

## A Rheological Characterization of SBS Block Copolymers

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### Synopsis

The dynamic viscosities of styrene-butadiene-styrene (SBS) block copolymer melts with different end- and midblock sizes are given as a function of frequency at several different temperatures. The data exhibit two distinct regions, a high frequency region where the response is typical of thermoplastics and a low frequency region where the viscosity continually increases with decreasing deformation rates. These results are successfully explained in terms of the formation of polystyrene domains in the low frequency region. The correlations given for the rheological properties should provide additional insight to the processing of these materials.

### INTRODUCTION

The unusual melt properties of three-block copolymers have motivated several studies<sup>1,2</sup> to characterize the rheological behavior of these materials. Of primary interest is the processability of the copolymers in conventional fabricating equipment. Three rheological properties which distinguish the melt behavior of the copolymers from that of conventional thermoplastics are the absence of an apparent Newtonian viscosity, the sensitivity of the viscosity to shear rate, and the sensitivity of viscosity to total molecular weight. An understanding of the dependence of viscosity on shear rate, temperature, and molecular parameters can provide valuable processing information. The ability to do this, however, requires an explanation of viscoelastic responses couched in terms of measurable molecular properties.

Most viscosity measurements previously reported for block polymers were obtained on the capillary rheometer, an instrument with limited accuracy in the low shear-rate range. Capillary data for styrene-butadiene-styrene (SBS) copolymers show the unusual viscosity behavior mentioned above along with other anomalous results. Problems inherent to the capillary rheometer motivated us to examine the rheological properties of block copolymers on the Weissenberg Rheogoniometer using a small-amplitude sinusoidal deformation. In our experiments, viscous and elastic responses are independent of the amplitude of deformation and may be analyzed using linear viscoelastic theory. The results of linear viscoelastic theory are generally more easily related to molecular structure. In addition, recent efforts<sup>3</sup> to relate the results obtained from small amplitude de-

formations to parameters measured in the presence of large deformations have been quite successful. Specifically, the dynamic viscosity versus frequency curves may sometimes be used to estimate steady state viscosities and normal forces as functions of shear rate.

In this report we present dynamic viscosity data for SBS melts of different polystyrene and polybutadiene block lengths. The data were taken in the frequency range 0.001 to 300 sec<sup>-1</sup> and for temperatures from 140°–200°C. These data are correlated in a way that demonstrates the domain-type structure suggested by earlier investigators<sup>1</sup> in the low frequency range and a thermoplastic behavior in the high frequency range. While our studies are focused on SBS copolymers, our results apply as well to other ABA three-block copolymers where the domain structure is formed.

### EXPERIMENTAL

The operation of the Weissenberg Rheogoniometer using a small-amplitude sinusoidal deformation is described briefly below:

A small amount of sample is placed in a cone and plate geometry and heated to the desired run temperatures. The lower platen is oscillated with an angular movement (shear) of

$$\gamma = \gamma_0 \exp(i\omega t) \quad (1)$$

where  $\omega$  is a known frequency,  $\gamma_0$  is a measured amplitude, and  $t$  is time. The shear rate is therefore

$$\dot{\gamma} = i\omega \gamma_0 \exp(i\omega t). \quad (2)$$

The resulting torque is also sinusoidal if  $\gamma_0$  is small. The oscillating shear stress (torque divided by platen area) is therefore

$$\sigma_{(t)} = \sigma_0 \exp[i(\omega t + \phi)] \quad (3)$$

where  $\phi$  is a phase angle and  $\sigma_0$  is the amplitude of the stress. The dynamic viscosity is defined as the ratio of oscillating stress to shear rate:

$$\eta^* = \frac{\sigma_{(t)}}{\dot{\gamma}} \equiv \eta' - i\eta'' \quad (4)$$

where  $\eta'$  is that portion of the stress to shear rate ratio in phase with the shear rate and  $\eta''$  is the portion 90° out of phase with the shear rate. The quantity of interest is  $\eta'$ , which may be calculated from

$$\eta'_{(\omega)} = \left(\frac{\sigma_0}{\gamma_0}\right) \frac{\sin\phi}{\omega}. \quad (5)$$

The amplitudes  $\gamma_0$  used in our experiments were varied over the available range of the instrument to give the highest possible resolution for any given run. A prerequisite to using linear viscoelasticity, however, is that  $\eta'$  be independent of  $\gamma_0$ . It was possible with our data reduction equipment to

TABLE I  
SBS Samples

SBS sample	Nominal block mol wt <sup>a</sup>	Slope of log $\eta'$ vs. log $\omega$
10-50	10-50-10	-0.36
14-50	14-50-14	-0.40
22-50	22-50-22	-0.66
14-60	14-60-14	-0.36
14-70	14-70-14	-0.36
MDPS/97 <sup>b</sup>	97	0.0

<sup>a</sup> In thousands.

<sup>b</sup> Monodispersed polystyrene, total molecular weight 97,000.

instantaneously determine the effect of  $\gamma_0$  on  $\eta'$ . Therefore, for each run condition a value of  $\gamma_0$  was selected which gave the highest resolution while still resulting in values for  $\eta'$  independent of  $\gamma_0$ . This procedure was followed for all data given in this paper. Referring to eq. (5),  $\eta'$  for a Newtonian sample will be independent of  $\omega$  and  $\phi$ ; the stress will be related to the shear rate by

$$\sigma_0 = \eta' (\omega \gamma_0) = \eta' \dot{\gamma}_0. \quad (6)$$

Most thermoplastic materials have this behavior for low frequencies. On the other hand, at higher frequencies,  $\phi$  decreases as the sample exhibits viscoelastic behavior. In the limit of perfect elasticity,  $\phi = 0$  and thus

$$\sigma_0 = \eta'' \omega \gamma_0 \equiv G \gamma_0 \quad (7)$$

where  $G$  is the elastic modulus.

The tests were performed on five experimental SBS samples (Table I) which were especially prepared for this investigation to give a range of different block sizes. A variety of analytical methods were used for identification of the chemical structure. Microstructure of the middle block and polystyrene content were primarily determined by infrared spectroscopy, and block molecular weights were established by a number of physical-chemical techniques. A narrow molecular weight distribution results from the standard polymerization technique used for the polymer preparations. The narrow distribution was confirmed by gel permeation chromatography. Gel content of the polymers was in all cases found to be less than 0.1% and usually below 0.01%.

The viscosity data for sample 22-50 are given on Figure 1. On this figure the dynamic viscosity ( $\eta'$  in eq. 4) is given versus frequency at four different temperatures. Also, a limited amount of steady-shear data are shown, viscosity ( $\eta$ ) and normal stress ( $\sigma_N$ ) versus shear rate. Several observations may be made: (1) At low frequencies, the slope of log  $\eta'$  versus log  $\omega$  is constant and independent of temperature, (2) a marked transition occurs in the  $\eta'$  versus  $\omega$  curve which is an apparent function of

temperature, and (3) the  $\eta'$  versus  $\omega$  curves for high frequencies resemble those for thermoplastic materials.

The unusual nature of the SBS material is clearly seen by comparing the data of Figure 1 with similar data taken on a monodispersed polystyrene

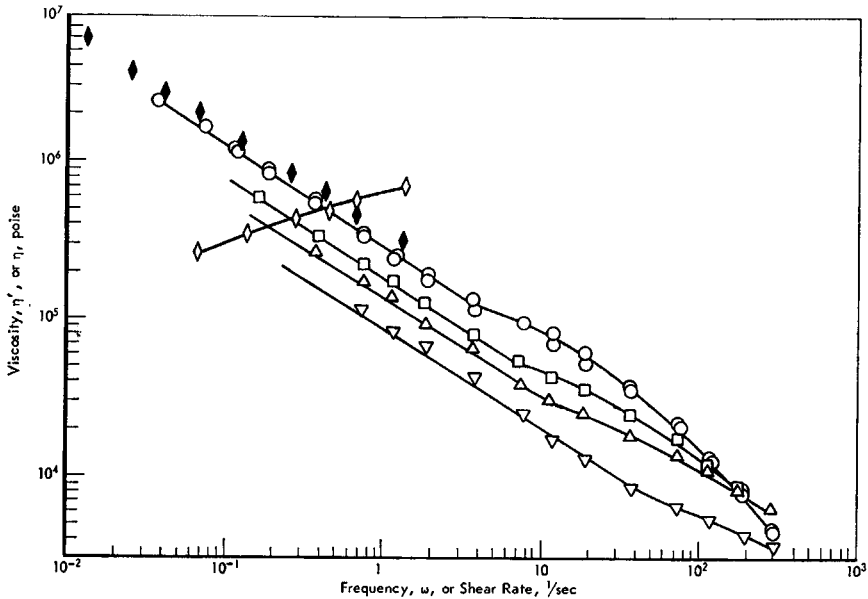


Fig. 1. Viscosity of SBS 22-50. Steady shear data (170°C): ( $\blacklozenge$ ) viscosity, poise; ( $\diamond$ ) normal stress, dynes/cm<sup>2</sup>. Dynamic data; (O) 170°C; ( $\square$ ) 180°C; ( $\Delta$ ) 190°C; ( $\nabla$ ) 200°C.

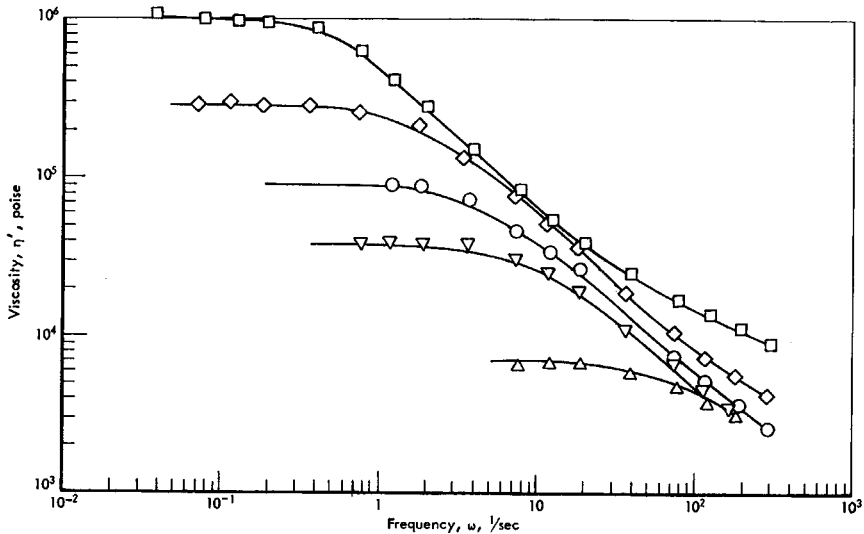


Fig. 2. Dynamic viscosity of MDPS/97: ( $\square$ ) 150°C; ( $\diamond$ ) 160°C; (O) 170°C; ( $\nabla$ ) 180°C; ( $\Delta$ ) 200°C.

sample having a molecular weight of 97,000 (MDPS/97) shown on Figure 2. Unlike SBS, the viscosity for polystyrene is constant (and equal to the steady state Newtonian viscosity) at low frequencies and declines at higher frequencies in the characteristic manner of thermoplastics. From the SBS data it is not possible to determine a Newtonian or zero-shear viscosity, and thus any attempt to correlate viscosity at low shear rates or shear stresses with molecular weight must be viewed with skepticism.

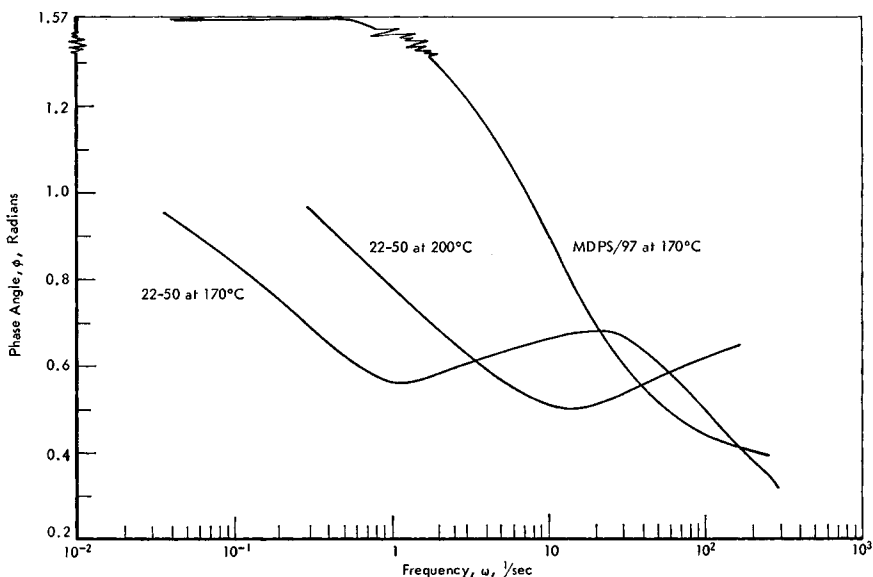


Fig. 3. Phase Angle for SBS 22-50 and MDPS/97.

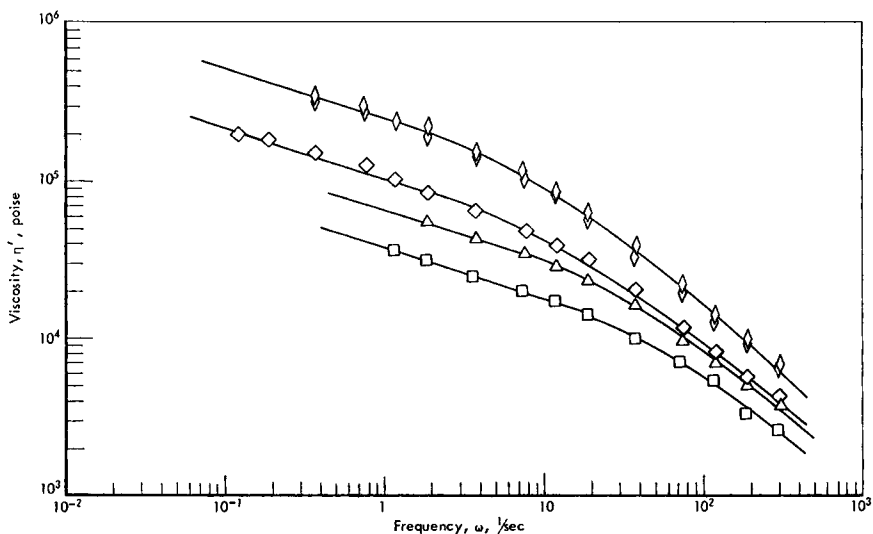


Fig. 4. Dynamic viscosity of SBS 10-50: ( $\diamond$ ) 150°C; ( $\diamond$ ) 170°C; ( $\Delta$ ) 180°C; ( $\square$ ) 200°C.

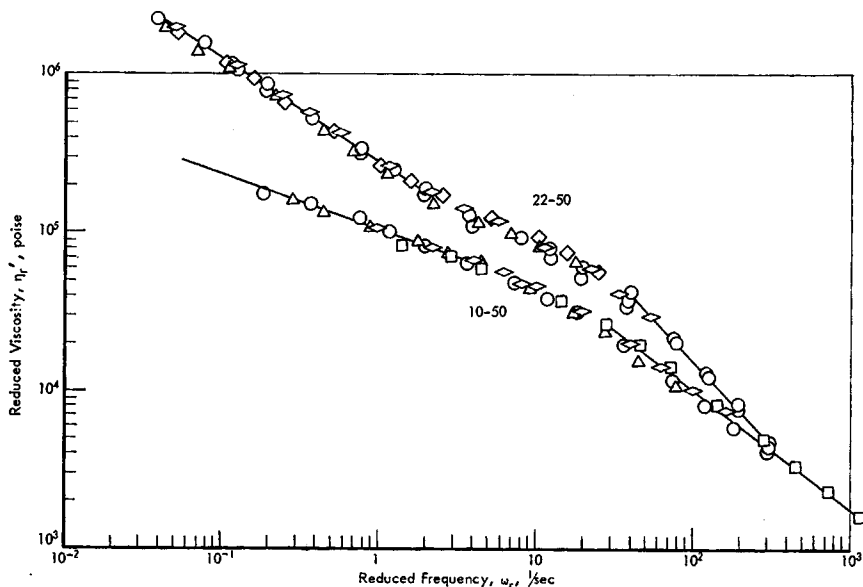


Fig. 5. Master curves for SBS 10-50 and 22-50: ( $\square$ ) 150°C; ( $\circ$ ) 170°C; ( $\diamond$ ) 180°C; ( $\diamond$ ) 190°C; ( $\Delta$ ) 200°C.

It was mentioned earlier that the phase shift,  $\phi$ , between the input deformation and resulting sinusoidal stress is also a measure of elasticity. A phase shift of  $90^\circ$  would be observed when the fluid is Newtonian since the stress would then be in phase with the rate of deformation; on the other hand, a perfectly elastic fluid would have a zero-phase shift. For most thermoplastics, a  $90^\circ$  shift (1.57 radians) is observed at low frequencies, with  $\phi$  dropping off sharply with increasing frequency as seen on Figure 3 for the MDPS/97 sample. On the same figure the results are given for SBS sample 22-50 at  $170^\circ$  and  $200^\circ\text{C}$ . The striking shape of the SBS curves suggest that the fluid undergoes a major transition in properties at well-defined frequencies and that the viscoelastic properties of the polymer are not going to be amenable to simple thermoplastic characterization.

Viscosity data for SBS sample 10-50 are given in Figure 4. The same general viscosity behavior is again observed, only the low frequency slope is smaller (less negative) than for SBS 22-50 and therefore the transition is less distinct. The data for both SBS samples suggest a temperature superposition technique based on the variables

$$\eta_r = \frac{\eta'}{a_T} \left( \frac{T^0}{T} \right) \left( \frac{\rho_0}{\rho} \right) \quad \text{and} \quad \omega_r = \omega a_T \quad (8)$$

where  $T^0$  is a reference temperature. If the superposition is successful, all of the data for a given sample would reduce to a single master curve of  $\eta'_r$  versus  $\omega_r$ , which is independent of temperature. The values of  $a_T$  would be a function of temperature alone. This method is empirical as stated,

TABLE II  
 $a_T$  Versus Temperature

SBS sample	Temperature, °C						
	140	150	160	170	180	190	200
10-50				1.0	0.52		0.237
14-50	31	11.2	4.0	1.0			
22-50		3.1		1.0	0.30	0.142	0.058
14-60			1.70	1.0	0.71		0.26
14-70		2.5	1.4	1.0	0.56	0.375	
MDPS/97		10.1	3.0	1.0	0.38		0.076

but it is suggested by several different molecular theories<sup>4</sup> and has found wide applicability for many viscoelastic functions. The temperature  $T^0$  is sometimes related to the glass transition temperature,  $T_g$ ; for block copolymers, however,  $T_g$  is not readily defined. We therefore arbitrarily choose  $T^0 = 170^\circ\text{C}$ . Further, we estimate the volumetric thermal expansion coefficient for SBS to be  $7 \times 10^{-4} \text{ l./}^\circ\text{C}$ , and thus the ratio  $(\rho_0/\rho)$  is negligible for the range of our data. Using the reduced variables given in eq. (8), the data of Figures 1 and 4 are shown in Figure 5. The superposition is seen to be quite good although some scatter is observed in the higher frequency region. The distinctive character of the SBS viscosity data, however, is still very apparent. The values of  $a_T$  used for the superposition are given in Table II.

The data for the other three samples are given in the reduced form in Figures 6, 7, and 8 for samples 14-50, 14-60, and 14-70, respectively; the

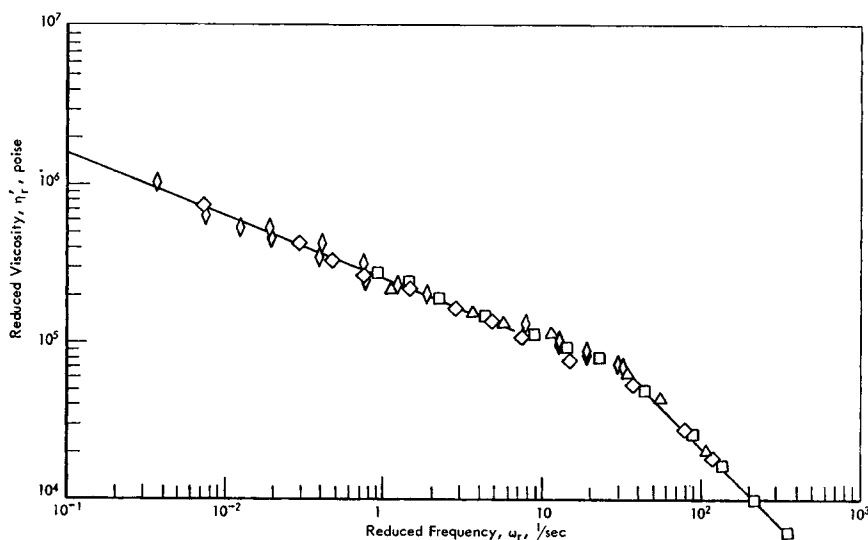


Fig. 6. Master curve for SBS 14-50; ( $\diamond$ )  $140^\circ\text{C}$ ; ( $\square$ )  $150^\circ\text{C}$ ; ( $\triangle$ )  $160^\circ\text{C}$ ; ( $\circ$ )  $170^\circ\text{C}$ .

values for  $a_T$  are also given in Table II. Once again the unusual rheological features of the block copolymers are seen in the curves.

The superposition of the data gathered at different temperatures provided an acceptable master curve for displaying the frequency dependence of the

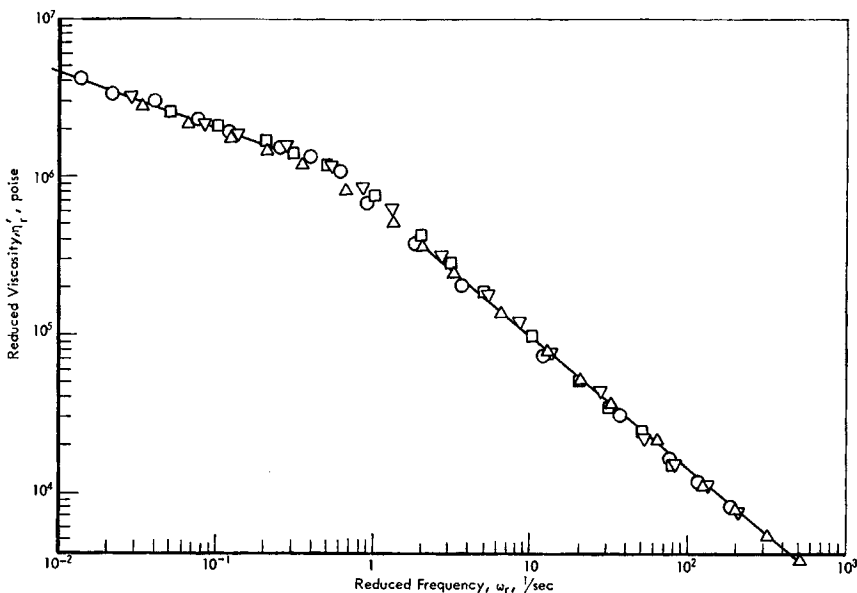


Fig. 7. Master curve for SBS 14-60: ( $\Delta$ ) 160°C; ( $\circ$ ) 170°C; ( $\nabla$ ) 180°C; ( $\square$ ) 200°C.

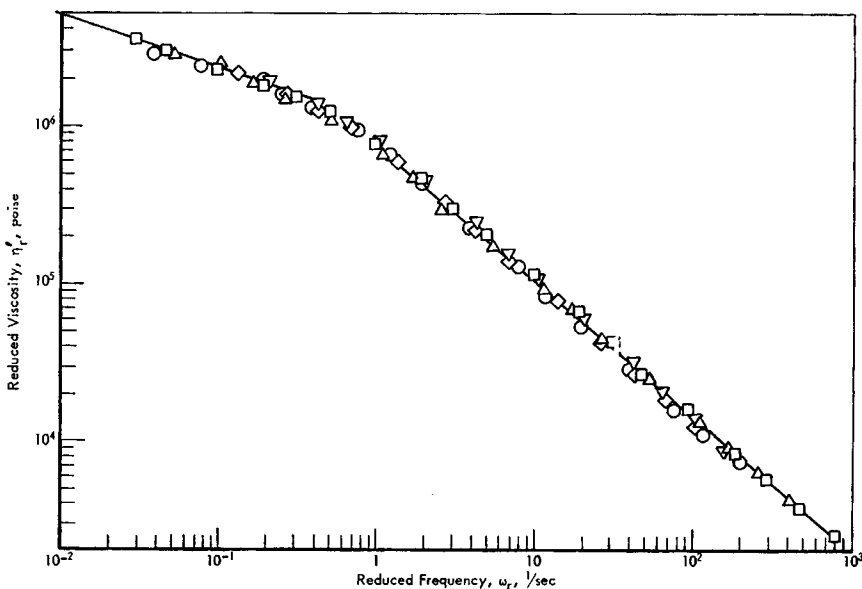


Fig. 8. Master curve for SBS 14-70: ( $\square$ ) 150°C; ( $\Delta$ ) 160°C; ( $\circ$ ) 170°C; ( $\nabla$ ) 180°C; ( $\diamond$ ) 190°C.



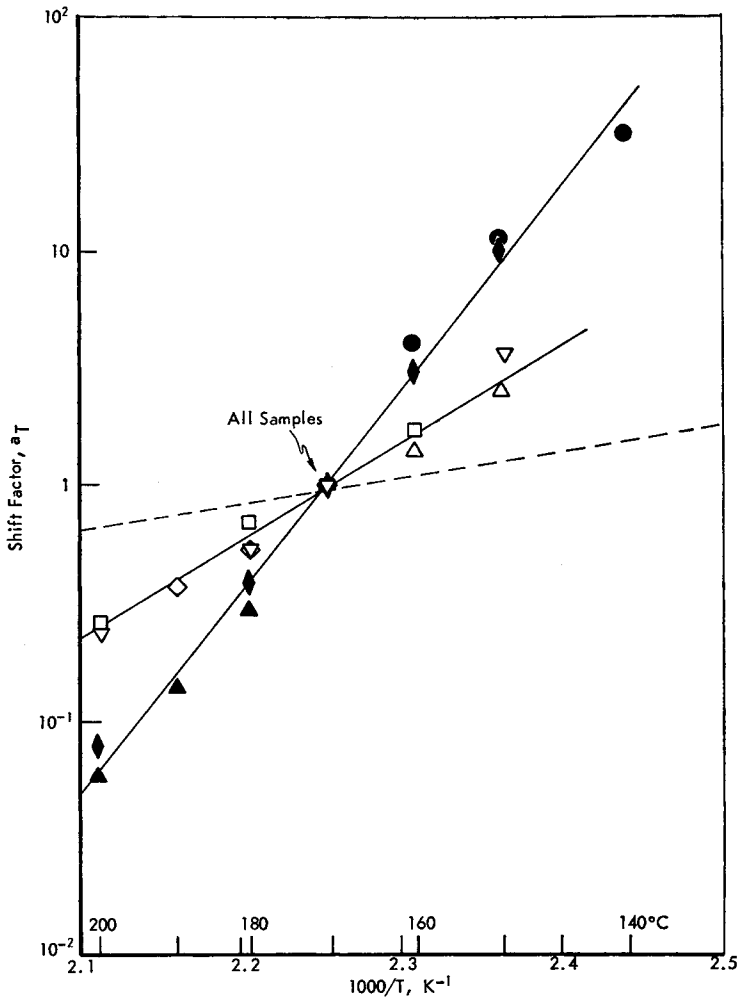


Fig. 9. Arrhenius plot of  $a_T$ : (●) SBS 14-50; (□) SBS 14-60; (◇) SBS 14-70; (▲) SBS 22-50; (▽) SBS 10-50; (◆) MDPS/97; (---) polybutadiene.<sup>6</sup>

dynamic viscosity for a given sample. The temperature dependence of the normalizing factor,  $a_T$ , is shown in Figure 9. Within experimental accuracy the data in this figure appear to fall on one of two lines. Using the Arrhenius relationship,

$$\log_e(a_T) = A + \frac{E}{RT} \quad (9)$$

activation energies  $E$  are calculated to be 38 and 19 kcal/mole for the two lines, respectively. A discussion of the temperature dependence of  $a_T$  on molecular structure is given in the next section.

## DISCUSSION OF RESULTS

The data presented in the previous section may be used directly to estimate the processing behavior of the SBS samples. In addition, they provide insight into the molecular mechanisms which govern these properties.

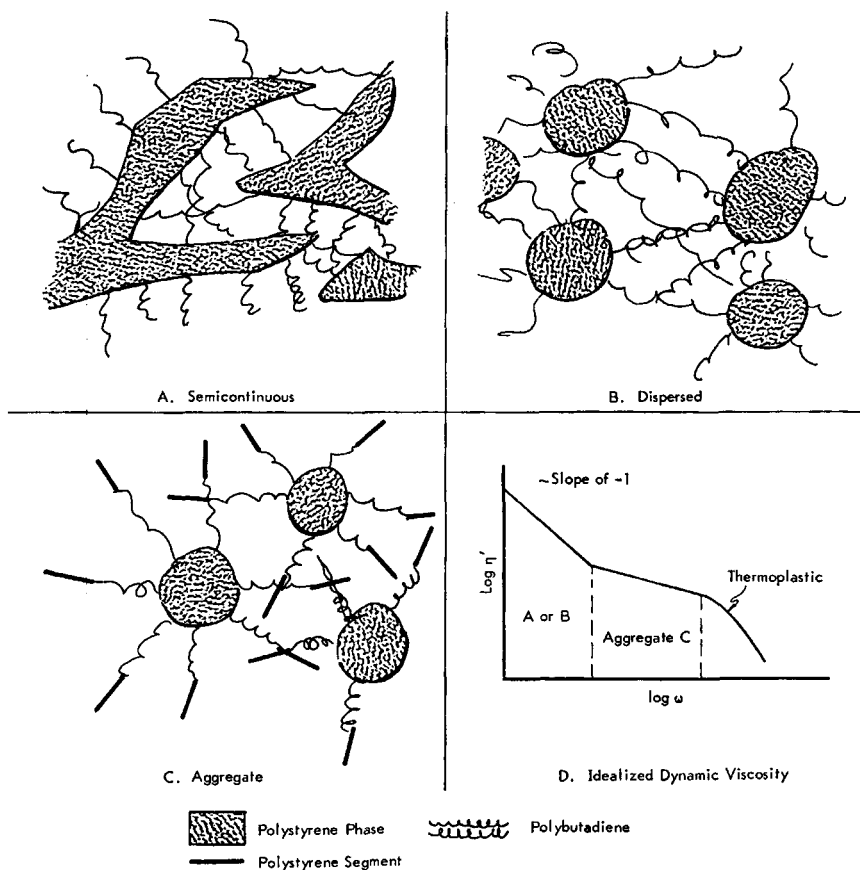


Fig. 10. Idealized structures.

A molecular theory<sup>5</sup> of domain formation in block copolymers provides the basic framework for our analysis. Because of domain formation, a three-dimensional network will be formed in A-B-A block copolymers and their rheology will be dominated by the interplay of processes tending to disrupt and to reform the network and domain systems. We believe that an A-B-A block copolymer can exist in three distinct states which depend on the rate of deformation. The stable state at rest or at very low deformation rates will be a state where the molecular network is essentially intact. This state is shown schematically in Figure 10a for a semicontinuous domain structure (formed when the polystyrene volume fraction is  $\sim 0.5$ ) and in Figure 10b for dispersed domains (low polystyrene volume fraction). At

intermediate deformation rates, the three-dimensional network will be disrupted. Domains and aggregates of many molecules still occur but they are not linked together to form a three-dimensional network. The system will behave as large star-shaped aggregates, shown schematically in Figure 10c. Finally, at high deformation rates, these aggregates will, in turn, be disrupted and the system will behave as an assemblage of individual, non-aggregated molecules. Briefly then, the theory would predict a network response at low shear stress levels (including a yield stress), an intermediate region of shear stress where the viscosity would be much higher than expected for molecules of the given molecular weight, and finally a region at high shear stresses where the behavior would be typical of ordinary thermoplastics of the same molecular weight. An idealized dynamic viscosity curve based on this theory is shown in Figure 10d.

The data presented in this work generally support the above theory. The "thermoplastic" response predicted at high deformation rates is clearly evident, as is the microphase structure at low rates. Since the transition from the "network" state to the "aggregate" state will be a gradual function of the deformation rate, we shall not differentiate between these states in our discussion. Hence, we center our discussion on two types of response, "domain" and "thermoplastic."

The temperature normalization used in this report resulted in activation energies for the shift factor  $a_T$ . In Figure 9, the data are seen to fit two distinct curves, one containing data for samples 14-50, 22-50, and MDPS/97 and one for 10-50, 14-60, and 14-70. In Table III, the activation energies are given along with the polystyrene volume fraction of the SBS molecule. It appears that two different mechanisms are involved, one for polystyrene fractions above 35% and one for fractions less than 31%. We feel that the abrupt change reflects two different types of domain structure in the low-frequency response region, one of a semicontinuous polystyrene phase, as shown in Figure 10a, and one of dispersed polystyrene domains, as shown in Figure 10b. When the semicontinuous polystyrene phase is present, the thermal properties of polystyrene would dominate and thus the curves for

TABLE III  
Volume Fraction of Polystyrene Segments

SBS sample	Polystyrene volume fraction <sup>a</sup>	Activation energy, kcal/mole <sup>b</sup>
MDPS/97	100	38
22-50	48	38
14-50	35	38
14-60	31	19
10-50	29	19
14-70	28	19

<sup>a</sup> The densities of polybutadiene and polystyrene in the melt phase are assumed equal.

<sup>b</sup> Approximate values.

samples 22-50 and 14-50 are nearly the same as for MDPS/97. On the other hand, when the polystyrene phase is dispersed in a continuous polybutadiene phase, the thermal properties would be more like those of polybutadiene (also shown in Figure 9). In this case, however, the presence of the polystyrene domains does influence the temperature dependence of the sample somewhat, resulting in a higher activation than that observed for polybutadiene. It seems apparent, then, that a transition in the melt structure occurs at some polystyrene composition between 31% and 35%. A similar conclusion is reached from results of other physical properties.<sup>1</sup>

We next consider the transition between the domain and thermoplastic responses. First, the success of the temperature superposition for each sample indicates that the product of the reduced transition viscosity  $(\eta'_r)_c$  and frequency,  $(\omega_r)_c$  is constant. By definition,

$$(\eta'_r)_c (\omega_r)_c = \eta_c \omega_c \left( \frac{T^0}{T} \right) = S \quad (10)$$

where  $S$  is constant. Over the temperature range of the data,  $\eta'_c$  varies by a factor of either 10 or 1000 depending on the activation energy. On the other hand,  $T^0/T$  varies by  $\pm 6\%$  and thus the product  $\eta'_c \omega_c$  for each sample may be considered as independent of temperature. If the data reported were steady state viscosities versus shear rate, the results of this constant product would be clear; the transition between microphase and thermoplastic behavior occurs at a constant stress and is essentially independent of temperature. The similarity between dynamic viscosity and steady state viscosity curves, as demonstrated in previous work, leads us to interpret our results in the same way. This, incidentally, is consistent with theoretical considerations discussed above.

The values of  $S$  as determined from the data for each sample are given in Table IV. Some freedom results when selecting the transition point due to both the scatter in the data and the method used to define the transition. Our method was to draw a straight line through the low frequency portion of the curve and mark the first departure from that line as the transition. It is interesting to note that for samples 22-50 and 14-50 the departure was up from the line, as opposed to down from the line for the other three SBS samples. These same two samples, of course, were identified as semicon-

TABLE IV  
Transitions at 170°C

SBS sample	$\eta'_c$ , poise	$\omega_c$ , l./sec	$\eta_c \omega_c = S$ , dynes/cm <sup>2</sup>
14-50	$12.5 \times 10^4$	5.5	$6.9 \times 10^6$
22-50	12.0	3.7	4.4
10-50	5.2	8	4.2
14-60	130	0.3	4.5
14-70	150	0.35	4.5

tinuous in the polystyrene phase. The values for  $S$  given in Table IV are seen to be relatively constant, with the exception of sample 14-50. A close examination of the curve for this sample indicates that it is a difficult transition to select and a value of  $S = 4.5 \times 10^5$  dynes/cm<sup>2</sup> is not unreasonable. It seems plausible, therefore, to conclude that  $S$  is essentially independent of the SBS block segment size and approximately equal to  $5 \times 10^5$  dynes/cm<sup>2</sup>.

The response observed at high frequencies is typical of that observed for other thermoplastic materials. All curves show a power law behavior with a slope essentially the same as that for polystyrene data. Our own studies and others reported in the literature<sup>7</sup> indicate that dynamic data of mono-dispersed polystyrenes have a slope of  $-1$  over the span of frequencies covered by the thermoplastic SBS data. For polystyrene, the stress level at which this slope of  $-1$  occurs is relatively independent of both molecular weight and temperature and has a value of about  $4 \times 10^5$  dynes/cm<sup>2</sup>. For the SBS samples, the slope also approaches  $-1$  in the power law region but occurs at a stress level of approximately  $20 \times 10^5$  dynes/cm<sup>2</sup>. This indicates a significant increase in molecular entanglement which the SBS molecule encounters when moving through the environment of other SBS molecules.

For two of the SBS samples, particularly SBS 22-50, the dynamic viscosity curve appears to level off and approach Newtonian behavior just before the microphase structure becomes dominant. Great care should be exercised in interpreting the data in this fashion, however, since the transition point from elastic to thermoplastic behavior undoubtedly occurs over a frequency range. Data in this range would exhibit both thermoplastic and domain behavior.\*

It was evident from the data presented in the previous section that the response in the low frequency region depended upon different block sizes. The slope of the  $\log \eta'$  versus  $\log \omega$  curve, however, was independent of temperature for a given sample. These slopes, tabulated in Table I, appear to be strongly dependent on the length of the polystyrene block and only weakly dependent on the length of the polybutadiene block. While heuristic arguments might be given to explain this observation, a complete explanation based on molecular structure is not presently offered.

## SUMMARY OF RESULTS

To sum up the previous discussion, we feel that the domain theory is well supported by the data presented. Further, in the absence of rheological

\* Several tests were conducted in which the order of viscosity determinations was altered for the same experimental conditions. Near the transition point, viscosities determined when decreasing frequency differed from those obtained when increasing, indicating that there was a range of frequencies in which one of several molecular structures might prevail depending on the deformation history. In these ranges average values are given in this report.

data on a particular SBS sample, we suggest that the dynamic properties may be estimated using the following guidelines:

A. The high frequency viscosity behavior should be qualitatively similar to that of thermoplastic polymers.

B. A transition between thermoplastic and domain behavior should occur at approximately  $\eta', \omega_r = 5 \times 10^5$  dynes/cm<sup>2</sup>.

C. The slope of the dynamic viscosity curve in the domain region appears to be strongly dependent on the polystyrene block size and to a lesser extent on the polybutadiene block size.

D. The temperature dependence of an SBS sample may be determined using the factor  $a_T$  which is given in terms of an activation energy  $E$ . The value of  $E$  will be approximately 38 kcal/mole for samples with polystyrene constant of greater than 35% and 19 kcal/mole for samples with less than 31% polystyrene.

### Nomenclature

- $A$  = constant, eq. (9)  
 $a_T$  = shift factor, eq. (8)  
 $T$  = absolute temperature, °K  
 $t$  = time, sec  
 $R$  = gas constant  
 $S$  = constant, eq. (10)  
 $\gamma$  = input sinusoidal shear, radians  
 $\gamma_0$  = amplitude of  $\gamma$ , radians  
 $\dot{\gamma}$  = shear rate,  $d\gamma/dt$ , sec<sup>-1</sup>  
 $\eta$  = steady shear rate viscosity, poise  
 $\eta^*$ ,  $\eta'$ ,  $\eta''$  = dynamic viscosity, eq. (4)  
 $\eta', \omega_r$  = reduced coordinates, eq. (8)  
 $(\eta')_c, (\omega)_c$  = transition values of  $\eta'$  and  $\omega$   
 $\rho$  = density, g/cc  
 $\sigma$  = shear stress, dynes/cm<sup>2</sup>  
 $\sigma_N$  = normal stress, dynes/cm<sup>2</sup>  
 $\phi$  = phase angle, radians  
 $\omega$  = frequency, sec<sup>-1</sup>

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