Dynamic Mechanical Properties of Block Copolymer Blends-A Study of the Effects of Terminal Chains in Elastomeric Materials I. Torsion Pendulum Measurements

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I. Torsion Pendulum Measurements

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Blends of well characterized polystyrene-polybutadiene (SB) diblock copolymers and polybutadiene continuous SBS triblocks provide network systems with controlled amounts of terminal chains of known molecular weight. Three different SB diblocks were blended in various amounts with a single SBS triblock. The mechanical properties of these materials were studied in free oscillation at about 0.2 Hz over a temperature range from −150°C to 100°C. The terminal chains act as an internal plasticizer lowering the storage modulus in the intertransition region. If their molecular weight is sufficiently large, a second, broad maximum appears in the loss modulus curve. Thus, the terminal chains can contribute to secondary loss mechanisms. The appearance of the polybutadiene transition region is unaffected by the amount of terminal chains.

INTRODUCTION

In conventionally crosslinked elastomers, a certain fraction of the polymer chains is covalently bonded to the network at only one end. This fraction of terminal chains affects the mechanical behavior of the material. Studies of entanglements in rubbers[1-4] have generally pointed to the important role of terminal chains. However, the inability to control the concentration, length, and length distribution of the terminal chains has prevented a clear

D

understanding of their effects from emerging. Only the effect of terminal chains on the equilibrium modulus (or compliance) of rubbers has been clearly established.[5]

A more detailed study of the effects of terminal chains would be possible if a suitable model system were available in which the amount of terminal chains and their length distribution could be controlled. Oberth[6] has used polyurethane elastomers to study the effects of terminal chains on the transient and ultimate mechanical properties. In this paper we report on the first stage of our efforts to use blends of block copolymers as model systems for a study of the effects of terminal chains on the dynamic mechanical properties of elastomers. Morton[7] has reported on the use of such blends as part of a study of the tensile strength of reinforced elastomers.

BLOCK COPOLYMER BLENDS AS MODEL NETWORK SYSTEMS

The phase separation of the dissimilar segments of block copolymers has been well established by electron microscopy. It is also well known that a triblock copolymer with relatively short glassy endblocks and a long rubbery center segment possesses, at temperatures below the glass temperature (T_g) of the endblocks, elastomeric properties, because the glassy regions or domains act as multifunctional crosslinks for the long rubbery chains which comprise the continuous phase. Above T_g of the hard segments the material will flow, and thus the name thermoplastic elastomer[8] has been proposed for block copolymers with such properties.

A schematic representation of a thermoplastic elastomer is shown at the upper left in Figure 1. It is immediately apparent that each of the rubbery center segments of a triblock must have both of its ends pinned in a glassy domain. Thus, at least to the extent that a pure triblock copolymer can be made, and that phase separation is complete, such materials will have no terminal chains. The continuous rubbery phase is not crosslinked, but it will bear stress at each of several entanglement points in addition to the glassy crosslinks. All of the entanglements are permanent since both ends of each rubbery segment are pinned; however, the positions of the entanglement points are not fixed because of the possibility of slippage[9] along the rubbery chains.

The diblock copolymer, shown schematically at the upper right in Figure 1, will exhibit a similar domain structure. In this case, however, the rubbery segments are pinned in a glassy domain at only one end. Such a diblock copolymer consists of multifunctional star-branched clusters in which the branches are all essentially terminal chains. The material will bear stress
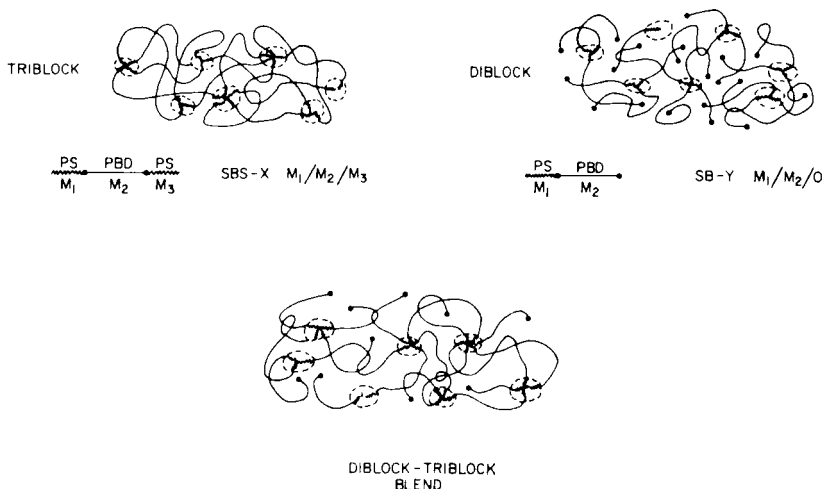
FIGURE 1 Block copolymer blends as model network systems.

only if an entanglement network is formed. The entanglements of this network are not permanent, however, because the free ends allow each rubbery segment to disentangle itself completely over a sufficiently long period of time.

It is a reasonable assumption that the styrene endblocks of diblock and triblock copolymer chains will mix without prejudice. Thus, by a judicious blending of such copolymers, one can, as shown schematically at the bottom of Figure 1, introduce a known fraction of terminal chains into the continuous rubbery phase of the blend. At the same time, it is possible to vary the length and even the length distribution of the terminal chains. Simultaneously, there will be a controlled combination of permanent (or trapped) and non-permanent (or untrapped) entanglements. The former arise from the entanglements between two of the triblock rubbery segments, while the latter involve a rubbery segment from at least one diblock molecule.

Evidently, diblock–triblock copolymer blends cannot be completely valid model systems for conventionally crosslinked elastomers. Below their glass transition temperature the polystyrene domains act essentially as a reinforcing filler. However, the time and temperature dependence of the filler affects the mechanical properties of the triblock copolymer even below T_g of the end blocks.[10] Furthermore, one cannot, in general, expect a sharp boundary between the two phases. The possibility of a mixed interfacial region in block copolymers has already been postulated in the literature.[11,12] Such an interlayer can seriously affect the mechanical properties in certain regions of time and temperature.[10]

Materials

We have chosen block copolymers of polystyrene and polybutadiene for use in our experiments. The triblock, a research grade material containing essentially no diblock fraction, was generously supplied by Shell Chemical Company. The material, designated TR-41-1648 by Shell, has an overall molecular weight of 110,000 with polystyrene endblocks of molecular weight 16,000 and a center polybutadiene segment of length 78,000 as determined in their laboratories. From these molecular weights the styrene weight fraction results as 0.29. Shell also determined the polybutadiene microstructure to contain 41% cis-1,4, 49% trans-1,4, and 10% 1,2 addition. Using NMR techniques,[13] we found a styrene weight fraction of 0.284, and a 1,2 addition of 8%, in satisfactory agreement with the Shell data. We were not able to estimate the cis:trans ratio by NMR measurements. In this paper the triblock material will be designated as SBS-8, 16/78/16, where the segment molecular weights, in thousands, are separated by the solidi.

Diblock materials were synthesized using well-known techniques of homogeneous anionic polymerization.[14] Details of the synthesis and characterization of the diblocks are given elsewhere.[15] The styrene contents and the amounts of 1,2 addition in the polybutadiene phase were again determined by the NMR method. The number average molecular weights were obtained using a Melabs osmometer. Three diblocks were synthesized. They will be referred to here under the designations: SB-5, 10/67/0; SB-6, 9/51/0; and, SB-7, 7/22/0. The numbers separated by solidi again refer to the segment molecular weights. All of the diblocks contained polybutadiene moieties with 8% 1,2 addition or less.

The glass transition temperatures of the polybutadiene phases of the triblock and the three diblocks were determined by differential thermal analysis. For all materials the T_g of the continuous phase was about $-90°C$. As in earlier work[16] with this type of material, the upper transition, characteristic of the polystyrene phase, could not be located reliably by DTA measurements. As indicated previously,[16] 83°C is a reasonable estimate for the upper transition.

Sample Preparation

The materials were blended by dissolving known weights of the triblock and one of the diblocks in benzene to form a solution of around 6% by weight of polymer. A trace amount (around 0.2%) of N-phenyl-2-naphthylamine was added as antioxidant. The solution was stirred for several hours and then poured carefully down a glass plate onto a mercury surface contained in a circular glass dish 10 cm in diameter. The glass plate was submerged below the mercury surface during pouring; this minimized the number of air

bubbles trapped at the mercury-solution interface. The benzene was allowed to evaporate over a period of several days. During this time the dish was covered, mounted on a vibration absorbing cork–rubber composite cushion, and stored in a dark, draft-free room. Using this technique, uniform thin films free of surface flaws or air bubbles could be obtained.

Because the soft material deposits on the sides of the dish as solvent evaporates, the edge of the circular film curved upward. This section of the film was discarded before cutting test specimens. However, a more serious effect of this adhesion to the sides of the dish was observed. Figure 2 shows
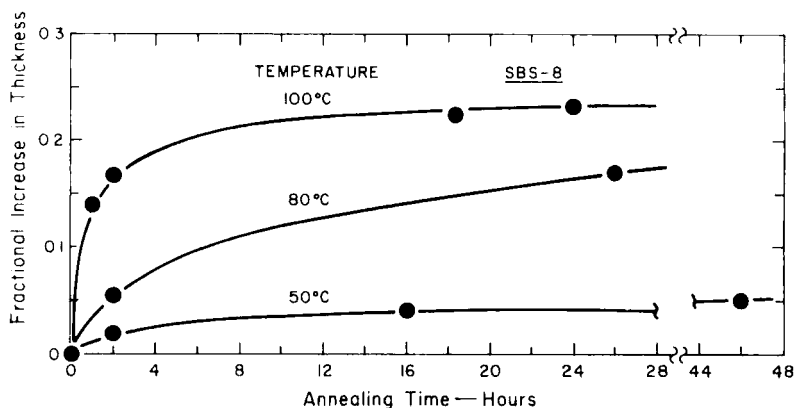

FIGURE 2 Effect of annealing on specimen dimensions.

the effect of annealing, i.e. the normalized change in thickness of a strip specimen as a function of time at various fixed temperatures. The specimens were cut from the center of one of the SBS-8 films. The increase in thickness (the length and width decreased commensurately) indicates that there is significant orientation in the radial direction as a result of the adhesion of the film to the side walls of the container in which it was cast.

Electron photomicrographs[17] show discrete, almost spherical polystyrene domains for annealed specimens; unannealed specimens show slightly elongated domains which appear to touch in some places. These observations are consistent with the annealing data shown in Figure 2. Especially important is the fact that at 50°C only minimal dimensional changes can be seen after very long times. Thus it appears that the radial orientation induced in the specimen during casting can only be removed by annealing at temperatures high enough to allow the polystyrene domains to soften. All of the specimens used in this work were annealed in vacuum at 100°C for twenty-four hours.

Apparatus and Experimental Procedures

The mechanical properties of the block copolymer blends were measured as a function of temperature at nearly constant frequency (about 0.2 Hz) on a freely oscillating torsion pendulum. The period and logarithmic decrement (natural logarithm of the ratio between successive displacements) were measured over a temperature range from −150°C to 100°C. The storage and loss moduli were calculated in the usual way[18] using tabulated corrections for a rectangular strip specimen.[19] A typical specimen had the following dimensions: length, 6.00 cm; width, 1.00 cm; thickness, 0.15 cm.

The torsion pendulum was built essentially along the lines of the apparatus described by Lawson.[20] This apparatus is similar to other freely oscillating torsion pendulums except for the displacement sensing device. The oscillating shaft has two magnets mounted on it in a sector-shaped configuration. Centered between the two magnets is a Hall effect device which, under the influence of a constant current, will convert changes in magnetic field strength to a changing voltage signal. This signal is then displayed without amplification on a strip chart recorder as a damped sinusoidal trace. The Hall device displacement sensor is simpler to balance and align than reflected light beam sensors. Because of its great sensitivity to very small changes in the magnetic field strength rather small angular displacements (± 1–2 degrees) can be employed. At these small angular displacements the relation between the displacement and the Hall device output may be regarded as linear with sufficiently good approximation.[20]

Below room temperature the specimen was encased in a Dewar flask containing a coil of stainless steel tubing. By passing cold nitrogen gas through the coil, temperatures as low as −160°C can be reached. The natural temperature rise is slow enough (around 10°C/hr) that no further control is necessary. A measurement is taken in less than one minute, and the effect of temperature change over this time interval is insignificant. At very low temperatures, especially near the glass transition temperature of the rubbery phase, the thermal gradient along the specimen caused a serious problem in obtaining reproducible measurements in early runs. This problem was solved by surrounding the specimen with a close-fitting (but not touching) brass cylinder to conduct heat evenly along the length of the specimen. Two thermocouples were placed through small holes in the brass cylinder, one near the top and one near the bottom of the specimen. Even at the lowest temperatures, the difference between the two thermocouples was less than 1°C.

Above room temperature the specimen, still surrounded by the brass cylinder, was placed in a glass container wrapped with electrical heating tapes. Again the temperature rise was negligible during a measurement, and the thermal gradient along the specimen was under 1°C. At the highest tempera-

tures, around 90 to 100°C, the specimen began to soften and narrow somewhat near the top clamp. The changing shape factor removes any hope of making precise measurements in this region.

A typical set of data obtained from the torsion pendulum experiments is shown in Figure 3. Here, the logarithms of the storage modulus, G', and
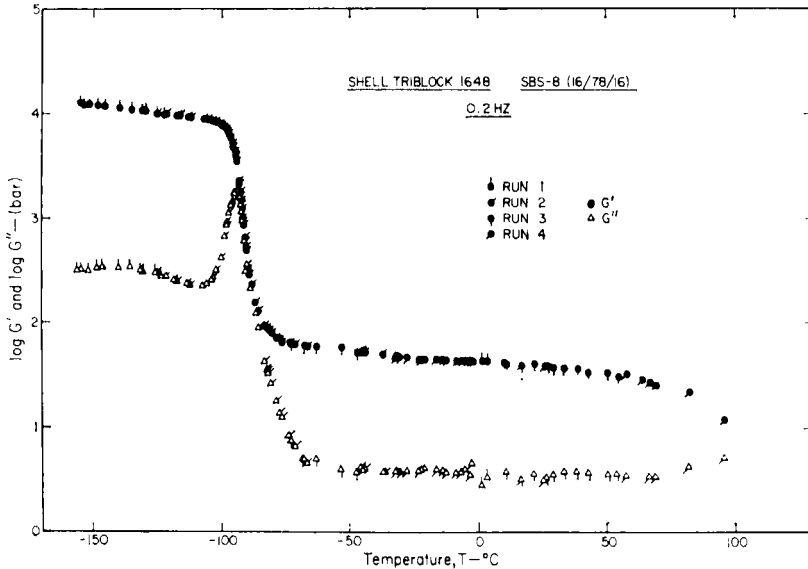

FIGURE 3   Typical data obtained from torsion pendulum—storage and loss modulus—SBS-8.

the loss modulus, G'', are plotted against temperature for SBS-8. The units of the moduli are bars (1 bar $= 10^6$ dynes/cm^2, or 14.5 psi). Each datum point represents an average value taken over at least eight cycles, except in the region of very high damping between $-100°C$ and $-90°C$. Here the number of cycles which could be obtained varied between eight and two. Figure 3 demonstrates the rather good reproducibility which can be obtained in the intertransition plateau between several repeat runs on the same specimen. The reproducibility was much poorer on specimens from unannealed samples.

Free oscillation data must be interpreted with caution. The complex modulus, $G^*(\omega, a)$, as calculated from such measurements, is a function of both the radian frequency, ω, and the damping, a. It becomes comparable to the modulus obtained in forced oscillation, $G^*(\omega)$, only if the damping

is negligible. The ensuing difference in notation and terminology has been suppressed here for simplicity but must be borne in mind when comparing our data with similar ones by other authors. A further complication arises from the fact that the measurements are not strictly isochronal. In our measurements the maximum range of frequencies over the temperature range tested was half a logarithmic decade. Isochronal measurements can be obtained by making several measurements at the same temperature in which the moment of inertia, the elastance of the suspension wire, the specimen geometry, or a combination of these factors is varied. In this way one can achieve a spread of frequency allowing interpolation to a constant frequency at each temperature. This method, however, is time consuming and is hardly warranted because damping and frequency cannot be controlled independently. Our measurements were made with the same moment of inertia, suspension elastance and specimen geometry throughout. In this way the data reported here are internally consistent and qualitative comparisons can be made between the various materials tested.

RESULTS

The experimental program is outlined in Table I. Blends of the various diblocks with the single triblock material are divided into three series. Measurements conducted on specimens within one of the series give information of the effect of varying the concentration of terminal chains of a given length. Comparing results from the three series yields information on the effect of the molecular weight of the terminal chains.

Figure 4 shows the behavior of the storage moduli of the materials of Series 1 in which the terminal chains have a number average molecular weight, $\overline{M}_n$, of 51,000. In the glassy and in the polybutadiene transition regions all materials exhibit identical behavior. At the base of the polybutadiene transition the curves diverge, with specimens containing more terminal chains having lower moduli. A quantitative representation of the terminal chain content is given by X, the weight fraction of the polybutadiene phase which is in the form of terminal chains. As X increases, the moduli in the intertransition regions drop away with temperature increasingly more steeply in addition to having lower values overall. The lowest curve, representing diblock behavior, was drawn from a minimum number of points because of experimental difficulties due to the tendency of this material to flow even at relatively low temperatures. For all of the curves, the data at the highest temperatures are in doubt due to a changing shape factor, as discussed earlier. There is present, however, a clear indication of the approaching polystyrene transition.
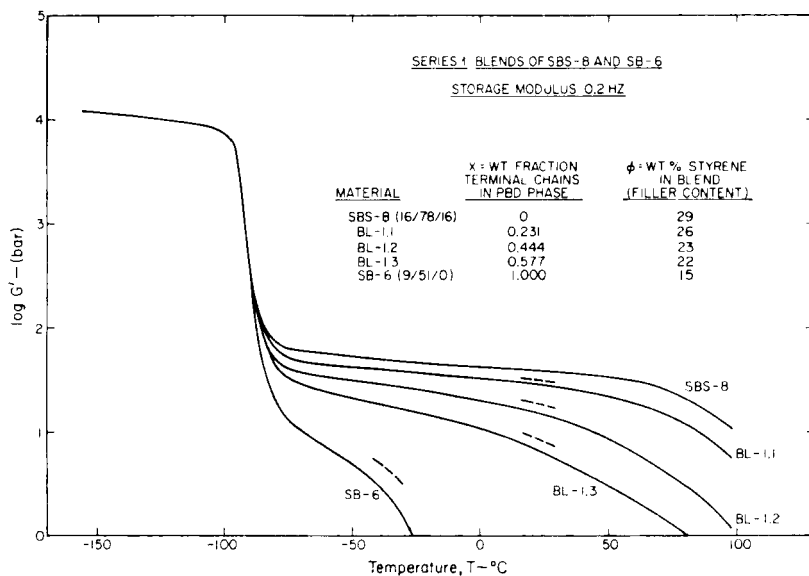
FIGURE 4   Log G' as a function of temperature—Series 1.

TABLE I

Series 1. Terminal chain $\bar{M}_n = 51{,}000$		
Sample Code	X	ϕ
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

In Figures 5 and 6, similar behavior is shown for the storage moduli of the
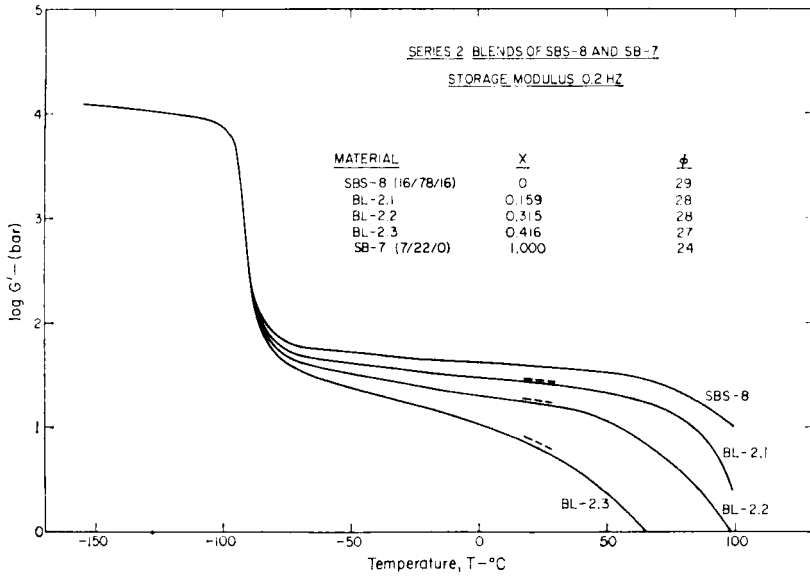materials in Series 2 and 3, in which the molecular weights of the terminal

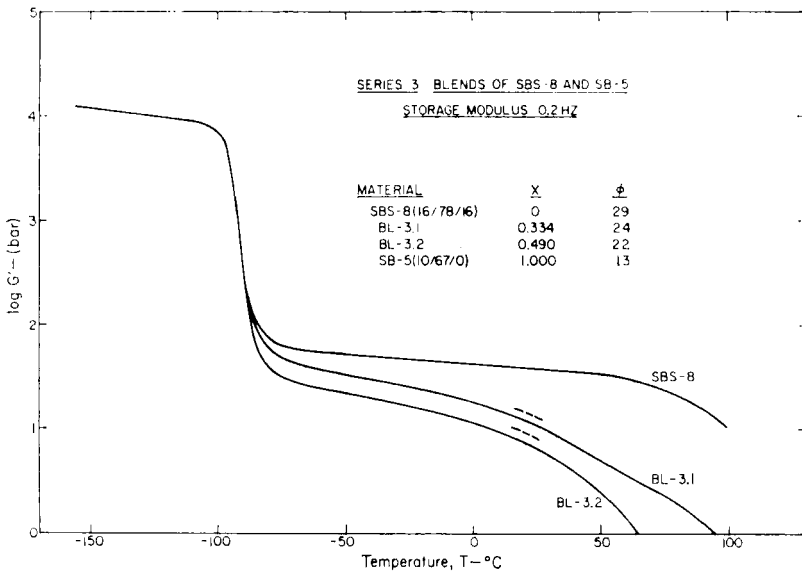FIGURE 5　Log G′ as a function of temperature—Series 2.

FIGURE 6　Log G′ as a function of temperature—Series 3.

chains are 22,000 and 67,000, respectively. A suitable specimen could not be prepared from the SB-7 diblock material, and the amount of the SB-5 diblock was not sufficient for testing. Thus the curves representing diblock behavior do not appear in Figures 5 and 6.

The loss moduli for the blends of Series 1 and 3 are shown in Figures 7 and 8. Each curve has been shifted successively downward by 0.5 decade for display purposes. Again, the glassy and transition regions show no effect of the terminal chains. At the base of the transition, a minimum appears and becomes more pronounced as X increases. From the minimum, the loss rises to a secondary peak and then falls off again at high temperatures. This general behavior appears for all blends of Series 1 and 3, that is, for terminal chains of molecular weight 51,000 and 67,000.

This secondary loss mechanism is quite obviously absent for the blends of Series 2 where the terminal chains have a molecular weight of 22,000. Figure 9 shows that even at rather high concentrations of terminal chains, there is no hint of a minimum at the base of the polybutadiene transition. There is some tendency for the loss to fall off at temperatures above 0°C but not nearly as rapidly as observed for the materials of Series 1 and 3.
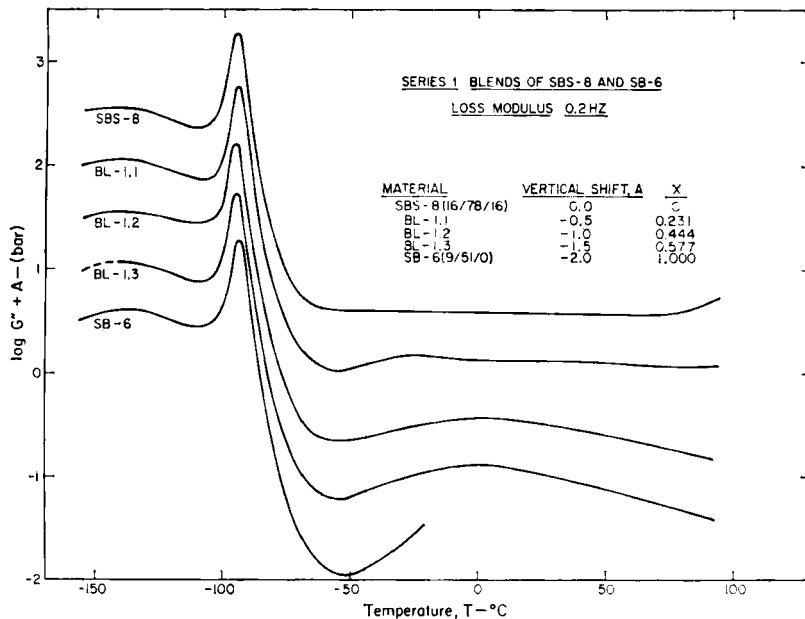

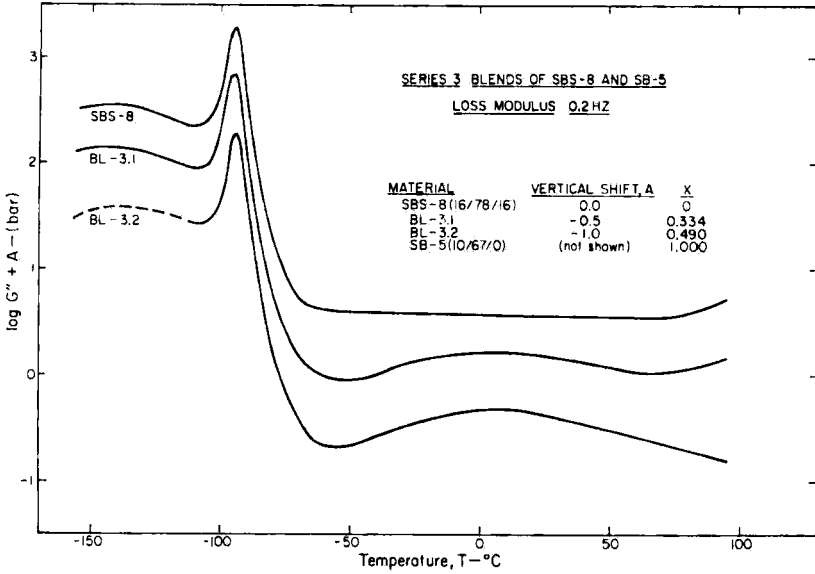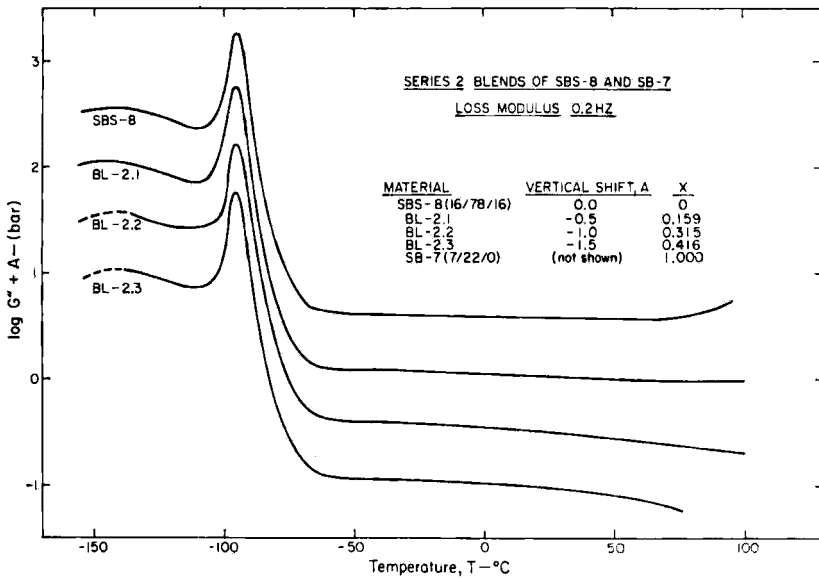FIGURE 7   Log G'' as a function of temperature—Series 1.

Discussion

Summarizing the results shown in Figures 4–9, we note two major effects of terminal chains on the dynamic moduli. First, the storage modulus is lowered in the intertransition plateau by an increase in the weight fraction of terminal chains. Second, if the terminal chains are sufficiently long, they can contribute to secondary loss mechanisms as evidenced by a minimum at the base of the polybutadiene transition and a broad secondary loss peak at higher temperatures. It is also apparent that the terminal chains have no effect on the glassy and polybutadiene transition regions in either storage or loss behavior. This is not unexpected because in the short range motions which dominate the mechanical behavior in these regions, all of the rubbery chains behave identically. It is only when the material becomes sufficiently soft, near the base of the polybutadiene transition, that the differences in longer range molecular motions first become noticeable.

One would expect the introduction of terminal chains to lower the storage modulus in the intertransition region in analogy to the reduction of the equilibrium modulus of crosslinked rubbers with increasing amounts of terminal chains.[5] However, it is also well known that the level of the modulus in this region is affected by the filler content. In general an increase in the filler content results in an increase in the modulus. In the diblock–triblock blends, the polystyrene domains are considered in the first approximation to be inert filler particles. Because the triblock and the diblocks contain different amounts of polystyrene, the filler content will vary slightly in a given series of blends. For example, in Series 1 the weight fraction of polystyrene varies from 0.29 in SBS-8 to 0.22 in blend BL-1.3. Thus, the data should be corrected for variation in the filler content.

Several correction factors can be used. The correction of the type proposed by Guth[21] has been applied successfully to account for the filler effect of polystyrene domains in triblock copolymers of styrene and isoprene.[8] This correction was applied in the intertransition region to normalize all data to a filler content of 29%. The short dashed curves in Figures 4–6 indicate the position of the various curves after this correction. A more sophisticated modulus correction for two-phase polymer systems has been proposed by Uemura and Takayanagi.[22] The corrections obtained using their method are smaller than those shown in Figures 4–6. Thus, only a relatively small proportion of the decrease in the storage modulus is ascribable to decreasing filler content, and the remainder must be attributed to the introduction of terminal chains into the material.

The storage modulus curve for the SB-6 diblock reveals a tendency to level into a plateau between -80 and $-50°$C. This must mean that the entangled chains are coupled loosely into a continuous stress bearing network

in this region. G' decreases, i.e. the untrapped entanglements uncouple, as temperature increases. Above −50°C the capability of the untrapped entanglements to bear stress is almost completely lost. Therefore the terminal chains from SB-6 become essentially non-stressbearing diluent in the rubbery networks of the blends of Series 1. The storage modulus vs. temperature curves could not be obtained for the SB-5 and SB-7 diblocks. However, it is likely that the storage modulus plateau, attributed to coupled untrapped entanglements, will be less distinct for the short polybutadiene chains of SB-7 and only slightly more distinct for the longer polybutadiene chains of SB-5 compared to the behavior observed for SB-6. Thus the decrease in storage modulus in the intertransition region with increased terminal chain content can be explained, at least qualitatively, in terms of the diluent effect of the terminal chains.

In an attempt to gain a somewhat more quantitative understanding of this diluent effect, the storage modulus data from Series 1 were plotted as shown in Figure 10. The values of G' were corrected for variations in the styrene content as discussed earlier, removing, in this way, any filler effect on the level of the modulus. As shown clearly in Figure 10, the intertransition region is not a plateau at all. There is no equilibrium value of G', indicating that slow relaxation processes are continuously taking place over the entire region. For each of the materials in Series 1, the dependence of G' on temperature in the intertransition region can be described by a straight line.
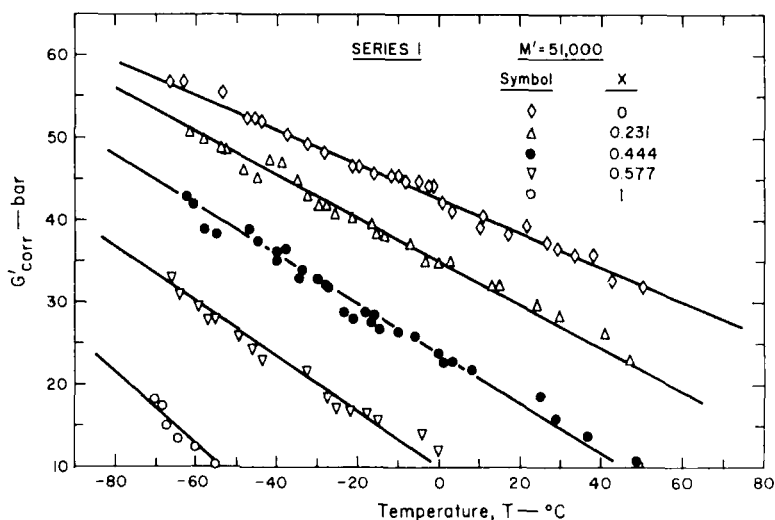

FIGURE 10   Effect of terminal chain content on the storage modulus in the intertransition region.

Such plots were also made from the data obtained with Series 2 and 3, and showed similar behavior. The slopes of the straight lines plotted against the amount of terminal chains, X, are shown in Figure 11. These plots again
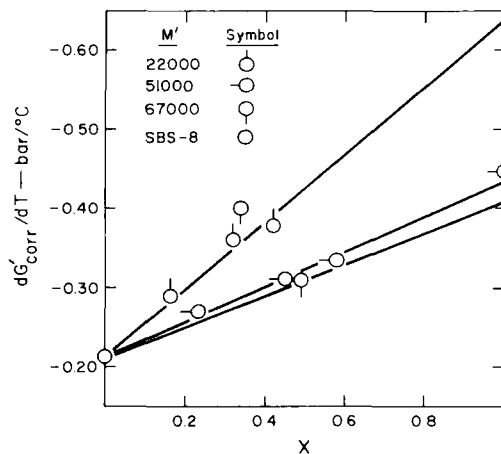

FIGURE 11   Effect of terminal chain content and length on the rate of decrease of the storage modulus in the intertransition region.

result in reasonable straight line fits. The point at $X = 0.334$ is clearly an outlier. These plots are offered merely as an observation because the data do not warrant a detailed interpretation. The observed simple behavior may be a consequence of an interplay between several mechanisms.[15,23] Figures 10 and 11 do serve, however, to show that in the intertransition region the storage modulus decreases with temperature and that the decrease is the more rapid as either the amount of terminal chains increases, or their length decreases.

We now turn our attention to the loss modulus data. Considering first the SB-6 curve in Figure 7 one sees that the loss modulus decreases from the base of the main transition up to about $-50°C$ where the loss begins to rise again. This decrease in the modulus reflects the general weakening of the network through a decrease in the number of stress bearing entanglement points. Evidence for the presence of a temporarily coupled network at these temperatures has already been mentioned in discussing the behavior of the storage modulus of the SB-6 diblock. Near $-50°C$ the terminal chains become sufficiently decoupled to slip and introduce internal frictional mechanisms which cause the loss to rise again. The resulting minimum in the loss curves is seen for all the blends of Series 1 and 3. The minimum is deeper for increased

terminal chain content. This is quite reasonable since a larger fraction of the network is susceptible to changes in entanglement coupling for higher terminal chain contents.

There has been some previous evidence to support the contention that the minima seen in the loss data for Series 1 and 3 arise from changes in entanglement coupling involving the terminal chains. In a study of very lightly crosslinked rubbers, Nielsen[24] observed minima in the loss moduli similar to those seen in this work. His materials were so lightly crosslinked that they contained a significant sol fraction; furthermore, the molecular weights between crosslinks were large and chain entanglements must have been contributing to the observed moduli in addition to crosslinks. In a conventionally crosslinked rubber, a high molecular weight between cross-links indicates the presence of long terminal chains. Therefore, the minima seen by Nielsen probably arise from the same effect of temperature on the number of coupled untrapped entanglements as seen here. He observed no minima in highly crosslinked rubbers. In general, a minimum on the low frequency side of the main loss peak derived from isothermal measurements of the viscoelastic functions is usually attributed to the presence of network strands which are coupled by entanglements.[25] In loss modulus vs. temperature curves, this corresponds to the high temperature side of the loss peak, exactly where the minima in the data occur in Series 1 and 3. Finally, Ferry *et al.*[26] have pointed out that temperature effects on the amount of entanglement coupling have a strong influence on the loss.

The entanglement coupling mechanism is quite obviously absent for all the materials of Series 2 since there is no evidence of a minimum in the loss modulus curves near $-50°C$ for these materials (see Figure 9). The implication is that the 22,000 molecular weight terminal chains were too short to engage in coupled entanglements with the rest of the network. Evidently the shorter terminal chains of Series 2 are already free enough at the base of the main transition to slip and contribute to the frictional loss mechanisms which began to occur around $-50°C$ for the longer terminal chains of Series 1 and 3.

One would expect entanglement coupling to extend throughout the system when the molecular weight of the rubbery segments is greater than twice[27] the entanglement molecular weight (M_e) for the material. For homopolymers of polybutadiene the values of M_e range between 2000 and 4000 depending upon the microstructure of the material.[28] The linear weighted average M_e for a polybutadiene containing about 45% *cis*-1,4, 45% *trans*-1,4, and 10% 1,2 addition is 2530. Thus, one should expect the onset of an entangled network system for molecular weights greater than about 5000 for homopolymers of polybutadiene. Gruver and Kraus[29] have observed a value of 5600 for a 50% *cis*-1,4 polybutadiene.

The fact that the entanglement coupling mechanism did not appear in the materials containing terminal chains of molecular weight 22,000 is difficult to understand in the light of the above discussion. However, it is important to note that the values of M_e quoted above were determined on *homopolymers* of polybutadiene. The terminal chains in the polybutadiene networks which we have studied can well have different entanglement characteristics because one of the chain ends is constrained to be at or near a polystyrene domain. Intuitively one would expect this constraint to increase the average length between entanglements because of a decrease in the relative freedom of movement. Thus it is quite possible that terminal chains of molecular weight 22,000 are not long enough to engage into a coupled network in our diblock–triblock copolymer blends. Similar considerations should also apply to the distance between the permanent entanglements in the triblock. Perhaps even more important is the fact that in a cast triblock elastomer the entanglements are formed simultaneously with the formation of the two-phase structure. By contrast, in a conventionally crosslinked rubber the entanglements were already present before crosslinking.

To resolve this problem, swelling measurements were conducted on the triblock material, SBS-8, to determine the average distance between entanglement points. Triblock copolymers can be swelled with a solvent which will penetrate the continuous rubbery phase and leave the dispersed glassy domains essentially untouched. Bishop and Davison[9] found that iso-octane satisfies these requirements for triblocks of polystyrene and polybutadiene. They also determined that it is necessary to correct the swelling ratio for the constraint on the swelling around each polystyrene domain, and that a correction of the type proposed by Kraus[30] for carbon black filled rubber could be applied successfully.

The equilibrium swelling ratio of the polybutadiene phase in iso-octane was determined for two separate specimens of SBS-8 with excellent reproducibility. No swelling creep[9] was detected even after several days, and less than 1% extractable material was recovered from the swelling solvent. The Kraus correction was applied, and the concentration of effective chains, v_e, was calculated from the Flory-Rehner equation[31,32] as used by Kraus[33]

$$v_e = -\frac{1}{V_s}\frac{ln\,(1 - v_r) + v_r + \chi\,v_r^2}{v_r^{1/3} - 2\,v_r/f} \qquad (1)$$

where V_s is the molar volume of the iso-octane solvent, v_r is the volume fraction of polybutadiene in the swollen network (corrected according to Kraus), f is the functionality of the crosslinks (trapped entanglements act as a tetrafunctional link), and χ is the polymer–solvent interaction parameter. Bishop and Davison[9] give the interaction parameter for the polybutadiene-iso-octane system as

E

$$\chi = 0.406 + 0.522 \, v_r \qquad (2)$$

The resulting value for v_e was 0.75×10^{-4} mole/cc of polybutadiene. The molecular weight between entanglements was then determined from the relation $M_e = \rho/v_e$ where ρ is the density of polybutadiene in grams/cc. This results in a value of about 13,000 for M_e in SBS-8; Bishop and Davison determined M_e to be about 16,000 for their SBS materials.

These results of the swelling experiments provide a satisfactory explanation for the absence of the entanglement coupling effect in Series 2 where the terminal chains had a molecular weight of 22,000. Assuming that the number of entanglements is the same in the triblock and the blends, a terminal chain molecular weight in excess of 26,000 (i.e. 2 M_e) would be required for the appearance of the entanglement coupling mechanism. Shorter terminal chains would not be engaged in the long-range coupled entanglements which form the temporary stress-bearing network necessary for this phenomenon to appear.

There have been some objections[34] raised concerning the validity of the entanglement molecular weights determined by swelling on block copolymer systems. In particular the level of the rubbery modulus is much too high to be accounted for by an entanglement molecular weight of 13,000, even after applying a correction[21] to remove filler effects. Although not entirely reliable for such calculations, the storage modulus data for SBS-8 in the intertransition region can be used to determine M_e from the relation $G = \rho RT/M_e$. The resulting entanglement molecular weights for the triblock obtained in this way vary between 800 and 2000 depending upon the particular temperature chosen.

These M_e values are much lower than the value predicted by the swelling data, and they are much closer to the entanglement molecular weights characteristic of homopolymers of polybutadiene. The discrepancy between the calculated values and those obtained by swelling could arise for several reasons but none of these seems to offer a satisfactory explanation. Thus, the swelling data could conceivably be in error due to some solubility of the polystyrene domains. However, as mentioned earlier only a minute quantity of extractable material could be recovered from the swelling solvent. Again, the Kraus correction might over-correct the swelling ratio. However, M_e values greater than 7000 are obtained from the swelling data when the Kraus correction is ignored. It is also possible that the calculation of the entanglement density from modulus data is not valid for these filled systems. The effective filler fraction may be significantly larger than predicted by the measured polystyrene content if there is a significant interlayer present or if the domain geometry is not spherical as presumed. In addition, the modulus data may

not represent equilibrium, although at the chosen frequencies and temperature they should be close to it.

If one accepts the rather low values of M_e calculated from the storage modulus data, the absence of entanglement coupling effects in Series 2 cannot be explained on the basis that the terminal chain length is less than twice the entanglement length for the system and therefore less than the critical length required for a coupled entanglement network. However, it has been suggested[34] that for these model networks the observed entanglement coupling phenomenon arises for reasons slightly different from those discussed above. If the polystyrene domains are assumed to be separated by a distance which is determined by the molecular weight (78,000) of the polybutadiene segments in the triblock, then diblock polybutadiene segment molecular weights in excess of 39,000 would be required before the terminal chains from neighboring domains could span the required distance to entangle with each other. Thus the terminal chains of molecular weights 51,000 and 67,000 are involved in coupled entanglements in this sense, whereas the shorter terminal chains of molecular weight 22,000 are not. This means that entanglements involving terminal chains from neighboring domains are required before the temperature effects on entanglement coupling become apparent. In this case the particular value of M_e characteristic of these systems is unimportant to the explanation of the mechanism's presence or absence. This is so because the critical terminal chain molecular weight for the appearance of the entanglement coupling effects is no longer defined in terms of M_e. Instead it depends only upon the molecular weight necessary to span the half-distance between neighboring domains and is roughly equal to half the triblock polybutadiene segment molecular weight.

In any case, there is overwhelming evidence in the data that the critical molecular weight for entanglement coupling is greater than 22,000 for these systems. Further studies of these systems using several more terminal chain lengths should help to decide which interpretation is the more reasonable.

The secondary loss peak located near 0°C and 10°C for Series 1 and 3 respectively, but absent for Series 2, is also related to the formation of a temporary network as discussed above. As the temperature increases, the entanglement coupling becomes weaker until finally the terminal chains are free to slip and completely disengage themselves from the network. The entanglement slippage and internal friction of the terminal chains will contribute to secondary viscoelastic mechanisms having relaxation times which are long compared to those governing the polybutadiene transition. Thus, a secondary peak in the loss behavior will occur at higher temperatures, and it becomes more pronounced as terminal chain content increases. This is consistent with the observations of increased relaxation in the storage behavior over the intertransition region as discussed earlier.

The secondary loss peak must be considered to be a combination of several effects. In addition to those described above, contributions from a possible interlayer region and from slippage of triblock chains between the trapped entanglements would be expected[23] to affect measurements in this region. There is no hope for separating the various high temperature phenomena with torsion pendulum measurements of the type described here. At present, isothermal forced oscillation measurements are underway on the materials of Series 1–3. The data already obtained indicate that a reasonable decomposition of the high-temperature process may be possible, and furthermore, that a more quantitative interpretation of the low-temperature entanglement coupling mechanism involving terminal chains can be made.[15] These results will be reported in a forthcoming publication.

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