

## Dynamic Rheological Properties of Polyisobutylene

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### Synopsis

The viscoelastic properties of polyisobutylene melts were investigated as functions of temperature, molecular weight, and molecular weight distribution. The effect of molecular weight distribution was studied through the use of blends of narrow distribution polymers. The Ninomiya and Ferry theory was used successfully to predict the viscosity of the blends. It was observed that the temperature coefficient for flow was independent of molecular weight distribution and of molecular weight. It was shown, at least in the case of polyisobutylene melts, that the temperature dependence of elasticity is less for polymers with greater polydispersity.

### INTRODUCTION

The purpose was to investigate the effect of temperature, molecular weight, and molecular weight distribution on the viscoelastic properties of polymer blends. Polyisobutylenes chosen had reasonably high molecular weights and exhibited high elastic character.

### EXPERIMENTAL

All measurements were made using a Weissenberg rheogoniometer Model R-18, employing cone-and-plate geometry. The mode of deformation was in all cases oscillatory. The temperature range was 50° to 242°C, and in all experiments the sample was protected with a nitrogen atmosphere. The frequency limits and amplitude range were 0.005 to 10 sec<sup>-1</sup> and 50 to 250 microns, respectively. The amplitudes and phase angles were both found to be reproducible within ±1%. Viscosity was found to be independent of the amplitude of the applied strain. The dynamic viscosity and the storage modulus  $G'$  were calculated using the methods of Walters.<sup>1</sup>

The polymers used in this study were supplied by Imperial Oil Enterprises Limited and Polysar Limited (Table I). The blends were made by preparing approximately 5% solutions of the components in toluene, then vacuum drying to constant weight.

### RESULTS AND DISCUSSION

#### Viscous Properties

Viscosity-frequency curves for the polyisobutylenes at 160°C are shown in Figure 1.

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TABLE I  
Molecular Weights of the Polyisobutylenes and Butyl Polymers<sup>a</sup>

Polymer	Manufacturer's code	$\bar{M}_w \times 10^{-5}$	$\bar{M}_w / \bar{M}_n$	$\bar{M}_z \times 10^{-6}$
	Polyisobutylene <sup>b</sup>			
I	LM-MS	0.847	2.99	0.214
II	L-80	8.48	2.54	1.33
III	L-100	12.3 <sub>6</sub>	2.70	2.00
IV	L-120	15.0 <sub>5</sub>	2.38	2.25
	Butyl <sup>c</sup>			
V	B-100	4.25 <sub>5</sub>	4.09	0.880

<sup>a</sup> Taken from GPC analysis performed at Polysar Ltd. by the Technical Development Division, Sarnia, Ontario.

<sup>b</sup> Supplied by Imperial Oil Enterprises Limited, Sarnia, Ontario.

<sup>c</sup> Supplied by Polysar Limited, Sarnia, Ontario.

Zero shear viscosities were determined from the data using the Cross method<sup>2,3</sup> based on the following equation:

$$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + \Upsilon\omega^b} \quad (1)$$

where  $\eta_0$  and  $\eta_{\infty}$  are the limiting values of viscosity at zero and infinite shear rate, respectively,  $\Upsilon$  (a material constant) is a representative relaxation time related to  $\eta_0$ ;  $\omega$  is the frequency; and  $b$  is a curve-fitting parameter. In this case,  $b = \frac{1}{2}$ .<sup>2,3</sup> The zero shear viscosities are given in Table II.

A plot of  $\log_{10}\eta'_0$  (zero shear dynamic viscosity) versus  $\log_{10} \bar{M}_w$ , for the data, results in a line with a slope of 3.4. With the exception of polymer I, the fit to this line was very good. This is in agreement with previous work on polyisobutylene melts<sup>4,5</sup> which have resulted in values from 3.2 to 4.0 for the slope (exponent in the Bueche equation<sup>6</sup>). A relatively recent study of the

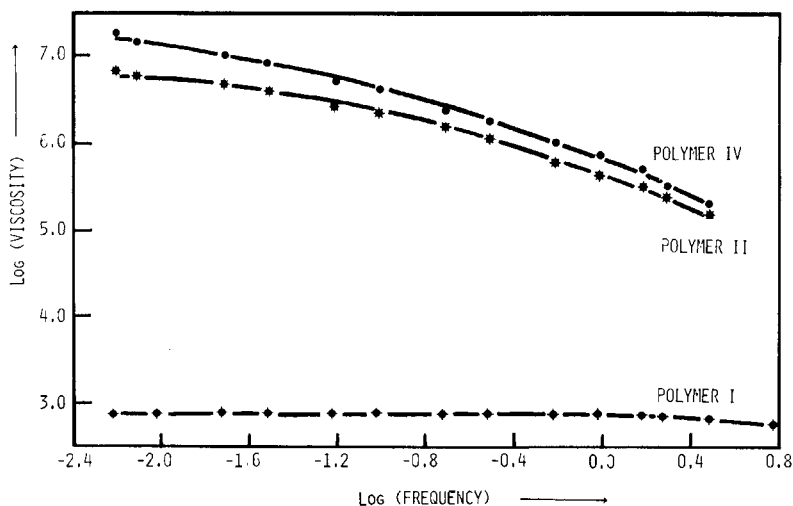


Fig. 1. Dynamic viscosity-frequency curves for the polyisobutylenes (as shown) at 160°C. Viscosity is in poises and frequency is in  $\text{sec}^{-1}$ .

TABLE II  
Viscosity Values at Zero Shear Rate for 160°C

Sample	$\log_{10} \eta'_0$ , poises
I	2.93
II	7.19
III	7.83 <sup>a</sup>
IV	8.00
V	6.16 <sup>a</sup>

<sup>a</sup> Although not included in Fig. 1, these values were obtained in the same manner.

dynamic viscosity of bulk polyisobutylene presented a value of 3.8 for this parameter.<sup>7</sup>

Polymers I, II, and IV were tested also over a range of temperatures and the zero shear viscosities determined (Table III). Arrhenius temperature coefficients of flow were calculated for the zero shear rate. Within experimental error, the values were independent of molecular weight over the molecular weight range [ $\bar{M}_w$  0.85 to  $15.0 \times 10^5$ ]. The average value is 12.8 kcal/mole. This is in very good agreement with values obtained by previous workers<sup>8</sup> from steady shear viscosity data.

The major aim was to investigate the rheological characters of blends. Blends were made using polymers I and II. It is readily apparent from Figure 2 that the addition of a small amount of the high molecular weight material to the low molecular weight species has much more effect than vice versa. Table IV gives the molecular weights and polydispersities of the blends along with the zero shear viscosities. A Ninomiya-Ferry theoretical plot<sup>9,10</sup> is compared with the experimental results, plotting  $\log_{10} \eta'_0$  versus weight per cent of the high molecular weight species (Fig. 3). The Ninomiya-Ferry prediction for the determination of  $\eta'_0$  can be written in the form<sup>7</sup>

$$\eta_0 = W_1 \left( \frac{\bar{M}_w}{\bar{M}_{w1}} \right)^{2.4} \cdot \eta_{01} + W_2 \left( \frac{\bar{M}_w}{\bar{M}_{w2}} \right)^{2.4} \cdot \eta_{02} \quad (2)$$

TABLE III  
Viscosity at "Zero Shear Rate"

Sample	Temperature, °C	$\log_{10} \eta'_0$ , poises
I	50	5.17 <sub>8</sub>
	74	4.50 <sub>9</sub>
	99	3.94
	121	3.53
	140	3.19 <sub>5</sub>
II	142	7.37
	174	6.95
	197	6.65
	222	6.39
	242	6.12
	IV	139
	179	7.79
	202	7.4
	222	7.13
	242	6.92

where  $\eta_0$  is the zero shear viscosity of the blend;  $\eta_{01}$  and  $\eta_{02}$  are the zero shear viscosities of components 1 and 2 with weight-average molecular weight  $\bar{M}_{w1}$  and  $\bar{M}_{w2}$ , respectively; and  $\bar{M}_w$  is the weight-average molecular weight of the blend. The agreement with experiment is better than was observed for polybutadiene blends.<sup>11</sup>

Zosel<sup>7</sup> also showed that the Ninomiya-Ferry equation gave a reasonable prediction of the viscosity of polyisobutylene blends. However, it is not possible to make any quantitative comparisons between the present study and the work of Zosel since this author did not report the polydispersities of the polymers studied.

A modified equation, which took into account the polydispersity of the materials to be blended and which was used for the polybutadiene blends,<sup>11</sup> resulted in a plot in poor agreement with the data. One possible explanation why the Ninomiya-Ferry theory fits the experimental data better here than for the polybutadiene blends is the overall distribution of the two materials in each blend. In the case of the polybutadiene blends, they were slightly more polydisperse.<sup>11</sup> The Ninomiya-Ferry theory would be expected to break down as the polydispersity of the polymers to be blended is increased.<sup>9,10</sup>

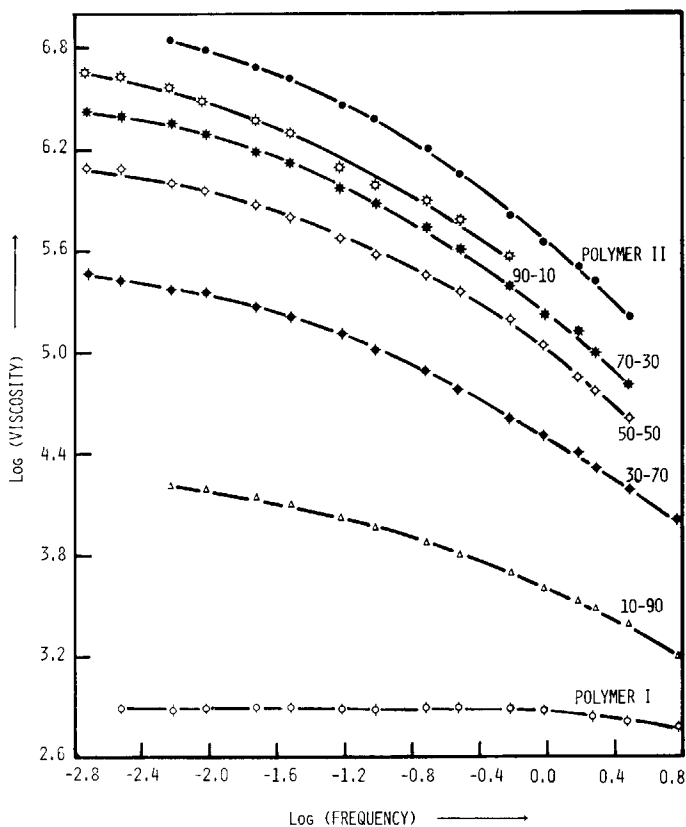


Fig. 2. Dynamic viscosity frequency plots for blends of polymers II and I at the weight percentage given. All viscosities were measured at 160°C. Viscosity is in poises and shear rate is in  $\text{sec}^{-1}$ .

TABLE IV  
Molecular Weights and Viscosity at Zero Shear for the Blends

Polymer Blend Ratio II-I	Weight-average molecular weight $\bar{M}_w \times 10^{-5}$	Polydispersity $\bar{M}_w/\bar{M}_n$	$\log_{10} \eta'_0$ , poises
0-100	0.847	2.99	2.93
10-90	1.61	5.18	4.34
30-70	3.13 <sub>9</sub>	8.02	5.62
50-50	4.76	9.14	6.15 <sub>9</sub>
70-30	6.19	7.85	6.62
90-10	7.72	4.81	6.89
100-0	8.48	2.54	7.19

The hypothesis of greater overall polydispersity also is supported by the fact that a  $\log_{10} \eta'_0$  versus  $\log_{10} \bar{M}_w$  plot for the blends of polymers I and II results in a straight line of slope 3.8. Although this slope is somewhat higher than the expected value of 3.4, it is still very acceptable in comparison with literature values. From the literature, it seems that a value higher than 3.4 is more common in cases of (i) plots over very large molecular weight ranges<sup>8</sup> and (ii) blends of monodisperse polymers.<sup>12,13</sup> It should be noted that  $\log_{10} \eta'_0$ -versus- $\log_{10} \bar{M}_w$  plots for the polybutadiene blends did not result in straight lines. One would expect the Bueche relationship to break down completely for blends of polymers exhibiting very broad molecular weight distributions. Thus, it appears that there is no need to attempt to modify the Ninomiya-Ferry theory for molecular polydispersity as long as the materials to be blended exhibit molecular weight distributions that are only relatively polydisperse. In fact, as noted above, the modified equation used in the previous work<sup>11</sup> overcompensated in this case.

Measurements at several temperatures were performed on the blends of polymers I and II. An example is the 50-50 blend (Fig. 4). Zero shear

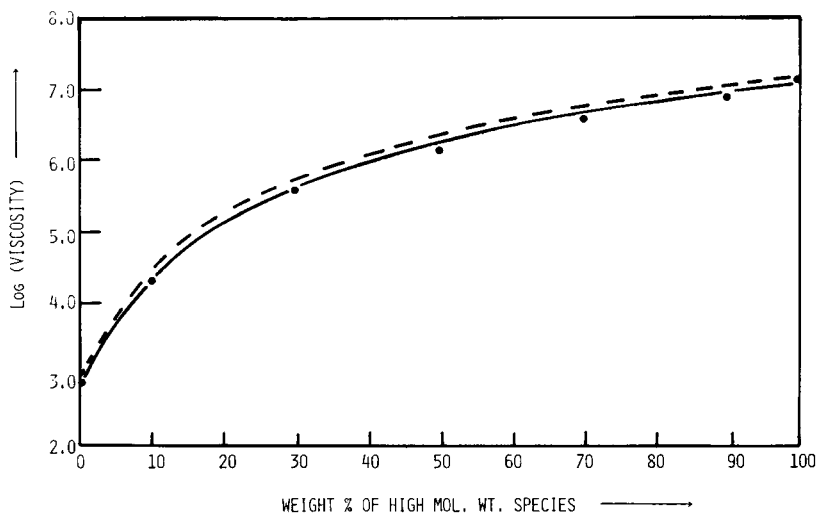


Fig. 3. Plot of  $\log_{10} \eta'_0$  (poises) vs. the weight per cent of polymer II added to polymer I. Temperature is 160°C. The dashed line is the curve predicted by the theory of Ninomiya and Ferry.

TABLE V  
Viscosity Values at Zero Shear Rate for Blends Polymers I and II

Polymer blend ratio II-I	Temperature, °C	log $\eta'_0$ , poises
10-90	115	5.0
	141	4.64 <sub>8</sub>
	160	4.34
	195	3.86
30-70	115	6.39 <sub>8</sub>
	141	5.88 <sub>6</sub>
	160	5.62
	195	5.13
50-50	116	6.86 <sub>9</sub>
	140	6.48 <sub>7</sub>
	160	6.15 <sub>9</sub>
	190	5.94
70-30	115	7.33
	141	7.07 <sub>5</sub>
	160	6.62
	195	6.23 <sub>7</sub>

viscosities also were determined by means of the Cross extrapolation (Table V). The temperature coefficient values calculated were found to be the same as for the unblended polymers, i.e., an average value of 12.7 kcal/mole. Thus, in the case of the polyisobutylenes, the zero shear temperature coefficient is apparently independent of molecular weight distribution as well as molecular weight.

On the curves for the 50-50 blend (Fig. 4), a plot for polymer V was superimposed. This polymer has approximately the same molecular weight as the 50-50 blend of polymer I and II ( $\bar{M}_w = 476,000$  for the blend and  $\bar{M}_w = 426,000$  for polymer V). However, it exhibits only about one half the polydispersity ( $\bar{M}_w/\bar{M}_n$  of 4.1 for polymer V as opposed to 9.1 for the blend). It is readily apparent that the less polydisperse sample exhibits a lower viscosity at zero shear rate and approaches Newtonian behavior more closely, that is, the decrease with increasing shear rate is less.

### Elastic Properties

From Figure 5, a plot of  $G'$  versus frequency, for blends of polymers I and II, it can be seen, as was the case for  $\eta'$  (Fig. 2), that the addition of a small amount of high molecular weight material to the low molecular weight species has much more effect than vice versa.

It should be noted that these curves exhibited a discontinuity around what will be described as the natural frequency of the system (i.e., platens and torsion head, with the polymer in place). The natural frequency was measured for only a few of the experimental conditions; and for those measured, this discontinuity did coincide with the measured natural frequency. In these cases, the data were "corrected" using a technique of Weeks and Reid,<sup>14</sup> which takes into account natural frequency. This modification did bring the data closer to the expected curve shape; but since in most cases the natural

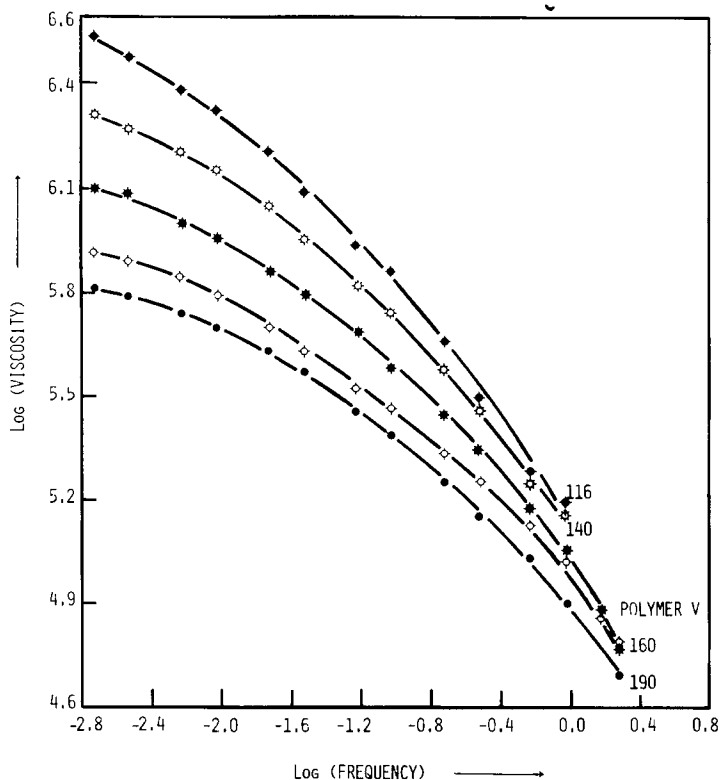


Fig. 4. Dynamic viscosity-frequency curves for the 50-50 weight per cent blend of polymers I and II at the temperatures ( $^{\circ}\text{C}$ ) shown. Superimposed on this plot is the curve for polymer V at  $160^{\circ}\text{C}$ . Viscosity is in poises and frequency is in  $\text{sec}^{-1}$  (for polymer V  $\bar{M}_w = 426,000$ ,  $\bar{M}_w/\bar{M}_n = 4.1$ ; for the 50-50 blend,  $\bar{M}_w = 476,000$ ,  $\bar{M}_w/\bar{M}_n = 9.1$ ).

frequency was not measured, this technique was not used extensively. Due to this lack of natural frequency data, no comment can be made on the validity of the "correction" technique.<sup>15</sup>

$Je^0$ , the low-frequency limit of the storage compliance, was determined as described by Prest and Porter<sup>16,17</sup> using the equation

$$J = \frac{G'}{G'^2 + G''^2} \quad (3)$$

where  $J'$  is the storage compliance,  $G'$  is the storage modulus, and  $G''$  is the loss modulus. The values were extrapolated to zero frequency to obtain  $Je^0$ .  $Je^0$  is plotted versus the weight fraction of the high molecular weight species, Figure 6. The shape of this curve is similar to that obtained by Zosel for polyisobutylene melts.<sup>7</sup>

Also shown on this graph is the  $Je$  curve calculated from a modified Rouse theory<sup>16</sup> as well as the curve determined using a theory developed by Graessley.<sup>16,18</sup>

The one feature of this plot that does not compare well with previous work<sup>7,16,17</sup> is the height of the maximum in the curve. The authors have no explanation for this; however, there is a lack of data in the important range in

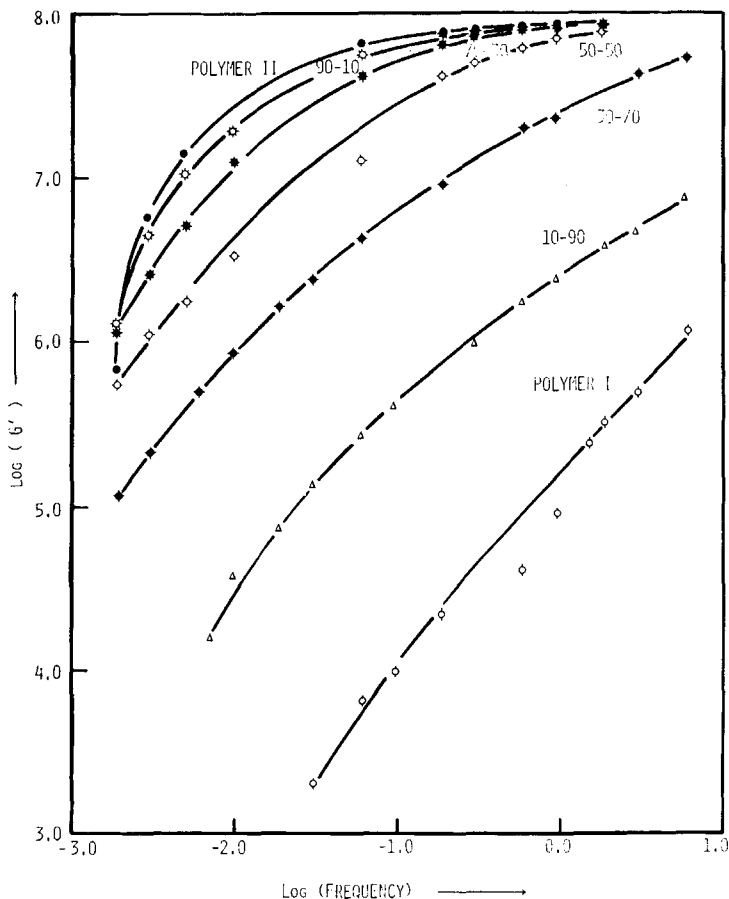


Fig. 5.  $G'$  vs. frequency plots for blends of polymers II and I at the weight percentage given.  $G'$  is in  $\text{dyne-cm}^{-2}$  and frequency is in  $\text{sec}^{-1}$ .

the present case. Noting the curve determined from the theory of Graessley, which has been shown to best represent the shape of the  $Je$  curve in this region,<sup>16</sup> it can be seen that possibly data are needed in the region at lower than 10 weight per cent of the high molecular weight species in order to show the "true" maximum.

As well, Kurata et al.<sup>19</sup> and Masuda et al.<sup>20</sup> have shown that the greater the difference between the molecular weights of the components blended, the greater the maximum in the  $Je^0$  plot. The molecular weight difference between the components is slightly less in the present paper than in the work of Zosel,<sup>7</sup> i.e., the weight-average molecular weights of the components are  $0.85 \times 10^5$  and  $8.5 \times 10^5$ , while in the work of Zosel the viscosity-average molecular weights were  $1.1 \times 10^5$  and  $13.0 \times 10^5$ .

In this present study, the authors were interested in the effect of the temperature on the  $G'$  curves with regard to molecular weight and molecular weight distribution. Figures 7, 8, and 9 are plots of  $G'$  at various temperatures for polymer II, polymer V, and 50-50 blend of polymers I and II. Comparing Figures 7 and 8, it can be seen that the lower molecular weight poly-



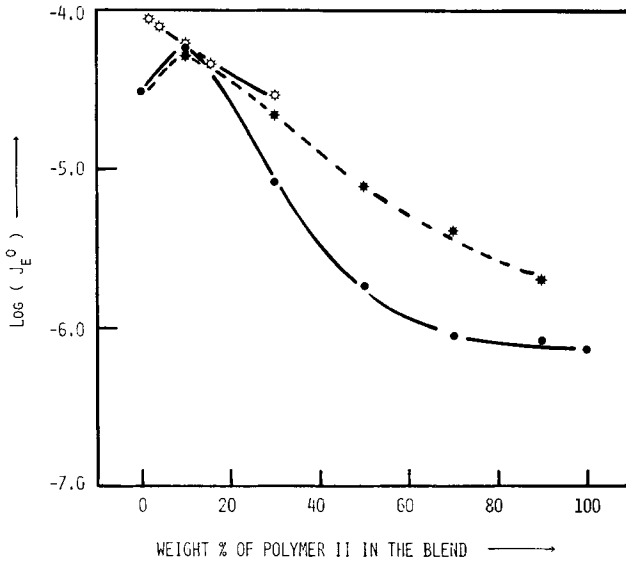


Fig. 6. Plot of  $Je^0$  [ $\text{cm}^2 \text{dyne}^{-1}$ ] vs. weight per cent of polymer II added to polymer I. Superimposed on this plot are the curves predicted using (a) a modified Rouse theory (\*), and (b) Graessley theory ( $\odot$ ).

mer, IV, exhibits a behavior more sensitive to changes in temperature than the higher molecular weight polymer, II. One possible explanation is that in polymer melts, elasticity is highly influenced by the number of "entanglements."<sup>21</sup> In the case of the high molecular weight polyisobutylenes, the "entanglements" are so great and the relaxation spectrum is so dominated by this fact that the changes due to changes in temperature are reduced. Thus, there is little or no change in the  $G'$  curve.

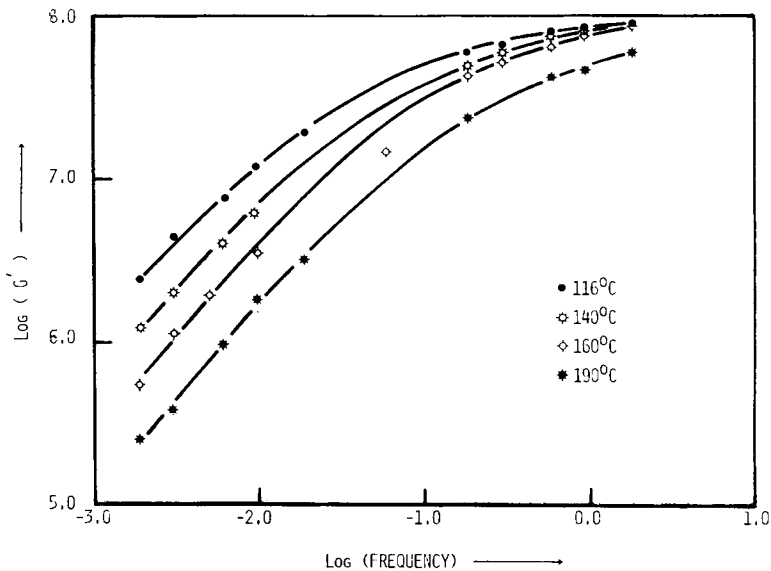


Fig. 7. Plot of  $G'$  ( $\text{dyne cm}^{-2}$ ) vs. frequency ( $\text{sec}^{-1}$ ) for polymer II at temperatures shown.

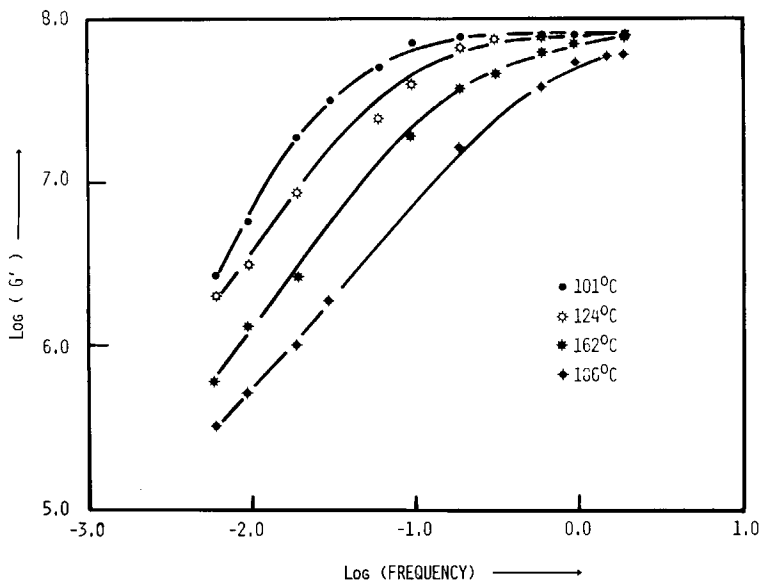


Fig. 8. Plot of  $G'$  (dyne  $\text{cm}^{-2}$ ) vs. frequency ( $\text{sec}^{-1}$ ) for polymer V at temperatures shown.

Figures 8 and 9 are for polymers exhibiting approximately the same weight-average molecular weight but having different polydispersities. It appears that the more polydisperse polymer (Fig. 9) is less temperature sensitive; this could be due to the influence of the relaxation spectrum of the high molecular weight portion of the blend. Further, the shape of the curves for the blend approximate those exhibited by the lower molecular species<sup>22</sup>; i.e., more so than the unblended polymer.

In this paper, the phase angle  $\phi$  between the stress and strain also was used

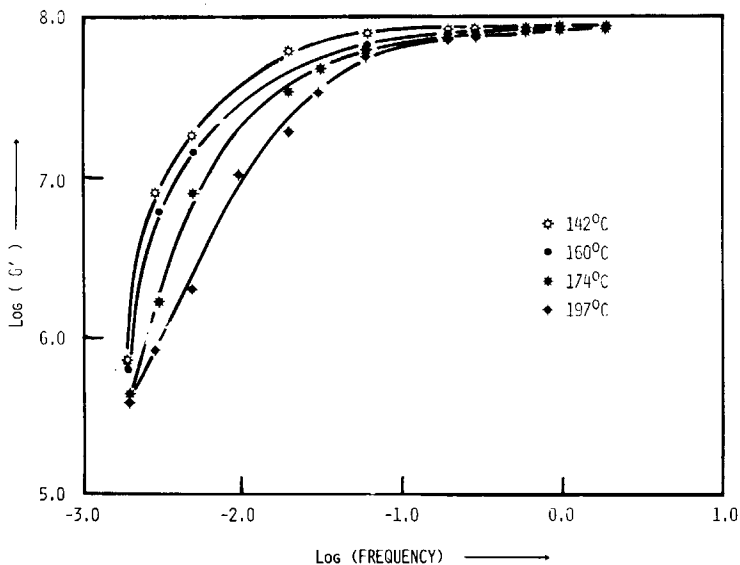


Fig. 9. Plot of  $G'$  (dyne  $\text{cm}^{-2}$ ) vs. frequency ( $\text{sec}^{-1}$ ) for the 50-50 blend of polymers I and II at temperatures shown.

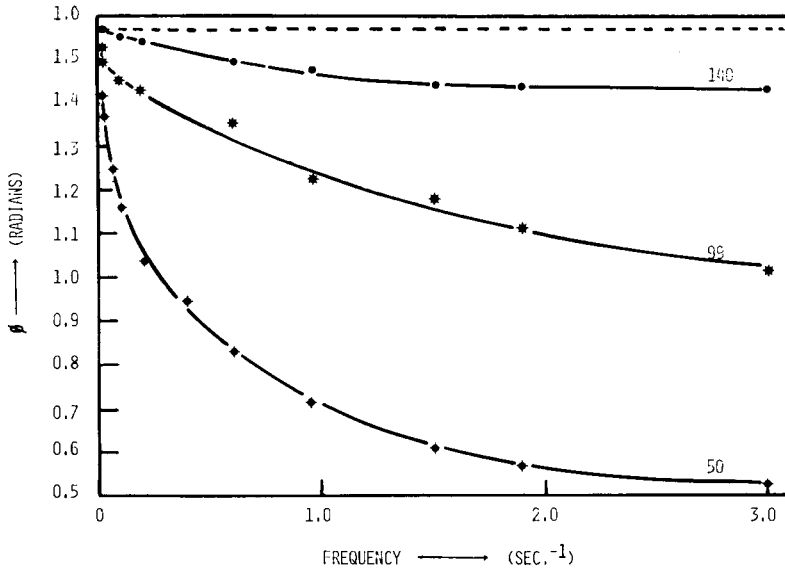


Fig. 10. Plot of phase angle (radians) vs. frequency ( $\text{sec}^{-1}$ ) at temperatures ( $^{\circ}\text{C}$ ) shown for polymer I.

to obtain a measure of elasticity.<sup>11</sup> Typical plots of the function  $\phi$  versus frequency are shown in Figure 10. All data for the polymers used in the paper were found to fit the equation

$$\phi = A[\omega\theta]^m + C \quad (4)$$

where  $C = 1.57$  radians ( $\equiv 90^{\circ}$ );  $\theta$  is a quantity having the dimensions of

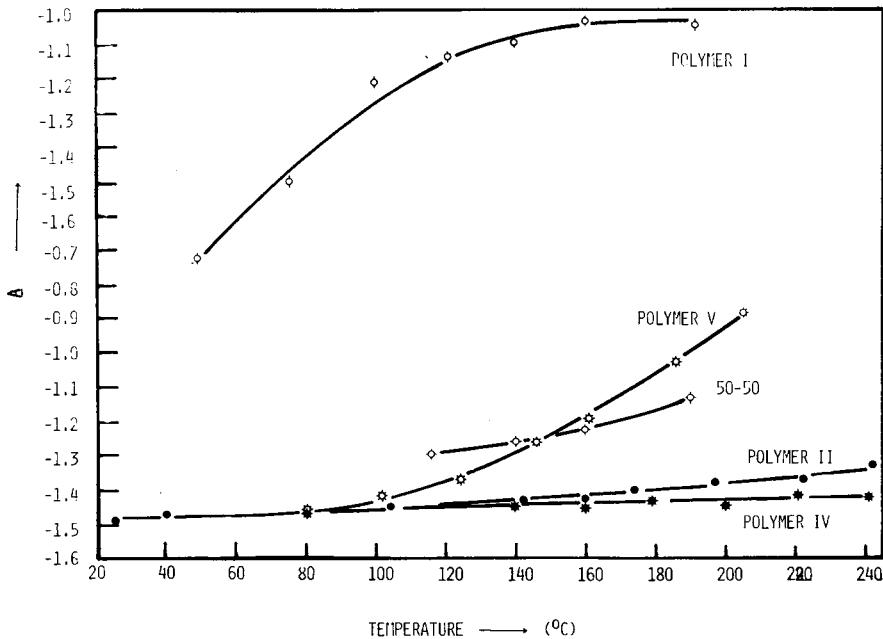


Fig. 11. Plot of  $A$  vs. temperature ( $^{\circ}\text{C}$ ) for samples shown.

time (in this case equal to 1 sec);  $\omega$  is frequency; and  $A$  and  $m$  are fit parameters for the polymer in question. Previously, it was described how  $A$  as a simply determined number could be used as a measure of elasticity.<sup>11</sup> No special theoretical significance is affixed to this parameter nor is the treatment intended to be rigorous.

The effect of temperature on elasticity, the value  $A$ , is shown in Figure 11. There are data on this graph at relatively low temperatures where the polyisobutylenes with the exception of polymer I could not be handled using the cone-and-plate geometry. Below 130°C, the solid sample holders previously described<sup>23</sup> were used for the high molecular weight polyisobutylenes. Considering Figure 11, it appears that the materials of medium molecular weight, polymers I and V, are more temperature sensitive than the high molecular weight species. Increasing molecular weight leads to decreasing sensitivity of elasticity to change in temperature. This may be due to the fact that the higher molecular weight polymer is more "entangled"<sup>21</sup>; thus, the relaxation spectrum is less sensitive to changes in temperature, the same deduction that was drawn from the  $G'$  curves earlier in the paper.

Further, it can be seen that there is very little difference between the curves for polymers II and IV; and, although not shown, data taken using polymer III result in a curve very close to that exhibited by polymer IV. Thus, it appears that for the very high molecular weight species where "entanglement" is high, the elasticity as measured by  $A$  exhibits very little dependence on molecular weight. It seems that at each end of the molecular weight scale, a limiting value is reached. This was observed for the low molecular weight polybutadienes<sup>11</sup> which are viscous in character and now for the polyisobutylenes which are quite elastic.

Comparing the studies of polybutadiene and the present work, it appears that, at a certain level of elasticity value  $A$ ,  $dA/d$  (molecular weight or temperature) tends to zero. Thus, it seems that superposition of the  $A$ -versus-molecular weight or temperature curves could be accomplished. However, much more work would be required before one could predict the shift factors necessary to achieve this.

Again, it is interesting to compare the 50-50 blend with polymer V. From Figure 11 at 180°C, one can see that the blend is more elastic ( $A$  is lower) than for polymer V. Again a possible explanation is that the long chain molecules in the high molecular weight end of the distribution curve of the blend result in long-range "entanglement networks," thus increasing the elasticity.<sup>21</sup> However, the elasticity of polymer V is much more temperature sensitive. In the case of the blend, the relaxation rate spectrum of the high molecular weight material is lagging in response. The relaxation time for polymer II does not shorten much with increasing temperature, probably due to the high "entanglement" which is influencing the response of the blend. Thus, due to the lower sensitivity of polymer II to temperature, at 150°C the curves cross and the blended sample exhibits less elasticity than polymer V.

## SUMMARY

The results for the unblended polymer (polyisobutylene) agreed well with those in the literature with regard to molecular weight and temperature de-

pendence, that is, the zero shear viscosities as measured follow the Bueche relationship, and the temperature coefficient as calculated confirms previous literature values.

From the blending experiments, it was shown that the temperature coefficient of flow is independent of molecular weight distribution as well as molecular weight over the ranges studied. Also, it was shown that the Ninomiya-Ferry theory correctly predicted the viscosity of the blends. It appears that there is no need to modify this theory to take into account the polydispersity of the materials blended unless this polydispersity is very large.

The effect of molecular weight, molecular weight distribution, and temperature on  $G'$  and on the elastic component of response, measured as  $A$ , also was considered. It appears that  $A$ , for the high molecular weight polyisobutylenes studied, reaches a limiting value where changes in molecular weight and/or temperature have no effect. Both of these relationships have been explained as being the result of a very high "entanglement" exhibited by these high molecular weight materials. This also is in agreement with the behavior of  $G'$  curves in the high molecular weight region. Thus, any change in relaxation time due to changes in temperature or molecular weight has little effect on the value of  $A$ . Again, as was shown using the  $G'$  curves, the temperature dependence of  $A$  is less for polymers with broad molecular weight distribution. This also was shown for low molecular weight polybutadiene polymers. Thus, although at the higher temperature conditions the broader the molecular weight distribution the higher the elasticity, lowering of the temperature can cause reversal of this behavior.

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