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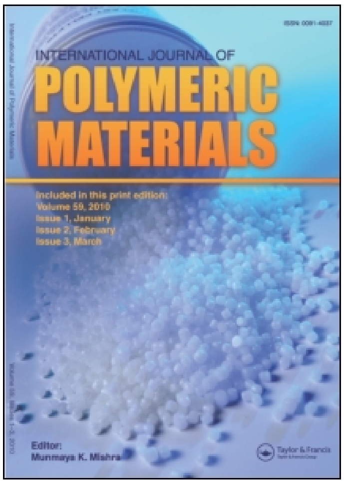

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Dynamic Mechanical Properties of Block Copolymer Blends-A Study of the Effects of Terminal Chains in Elastomeric Materials

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Dynamic Mechanical Properties of Block Copolymer Blends—A Study of the Effects of Terminal Chains in Elastomeric Materials

2. Forced Oscillation Measurements

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Three different polystyrene-1,4 polybutadiene (SB) diblock copolymers were blended with a single polybutadiene continuous SBS triblock to form rubbery networks with controlled amounts of terminal chains of known molecular weight. The mechanical properties of these materials were studied in dynamic uniaxial compression from 0.1 to 1000 Hz at various temperatures between −87 and 85°C. At high reduced frequencies in the glassy and polybutadiene transition regions the terminal chains have no perceptible effect on the components of the complex compliance. At intermediate reduced frequencies a temperature dependent entanglement coupling phenomenon appears if the terminal chains are sufficiently long. At low reduced frequencies the terminal chains contribute to entanglement slippage processes which result in an increase in both the storage and loss compliance.

INTRODUCTION

In the first paper of this series,[1] we have discussed the advantages and limitations of block copolymer blends as model materials for the study of the effects of terminal chains in elastomers. A triblock copolymer with glassy endblocks and a rubbery center segment provides a rubbery network with no terminal chains and serves as a base material for the model system. By blending it with well characterized diblock copolymers, rubbery networks with controlled amounts of terminal chains of known molecular weight are obtained.

We have previously reported[1] on free oscillation (isochronal) measurements conducted on three series of blends of polystyrene-1,4 polybutadiene (SB) diblock and polystyrene-1,4 polybutadiene-polystyrene (SBS) triblock copolymers. These measurements provided qualitative information on the effect of terminal chain content and terminal chain length on the storage and loss moduli of the blends. In this paper we report isothermal forced oscillation measurements on the same materials. The measurements were made in uniaxial compression. They corroborate the earlier results but are more amenable to quantitative interpretation and, therefore, provide more information on the molecular mechanisms involving the terminal chains.

MATERIALS AND SAMPLE PREPARATION

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The earlier paper[1] described the materials used in this work in detail. Their compositions are repeated in Table I. The numbers separated by the solidi indicate the individual block molecular weights in thousands. In this paper we examine the SBS-8 triblock (the base material), all blends of Series 1,

TABLE I

Sample Code	X	ϕ
Series 1. Terminal chain $\bar{M}_n = 51{,}000$		
SBS-8, 16/78/16	0	29
BL-1.1	0.231	26
BL-1.2	0.444	23
BL-1.3	0.577	22
SB-6, 9/51/0	1.000	15
Series 2. Terminal chain $\bar{M}_n = 22{,}000$		
SBS-8	0	29
BL-2.1	0.159	28
BL-2.2	0.315	28
BL-2.3	0.416	27
SB-7, 7/22/0	1.000	24
Series 3. Terminal chain $\bar{M}_n = 67{,}000$		
SBS-8	0	29
BL-3.1	0.334	24
BL-3.2	0.490	22
SB-5, 10/67/0	1.000	13

X = weight fraction of terminal chains in rubbery phase.
ϕ = weight percent polystyrene.

and blends BL-2.3 and BL-3.2 from Series 2 and 3, respectively. None of the pure diblock copolymers was studied since they were too soft to prepare specimens suitable for our apparatus.

The techniques for preparing uniform thin films of the various diblock–triblock blends have been discussed previously.[1-4] The thickness of a typical film was not sufficient for direct use in the dynamic tester and therefore laminated specimens were made.[3,4] In this study the uniaxial compression was imposed perpendicular to the laminations. Mechanical properties measured parallel and perpendicular to the laminations of one triblock specimen had been found to be essentially identical[3,4] and thus the necessity for using multilayer specimens is not considered to be a problem.

The importance of annealing the block copolymer films has also been discussed previously.[1-4] The laminated sheets from which the small specimens were cut were annealed in vacuum for 6 hours at 100°C.

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APPARATUS AND EXPERIMENTAL PROCEDURES

The rheometer and the method of obtaining the complex moduli or compliances of the materials tested has been described by Fesko,[3] and by Fesko and Tschoegl.[4] The operation of the rheometer can be summarized as follows. A voltage signal is supplied to a confined stack of piezoelectric disks. As a result, a flat driver plate experiences a sinusoidal displacement. The maximum amplitude of this displacement is estimated[3,4] to be around 300 nm (3000 Å). The specimen is compressed between the driver and a force monitor plate. The force transmitted to the monitor plate is converted to an electrical charge signal by a very small deformation of a piezoelectric force transducer. This deformation is small enough to be neglected in comparison with the drive displacement.[3,4] Thus, a typical specimen experiences exceedingly small compressional strains (ca 0.01 %). Because of these small strains distortion of the specimen by bulging may be neglected.

Each material was tested over four decades of frequency (from 0.1 to 1000 Hz) at a minimum of 17 different temperatures. The temperature range extended roughly from −87° to 85°C. Measurements always began at 50°C, and the apparatus with specimen in place was allowed to equilibrate at that temperature for 24 hours. This procedure assured good adhesion between the specimen and the confining plates and improved the reproducibility of the data. The test temperature was progressively lowered in intervals of 5–10°C until data had been obtained at the lowest temperature of interest; measurements were then made at temperatures above 50°C. A blanket of nitrogen gas was maintained around the specimen to prevent oxidation.

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RESULTS

The data are presented as the components of the complex compressional compliance, the storage compliance, $D'(\omega)$, and the loss compliance, $D''(\omega)$. Shifting the isothermal segments into master curves presents a particular problem for the two-phase block copolymer systems studied here. It has been shown on theoretical grounds[3,8] that the conventional shifting procedure[5] commonly employed for thermorheologically simple materials cannot be valid in all regions of time and temperature for the materials studied here. In the detailed study of the time–temperature characteristics of the SBS-8 triblock conducted by Fesko and Tschoegl[3,4] it was established that for temperatures below 40°C the temperature dependence of the mechanical properties was dominated by the contribution from the polybutadiene phase. Furthermore, below this temperature contributions to the compliance arising from a softening interlayer[3,6,7] or from the polystyrene domains themselves can be neglected.[3,4] To extend the analysis to higher temperatures it would be necessary to use point-wise shifts calculated from a model such as the one proposed by Fesko and Tschoegl[8] to account for the thermorheological complexity of the two-phase system.

For the base material, the SBS-8 triblock, the segments corresponding to temperatures of 40°C and below were assembled into storage and loss compliance master curves. The data above 40°C could not be superposed by simple horizontal shifting, and therefore these data were disregarded. The empirical shift factors, log a_T, required to effect superposition are plotted against temperature, T, in Figure 1 for two separate specimens (denoted u and uA)

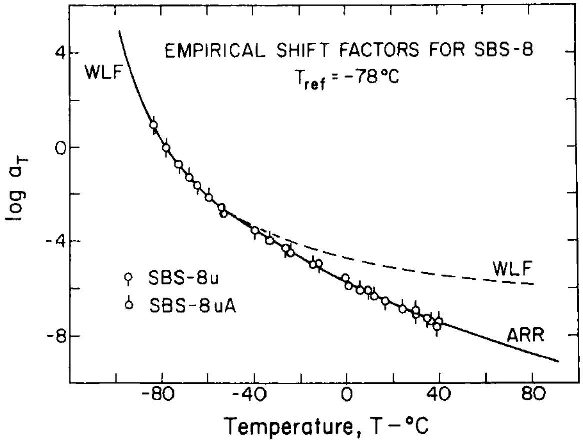

FIGURE 1 Empirical shift factors for the SBS-8 triblock.

of SBS-8. Below about $-60°C$, the temperature dependence of the mechanical properties of SBS-8 could be described by a WLF equation.[5] At higher temperatures the shift factors followed an Arrhenius equation. The solid line in Figure 1 is represented rather well by the following composite equation:

$$\log a_T = \begin{cases} -7.76\,(T + 78.0)/(129.1 + T) & T \leq -60°C \\ 3600\left(\dfrac{1}{T + 273.2} - 5.25\right) & T > -60°C \end{cases} \tag{1}$$

where T is the temperature in °C and the various constants are found from the data by suitable curve fitting procedures.[5]

A shift factor equation comprising a WLF and an Arrhenius portion has been proposed in an earlier paper from this laboratory[9] to represent what was then thought to be the separate contributions of a hard and a soft phase in a two-phase material. Later work[3,8] showed that this interpretation was not correct, and that the observed departure from WLF-behavior at higher temperatures (below the glass transition of the polystyrene phase, however) appeared to result from the existence, in the polybutadiene phase, of two mechanisms: the usual main transition, and entanglement slippage. According to this view the polybutadiene phase itself is not thermorheologically simple. The data presented here are not precise enough to allow a clear separation of the temperature dependences of the two mechanisms. Fortunately, however, in the region where the two mechanisms overlap, the compliance curves are relatively flat and the difference between WLF and Arrhenius behavior is small. Therefore master curves obtained by shifting according to Eq. (1) in this region should not differ markedly from those one would obtain from a more sophisticated shifting procedure if one were available.

Equation (1) differs slightly in form from the equation used by Fesko,[3] and by Fesko and Tschoegl.[4] It yields a shift factor curve which is smooth over the entire temperature range rather than exhibiting a sudden break at an arbitrary temperature, and this results in somewhat better overall superposition in the compliance master curves.

Application of the shift factors shown in Figure 1 to the compliance data for SBS-8 results in the master curves for a reference temperature of $-78°C$ shown in Figure 2. Here the logarithms of the reduced compressional storage compliance, $D'_p(\omega a_T)$, and the reduced compressional loss compliance, $D''_p(\omega a_T)$, are plotted against the logarithm of the reduced frequency. The subscript p indicates that the temperature correction T/195 (°K) has been applied to the data. The superposition of the data is quite good over the entire reduced frequency range, although it is generally somewhat better for the storage compliance. This reflects the relative ease with which the latter measurements can be obtained. The storage compliance rises from very low values

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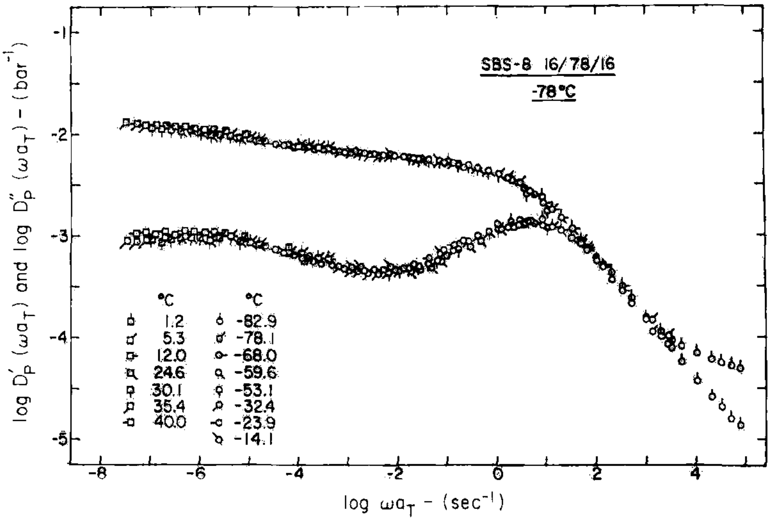

FIGURE 2 Storage and loss compliance master curves for SBS-8.

in the glassy region (low temperature and high frequency) through the polybutadiene transition and continues to rise, although much more slowly, across the intertransition region. The loss compliance exhibits a peak in the polybutadiene transition and a broad secondary maximum at much lower frequencies. The polystyrene transition would appear at still lower frequencies but is not seen here since all data above 40°C were excluded.

In shifting the data for the blends, best results were found when the data were fitted into superposition in the region of the main polybutadiene transition and at the low reduced frequency end of the master curves. In addition to providing the best overall superposition for all the blends studied, this procedure resulted in log a_T vs. T plots which were essentially identical to that established for the triblock material. Figure 3 shows the empirical shift factors for the five blends with the solid line again representing Eq. (1). Since the triblock represents the base material for the three series, it is reasonable to use its temperature dependence for reduction of the data for all of the blends. In this way it is certain that any differences appearing in the various master curves must arise from changes in material behavior, and not from differences in the method used to reduce the data.

Figure 4 shows the storage and loss compliance master curves for one of the blends of Series 1, BL-1.2. The data superpose well at high reduced frequencies, i.e. in the glassy and transition regions. At the beginning of the intertransition region there is a significant lack of superposition on the low frequency side of the main loss peak. At still lower reduced frequencies the

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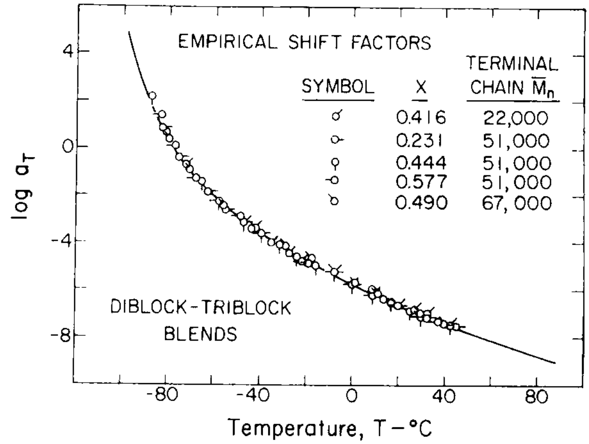

FIGURE 3 Empirical shift factors for the diblock-triblock blends.

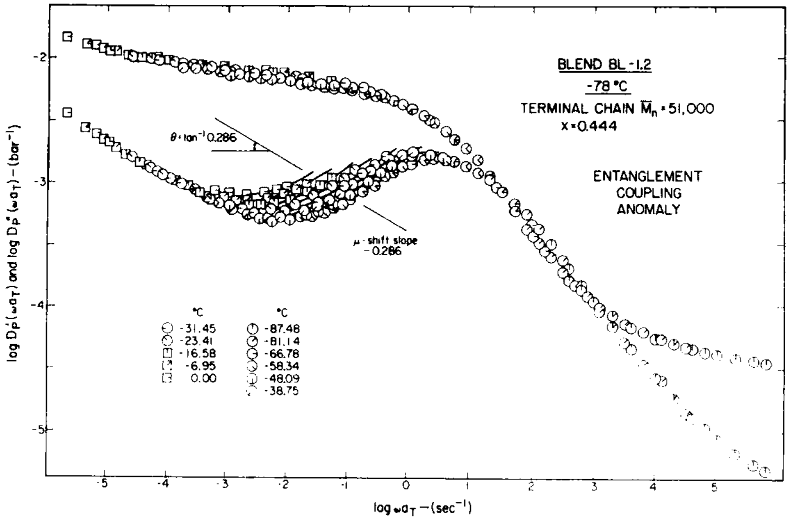

FIGURE 4 Storage and loss compliances for blend BL-1.2 reduced by shift factors of Figure 3.

data again superpose well. Only data for temperatures 0°C and below are shown here for clarity. The low frequency ends of the storage and loss compliance curves obtained at temperatures between 0°C and 40°C (not shown in Figure 4) all superposed well. Superposition anomalies similar to the behavior seen in Figure 4 were also observed for the other two blends of Series 1 and for the single blend studied from Series 3.

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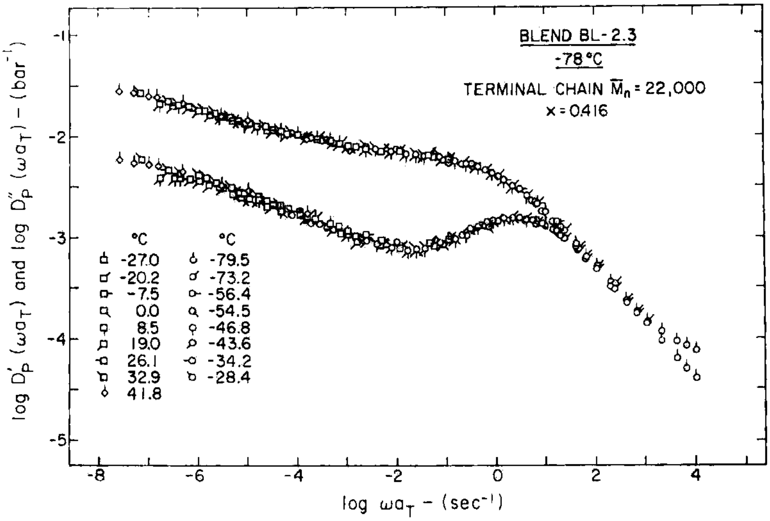

FIGURE 5 Storage and loss compliances for blend BL-2.3 reduced by shift factors of Figure 3.

The blend from Series 2 did not exhibit the superposition anomaly seen in Series 1 and 3. Figure 5 shows the storage and loss compliance data for this blend. The data superpose well over the entire frequency range. BL 2.3 was the only blend studied from Series 2, but since it contained the largest concentration of terminal chains in that series it offered the most rigid test of the data.

DISCUSSION

Glassy and transition regions

Our earlier measurements[1] in free oscillation had shown that the terminal chains in the model networks of Series 1–3 had essentially no effect on the mechanical properties in the glassy and the polybutadiene transition regions. This is borne out by a comparison of Figures 2, 4, and 5. Figure 6 shows the loss tangents ($\tan \delta = D''/D'$) in forced oscillation for the SBS-8 triblock and the three blends of Series 1. In the glassy and transition regions ($\log \omega a_T > 0$) the narrow band of curves indicates the essential agreement among the various sets of data. The $\tan \delta$ curves for the two blends from Series 2 and 3 are not shown but would appear within the envelope of curves in Figure 6 above $\log \omega a_T = 0$.

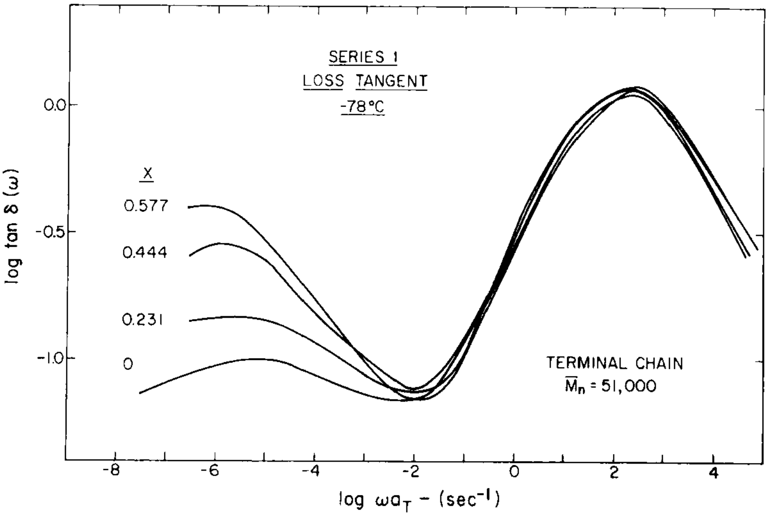

FIGURE 6 Loss tangents for SBS-8 and the blends of Series 1.

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The essentially identical response to forced oscillation in the glassy and transition regions supports the earlier proposal[1] that the short-range motions dominating the mechanical response in these regions occur without regard to the nature of the chain-end restrictions in the network. Thus in all the materials studied here terminal chains (engaged in the network at only one end) and network chains (both ends engaged) behaved identically at high reduced frequencies.

In the free oscillation measurements the location of the transition region on the temperature axis was also unaffected by the presence of terminal chains.[1] The location of the transition region on the frequency scale is determined primarily by the monomeric friction coefficient which in turn depends upon the amount of free volume in the material. The frictional resistance per monomer unit decreases with increasing free volume and results in a shift of the transition to higher frequencies. The presence of chain ends in polymeric systems can cause a significant increase in free volume; however, when the molecular weight of the polymer molecules is greater than about 20,000, the effects of changing free volume due to differences in the amount of free chain ends becomes imperceptible.[5] This explains the observed insensitivity of the location of the transition region to the terminal chain content in this study. Since terminal chains introduce only one free end each, they affect the free volume in a manner similar to homopolymer chains of twice the molecular weight. Thus the shortest terminal chains employed here ($\bar{M}_n$ = 22,000) are much too long to cause significant changes in the free volume. A significant fraction of terminal chains of molecular weight below 10,000 would be necessary to change the location of the transition region along the frequency scale.

Temperature-dependent entanglement coupling

Our previous experiments on these materials[1] indicated that the long terminal chains in the blends of Series 1 and 3 can be engaged in a temporarily coupled network of untrapped entanglements within the permanent network of trapped entanglements provided by the triblock. The effect of this temperature-dependent mechanism was most noticeable in the loss properties.[1] The coupling of the untrapped entanglements weakened as temperature increased. Further, in these earlier experiments no temporary entanglement coupling could be detected in the blends of Series 2. Thus we should expect to find manifestations of a second temperature dependence, in addition to the basic time–temperature relationship of Eq. (1), for the blends of Series 1 and 3 but not for the blends of Series 2.

Since good superposition was obtained for SBS-8 and BL-2.3 data, the shift factors of Figures 1 and 3 represent the temperature dependence of the mechanical properties of the polybutadiene phase of these materials. For the blends of Series 1 and 3, however, these shift factors were not sufficient to bring the data into superposition as evidenced by reduction anomalies of the type seen in Figure 4.

Reduction anomalies of this type have already been observed by Ferry and coworkers in the behavior of several high molecular weight methacrylate polymers and their solutions.[10–13] In one of these studies[11] a method for reducing the anomaly was developed through considerations of the effect of temperature on the temporary entanglement network formed in these materials. Because there is no entanglement slippage in the region of the anomaly (slippage occurs at lower reduced frequencies), the predictions of the molecular theories for cross-linked and entanglement networks (Ref. 5, Ch. 10) are applicable here. These theories indicate that the magnitude of the complex compliance is inversely proportional to the number of junction points in a network while the location of the same compliance value along the reduced frequency scale is directly proportional to the square of this number. Ferry and coworkers reasoned that in an entanglement network the number of junction points, i.e. the number of untrapped entanglements, could be affected by changes in temperature. In particular, a change in temperature which would alter the number of entanglement points by a factor f would consequently result in a change in magnitude of the compliance by a factor $1/f$ and a shift in its location on the frequency scale by a factor f^2. The unknown factor f associated with each temperature was determined by shifting the

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anomalous compliance data along the theoretical slope of −1/2 on the log–log plots and recording the distance required to obtain superposition. The "*f*-shift"[11] factors obeyed Arrhenius equations with apparent activation energies ranging from 1.6 to 2.3 kcal/mole depending upon the material.

The method resulted in excellent reduction of the superposition anomaly for the various methacrylate polymers. The basic reasons for the observed nonsuperposition were also made apparent by Ferry's analysis. Experiments carried out at different temperatures, while conducted on the same specimen, actually tested a material with a different structure in each case. At higher temperatures there was a larger average distance between entanglement points and therefore fewer entanglements comprising the network. Consequently the material became more compliant (i.e. the compliances were shifted upward) and its overall mechanical response shifted to lower frequencies than predicted by the conventional temperature reduction. These changes in structure of the material were compensated for by the *f*-shift as described above, and therefore the superposition of the data was restored.

The superposition anomaly in the mechanical behavior of the methacrylate polymers is remarkably similar to the anomaly seen for blend BL-1.2 in Figure 4, for the remaining two blends of Series 1 and for the single material BL-3.2, studied from Series 3. Therefore, a diagonal shifting scheme similar to the "*f*-shift" seems indicated to resolve the anomalies here. The blends differ from the methacrylates, however, in that only a portion of the networks, the untrapped entanglement portion, will be affected by a change in entanglement coupling with temperature since the trapped entanglements are fixed in number as long as the polystyrene domains remain intact. The methacrylate networks were comprised entirely of untrapped entanglements and therefore the total system was affected by changes in temperature. Qualitatively, then, one would expect the vertical, or compliance component of the diagonal shift to be smaller for our networks than for the methacrylates. Following this line of reasoning, one should use slopes of absolute magnitude less than 1/2 to resolve the superposition anomalies in the blends, and furthermore these slopes should increase toward a limiting magnitude of 1/2 as terminal chain content increases. Since the magnitudes of the slopes of the low frequency losses in the blends were always less than 1/2 and increased with increasing terminal chain content, shifting along these slopes appeared to be a convenient and meaningful way to resolve the superposition anomaly in these materials. Since the slopes were composition-dependent and different from −1/2, the diagonal shift scheme used here has been designated as the "μ-shift" to distinguish it from Ferry's "*f*-shift." In the Appendix it is shown that our μ-shift reduces to Ferry's *f*-shift for the particular case of a diagonal slope of −1/2. In Figure 7 the μ-shift slopes are plotted against the weight fraction of terminal chains, X. The value for the base material, SBS-8, is

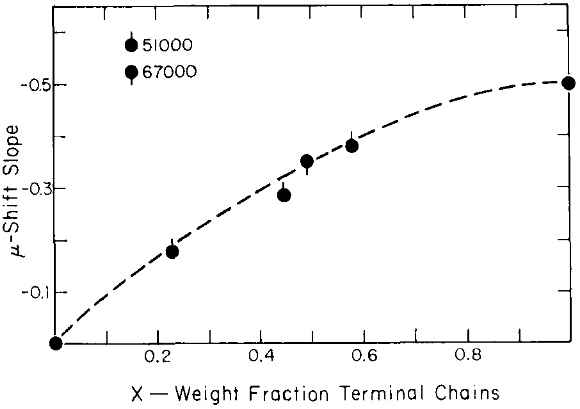

FIGURE 7 μ-shift slopes as function of terminal chain content.

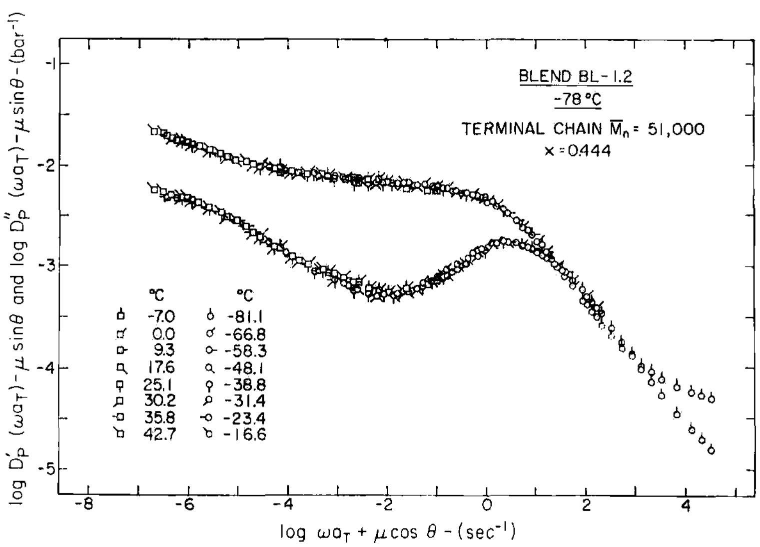

FIGURE 8 Storage and loss compliances for blend BL-1.2 reduced by both log a_T and μ-shift factors.

included as the point at the origin. The *f*-shift value of $-1/2$ is also included as the point for $X = 1$. The slopes all fall on a smooth curve which may approach $-1/2$ for a terminal weight fraction of unity.

By moving the individual isotherms down and to the right along the appropriate slope, the data collapsed into a single master curve exhibiting good superposition over the entire frequency range. Figure 8 illustrates this behavior for blend BL-1.2 where the horizontal and vertical coordinates now

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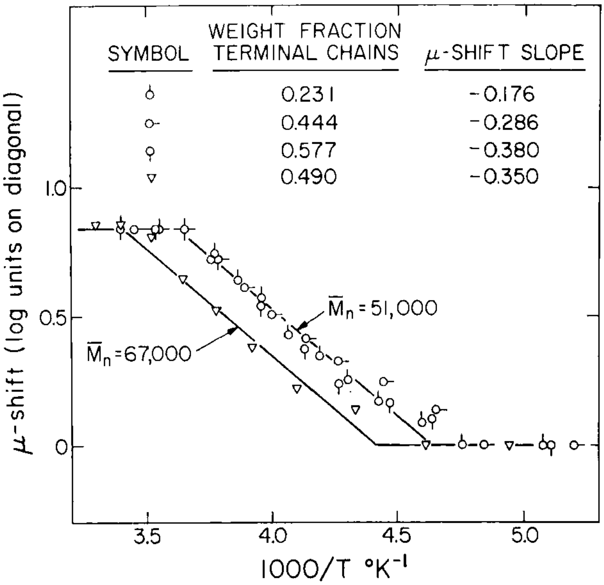

FIGURE 9 μ-shift factors for the blends of Series 1 and for blend BL-3.2.

include the appropriate component of the diagonal shift or "μ-shift". The μ-shift factor corresponding to a given temperature is taken as the distance along the diagonal, in logarithmic units, required to effect superposition of the particular isotherm under consideration with the rest of the data.

The μ-shift factors for the four blends under consideration are plotted against inverse temperature in Figure 9. A different μ-shift slope was employed for each material, steeper slopes corresponding to higher terminal chain contents. For Series 1 the μ-shift factors for all three blends (represented by the circles in Figure 9) scatter moderately around a single straight line over the region of temperature in which the superposition anomaly was apparent. At low temperatures the compliance data superposed very well and no μ-shift was necessary; the choice of $\mu = 0$ at low temperature assures that both shifting procedures (log a_T and μ) have been referred to a temperature, −78°C, within the transition region. The maximum value of μ is somewhat arbitrary as a result of the limited length of the compliance isotherms. This upper limit corresponds to the highest temperature for which the compliance data reached into the region where the reduction anomaly was apparent. Data at still higher temperatures superposed quite well and therefore no further μ-shift was required.

For the single blend of Series 3, BL-3.2, the lack of superposition in the compliance data could also be resolved successfully by the same μ-shift

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procedure. As shown by the triangles in Figure 9, the μ-shift factors for this material could be fitted by a straight line parallel to the one used for Series 1. The μ-shift data for this blend are sparse, but they do indicate that the increase in terminal chain length from 51,000 to 67,000 had no effect on the controlling mechanism except that it was shifted to higher temperatures.

An apparent activation energy, ΔH_a, in units of kcal/mole cannot be calculated directly from the μ vs. 1000/T plot in Figure 9 since only a portion of each model network takes part in the temperature-dependent entanglement coupling mechanism. The active proportion of the network increases as terminal chain content increases; however this concentration dependence has been effectively removed by employing the various selected μ-shift slopes indicated in Figure 9. Thus we may assume that when all of the model network takes part in this entanglement coupling phenomenon, i.e. when $X = 1$ and the magnitude of the μ-shift slope is 1/2, the slope of the μ vs. 1000/T plot in Figure 9 will remain unchanged. In that case we can calculate the apparent activation energy associated with the temperature-dependent entanglement coupling mechanism for our polybutadiene material from the relation:

$$\Delta H_a = 0.447\,(2.303\ RS) \qquad (2)$$

The numerical factor 0.447 accounts for the geometry discussed in the Appendix, the factor of 2.303 converts decadic to natural logarithms, R is the gas constant in appropriate units, and S is the magnitude of the slope of the μ vs. 1000/T plot shown on Figure 9.

The resulting value of 1.7 kcal/mole for ΔH_a associated with the μ-shift for these materials is in excellent agreement with the values of 1.6 to 2.3 kcal/mole reported by Ferry and coworkers[5,11] for the methacrylate polymers. This close agreement is probably fortuitous since the systems are quite different. In fact, the general interpretation of these apparent activation energies as heats of dissociation, with an implied equilibrium existing between the untrapped entanglements and a large excess of entanglement sites[5,11] should not be taken too literally. It is perhaps sufficient to view the μ-shift as a convenient method for reducing superposition anomalies of the type shown above. There is, however, ample evidence from our previous studies of these materials[1] and the earlier studies on methacrylate polymers[10–13] to suggest that the systematic superposition anomalies observed here result from a decrease in the amount of entanglement coupling with increasing temperature.

It remains to explain the obvious absence of any entanglement coupling effects in Series 2, in which the terminal chain molecular weight is 22,000. Figure 5 shows clearly that no μ-shift was required to obtain good superposition of the data on blend BL-2.3 in the region in which the superposition anomaly appeared in the blends of Series 1 and 3. This is consistent with the earlier observation[1] that no minima developed in the loss modulus curve

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derived from free oscillation data for Series 2. We have discussed this problem extensively in the earlier paper and have concluded that terminal chains with molecular weight of 22,000 are short enough to be below the molecular weight required for coupled untrapped entanglements in these systems.[1] As a result the response of blend BL-2.3 is not affected by changes in temperature in the manner discussed above.

It is not clear why the entanglement coupling anomaly is so apparent in the methacrylate polymers and the block copolymer blends reported on here but is completely absent in virtually all other systems whose properties have been reported in the literature. One possible explanation[5,11] is based on the presence of high molecular weight aggregates in the methacrylate polymers due to regions of tactic ordering.[14] Presumably the effects of temperature on entanglement coupling are more prominent when the entanglement structure is enhanced by these regions of high aggregation.[5] It is interesting that an entanglement coupling mechanism so strikingly similar to that seen in the methacrylates should appear in the mechanical behavior of our model networks. Especially interesting is the fact that the glassy domains act as multifunctional linkage points from which the uncross-linked polybutadiene segments emanate. The domains may affect the entanglement topology in much the same way as the regions of tactic ordering do in the methacrylates, and this may conceivably account for the appearance of prominent entanglement coupling effects in our data. Further studies of entanglement networks containing regions of high aggregation should help to establish the validity of this explanation.

ENTANGLEMENT SLIPPAGE

The slippage of trapped and untrapped entanglements will cause secondary relaxation or retardation effects to appear in the mechanical response curves at low reduced frequencies. Untrapped (diblock–diblock and diblock–triblock) entanglements become completely disengaged through this entanglement slippage process so that their contribution to the mechanical properties disappears at very long times. Trapped (triblock–triblock) entanglements cannot become disengaged since all four chains radiating from these entanglements eventually find their way to a glassy domain. However, at low enough reduced frequencies, when slippage of these chains is permitted, the positions of the trapped entanglements will change continuously as the network seeks to accommodate the imposed stresses or strains.

The free oscillation data obtained earlier[1] suggested that the entanglement slippage processes resulted in a decrease in the storage modulus but contributed at the same time to additional frictional mechanisms which increased

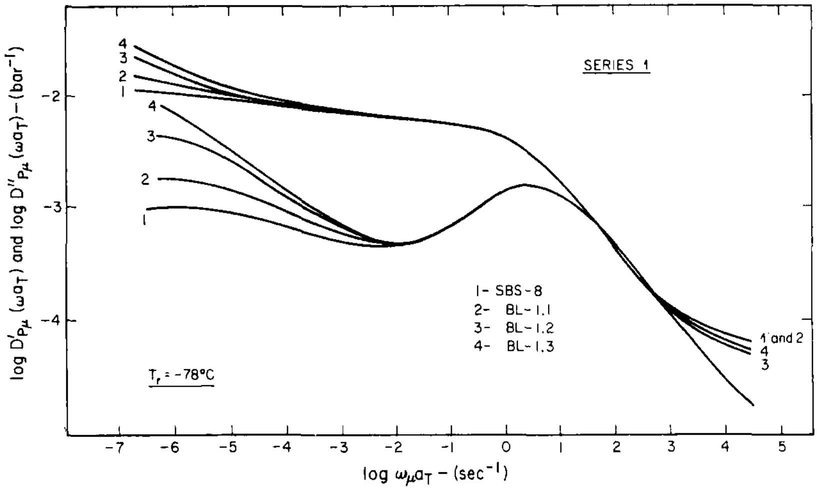

FIGURE 10 Fully reduced storage and loss compliances for SBS-8 and the blends of Series 1.

the loss. Figure 10 shows that similar effects appear in the forced oscillation compliance data. Here the double subscripts on $D'_{p_\mu}(\omega a_T)$ and $D''_{p_\mu}(\omega a_T)$ indicate that the μ-shift has been taken into account for the blends. The storage and loss compliance master curves for Series 1 shown in Figure 10 are essentially identical above $\log \omega a_T = -2$ where entanglement slippage is not important. At lower reduced frequencies the slippage mechanisms result in an increase in both the storage and the loss compliance.

The broad secondary maximum seen in the loss compliance for the triblock material appears to represent the dispersion due to trapped entanglement slippage.[3,4] As terminal chains are added to the networks the low frequency losses increase and the location of the overall dispersion shifts to lower frequencies. This shift in location is seen more clearly in Figure 6 since the secondary peaks in tan δ are more pronounced than those in the loss compliance curves. Figure 6 also reveals that the loss is affected to a much greater extent than the storage by enhanced entanglement slippage since the low frequency values of tan δ increase with terminal chain content, X. The increase of the storage compliance with X is a result of the increased amount of untrapped entanglements in the network which eventually become disengaged and no longer contribute to the stress bearing capacity of the material. At the same time, the friction or loss contribution is greatly increased as the network becomes looser and the amount of long-range dissipative motion increases.

In the earlier study[1] of these model materials, the length of the terminal

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chains in the network appeared to influence the location of the various entanglement slippage processes along the temperature scale; longer terminal chains contributed at higher temperatures. Similar conclusions may be drawn by inspection of the forced oscillation data presented here. It appears that the short terminal chains of Series 2 were not engaged in a coupled entanglement network since no μ-shift mechanism was observed in the temperature dependence of blend BL-2.3. Thus these short terminal chains were already free to take part in slippage processes at intermediate reduced frequencies. This is seen in Figure 5 in the shallower minimum in the loss compliance of blend BL-2.3 near $\log \omega a_T = -2$ and the overall more rapid rise in the storage compliance as compared to the Series 1 master curves. Although not shown here, the loss compliance master curve obtained on blend BL-3.2 from Series 3 exhibited a deeper minimum, and the secondary rise in the storage compliance was shifted to lower frequencies compared to the Series 1 data. This indicates a paucity of intermediate-frequency slippage processes in favor of those at lower frequencies for the long terminal chains of Series 3.

The mechanical behavior at low frequencies observed here is not unlike that found by Ferry and coworkers[15–22] in their studies of entanglements in conventionally crosslinked elastomers. However, it is particularly useful that our model systems have networks which are well-characterized in terms of terminal chain molecular weight and terminal chain content, X. In the next paper of this series a mathematical model will be developed to predict the low-frequency mechanical response in terms of these two parameters. The model successfully accounts for the observations discussed above concerning the changing strength and location of the various entanglement slippage processes as terminal chain content and length are varied.

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APPENDIX—THE μ-SHIFT

The μ-shift factors are taken as the shift, in logarithmic units, along a line with a slope of $\tan \theta$ as illustrated in Figure 11 for the loss compliance. We have

$$\log D''_{p_\mu}(\omega a_T) = \log D''_p(\omega a_T) - \mu \sin \theta \tag{3}$$

and

$$\log \omega_\mu a_T = \log \omega a_T + \mu \cos \theta \tag{4}$$

The relations for the storage compliance are analogous.

Equating Ferry's f-shift with our μ-shift we have

$$-\log f = \mu \sin \theta \tag{5}$$

and

$$2 \log f = \mu \cos \theta \tag{6}$$

which is only true for $\tan \theta = -1/2$.

The numerical factor in Eq. (2) is simply

$$0.447 = \sin (\tan^{-1} 0.5) \tag{7}$$

where the slope is taken with the positive sign because we are concerned only with its magnitude.

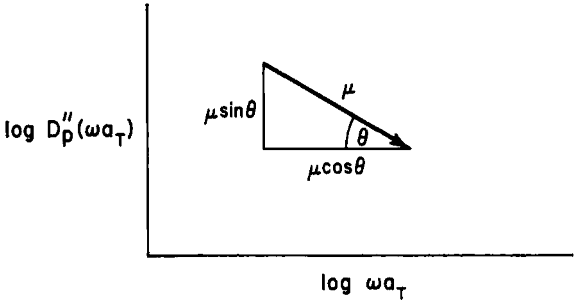

FIGURE 11 The μ-shift.

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