

Dynamic Rheological Properties of Bromine-Terminated Polybutadiene Melts

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Synopsis

The viscous and elastic properties of bromine-terminated polybutadiene were investigated as functions of temperature, molecular weight, and molecular weight distribution. They were found to depend on these variables in a manner similar to other polybutadienes. It was shown that the effect on the viscous properties due to bromine terminal functionality is not as great as for carboxyl and/or hydroxyl terminal functionality. In this study it was shown that the viscosity resultant from the blending of two samples of the same polymer differing in molecular weight is dependent on the polydispersity of the polymers from which the blend is prepared. A form of the Ninomiya and Ferry theory was modified and compared with experiment. As a result of the experiments involving blending, it was shown that the temperature dependency of elasticity is less for polymers exhibiting greater polydispersity.

INTRODUCTION

The rheology of low molecular weight terminally reactive polybutadienes has been considered previously.^{1,2} The work was carried out with terminally carboxylated and hydroxylated materials. Bromine has also been introduced for use as a terminal functional group in the polymer, i.e., bromine-terminated polybutadienes. In all cases these systems offer the ease of handling of liquid prepolymers and provide idealized chain extension and crosslinking systems.³

The carboxyl- and hydroxyl-terminated polymers, because of hydrogen bonding and polarity, have enhanced melt viscosity over pure polybutadiene. However, bromine-terminated polybutadiene, although the C-Br bond is highly polar, is not capable of hydrogen bonding, and thus the endgroup should not have as great an effect on viscosity. Comparisons between the effect of these terminal functionalities will be made in this paper.

Not all of the polymers that were studied can be considered to be prepolymers, since they are already of relatively high molecular weight. The reason for including these materials in the study was to carry out a general investigation regarding the effect of temperature, molecular weight, and

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molecular weight distribution on the elastic viscous properties of polymer melts.

EXPERIMENTAL

The polymers used were supplied by the Polymer Corporation Limited (Table I). These are free radical-produced polybutadienes.⁴

TABLE I
Molecular Weights of the Bromine-Terminated Polybutadienes

Polymer	\bar{M}_w^a	\bar{M}_w/\bar{M}_n^a	\bar{M}_z^a
A	7,440	1.5	11,180
B	11,570	1.5	15,900
C	11,600	2.2	23,110
D	18,270	1.7	23,200
E	27,400	3.0	70,600
F	43,200	3.1	142,500
G	82,700	5.3	347,000
H ^b	330,000	2.6	669,000

^a Taken from GPC analysis as performed by Polymer Corporation Research and Development Division.

^b An anionically produced nonfunctional polybutadiene.

Measurements were made using a Weissenberg rheogoniometer Model R-18, employing cone-and-plate geometry.⁵ The mode of deformation was in all cases oscillatory. The temperature range was 24°C to 120°C, and in all experiments the sample was protected with a N₂ atmosphere. The frequency range and amplitude range were 0.006 to 6 sec⁻¹ and 50 to 500 microns, respectively. Thus, these experiments were considered to involve small-amplitude sinusoidal deformations. The amplitudes and the phase angles were both found to be reproducible well within ±1%. Viscosity was found to be independent of the amplitude of the applied strain.

The phase difference ϕ , the movement of the plate (stress) P_0 , and the movement of the cone (strain) γ_0 are measured. The dynamic viscosity is calculated using an equation of the form developed by Weissenberg⁶:

$$\eta' = \frac{P_0}{\gamma_0} \frac{K}{\sin \phi} \text{ (poise)} \quad (1)$$

where K is a constant (dependent on the torsion bar constant, the cone angle, and the cone radius). A number of "correction" terms can be added as well to account for fluid inertia and viscous damping.⁶

For representation of the results, viscosity is plotted versus shear rate. The rate of shear in oscillatory deformation is the first derivative of the shear strain, and for the cone-and-plate geometry on the Weissenberg rheogoniometer, the maximum⁵ is

$$\text{shear rate} = \frac{\omega\gamma_0}{567\alpha} \text{ (sec}^{-1}\text{)} \quad (2)$$

where α is the cone angle, and ω is frequency. In this paper, the shear rate has been calculated using the above equation.

RESULTS AND DISCUSSION

The response to deformation of a viscoelastic material can be divided into a viscous component and an elastic component. For convenience, the results in this paper will be discussed under these headings.

Viscous Properties

Effect of Temperature

Viscosity-shear rate curves were constructed from data taken on all samples over a temperature range of 24° to 120°C. Examples of these curves are given in Figures 1, 2, and 3. Polymer C (Fig. 1) is a very low molecular weight prepolymer, and the behavior is Newtonian. As the molecular weight is increased, the behavior becomes somewhat non-Newtonian (Fig. 2, polymer F), and the relatively high molecular weight polymer, G, exhibits a markedly pseudoplastic behavior.

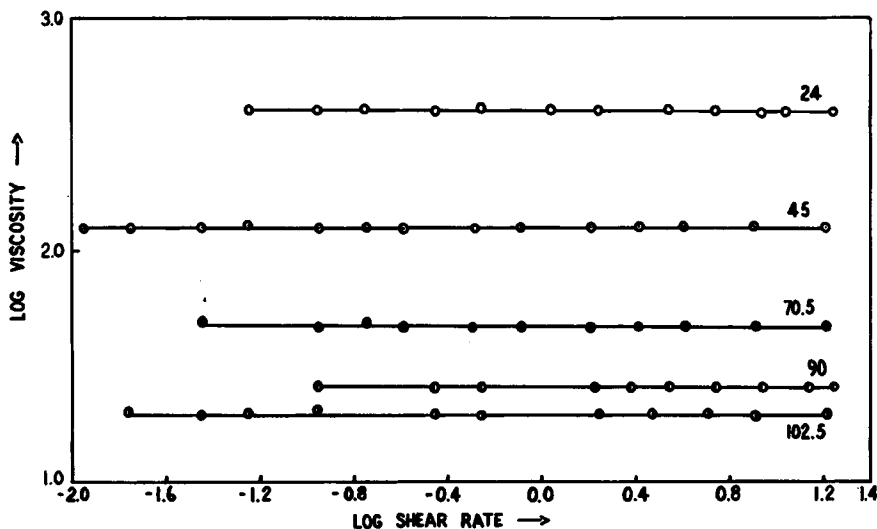


Fig. 1. Plots of \log_{10} viscosity (poise) vs. \log_{10} shear rate (sec^{-1}) for polymer C ($\bar{M}_w = 11,600$, $\bar{M}_w/\bar{M}_n = 2.2$) at the temperatures ($^{\circ}\text{C}$) indicated.

In this paper, the zero-shear viscosities were determined by extrapolation and by a method of Cross⁷ based on the following equation:

$$\eta = \eta_{\infty} + \frac{\eta_0 + \eta_{\infty}}{1 + \tau\omega^p} \quad (3)$$

where η_0 and η_{∞} are the limiting values of viscosity at zero and infinite shear rate, respectively; τ (a material constant) is a representative relaxa-

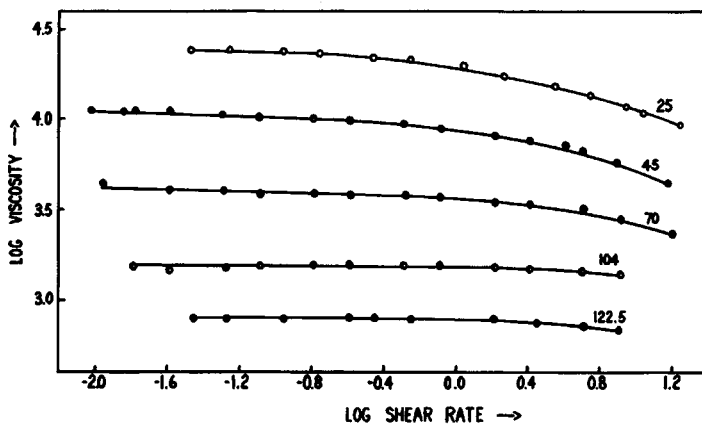


Fig. 2. Plots of \log_{10} viscosity (poise) vs. \log_{10} shear rate (sec^{-1}) for polymer F ($\bar{M}_w = 43,200$, $\bar{M}_w/\bar{M}_n = 3.1$) at the temperatures ($^{\circ}\text{C}$) indicated.

tion time related to η_0 ; ω is the frequency; and b is a curve-fitting parameter. The η'_0 (zero-shear dynamic viscosity) is determined from the intercept of a plot of $1/\eta'$ -versus-(frequency)^{1/2}. Using $b = 1/2$ which has been used successfully for other studies using oscillatory motion,^{7,8} resulted in

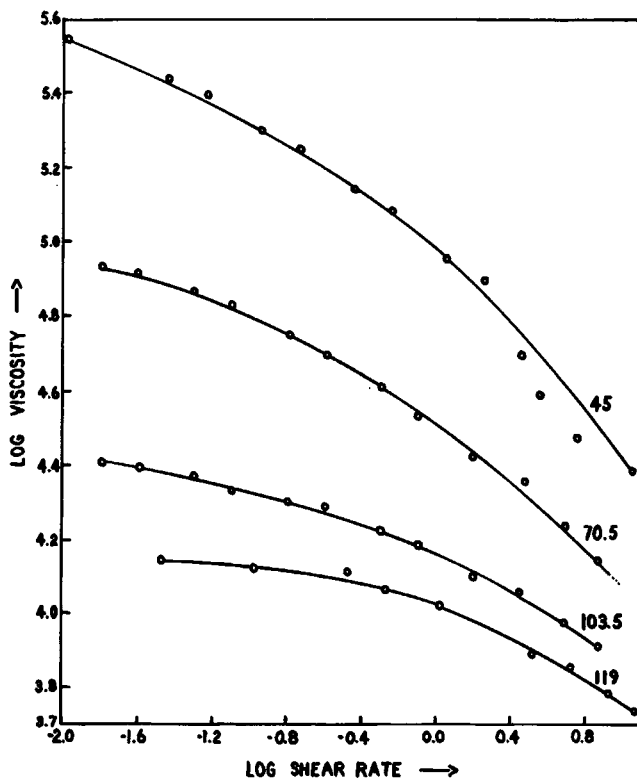


Fig. 3. Plots of \log_{10} viscosity (poise) vs. \log_{10} shear rate (sec^{-1}) for polymer G ($\bar{M}_w = 82,700$, $\bar{M}_w/\bar{M}_n = 5.3$) at the temperatures ($^{\circ}\text{C}$) indicated.

$1/\eta'$ -versus-(frequency)^{1/2} plots that all had good correlation coefficients, greater than 0.95, and the standard error in $1/\eta'$ was $\pm 4\%$. The zero-shear values determined using the Cross method agreed very well with simple extrapolation. Simple extrapolation could be and only was carried out where the viscosity-shear rate curve either was approaching rapidly, or was in, the upper Newtonian region. The zero-shear viscosities are given in Table II.

The Arrhenius temperature coefficients of flow were calculated. The zero-shear Arrhenius temperature coefficients are independent of molecular weight over the range 7,440 to 43,200 \bar{M}_w , and molecular weight distribution up to $\bar{M}_w/\bar{M}_n \sim 3.0$. The average Arrhenius temperature coefficient of flow at zero shear rate for all bromine-terminated polybutadiene samples, except polymer G, was 8.4 kcal/mole (Table II). Polymer G exhibited an

TABLE II
The Viscosity Values at Zero-Shear Rate for the Bromine-Terminated Polybutadienes

Sample	Temperature, °C	$\log_{10} \eta_0'$ (poise)	E , kcal/mole
A	24	2.10 ^a	8.3
	45	1.60 ^a	
	71	1.105 ^a	
	102	0.74 ^a	
B	24	2.615 ^a	8.3
	45	2.105 ^a	
	70	1.675 ^a	
	102	1.27 ^a	
C	24	2.60 ^a	8.5
	45	2.10 ^a	
	70.5	1.67 ^a	
	90	1.40 ^a	
	102.5	1.28 ^a	
D	24	3.33 ^a	8.8
	45	2.80 ^a	
	70	2.37 ^a	
	104	1.855 ^a	
E	25	3.68 ^a	8.4
	45	3.19 ^a	
	70.5	2.81 ^a	
	103	2.35 ^a	
	120	2.16 ^a	
F	25	4.38 ^{a,b}	8.3
	45	4.04 ^{a,b}	
	70	3.60 ^a	
	104	3.19 ^a	
	122.5	2.90 ^a	
G	45	5.68 ^b	11.5
	70.5	5.09 ^b	
	103.5	4.50 ^{a,b}	
	119	4.18 ^{a,b}	

^a Determined by simple extrapolation.

^b Determined by method of Cross.⁷

Arrhenius temperature coefficient of 11.5 kcal/mole. This high value will be discussed later in the paper.

The average value of the Arrhenius parameter is just slightly higher than the highest value obtained by Vinogradov et al.⁹ on nonfunctionally terminated polybutadiene for their sample with the highest trans-1,4 content. The polybutadienes studied by Vinogradov et al. were titanium-initiated polybutadienes. Their results with the trans-1,4-content are:

<i>E</i> , kcal/mole	Trans-1,4, %
8.0	30
7.4	15
5.6	5

The present material exhibits a trans-1,4 content of the order of 60%.

The Arrhenius values presented by Vinogradov et al.⁹ were determined over temperature and molecular weight ranges roughly equivalent to the present work. The results were also found to be independent of molecular weight above a "critical" molecular weight which as well is in agreement with the work of Fox and Flory.¹² For *n*-butyllithium-initiated polybutadienes (again nonfunctional) which also have relatively high trans-1,4 content (around 40%), an E_{η_0} value of 8.0 kcal/mole was obtained.^{10,11} Thus, the present value of 8.4 kcal/mole appears to be in good agreement with these other values. It should be noted that the results for butyllithium- and titanium-initiated polybutadienes were obtained by steady-shear methods.

Effect of Molecular Weight

If one compares Figures 1, 2, and 3, it is readily apparent that, as the molecular weight is increased at a constant shear rate and temperature, the viscosity increases. The well-known representation of the dependency of viscosity on molecular weight is given in Figure 4, a plot of zero-shear viscosity versus molecular weight.¹³ The slope of this line is 3.4. Note

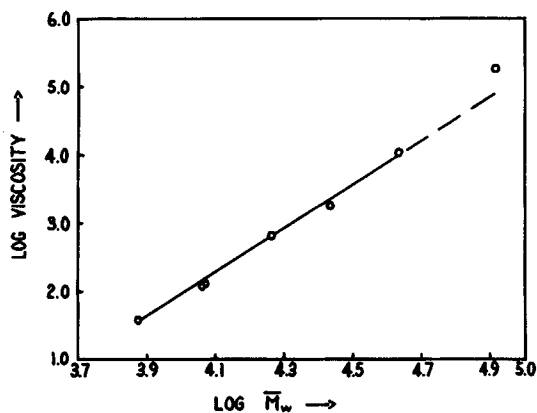


Fig. 4. Plot of \log_{10} viscosity vs. $\log_{10} \bar{M}_w$. Slope of the line is 3.4.

that polymer G, which exhibits a polydispersity (\bar{M}_w/\bar{M}_n) much greater than the other polymers (Table I), does not lie on the curve.

The dependency of viscosity on a 3.4 power of \bar{M}_w is in agreement with the results observed with butyllithium- and titanium-initiated (nonfunctional) polybutadienes.⁹⁻¹¹ The microstructure is different. Thus, it appears that over this full range of microstructure (cis-1,2 90% to 17%; the cis content of the present polybutadiene is approximately 17%), the polybutadienes of polydispersity ≤ 3.0 approximately obey a 3.4 power law.

Effect of Terminal Functionality

From Table III one can see that this terminal group has less effect on viscosity and the Arrhenius temperature coefficient than carboxyl (COOH) or hydroxyl (OH) termination. The COOH and OH termination results are taken from Boyce et al.¹ and Collins et al.² It is believed that these polybutadienes were butyllithium catalyzed. The nonfunctional polybutadiene was a butyllithium-initiated polybutadiene. The temperature range for all the E_{η_0} values shown was approximately 20° to 100°C.

TABLE III
Effect of Terminal Functionality of Rheological Properties

Polymer	\bar{M}_w	\bar{M}_w/\bar{M}_n	η_0 (25°C), poise	E_{η_0} , kcal/mole
PBD—carboxyl ^a	8310	1.6	625	11.8
PBD—hydroxyl ^a	9510	1.7	500	12.1
PBD ^a	8460	1.2	75	8.3
PBD—bromine	7440	1.5	98	8.3

^a Reference 2.

Collins² suggested that the high viscosity of the COOH- and OH-termination material as opposed to nonfunctionally terminated polybutadienes is due to polarity and association (hydrogen bonding) of the functional group. The Br endgroup is more polar than carboxyl or hydroxyl functionalities,¹⁴ and yet the polymer is much lower in viscosity. In point of fact, the bromine termination results in a 23% increase in viscosity whereas the carboxyl termination results in an 880% increase in viscosity. Thus, it seems that polarity is of much less importance than association. This fact has also been borne out by a recent article that involved the study of a low molecular weight bromine-terminated polybutadiene.¹⁵ As well, COOH is capable of stronger association than OH,¹⁶ and, as would be expected, the viscosity resulting from carboxyl termination is higher. This viscosity difference is quite important in prepolymers, because of the advantage of easier processing for lower viscosities.

The fact that the Arrhenius coefficient is greater when there is hydrogen bonding present has been explained by means of a temporary crosslinking mechanism.¹⁷

There is also some experimental evidence that long-chain branching can increase the Arrhenius value.¹⁸ Presumably the temperature coefficient is increased by the interaction of long-chain branches giving rise to temporary crosslinks analogous to hydrogen bonding. It is also well documented that branching increases the dependency of viscosity on \bar{M}_w .^{19,20} Since polymer G has a broad molecular weight distribution and is produced by free-radical polymerization, it is believed to contain a large amount of branching.⁴ The above evidence implies that the anomalies in the viscosity and the Arrhenius value for polymer G are due to branching.

Combs et al.²¹ showed that E increases with increasing molecular weight. Thus one may argue that the larger E exhibited by polymer G is due to the higher molecular weight. However, if one considers samples E and F, which have about the same polydispersity yet exhibit different weight-average molecular weights, the E values are similar. The present suggestion of a lack of dependency of E on molecular weight (above a critical molecular weight) also is in agreement with the results of Vinogradov et al.⁹ as well as Fox and Flory.¹²

Effect of Molecular Weight Distribution

In order to study samples exhibiting greater polydispersity, blends of C and G in the weight per cent ratios of 10-90, 30-70, 50-50, 70-30, and 90-10 were made. These blends exhibit a fair amount of overlap in their molecular weight distributions. This is seen in Figure 5, which represents a 50-50 blend of polymers C and G. A second set of blends were also prepared that would exhibit less overlap in their molecular weight distributions, i.e., blends of C and H (Fig. 6). H is not, however, a bromine-terminated or free-radical polymerization-produced polybutadiene. It is anionic-initiated polybutadiene and has a trans-1,4 content of almost 35%.

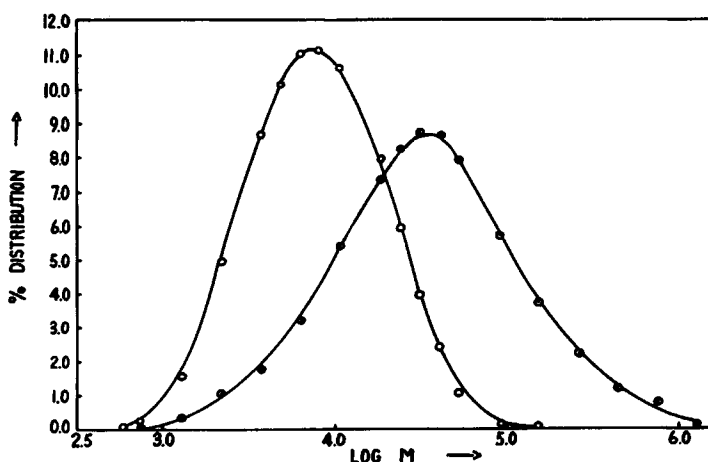


Fig. 5. Molecular weight distributions of polymers C ($\bar{M}_w = 11,600$) (○) and G ($\bar{M}_w = 82,700$) (○).

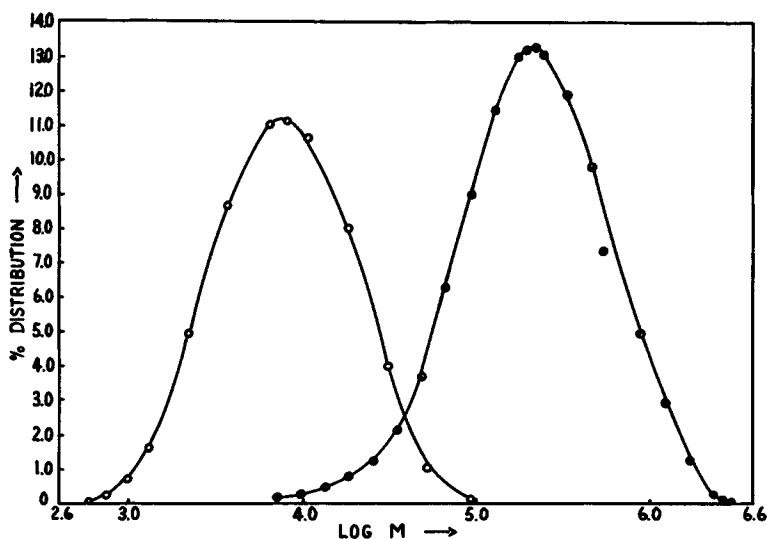


Fig. 6. Molecular weight distributions of polymer C ($\bar{M}_w = 11,600$) (○) and polymer H ($\bar{M}_w = 330,000$) (⊙).

Figure 7 is a series of flow curves for the blends of C and G at 45°C. As the amount of polymer G is increased in the blend, the viscosity at any given shear rate increases. Table IV gives the molecular weight and polydispersities of the blends. From Figure 8, it can be seen that the viscosity increases linearly with increasing weight per cent of polymer G.

TABLE IV
Molecular Weights^a and Viscosity at Zero-Shear Rate for Blends of
Polymers C and G (at 45°C)

Weight ratio	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n	$\log_{10} \eta'_0$ (poise)
C	5,360	11,600	2.2	2.09
90-10	5,940	18,700	3.1	2.53
70-30	6,680	32,900	4.8	3.25
50-50	8,000	48,200	6.0	4.03, 4.08 ^b
30-70	9,960	61,400	6.2	4.42, 4.26 ^b
10-90	13,200	75,700	5.8	5.23
G	15,700	82,700	5.3	5.62

^a The molecular weight averages for the blends were calculated from the following equations:

$$\bar{M}_n = \frac{\sum w_i}{\sum (w_i/M_i)} \quad (\sum w_i = 1)$$

$$\bar{M}_w = \frac{\sum w_i M_i}{\sum w_i}$$

where w_i is the weight fraction of species i and M_i is the molecular weight of species i .

^b Duplicate experiments.

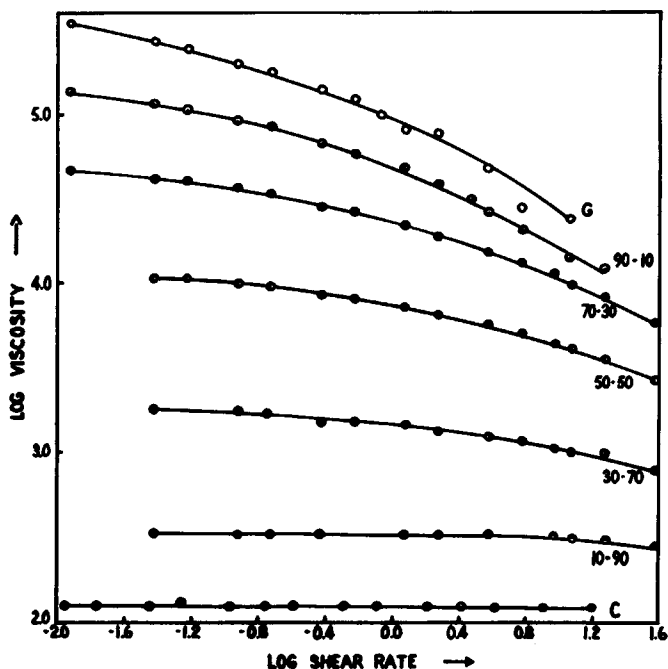


Fig. 7. Plots of \log_{10} viscosity vs. \log_{10} shear rate at 45°C for blends of polymer C and polymer G at the given weight percentages.

This result is somewhat unexpected, as it is generally accepted that the addition of a high molecular weight species to low molecular weight material results in a large increase in viscosity²² and the addition of a low molecular weight species to high molecular weight material results in very little decrease of the viscosity, similar in behavior to the dashed line in Figure 8.

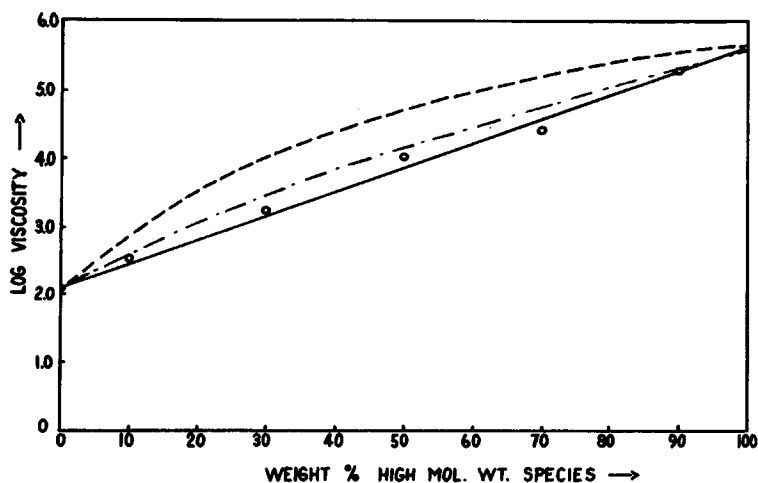


Fig. 8. Plot of \log_{10} zero-shear viscosity vs. weight per cent of polymer G. The (—) line is predicted by eq. (4); (---) line is predicted by eq. (5).

The dashed line in this figure is the prediction of a semiempirical theory developed by Ninomiya and Ferry.^{23,24} Their equation can be written²⁵ in the form

$$\eta_0 = W_1 \left(\frac{\bar{M}_w}{\bar{M}_{w_1}} \right)^{2.4} \cdot \eta_{01} + W_2 \left(\frac{\bar{M}_w}{\bar{M}_{w_2}} \right)^{2.4} \cdot \eta_{02} \quad (4)$$

where η_0 is the zero-shear viscosity of the blend; η_{01} and η_{02} are the zero-shear viscosities of components 1 and 2 with weight-average molecular weight \bar{M}_{w_1} and \bar{M}_{w_2} , respectively; W_1 and W_2 are the weights per cent of components 1 and 2 in the blend; and \bar{M}_w is the weight-average molecular weight of the blend. This has been shown to be quite applicable to the blends of relatively monodisperse ($\bar{M}_w/\bar{M}_n < 2.0$) polymer melts by various workers.^{23,25} The predicted curve does not fit the experimental data. In this case, addition of a small amount of high molecular weight species does not have as large an effect on viscosity as would be expected. Some of the lack of agreement may be due to the fact that the two polymers blended have fairly broad molecular weight distributions. It is thought that the results can be explained on the basis of a great deal of overlap in the molecular weight distribution. There is not a "clean" influence of a high molecular species being added to low molecular weight polymer, since the low molecular weight material already contains a small portion of high molecular weight material in its molecular weight distribution.

An attempt was made to modify the theory of Ninomiya and Ferry to compensate for this overlap in the molecular weight distributions by adding a polydispersity term. Using polydispersity to the 2.4th power, the same power as the molecular weight dependency in the Ninomiya and Ferry theory, was considered. This overcompensated, and the fit was not as good as that predicted by Ninomiya and Ferry. A polydispersity term of the first order resulted in an equation which predicted a curve that more closely approached the experimental data (Fig. 8):

$$\eta_0 = W_1 \left(\frac{\bar{M}_w}{\bar{M}_{w_1}} \right)^{2.4} \cdot \left(\frac{\bar{M}_{w_1}}{\bar{M}_{n_1}} \right)^{-1} \cdot \eta_{01} + W_2 \left(\frac{\bar{M}_w}{\bar{M}_{w_2}} \right)^{2.4} \cdot \left(\frac{\bar{M}_{w_2}}{\bar{M}_{n_2}} \right)^{-1} \cdot \eta_{02}. \quad (5)$$

There is a precedent for the use of a first-order polydispersity correction term. Middleman²⁶ used this type of modification in his extension of Bueche's theory to polydisperse polymers.

As stated above, C and H blends were studied in order to examine a series of blends whose molecular weight distributions exhibited less overlap. Figure 9 shows the viscosity-shear rate plots of these blends at 100°C. Values of the molecular weight and polydispersity are given in Table V. It can be seen that in this case the addition of the high molecular weight species to the low molecular weight polymer has a much greater effect on viscosity than vice versa. This fact is easier to see in Figure 10. It can also be noted that in this case the theory of Ninomiya and Ferry more closely predicts the actual experimental results than for the previous blend. However, in both cases the data agree better with eq. (5) (the modified equation).

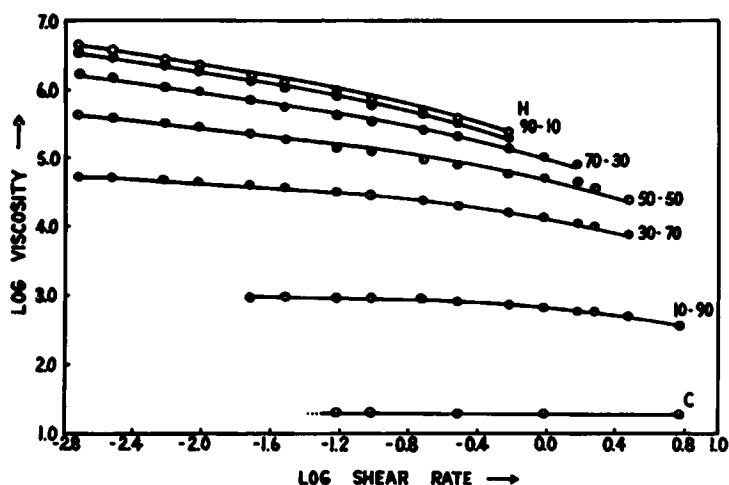


Fig. 9. Plots of \log_{10} viscosity vs. \log_{10} shear rate at 100°C for blends of polymer C and polymer H at the percentages indicated.

It seems from the above results that if there is a great deal of overlap in the molecular weight distribution of two blends, then the normally expected effects on viscosity do not occur. One should also keep in mind that in this case there is a greater difference in molecular weights for the C and H blend than the C and G blend.

Neither blend system obeys the 3.4 power law; in fact, plots of $\log_{10} \eta'_0$ versus $\log_{10} \bar{M}_w$ were not even linear. This is not surprising as the degree of polydispersity is high, and Bucche's theory was not developed for these conditions.¹³ However, even though the C and H blends have a greater polydispersity, they approach linear behavior more closely than the C and G blends in their molecular weight dependence. This is possibly because the individual polymers have lower polydispersity (polymer H). Plots of \log_{10} viscosity versus $\log_{10} \bar{M}_w$ for blends of monodisperse polymers result in behavior that is in agreement with the prediction of Bucche,¹³ although the slope of the line is generally greater than 3.4.²⁵

TABLE V
Molecular Weights^a and Viscosities at Zero-Shear Rate η'_0 for
Blends of Polymer C and H (at 100°C)

Weight ratio	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n	$\log_{10} \eta'_0$ (poise)
C	5,360	11,600	2.2	1.30
90-10	5,930	43,500	7.3	2.97
70-30	7,750	74,200	9.6	4.81
50-50	10,300	170,900	16.6	5.89
30-70	16,300	234,500	14.4	6.70
10-90	38,800	298,300	7.7	7.30
H	126,400	330,000	2.6	7.35

^a See Table IV.

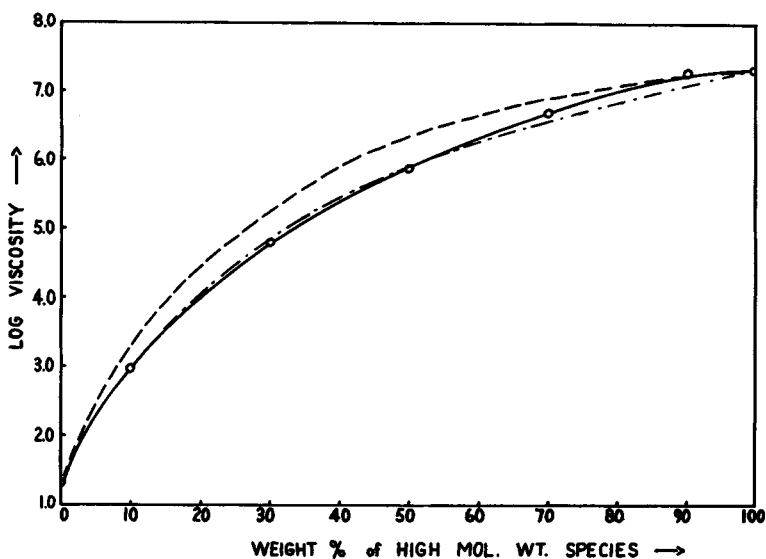


Fig. 10. Plot of \log_{10} zero-shear viscosity vs. weight per cent of polymer H. The (---) line is predicted by eq. (4); The (-·-) line is predicted by eq. (5).

These results underline the importance of knowing the complete molecular weight distribution. Although the C and H blends have greater polydispersities, knowledge of the whole distribution tells us that the C and H blends have distinct bimodal distributions while the C and G blends approximate one broad distribution. It has just been shown that this fact can drastically effect the viscosity characteristics of blends.

The influence of polydispersity on the viscosity-shear rate curve is shown in Figure 11. This is a series of \log_{10} viscosity-versus- \log_{10} shear rate plots for the 50-50 blend of polymers C and G. Superimposed on the curve at 45°C is the viscosity-shear rate curve for polymer F at 45°C. Polymer F has approximately the same \bar{M}_w as the 50-50 blend, however, it exhibits a polydispersity about one half as great. As can be seen from the figure, the sample with the lower polydispersity is much more Newtonian in behavior.

The Arrhenius coefficient of flow for the 50-50 blend is 8.5 kcal/mole. Thus, it appears that the $E\eta'$ is independent of polydispersity. This is in agreement with the results of Combs et al.²¹ However, because of the previous results on polymer G, it would be best not to attempt to draw any conclusions from this result. The other difficulty in considering the results for polymer G is the extrapolation to η'_0 (Table I). The lowest shear rate value measured is far removed from any plateau region. Thus, achieving this arbitrary value must be subject to greater error than for the other polymers which are less pseudoplastic in behavior.

Elastic Properties

The phase angle ϕ between the stress and strain was used to obtain a measure of elasticity. This angle can be considered in terms of viscous and

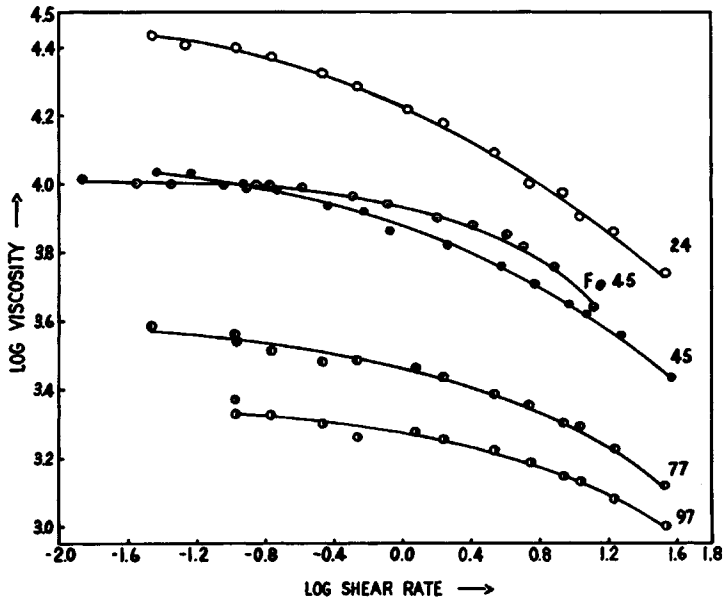


Fig. 11. Viscosity shear rate plots for 50-50 blend of polymers C and G at the temperatures ($^{\circ}\text{C}$) shown. Superimposed on this plot is a viscosity-shear rate curve for polymer F at 45°C (for polymer F, $\bar{M}_w = 43,200$, $\bar{M}_w/\bar{M}_n = 3.1$; and for the 50-50 blend, $\bar{M}_w = 48,200$, $\bar{M}_w/\bar{M}_n = 6.0$).

elastic components. A material that is totally or perfectly viscous when deformed absorbs all the energy in deformation, and the response is 90° out of phase. However, if a material is perfectly elastic, all the energy is released in a rebound, i.e., the response to a deformation is exactly in phase with the strain.

Typical plots of the function ϕ versus frequency are shown in Figure 12. All were found to fit the equation

$$\phi = A (\omega\theta)^m + C \quad (6)$$

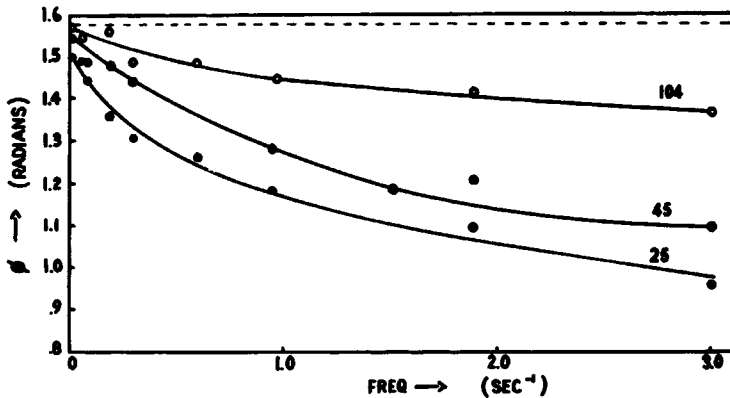


Fig. 12. Plot of ϕ vs. frequency for polymer F at the temperatures ($^{\circ}\text{C}$) indicated.

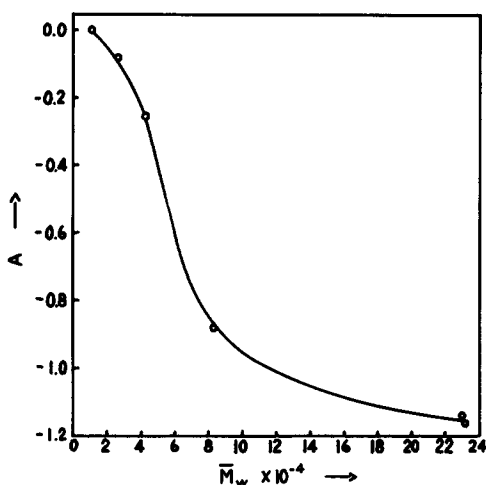


Fig. 13. Plot of coefficient A vs. molecular weight for bromine-terminated polybutadiene at 45°C. The 230,000 \bar{M}_w sample was a "solid" under test conditions, thus the solid sample holders described before were used.²⁷

where $C = 1.57$ (phase angle in radians = 90°); θ is a quantity having dimensions of time (in this case equal to 1 sec); and A and m are fit parameters for the polymer in question. The agreement with the equation was tested by means of an F -test at 95% confidence limits. The behavior of A and m has been discussed previously.²⁷ For a viscous fluid, $A = 0$, i.e., a viscous fluid gives stress 90° out of phase with the strain (a line $\phi = 1.57$). As a material approaches a completely elastic state, A approaches -1.57 . This then allows one to use a single number as a measure of elasticity for studying the dependency of elasticity on such parameters as temperature, molecular weight, and molecular weight distribution.

In Figure 13 one can see that the molecular weight dependence of A is greater for the medium molecular weights, i.e., for bromine-terminated polybutadiene at 45°C over the range of about $(1-10) \times 10^4 \bar{M}_w$. Guillet et al.²⁸ showed that increasing the polydispersity and the branching increased the melt recovery, whereas increasing molecular weight of narrow fractions had no influence on melt recovery for polyethylene. Thus, it could be argued that the present observed increase in elasticity may be due to an increased polydispersity (Table I); however, if one considers samples E and F, the value A changes even though both sample exhibit approximately the same molecular weight.

The dependency of the value of A on \bar{M}_w appears to be leveling out in the region of 200,000 to 250,000 \bar{M}_w . Note that the sample at 230,000 \bar{M}_w is not a bromine-terminated polybutadiene although it is free-radical produced, so that the microstructure should be similar to the brominated polybutadienes; and, as well, the results in the previous section imply that there should be very little difference between the properties of the nonfunctional and the bromine-terminated samples.

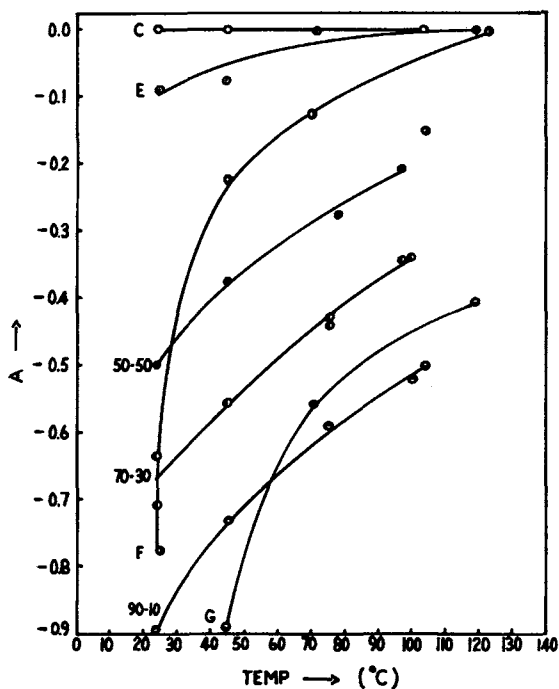


Fig. 14. Plot of A vs. temperature for the polymer and blends of polymers C and G indicated.

Considering the results of Vinogradov et al.⁹ for a high cis-content polybutadiene, the dependency of elasticity (as measured by recoil experiments) on molecular weight appears to begin to diminish at about $300,000 \bar{M}_w$ (this work was performed at a slightly higher temperature than the present work). This behavior is very similar to the present results.

One possible explanation for A reaching a limiting behavior is due to the fact that at the high molecular weight there is a high entanglement density. The elasticity of a polymer melt is very dependent on entanglement density.²⁹ Once a very high entanglement density is reached, one might expect no further increase with increasing molecular weight.

Elasticity measurements as described by the value A from eq. (6) were determined for the polymers over the temperature range 25° to 124°C . Over this temperature range, polymers A, B, and D are all perfectly viscous (i.e., A from eq. (6) exhibited a value of zero). From Figure 14, one can observe that the temperature dependency of the value A is exaggerated with increasing molecular weight over this range of molecular weight, i.e., $7,440$ to $82,700 \bar{M}_w$. For the low molecular weight material, there is no change in A with temperature. In the case of the higher molecular weight material, the value A changes by a factor of 2 over the same temperature range.

Values of A were also determined over the temperature range for the C and G blends and superimposed on the curves for unblended polybutadienes

(Fig. 14). The first thing that one notices is that the temperature dependence of the blends is less than for the unblended polymers. Polymer F has the same approximate weight-average molecular weight as the 50-50 blend yet is much less polydisperse, so a direct comparison of the temperature dependency for different polydispersity can be made in this case. The more polydisperse polymer is more elastic down to about 38°C. However, at this point, due to the lower sensitivity with temperature, the lines cross and the polydisperse sample is less elastic. Guillet and co-workers³⁰ have shown that melt recovery (directly related to elasticity) increases as the molecular weight distribution broadens, although this work was not performed with temperature as a variable.

Combs et al.²¹ observed an increase in melt recovery, thus elasticity, with increasing temperature at constant high-shear stress. This discrepancy with the present results could possibly be explained by the fact that in the present investigation (because of the nature of the experiment) the shear stress is lower at any given shear rate at a higher temperature. It is difficult to make any direct comparisons, as the work of Combs et al. was performed under higher shear stress-shear rate conditions than the present work.

Chartoff and Maxwell³¹ have suggested that polydisperse polymers should have viscoelastic properties which are less temperature dependent. Qualitatively, they explained this phenomenon on the basis of a reduction in the temperature dependence of the relaxation spectrum caused by the low molecular weight portion of the molecular weight distribution. These authors used an expression Ferry derived for the relaxation spectrum of a polydisperse polymer in the terminal zone which has the following form:

$$H(\lambda) = \frac{\rho RT_0}{\bar{M}_n} \int_0^\infty \sum_{p=1}^N \lambda_p \delta(\lambda - \lambda_p) \Phi(M) dM \quad (7)$$

where the p th relaxation time is given by

$$\lambda_p = \frac{n\sigma^2 N^2 (f_0 Q_e) M}{\pi^2 p^2 \rho R T_0}$$

$$p = 1, 2, 3 \dots N$$

and δ is the Dirac delta function; $\Phi(M)$ is the molecular weight distribution function for a given material such that $\int M \Phi(M) dM = \bar{M}_n$. Chartoff and Maxwell³¹ suggest, "For the limiting case of a monodisperse polymer, eq. (7) reduces to the equivalent expression given by the Rouse-Bueche theory, which qualitatively represents the viscoelastic behavior of polymers in the terminal zone. The quantity f_0 , the friction factor for segmental motion, is known to have a comparatively low temperature dependence in structures with large relative free volumes. Therefore, the temperature dependence of $H(\lambda)$ and all other viscoelastic properties should be reduced for polydisperse polymers, since the relaxation spectrum enters the expression for all functions."

In the present case, the author pictures the behavior as the relaxation spectrum and ultimately the elasticity not changing as rapidly with temperature because the relaxation time of the low molecular weight portion is still quite fast, even at the low temperatures. As the temperature is decreased, the influence of the low molecular weight material is greater relative to that of the high molecular weight portion. In the case of processing low molecular weight prepolymers, this fact should be kept in mind because low-temperature processing is a possibility.

SUMMARY

The results for the prepolymer, bromine-terminated polybutadiene, indicate that the viscous properties of this polymer change with such variables as temperature and molecular weight similarly to other polymers as long as chain extension does not take place during testing. However, the viscosity can be influenced by the endgroup on the prepolymer. In the case of bromine-terminated polybutadiene, the effect of the bromine-terminal functionality on the viscosity and viscosity-temperature characteristics is not as great as for hydroxyl and carboxyl endgroups.

From the experiments on blending, it was shown that the viscosity of a blend of two polymers (of the same material) differing in weight-average molecular weight is dependent on the amount of overlap of the molecular weight distributions of the two polymers used to prepare the blend; i.e., it is advantageous to take polydispersity into account when predicting the viscosity behavior of blends, as is done in eq. (5).

Also as a result of the blending experiments, it was shown that the temperature dependence of elasticity is less for polymers with broad molecular weight distributions (distributions that contain a significant proportion of each of a high or low molecular weight material). Thus, although under most circumstances broad molecular weight distributions result in higher elasticity, changing the temperature can cause reversal of this behavior.

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