viscoelastic spectra of typical samples. Figure 7-6(a), 7-7(a) and 7-8(a) show the relaxation moduli G(s) computed from these spectra with eq. 7-5 for samples A2, F1 and K2. The result of the computation for the rest of the samples can be found in Appendix 3. Notice that although the discrete spectra are non-uniform and the spectra computed from dynamic viscosity look a little different from those computed from dynamic storage moduli, the curves of the relaxation moduli appear almost identical.

Fig. 7-11 ~ 7-13 show the dynamic viscosities and the dynamic storage moduli from experimental measurements, from the spectra computed from the dynamic viscosities, and from the spectra computed from the dynamic storage moduli. All of these three types of curves appears identical except at higher end of the frequency for the dynamic viscosity curve. This good agreement justifies the use of the discrete spectrum.

The exceptional behavior of the dynamic viscosity curve at the higher end of the frequency is in a region where the viscosity is larger than the straight line power law slope due to the effect of the infinite viscosity \( \eta'_\infty \). When \( \eta' - \eta''^{**} \) is used instead of \( \eta' \) in this spectrum, the agreement is somewhat better but did not agree

** \( \eta'_\infty \) computed by eq. 6-27 from concentration only used in the Carreau equation (eq. 7-23).
Fig. 7-11 Linear Viscoelastic Properties
Experimental Data and Values Computed from Discrete Linear Viscoelastic Spectrum Sample: A2 Narrow Distribution Polystyrene $M_w=2,000,000$
0.15 g/ml in 1-CN

![Graph showing viscoelastic properties with axes for frequency and stress or strain](image-url)
Fig. 7-12 Linear Viscoelastic Properties
Experimental Data and Value computed from Discrete Linear Viscoelastic Spectrum
Sample: F1 Star Branched Polystyrene
HA31 0.45g/ml in 1-CN
Fig. 7-13 Linear Viscoelastic Properties
Experimental Data and Value Computed from Discrete Linear Viscoelastic Spectrum Sample: K2 Commercial Polystyrene STYRON with Broad Molecular Weight Distribution 0.473 g/ml in 1-CN
completely. (As the solvent viscosities are low for solvents used in this study \( \eta_s \) has been omitted.)

5. Conclusion

As a result of these computations, we arrived to the following conclusions:

1) A discrete spectrum can predict \( \eta' \) from \( G' \) and \( G' \) from \( \eta' \) accurately within reasonable experimental error for our samples.

2) The good agreement between the experimental data and the prediction from the discrete spectra demonstrates the reliability of experimental measurements of linear viscoelastic properties.

The only exception is for Sample E1 which has the highest concentration \([c = 0.62 \text{ g/ml}]\) among the sample solutions. During the measurement, a number of abnormalities such as shear stress decreasing by time, or lack of reproducibility were observed which suggests an irreversible structure collapse or some other problem. It shows that when experimental measurement is not linear viscoelastic or wrong the spectra from \( \eta' \) and \( G' \) may not agree well.

3. The distribution of \( a_i \tau_i \) depends on the molecular weight distribution. For narrow molecular weight distribution polymers, the \( a_i \tau_i \) is almost constant over the entire time scale and suddenly reduces to zero beyond a certain critical time.

In contrast, for broad molecular weight distribution polymers \( a_i \tau_i \) appears almost constant just like narrow distribution polymers but decreases gradually at the higher end of the spectrum.
4) The distribution of $a_i \tau_i$ for star-branched polystyrene shows no distinctive difference in the shape from the distribution of $a_i \tau_i$ for narrow distribution linear polystyrene except star-branched polystyrene starts decreasing at smaller $\tau_i$ than linear samples of comparable molecular weight.
CHAPTER VIII. THEORETICAL STUDY - NON-LINEAR PROPERTIES

1. Non-linear viscoelastic constitutive equations

The objective of this chapter is to explain the analogies or the deviations from the analogies from a constitutive equation. Mathematical derivations of constitutive equations of non-linear viscoelasticity will be performed to fit our experimental data into constitutive equations.

The capability of constitutive equations to fit the experimental deviations from the analogies is an important aspect of the evaluation of the models. To evaluate the non-linear viscoelastic character of rheological models, time dependent shear properties and/or amplitude dependent oscillatory properties have been used as more vigorous tests than steady shear properties (105, 106, 107, 108).

However, as reviewed in Chap. 1, many of the models which were moderately successful in predicting such time dependent properties fail to predict the simple steady shear properties and linear viscoelastic properties at a high shear rate and frequency accurately enough for practical applications.

Therefore, it is worthwhile to evaluate some of the constitutive equations which have the capability to fit the deviations from the analogies to find out a model which can satisfy actual linear and non-linear viscoelastic properties without prohibitive mathematical complexities.
Such a constitutive equation will predict the steady shear properties and time dependent shear flow properties from the linear viscoelastic spectrum as obtained in Chap. 5 and some form of the non-linear spectrum function which will be obtained by fitting the deviation from the analogies into the constitutive equation.

Among the constitutive equations of non-linear viscoelasticity reviewed in Chap. 1, the Goddard expansion and the modified rubber-like liquid model of Wagner were chosen to fit our data. Most of the models either lack the ability to predict any rheological analogy or predict a horizontal shift along the shear rate/frequency axis as the sole source of the deviations from the analogies. Those models could not fit our experimental observation of the deviations from the analogies. As shown in Chapter 5, the deviations did exist and could not be explained by simple shifts of curves.

These two constitutive equations have different ways to accommodate the non-linearity of the viscoelasticity in addition to the linear viscoelasticity.

The Goddard expansion is an R-type model (rate of strain dependent non-linear function) and expresses the non-linear character as multiple integrals over the history of products of the rate of deformation measure. The linear viscoelastic spectrum is contained in its first term.

On the other hand, Wagner's model is an S-type model (strain dependent non-linear function) and uses a single integral type constitutive equation [with a memory function inside the single integral].
Linear properties are expressed with a linear memory function, \( u(t-t') \) and the non-linear properties are expressed by the full non-linear memory function which factors into a linear term, the linear memory function \( u(t-t') \) and a non-linear strain dependent damping function. Wagner's model is based on an assumption that the non-linear memory function inside the single integral can be separated into a linear viscoelastic spectrum and a strain dependent function. Experimental results have shown that this is an acceptable assumption (30)(43)(109) and from the step strain experiments, the separability was demonstrated for polystyrene solutions (110) and polyethylene melts over wide range of strain (43).

The Goddard expansion is not restricted by specific physical assumptions like the "separability", but the expansion is too general to fit experimental data directly, and it has been necessary to simplify the expansion by some assumptions about the forms of kernel functions in the higher order integrals (13). No exact, general solution of higher order kernels, \( G_{II}, G_{III} \) or \( G_{IV} \) has ever been obtained.

2. The modified rubber-like liquid theory

The single integral type constitutive equation such as Lodge's rubber-like liquid is known to describe linear viscoelastic properties completely with a linear memory function: \( u \).
\[ \Xi = \int_0^\infty \mu(t-t') \gamma'[0](t,t') d(t-t') \]  \[ [8-1] \]

\[ \mu(t-t') = \overset{\circ}{\mu}(t-t') \]  \[ [8-2] \]

\[ \overset{\circ}{\mu}(t-t') = \sum_i a_i \exp(-\frac{t-t'}{\tau_i}) \]  \[ [8-3] \]

Non-linear properties can be described by replacing the memory function by the product of the linear memory function and a strain dependent function.

\[ \mu(t-t') = \overset{\circ}{\mu}(t-t') \cdot h(I_{\gamma'0}, I_{\gamma'0}) \]  \[ [8-4] \]

Wagner (111) has proposed that with the discrete spectrum, eq. 8-3, and an exponential type damping function \( h \), satisfactory predictions of non-linear properties are possible.

For steady shear flow, both strain invariants can be written in terms of the magnitude of shear \( \gamma_{t,t'} \). This we let

\[ h(I_{\gamma'0}, I_{\gamma'0}) = h(\gamma_{t,t'}) \]  \[ [8-5] \]

Osaki et al. have previously shown from the step strain experiments that \( G(t;\gamma) \) of polystyrene solutions can be separated into \( G(t) \), the linear relaxation modulus, and a strain dependent function* (110).

*Similar results have been observed for solid rubber-like materials, in particular by Smith (112).
\[ G(t) = G(t;\gamma)/h(\gamma) \quad [8-6] \]

Laun measured the damping function, \( h \), directly with polyethylene melts and showed \( h(\gamma) \) can be fitted with the following equation.

\[ h(\gamma) = f_1 \exp(-n_1\gamma) + (1-f_1) \exp(-n_2\gamma) \quad [8-7] \]

He obtained a master curve of \( G(t) \) with eq. 8-7 as a fitting parameter up to \( \gamma = 13 \).

Wagner showed that steady shear viscosity and normal stress difference of various polymer solutions and melts can be fitted satisfactorily with a single exponential damping function.

\[ h(\gamma) = \exp(-n\gamma) \quad [8-8] \]

The value of \( n \) ranges from 0.13 to 0.20 (109). The modified rubber-like liquid model leads to the following expressions of linear viscoelastic properties and viscometric properties with the use of the discrete linear spectrum.

\[
\begin{align*}
\eta'(\omega) &= \sum_{i=1}^{m} \frac{a_i\tau_i^2}{1+\omega^2\tau_i^2} \\
G'(\omega) &= \sum_{i \neq 1}^{m} \frac{a_i\tau_i \cdot \omega^2\tau_i^2}{1+\omega^2\tau_i^2} 
\end{align*}
\quad [8-9, 8-10]
\]

When eq. 8-8 is used as the damping function, the following viscometric
functions are found.

\[ n(\dot{\gamma}) = \sum_{i=1}^{m} \frac{a_i \tau_i^2}{(1+n\dot{\gamma} \tau_i)^2} \]

\[ \psi_1(\dot{\gamma}) = 2 \sum_{i=1}^{m} \frac{a_i \tau_i^3}{(1+n\dot{\gamma} \tau_i)^3} \]

*Notice there is a typographical error in p. 9 eq. 2

eq. 8-12 is the correct form.

** In eq. 8-12

as \( \dot{\gamma} \to \infty \)

\[ N_1 = \dot{\gamma}^2 \psi_1 = 2 \sum_{i=1}^{m} \frac{a_i \tau_i^3 \dot{\gamma}^2}{(1+n\dot{\gamma} \tau_i)^3} \]

\[ \sim 2 \sum_{i=1}^{m} \frac{a_i}{n^3} \dot{\gamma}^{-1} \]

It may appear that \( N_1 \) decreases as \( \dot{\gamma} \) increases at very rate. This is not true. When using discrete spectrum value outside the range of spectrum can be meaningless.

As shown in Fig. 8-1, it is practically inevitab' both sides of spectrum \( (a_i \tau_i) \) at \( \tau_i \to 0 \) and \( \tau_i \to \infty \). at \( (\tau_i)_{\text{max}} \) causes little problem because always a. \( \tau_i \to \infty \). But \( a_i \tau_i \) does not approach zero as \( \tau_i \) approac \( (\tau_i)_{\text{min}} \). In other words the above expression for \( N_1 \) follows if large \( \dot{\gamma} \) or short time scale is to be discu
\[ N_1 = 2 \sum_{i=1}^{m} \frac{a_i}{n^{\frac{3}{\gamma}}} \frac{1}{\gamma - 1} + 2 \sum_{i=1}^{0} \frac{a_i}{n^{\frac{3}{\gamma}}} \frac{1}{\gamma - 1} = \frac{2}{3} \sum_{i=1}^{m} a_i + \sum_{i=\infty}^{0} a_i \]

from experimental observation, \( a_i \tau_i \geq a_{i+1} \tau_{i+1} \) as \( \tau_{i+1} > \tau_i \)

In other words, \( \sum_{i=\infty}^{0} a_2 \) may have infinite positive value. Therefore asymptotic discussion is not useful to predict the trend of viscometric properties at high shear rate. To discuss high shear rate properties, corresponding short time scale linear spectrum at \( \tau_i \sim (1/\dot{\gamma}) \) must be added to the \( a_i \tau_i \) spectrum. See Fig. 8-6 and 8-10 at which \( N_1 \) always increases as \( \dot{\gamma} \) increase within the range of spectrum where data are picked. Highest value is not accurate as it is affected significantly by the truncation of \( a_i \tau_i \) at \( \tau_i \to \infty \).

**Fig. 8-1 Theoretical Prediction by Modified Rubber-like Liquid Theory**

Data from ref. (32)
when eq. 8-7 is used we get

\[ n(\dot{\gamma}) = \sum_{i=1}^{m} \left[ \frac{f_1}{(1+n_1 \dot{\gamma} \tau_i)}^2 + \frac{1-f_1}{(1+n_2 \dot{\gamma} \tau_i)} \right] a_i \tau_i^2 \]  \hspace{1cm} [8-13]

\[ \psi_1(\dot{\gamma}) = 2 \sum_{i=1}^{m} \left[ \frac{f_1}{(1+n_1 \dot{\gamma} \tau_i)^3} + \frac{1-f_1}{(1+n_2 \dot{\gamma} \tau_i)^3} \right] a_i \tau_i^3 \]  \hspace{1cm} [8-14]

If it is necessary to include a larger number of exponentials to fit experimental data, eq. 8-10 and eq. 8-11 can be extended as shown below.** (43)

\[ h(\gamma) = \sum_{j=1}^{m} f_j e^{-n_j \gamma} \]  \hspace{1cm} [8-15]

\[ n(\dot{\gamma}) = \sum_{i=1}^{k} \left[ a_i \tau_i^2 \sum_{j=1}^{m} \frac{f_2}{(1+n_j \dot{\gamma} \tau_i)^2} \right] \]  \hspace{1cm} [8-16]

\[ \psi_1(\dot{\gamma}) = 2 \sum_{i=1}^{k} \left[ a_i \tau_i^3 \sum_{j=1}^{m} \frac{f_j}{(1+n_j \dot{\gamma} \tau_i)^3} \right] \]  \hspace{1cm} [8-17]

where \( \sum_{j=1}^{m} f_j = 1 \).

**Weinberg and Armstrong(113) have suggested that a damping function expressed in the form of eq. 8-18 fit the power law region of \( n(\dot{\gamma}) \) observed for an elastomer better than a single exponential type damping function of eq. 8-8.

\[ h = \gamma^{-d} \]  \hspace{1cm} [8-18]

\[ d: \text{ power law slope of } n(\dot{\gamma}) \]

They attributed the difference to the fact that eq. 8-18 decreases slower than single exponential damping function of eq. 8-8 as \( \dot{\gamma} \to \infty \).
As shown in Fig. 8-2, Wagner has recently shown that $\eta(\dot{\gamma})$ and $N_1(\dot{\gamma})$ as well as $\eta'(\omega)$ and $G'(\omega)$ curves of a narrow molecular weight distribution polyisoprene solution in tetradecan (68) can be fitted with eq. 8-9, 8-10, 8-11 and 8-12 (114). However, at high shear rate it appears that there is some difference between the experimental data and the theoretical prediction for both $\eta(\dot{\gamma})$ curve and $N_1(\dot{\gamma})$ curve.

We used eq. 8-8 to describe $h$ for our samples and computed values of $n$ from our experimental data with the linear viscoelastic spectra obtained in Chapter 7. Then $n$ values were computed for several data points of $\eta(\dot{\gamma})$ and $N_1(\dot{\gamma})$ by solving eq. 8-11 and eq. 8-12.

Table 8-1 shows the result of the solutions as functions of shear rate of each data point and Fig. 8-3 shows concentration dependence of damping constants, $n$. The damping constant, $n$, in the single exponential type damping function $h(\gamma)$ of eq. 8-8, are not single value for each samples as was shown by Wagner (109) but smaller $n$ is required to fit $\eta(\dot{\gamma})$ at larger $\dot{\gamma}$ as shown in Fig. 8-4 and Fig. 8-5.

The damping constants obtained from the normal stress data of narrow molecular weight distribution polystyrene solutions are
Fig. 8-2 Concentration Dependence of Damping Constants from Steady Shear Viscosity based on Wagner Model

Symbols:
- A1
- A2
- A3
- B1
- C1
- C2
- F1
- F2
- G1
- K1
- K2
- K3
- K4
- K7
- K8

n: damping constants

Concentration (g/ml)
Fig. 8-3 Dependence of $n$: Damping Constants from $\eta$ on $\dot{\gamma}$ of $\eta$

Data Points of Steady Shear Viscosity

Symbols: same as Fig. 8-2

$n$: Damping Constants

0.3

0.1

Shear Rate ($s^{-1}$)
Fig. 8-4 Dependence of Damping Constants, $n$ from $\Psi_1$ on $\dot{\gamma}$ of Data Points

Symbols; same as Fig. 8-2
### Table 8-1

Damping Constants in the Modified Rubber-like Liquid Theory from Steady Shear Viscosity

<table>
<thead>
<tr>
<th>Sample</th>
<th>(n) from (\eta(\dot{\gamma})) at (\dot{\gamma} = 1)</th>
<th>(n) from (\eta(\dot{\gamma})) at (\dot{\gamma} = 10)</th>
<th>(n) from (\eta(\dot{\gamma})) at (\dot{\gamma} = 100)</th>
<th>(n) from (\eta(\dot{\gamma})) at (\dot{\gamma} = 1000)</th>
<th>(n) from (\eta(\dot{\gamma})) at (\dot{\gamma} = 10000)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.195</td>
<td>0.126</td>
<td>0.091</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A2</td>
<td>0.147</td>
<td>0.208</td>
<td>0.172</td>
<td>0.127</td>
<td>0.096</td>
</tr>
<tr>
<td>A3</td>
<td>0.201</td>
<td>0.233</td>
<td>0.175</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td></td>
<td>0.133</td>
<td>0.082</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td></td>
<td>0.163</td>
<td>0.104</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td></td>
<td>(0.152)</td>
<td>0.181</td>
<td>0.215</td>
<td></td>
</tr>
<tr>
<td>F1</td>
<td>0.281</td>
<td>0.244</td>
<td>0.137</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F2</td>
<td></td>
<td></td>
<td>0.250</td>
<td>0.188</td>
<td></td>
</tr>
<tr>
<td>G1</td>
<td></td>
<td>0.212</td>
<td>0.147</td>
<td></td>
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</tr>
<tr>
<td>K1</td>
<td>0.230</td>
<td>0.102</td>
<td>0.126</td>
<td></td>
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<td>K2</td>
<td>0.172</td>
<td>0.174</td>
<td>0.133</td>
<td>0.061</td>
<td></td>
</tr>
<tr>
<td>K3</td>
<td></td>
<td>(0.211)</td>
<td>0.133</td>
<td>0.061</td>
<td></td>
</tr>
<tr>
<td>K4</td>
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<td>0.144</td>
<td>0.140</td>
<td>0.085</td>
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<td>K7</td>
<td></td>
<td>0.161</td>
<td>0.120</td>
<td>0.065</td>
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</tr>
<tr>
<td>K8</td>
<td></td>
<td>0.164</td>
<td>0.075</td>
<td>0.030</td>
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</tbody>
</table>
Fig. 8-5  Viscometric Properties
Experimental Data and Predictions from Wagner Model with Single term Damping Functions

Sample: (A2) Narrow Distribution Polystyrene
$M_W = 2,000,000$  $0.15$ g/ml in 1-CN

Filled triangles and circles; experimental data
Fig. 8-6: Viscometric Properties
Experimental Data and Theoretical Prediction from Wagner
Sample: A2 Linear Narrow Distribution Poly(styrene) M_w = 2x10^6

Filled circles and triangles: experimental data

Shear Rate (s^-1) or Frequency (rad/s)

(Pa-s or Pa)

10^4  10^3  10^2  10^1  10^0
Fig. 8-7  Viscometric Properties
Experimental Data and Theoretical Predictions from Wagner Model with Single
Term Damping Function  Sample: Star Branched Polystyrene HA31 0.45 g/ml
in 1-CN

\( \eta \quad n=0.137 \)
\( \eta' \quad n=0.244 \)
\( N_{1/2} \quad n=0.281 \)

(\( \text{Pa} \cdot \text{s or Pa} \))

\( 10^5 \)
\( 10^4 \)
\( 10^3 \)
\( 10^2 \)
\( 10 \)

10^0 10^1 10^2 10^3 10^4
Shear Rate \( (s^{-1}) \) or Frequency \( (\text{rad/s}) \)

filled circles and triangles; experimental data
Fig. 6 8 Viscosometric Properties Experimental Data and Theoretical Prediction from Wagner Model with Single Term Damping Function Sample K2 Broad Distribution Commercial Polystyrene SYRION in 1-CN 0.42 g/ml

n=0.126
n=0.172, 0.174

N
\eta

Shear Rate (s^-1) or Frequency (rad/s)
Solid lines; theoretical, filled circles and triangles; experimental
different depending on the shear rate. The differences are smaller than the differences from steady shear viscosity as can be seen by comparing Fig. 8-4 which lists damping constants computed from \( \eta(\dot{\gamma}) \) to Fig. 8-7 which lists damping constants from \( N_\eta(\dot{\gamma}) \) of same samples.

As the differences of damping constants for the same samples are systematic, it would not be meaningful to average or to use linear regression to obtain single values for each sample.

In Fig. 8-3 there appears no concentration dependence of these damping constants, \( n \), for polystyrene solutions although errors or scatters might be large.

Figure 8-6 - 8-8 show the comparison between theoretical predictions from these damping constants(\( n \)) and experimental data.

As expected, the values of \( n \) computed from the same viscosity curve but different data points at various shear rate are different. In order to fit the high shear rate viscosity, smaller value of \( n \) is necessary than the value of \( n \) to fit the low shear rate viscosity.

However, the viscosity curves of most of the broad distribution polystyrene solutions can be fitted by single \( n \) value except at very high shear rate. For these samples, eq. 8-11 and eq. 8-12 fit experimental data satisfactorily.

Similarly, the damping constant \( n \) obtained from \( N_\eta \) for the Styron solutions were mostly the same for the same sample.

When a single exponential type of the strain dependent damping function is used, the deviation from the analogy becomes a compromise between the horizontal shift and the slope difference type. Recall
that
\[ \eta' = \Sigma \frac{a_i \tau_i}{1 + \tau_i \omega^2} \quad [8-9] \]

and from eq. 8-11
\[ \eta = \Sigma \frac{a_i \tau_i}{1 + 2n \tau_i \omega / (1 + n \tau_i^2 \gamma^2)} \quad [8-19] \]

For comparison, a horizontal shift is represented by eq. 8-20
\[ \eta = \Sigma \frac{a_i \tau_i}{1 + n^2 \tau_i^2 \gamma^2} \quad [8-20] \]

in which \( \omega \) of eq. 8-10 is replaced by \( n \gamma \), so that the shift factor is \( 1/n \).

---

**Fig. 8-9** The Sape of Viscosity Curve and Forms of Theoretical Models from Wagner Model and from Carreau Eq.
Table 8-2
Damping Constants in the Modified Rubber-like Liquid
Theory from Primary Normal Stress Difference

<table>
<thead>
<tr>
<th>Sample</th>
<th>( n ) from ( N_1(\gamma') ) at ( \gamma' = 1 )</th>
<th>( n ) from ( N_1(\gamma') ) at ( \gamma' = 10 )</th>
<th>( n ) from ( N_1(\gamma') ) at ( \gamma' = 31.6 )</th>
<th>( n ) from ( N_1(\gamma') ) at ( \gamma' = 10^2 )</th>
<th>( n ) from ( N_1(\gamma') ) at ( \gamma' = 10^4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2</td>
<td>0.214</td>
<td>0.236</td>
<td></td>
<td>0.159</td>
<td></td>
</tr>
<tr>
<td>A3</td>
<td></td>
<td>0.287</td>
<td></td>
<td>0.206</td>
<td></td>
</tr>
<tr>
<td>F2</td>
<td></td>
<td></td>
<td></td>
<td>0.147</td>
<td>0.153</td>
</tr>
<tr>
<td>K1</td>
<td>0.168</td>
<td>0.127</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K3</td>
<td>0.120</td>
<td>0.133</td>
<td>0.083</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K7</td>
<td>0.150</td>
<td>0.150</td>
<td>0.135</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K8</td>
<td>0.198</td>
<td>0.189</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K4</td>
<td></td>
<td>0.192</td>
<td></td>
<td>0.185</td>
<td></td>
</tr>
</tbody>
</table>
The difference between eq. 8-20: horizontal shift and eq. 8-19, Wagner's model, also depends upon the distribution of \( a_i(\tau_i) \) through the 2n\( \pi_i \gamma \) term of eq. 8-18. Notice there is no non-linear fitting parameter in this shape fitting. The shape of \( \eta(\dot{\gamma}) \) depends solely on the linear spectrum when \( n \): the magnitude of the deviation is determined.

In order to eliminate the error between theoretical predictions and experimental data caused by the single exponential type damping function eq. 8-7 proposed by Laun is used (43).

As this damping function has three adjustable parameters, and we did not have the facility to measure \( h(\gamma) \) directly for our sample solutions, three experimental data points for each sample were taken either from the steady shear viscosity or normal stress difference curve. Then eq. 8-13 and eq. 8-14 were solved iteratively with the physical constraints:

\[
\begin{align*}
n_1, n_2 &> 0 \\
1 &> f_1 > 0
\end{align*}
\]

Table 8-3 shows these damping parameters obtained for all the samples for which viscometric data were available over a sufficiently wide range to take three data points at spacings of one decade of \( \dot{\gamma} \) on logarithmic scale. Figures 8-10, 8-11, and 8-12 show the comparison between the experimental data and theoretical predictions from these damping parameters of Table 8-3.
Table 8-3
Damping Function Parameters from $\eta(\dot{\gamma})$

<table>
<thead>
<tr>
<th>Sample</th>
<th>$n_1$</th>
<th>$n_2$</th>
<th>$f_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2</td>
<td>0.725</td>
<td>0.0313</td>
<td>0.821</td>
</tr>
<tr>
<td>C2</td>
<td>0.165</td>
<td>0.052</td>
<td>0.987</td>
</tr>
<tr>
<td>F1</td>
<td>0.373</td>
<td>0.0372</td>
<td>0.884</td>
</tr>
<tr>
<td>K1</td>
<td>0.547</td>
<td>0.0472</td>
<td>0.716</td>
</tr>
<tr>
<td>K2</td>
<td>0.177</td>
<td>0.0486</td>
<td>0.990</td>
</tr>
<tr>
<td>K7</td>
<td>0.442</td>
<td>0.0424</td>
<td>0.574</td>
</tr>
</tbody>
</table>

Footnote 1: Most of the iterations did not converge completely with reasonable value under physical constraints but converged close to data points.

Footnote 2: Because of experimental scatter, it was not feasible to obtain two exponent damping functions from primary normal stress difference.
Fig. 8-10  Theoretical Predictions of Viscometric Properties from Wagner Model with Two Exponential Damping function

Filled circles and triangles; experimental
Solid lines; theoretical

Sample: (A2) Narrow distribution polystyrene $M_w = 2,000,000$
0.15 g/ml in 1-CN

$10^4$
$10^3$
$10^2$
$10^1$
$10^0$

Shear Rate (s$^{-1}$) or Frequency (rad/s)
Fig. 8-11 Viscometric Properties Predicted by Wagner Model with Two Exponential Damping Function

Filled circles; experimental solid lines; theoretical

Sample: (P2) Star branched polystyrene (HA31)
0.45 g/ml in 1-CN
Fig. 8-12 Viscometric Properties Predicted by Wagner Model with Two Exponential Damping Functions

Sample: (X2) Commercial polystyrene STPBN with broad molecular weight distribution 0.42 g/ml in N2-0

\[ 10^{-1} \] \[ 10^0 \] \[ 10^1 \] \[ 10^2 \] \[ 10^3 \] \[ 10^4 \]

Shear Rate (s\(^{-1}\)) or Frequency (rad/s)

\[ 10^{-2} \] \[ 10^{-1} \] \[ 10^0 \] \[ 10^1 \] \[ 10^2 \] \[ 10^3 \] \[ 10^4 \]

\[ (\text{Pa.s or Pa}) \]

\[ N_0 \] \[ \eta \]
The result for sample A2 in Fig. 8-11 shows that the damping function computed from $\eta$ does not give exact fit with $N_1$. It may be caused by experimental error, or computation of $h$ is too sensitive and converged to a wrong set of parameters, or it may be a real phenomenon.

Previously it has been observed that the strain dependent part of the memory function in the Kaye-BKZ type constitutive equation (which include Wagner's model) had different form when computed from steady shear viscosity and from normal stress difference (80) (115).

3. The Goddard Expansion*

The Goddard expansion has a capability of predicting the deviations from the analogies with higher order kernel functions in multiple integrals. First, the expansion terms of larger than triple integrals were truncated as there were some evidences that use of up to a triple integral may predict the non-linear properties sufficiently (13).

$$\eta(\dot{\gamma}) = \int_0^\infty G_1(s) \cos \dot{\gamma} ds$$

$$+ \dot{\gamma}^2 \int_0^\infty \left[ \int_0^\infty \left[ 2G_{III} \cos \gamma s \cos \dot{\gamma}(s' - \gamma) + G_{IV} \cos \dot{\gamma}(s'' - s' + s) \right] ds ds' ds'' \right]$$

[8-21]

*Part of the result in this section is the work of Mr. Frank Smith III.
\[
\frac{\dot{\gamma}}{2} \psi_1(\dot{\gamma}) = \int_0^\infty G_I(s) \sin \dot{\gamma} ds \\
+ \gamma^2 \int_0^\infty \int_0^\infty [2G_{III} \sin \dot{\gamma}s \cos(\dot{\gamma}s' - s'') + G_{IV} \sin \dot{\gamma}(s'' - s' + s)] ds'ds''
\]

[8-22]

In this chapter, the general capability of the Goddard expansion to fit the deviations from the analogies was examined and we reached rather negative conclusions. Also the Goddard expansion with special choices of higher order kernel functions are examined based on experimentally obtained data.

a. Attempt to solve the triple integral terms of the Goddard expansion without special assumption about the kernel functions $G_I, G_{III}, G_{IV}$.

In this section we attempted to solve the Goddard expansion for viscometric properties, namely eq. 8-23 and eq. 8-24 from the experimental data of the deviation from the analogies (right sides of eq. 8-31 and eq. 8-32) without assuming special forms for higher order kernels $G_{III}$ and $G_{IV}$ or first order kernel $G_I$.

\[
n - n' = \gamma^2 \int_0^\infty F_2[G_{III}, G_{IV}] \]

[8-23]

\[
\frac{\dot{\gamma}}{2} \psi_1 - n'' = \gamma^2 \int_0^\infty F_1[G_{III}, G_{IV}] \]

[8-24]
From mathematical derivations without any assumption the details of which are found in the appendix-5, the following equations with double integrals and single integrals are obtained.

\[
\int_0^\infty \int_0^\infty \left[ 2G_{III} + G_{IV} \right] \cos \dot{\gamma}(s'-s'') \, ds'' \, ds' \\
= \frac{1}{2\pi} \int_0^\infty \left[ \left( \frac{n-n'}{\dot{\gamma}^2} \right) \cos \dot{\gamma}s + \left( \frac{2}{\dot{\gamma}^2} \right) \sin \dot{\gamma}s \right] \, d\dot{\gamma} \quad [8-25]
\]

\[
\int_0^\infty G_{IV} \sin \dot{\gamma}(s'-s'') \, ds'' \, ds' \\
= \frac{1}{2\pi} \int_0^\infty \left[ \left( \frac{n-n'}{\dot{\gamma}^2} \right) \sin \dot{\gamma}s - \left( \frac{2}{\dot{\gamma}^2} \right) \cos \dot{\gamma}s \right] \, d\dot{\gamma} \quad [8-26]
\]

We could not find a way to obtain single integral expressions for the Goddard expansion model analytically. But expressions of eq. 8-25 and eq. 8-26, may be useful to evaluate certain forms of mathematical expressions for \( G_{III} \) and \( G_{IV} \) when they are derived from a molecular theory or empirical forms are proposed because the right side of the equation can easily be obtained from numerical integrations of data.

We could also have some idea about the form of \( G_{III} \) and \( G_{IV} \) by computing the right side of the equations numerically. The result will tell whether such assumptions as \( G_{IV} = 0 \) or \( G_{III} = 0 \) is reasonable.

Define \( D_1 = \frac{n-n'}{\dot{\gamma}^2} \)  \quad [8-27]
D_2 = \frac{\psi_{1-n}}{\gamma^2} \equiv \frac{N_1/2 - G}{\gamma^3}

\text{[8-28]}

then

\text{[8-25]} = \frac{1}{2\pi} \int_0^\infty [D_1 \cos \dot{\gamma} s + D_2 \sin \dot{\gamma} s] d\gamma \quad \text{[8-29]}

\text{[8-26]} = \frac{1}{2\pi} \int_0^\infty [D_1 \sin \dot{\gamma} s - D_2 \cos \dot{\gamma} s] d\gamma \quad \text{[8-30]}

Figure 8-14 shows sketch of these D_1, D_2.

Fig. 8-13 Schematic Shapes of Deviation Functions
D_1(\dot{\gamma}), D_2(\dot{\gamma}), \eta(\dot{\gamma}) and \eta'(\omega)
As D1 and D2 are small quantities at high shear rate, it was not convenient to obtain D1 and D2 directly from data. Instead D1 and D2 are computed from \( \eta, \eta', N_1 \), and \( G' \) assuming either Carreau model or Wagner model.

b. Numerical integration of the Goddard expansion with the modified rubber-like liquid theory

The mathematical expressions for \( \eta'(\omega), \eta(\dot{\gamma}), \psi_1(\dot{\gamma}) \) and \( G'(\omega) \) from the modified rubber-like liquid theory eq. 8-31 and 8-32, are supplied into the right sides of eq. 8-29 and eq. 8-30.

\[
D_1 = \frac{1}{\gamma^2} \left[ \sum \frac{a_i \tau_i}{i (1+\gamma n \tau_i)^2} - \sum \frac{a_i \tau_i}{1+\gamma^2 \tau_i^2} \right] \tag{8-31}
\]

\[
D_2 = \frac{1}{\gamma^2} \left[ \sum \frac{a_i \tau_i^3}{i (1+\gamma n \tau_i)^3} - \sum \frac{a_i \tau_i}{1+\gamma^2 \tau_i^2} \right] \tag{8-32}
\]

The linear viscoelastic spectra obtained in Chap. 7 and the damping function with a single exponential obtained in the sec. 1 of this chapter are used in these equations. Fig. 8-14 (a)(b)(c) show D1 and D2 obtained from eq. 8-31 and eq. 8-32 as well as those from Wagner's model with the double exponential damping function. D1 and D2 from the Wagner model with single exponential damping function differed completely with those from the Wagner model with double exponential damping function. No numerical integration was performed for any of the D1 and D2 as error due to the model appears large.
b-2) Numerical integration with the modified Carreau equations.

As shown in Chap. 5, viscometric properties and linear viscoelastic properties can be reasonably fitted with the following modified Carreau viscosity equation type expression.

\[ \eta' (\omega) = \eta_0 \left( 1 + \lambda' \omega^2 \right)^{n'-1} / 2 \]  \[8-33]^*

\[ \eta(\dot{\gamma}) = \eta_0 \left( 1 + \lambda_2 \dot{\gamma}^2 \right)^{n-1} \]  \[8-34]\n
\[ \frac{2}{\omega^2} G'(\omega) = \psi_1^o \left( 1 + \lambda e \dot{\gamma} \right)^{b'} \frac{m-2}{b} \]  \[8-35]^{**}

\[ \psi_1(\dot{\gamma}) = \psi_1^o \left( 1 + (\lambda' e \dot{\gamma})^{b'} \right) \frac{m'-2}{b'} \]  \[8-36]^*

D1 and D2 were computed by using equations 8-33 - 8-36 with experimentally obtained parameters and eq. 3-27, eq. 8-28.

Fig. 8-14 (a)(b)(c) show the results. Note that D1 and D2 thus obtained are different both in magnitude and time scale from D1 and D2 obtained from the Wagner model.

*Curve fitting parameters in [5-7][5-8] are close to 2 for narrow distribution polymer solution.

** See equations[5-14][5-15]
Fig. 8-14a Deviation functions
D1 for sample A2 from three models

- a. Carreau
- b. Wagner's model with single exponential
- c. Wagner's model with double exponential (negative)
Fig. 8-14b Deviation function; D2 for sample A2 from three models

- b. Wagner's model with single exponential
- a. Carreau eq.
- c. Wagner's model with double exponential
Fig. 8-14c Deviation function A2 for sample F1 from three different models

- a. Carreau eq.
- b. Wagner's model with single exponential
- c. Wagner's model with double exponential

\( \gamma \; \text{s}^{-1} \)

\( \text{Pa.s}^3 \)
Fig. 8-15 Higher Order Kernels in Goddard Expansion
from Carreau Eq.
Numerical integration by eq. 8-29 was carried out for sample 6A3 only which is shown in Fig. 8-15. $F_Y$ is the contribution of $D_1 \cos \dot{\gamma}$ term in eq. 8-29 while $F_E$, that of $D_2 \sin \dot{\gamma}$. $F$ is the total result of integration of eq. 8-29.

No further integration was performed as the significance of the quantity $F$ or integrations eq. 8-29 and eq. 8-30 became very questionable as will be discussed in the next section.

C. **Fundamental Problem of the application of the Goddard expansion for the study of the analogies**

We found that the mathematical formulation of the Goddard expansion does not have the capability to predict high shear rate flow behavior, also, it is too complicated to apply to actual polymer flow problems.

As shown in eq. 8-25 and eq. 8-26 experimental data enter the expansion through the following two terms only.

\[
\frac{\eta - \eta'}{\dot{\gamma}^2} \equiv D_1(\dot{\gamma}) \quad [8-27]
\]

\[
\frac{2}{\dot{\gamma}^2} \psi_{1-n''} \equiv D_2(\dot{\gamma}) \quad [8-28]
\]

We evaluated numerical value of these terms. In order to do the calculation,

i) Modified Carreau viscosity equation, 8-33 - 8-36, and

ii) Wagner's model equation 8-31, 8-32 are used to compute these
four material functions \( (\eta, \eta', \psi_1, \eta'') \).

Fig. 8-14 ~ Fig. 8-16 show the results for D1 and D2 from typical sample solutions A2, F1 and K2. It is very clear that D1 and D2 decrease rapidly and almost vanishes at moderate shear rates. In the double logarithmic plot both D1 and D2 decrease at slopes steeper than -2 at high shear rate. The shear rate when both D1 and D2 are almost zero and negligible is no greater than 10 \( \dot{\gamma}_0 \) as shown in Fig. 8-14 ~ Fig. 8-16. These values enter eq. 8-29 and eq. 8-30 and are multiplied by \( \cos \dot{\gamma}s \) and \( \sin \dot{\gamma}s \) which do not particularly weigh high \( \dot{\gamma} \) data heavily. As a consequence no high shear viscosity data or data at power law zone enters these equations and \( G_{\text{III}} \) and \( G_{\text{IV}} \) are determined by the small difference between \( \eta \) and \( \eta' \) below \( \dot{\gamma}_0 \) and \( \omega_0 \).

More generally, the mathematical formulation of this expansion has a following form.

\[
\eta - \eta' = A \cdot \dot{\gamma}^2 + B \cdot \dot{\gamma}^4 + \ldots \quad [8-37]
\]

Here \( \eta - \eta' \) has a peak but decreases rapidly at high shear rate. Although higher power of \( \dot{\gamma} \) terms \((B\ldots)\) are expected to improve the expansion systematically, \( B \) is affected by smaller shear rate behavior because

\[
\frac{\eta - \eta'}{\dot{\gamma}^4} = B + \ldots \quad [8-38]
\]
The expansion, of course, offers better approximation with higher order terms, but it does not imply to offer approximation at higher shear rate with higher order terms systematically and the value of the left side of eq. 8-38 decreases more rapidly than $\dot{\gamma}^4$.

It can be argued that by using the modified Carreau equations (eq. 8-33 ~ eq. 8-36) fitting their parameters with high $\dot{\gamma}$ property, one can use eq. 8-29 and 8-30 to estimate $G_{III}$ and $G_{IV}$. Then $G_{III}$ and $G_{IV}$, determined this way, will predict high shear rate properties again. This argument is obviously wrong because there is no evidence either experimentally or theoretically that the modified Carreau equations are exactly the same as the experimental curves at low shear rate/frequency.

As a conclusion, we found that the Goddard expansion, which has attracted strong interests (because of its general nature and apparent capability of systematic improvement to describe non-linear properties which at the same time the expression for the deviations from the analogies), is not suitable to do any of these at high shear rate. This deficiency is based on its mathematical formulation in regard to the actual behavior of material properties. (i.e. $\dot{\gamma} - n'$ and $\dot{\gamma}^2 - n''$ decreasing functions of $\dot{\gamma} = \omega$ at high $\dot{\gamma} = \omega$).

These basic deficiencies have never been noticed probably because exact solution of the expansion was believed to be too complicated and has never been obtained.

Rather, attempts were made under several assumptions about the kernels and/or material functions, the results of which were not accur-
ate enough to evaluate actual high shear rate properties.

NOTE:

If the above argument is not enough to show that the Goddard expansion is not suitable to describe high shear rate flow properties, the following additional evidence should be considered. Remember there has been no assumptions made to the expansion (except the truncation of higher than fourth power terms).

In eq. 8-35 and eq. 8-36 the left sides contain kernels and right sides contain mathematical functions both weighted by trigonometric functions:

On the left side it can be shown that

\[ \int_{0}^{\infty} [D_1 \cos \dot{\gamma}s + D_2 \sin \dot{\gamma}s] \, d\dot{\gamma} \]

\[ = \sum_{i=1}^{\infty} [D_1(\dot{\gamma}_i) \cos \dot{\gamma}_i s + D_2(\dot{\gamma}_i) \sin \dot{\gamma}_i s] \Delta \dot{\gamma} \]

\[ = \sum_{i=1}^{m} [D_1(\dot{\gamma}_i) \cos \dot{\gamma}_i s + D_2(\dot{\gamma}_i) \sin \dot{\gamma}_i s] \]

\[ + \sum_{i=m+1}^{\infty} [D_1(\dot{\gamma}_i) \cos \dot{\gamma}_i s + D_2(\dot{\gamma}_i) \sin \dot{\gamma}_i s] \cdot \Delta \dot{\gamma} \]

where

\[ \dot{\gamma}_i = \Delta \dot{\gamma}(i - 1/2) \]

As D1 and D2 decrease as the -2.5 - -3 power of \( \dot{\gamma} \),
\[ \sum_{i=1}^{m} D1(\dot{\gamma}_i) \gg \sum_{i=m+1}^{\infty} D1(\dot{\gamma}_i) \]
\[ \sum_{i=1}^{m} D2(\dot{\gamma}_i) \gg \sum_{i=m+1}^{\infty} D2(\dot{\gamma}_i) \]

and as \(|\sin| < 1 \) and \(|\cos| < 1\),

\[ \sum_{i=1}^{m} D1(\dot{\gamma}_i) \cos \dot{\gamma}_i s \gg \sum_{i=m+1}^{\infty} D1(\dot{\gamma}_i) \cos \dot{\gamma}_i s \]
\[ \sum_{i=1}^{m} D2(\dot{\gamma}_i) \sin \dot{\gamma}_i s \gg \sum_{i=m+1}^{\infty} D2(\dot{\gamma}_i) \sin \dot{\gamma}_i s \]

and

\[ \sum_{i=1}^{m} D1(\dot{\gamma}_i) \cos \dot{\gamma}_i s + D2(\dot{\gamma}_i) \sin \dot{\gamma}_i s \gg \]
\[ \sum_{i=m+1}^{\infty} D1(\dot{\gamma}_i) \cos \dot{\gamma}_i s + D2(\dot{\gamma}_i) \sin \dot{\gamma}_i s \]

unless both sides are zero.

Therefore

\[ \int_{0}^{\infty} [D1 \cos \dot{\gamma}s + D2 \sin \dot{\gamma}s] d\dot{\gamma} \approx \int_{0}^{\dot{\gamma}_m} [D1 \cos \dot{\gamma}s + D2 \sin \dot{\gamma}s] d\dot{\gamma} \]

where \( \dot{\gamma}_m = \dot{\gamma}_0 \) (critical shear rate) which means kernel functions \( G_{III}, G_{IV} \) only depend on steady shear properties at shear rates lower than critical shear rate.

Another fact we noticed is that \( D1 \) and \( D2 \) from Wagner's model with \( h(\dot{\gamma}) \) of double exponent is not good at low \( \dot{\gamma} \). Because all parameters are chosen to fit high shear rate properties, \( D1 \) and \( D2 \) which
depend on low shear rate properties are different from those computed from other methods. In general, if discrete spectrum is used, there is some oscillating of \( n' \) and \( n \) at low shear rates, i.e. they do not exactly approach a constant value of \( n_0 \) monotonically as they should. The oscillating noise caused by the discrete spectrum drives D1 and D2 to go to either very large negative or very large positive value at small \( \dot{\gamma} \). Of course we do not yet know whether D1 and D2 really are zero or have finite negative or positive value as shear rate approaches zero.*

* 

\( n \) and \( n' \) are both even functions of their arguments

\[
n = n_0 - a_1 \dot{\gamma}^2 + a_2 \dot{\gamma}^4 - \cdots
\]

\[
n' = n_0 - b_1 \omega^2 - b_2 \omega^4 - \cdots
\]

\[
D1(\dot{\gamma}) = \frac{n(\dot{\gamma}) - n'(\dot{\gamma})}{\dot{\gamma}^2} = (b_1 - a_1) + (a_2 - b_2)\dot{\gamma}^2 + \cdots
\]

Clearly \( D1(0) \) is finite, but whether it is positive or negative depends on whether \( b_1 > a_1 \) or \( b_1 < a_1 \). Similar considerations apply to D2. Therefore, real values of D1 and D2 at \( \dot{\gamma} = 0 \) are finite but we do not know if they are positive or negative as yet.
d. Analytical integration of the expansion

It was postulated that higher order kernels \( G_{III}, G_{IV} \) can be expressed as products of some powers of \( G_I \) (linear relaxation modulus). as shown below

\[
G_{III}(s,s',s'') = k_3 \ G_I^a(s) \ G_I^b(s') \ G_I^c(s'') \quad [8-39]
\]

\[
G_{IV}(s,s',s'') = k_4 \ G_I^d(s) \ G_I^e(s') \ G_I^f(s'') \quad [8-40]
\]

As \( G_{III} \) and \( G_{IV} \) have similar physical meanings as \( G_I \), the dimension should be the same.

\[
a + b + c = 1 \quad [8-41]
\]

\[
d + e + f = 1 \quad [8-42]
\]

**d-1**) The Segalman model

As derived in Chapter 7,

\[
\eta' (\omega) = \eta_0 (1 + \lambda^2 \omega^2)^{\frac{n-1}{2}} \cos [(1-n)\tan^{-1}\lambda \omega] \quad [8-43]
\]

*partly because it is the simplest way to separate the variables and minimize the number of parameters*
To simplify the computation, an assumption is made.

\[ G_{IV} = 0 \text{ and } G_{III} \neq 0 \]

After analytical integrations, details of which can be found in the appendix -5, the following expression for the steady shear viscosity was obtained.

\[
\eta'_{\gamma=\omega} = \eta' + 2k_3 \eta_0 \lambda^2 \omega^2 \frac{\Gamma(1-an)\Gamma(1-bn)\Gamma(1-cn)}{\Gamma(1-n)}
\cdot \cos \left\{ (1-an)\tan^{-1}\left(\frac{\omega \lambda}{a}\right) \right\} \cos \left\{ (1-bn)\tan^{-1}\left(\frac{\omega \lambda}{b}\right) - (1-cn)\tan^{-1}\left(\frac{\omega \lambda}{c}\right) \right\}
\cdot \frac{a^{2\omega^2 - \lambda^2} - an-1}{2} \left( b^{2\omega^2 - \lambda^2} - bn-1 \right) \left( c^{2\omega^2 - \lambda^2} - cn-1 \right) \frac{2}{2} \tag{8-44}
\]

\[ k_3 = \text{constant} \]

Experimental observations require that at high \( \omega \), \( \eta > \eta'_{\gamma=\omega} \),

so that both cosine functions must always be positive therefore,

\[ 0 < a < \frac{2}{\eta} \]

\[ \frac{1}{\eta} < b+c < \frac{3}{\eta} \]

This requirement is not compatible with \( 0 < n < 1 \). Thus the previous assumption \( G_{IV} = 0 \) was wrong.

Next it is assumed that \( G_{IV} \neq 0 \) and \( G_{III} = 0 \). Then it follows that
\[ n' = n + \frac{n_0 \lambda^2 \omega^2}{\Gamma(1-dn) \Gamma(1-en) \Gamma(1-fn)} \]

\[ - (d^2 \lambda^2 + \omega^2)^{\frac{dn-1}{2}} (e^2 \lambda^2 + \omega^2)^{\frac{en-1}{2}} (f^2 \lambda^2 + \omega^2)^{\frac{fn-1}{2}} \]

\[ - \cos \left\{ (1-dn)\tan^{-1}\left(\frac{\omega \lambda}{d}\right) - (1-en)\tan^{-1}\left(\frac{\omega \lambda}{e}\right) + (1-fn)\tan^{-1}\left(\frac{\omega \lambda}{f}\right) \right\} \quad [8-45] \]

\[ \cos \big\{ \big\} = 1 \text{ when } \omega = 0 \]

Same as before, cosine function must always be positive at \( 0 < \omega < \infty \). Which means inside \( \big\} \) must be between \( -\pi/2 \) and \( \pi/2 \).

In order to satisfy the condition, \( d, e \) and \( f \) must satisfy one of the following conditions as well as \( d+e+f = 1 \).

(i) \( d > 0 \quad f > 0 \quad \frac{1}{2} > e > 0 \)

(ii) \( d > 0 \quad e < 0 \quad 0 > f > \frac{1}{2} - \frac{1}{n} \)

(iii) \( d < 0 \quad e > 0 \quad \frac{1}{2} > f > 0 \)

(iv) \( e > 0 \quad f < 0 \quad \frac{1}{2} > d > 0 \)

(v) \( e < 0 \quad f > 0 \quad 0 > d > \frac{1}{2} - \frac{1}{n} \)

These are easy conditions to satisfy.

The results of numerical computation of these expressions are shown in Fig. 8. The troubles with the Segalman model appear more strongly here than in the case of the dynamic viscosity. Qualitatively, this model can predict the difference between the dynamic viscosity and the steady shear viscosity with arbitrary choices of \( d, e \) and \( f \) for the expression of \( G_{IV} \). But it is unlikely one can fit these \( d, \)
Fig. 8-16(a) Dynamic and Complex Viscosities from Segalman Kernal and Steady Shear Viscosity from Goddard Expansion with Various Assumptions Sample:A3

$G_{III} = 0 \quad G_{IV} = G_{I}^a(s) G_{I}^b(s') G_{I}^c(s'') \quad a=3, b=-1, c=-1$

to get best fit with data at high shear rate ($\dot{\gamma} = 10^3$)
Fig. 8-16(b) Dynamic and Complex Viscosities from Segalman Kernel and Steady Shear Viscosity from Goddard Expansion with Various Assumptions: different value of a, b, c from (a) to get best fit with the Cox-Merz rule

Assumptions: $G_{III} = 0$, $G_{IV} = G_I(s) G_I(s') G_I(s'')$

$a = 10^{-6}, b = 2, c = -1$

$G_I$; Segalman Kernel
e, and f from experimental data with the presence of large errors due to the inaccurate prediction of the model both around the critical shear rate and in the power law zone of high shear rate.

\[ d-2) \text{Combination of the discrete linear spectrum and the assumptions of eq. 8-39 or eq. 8-40} \]

As the simplest form of a discrete spectrum, a binomial expression, as shown below, was used to check the feasibility of an analytical solution under these assumptions

\[ G_{I}(s) = a_1 e^{-s/\lambda_1} + a_2 e^{-s/\lambda_2} \quad [8-46] \]

\[ G_{III}(s) = G_{I}^2(s) G_{I}^{-2}(s') G_{I}(s'') \quad [8-47] \]

\[ G_{IV}(s) = 0 \]

Mathematical deviation from eq. 8-46, 8-47 and eq. 8-21 was not convenient to perform as shown in appendix - 5 even under this simplest form. It was concluded that the use of discrete linear spectrum combined with assumptions like eq. 8-47 is not a feasible way to fit the deviations from the analogies by the Goddard expansion.
4. Non-linear constitutive equations to predict the Cox-Merz rule

There are a few constitutive equations that predict some kind of deviations from the rheological analogies but none of the well studied constitutive equations predict the Cox-Merz rule. As detailed in Chap. 1, theoretical derivations of the Cox-Merz rule by Pao (16) and Bueche (15) are not correct.*

There is one 'Bird-Armstrong-Hassager' model that predicts the Cox-Merz rule (P. 378 of ref. 7) as shown in eq. 8-47 and 8-48.

\[ \eta = \eta_0 \frac{1 + (\lambda_2 \dot{\gamma})^2}{1 + (\lambda_1 \dot{\gamma})^2} \quad [8-47] \]

\[ \eta^* = \eta_0 \frac{1 + (\lambda_2 \omega)^2}{1 + (\lambda_1 \omega)^2} \quad [8-48] \]

But this 'model' has a few critical deficiencies which are similar to those of the 3-constant Oldroyd model. They are,

1) \( \eta \) and \( |\eta^*| \) have S-shape curves on a double logarithmic plot

*It is not clear if the derivation of an expression similar to the Cox-Merz rule by Osaki (116) from his correction of Pao's error in his derivation is totally free from errors committed by Pao and Bueche.
2) $\eta_\infty = \lambda_2/\lambda_1$, for most of polymeric liquids $\lambda_2 \ll \lambda_1$

3) power law slope is -1 when $\lambda_2 \ll \lambda_1$ and no adjustment is possible

As the experimental result on polystyrene solutions as well as some of the data on literature support the Cox-Merz rule, there is a strong desire to have a simple constitutive equation which predicts the Cox-Merz rule with decent success in predicting the linear viscoelastic properties and the non-Newtonian properties.
CHAPTER IX  CONCLUSIONS AND DISCUSSION

1. Conclusion

The following conclusions have been obtained as a result of this study.

A. Phenomenological Observation of the Analogies

1. The Cox-Merz rule is applicable over wide range of shear rate for both linear and star branched polystyrene solutions with some exceptions as mentioned in 2. The Cox-Merz rule has never been examined for star branched polymers before.

2. Exceptions to the application of the Cox-Merz rule to polystyrene are

   2-1) $cM_w > 5 \times 10^5$ when $|\eta^*| > \eta$ at high $\dot{\gamma}$ and $\dot{\gamma}_0 > \omega_0$

   2-2) polystyrene with broad molecular weight distribution when $\eta > |\eta^*|$ at high $\dot{\gamma}$

3. The deviations from the analogies are due to the difference in the power law slopes and not the result of shift of $\dot{\gamma}$ and $\omega$ between $\eta$ and $\eta'$ for narrow distribution polymers.

4. The difference between $\dot{\gamma}_0$ and $\omega_0$ ($\dot{\gamma}_0 > \omega_0$) are caused by
a broad distribution of molecular weight. For narrow distribution polymers, \( \lambda = \lambda' \) and \( \dot{\gamma}_o = \omega_0 \) and for broad distribution \( \dot{\gamma}_o = 1.7\omega_0 \)

5. There are correlations between power law slopes of \( n \) and \( n' \).

\[
d = d' - 0.26 \quad \text{narrow distribution (} \frac{M_w}{M_n} = 1 \text{)}
\]

\[
d = d' - 0.13 \quad \text{broad distribution (} \frac{M_w}{M_n} \approx 3.4 \text{)}
\]

6. There is deviation from analogy between \( N_1/2 \) and \( G' \)

\[
N_1/2 > G' \quad \text{at large } \dot{\gamma}, \omega
\]

\[
N_1/2 = G' \quad \text{at small } \dot{\gamma}, \omega
\]

We are unaware of a simple correction to this analogy which works as good as the Cox-Merz does for the viscous part of the analogy.

7. No effect of star branching observed for any of above (1-6) conclusions.

B. Phenomenological Observations of Rheological Properties (other than analogies)

8. The correlations of \( \beta_0, \beta_0' \) (reduced critical shear rate and frequency) vs. \( cM_w \) were consistent with previous literature results in the literature.

9. The correlations of power law slopes \( d \) vs \( c[\eta] \) and \( d' \) vs \( c[\eta] \)
were observed, and were similar to published results except at large \( c[\eta] \) \((\sim 100)\) constant value of \( d \) was not yet reached.

10. The correlation of \( J_e^o \) vs \( cM \) was observed and agreed well with published results.

11. No enhancement effect of star branching was observed for zero shear rate viscosity.

12. Small enhancement effect of star branching was observed for \( J_e^o \) but the effect was not much larger than experimental scatter of \( J_e^o \).

13. The effect of star branching was quantitatively characterized with \( g^* \) although \( g \) was theoretically derived at infinite dilution.

C. Temperature Dependence and Concentration Dependence of Zero-Shear Rate Viscosity

14. The time-temperature superposition principle is applicable for polystyrene solutions for both linear viscoelastic properties and

\[ g^* \text{: ratio of radius of gyration for star branched polymer/linear polymer of same molecular weight eq. 1-25.} \]
viscometric properties.

15. The time-temperature superposition was good for linear viscoelastic properties of polystyrene melts but apparently failed to superpose viscometric properties with the same shift factors. Similar anomaly of steady shear viscosity superposition was reported by Graessley et al. Experimental errors are suspected.

16. Approximate concentration dependence was obtained with,

\[ \eta_0 = k c^{6.8} \overline{M}_w^{3.4} \]

a better correlation was obtained with,

\[ \eta_0 = (k_1c)^c \cdot k_2 \cdot c \cdot \overline{M}_w^y \]

\[ y = 3.4 \quad \text{if } \overline{cM}_w > M_c \]
\[ y = 1 \quad \text{if } \overline{cM}_w < M_c \]

\[ K_1 = 6.31 \times 10^{11} \]
\[ K_2 = 8.5 \times 10^{-2} \]

17. No single unified curve of \( \eta(\dot{\gamma}, T, c, M, f) \) was possible. While \( \eta_0(T, c, M, f) \) and \( \eta(\dot{\gamma}, T) \) were obtained as unified curves. This is because the power law slopes and shape of \( \eta \) curve depends on \( c \) and \( M \).
D. Theoretical Interpretation of Linear Viscoelastic Properties

18. Discrete spectrum gives good description of linear viscoelastic properties if time constants ($\tau_i$) are spaced at half decade intervals.

19. Distribution of $a_i \tau_i$, weighting factors, of discrete spectrum differs depending on molecular weight distribution. For narrow distribution polystyrene, $a_i \tau_i$ is almost constant up to a certain value of $\tau_i$ ($= \tau_{\text{max}}$) then rapidly drops to zero. Whereas for broad distribution polystyrene, $a_i \tau_i$ appears almost constant up to a certain value $\tau_{\text{max}}$ similar to narrow distribution but decreases gradually to zero as $\tau_i$ increases beyond $\tau_{\text{max}}$.

20. No effect of star branching on the distribution of $a_i \tau_i$ was observed.

E. Theoretical Interpretation of Non-linear Viscometric Properties

21. The modified rubber-like liquid theory (Wagner's model) gave a moderately successful description of the non-linear properties, especially the deviations from the analogies.

22. In Wagner's model, if single exponential type $h(\gamma)$ is used as
a damping function* for narrow distribution polymers, either the
high shear rate or the low shear rate property prediction differs
from experimental data depending on how the damping constant was
determined. But for broad distribution polymers, a single exponen-
tial $h(\gamma)$ gives sufficiently good prediction.

23. If double exponential type damping function is used,
Wagner's model gives good predictions at high shear rate as well
as at low shear rates for both broad distribution and narrow distri-
bution polymers.

24. The Goddard expansion is not a useful model for describing
the deviations from the analogies. Its higher order kernels are
formulated at high shear rate/frequency in such a way that they re-
fect low to moderate shear rate properties heavily but high shear
rate properties affect the higher order kernels very little.

25. The Goddard expansion was solved with special choices
for the higher order kernels ($G_{III}$ and $G_{IV}$) but no satisfactory
description of viscometric properties was obtained.

* damping function $h(\gamma)$ is a strain dependent scaling factor between
non-linear and linear memory functions $M(s,\gamma) = M(s) h(\gamma)$ ($s=t-t'$)
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F. Experimental Measurements of Linear Viscoelastic and Steady Shear Properties

26. The analogies of very high concentration (up to 0.62 g/ml), and low molecular weight solution in the power law zone were, for the first time, observed with the use of a capillary rheometer and the Mechanical Spectrometer.

27. Shear fracture is evident for all high shear rate flows in the cone and plate geometry or in the parallel plate geometry. There is no proven way to estimate the effect of the shear fracture and to separate it from that of the stress overshoot.

28. Star branched polystyrene solutions showed more severe shear fracture than linear polystyrene solutions.

2. Implication and Application of this Study and Future Work Suggested from the Results

For practical application of the analogies, we found three different ways to estimate high shear rate viscosities.

The Cox-Merz rule can be used to estimate high shear rate viscosity with some confidence. Our data as well as review of recent literature proved that, unless cM is extremely high or the system is heterogenous, one can use this empiricism up to high
frequency where the effect of infinite viscosity becomes apparent.

Another way to estimate steady shear viscosity is to use the correlation between power law slopes. For example, if

$$
\eta' = \eta_0 (1 + \lambda^2 \omega^2 \frac{-d'}{2})
$$

then

$$
\eta = \eta_0 (1 + \lambda^2 \gamma^2 \frac{-d}{2})
$$

$$
d = d' - 0.25 \text{ for narrow distribution polystyrene}
$$

Third way to estimate steady shear viscosity is the use of the Wagner's model. It has been known that the damping constant is $0.13 \sim 0.20$.

If

$$
\eta' = \sum_{i=1}^{m} \frac{a_i \tau_i^2}{1 + \omega^2 \tau_i^2}
$$

then

$$
\eta = \sum_{i=1}^{m} \frac{a_i \tau_i^2}{(1 + n \gamma \tau_i)^2}
$$

and

$$
\psi_1 = \sum_{i=1}^{m} \frac{a_i \tau_i^3}{(1 + n \gamma \tau_i)^3}
$$

One can safely use $n = 0.15$ as approximation in the above equations. This method gives both $\eta$ and $\psi_1$ while two others give $\eta$ only. The power law slopes from Wagner's model are less steep than experimental values for narrow distribution polymers but very close to data for
broad distribution polymers.

In the industrial application of rheology, some people use 'viscosity ratio' which is a ratio of observed viscosities at two different shear rates with a concentric viscometer. This parameter is actually an indirect representation of the power law slope, because most industrial polymeric fluids have a broad power law zone.

From our correlation it is possible to use the power law slope of $\eta'$ or that of $|\eta^*|$ as the characteristic parameter of the fluid rather than very empirical values like 'viscosity ratio'.

In the more sophisticated mathematical modelling of the polymer processing system, one can use Wagner's model to acquire numerical values of steady shear flow properties. If extremely high shear rate viscosity is important the correlation of power law slope is the next best method to the actual measurement with a capillary rheometer.

While Mendelson has observed the effect of long chain branching of polyethylene melts on the deviations from the analogies as a failure of the Cox-Merz rule, we observed no effect of star branching on the Cox-Merz rule or the correlation between linear and non-linear properties.

It may be that only in the enhancement region one can observe the effect of star branching on the deviations from the analogies. In order to get the enhancement effect on $\eta$ for polystyrene cM should be above $10^6$. However, as mentioned in conclusion no. 2, linear
polystyrene solution is known to show abnormal steady shear property and abnormal analogical phenomena at such high cM. Therefore, it is very questionable if the enhancement by the star branching can be observed besides the enhancement by extremely high cM. The enhancement measured in such a case cannot be taken simply as the effect of branching.

It will be more interesting to check the analogical phenomena for star branched polyisoprene and polybutadiene which show strong enhancement on viscosity at moderate cM. All materials and instruments are available for such experiments.

In our study, star branching showed no enhancement of viscosity and only a slight enhancement of $J_e^0$ as was previously demonstrated. It would be interesting to study the behavior of star branched polystyrene melts to check the enhancement effect on $J_e^0$ with the same well characterized star branched polymer samples used in this study.

Also it is interesting to check the time-temperature superposition of steady shear properties for polystyrene melts. To accomplish these two objectives, a small scale capillary or slit die rheometer with high sensitivity is necessary. Current instruments are not suitable for that purpose because of large friction force (Instron 3211) or the lack of ability to attain steady shear flow (Monsanto) or the requirement of large amount of sample (Göttfert).

In our study, quantitative measurement of $\Psi_1$ at high shear rate was not possible for most of samples. With a high sensitivity, small
capacity slit die rheometer, quantitative measurement of $\psi_1$ should be possible. It would be interesting to acquire such data to check the correlation between $\psi_1$ and $G'$ in terms of critical shear rates $\dot{\gamma}_c$ and $\omega_c$ as well as power law slopes $n$ and $m'$ as was obtained for $\eta$ and $n'$ in this study.

As the deviation from the analogy between $\eta$ and $\eta'$ does exist generally and does not take the form of the difference between the critical shear rate and the critical frequency but rather appears as the difference in power law slopes, many constitutive equations apparently failed. They fail to accommodate the simplest relationship between non-linear and linear properties qualitatively.

The difference between $\dot{\gamma}_0$ and $\omega_0$ appears to be caused by the broad distribution of molecular weight.

From these evaluations of constitutive equations, the modified rubber-like liquid theory (Wagner's model) with an adjustable damping function showed the best results in predicting steady shear properties from linear viscoelastic properties.

Neither a single exponential nor double exponential type of the damping function gave an exact fit for both steady shear viscosity and primary normal stress difference but they both gave qualitatively good predictions of them.

It will be interesting to obtain damping function $h$ at very high strain experimentally to compute viscometric properties $\eta$ and $\psi_1$ without extrapolation to high $\gamma$ as has been done in various studies including this one. Some researchers suggested that the
error of prediction at high shear rate power law region may be
due to the error of extrapolation with single or double exponential
type damping function up to extremely high strain which is necessary
to compute and $\psi_1$.

If experimentally more accurate damping function can give
better prediction of $\eta$ and $\psi_1$, it will be a fundamental justification
of the modified rubber-like liquid model.

In other words, we want to know which of the following caused
the difference between data and prediction from the model.

1) Wagner's model is a perfect description of the rheological
phenomena and the inaccuracy of $\eta$ is the sole origin of the error.
2) Like the most of the constitutive equations, the model is
an approximation of rheological phenomena and even if an optimum
form of $\eta$ is obtained, resulting steady shear properties will
not be an exact match with physical behaviors.

The Goddard expansion is more sensitive to low shear rate
properties than to high shear rate properties. It cannot take into
account the difference between $\eta$ and $\eta'$ at the power law zone directly.

The fit of experimental data into the Goddard expansion can be
done as follows if the mathematics are possible.

1) Fit of experimental data at high shear rate into a model
(for example Wagner's model or Carreau model).
2) Compute low shear rate properties from the model under the
assumption that the model is accurate at the low shear rate.
3) Compute higher order kernels from the low shear rate properties computed in step 2.
4) Calculate high shear rate properties from the higher order kernels and check against experimental data.

In principle, one can iterate the above process to converge to a set of higher order kernels which predict experimental data with sufficient accuracy. But obviously in step 2) an assumption was made without experimental verification which will be very hard to obtain as the deviations from the analogy are very small at low shear rate.

Thus the prediction can be no more general or no more accurate than those obtained from the model used in step 1 without using the Goddard expansion.

It is desired to have a general constitutive equation which has the capability to fit higher shear rate properties systematically with higher order terms (or kernels).

Following are the implications of our findings in the experimental rheology.

It is very important to use the combination of a rotary rheometer and a die (capillary or slit) rheometer or a rheometer with a enclosed geometry to obtain wide range of shear rate. In the power law zone, data from the rotary (open geometry) rheometer are not necessarily reproducible or reliable. Independent verification from a capillary or
a slit die geometry proves the accuracy of the measurement.

Dynamic data from ERD and the forced oscillation of cone and plate mode agreed acceptably well. The forced oscillation has a wider range for low viscosity samples. But the result from forced oscillation was processed through a phase analyzer and not much was disclosed as to how these dynamic properties are computed. One needs extreme caution to use the result with small amplitude, or small force, or large amplitude, or high frequency as error in computation tends to be big in such cases, and should at least check the shape of torque signals on the chart.

The ideal rotary rheometer for steady shear flow measurements should have the following features in addition to those found on the Mechanical Spectrometer or Instron 3250 rheometer.

1) No or little temperature gradient within sample fluid (0.5° C, maximum, necessary for polystyrene melts, (hopefully between -100° C and 300° C).

2) Low and constant rotation of $10^{-4} \sim 10^{-6}$ rad/s (to measure $\eta_0$ of broad distribution polymer melts).

3) Force transducer has a stable base line (temperature compensated or heat insulated).

4) Strong resistance (10 ~ 100 kg) against x- and y- directional forces (Mechanical Spectrometer can withstand up to 1000g safely).
References


62. 


84. Operation Manual, Monsanto Capillary Rheometer.


119. W. Gheissle, paper read at meeting of German Society of Rheology.
Appendix-1

List of Symbols

Symbols are taken from (5) and (7) as much as possible.

\[ a \] offset between axis of two rotating disks.
\[ a, a' \] curve fitting parameters in the modified Carreau viscosity equation
\[ a_i \] weighting factor in the modified rubber-like liquid theory
\[ a_T \] shift factor
\[ c \] concentration g/ml
\[ d, d' \] power law slopes in the modified Carreau viscosity equation
\[ D \] diameter of a capillary
\[ e \] end correction factor for capillary rheometer
\[ E_a \] activation energy
\[ f \] number of arms in a polymer molecule
\[ F_x, F_y, F_z \] X-, Y- and Z-directional forces
\[ g \] ratio of mean square radius of gyration between branched and linear polymer molecule
\[ G_2 \] size correction factor for Je\(^0\) from branching
\[ G \] relaxation modulus
\[ G_{I,II,...} \] kernel functions in corotational memory integral expansion
\[ G' \] dynamic storage modulus
\[ G'' \] dynamic loss modulus
\[ [G'] \] intrinsic storage modulus
[G"] intrinsic loss modulus

h damping function in the modified rubber-like liquid

H separation between two disks in ERD mode

H(τ) relaxation spectrum

J_e^o reduced steady shear compliance

k Boltzmann's constant

m parameter in power law viscosity model

m,m' power law slope parameters in the Modified Carreau equation for elastic properties

M(t-t') memory function

M molecular weight

M_n number average molecular weight

M_w weight average molecular weight

M_v viscosity average molecular weight

n,n' power law slope parameters in the modified Carreau viscosity equation

n_1,n_2 damping constants in the modified rubber-like liquid theory

N_1,N_2 primary and secondary normal stress coefficient

Q volume flow rate

R radius or
gas constant

<s^2> mean square radius of gyration

t time

t' past time

T temperature
\( T_g \)  
glass transition temperature

\( J \)  
torque

\( v \)  
velocity or volume fraction (%)

\( w \)  
weight fraction (%)

\( w \)  
angular velocity

\( (2G'/\omega^2)_0 \)  
zero frequency limiting value of \( 2G'/\omega^2 \)

\( \dot{\beta}_0' \)  
reduced critical shear rate and critical frequency

\( \gamma, \gamma' \)  
empirical shift factors

\( \gamma \)  
shear strain

\( \dot{\gamma} \)  
rate of strain tensor

\( \dot{\gamma} \)  
shear rate

\( \dot{\gamma}_0 \)  
critical shear rate

\( \dot{\gamma}_0^R \)  
reduced critical shear rate

\( \dot{\gamma}_e \)  
critical shear rate for \( N_1 \)

\( \dot{\gamma}_0^{[0]}, \dot{\gamma}_0^{[n]} \)  
strain tensors

\( \dot{\gamma}_e^{[n]}, \dot{\gamma}_e^{[n]} \)  
codeformational kinematic tensors

\( \Gamma \)  
gamma function or surface tension

\( \omega \)  
corotating rate of strain tensor

\( \delta \)  
phase angle between stress and strain

\( \delta \omega \)  
unit tensor

\( \eta \)  
steady shear viscosity

\( \eta^* \)  
complex viscosity

\( \eta' \)  
in-phase components of \( \eta^* \), dynamic viscosity

\( \eta'' \)  
out-of-phase components of \( \eta^* \)

\( \eta_s \)  
solvent viscosity
\[ \eta_0 \quad \text{zero shear rate viscosity} \]
\[ \eta_\infty, \eta'_\infty \quad \text{limiting value of} \ n \ \text{and} \ n' \ \text{with infinite} \ \dot{\gamma} \ \text{and} \ \omega \]
\[ [\eta] \quad \text{intrinsic viscosity} \]
\[ \theta_0 \quad \text{cone angle} \]
\[ \tau \quad \text{time constant} \]
\[ \mu \quad \text{viscosity of Newtonian fluid} \]
\[ \rho \quad \text{density} \]
\[ \mathbf{T} \quad \text{stress tensor} \]
\[ \tau, \tau_i \quad \text{relaxation time} \]
\[ \psi_1, \psi_2 \quad \text{primary and secondary normal stress difference coefficients} \]
\[ \psi_1^0, \psi_2^0 \quad \text{zero-shear-rate normal stress difference coefficients} \]
\[ \omega \quad \text{frequency} \]
\[ \omega_0 \quad \text{critical frequency} \]
\[ \omega_0^R \quad \text{reduced critical frequency} \]
\[ \omega_c \quad \text{critical frequency for} \ G' \]
\[ \Pi \quad \text{total stress tensor} \ (\rho \dot{\delta} + \mathbf{T}) \]
\[ \Pi^*, \Pi^*_{\gamma} \quad \text{scalar invariants of} \ \dot{\gamma} \]
Appendix 2  Experimental Data

A2 - 1  Linear Viscoelastic Properties

Master curves of dynamic viscosities, compl dynamic storage moduli and loss moduli from ei rotating disk mode (ERD) or cone and plate o listed in this section. Table A2-1 lists figu section.

Table A2-1  Figures in Section A2-1

<table>
<thead>
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<th>Sample</th>
<th>from ERD</th>
<th>from cone oscillat</th>
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Fig. A2-1 Linear Viscoelastic Properties from ERD Mode
Polyethylene, $M_w = 2,000,000$
Reference Temperature = 25°C
Sample: (A1) Narrow Molecular Weight Distribution
0.30 g/ml in 1-CN
Fig. A2-2
Linear Viscoelastic Properties from ERD mode
Sample: (A1) $M_w = 2,000,000$ 0.30 g/ml in 1-CN
Reference Temperature = 25°C
Fig. A2-3 Linear Viscoelastic Properties from ERD Mode

Sample: (A3, ) Narrow Molecular Weight Distribution
Polystyrene, $M_w = 2,000,000$ 0.088 g/ml in 1-CN

Reference Temperature = 25°C

$\omega \cdot a_T (rad/s)$
Fig. A2-4
Sample: (A3) Narrow Molecular Weight Distribution
Polystyrene, $M_w = 2,000,000$ 0.088 g/ml in 1-CN
Reference Temperature = 25 °C
Fig. A2-5 Linear Viscoelastic Properties; Reduced Dynamic Viscosity and Reduced Complex Viscosity from ERD Mode

Sample: (B1) $\bar{M}_w = 390,000$ Narrow molecular weight distribution polystyrene 0.45 g/ml in 1-CN

Reference Temperature = 25°C
Fig. A2-6 Linear Viscoelastic Properties; Reduced Dynamic Storage Modulus and Reduced Dynamic Loss Modulus from ERD Mode
Sample: (B1) $\tilde{M}_w = 390,000$ Narrow molecular weight distribution polystyrene 0.45 g/ml in 1-CN
Reference Temperature = 25°C
Fig. A2-7  Linear Viscoelastic Properties; Reduced Dynamic Viscosity and Reduced Complex Viscosity from Cone and Plate Oscillatory Mode

Sample: (B1) Narrow molecular weight distribution polystyrene

\( M_w = 390,000 \)  0.45 g/ml in 1-CN  Reference Temperature = 25°C
Fig. A2-8 Linear Viscoelastic Properties; Reduced Dynamic Storage Modulus and Reduced Dynamic Loss Modulus from Cone and Plate Oscillatory Mode

Sample: (B1) Narrow molecular weight distribution polystyrene $\bar{M}_w = 390,000$ 0.45 g/ml in 1-CN

Reference Temperature = 25°C
Fig. A2-9  Linear Viscoelastic Properties; Reduced Dynamic Viscosity and Reduced Complex Viscosity from ERD Mode

Sample: ( B2 ) Narrow molecular weight distribution polystyrene \( \overline{M_w} = 390,000 \) 0.30 g/ml in 1-CN

Reference Temperature = 25°C
Fig. A2-10 Linear Viscoelastic Properties; Reduced Dynamic Storage Modulus and Reduced Dynamic Loss Modulus from ERD Mode

Reference Temperature = 25 C
Sample: (B2) Narrow molecular weight distribution polystyrene $M_w = 390,000$ 0.30 g/ml in 1-CN
Fig. A2.11 Linear Viscoelastic Properties; Reduced Dynamic Viscosity and Reduced Complex Viscosity from EBR Mode

Sample: (C1) Narrow molecular weight distribution
Polystyrene $M_w = 110,000$ g/mol in 1-CN
Reference Temperature = 25°C

$\eta' \propto 10^4$
$\eta'' \propto 10^2$
$\omega \cdot Q_r (rad/s)$
Fig A2-12 Linear Viscoclastic Properties, Reduced Dynamic Storage Modulus and Reduced Loss Modulus from ERD Mode
Sample: (C1) Narrow molecular weight distribution polystyrene $M_w = 110,000$ 0.52 g/ml in 1-CN
Reference Temperature = 25°C
Linear Viscoelastic Properties; Reduced Dynamic Viscosity and Reduced Complex Viscosity from Cone and Plate Oscillatory Mode

Sample: (C1) Narrow molecular weight distribution polystyrene

$M_w = 110,000$ $0.52$ g/ml in 1-CN  Reference Temperature = 25°C
Fig A2-14 Linear viscoelastic Properties; Reduced Dynamic Storage Modulus and Reduced Dynamic Loss Modulus from Cone and Plate Oscillatory Mode

Sample: (C1) Narrow molecular weight distribution polystyrene, $\bar{M}_w = 110,000$, 0.52 g/ml in 1-CN Reference Temperature = 25°C

$G'$
- $-5$ C
- $5$ C
- $25$ C

$G''$
- $-5$ C
- $5$ C
- $25$ C

$\omega \cdot \alpha_T (\text{rad/s})$
Fig. A2-15 Linear Viscoelastic Properties; Reduced Dynamic Properties
Viscosity and Reduced Complex Viscosity from ERD Mode
Sample: (C2) Narrow molecular weight distribution
polystyrene  $\bar{M}_w = 110,000$  0.45 g/ml in 1-CN
Reference Temperature = 25°C
Fig. A2-16 Linear Viscoelastic Properties: Reduced Dynamic Storage Modulus and Reduced Dynamic Loss Modulus from ERD Mode
Sample: (G2) Narrow molecular weight distribution polystyrene
\[ M_w = 110,000 \] 0.45 g/ml in 1-CN Reference Temperature = 25°C
Fig. A2-17 Linear Viscoelastic Properties; Reduced Dynamic Storage Modulus and Reduced Loss Modulus from ERD mode

Sample: (D1) Narrow molecular weight distribution

Polystyrene $\bar{M}_w = 37,000$ 0.62 g/ml in 1-CN

Reference Temperature = 25°C
Fig. A2-18 Linear Viscoelastic Properties; Reduced Dynamic Viscosity and Reduced Complex Viscosity from ERD Mode

Sample: (D1) Narrow molecular weight distribution polystyrene $\bar{M}_w = 37,000$ 0.62 g/ml in 1-CN

Reference Temperature = 25 C
Fig. A2-19 Linear Viscoelastic Properties; Reduced Dynamic Viscosity and Reduced Complex Viscosity from ERD mode
Sample: (D2) Narrow molecular weight distribution polystyrene $\bar{M}_w = 37,000$, 0.45 g/ml in 1-CN
Reference Temperature = 25°C

$\eta^* (Pa \cdot S)$

$\omega \cdot a_T (rad/s)$
Fig.A2-20 Linear Viscoelastic Properties; Reduced Dynamic Storage Modulus and Reduced Dynamic Loss Modulus from ERD Mode

Sample: (D2) Narrow molecular weight distribution polystyrene $\overline{M}_w = 37,000$ 0.45 g/ml in 1-CN

Reference Temperature = 25 C
Fig: A2-21 Linear Viscoelastic Properties; Reduced Dynamic Viscosity and Reduced Complex Viscosity from Cone and Plate Oscillatory Mode
Sample: (D2) Narrow molecular weight distribution polystyrene
$M_w = 37,000 \quad 0.45 \text{ g/ml in 1-CN} \quad \text{Reference Temperature} = 25^\circ C$
Fig. A2-22 Linear Viscoelastic Properties; Reduced Dynamic Storage Modulus and Reduced Dynamic Loss Modulus from Cone and Plate Oscillatory Mode
Sample: (D2) Narrow molecular weight distribution polystyrene $\bar{M}_w = 37,000$ 0.45 g/ml in 1-CN
Reference Temperature = 25 °C
Fig. A2-23 Linear Viscoelastic Properties; Reduced Dynamic Viscosity and Reduced Complex Viscosity from EMD Mode
Sample: \( ( E1 ) \) Narrow molecular weight distribution polystyrene \( \overline{M}_w = 17,500 \) \( 0.62 \text{ g/ml in 1-CN} \)
Reference Temperature = 25°C
Fig A2-24 Linear Viscoelastic Properties; Reduced Dynamic Storage Modulus and Dynamic Loss Modulus from ERD Mode
Sample: (E1) Narrow molecular weight distribution polystyrene $\bar{M}_w = 17,500 \ 0.62 \text{ g/ml in 1-CN}$
Reference Temperature = 25°C
Fig. A2-25 Linear Viscoelastic Properties; Reduced Dynamic Viscosity and Reduced Complex Viscosity from Cone and Plate Oscillatory Mode
Sample: (E1) Narrow molecular weight distribution polystyrene $\bar{M}_w = 17,500$ 0.62 g/ml in 1-CN
Reference Temperature = 25 C
Fig. A2-26. Linear Viscoelastic Properties: Reduced Dynamic Storage Modulus and Reduced Dynamic Loss Modulus from Cone and Plate Oscillatory Mode

Sample: PS (B1) Narrow molecular weight distribution

polystyrene $M_w = 17,500$ g/mol in 1-CN

Reference Temperature = 25°C

$G'$ $G''$
Fig. A2-27 Linear Viscoelastic Properties; Reduced Dynamic Viscosity and Reduced Complex Viscosity from ERD mode
Sample: (F2) Star shaped polystyrene (HA31) 0.30 g/ml in 1-CN
Reference Temperature = 25°C
Fig. A2-28 Linear Viscoelastic Properties; Reduced Dynamic Storage Modulus and Reduced Dynamic Loss Modulus from ERD Mode

Sample: (F2) Star shaped polystyrene (HA31) 0.30 g/ml
in 1-CN Reference Temperature = 25 °C
Fig. A2-29 Linear Viscoelastic Properties; Reduced Dynamic Storage Modulus and Reduced Loss Modulus from ERD Mode
Sample: (G1) Star shaped polystyrene (HA29) 0.45 g/ml in 1-CN Reference Temperature = 25°C
Fig. A2-30  Linear Viscoelastic Properties; Reduced Dynamic Viscosity and Reduced Complex Viscosity from ERD mode
Sample: (G1) Star shaped polystyrene (HA29) 0.45 g/ml in 1-CN
Reference Temperature = 25 C
Fig. A2-31 Linear Viscoelastic Properties; Reduced Dynamic Viscosity and Reduced Complex Viscosity from Cone and Plate Oscillatory Mode

Sample: (G1) Star shaped polystyrene (HA29) 0.45 g/ml
in 1-CN

Reference Temperature = 25°C
Fig. A2-32 Linear Viscoelastic Properties; Reduced Dynamic Storage Modulus and Reduced Dynamic Loss Modulus from Cone and Plate Oscillatory Mode.

Sample: (G1) Star shaped polystyrene (HA29) 0.45 g/ml in 1-cm  
Reference Temperature = 25°C
Fig. A2-33 Linear Viscoelastic Properties: Reduced Dynamic Viscosity and Reduced Complex Viscosity from ERD Mode

Sample: (• H1) Star shaped polystyrene (HA26) 0.45 g/ml in 1-CN  Reference Temperature = 25°C
Fig. A2-34  Linear Viscoelastic Properties; Reduced Dynamic Storage Modulus and Reduced Dynamic Loss Modulus from ERD Mode
Sample: (H1) Star shaped polystyrene (HA26) 0.45 g/ml
in 1-CN
Reference Temperature = 25°C
Fig. A2-35  Linear Viscoelastic Properties; Reduced Dynamic Viscosity and Reduced Complex Viscosity from Cone and Plate Oscillatory Mode.
Sample: (H1) Star shaped polystyrene (HA26) 0.45 g/ml
in 1-CN
Reference Temperature = 25°C
Fig. A2-36 Linear Viscoelastic Properties: Reduced Dynamic Storage Modulus and Reduced Dynamic Loss Modulus from Cone and Plate Oscillatory Mode

Sample: (H1) Star shaped polystyrene (HA26) 0.45 g/ml
in 1-CN
Reference Temperature = 25 C
Fig. A2-37 Linear Viscoelastic Properties; Reduced Dynamic Viscosity and Reduced Complex Viscosity from ERD Mode
Sample: ( J1 ) Star shaped polystyrene ( HA27 ) 0.45 g/ml
in 1-CN  Reference Temperature = 25°C

\[ \eta' \]
Fig. A2-38 Linear Viscoelastic Properties; Reduced Dynamic Storage Modulus and Reduced Dynamic Loss Modulus from ERD Mode
Sample: (J1) Star shaped polystyrene (HA27) 0.45 g/ml in 1-CN
Reference Temperature = 25°C
Fig. A2-39  Linear Viscoelastic Properties, Reduced Dynamic Viscosity and Reduced Complex Viscosity from Cone and Plate Oscillatory Mode

Sample: (J1) Star shaped polystyrene (HA27) 0.45 g/ml in 1-CN

Reference Temperature = 25°C

\[ |\eta^*| \times 1 -5°C
g 5°C
g 25°C

\[ \eta' \] + -5°C
\times 5°C
\triangleright 25°C

\[ \omega \cdot \alpha_T (\text{rad/s}) \]
Fig. A2-40 Linear Viscoelastic Properties, Reduced Dynamic Storage Modulus and Reduced Dynamic Loss Modulus from Cone and Plate Oscillatory Mode.

Sample: (J1) Star shaped polystyrene (HA27) 0.45 g/ml in 1-CN
Reference Temperature = 25°C

\[ G', G'' \] vs. \( \omega \cdot Q_T \) (rad/s)
Fig A2-41 Linear Viscoelastic Properties; Reduced Dynamic Viscosity and Reduced Complex Viscosity from ERD Mode
Reference Temperature = 25°C

Sample: (X1) Commercial polystyrene STYRON with broad molecular weight distribution 0.473 g/ml in 1-CN

\( \omega \cdot \alpha_T (\text{rad/s}) \)
Fig. A2-42 Linear Viscoelastic Properties; Reduced Dynamic Storage Modulus and Reduced Dynamic Loss Modulus from ERD Mode

Reference Temperature = 25°C

Sample: (K1) Commercial polystyrene STYRON with broad molecular weight distribution 0.473 g/ml in 1-CN
Fig. A2-43 Linear Viscoelastic Properties; Reduced Dynamic Viscosity and Reduced Complex Viscosity from ERD Mode

Reference Temperature = 25 C

Sample: (K2) Commercial polystyrene STYRON with broad molecular weight distribution 0.42 g/ml in 1-CN.
Fig. A2-44 Linear Viscoelastic Properties; Reduced Dynamic Storage Modulus and Reduced Dynamic Loss Modulus from ERD Mode
Reference Temperature = 25°C
Sample: (K2) Commercial polystyrene STYRON with broad molecular weight distribution 0.42 g/ml in 1-CN
Fig A2-45  Linear Viscoelastic Properties; Reduced Dynamic Viscosity and Reduced Complex Viscosity from ERD Mode

Reference Temperature = 25°C

Sample: (K3) Commercial polystyrene STYRON with broad molecular weight distribution 0.368 g/ml in DMP
Fig. A2-46 Linear Viscoelastic Properties; Reduced Dynamic Storage Modulus and Reduced Dynamic Loss Modulus from ERD Mode
Reference Temperature = 25 °C

Sample: (K3) Commercial polystyrene STYRON with broad molecular weight distribution 0.368 g/ml in 1-CN

$\omega \cdot Q_T (rad/s)$
Fig. A2-48 Linear Viscoelastic Properties; Reduced Dynamic Storage Modulus and Reduced Dynamic Loss Modulus from ERD Mode

Reference Temperature = 25°C

Sample: (K4) Commercial polystyrene STYRON with broad molecular weight distribution 0.315 g/ml in 1-CN
Fig. A2-49 Linear Viscoelastic Properties: Reduced Dynamic Viscosity and Reduced Complex Viscosity from ERD Mode

Reference Temperature = 25°C

Sample: (X5) Commercial polystyrene STYRON with broad molecular weight distribution 0.368 g/ml in DMP
Fig A2-50 Linear Viscoelastic Properties; Reduced Dynamic Storage Modulus and Reduced Dynamic Loss Modulus from ERD Mode

Reference Temperature = 25°C

Sample: (K5) Commercial polystyrene STYRON with broad molecular weight distribution 0.368 g/ml in DMP
Fig A2-51: Linear Viscoelastic Properties: Reduced Dynamic Viscosity and Reduced Complex Viscosity from ERD Mode

Sample: (K6) Commercial polystyrene STYRON with broad molecular weight distribution 0.315 g/ml in DBP

Reference Temperature = 25°C

ω * η (rad / s)

log(η)

log(10^4)

10^2

10^0
Fig. A2-52 Linear Viscoelastic Properties; Reduced Dynamic Viscosity and Reduced Complex Viscosity from ERD Mode
Reference Temperature = 25°C

Sample: (K6) Commercial polystyrene STYRON with broad molecular weight distribution 0.315 g/ml in DBP

\[ G' \]
\[ G'' \]

\[ \omega \cdot \alpha_i \text{ (rad/s)} \]

\[ 10^0 \]
\[ 10^1 \]
\[ 10^2 \]
\[ 10^3 \]
\[ 10^4 \]
Fig. A2-53 Linear Viscoelastic Properties; Reduced Dynamic Viscosity and Reduced Complex Viscosity from ERD Mode
Reference Temperature = 25 C
Sample: (K8) Commercial polystyrene STYRON with broad molecular weight distribution 0.315 g/ml in KMC-A

![Graph showing viscosity and complex viscosity data points at different temperatures.](image)
Fig. A2-54 Linear Viscoelastic Properties: Reduced Dynamic Storage Modulus and Reduced Dynamic Loss Modulus from ERD Mode

Sample: (X8) Commercial polystyrene STYRON with broad molecular weight distribution 0.315 g/ml in KMC-A

Reference Temperature = 25 °C
A2-2 Comparison between viscometric properties and linear viscoelastic properties

Master curves of $\eta$ and $N_1/2$ are compared in this section to master curves of $\eta^*$, $|\eta^*|$ and $G'$ which already appeared in A2-1. Figures in this section are listed in Table A2-2.

Table A2-2  Figures of Graphical Comparison between Viscometric and Linear Viscoelastic Properties

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<th>Figures</th>
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Fig. A2-55  Comparison between the Viscometric Properties and the Linear Viscoelastic Properties; reduced to Reference temperature = 25°C.

Sample: (A1) Narrow Molecular Weight Distribution
Polystyrene $M_w = 2,000,000$ 0.30 g/ml in 1-CN

$\eta$ and $N_1$

+ for -5°C
× for 5°C
▼ for 15°C
▼ for 25°C
▲ for 35°C
▲ for 40°C
O from capillary at 25°C

$\omega \cdot a_T$ (rad/s) or $\dot{\gamma} \cdot a_T$ (s$^{-1}$)
Fig. A2-56 Comparison between the Viscometric Properties and the Linear Viscoelastic Properties; reduced to Reference temperature = 25°C

Sample: (A3) Narrow Molecular Weight Distribution
Polystyrene, $\bar{M}_w = 2,000,000$ 0.088 g/ml in 1-CN

$\eta$ and $N_1$

+ -5°C
$\times$ 5°C
$\triangle$ 15°C
$\diamond$ 25°C
$\triangleleft$ 35°C
$\Delta$ 40°C

〇 from capillary at 25°C
Fig. A2-57 Comparison between the Viscometric Properties and the Linear Viscoelastic Properties; reduced to Reference temperature = 25°C

Sample: (B1) \( M_w = 390,000 \) Narrow molecular weight distribution polystyrene 0.45 g/ml in 1-CN

\[ \omega \cdot A_T (\text{rad/s}) \] or \[ \delta \cdot A_T (\text{s}^{-1}) \]
Fig. A2-58 Comparison between the Viscometric Properties and the Linear Viscoelastic Properties; reduced to Reference temperature = 25°C

Sample: (B2) Narrow molecular weight distribution polystyrene

\[ \overline{M_w} = 390,000 \quad 0.30 \text{ g/ml} \]
Fig. A2-59  Viscometric Properties and Dynamic Properties

Sample: (C1)  Narrow molecular weight distribution
polystyrene  $M_n = 110,000$  0.52 g/ml in 1-CN

$\eta$ and $N_1$

+ $-5\,\text{C}$
$\times$ $5\,\text{C}$
$\triangleright$ $15\,\text{C}$
$\triangle$ $25\,\text{C}$
Fig. A2-61  Viscometric Properties and Dynamic Properties

Sample: (D2) Narrow molecular weight distribution
Polystyrene $\bar{M}_w = 37,000$ 0.45 g/ml in 1-CN
Reference Temperature = 25 C
Fig. A2-62  Viscometric Properties and Dynamic Properties

Sample: (E1) Narrow molecular weight distribution polystyrene \( M_w = 17,500 \) 0.62 g/ml in 1-CN Reference Temperature = 25 C
Fig. A2-63 Comparison between the Viscometric Properties and the Linear Viscoelastic Properties; reduced to Standard
Sample: (E2) Narrow molecular weight distribution polystyrene $M_w = 17,500$ 0.45 g/ml in 1-CN
Reference Temperature = 25°C

$\eta$ and $N_1$

+ -5°C
× 5°C
▼ 15°C
▼ 25°C
△ 35°C
△ 40°C

from capillary
at 25°C

$\omega \cdot \eta$ (rad/s) or $\omega^2 \cdot \eta$ (s⁻¹²)
Fig. A2-64 Comparison between the Viscometric Properties and the Linear Viscoelastic Properties; reduced

Sample: (F2) Star shaped polystyrene (PA31) 0.30 g/ml
in 1-CN Reference Temperature = 25°C

\[ \Omega \cdot Q_{T} (\text{rad/sg}) \text{ or } \dot{\gamma} \cdot A_{T} (\text{s}^{-1}) \]
Fig. A2-65 Viscometric Properties and Dynamic Properties

Sample: (G1) Star shaped polystyrene (HA29) 0.45 g/ml
in 1-CN
Reference Temperature = 25°C
Fig. A2-66  Viscometric Properties and Dynamic Properties

Sample: (H1) Star shaped polystyrene (HA26) 0.45 g/ml
in 1-CN  Reference Temperature = 25°C
Fig. A2-67: Viscosimetric properties and dynamic properties of samples (11) Star shaped polystyrene (HA27) 0.45 g/ml in 1-CN. Reference temperature = 25°C.
Fig. A2-68  Viscometric Properties and Dynamic Properties
Sample: (K1) Commercial polystyrene STYRON with broad molecular weight distribution 0.473 g/ml in 1-CN
Reference Temperature = 25°C
Fig. A2-69  Viscometric Properties and Dynamic Properties
Sample: (K3) Commercial polystyrene STYRON with broad molecular weight distribution 0.368 g/ml in 1-CN
Reference Temperature = 25°C
Fig. A2-70 Viscometric Properties and Dynamic Properties

Sample: (K4) Commercial polystyrene STYRON with broad molecular weight distribution 0.315 g/ml in 1-CN
Reference Temperature = 25°C
Fig. A2-71 Viscometric Properties and Dynamic Properties

Sample: (K6) Commercial polystyrene STYRON with broad molecular weight distribution 0.315 g/ml in DBP
Reference Temperature = 25°C
Fig. A2-72 Comparison between the Viscometric Properties and the Linear Viscoelastic Properties; reduced to Reference temperature = 25°C
Sample: (X8) Commercial polystyrene STYRON with broad molecular weight distribution 0.315 g/ml in XMC-A
A2-3  Steady shear viscosity from the Instron Capillary Rheometer 3211

Steady shear viscosities measured with the Instron Capillary Rheometer are listed in this section.

Table A2-3  Steady Shear Viscosities from Instron 3211

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<td>2.88E 01 9.56E 01 2.88E 02 9.56E 02 2.88E 03 9.56E 03</td>
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<td>Date</td>
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<td>P1</td>
<td>HA31</td>
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<td>HA29</td>
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- **Date:** 78/9/13
- **Styron 429.45**

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### Sample K1

- **Styron:** 473 79/9

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- **Styron:** 42 78/3/2

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- **Styron:** 368 78/3/7

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- **Styron:** 315 78/3/7

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A2-4  Steady shear flow properties from parallel plate mode

Master curves of viscometric properties at reference temperature 25 C are shown in figures which are listed in Table A2-4

Table  A2-4  Master Curves in A2-4

<table>
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<td>K7</td>
<td>A2-108</td>
<td>A2-109</td>
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</table>
\[ \frac{\eta}{\eta_0} \]

Fig A2-73 Reduced Steady Shear Viscosity from Parallel Plate Mode
Reference Temperature = 25°C

Sample: (A3) Narrow Molecular Weight Distribution
Polystyrene, \( M_w = 2,000,000 \) 0.088 g/ml in 1-CN

gap = 0.2 cm \( R = 1.25 \) cm
Fig. A2-76 Reduced from Parallel Plate Mode

Reference Temperature = 25°C

Sample: (A3) Narrow Molecular Weight Distribution
Polystyrene, $M_w = 2,000,000$, 0.088 g/ml in 1-CN

$R = 36$ mm gap = 1.3 mm
Fig A2-77 Reduced Steady Shear Viscosity from Parallel Plate Mode
Reference Temperature = 25°C

Sample: (B1) $\bar{M}_w = 990,000$ Narrow molecular weight
distribution polystyrene 0.45 g/ml in 1-CN
$R = 12.5$ mm $\quad$ gap = 1 mm

$\gamma : a_T$ (s$^{-1}$)
Fig. A2-7P Reduced $\psi_{1} - \psi_{2}$ from Parallel Plate Mode

Sample: (P2) Narrow molecular weight distribution
Polystyrene $M_w = 350,000$
Standard temperature $= 250^\circ C$
$R = 12.5$ mm $\Delta Y_p = 1.5$ mm
Fig. A2-01  \( \psi_1 - \psi_2 \) from Parallel Plate Mode
Reference Temperature = 25°C

\( R = 12.5 \text{ mm} \)  \( \text{gap} = 2.7 \text{ mm} \)

Sample: (G1) Narrow molecular weight distribution polystyrene
\( \bar{M}_w = 110,000 \)  0.52 g/ml in 1-CN

\( \gamma \cdot \alpha \)
Fig. A2-82 Steady Shear Viscosity from Parallel Plate Mode

Reference Temperature = 25°C

Sample: (02) Narrow molecular weight distribution polystyrene

\[ M_w = 110,000 \quad 0.45 \text{ g/ml in 1-ON} \]

R = 12.5 mm  gap = 1 mm

\[ \gamma \cdot \Omega_T \ (s^{-1}) \]
Fig. A2-84 Steady Shear Viscosity from Parallel Plate Mode

Reference Temperature = 250°C

Sample: (C2) Narrow molecular weight distribution polystyrene

$\bar{M}_w = 110,000$ 0.45 g/ml in 1-CN

$R = 1.25$ cm gap = 0.2 cm

$\sqrt{\dot{\gamma} \Delta T}$ (s⁻¹)
Fig. A2-85 $\Psi_1 - \Psi_2$ from Parallel Plate Mode

Reference Temperature = 25°C

Sample: (C2) Narrow molecular weight distribution
polystyrene $M_w = 110,000$ 0.45 g/ml in 1-CN

$R = 12.5$ mm  gap = 2 mm

$\dot{\gamma}$: $\dot{\gamma}_T$ (s$^{-1}$)
Fig. A2-87 \( \Psi_1 - \Psi_2 \) from Parallel Plate Mode

Sample 1: (D1) Narrow molecular weight distribution
Polystyrene \( M_n = 57,000 \) 0.62 g/ml in 1-CN
Reference Temperature = 25°C

\( R = 12.5 \text{ mm} \)  \( \text{gap} = 1 \text{ mm} \)

\( \dot{\gamma} \cdot \eta_T (s^{-1}) \)
Fig. A2-92 Steady Shear Viscosity from Parallel Plate Mode

Sample: (E2) Narrow molecular weight distribution
polystyrene $M_w = 17,500$ 0.45 g/ml in 1-Ch
Reference Temperature = 25°C $R = 12.5$ mm gap = 1 mm

$\gamma \cdot \alpha_T$ (s⁻¹)

$\eta/\eta_0$

-5°C
5°C
10°C
25°C
35°C
40°C
Fig. A2-9b: Steady Shear Viscosity from Parallel Plate Mode
Sample: (P) Star shaped polystyrene (HA31) 0.30 g/ml.
In 1-cm Chamber Reference Temperature = 25°C
R = 36 mm gap = 1 mm

$\eta/\eta_0$ versus $\dot{\gamma} \cdot \alpha_T \ (S^{-1})$
Fig. A2-95 from Parallel Plate Mode

Sample: (P2) Star shaped polystyrene (Mw=1) 0.30 g/ml in 1-CN
Reference Temperature = 25°C

R = 36 mm gap = 1 mm
Fig. A2-96 Steady Shear Viscosity from Parallel Plate Mode

Sample: (P2) Star shaped polystyrene (HA31) 0.30 g/ml in 1-CN
Reference Temperature = 25°C

\[ \gamma: \alpha_T (s^{-1}) \]

\[ \frac{\eta}{\eta_s} \]

\( R = 12.5 \text{ mm} \quad \text{gap} = 2 \text{ mm} \)

-5°C  
5°C  
15°C  
25°C  
35°C  
40°C
Fig. A2-97 $\Psi_1 - \Psi_2$ from Parallel Plate Mode

Sample: (P2) Star shaped polystyrene (HA31) 0.30 g/ml
In 1-CN Reference Temperature = 25°C

$R = 12.5$ mm gap = 2 mm

$\dot{\gamma} \cdot \eta_\tau (s^{-1})$
Fig. A2-98 Steady Shear Viscosity from Parallel Plate Mode

Sample: (01) Star shaped polystyrene (Mw29) 0.45 g/ml

in 1-ON Reference Temperature = 25°C

R = 12.5 mm gap = 1.2 mm
Fig. A2-99  $\Psi - \Psi_2$ from Parallel Plate Mode

Sample 1 (91) Star shaped polystyrene (HA29) 0.45 g/ml
in 1-CN  Reference Temperature = 25 C

$R = 12.5$ mm  gap = 1.2 mm

-5 C  5 C  15 C  25 C  35 C  40 C
Fig. A2-100 Steady Shear Viscosity from Parallel Plate Mode

Sample: (K1) Commercial polystyrene STYRON with broad molecular weight distribution 0.368 g/ml in 1-ON
Reference Temperature = 25°C
R = 12.5 mm  gap = 2 mm
Fig. A2-101  $\psi_1 - \psi_2$ from Parallel Plate Mode

Sample: (K3) Commercial polystyrene STYRON with broad molecular weight distribution 0.368 g/ml in 1-ON

Reference Temperature = 25°C

$R = 12.5$ mm  $\text{gap} = 2$ mm
Fig.A2-102 Steady Shear Viscosity from Parallel Plate Mode

Sample: (K3) Commercial polystyrene STYRON with broad molecular weight distribution 0.368 g/ml in 1-CN

Reference Temperature = 25°C

R = 36 mm  gap = 1.55 mm
Fig. A2-103 \( \Psi_1 - \Psi_2 \) from Parallel Plate Mode

Sample: (K3) Commercial polystyrene STYRON with broad molecular weight distribution 0.368 g/ml in 1-CN

Reference Temperature = 25°C

\( R = 36 \text{ mm} \) gap = 1.55 mm
Fig A2-104 Steady Shear Viscosity from Parallel Plate Mode

Sample: (X5) Commercial polystyrene STYRION with broad molecular weight distribution 0.368 g/ml in IMP
Reference Temperature = 25°C
Fig. A2-105  from Parallel Plate Mode
Sample: (K5), Commercial polystyrene STYRON with broad molecular weight distribution 0.560 g/ml in IMP
Reference Temperature = 25°C

\[ \frac{\Phi(\gamma)}{2} \times 10^4 \]

\[ 10^1 \]

\[ 10^2 \]

\[ 10^3 \]

\[ 10^{-2} \]

\[ 10^{-1} \]

\[ 10^0 \]

\[ 10 \]

\[ 10^2 \]

\[ 10^3 \]

\[ \theta' \alpha_r \text{ (S}^{-1}) \]
Fig. A2-107 from Parallel Plate Mode

Sample: (K8) Commercial polystyrene STYRON with broad molecular weight distribution 0.315 g/ml in KMC-A

Reference Temperature = 25°C  R = 36 mm  gap = 2.15 mm
Fig. A2-108 Steady Shear Viscosity from Parallel Plate Mode

Sample: (M&7) Commercial polystyrene STYRON with broad molecular weight distribution, 0.315 g/ml in DBP

Reference Temperature = 25°C, R = 36 mm, gap = 1.85 mm
Fig. A2-109 Reduced $\Psi_1 - \Psi_2$ from Parallel Plate Mode

Samples: (x) Commercial polystyrene STYRON with broad molecular weight distribution 0.315 g/ml in DMP
Reference Temperature $= 25^\circ C$ $R = 36$ mm gap = 1.25 mm
A2-5  Intrinsic Viscosity

Intrinsic viscosities of linear polystyrene samples with narrow molecular weight distribution were measured in 1-Chloronaphthalene at 35 C with a Finske-type viscometer Kimax #100.

Table A2-5  Intrinsic Viscosities of Polystyrene

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<td>125</td>
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<td>22</td>
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<tr>
<td>17,500</td>
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</table>

Following relationship was obtained by a least square fit of data.

$$ = 7.81 \times 10^{-3} \left( \frac{M_w}{M_n} \right)^{0.754} $$

A2-6  Concentration dependence of zero shear rate viscosity

Unsuccessful attempts to correlate concentration dependence of zero shear rate viscosity to $c$ and $M$ by the Martin equation and by the Simha plot are shown here.

Martin equation is usually applicable up to a moderate concentration of a polymer solution because it predicts zero shear viscosities from dilute solution properties and concentration only. It contains no information about polymer chain-chain interaction. The Martin equation is

$$ \frac{\eta_{sp}}{c [\eta]} = \exp \left( k'[\eta] c \right) $$
Fig. A2-110  Martin Equation Plot for Good Solvents
Sample: Polystyrene in 1-CN

\[ \frac{\eta_s}{cM_w^{0.75}} \]
Fig. A2-111 Martin Equation Plot for Poor Solvents
Sample: Polystyrene in 1-CN

\[ \frac{\eta_s}{cM_w^{0.5}} \]
Fig. A2-112 Martin Equation Plot for Good Solvents
Sample: Polystyrene in Aroclor

\[ \frac{\eta_0}{c_{M_w}^{0.75}} \text{ or } \frac{\eta_0}{c (g_{M_w})^{0.75}} \]

\[ c_{M_w}^{0.75} \text{ or } c (g_{M_w} \cdot g)^{0.75} \]
Fig. A2-113 Simha Plot
Sample: Polystyrene in 1-CN

\[ \frac{\eta_o}{c^M^{0.75}} \]

\[ c(\text{g/ml}) \]
Appendix 3  Theoretical interpretation of data

A3-1  Linear relaxation moduli and discrete linear viscoelastic spectra

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Sample: (A1) Narrow Molecular Weight Distribution
Polystyrene, M_w = 2,000,000 0.30 g/ml in 1-CN
Fig. A3-2a Linear relaxation modulus: $G(s)$

- $\times$ from $G'$
- $\dagger$ from $G''$

Sample: (A3) Narrow Molecular Weight Distribution Polystyrene, $M_w = 2,000,000$ 0.088 g/ml in 1-CN

Fig. A3-2b Discrete linear viscoelastic spectrum: $a_i \tau_i$

- $\triangle$ from $G'$
- $\dagger$ from $G''$
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Fig. A3-3a Linear relaxation modulus: $G(s)$

- $\times$ from $G'$
- $\triangle$ from $G''$

Fig. A3-3b Discrete linear viscoelastic spectrum: $a_1 \tau_i$

- $\triangle$ from $G'$
- $\times$ from $G''$

Sample: (B1) $M_w = 390,000$ Narrow molecular weight distribution polystyrene $0.45$ g/ml in 1-CN

Reference Temperature = 25°C
## RELAXATION MODULUS FROM DISCRETE SPECTRA

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Fig. A3-4a  Linear relaxation modulus: $G(s)$

$\times$ from $G'$
$\dagger$ from $G''$

Sample: (C1) Narrow molecular weight distribution polystyrene $M_w = 110,000$ 0.52 g/ml in 1-CN

Fig. A3-4b Discrete linear viscoelastic spectrum: $a_i \tau_i$

$\triangle$ from $G'$
$\dagger$ from $G''$
Fig. A3-5a Linear relaxation modulus: $G(s)$

- $\times$ from $G'$
- $\triangle$ from $G''$

Sample: (C2) Narrow molecular weight distribution polystyrene. $M_w = 110,000$ 0.45 g/ml in 1-CN

Standard temperature = 25°C

Fig. A3-5b Discrete linear viscoelastic spectrum: $a_l \tau_i$

- $\triangle$ from $G'$
- $\triangle$ from $G''$
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Fig. A3-6a  Linear relaxation modulus: $G(s)$

$\times$ from $G'$
$+$ from $G''$

Sample: (E1) Narrow molecular weight distribution polystyrene $M_w = 17,500$ 0.62 g/ml in 1-CN

Fig. A3-6b  Discrete linear viscoelastic spectrum: $a_i \tau_i$

$\triangle$ from $G'$
$+$ from $G''$
Fig. A3-7a  Linear relaxation modulus: $G(s)$

- $\times$ from $G'$
- $+$ from $G''$

Sample: (P2) Star shaped polystyrene (HA31) 0.30 g/ml in 1-CN

Reference Temperature = 25°C

Fig. A3-7b  Discrete linear viscoelastic spectrum: $a_1 \tau_1$

- $\triangle$ from $G'$
- $+$ from $G''$
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**Fig. A3-8a**  Linear relaxation modulus: $G(s)$

- $\times$ from $G'$
- $+$ from $G''$

Sample: (G1) Star shaped polystyrene (HA29) 0.45 g/ml in 1-CN

**Fig. A3-8b**  Discrete linear viscoelastic spectrum: $a_1 \tau_1$

- $\triangle$ from $G'$
- $+$ from $G''$
Fig. A3-9a  Linear relaxation modulus: $G(s)$

- $\times$ from $G'$
- $+$ from $G''$

Sample: (H1) Star shaped polystyrene (HA26) 0.45 g/ml in 1-CN

Fig. A3-9b  Discrete linear viscoelastic spectrum: $a_i \tau_i$

- $\triangle$ from $G'$
- $+$ from $G''$
## Relaxation Modulus from Discrete Spectra

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Fig. A3-10a Linear relaxation modulus: $G(s)$

- $\times$ from $G'$
- $\dagger$ from $G''$

Sample: (K3) Commercial polystyrene STYRON with broad molecular weight distribution 0.36 g/ml in 1-CN

Fig. A3-10b Discrete linear viscoelastic spectrum: $a_i \tau_i$

- $\triangle$ from $G'$
- $\dagger$ from $G''$
Fig. A3-11a Linear relaxation modulus: $G(s)$

$\times$ from $G'$  
$\div$ from $G''$

Sample: (K4) Commercial polystyrene STYRON with broad molecular weight distribution C.315 g/ml in 1-CN

Fig. A3-11b Discrete linear viscoelastic spectrum: $a_i \tau_i$

$\Delta$ from $G'$  
$\div$ from $G''$
**RELAXATION MODULUS FROM DISCRETE SPECTRA**

Sample K5

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Sample: (K5) Commercial polystyrene STYRON with broad molecular weight distribution 0.368 g/ml in DMF

Fig. A3-12b Discrete linear viscoelastic spectrum: \( a_1 \tau_i \)

\[ \triangle \text{ from } G' \]
\[ \dagger \text{ from } G'' \]
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Fig. A3-13a Linear relaxation modulus: $G(s)$

- $\times$ from $G'$
- $\pm$ from $G''$

Sample: (K7) Commercial polystyrene STYRON with broad molecular weight distribution. 0.315 g/ml in DEP

Fig. A3-13b Discrete linear viscoelastic spectrum: $a_i \tau_i$

- $\triangle$ from $G'$
- $\pm$ from $G''$
Fig. A3-14a Linear relaxation modulus: $G(s)$

- $\times$ from $G'$
- $+$ from $G''$

Sample: (ES) Commercial polystyrene STYRON with broad molecular weight distribution 0.515 g/ml in Exxon-A

Fig. A3-14b Discrete linear viscoelastic spectrum: $a_i \tau_i$

- $\triangle$ from $G'$
- $+$ from $G''$
Appendix 4  Representative computer programs

Representative Computer programs used in this study are listed in this section. These programs are shown below.

1) Subroutine to reduce data from the cone and plate mode
2) Program to compute reduced viscosity and primary normal stress difference from cone and plate mode data and to plot these data on double logarithmic scale
3) Program to compute reduced dynamic viscosity and dynamic storage modulus from ERD mode
4) Program to reduce data from parallel plate mode
5) Program to compute discrete linear spectra from dynamic storage modulus
6) Program to compute discrete linear spectrum and damping function in the modified rubber-like liquid from viscosity and dynamic viscosity
7) Program to compute the Segalman kernel function from parameters of the modified Carreau equation.
8) Program to plot dynamic viscosity on double logarithmic scale computed from the Segalman kernel
9) Program to compute $G(s)$ in the Goddard expansion by numerical integration from dynamic viscosity
10) Program to compute steady shear viscosity by the Goddard expansion with the Segalman kernel assuming $G_{III}=G_{I}(s)G_{I}(s)$ $G_{I}(s)$
1) Subroutine to reduce data from the cone and plate mode

// FOR
LIST SOURCE PROGRAM
SUBROUTINE CPSTD
DIMENSION X(50), Y(50), ZC(50)
COMMON NDATA, TEMP, PI4, X, Y, Z
C VISCOSITY. VIS (POISE) = FIRST NORMAL STRESS DIFFERENCE, PSI1 (DYNE/CM2)
C FROM CONE AND PLATE GEOMETRY STEADY SHEAR FLOW MEASUREMENT
C NEGATIVE NORMAL FORCE CORRECTION 77.11.10
READ (2, 30) R, THETA, TEMP, NDATA
30 FORMAT (3F10.0, 1I0)
CALL PLTP
A = 3.1415 * R**2
WRITE (3, 120) R, THETA, TEMP, NDATA
120 FORMAT (/ 'RADIUS = ', F6.2, 'CM', ' CONE ANGLE = ', F6.2, 'CM', ' TEMP = ', F5.1)
WRITE (3, 333)
333 FORMAT(1H ' PEAK HEIGHT OF TORQUE, TOOCH(INCH) FULL RANGE OF TORQUE, TOOFL
C (GACH/10INCH) PEAK HEIGHT OF NORMAL FORCE, NFCH(INCH) FULL RANGE OF
C NORMAL FORCE, NFFUL
DO 888 I = 1, NDATA
READ (2, 40) SPEED, T00CH, F00CH, X00FL, F00FUL
40 FORMAT (6F10.0)
C COMPUTE SHEAR VISCOITY AND FIRST NORMAL STRESS DIFFERENCE PSI1
TOOl = TOOCH * TOOFL/20 * 980.
\* = SPFED * XSP
SHEAR = \* / THETA
FNUC = F00CH * F00FUL / 10. * 980.
FN = F00NC + FNUC
VIS = TOO * 1.5 / SHEAR / A / R
PSI1 = FN + 2. / A / SHEAR**2
IF (F00CH < 0.003001) 3, 4
3 PSI1 = 0
4 CONTINUE
PSAGY = PSI1 * SHEAR **2 / 2.
WRITE (3, 130) \* * TOO, FN, SHEAR, VIS, PSI1, PSAGY
130 FORMAT (3E15.4, 5E20.4, 3E15.4, /)
X(I) = ALOG (SHEAR) / ALOG (10.)
Y(I) = ALOG (VIS) / ALOG (10.)
Z(I) = ALOG (PSI1) / ALOG (10.)
IF (Y(I) > 7) 801, 802
801 Y(I) = 7
802 IF (Z(I) > 7) 803, 804
803 Z(I) = 7
804 CONTINUE
888 CONTINUE
RETURN
END
2) Program to compute reduced viscosity and primary normal stress difference from cone and plate mode data and to plot these data on double logarithmic scale

```fortran
C DIMENSION DV(50), GD(50), FQ(50)

C PLOT LOG(REDS SHEAR) AND LOG(IN/2) VS ALOG(REDS VISe)

C CONVON NDATA, TEMP, IPNT, X, Y, Z, CDE

L=2
STDP=25
1 CONTINUE

CALL SCALF(1,5,1,5,-6,-8)
CALL FQID(0,4,0,1,1)
CALL FQID(1,0,5,-1,1)
CALL FQID(2,4,5,1,9)
CALL FQID(3,4,6,1,6)
CALL FPLCT(1,-6,-8)
CALL CAPLT

105 CONTINUE
CALL VRS1
IF(VODE) 2,3,3

C VISO ZEROSHEEL AT THIS TEMP VISTD ZEROSHEAR AT STD TP

3 READ (2,6) VISO, VISTD
6 FORMAT (2F10.0)

4 READ (2,6) R, THETA, TEMP, NDATA

4 FORMAT (3F10.0, I10 )

CALL PLTP
ST=(273+STDP)/(TEMP+273)

AT=ST*VISO/VISTD
WRITE (3,7) AT, ST, VISO, TEMP

7 FORMAT (4E20.3) !
A = 2.1415 * R **2
DO 201 J = 1, NDATA

210 READ (L+40) SPEED, TOOCH, FNC, XSP, TOOFL, FNFUL
40 FORMAT (6F10.0)
310 TOO = TOOFL + TOOCH * 49.

W = SPEED * XSP
FNUC=FNC*FNFUL/10.*980.
FNC = 3./40.314151.1*R**4*N**2
FN = FNC + FNUC

IF(FNC) 84, 85, 84

85 FN=0.

84 CONTINUE

SHEAR = W / THETA

VIS = TOO + 1.5 / SHEAR / A / R

PSI1 = FN * 2 / A / SHEAR**2

PSAGY = PSI1 * SHEAR**2 / 2

VISO = VIS/VISO * VISTD

SHRP = SHEAR AT

PSAGP = PSAGY * ST

PSI1P=PSI1*ST/AT**2

5 FORMAT (4E25.3)

DV(J)=ALOG(VISO)/ALOG(10.)
GD(J)=ALOG(PASGP)/ALOG(10.)
FQ(J)=ALOG(SHRP)/ALOG(10.)
FQ(J)=FQ(J)-1.
IF(GD(J)+7) 24, 24, 25
24 GD(J)=7.
25 IF(DV(J)+7) 30, 30, 31
30 DV(J)=7
```
PAGE 2

11 IF(GD(J)==6.2)32,33,33
33 GD(J)=6.2
32 IF(DV(J)==6.2)39,39,39
39 DV(J)=6.2
38 CONTINUE
201 CONTINUE
   CALL SCalf(1,5,1.5,-6.,-8)
   DO 202 I=1,Ndata
   CALL Fplot(-2,FO(I),DV(I))
      CALL Point(IPNT)
      CALL Fplot(1,FO(I),DV(I))
      CONTINUE
   202 CONTINUE
   DO 102 I=1,NData
   CALL Fplot(-2,FO(I),GD(I))
   CALL Point(IPNT)
   CALL Fplot(1,FO(I),GD(I))
102 CONTINUE
   CALL Fplot(1,-6.,-8)
   GO TO 105
2 CALL Fplot(1,4.,-8)
   GO TO 1
END

********** INTERRUPT REQUEST **********
3) Program to compute reduced dynamic viscosity and dynamic storage modulus from ERD mode

```
LIST SOURCE PROGRAM
*ICCS(TYPPE=WITER,KEYBOARD+DISK,CARD,1132PRINTER)
DIMENSION X(150),Y(150),YC(150),Z(150)
2 FORMAT('FREQ, DVIS, COVIS, GSTR, GS*2/F2
*','+','RADS/PAS, PAS, PAS, N/M2, N*2/M2')
*\)
3 FORMAT('AT',E13.3,'BT',F7.3,'VISOS',F7.0,'PA.S, TEMP',F5.1,'//
*','F5.1','C','+','RADIUS',F10.3,'GAP',F10.3,'/'))
5 FORMAT(5E12.3)
6 FORMAT(15A1)
7 FORMAT(15A1)
8 FORMAT(15A1)
9 FORMAT(15A1)
10 FORMAT(15A1)
11 FORMAT(15A1)
12 FORMAT(15A1)
23 FORMAT(15A1)
DO 102 J=1,50
WRITE(3,23)
READ(2,7)A1,A2,A3,A4,A5,A6,A7,A8,A9,B1,B2,B3,B4,B5,B6
WRITE(3,8)
READ (2,10)R,TEMP,GAPX,OFSTY,NDATA
BT=(273.+STDP)/(TEMP+273.)*(1.+2.65/1000.*(TEMP-STDP))
AT = BT * VIS0 / VSTD
GAP = GAPX - 1.01 * (TEMP - 25.0)
VIS0=VIS0/10.
WRITE(3,24)
WRITE(3,25)
DO 100 J=1,NDATA
READ(2,20)SPEED,FXC=,FYCH,XSP,XFULL,YFULL
20 FORMAT(15A1)
A = 3.1415 * R**2
FXM= FCH*XFULL/2C. *980.
FY0= FYCH*YFULL/2O. *980.
XX = 3.4 / 1C.**5
YY = 2.5 / 1C.**5
X= OFFSET = SGRT (OFSTY**2 = 2. OFSTM = YK * FYM + ( YK * FYM ))
FY = FYM / OFSET + OFSTEM + FYM + ( X* - X) / FYM)
FX = FXM / OFSET + OFSTEM + FYM + ( X - YK **2)
RATIO = OFSET/GAP
GSTR = FY / RATIO / A/10.
IF[FYCH=600R,607,608]
607 GSTR=0.
608 CONTINUE
GLOSS = FX / RATIO / A/10.
FREQ = SPEED*XSP
COVIS = SGRT (GLOSS**2+GSTR**2)/FREQ
GSTAG = GSTR * 2. / ( FREQ**2 )
DVIS = GLOSS/FREQ
X(J) = FREQ*AT
Y(J) = DVIS/ VISP
Y(J) = COVIS/VISP
Z(J) = GSTAG*BT/AT**2
WRITE(3,5) FREQ, DVIS, COVIS, GSTR, GSTAG
```
100 CONTINUE
   WRITE(3,6)
   DO 101 J=1,NDATA
      WRITE(3,9) X(J), Y(J), YC(J), Z(J)
101 CONTINUE
102 CONTINUE
END
4) Program to reduce data from parallel plate mode

```c
4 LIST SOURCE PROGRAM
+IOCS1(TYPWRITER,KEYBOARD,DISK,CARD,1132PRINTER)
DIMENSION SHEAR(40),X(40),Y(40),Z(40),U(40),V(40),PSIZ(40),PSI12(40),VIS(40)
COMMON NDATA,TEMP,IPNT,X,Y,PSIZ,SHC3,MODE,SHEAR,PSI12,U,V,PSIZ
5 FORMAT(2F10.3)
6 FORMAT(6X,1AT,'F7.3)' TO/T='F7.3',VIS='F11.1',PA='S'/)
7 FORMAT(17A)
8 FORMAT(3F10.3)
9 FORMAT(E19.3,2E12.3)
10 FORMAT(I10)
11 FORMAT(3F10.6)
10 CONTINUE
WRITE(3,38)
38 FORMAT(11H)
  READ(2,7)A,A1,A2,A3,A4,A5,A6,A7,A8,A9,B,B1,B2,B3,B4,B5,B6
WRITE(3,39)A,A1,A2,A3,A4,A5,A6,A7,A8,A9,B,B1,B2,B3,B4,B5,B6
  READ(2,11)OME
READ(2,5) VISO,VISTD
STDTP=25.
  READ (2,75) R, TEMP, GAPX, NDATA
BT=(273.†STDTP)/(TEMP+273.)
A T=BT*VISO/VISTD
VISO=VISO/10.
WRITE(3,36)AT,B,VISO
  GAP = GAPX - .0001 *( TEMP - 25. )
WRITE (3,224) R, TEMP, GAP, NDATA
224 FORMAT('/6X,'RADIUS='F5.2,'CM TEMP='F5.1,'C GAP='F6.4,'CM
* NO OF DATA='I3) NFI=2
234 WRITE (3,343)
  FORMAT(1H',/10X,'SHEAR,'8X,'VIS','8X,'PSI1-PSI2,'4X,'*
  * PSAGY','/11X 'S-1','9X,'PA,'8X,'N=2/V2','5X,'N/V2','/)
DO 99 I = 1, NDATA
  READ (2,71) SPEED, TOUCH, FNCH, XSP, TOOFL, FNFUL
71 FORMAT (6F10.0)
  YC(I)=FNCH-
  TOO=TOOFL+TOOFL/20.*990.*
  %SPEED=XSP
  FNUC=FNCH*FNFUL/10.*980.*
  FNCH = 3.3/40.*3.1415*1.1*R**4*K**2
  FX = FNUC + FNUC
  SHEAR(I) = W *R/GAP
  X(I) = TOO /(2.*3.1415*(R**3))
  Y(I) = FN / (3.1415*R**2)
  UI(I) = ALOG(X(I))
  VI(I) = ALOG(Y(I))
  Z(I) = ALOG(SHEAR(I))
IF(FNCH<.0001) 13+13+14
13 PSIZ(I) = 0.
  GO TO 99
14 PSIZ(I) = 1.
99 CONTINUE
DO 77 J = 1, NDATA
  SUMU=0.
  SUMV=0.
  SUMZ=0.
  SUMV2 = 0.
```
SUUV = 0
SUUZ = 0
SUUY = 0
SUVZ = 0
SUYY = 0
SZZ = 0

IF(j-3) 1, 2, 3, 4

1) INIT = 1
IEND = J + NFFT
MSUM = J + NFFT
GO TO 10

2) INIT = J - NFFT

3) IEND = NDATA
MSUM = NDATA - J + 3
GO TO 10

4) IEND = J + NFFT
MSUM = 5

10 CONTINUE
SUM = FLOAT(MSUM)

DO 55 K = 1, INIT, IEND
SUUV = SUUV + U(K)
SUUZ = SUUZ + Z(K)
SUUY = SUUY + U(K)*Z(K)
SUUV = SUU + U(K)**2
SUUY = SUUY + U(K)**2

55 CONTINUE
SUM = SUM + 1

50 CONTINUE
55 CONTINUE
DUDZ = (SUUV*(SUUV**2/SUM)) / (SUUV**2/SUM)
DVZ = (SUUVZ*(SUUV**2/SUM)) / (SUUVZ**2/SUM)
DTRUZ = (SUUVZ/SUM)

PSI12(J) = PSI12(J) + (S**2*(PSI12(J) + DUDZ) / 10.)
W = SHEAR + GAP / R

IF(PSI12(J)) 305, 305, 306

305 PSI12(J) = 0.
306 CONTINUE

WRITE(W,73) (VIS,J), PSI12(J), PS1, PS2

77 CONTINUE

WRITE(W,342)

342 FORMAT(1X, 8X, 'RED SHEAR', 8X, 'RED VIS', 8X, 'RED', 8X, 'PS1', 8X, 'PS2')

DO 57 J = 1, NDATA
RVis = VIS(J) / VIS0 * 10.
RSHR = SHEAR(J) * AT
RPS12 = PSI12(J) * BT / AT * AT
WRITE(W,95) RSHR, RVis, RPS12

57 CONTINUE
GO TO 101
END

PAGE 3
5) Program to compute discrete linear spectra from dynamic storage modulus

```
// FOR
*LIST SOURCE PROGRAM
*IOCS TYPE=WRITER *KEYBOARD DISK CARD 1132PRNTER PLOTTER
DIMENSION GSTD(20), TAU(20), AT(20), CVIS(20), ACOEF(20,20), FREQ(20)

1/2 DECADE WISE MODIFICATION OF GAUSS SEIDEL ITERATIVE SOLUTION OF
COMPUTE L V E SPECTRUM FROM GAUSS-SEIDEL METHOD TO SOLVE SIMUL ED.
DO 112 NSLPL = 1, 10
READ(2,1) IDCO,NDCOE,ATO
1 FORMAT(2I10,F10.0)
NDC = NDCOE * 2 - 1
READ(2,2) GSTD(J), J = 1, 8
WRITE(3,14)
14 FORMAT(1H1,15X,'L V E SPECTRUM FROM GS TO DVIS AND GS 1/2
*DECAY WISE ATI AND GS DV ')
READ(2,2) GSTD(J), J = 9, NDC
2 FORMAT(8F9.0)
DO 107 I = 1, NDC
TAU(I) = 10.0 *(FLOA(T(I))/2.0 - FLOA(IDCO))
FREQ(I) = 1.0 / TAU(I)
AT(I) = ATO
TAU(I) = 1.0 / FREQ(I)
107 CONTINUE
DO 106 I = 1, NDC
DO 105 J = 1, NDC
ACOEF(I,J) = TAU(I)**2 * FREQ(J)**2 / (1.0 + FREQ(J)**2 * TAU(I)**2)
105 CONTINUE
106 CONTINUE
DO 100 ITRN = 1, 20
DO 101 J = 1, NDC
ASUM = 0.0
DO 102 I = 1, NDC
ASUM = ASUM + AT(I) * ACOEF(I,J)
102 CONTINUE
ASUM = ASUM - AT(J) * ACOEF(J,J)
AT(J) = GSTD(J) - ASUM / ACOEF(J,J)
101 CONTINUE
C *************** CONSTRAINT = 1 ALL AT POSITIVE OR ZERO ***************
IF(AT(J)) .GT. 200, 201, 201
200 AT(J) = 0.0
201 CONTINUE
100 CONTINUE
C ********** NO CONSTRAINT OF ZERO VIS **********
20 CONTINUE
DO 103 J = 1, NDC
CVIS(J) = 0.0
GSTR(J) = 0.0
DO 104 I = 1, NDC
GSTR(J) = GSTR(J) + AT(I) * ACOEF(I,J)
CVIS(J) = CVIS(J) + AT(I) * ACOEF(I,J)
104 CONTINUE
103 CONTINUE
DFGS = 0.0
DO 109 J = 1, NDC
DFGS = DFGS + GSTR(J) / GSTD(J)
109 CONTINUE
C IF (DFGS .LT. 0.0) 110, 110, 111
111 WRITE(3,11) DFGS
11 FORMAT(F20.3)
100 CONTINUE
110 CONTINUE
```
DO 119 J=1,NDCD
  WRITE(3,10) GSTD(J),GSTR(J),CVIS(J),AT(J),TAU(J),FREQ(J)
10 FORMAT(/10X,6E12.3)
113 CONTINUE
  CALL SCALF (1.,1.,-1.,-1.,-5.)
  CALL FGRID(0, 0.,-4.,1.,6.)
  CALL FGRID(1, 6.,-4.,1.,8.)
  CALL FGRID(2, 6.,-4.,1.,6.)
  CALL FGRID(3, 0., 4.,1.,8.)
  DO 119 I=1,NDCD
119 IF (AT(I) .LE. 05.) GO TO 207
  IF (AT(I) .GE. 105.) GO TO 306
  205 PTL=ALOG(AT(I))/ALOG(10.)
  GO TO 207
  207 206 TL=ALOG(TAU(I))/ALOG(10.)
  CALL FPLOT(-2,ATL,TL)
  CALL POINT(1)
  CALL FPLOT( 1,ATL,TL)
119 CONTINUE
  CALL FPLOT(-2,ATL,-5.)
  CALL SCALF (1.,1.,-1.,-1.,-5.)
  CALL FGRID(0, 0.,-4.,1.,6.)
  CALL FGRID(1, 6.,-4.,1.,8.)
  CALL FGRID(2, 6.,-4.,1.,6.)
  CALL FGRID(3, 0., 4.,1.,8.)
  DO 118 I=1,NDCD
118 IF (ATL .LE. -5.) GO TO 306
  F=ALOG(FREQ(I))/ALOG(10.)*(-1.)
  CV=ALOG(CVIS(I))/ALOG(10.)
  GC=ALOG(GSTR(I))/ALOG(10.)
  GD=ALOG(GSTD(I))/ALOG(10.)
  CALL FPLOT(-2,GD,F)
  CALL POINT(0)
  CALL FPLOT( 1,GD,F)
  CALL FPLOT(-2,GC,F)
  CALL POINT(2)
  CALL FPLOT( 1,GC,F)
  CALL FPLOT(-2,CV,F)
  CALL POINT(1)
  CALL FPLOT( 1,CV,F)
118 CONTINUE
  CALL FPLOT(-2,8.,-5.)
112 CONTINUE
C GS(DATA) GS(CAL) DVIS(CAL)
END
6) Program to compute discrete linear spectrum and damping function in the modified rubber-like liquid from viscosity and dynamic viscosity

```c
// FOR
*LIST SOURCE PROGRAM
*IOCS(TYPEWTR,KEYBD,DISK,CARD,1132PRNT)

DIMENSION DVIS(20),TAU(20),AT(20),CVIS(20),ACOEF(20),FREQ(20)
*GSTR(20),PS(20),SV(15),SHR(5)

C COMPUTE L V E SPECTRUM FROM GAUSS-SEIDEL METHOD TO SOLVE SIMUL EQU.
DO 112 NSLPL=1,10
NSL=NSLPL
READ(2,1) IDCD,NDCDE,ATO
1 FORMAT(2I10,F10.0)
NDCD=NDCDE+2-1
READ(2,2)(DVIS(J),J=1,8)
 READ(2,2)(DVIS(J)+J=9,NDCD)
 WRITE(14,14)
15 X ' L V E SPECTRUM FROM DVIS TO DVIS AND CSS'
2 FORMAT(8F9.0)
DO 107 I=1,NDCD
TAU(I)=10.***FLOAT(I)/2.-FLOAT(IDCD))
FREQ(I)=1./TAU(I)
AT(I)=ATO
107 CONTINUE
DO 106 J=1,NDCD
ACOEF(I,J)=1./FREQ(J)**2/FREQ(I)**2/FREQ(I)
105 CONTINUE
106 CONTINUE
DO 100 ITRN=1,20
DO 101 J=1,NDCD
ASUM=0.
 DO 102 I=1,NDCD
 ASUM=ASUM+AT(I)*ACOEF(I,J)
102 CONTINUE
ASUM=ASUM+AT(J)*ACOEF(J,J)
C(J)=DVIS(J)-ASUM/ACOEF(J,J)
C
C ******** 2ND CONSTRAINT ZERO VIS VALUE OKART ***************
C
C ******** 2ND CONSTRAINT ZERO VIS VALUE OKART ***************
C
C **** ITRN 4 OR LARGEP ONLY ****
C
203 CONTINUE
VISOC=0.
AT3=0.
DO 113 J=1,NDCD
AT3=AT3+AT(J)*TAU(J)**2
VISOC=VISOC+AT(J)*TAU(J)
113 CONTINUE
ZVISR=DVIS(1)-VISOC
DO 114 J=1,NDCD
AT(J)=AT(J)+ZVISR*AT(J)*TAU(J)/AT3
114 CONTINUE
202 CONTINUE
DO 103 J=1,NDCD
CVIS(J)=0.
GSTR(J)=0.
DO 104 I=1,NDCD
CVIS(J)=CVIS(J)+AT(I)*ACOEF(I,J)
GSTR(J)=GSTR(J)+AT(I)*ACOEF(I,J)*TAU(I)
```
CONTINUE
GSTR(J)=GSTR(J)*FREQ(J)**2
CONTINUE
DFVIS=0.
DO 109 J=1,NDCD
   DFVIS=DFVIS+SORT((DVIS(J)-CVIS(J))**2)/DVIS(J)
109 CONTINUE
IF(DFVIS=.001)110,110,111
WRITE(3,11)DFVIS
11 FORMAT(F20.3)
110 CONTINUE
111 CONTINUE
   DO 115 J=1,NDCD
      WRITE(3,10)DVIS(J),CVIS(J),GSTR(J),AT(J),TAU(J),FREQ(J)
10 FORMAT(*10X,6E12.3)
115 CONTINUE
   CALL SCALF(1.,1.,-1.,1.,-5.)
   CALL FGRID(0.,0.,-1.,-1.,6.)
   CALL FGRID(1.,0.,-1.,7.,8.)
   CALL FGRID(2.,0.,-4.,1.,6.)
   CALL FGRID(3.,0.,-4.,1.,8.)
   DO 118 I=1,NDCD
      F=ALG(FREQ(I))/ALOG(10.*)**(I-1.)
      CV=ALG(CVIS(I))/ALOG(10.*)
      DV=ALG(DVIS(I))/ALOG(10.*)
      CALL FPLOT(-2.,DV,F)
      CALL POINT(0)
      CALL FPLOT(-2.,CV,F)
      CALL POINT(1)
      CALL FPLOT(1.,CV,F)
      CALL POINT(1)
   118 CONTINUE
   DO 124 I=1,NDCD
      F=ALG(FREQ(I))/ALOG(10.*)**(I-1.)
      GS=ALG(GSTR(I))/ALOG(10.*)
      CALL FPLOT(-2.,GS,F)
      CALL POINT(2)
      CALL FPLOT(1.,GS,F)
   124 CONTINUE
   CALL FPLOT(1.,-1.,-5.)
C ********** NON-LINEAR VISCOELASTICITY **********
C ********** ADJS1=3000.
C ADJS2=300.
READ(2,26)NDATA,A1,A2,A3,A4,A5,A6
26 FORMAT(1G9.3)
WRITE(3,28)A1,A2,A3,A4,A5,A6
28 FORMAT(/,15X,9A3,/)WRITE(3,27)A1,A2,A3,A4,A5,A6
27 FORMAT(/,1H1,*/15X,9A3,/)READ(2,25)
(SHR(IN)+IN=1,NDATA),(SVISD(IN)+IN=1,NDATA)
SHR1=SHR(1)
SHR2=SHR(3)
25 FORMAT(7F10.0)
21 FORMAT(/,3F10.2,/)EN1=.5
EN2=.05
F1=.5
WRITE(3,16)
16 FORMAT(15X, 'NON-LINEAR DUMPING FUNCTION OF LAU.\n IN WAGNER,\n *S MODIFIED RUBBER-LIKE LIQUID MODEL',\n *' ITERATION: TO COMPUTE N1,N2, SVIS1,SVIS2, DEN1, DEN2,\n *K, F11, F1, SV21, SV22', '//'\n) DO 116 I=1,20
 SVSI=0
 SVS2=0
 DO 117 K=1,NDCD
 SVSI=SVSI+AT(K)*TAU(K)*((1.+EN1*TAU(K)*SHR1)**(-2))*F1+(1.+EN2*TAU(K)*\n *K)*SHR1)**(-2)*F1+(1.-F1))
 SVS2=SVS2+AT(K)*TAU(K)*((1.+EN1*TAU(K)*SHR2)**(-2))*F1+(1.+EN2*TAU(K)*\n *K)*SHR2)**(-2)*F1+(1.-F1))
 117 CONTINUE
 DEN1=1./SVSI-1./SVISD(I)
 DEN2=1./SVS2-1./SVISD(3)
 EN1=EN1-DEN1*ADJS1/SHR1
 EN2=EN2-DEN2*ADJS2/SHR2
 IF(I=-4) 312,312,315
 315 CONTINUE
 SVS21=0.
 SVS22=0.
 DO 129 K=1,NDCD
 SVS21=SVS21+AT(K)*TAU(K)*((1.+EN1*TAU(K)*SHR2)**(-2))*F1+(1.+EN2*TAU(K)*\n *K)*SHR2)**(-2)*F1+(1.-F1))
 SVS22=SVS22+AT(K)*TAU(K)*((1.+EN1*TAU(K)*SHR2)**(-2))*F1+(1.+EN2*TAU(K)*\n *K)*SHR2)**(-2)*F1+(1.-F1))
 129 CONTINUE
 F11=(SVISD(2)-SVS22)/(SVS21-SVS22)
 IF(F11=0.01) 310,310,311
 310 F11=0.01
 311 IF(F11=-99) 314,314,313
 313 F11=-99
 314 CONTINUE
 F1=(F1+F11)/2.
 312 CONTINUE
 WRITE(3,15) SVSI,SVS2,EN1,EN2,F11,F1,SVS21,SVS22
 15 FORMAT(10E9.2)
 116 CONTINUE
 302 CONTINUE
 WRITE(3,17) SHR, VIS, N1/2)
 17 FORMAT(//, 'SHR', VIS, N1/2)
 DO 120 I=1,NDCD
 PSI=0.
 DO 121 K=1,NDCD
 SVIS=SVIS+AT(K)*TAU(K)*((1.+EN1*TAU(K)*FREQ(I))**(-2))*F1+(1.+EN2*\n *TAU(K)*FREQ(I))**(-2)*F1+(1.-F1))
 C PSI ACTUALLY A NSI
 PSI=PSI+AT(K)*TAU(K)**2*(((1.+EN1*FREQ(I)*TAU(K))**(-3))*F1+(1.+EN2*\n *FREQ(I)*TAU(K))**(-3)*F1+(1.-F1))
 121 CONTINUE
 PSI=PSI+FREQ(I)**2
 SV(I)=ALOG(SVIS)/ALOG(10.)
 PS(I)=ALOG(PSI)/ALOG(10.)
 WRITE(3,18) FREQ(I),SVIS,PSI
 18 FORMAT(//,6E15.2)
 120 CONTINUE
 DO 122 I=1,NDCD
 F=ALOG(FREQ(I))/ALOG(10.)*(-1.)
 CALL FPLT(-2.,SV(I),F)
 CALL POINT(3)
CALL FPLCT( 1, SV(I)+F)
122 CONTINUE
DO 123 I=1, NDCD
   F=ALOG(FREQ(I))/ALOG(10.)*(-1.)
   CALL FPLCT(-2, PS(I)+F)
   CALL POINT(5)
   CALL FPLCT( 1, PS(I)+F)
123 CONTINUE
   CALL FPLCT( 1,-1.,-5.)
301 CONTINUE
   WRITE(3,19)EN1,EN2,F1,SHR1,SHR(2),SHR(3),SVISD(1),SVISD(2),SVISD(3)
*     WRITE(3,25) ADJS1, ADJS2
19 FORMAT(///
      N1, N2, F1, SHR1, SHR2, SHR3, SVIS1, SVIS2, SVI
      *S3, ADJS1, ADJS2
*     *2E10.2,F10.4,3F8.1,3F8.2,2F8.0)
   CALL FPLCT(1,7.,-5.)
112 CONTINUE
   END
7) Program to compute the Segalman kernel function from parameters of the modified Carreau equation.

```fortran
// FOR
*LIST SOURCE PROGRAM
*IOCS(TYPEWRITER,KEYBOARD,DISK,CARD,1132PRINTER)
C RELAXATION MODULUS BY SEGALMAN EQ.
  1 FORMAT(F20.4,E20.3,F34.3,F20.3)
  2 FORMAT(3F10.3)
  6 FORMAT(//,1X,SEGALMAN EQ G(S) RELAXATION MODULUS FROM RMS',//)
  "ZERO VIS=",F6.0," N=",F7.4," LAMDA=",F7.4,"//")
  4 READ(2,2) VIS0,EN,RAMDA
  IF(VIS0) 3,3,5
  3 STOP
  5 WRITE(3,6) VIS0,EN,RAMDA
  DO 100 I=1,50
   S=10.**(I*2.-5.)
   CALL GAM(A(I-1,EN,GX,IR))
   GS= VIS0/RAMDA/GX*(RAMDA/S)** EN /EXP(S/RAMDA)
   SLOG=I*2.-5.
   GSLOG=ALOG(GS)/ALOG(10.)
  100 WRITE(3,1) S,GS, SLOG,GSLOG
  GO TO 4
END

FEATURES SUPPORTED
IOCS

CORE REQUIREMENTS FOR COMMON O VARIABLES 34 PROGRAM 232
8) Program to plot dynamic viscosity on double logarithmic scale computed from the Segalman kernel

// FOR
*LIVE SOURCE PROGRAM
*IOCS(TYPE=FILE,KEYBOARD,DISK,CARD,1132PRINTER,PLTTER)
*DIMENSION X(50),Y(50),YC(50),Z(50)
*COMMON NDATA,TEMP,IPNT,X,Y,YC,Z,MODE
C 74 4 21
C 12 FORMAT(3F10.3)
C 6 FORMAT(/'SEGALMAN EO G(S) DVIS FROM SEGALMAN EO BY PARAMET')
C 3 *FRES FROM EXP. TO COMPAIR EXP DVIS GIV'/,
C 1' ZERO VIS='F5.0,' N='F7.4,' LAMDA='F5.2,' D='F5.2,' E='F5.2,' F='F5.2,' S='F5.2,' GSP=',/
C 7 FORMAT(3E13.3)
C 4 READ(2,12)VIS0,EN,RAMDA
C 3 READ(2,12) A,B,C
C 3 IF(VIS0) 3,3,5
C 3 STOP
C 5 WRITE(3,6) VIS0,EN,RAMDA,A,B,C
C 3 CALL GAMMA(1.,-EN,GX1,IER)
C 3 CALL GAMMA(1.-A*EN,GX2,IER)
C 3 CALL GAMMA(1.-B*EN,GX3,IER)
C 3 CALL GAMMA(1.-C*EN,GX4,IER)
C 3 DO 100 I=1,50
C 10 FREQ=10.**(I-1.)
C 3 CDVIS=VIS0*(1.+RAMDA**FREQ)**2*(((EN-1.)/2.)**2)
C 5 DVIS=CDVIS*DOS((1.-FN)*ATAN(RAMDA*FREQ))
C 3 FRLG=I**(1.-1.)
C 3 CDVLG=ALOG(CDVIS)/ALOG(10.)
C 3 DVLG=ALOG(DVIS)/ALOG(10.)
C 3 X(I)=FRLG
C 3 FR=FREQ*RAMDA
C 3 FR2=FREQ**2*RAMDA**2
C 3 VF1=VIS0*RAMDA**2*2.*GXB*GXB/GXC/GX1/(FR2+FR**2)**2*(((1.-A*EN)**2)/(FR2+B**2)**2*(((1.-B*EN)**2)/(FR2+C**2)**2*(((1.-C*EN)**2)/2.)**2)
C 3 P=(1.-A*EN)*ATAN(FR/AF)
C 3 Q=(1.-B*EN)*ATAN(FR/B)
C 3 R=(1.-C*EN)*ATAN(FRC/C)
C 3 VDI=CSQ(P-Q*R)*VF1*FREQ**2
C 3 SVIS=UVIS+VDIF
C 3 SVLOG=ALOG(SVIS)/ALOG(10.)
C 10 GSTR= .(FR2+1.)**2*(((EN-1.)/2.)*SIN((1.-EN)*ATAN(FR)))*VIS0*FREQ
C 10 GSTR= .(FR2+1.)**2*(((EN-1.)/2.)*SIN((1.-EN)*ATAN(FR)))*VIS0*FREQ
C 3 IF(Y(I)>8,106,106+107)
C 106 Y(I)=.7
C 107 IF(SVLOG+.8,104,104+.105)
C 104 YC(I)=.7
C 105 YC(I)=SVLOG
C 108 CONTINUE
C 108 CUVIS=SQRT(DVIS**2*(GSTR/FREQ)**2)
C 108 Z(I)=ALOG(CUVIS)/ALOG(10.)
C 108 IF(Z(I)>7,111,111+112)
C 111 Z(I)=.7
C 112 CONTINUE
C 10 CONTINUE WRITE(3,7)FREQ,CDVIS,DVIS,VDIF,SVIS,GSTR,COVIS,QR
C 100 CONTINUE
C 100 IPNT=0
CALL PLT4.
IPNT=4
CALL PLT5
CALL SCALF(1.5,1.5,-6,-8)
CALL FGRID(0,-4,0,1,8)
CALL FGRID(1,4,0,1,6)
CALL FGRID(2,4,6,1,6)
CALL FGRID(3,-4,6,1,6)
CALL FPLT(-2,6,-8)
GO TO 4
END
9) Program to compute G(s) in the Goddard expansion by numerical integration from dynamic viscosity

```
// FOR
*LIST SOURCE PROGRAM
*I0CS* TYPEWRITER* KEYBOARD* DISK* CARD* 1132 PRINTER* PLOTTER
CALL SCALE(1.5*1.5*1.5*3.3*3.3)
CALL FGRID(0.1*4.1*3.5*1.3)
CALL FGRID(0.2*2.3*3.3*1.3)
CALL FGRID(0.1*2.3*3.3*1.3)
DO 102 K=1,120
   READ(2,1) VISQ, ENS, RAMS, AS, END, RAD, AD, A1, A2
   WRITE(3,2) VISQ, ENS, RAMS, AS, END, RAD, AD, A1, A2
1 FORMAT(7F10.0,2A4)
2 FORMAT(7E10.2,2A4)
   DO 101 J=1,10
      S=10.**((FLOOR(J)-15.1)/5.)
      IF(J<5)60,60,61
60 CONTINUE
   MAXX=1000
   DX=0.02
   A=FLOAT(MAXX)*DX/2.*(-1.)
   XMAX=A+DX*MAXX
   XMIN=A
   SUMV=0.
   CARPV=0.
   SUME=0.
   CAREP=0.
   DO 120 I=1,XMAX
      A=A+DX
      FREQ=EXP(A)
      CARV=FREQ*COS(FREQ*S)*(1.0+RAMS**AS+FREQ**AS)**((ENS-1.0)/AS)
      SUMV=SUMV+(CARV+CARPV)/2.*DX
      CARV=CARPV
120 CONTINUE
   GIDV=2./3.1415*SUMV*VISQ
   GO TO 121
61 IF(J<15)62,62,63
62 NMAX=4
   IMAX=500
   GO TO 64
63 IMAX=200
   NMAX=10
64 CONTINUE
   DX=3.1415/S/IMAX
   SUMI=0.
   DO 100 I=1,IMAX
      FREQ=I*DX
      SUMI=0.
      DO 103 N=1,NMAX
         SUMI=SUMI+(1.0+(RAMS**AS+FREQ**AS)**((ENS-1.0)/AS))
103 CONTINUE
      SUMI=SUMI+COS(S*FREQ)*SUMI*DX
100 CONTINUE
   GIDV=SUMI*2./3.1415*VISQ
   IF(GIDV < 98.99)100,99,99
3 FORMAT(E50.3,E20.3)
99 CONTINUE
```
121 CONTINUE
   WRITE(3,3) S, G1DV
   X = ALOG(S)/ALOG(10.)
   Y = ALOG(G1DV)/ALOG(10.)
   Y = Y - 2.
   IF(Y > 3.4) GO TO 800, 801, 901.
800 Y = -3.4
801 CONTINUE
   CALL FPLOT(-2. * X, Y)
   CALL POINT(IPNT)
101 CONTINUE
99 CONTINUE
   CALL FPLOT(1., -5., -3., 5.)
102 CONTINUE
   XMIN = EXP(XMIN)
   XMAX = EXP(XMAX)
   WRITE(3,4) XMIN, XMAX, DX
4 FORMAT(/'XMIN=', 'E9.3/', 'XMAX=', 'E9.3/', 'DX=', 'E9.3/')
END
10) Program to compute steady shear viscosity by the Goddard expansion with the Segalman kernel assuming $G_{III} = G_I(s) G_I(s)$

\[ G_I(s) \]

// FOR
*LIST SOURCE PROGRAM
*ICCS(TYPEWRITER,KEYBOARD,DISK,CARD,1132PRINTER)
DIMENSION FREQ(50)
2 FORMAT(3F10.3)
3 FORMAT(6E18.3)
11 FORMAT(1G3=G1**,F6.3,**G1**,F6.3,**G1**,F6.3,/,READ(2,2) A,B,C
WRITE(13,11) A,B,C
C TRY CARREAU KERNEL BY NUMERICAL INTEGRATION UP TO GODDARD HIGH KERNELS
VISSR=ROO.
RAM2=.5
CALL GAMMA(.5,G2,IER)
SXP =0.
CXP =1.
AXP=0.
DO 101 J=1,9
FREQ(J)=10.**(J+6)/1000
SUMPS=0.
SUMCS=0.
SUMCC=0.
SUMV=0.
SUMBC=0.
SUMAC=0.
T=0.
SUMGS=0.
DO 102 K=1,3
IF(K-2)1301,302,303
301 INIT=2
IMAX=50
DT=.001
GO TO 304
302 INIT=51
IMAX=101
DT=.01
GO TO 304
303 INIT=102
IMAX=151
DT=.1
304 CONTINUE
IF(FREQ(J)=13,1305,305,306
306 DT=1./FREQ(J)/4.
INIT=2
IMAX=500
305 CONTINUE
DO 100 I=INIT,IMAX
T=T+DT
CALL BESK(T,G0,BK,IER)
AXN =2.*VISSR/ 1.7729 /RAM2/G2*BK
CXR =COS(FREQ(J)*RAM2*T)
SNX =SIN(FREQ(J)*RAM2*T)
SUMGS=SUMGS+(AXN *SNX +AXP *SXP )*RAM2/2.*DT
C
O
SUtv = SUtv + (AXN * CXN + AXP * CXP) * RAM2/2 * DT
SUtvAC = SUtvAC + (AXN * A* CXN + AXP * A* CXP) * RAM2/2 * DT
SUtvCC = SUtvCC + (AXN * C* CXN + AXP * C* CXP) * RAM2/2 * DT
SUtvCS = SUtvCS + (AXN * C* SXN + AXP * C* SXP) * RAM2/2 * DT
SUtvBC = SUtvBC + (AXN * B* CXN + AXP * B* CXP) * RAM2/2 * DT
SUtvBS = SUtvBS + (AXN * B* SXN + AXP * B* SXP) * RAM2/2 * DT

100 CONTINUE
102 CONTINUE
DVIS = SUMV
SVIS = DVIS + FREQ(J) * 2 * (SUMAC * (SUMBC * SUMCC * SUMBS * SUMCS))
DVAL = VISO / SORT (1 + FREQ(J) * 2 * RAM2 * 2)
GSTR = SUMGS * FREQ(J)
CCVIS = SORT (DVIS * 2 * SUMGS * 2)
WRITE(3, 3) FREQ(J), DVIS, DVAL, GSTR, CCVIS, SVIS

101 CONTINUE
END
Appendix 5 Mathematical Derivations

Mathematical derivations which could not be included in main chapters are shown here.
\[ \eta^# = \eta - i \frac{\dot{\eta}}{2} \psi_1 = \int_0^\infty G_I(s) e^{-i \dot{\eta}s} ds + \dot{\eta}^2 \int_0^\infty \int_0^\infty 2G_{III}(s,s',s'') \cos \dot{\eta}(s'-s'') e^{-i \dot{\eta}(s''-s'+s)} ds'' ds' ds \]

\[ \eta^# = \int_0^\infty G_I(s) e^{-i \dot{\eta}s} ds = \dot{\eta}^2 \int_0^\infty \int_0^\infty (2G_{III} \cos \dot{\eta}(s'-s'') + G_{IV} \cos \dot{\eta}(s'\!-\!s'') + i G_{IV} \sin \dot{\eta}(s'-s'')) ds'' ds' ds \]

\[ = \dot{\eta}^2 \int_0^\infty \left[ \int_0^\infty (2G_{III} + G_{IV}) \cos \dot{\eta}(s'-s'') + i G_{IV} \sin \dot{\eta}(s'-s'') \right] ds'' ds' \]

\[ \int_0^\infty G_I(s) e^{-i \dot{\eta}s} ds = (\eta - i \frac{\dot{\eta}}{2} \psi_1) - (\eta' - i \dot{\eta}' ) \mid_{\omega = \dot{\eta}} \]

\[ = (\eta - \eta') - i (\frac{\dot{\eta}}{2} \psi_1 - \eta'') \]

\[ F_{3,4} = \int_0^\infty (2G_{III} + G_{IV}) \cos \dot{\eta}(s'-s'') ds'' ds' \]

\[ F_4 = \int_0^\infty G_{IV} \sin \dot{\eta}(s'-s'') ds'' ds' \]
\[ D1 - iD2 = \int_0^\infty (F_{3,4}(s) + iF_4(s)) e^{-i\dot{\gamma}s} ds \]

\[ D1 - iD2 = \int_0^\infty \left( [F_{3,4}(s) \cos \dot{\gamma}s + F_4(s) \sin \dot{\gamma}s] \right) ds \]

\[ + i[F_4(s) \cos \dot{\gamma}s - F_{3,4}(s) \sin \dot{\gamma}s] ds \]

\[ D1 = \int_0^\infty F_{3,4}(s) \cos \dot{\gamma}s ds + \int_0^\infty F_4(s) \sin \dot{\gamma}s ds \]

\[ D2 = \int_0^\infty F_{3,4}(s) \sin \dot{\gamma}s ds - \int_0^\infty F_4(s) \cos \dot{\gamma}s ds \]

\[ D1 + iD2 = \int_0^\infty [F_{3,4}(s) - iF_4(s)] e^{+i\dot{\gamma}s} ds \]

by Fourier inversion,

\[ F_{3,4}(s) - iF_4(s) = \frac{1}{2\pi} \int_0^\infty (D1 + iD2) e^{-i\dot{\gamma}s} \, d\dot{\gamma} \]

\[ F_{3,4}(s) = \int_0^\infty \left( (2G_{III} + G_{IV}) \cos \dot{\gamma}(s'-s) \right) ds'' ds' \]

\[ = \frac{1}{2\pi} \int_0^\infty \left( \left( \frac{\eta-\eta'}{\dot{\gamma}^2} \right) \cos \dot{\gamma}s + \left( \frac{\dot{\gamma}^2 + \eta''}{\dot{\gamma}^2} \right) \sin \dot{\gamma}s \right) d\dot{\gamma} \]

\[ F_4 = \int_0^\infty G_{IV} \sin \dot{\gamma}(s'-s) ds'' ds' = \]

\[ = \frac{1}{2\pi} \int_0^\infty \left( \left( \frac{\eta-\eta'}{\dot{\gamma}^2} \right) \sin \dot{\gamma}s - \left( \frac{\dot{\gamma}^2 + \eta''}{\dot{\gamma}^2} \right) \cos \dot{\gamma}s \right) d\dot{\gamma} \]
It was not clear whether $x=0$ or $x=-\infty$

but if $x=-\infty$

\[ P_{3,4} = \frac{1}{\pi} \left( \frac{\eta-\eta'}{\dot{\gamma}^2} \right) \cos \dot{\gamma}s \, d\dot{\gamma} \]

\[ P_4(s) = \frac{1}{\pi} \left( \frac{\dot{\gamma} \psi - \eta'}{\dot{\gamma}^2} \right) \cos \dot{\gamma}s \, d\dot{\gamma} \]
A5-2 from eq. 8-43 to eq. 8-44

\[
\eta'(\omega) = \frac{\eta_0}{(\lambda \omega^2 + 1)^{1-n}} \cos^\lambda (1-n) \tan^{-1}(\lambda \omega) \text{ from Segalman kernel}
\]

\[
\frac{\eta - \eta'}{\eta^2} = \int_0^\infty 2G_{III}(s, s', s'') \cos \omega s \cos \omega (s' - s'') ds'' ds' ds
\]

and assume \( G_{III} = G_I(s)^a G_I(s')^b G_I(s'')^c, a + b + c = 1 \)

\[
G_I(s) = \frac{\eta_0 \lambda^{n-1}}{\Gamma(1-n)} (s^{-n} - s/\lambda) : \text{Segalman kernel}
\]

\[
D_1 = \frac{2 \eta_0 \lambda^{n-1}}{\Gamma(1-n)} (s^{-n} - s/\lambda)^a (s' - n_e - s'/\lambda)^b (s'' - n - s''/\lambda)^c \cos \omega s' \cos \omega s'' ds'' ds' ds
\]

\[
= \frac{2 \eta_0 \lambda^{n-1}}{\Gamma(1-n)} s^{-n} - a s/\lambda \cos \omega s ds (\int_0^\infty s^{-b} - b e^{-bs}/\lambda \cos \omega s ds')
\]

\[
\int_0^\infty s'^{-c} - c e^{-cs}/\lambda \cos \omega s' ds'' + \int_0^\infty s'^{-b} - b e^{-bs}/\lambda \sin \omega s' ds' + \int_0^\infty s'^{-c} - c e^{-cs}/\lambda \sin \omega s' ds''
\]

\[
\int_0^\infty s'^{-c} - c e^{-cs}/\lambda \sin \omega s' ds''
\]
from eq. 3.944-5 of reference (118)

\[
D_1 = \frac{\Gamma(1-an) \Gamma(1-bn) \Gamma(1-cn)}{(a^2/x^2+\omega^2)^{1-an/2} (b^2/x^2+\omega^2)^{1-bn/2} (c^2/x^2+\omega^2)^{1-cn}} \cdot \cos (1-bn) \tan^{-1}(\frac{\omega\lambda}{b}) - (1-cn) \tan^{-1}(\frac{\omega\lambda}{c})
\]

Similarly \(G_{III}=0\), \(G_{IV}=G_I(s)^d G_I(s^1)^e G_I(s^2)^f\), \(d+e+f=1\)

\[
D_1 = \frac{\Gamma(1-dn) \Gamma(1-en) \Gamma(1-fn)}{\Gamma(1-n) (d^2/x^2+\omega^2)^{1-an/2} (e^2/x^2+\omega^2)^{1-en/2} (f^2/x^2+\omega^2)^{1-fn/2}} \cdot \cos \left\{ (1-dn) \tan^{-1}(\omega\lambda/d) - (1-en) \tan^{-1}(\omega\lambda/e) + (1-fn) \tan(\omega\lambda/f) \right\}
\]
A5-3 from eq. 8-46 and 8-47 to be used in the Goddard expansion as a model of discrete spectrum

\[ G_I = a_1 \exp(-s/\lambda_1) + a_2 \exp(-s/\lambda_2) \]

\[ \eta'(\omega) = \int_0^\infty G_I(s) \cos \omega s \, ds \]

\[ = a_1 \int_0^\infty \exp(-s/\lambda_1) \cos \omega s \, ds + a_2 \int_0^\infty \exp(-s/\lambda_2) \cos \omega s \, ds \]

from eq. 3.893-2 of ref. (118)

\[ \frac{a_1 \lambda_1}{1 + \lambda_1^2 \omega^2} + \frac{a_2 \lambda_2}{1 + \lambda_2^2 \omega^2} \]

then assume \( G_{IV} = 0 \), \( G_{III} = G_I(s)^2 G_I(s')^{-2} G_I(s'') \)

\[ D_1 = \int_0^\infty \left[ a_1 \exp(-s/\lambda_1) + a_2 \exp(-s/\lambda_2) \right]^2 \cos \omega s \, ds \Rightarrow I_1 \]

\[ \cdot \left[ \int_0^\infty \left[ a_1 \exp(-s'/\lambda_1) + a_2 \exp(-s'/\lambda_2) \right]^2 \cos \omega s' \, ds' \right]^{-2} \]

\[ \cdot \left[ a_1 \exp(-s''/\lambda_1) + a_2 \exp(-s''/\lambda_2) \right] \cdot \left( \cos \omega s' \cdot \cos \omega s'' + \sin \omega s' \cdot \sin \omega s'' \right) \, ds'' \, ds' \]

\[ = I_1 \left[ \int_0^\infty \left[ a_1 \exp(-s'/\lambda_1) + a_2 \exp(-s'/\lambda_2) \right]^2 \cos \omega s' \, ds' \right] \Rightarrow I_2 \]

\[ \cdot \left[ \int_0^\infty \left[ a_1 \exp(-s''/\lambda_1) + a_2 \exp(-s''/\lambda_2) \right] \cos \omega s'' \, ds'' \right] \Rightarrow I_3 \]

\[ + \int_0^\infty \left[ a_1 \exp(-s'/\lambda_1) + a_2 \exp(-s'/\lambda_2) \right]^2 \sin \omega s' \, ds' \Rightarrow I_4 \]
\[ I_1 = \int_0^\infty \left[ a_1 \exp(-s/\lambda_1) + a_2 \exp(-s/\lambda_2) + 2a_1a_2 \exp(-s/\lambda_1-s/\lambda_2) \right] \cos \omega s \, ds \, \text{by eq. 3.893-1 and 2 of ref. (118)} \]

\[ = \frac{2a_1\lambda_1}{4+\lambda_1^2 \omega^2} + \frac{2a_2\lambda_2}{4+\lambda_2^2 \omega^2} + \frac{a_1a_2(1/\lambda_1 + 1/\lambda_2)}{(1/\lambda_1 + 1/\lambda_2)^2 + \omega^2} \]

similarly

\[ I_3 = \frac{a_1\lambda_1}{1+\lambda_1^2 \omega^2} + \frac{a_2\lambda_2}{1+\lambda_2^2 \omega^2} \]

\[ I_5 = \frac{a_1\lambda_1}{1+\omega^2 \lambda_1^2} + \frac{a_2\lambda_2}{1+\omega^2 \lambda_2^2} \]

but neither \( I_2 \) nor \( I_4 \) could be solved by analytical integrations found in ref. (118).

\[ I_2 = \int_0^\infty \frac{\cos \omega s' \, ds'}{a_1 \exp(-s'/\lambda_1)^2 + a_2 \exp(-s'/\lambda_2) + 2a_1a_2 \exp(-1/\lambda_1-1/\lambda_2)s'} \]
Appendix-6
Corrections and Errors in Rheological Measurement

Necessary corrections to the data from rheological measurements and possible errors in the measurements are discussed in this section. Corrections A6-1 - A6-3 are incorporated into the computer programs for data reduction which appear in Appendix-4.

A6-1 Negative normal force correction

In a steady shear flow experiment with the cone and plate mode or parallel plate mode of a rotary rheometer, negative normal force \( F_N \)* due to centrifugal force to sample fluid is observed at high shear rates. Equation 6-1 gives the normal force due to the centrifugal force (11). Same negative normal force exists for measurements with non-Newtonian fluids and it must be corrected from the normal stress measurements.

\[
F_N = -\frac{3\pi \eta \Omega^2 R^4}{40} \quad \text{[A6-1]}
\]

\[R: \text{ radius}\]
\[\Omega: \text{ angular velocity}\]

*Normal force which pushes the upper and lower plates (or a plate and a cone) apart is called positive. Negative normal force pulls two plates together.
Equation A6-1 is applicable for both the cone and plate mode and the parallel plate mode steady shear flow and is not affected by gap or cone angle. Equation A6-1 was examined experimentally with glycerin and with polydimethylsiloxane oil (Dow Corning DC710) both of which are apparently Newtonian fluids. Steady shear flow measurements were performed with the cone and plate model and with the parallel plate mode of the Rheometers Mechanical Spectrometer.

Figure A6-1 shows the observed normal force measurements with the parallel plate mode with various gap as well as with the cone and plate mode. In the case of the parallel plate steady shear flow, larger than theoretical value of negative normal force was observed in Fig. A6-1 for small gaps like 800μ and 500μ. If gap is wide enough (1500μ) observed negative normal force is equal to theoretical value from eq. A6-1 and equal to the negative normal force observed with the cone and plate steady shear flow.

Figure A6-2 shows negative normal forces with DC710 fluid with the cone and plate steady shear flow and with the parallel plate steady shear flow of the Mechanical Spectrometer. Similar to the observation with glycerin, DC710 showed larger than theoretical negative normal force for a small gap, 800μ but a good agreement with theoretical value for a large gap of 1400μ. The cone and plate mode (R=3.6cm and φ=0.04 rad.) resulted in an error of larger than theoretical negative normal force at low shear rate similar to small gap parallel plate mode.

Figure A6-3 shows viscosity measurements of glycerin and DC710
Fig. A6-1 Negative normal force measurement
sample: Glycerin, radius = 3.6 cm, cone angle = 0.04 rad
Fig. A6-2 Negative normal force measurement
sample: Polydimethylsiloxane oil, radius = 3.6 cm
cone angle = 0.04 rad
Fig. A6-3 Steady shear viscosity of Newtonian fluids
fluid to show that these liquids behaved as Newtonian over the shear rates used in these negative normal force observation. As a conclusion, eq. A6-1 is good for the parallel plate steady shear flow and the cone and plate steady shear flow if gap is wide (larger than 1.5mm for our sample solutions and fixtures) or shear rate is large which was usually satisfied for steady shear measurements of polystyrene solutions and melts in this study. Normal stress was corrected for all of our cone and plate mode and parallel plate mode measurements with eq. A6-1 and eq. A6-2

\[ F_z(\text{real}) = F_z(\text{measured}) - F_N \]  

[A6-2]

A6-2 Correction for thermal expansion

A forced convection oven which surrounds sample fluid, an upper fixture and a lower fixture is used for the Rheometrics Mechanical Spectrometer to control the temperature of measurement. As shown in Fig. A6-4, parts of the fixtures inside the oven shrink or expand due to temperature change while the rest of the instrument stays at room temperature. As a result, the gap shrinks at higher than room temperature and expands at lower than room temperature.

We knew from our experimental measurements that thermal expansion constant is

\[ 1.0 \times 10^{-3} \text{ mm./°C between -5 to 250° C or} \]

within the temperature range of our experiment. The thermal expansion correction was used to correct the gaps of ERD, parallel plate and cone and plate mode measurements with the Mechanical Spectrometer.
Fig. A6-4  Effect of thermal expansion to the gap between plates
An alternative way of thermal expansion correction without knowing the thermal expansion coefficient may be done by adjusting the gap at measurement temperature. If temperature change during measurement is required, which was often the case to study temperature dependence of rheological properties for the time-temperature superposition, the alternative method results in the additional trouble of removing the sample and cleaning up the gap for each temperature and we recommend the use of thermal expansion coefficient.

A6-3 Instrument Compliance Correction

In the ERD measurements with the Mechanical Spectrometer, if the sample is rigid, large X- and Y- directional forces act on the instrument and tilt upper and lower plates. The geometry, as a result, becomes different from the one in the absence of X- and Y- directional forces with accurate parallelness between plates and designated offset between two rotating axis. Necessary correction has been developed by Macosko and Davis (81). We measured X- and Y- directional compliances, $K_x$, $K_y$, of our Mechanical Spectrometer necessary for the correction. They are

\[ K_x = 3.39 \times 10^{-6} \text{ m/N} \]
\[ K_y = 2.50 \times 10^{-6} \text{ m/N} \]

The equations for corrections are (81)

\[ \frac{n'_m}{n'_t} = \frac{(1-K_y G'_m A/h)^2 + (K_x G'_m A/h)^2}{1-G'_m (K_x-K_y)^2 A/h} \]  

\[ \text{[A6-3]} \]
\[
G'_m = \frac{(1-K_y G'_m A/h)^2 + (K_x \Omega^2 n'_m A/h)^2}{1-K_y G'_m A/h - K_x \Omega^2 n'_m A/h / G'_m}
\quad [A6-4]
\]

- \(n'_m\) dynamic viscosity, without correction
- \(n'_t\) dynamic viscosity, real
- \(G'_m\) dynamic storage modulus, without correction
- \(G'_t\) dynamic storage modulus, real
- \(\Omega\) angular velocity
- \(A/h\) amplitude of strain

Macosko et al. gave a criterion \(G'\), measured > \(2\times10^4\) Pa in which range of \(G'\) these corrections are beyond ±3% of \(G'\) which is the magnitude of experimental error (81). This criterion was not applicable for many of our samples but the corrections were included in our computer program (see Appendix 4) and corrected for all data from ERD mode to avoid unnecessary confusion.

A6-4 Errors from temperature gradient inside sample and errors of temperature measurement

Fig. A6-5a shows the top view and the side view of the settings for the cone and plate steady shear flow measurements inside the air convection oven of the Mechanical Spectrometer. Temperature of experiment is controlled by a thermocouple inside the oven upstream from the cone and the plate fixtures. In our EC-1000 oven shown in Fig. A6-5b strong air flow directly blows the sample and the fixtures.
Air temperature is controlled as good as ±0.5° C.

Major errors were caused by 1) errors in temperature measurement and 2) temperature gradient inside sample liquid.

Sample temperature is measured by a thermo couple in a stainless steel protective tube which is in contact with the back side of the center of the cone (or the upper plate) as shown in Fig. A6-5*.

As shown in Fig. A6-5, there are four windows in the wall that connects the cone (or plate) to the drive shaft. Depending on the location of the window, air either blows directly to the thermocouple tube (Fig. A6-6(a)) or air is blocked by the wall and blows indirectly (Fig. A6-6(b)). If the temperatuer of the oven is significantly higher than room temperature, the cone or the plate upper fixture, thermocouple tube, and the drive shaft work as effective heat sinks. As a result, temperature indication which is the local temperature at the tip of the thermocouple is high for case (b) and low for case (a). Fig. A6-7 shows the different temperature indication for the cone and plate mode without sample liquid for the cases

*For the Instron 3250, the thermocouple is imbedded in the lower fixture and wire is hooked to the lower fixture. This eliminates error from the bad content between the thermocouple and the fixture but does not help to prevent other causes of errors. A serious drawback is that lower fixture (plate) cannot rotate, that is, temperature measurement in the ERD mode is impossible. Also, the wire hook up to the lower fixture which is connected to the free transducer may cause noise for very sensitive measurements.
Fig. A6-5(a) Temperature control and measurement of sample liquid in cone and plate mode of the Mechanical Spectrometer
Fig. A6-5(b) Top section of the environmental chamber EC-1000 of the Rheometrics Mechanical Spectrometer

(a) wind blocked

(b) wind blow directly

Fig. A6-6 Relationship between thermocouple and side walls of cone/plate upper fixture
Fig. A6-7 Difference in temperature indication depending wind blow to the thermocouple; cone and plate without sample fluid
of (a) wind is blocked by the wall, (b) wind blows directly through the window to thermocouple and (c) upper fixture is rotating and air flow is partly blocked.

Temperature indications are different by 4-9° C and the difference is larger for higher temperatures. In our study of undiluted polystyrene, temperature indication with the upper fixture rotating is used as measurement temperature. Temperature gradient inside sample liquid causes error. As mentioned earlier both upper and lower fixtures are made of stainless steel and act as heat sinks at elevated temperatures. Heat is transferred to sample fluid from air through the surface between air and sample and then transferred to metal plates (or a cone). As a result temperature gradient exists inside sample liquid.

Local temperature measurements with an exposed thermocouple dipped into sample liquid showed that sample temperature is highest at (2 in Fig. A6-7) the rim directly facing hot air flow and lowest at the smallest gap between the cone and the plate (1 in Fig. A6-5). Fig. A6-8 shows local sample temperature measured at 1 and 2 as well as temperature indications under the same conditions as in Fig. A6-7 with the cone and plate mode filled with polystyrene (Styron) melt, as functions of temperature settings.

In Fig. A6-8, it was observed that the temperature gradient inside sample fluid is larger if temperature is higher, and the average sample temperature is between the temperature indications with air blocked (Fig. A6-6(a)) and the indication with upper fixture rotating.
Fig. A6-8 Actual sample temperature and temperature indications in cone and plate mode of the Mechanical Spectrometer.
This large temperature gradient is one of the reasons why large error is expected for the study of temperature dependent rheological properties of polystyrene melts which are very temperature sensitive. Such study is not suitable for the Mechanical Spectrometer or any other commercially available rotary rheometer we know of.

Note that current models of the Mechanical Spectrometer are equipped with a modified air convection oven with slower and indirect air flow. The error with temperature measurement is probably reduced appreciably. However, the error caused by the temperature gradient is unaffected by the modification. The Instron 3250 rotary rheometer is equipped with a radiant type oven which eliminated air flow and turbulence caused by air flow. However, the error from temperature gradient is expected to be more serious than air convection oven because of reduced heat flux into sample fluid.
A6-5 Errors from shear fracture

As briefly discussed in Chapter 3 and Chapter 4, shear fracture which accompanies almost all high shear rate measurements with a rotary rheometer constitutes a serious source of error. Fig. A6-9 shows an ideal free surface in a cone and plate rheometer. During very low shear rate flow measurement this ideal spherical surface is preserved. But as shear rate increases stripes as shown in Fig. A6-10 are observed at the surface as a result of
At a still higher shear rate, sample fluids are extruded from the space between a cone and a plate and void appears inside the sample fluid as shown in Fig. A6-11. When these phenomena occur the apparent shear stress and apparent shear strain decrease because both effective surface area and effective shear rate decrease. Walters (RHY) has shown a representative form of shear fracture which appeared in Fig. 3-1.

Shear fracture has been studied extensively by Hutton (29). He proposed an energy criterion critical first normal stress difference \( (N_1)_c \) Eq. A6-5 is for the cone and plate geometry for the occurrence of shear fracture.

\[
(N_1)_c = \frac{n' \Gamma}{R \theta_0}
\]

\( n' \): empirical factor  
\( \Gamma \): surface tension*  
\( R \): radius  
\( \theta \): cone angle
Fig. A6-9  Ideal Free Surface

Fig. A6-10  Shear Fracture at the Free Surface
Fig. A6-11  Severe Shear Fracture that results in Extrusion of Sample Fluids
critical surface tensions of polymers measured from the wettability with series of solvents are listed in ref. (78). Due to experimental errors and arbitrary choices of solvents, value of critical surface tension varies significantly. Those measurements made in the same laboratory can be seen as consistent. Measurements made by L.-H. Lee show that

\[
x \times 10^{-3} \text{ N/M}
\]

<table>
<thead>
<tr>
<th>Material</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>High density polyethylene</td>
<td>31</td>
</tr>
<tr>
<td>Low density polyethylene</td>
<td>31</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>36</td>
</tr>
<tr>
<td>Atactic polystyrene</td>
<td>36</td>
</tr>
<tr>
<td>Polybutadiene (cis or trans)</td>
<td>31-32</td>
</tr>
<tr>
<td>Polyisoprene (cis or trans)</td>
<td>30-31</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>29</td>
</tr>
</tbody>
</table>
The energy criterion in Eq. A6-9 states that shear fracture occurs beyond critical value of primary normal stress difference which is consistent with our observation with polystyrene melts and solutions.

The equation predicts that the shear rate beyond which shear fracture occurs is higher for sample solutions with high molecular weight, M, and low concentration, C, than solutions with low and high even when critical shear rate, \( \dot{\gamma}_0 \), is comparable. This is the result of the fact that zero shear rate primary normal stress \( N_1^0 \) is smaller for solutions of high M and low C than for solutions of low M and high C with comparable \( \dot{\gamma}_0 \). Fig. A6-12 shows schematic explanation of the different critical normal stresses for two different solutions. Although solution (A) has lower \( \dot{\gamma}_0 \) than solution (B) (A) has lower zero shear normal stress difference coefficient \( \psi_1^0 \). As a result solution (A) reaches critical shear rate \( (N_1)_{cr} \) at much higher shear rate than solution (B) and a wide range of power law zone can be observed with cone and plate shear flow (or parallel plate mode) while only Newtonian zone can be observed for solution (B) which has large \( \psi_1^0 \). This is consistent with the observation by Graessley et al. (68) that high shear rate steady shear measurement of power law zone with the cone and plate mode is only possible with high M, low C polyisoprene solutions.

The fact that polystyrene melts show shear fracture at lower shear rates than polyethylene melts can be explained by the difference in surface tension with Eq. A6-9. Polystyrene has a lower
Fig. A6-12 Limit of Steady Shear Measurement and Normal Stress Difference

(A) large M, small c
(B) small M, large c
surface tension than polyethylene.

As explained in Chapters 4 and 5 shear fracture is one of the causes of the apparent 'stress overshoot' phenomena observed with most high shear rate steady shear flow measurement. Fig. A6-13 shows one such example with polystyrene melt (Styron). Shear rate, $\dot{\gamma}$, is increased step wise. With $\dot{\gamma} = 0.1 \text{ (S-1)}$ torque which is proportional to shear stress $\tau_{12}$ increased rapidly and went through maximum in less than 5 seconds. In 30 ~ 45 seconds shear stress reached an apparently constant value. This shear rate, shear fracture at the free surface of polymer (stripe) is observed. When $\dot{\gamma} = 0.16$ constant value of shear stress is some 60% of maximum and serious shear fracture started. If $\dot{\gamma}$ is still higher, $\dot{\gamma} = 0.25$, shear fracture is catastrophic, and the torque does not reach a constant but rather starts increasing and so called 'rolling' or 'milling' of flow units of polymer is observed rather than uniform steady shear flow.

We want to emphasize the importance of surface observation during the steady shear flow measurement especially at high shear rates at which apparent 'stress overshoot' is observed. If the surface of polymeric liquid stayed ideally spherical, it is safe to assume the stress overshoot recorded on the chart is a real phenomenon. For most of polymeric melts and concentrated solutions this was not the case.
Fig. A6-13 Apparent Stress Overshoot or Shear Fracture in Cone and Plate Mode Sample: Undiluted Polystyrene 160°C Cone Angle = 0.1 rad  Radius = 1.25cm Apparent Extrusion of Polystyrene started at $\dot{\gamma} = 10^{-1} \text{ s}^{-1}$
A6-6 Errors from surface irregularities other than shear fracture with a rotary rheometer

Irregularities other than shear fracture at the surface of sample fluids also cause errors in measurement. Slip between plate or cone and sample as shown in Fig. A6-12, and deformation of sample shape by centrifugal force as shown in Fig. A6-13 are mentioned in this section.

Slip at the surface between sample and plate (or cone) occurs in the steady shear flow measurement of a rotary rheometer as well as ERD measurement of a rotary rheometer when the sample is rigid or adhesion between sample and plate (or cone) is poor. Polymers with low surface energy, such as polydimethylsiloxane and polytetrafluoroethylene often show slip. The slip results in a lower than expected shear rate thus lower observed stress than it should be without slip.

In the ERD measurement at high speed rotation, deformation of sample shape as shown in Fig. A6-13, is apparent. If the viscosity of the liquid is low the sample fluid flies away in small particles because of centrifugal force. If the viscosity is sufficiently high and cohesion of the fluid is good, the sample liquid holds together rather than fly away but the shape is deformed by the centrifugal force. Effective surface area between sample and plate becomes smaller by the deformation which results in lower storage modulus, G', and loss modulus, G".
A6-6 Errors from surface irregularities other than shear fracture with a rotary rheometer

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Fig. A6-14  Separation of Sample from Plate/Cone due to Poor Adhesion

Fig. A6-15  Distortion of the Shape of Sample due to Centrifugal Force
Appendix-7

Instruments

Among the instruments for rheological measurements, rheometers not described fully in Chap. 2 are described here in detail.

A7-1 Instron rotary rheometer model 3250 (IRR)

The comparison between the Rheometrics Mechanical Spectrometer (RMS) and Instron Rotary Rheometer (IRR) has been given in Table 2-7. IRR appeared in the market several years later than RMS. The two rheometers have comparable but different performance specifications. Basic differences between the two models of rheometers are in 1) force transducer, 2) lower table parallel adjustment, and 3) drive control.

The following evaluation of IRR in comparison to RMS is based on our experience with both instruments and discussions with the rheologists at both manufacturers. The force transducer of the RMS measures torque and X-, Y- and Z- directional forces simultaneously and forces are measured at 4 points for 4 directions with 16 strain gauges. X- and Y- directional forces are measured from the tilt of the lower plate axis to S- and Y- directions (See Fig. A7-1) while Z- force is from Z- directional displacement and torque from rotational displacement of the lower plate. In computing these forces, sometimes an error called 'cross talk' appears in the torque signal. It is an effect of Z-force to T-signal. In case
Fig. A7-1 Force transducer of the Rheometrics Mechanical Spectrometer; above shows schematically the deflection due to $F_Y$. Effect of the calibration is the same. Below is the wheatstone bridge circuit used to convert the resistance changes of the strain gauges to a voltage imbalance.
of bad adjustment we have observed 2% of Z-force in torque channel as an apparent torque even though there is no real torque. This magnitude of error is significant for steady shear measurement at high shear rate when torque is small as a result of shear thinning while normal force increases at almost second power of shear rate. There is an electronic circuit to compensate the cross talk automatically and the correction may be adjusted statically whenever necessary by weights or dynamically with viscoelastic fluids.

IRR utilizes two force transducers for the different modes of measurement. The normal force and torque transducer is used for simple shear flow measurements and the orthogonal transducer which measures X- and Y-force is used for ERD measurements.

Each force is detected independently and no electronic cross talk as we saw with RMS exists with IRR. But we observed small cross talk (from Z-force to torque up to 0.1%) which is probably due to slight assymmetry of the instrument. There is no circuit to compensate this cross talk.

The parallelness between upper and lower plates can be adjusted for IRR by changing the tilting of the lower plate through the use of a hemispherical setting of the lower assembly; while for RMS the parallelness is fixed and no adjustment can be made (a certain amount of "shimmin" is possible by trial and error). IRR is probably more accurately parallel but usually does not make a difference in the results. Each time a sample is changed or transducer is changed in the IRR it is necessary to readjust parallelness which takes a
few minutes. For the sensitive transducer less than 1 kg of force may break the parallelness. Check of parallelness after measurement is necessary to make sure upper and lower plate are aligned accurately. Therefore, IRR is much more time consuming to operate and data productivity is usually far less compared to RMS.

Designers of IRR adopted digital position control to regulate angular velocity as contrasted to the analog speed control used for RMS. Digital control enabled fast start up and fast speed change to be made*. More importantly, it was anticipated that digital control made very low angular velocity (as low as $10^{-6}$ rad/s) possible compared to $10^{-3}$ rad/s of RMS. However IRR has a total of 128,000 steps (substeps) to monitor and control the position. 125 substeps are grouped into a control step. There are 1024 control steps for a revolution, and only at these 1024 control steps, speed and position are exactly adjusted to the command. At the slowest speed of $10^{-6}$ rad/s the rotating drive shaft encounters these control steps only once in every 6100 seconds (almost 2 hours!) and encounters the substeps once in every 49 seconds.

*The actual speed change depends on the acceleration of the mass of the fixtures and the drive shaft by a motor which has limited torque.
Obviously steady shear flow could not be obtained from such control at the lowest rotation rates.

The digital position control method of velocity control results in stepwise rotation rather than constant speed rotation as it should be. Schematic comparison of this is in Fig. A7-2a. The stepwise shear strain does not necessarily appear in observed stress and sometimes the error in shear rate is unnoticed as strain or shear rate of IRR are not observed directly. As shown in Fig. A7-2, polymeric material is viscoelastic and it damps some of the stepwise motion. The observed stress appears smooth and the shape is not much different from those observed with real steady shear flow.

If relaxation time is appreciably longer than the time interval between digital drive as in the case of Fig. A7-2b, the observed stress appears smoother and not much different from other background noise.

Fig. A7-3 shows examples of stress measurements that show speed control errors with IRR. Fig. 7A-3(a) is with sample F1 while (b) (c) and (d)(e) is with sample A2 which has longer relaxation time than F1. In (a) and (b) at speeds about 10 or 6 times faster than the slowest, the stepwise nature of strain is apparent from the sharp peak of stress (actually torque) in the signal. Each peak corresponds to one of 128,000 steps of one revolution. In Fig. A7-3(c) beside substeps the error from control steps (1024 steps per revolution) appears as 5 sharp large peaks for both clockwise and counter clockwise rotation. Speed was $10^{-4.2}\text{rad/s}$. In Fig. A7-3(d) and (e)
Fig. A7-2a  Speed Control of Instron 3250

\[ v \text{ (rad/s)} \]

Actual (Stepwise)

Constant (Designed)

Time (s)

Fig. A7-2b Shear Stress as a Result of Stepwise Rotation of Fig. A7-1 for Two Liquids of Different Relaxation Time, \( \tau_a \), \( \tau_b \)
Fig. A7-3  Shear Stress Observed With Instron Rotary Rheometer

(a) Sample: F1
Speed: $10^{-4}$ rpm
$10^{-5}$ rad/s
Shear Rate: $1.5 \times 10^{-4}$ s$^{-1}$

(b) Sample: A2
Speed: $10^{-4.2}$ rpm
$10^{-5.2}$ rad/s
Shear Rate: $9.5 \times 10^{-5}$ s$^{-1}$
Fig. A7-3 (c)  Sample: A2
Speed: $10^{-4.2} \text{rad/s}$
Shear Rate: $9.5 \times 10^{-4}$
Fig. A7-3 (d) Sample: A2
Speed: $10^{-3.2}$ rad/s
Shear Rate: $9.5 \times 10^{-3}$ s$^{-1}$
Fig. A7-3 (e)  Sample: A2
Speed: \(10^{-2.2}\text{rad/s}\)
Shear Rate: \(9.5\times10^{-2}\text{s}^{-1}\)
in which rotational speeds are $10^{-3.2}\text{rad/s}$ and $10^{-2.2}\text{rad/s}$, the
torque signals are smooth enough to measure their magnitudes. But
oscillations resulting from the stepwise rotation is apparent. The
small magnitude of such oscillation in (e) may suggest small step-
wise rotation overlapped on steady rotation but may be a result of
damping by sample fluid or limit of recorder performance. The
magnitude of the oscillatory shear rate overlapped on the steady
shear rate could be longer than the figure suggests and needs to be
checked.

The major advantage of using a very low rotational velocity
and very low shear rate was to measure zero-shear-rate viscosity of
industrial polymers with broad molecular weight distribution. It
has often been impossible to get zero shear rate viscosity with many
commercial polyethylene or polystyrene samples with conventional
rheometers like RMS at the lowest rotational velocity. But as a
result of speed control error we found with IRR, it is only safe
to use $10^{-2}\text{rad/s}$ (200 substeps/s and 1.6 control step/s) as lowest
rotational speed. If substeps are adjusted better, $10^{-3}\text{rad/s}$ or
a little lower speed may be used. In any case it does not appear
feasible to obtain steady shear flow at $10^{-6}\text{rad/s}$ with 128,000 steps
and IRR does not offer particular advantage over RMS for low shear
rate measurements.

At any speed, special caution is required if particular rheo-
logical phenomena of interest could be affected by the superposition
of oscillation or vibration over the steady shear flow. IRR is not
appropriate for such experiments.
Fig. A7-4 Schematic Comparison between Sinusoidal Strain and Digitally Controlled Rotation to Approximate One
The error from digital control may affect sinusoidal osc
to more severely than steady shear flow. Fig. A7-4 gives an explanation of the difference between real sinusoidal osc and those by digital control. As shown in the figure de
d by sinusoidal oscillation and the deformation by digital are basically different. Further study will be necessar
treating data output from IRR sinusoidal oscillation mea
by a conventional phase analyzer to compute the apparent properties.

A7-2 Monsanto capillary rheometer

As shown in Fig. A7-5, this capillary rheometer has mechanism than Instron capillary rheometer 3211 which we our experiments and described in Chap. 2. The Monsanto rheometer is compared to the Instron 3211 in Table A7-1. difference between the two capillary rheometers comes fr that Instron 3211 is a flow rate control type. There is no advantage for Monsanto rheometer over Instron capillar and that is the reason Monsanto rheometer was not used.

Figure A7-5 shows overall mechanism of the Monsanto rheometer. A plunger is driven by air pressure (p) and meric liquid through a capillary of length, L and radius time required to travel certain length is measured by t Four measurements with four timers are possible for eac condition of the measurement is determined by the air p the choise of capillary (L, R).
Fig. A7-5  Monsanto Capillary Rheometer

pressure gauge

pressure

$P$

$N_2$

timer 1

timer 2

timer 3

timer 4

capillary

exit
To compute the shear rate from Eq. 2-10, we must know the volume flow rate, $Q$ from time measurements and the wall shear stress, $\tau_R$ from the air pressure. To plot eq. 2-12 for a fixed value of $Q/\pi R^3$ in order to obtain an end correction factor, number of runs are necessary as it is impossible to predetermine $Q$ or plunger speed.

It is not possible to know whether steady shear flow is attained and sustained during the measurement as there is no means of instantaneous observation of shear flow. With Instron capillary rheometer shear stress can be observed continuously on a chart.

As another advantage of instantaneous stress observation, Instron capillary rheometer can measure with about 10 different conditions for each run.

For accurate time measurement on the Monsanto capillary rheometer, the length of time must be above 15 sec. while polymer degradation and other errors require measurement be shorter than 10 to 15 min. Less than two decade of shear rates are possible with a capillary compared to three to four decades for force measurements with the Instron capillary rheometer.
### Table A7-1 Comparison Between Two Types of Capillary Rheometers

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<thead>
<tr>
<th></th>
<th>Instron 3211</th>
<th>Monsanto</th>
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<tbody>
<tr>
<td>Force to drive plunger</td>
<td>Measured by a force transducer, variable</td>
<td>Constant (preset)</td>
</tr>
<tr>
<td>Plunger speed</td>
<td>Constant (preset)</td>
<td>Measured by time to travel certain distance,</td>
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<tr>
<td>Plunger drive</td>
<td>Screw driven</td>
<td>Air pressure driven</td>
</tr>
<tr>
<td>Measurement</td>
<td>Force to drive plunger instantaneous observation</td>
<td>Time for a plunger to travel certain length—average volume flow rate over the time</td>
</tr>
<tr>
<td>End correction</td>
<td>Easy</td>
<td>Difficult, needs many runs</td>
</tr>
<tr>
<td>Shear rate range with</td>
<td>Wide</td>
<td>Small</td>
</tr>
<tr>
<td>single capillary</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
illary Rheometers

Kansanto

Constant (preset)

measured by time to travel certain distance,

or pressure driven

time for a plunger to travel certain length—average volume flow rate over the time

difficult, needs many runs

small