Macromolecules **1980**, *13*, 1571-1577

(19) Miller, A. A. *J. Chem. Phys.* **1968**, *49*, 1393 (Table II).
(20) Simha, R.; Boyer, R. F. *J. Chem. Phys.* **1962**, *37*, 1003.
(21) Olabisi, O.; Simha, R. *Macromolecules* **1975**, *8*, 208 (eq 3, Table X (LPE)).
(22) Extrapolation of the specific volume by the same equation leads to $V = 1.072$ cm^3/g at 200 K, compared to our value of 1.080 cm^3/g.
(23) Boyer, R. F. *J. Macromol. Sci.—Phys.* **1973**, *B7*, 487.

Rubber Networks Containing Unattached Macromolecules. 5. Stress Relaxation in Styrene–Butadiene–Styrene Block Copolymer with Unattached Linear and Star Polybutadienes[1]

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ABSTRACT: Stress relaxation has been studied in networks of styrene–butadiene–styrene block copolymer with spherical styrene domain structure containing 0.10 weight fraction of unattached linear or star-branched polybutadiene with the same microstructure as the butadiene block. Stress relaxation measurements were also made on networks containing no unattached species and containing the same weight fraction of hydrocarbon oil and on one of the linear polybutadienes. Equivalent viscoelastic data for the other uncross-linked polybutadienes were obtained from measurements of dynamic storage and loss moduli by Graessley and creep by Plazek. The stretch ratio was usually 1.15 and the temperature range from −20 to +20 °C. The Young's relaxation modulus was calculated from the neo-Hookean stress–strain relation. For the uncross-linked linear polymers (M_w = 203 000, 389 000, and 813 000), the time dependence of the relaxation modulus agreed rather well with the Doi–Edwards theory as modified for a slight degree of molecular weight distribution, and the disengagement time was proportional to the third power of the molecular weight. For the star-branched uncross-linked polymers (3-arm, M_w = 204 000; 4-arm, 88 000 and 226 000), the relaxation was much more gradual but eventually reached low modulus values. The contribution of the unattached species in the network to the relaxation modulus, $E_1(t)$, was calculated by difference; after multiplication by $(1 - v_2'^2)^{-1}$, where v_2' is the volume fraction of polybutadiene block in the continuous polybutadiene phase, it was compared with the relaxation modulus measured directly for the uncross-linked polymer, $E_{11}(t)$, for each unattached species. For the linear polymers, the relaxation was slower in the network than in the environment of the linear species alone by about half an order of magnitude, but the form of the time dependence was the same. For the star-branched polymers, the relaxation was very much slower in the network. It may be concluded that the suppression of reptation by branching is much more effective when the topological obstacles are trapped entanglements on strands with anchored ends than when they are untrapped entanglements on strands with free ends.

In previous papers in this series,[3-6] viscoelastic properties have been reported for conventionally cross-linked[3-5] and end-linked[6] networks containing unattached linear macromolecules, whose relaxation can be attributed to reptation[7] or contour diffusion processes.[8,9] A question of particular interest has been the influence of branching on reptation. It is well-known that long-chain branching with sufficiently long branches increases the viscosity of an uncross-linked polymer enormously and prolongs the relaxation times in the terminal zone.[10] Specifically, de Gennes has pointed out that long-chain branching should essentially eliminate the reptation mechanism for relaxation.[11] We have undertaken a comparison of relaxation of linear and star-branched molecules in still another type of network, namely, that formed by domain separation in a poly(styrene–butadiene–styrene) triblock copolymer (SBS). The unattached molecule is a polybutadiene whose microstructure matches that of the butadiene block to ensure compatibility. Viscoelastic properties of blends of this type with linear unattached molecules have been examined previously by Toy, Niinomi, and Shen[12] and Kraus and Rollmann.[13] In the latter study (in which a (SB)$_n$ multiblock copolymer was used), the frequency location of the viscoelastic loss associated with relaxation of the unattached species, as judged by either the loss tangent maximum or the loss modulus maximum, was found to be approximately inversely proportional to the third power of the molecular weight, as predicted for the reptation mechanism.[7-10] In our experiments, three linear and three star-branched polybutadienes have been studied and their contributions to stress relaxation in a triblock copolymer network have been compared with the relaxations of the respective uncross-linked polymers themselves. The volume fraction of the unattached species in the polybutadiene phases of the SBS network was 0.15. Thus we compare motions of the same molecule in its own loose entanglement network and in a network whose entangled strands are anchored by polystyrene domains. The essential difference between the two media in which the unattached molecules are relaxing is that the entanglements of the surrounding molecules are untrapped and trapped, respectively. However, the steric effects of the polystyrene domains may also influence the mobility of the unattached species.

Experimental Section

The SBS block polymer and one linear (389L), one 3-arm star (204S3), and one 4-arm star (226S4) polybutadiene were synthesized at The University of Akron. The synthesis followed procedures outlined elsewhere.[14-16] *sec*-Butyllithium was used as the initiator with benzene as the polymerization solvent. All reactions were carried out at about 30 °C. Methyltrichlorosilane and silicon tetrachloride were used as the linking agents for the formation of the 3- and 4-arm polybutadiene stars.

The GPC analysis of these near-monodisperse polymers was carried out by using a seven-column Styragel set with tetrahydrofuran as the carrier solvent. The characteristics of this

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Table I
Characterization of Polymers

sample	source[a]	$10^{-3}\overline{M}_n$	$10^{-3}\overline{M}_w$[b]	$10^{-3}\overline{M}_w$[c]	$\overline{M}_w/\overline{M}_n$[c]	$[\eta]_{THF}$, dL/g	PB, microstructure cis	trans	vinyl
SBS	A	69		72	1.05	0.77_4[d,f]	41	51	8
203L	G	196	199	203	<1.05	2.17[e]	g		
389L	A	360	385	389	1.09	3.36[d,f]	41	51	8
813L	G	700	791	813	<1.05	6.15[e]	g		
204S3	A	178	195	204		1.57[d,f]	g		
88S4	G	80	85	88	1.08	0.93_5[e]	g		
226S4	A	212	230	226	1.09	1.54_5[e,f]	g		

[a] A = synthesized at The University of Akron; G = gift of Professor W. W. Graessley. [b] From light scattering. [c] From gel permeation chromatography via universal calibration approach. [d] Measured at 30 °C. [e] Measured at 25 °C. [f] Measured also at the University of Wisconsin. [g] Should have similar microstructure due to the similar preparation method.

column arrangement are available elsewhere.[17] The columns were calibrated with 11 polystyrene standards for the application of the universal calibration analysis[18] and also calibrated by using 5 polybutadiene standards which were synthesized and characterized in these laboratories. The application of the universal calibration procedure was identical with that reported elsewhere.[16] The number-average molecular weights were determined in toluene at 37 °C, using a Hewlett-Packard membrane osmometer; S and S-08 membranes were used.

The gel permeation chromatography analysis of the 3-arm star polybutadiene star revealed that about 3% of the linear arm was present. This material was used without fractionation. The 4-arm star polybutadiene was fractionated prior to use. The GPC analysis showed that virtually all of the linear arm was removed.

The triblock polymer was synthesized by a three-step sequential process. The crossover reaction of butadienyllithium with styrene was accelerated by the addition of a small amount of tetrahydrofuran (THF/RLi $\simeq$ 5). A 1-mm cell was attached to the reactor in order to ensure that no significant chain termination took place on the addition of the second styrene charge. The spectroscopic determination (λ_{max} 334 nm) of the styryllithium concentration at the end of the block polymer synthesis showed that this concentration was unchanged from that measured prior to the addition of the butadiene. It should be noted that Bywater and Worsfold have shown[19] that small amounts of tetrahydrofuran do not change the extinction coefficient relative to that of styryllithium in pure benzene. Thus, the spectroscopic analysis indicates that essentially pure triblock polymer was obtained. This conclusion is partially fortified by the fact that the GPC measurements did not show the presence of homopolystyrene in this sample. Free polystyrene would result if the addition of butadiene caused some termination of the chain ends of the first polystyrene segment. Figure 1 shows the chromatogram of this triblock polymer. The styrene content was 27.6% by weight, corresponding to block molecular weights of approximately (10–50–10) × 10^3.

Weight-average molecular weights ($\overline{M}_w$) were obtained from light scattering measurements made at 25 °C with a Sofica PGD instrument; cyclohexane was the solvent and the solutions were clarified by filtration through Millipore 0.45-mμ filters. Number-average molecular weights ($\overline{M}_n$) were obtained from osmometry in toluene at 37 °C; intrinsic viscosities were measured in tetrahydrofuran at 25 or 30 °C. The precision of $\overline{M}_w$ and $\overline{M}_n$ is believed to be within about 5%.

In addition, one 4-arm star (88S4) and two linear (203L, 813L) polybutadienes were generously given us by Professor W. W. Graessley, identifiable by their code numbers given by Rochefort et al.[20]

The microstructures of the linear and star-branched polybutadienes, where determined, matched that of the butadiene block of the SBS triblock reasonably well and otherwise are expected to be closely similar because of the method of synthesis. These data, together with molecular weights and intrinsic viscosities, are recorded in Table I. The code numbers reflect the weight-average molecular weights as in the notation of Rochefort.[20]

A hydrocarbon motor oil with no additives (Exxon Chemical Co. S-100-NLP ck 35389, ρ_{25} = 0.8385 g/mL), obtained from Professor J. L. Schrag, was used to prepare a network in which the SBS was diluted with this low molecular weight diluent instead of a polymeric unattached species.

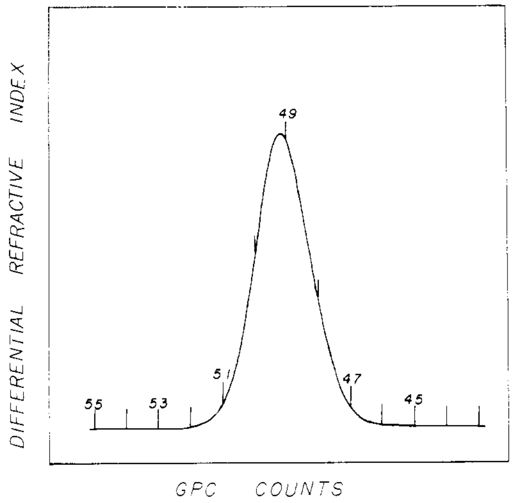

Figure 1. Gel permeation chromatogram of SBS triblock copolymer.

To cast films for stress relaxation measurements, the SBS was dissolved in a mixture of 9 parts of benzene and 1 part of *n*-heptane by volume, at a concentration of about 0.20 g of polymer/mL, together with 0.2% (based on the polymer) of the antioxidant 2,6-di-*tert*-butyl-4-methylphenol. When an unattached polybutadiene species (or oil) was to be added, it was first dissolved in the mixed solvent at a concentration of 0.02 g/mL, and after 1 day the SBS was added. The weight fraction of unattached species (or oil) was always 0.10. After about 1 day, the viscous solution was stirred for about 1 h and then poured into a leveled Teflon mold. The solvent was allowed to evaporate slowly for about 1 day. The mold and film were transferred to a desiccator and evacuated for 1 week. Then the film was removed from the mold and stored under nitrogen at about 5 °C until used. The final dry films, usually about 0.6-mm thick, of pure SBS and SBS containing oil were clear; those of SBS containing unattached polybutadienes were slightly hazy.

Casting from the solvent used should result in morphology with spherical polystyrene domains distributed rather regularly in a polybutadiene matrix.[21] This was checked at The University of Akron by electron microscopy of ultrathin sections stained by osmium tetraoxide for pure SBS and for SBS containing 10% by weight of polybutadiene 389L; the procedures have been described previously[15] and the electron micrographs are shown elsewhere.[22] The average diameter of a polystyrene sphere was estimated to be 170 Å for both networks. On the basis of a hexagonal-close-packed array, the minimum distance between spheres is estimated to be of the order of 100 Å. This may be compared with an unperturbed root-mean-square length of 200 Å for the butadiene block and about 400–800 Å for the linear unattached species used.

The unattached polybutadiene, or the diluent oil, is expected to be confined to the continuous polybutadiene phase of the SBS network. Its actual volume fraction in that phase (v_1') depends on whether each polystyrene domain is surrounded by a boundary layer from which the other component is also excluded. In the absence of a boundary layer, the volume fraction v_1' is calculated from the composition and densities (0.9323 g/mL measured for SBS at 25 °C, 0.895 taken for polybutadiene at 25 °C), assuming volume additivity, to be 0.133 for polybutadiene and 0.141 for the oil. A boundary layer 20-Å thick would increase these values to 0.147 and 0.157, respectively. Somewhat arbitrarily because of better agreement with the effect of dilution on modulus, the latter values are chosen, and the composition of the continuous phase is expressed below as the volume fraction of polybutadiene block, $v_2' = 1 - v_1'$, based on the assumption of a boundary layer.

Stress relaxation experiments in uniaxial extension were performed on network strips, 6-cm long and 4-mm wide, cut from the cast films. A separate strip was used for each experiment. The apparatus and experimental procedure have been described previously.[6] Measurements were usually made with the stretch ratio $\lambda = 1.15 \pm 0.01$ at −20.0, −10.0, +5.0, and +20.0 °C. The uniformity of strain was checked with fiducial marks. The stress relaxation data were calculated in terms of the apparent Young's modulus, $E_a(t)$, defined as

$$E_a(t) = 3f(t)/A_0(\lambda - \lambda^{-2}) \tag{1}$$

where $f(t)$ is the time-dependent force and A_0 is the original cross-sectional area, determined from the weight of a strip of measured length and the network density. If the stress–strain relation is neo-Hookean, this should provide the true Young's relaxation modulus of linear viscoelasticity; deviations at this strain magnitude are expected to be small. Four experiments on samples of SBS and three SBS containing linear polybutadienes were made with $\lambda \cong 1.08$ at −20.0 °C to explore the possible strain dependence on modulus. Comparison with data at $\lambda = 1.15$ showed $E_a(t)$ to be higher by about 12% at the smaller strain, but the difference was almost independent of time and of whether an unattached species was present. Hence, eq 1 was used in all subsequent calculations for constant $\lambda = 1.15$ to provide data which are comparable on a relative basis.

The relaxation modulus of each linear and star polybutadiene, denoted by $E_{11}(t)$, was also obtained from measurements on the pure species for comparison with relaxation in the SBS network. That of the highest molecular weight linear polymer, 813L, was measured directly in uniaxial extension at $\lambda = 1.08$ at −20 °C. Those for the linear samples 203L and 389L, and the 4-arm stars 88S4 and 226S4, were calculated indirectly from oscillatory shear measurements of the storage and loss shear moduli G' and G'' generously provided by Professor W. W. Graessley and collaborators;[20,23] data for 203L and 88S4 were available, and 389L and 226S4 were assumed to be closely similar to other samples with nearly the same microstructure and molecular weights, namely, 347L and 217S4, respectively. (However, the time scale for 347 was adjusted for the third power of the molecular weight ratio of 389 and 347, a procedure justified by the observed dependence of relaxation times on molecular weight as described below.) The conversion of G' and G'' to $E_{11}(t)$ was made by the method of Schwarzl[24] (his eq 25 and 26). Finally, $E_{11}(t)$ of the 3-arm star, 204S3, was calculated from data for the creep compliance $J(t)$ generously given us by Professor D. J. Plazek,[25] by the conversion method of Leaderman[26]

$$E(t) = 3 \sin (m\pi)/m\pi J(t) \tag{2}$$

where m is the slope of a doubly logarithmic plot of $J(t)$. Temperature shifts associated with these calculations are described below.

Results

Pure Triblock Network and Network with Oil. In the upper part of Figure 2, $E_a(t)$ is plotted logarithmically against time for the pure SBS network at four temperatures as indicated. Only a small fraction of the data points taken is plotted. For purposes of subsequent calculations, the magnitude of E_a has been reduced to a reference temperature of 20 °C (T_0 = 293 K) by the factor $T_0\rho_0/T\rho$, where ρ_0 is the density at T_0 and ρ that at the temperature of measurement, T. In this calculation, the thermal expansion coefficient was taken as 7.5×10^{-4} deg^{-1}. There is significant relaxation with apparently no approach to an equilibrium value. These curves could be superposed by empirical shifts log a_T to give the composite curve shown in Figure 3; the shift factors are plotted against temperature in Figure 4.

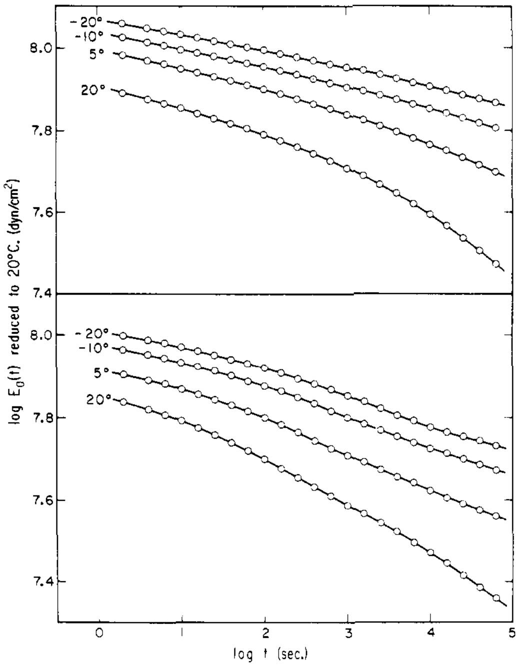

Figure 2. Logarithmic plots of the apparent Young's modulus $E_a(t)$ against time for pure SBS network (top) and a network containing linear polybutadiene 813L (bottom) at four temperatures as indicated. Many points have been omitted to avoid confusion. Modulus magnitude reduced to 20 °C.

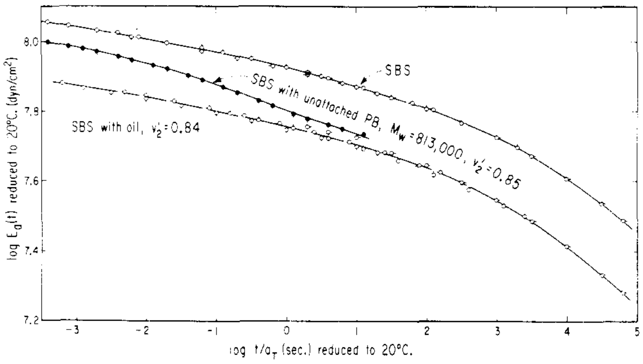

Figure 3. Logarithmic plot of $E_a(t)$ against time for SBS network, upper data of Figure 1 reduced to 20 °C, compared with similar plots for networks containing hydrocarbon oil and linear polybutadiene 813L (at −20 °C only). Volume fraction of network polybutadiene block in polybutadiene phase is v_2'. Pip down, data at −20 °C; successive rotations clockwise, −10, +5, and +20 °C.

Similar data at four temperatures for a network containing hydrocarbon oil to reduce the volume fraction of network in the butadiene phase to $v_2' = 0.84$ provided the lower composite curve in Figure 3; the temperature shift factors are almost identical, as shown in Figure 4. The two composite curves match closely if the upper is shifted vertically by −0.15 and horizontally by −0.25. The former corresponds to the factor log $v_2'^2$ expected for reduction of the concentration of trapped entanglement strands by dilution; the latter corresponds to the effect of dilution on the monomeric fraction coefficient as calculated[22] from the change in fractional free volume f if the derivative $\beta' = (\partial f/\partial v_1')_T = 0.06$, a reasonable value[27] (although 0.10 was found for a similar comparison in an end-linked polybutadiene network[6]).

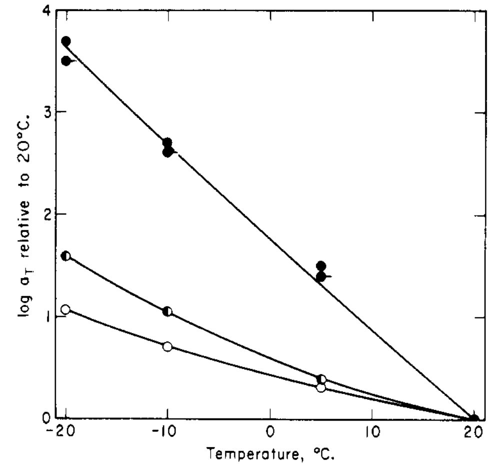

Figure 4. Shift factors log a_T plotted against T. Black circles, $E_a(t)$ for SBS network; black with pips, SBS network with oil; half black, $E_1(t)$ for unattached polybutadienes in SBS network; open circles, $E_{11}(t)$ for homogeneous uncross-linked polybutadienes (calculated).

Networks Containing Unattached Species. In Figure 3, the apparent Young's relaxation modulus $E_a(t)$ is also plotted for a network containing unattached linear polybutadiene at nearly the same volume fraction as the oil ($v_2' = 0.85$), at a single temperature of -20 °C. At short times, it is close to the undiluted network, but at longer times it shows additional relaxation and approaches the curve for the network diluted with oil. This curve is also reproduced in the lower part of Figure 2 together with modulus-time curves for the same network at different temperatures.

These curves of E_a for the network containing polymer 813L, and for the other networks with unattached species, do not superpose accurately when data at different temperatures are empirically shifted; the temperature dependencies of the two species appear to be different despite the match of polybutadiene microstructure. The contribution of the unattached species to the relaxation modulus is therefore determined by subtraction of data as portrayed in Figure 2 at each individual temperature, as done previously for end-linked networks.[6] In the latter case, the subtraction was based on comparison of the equilibrium moduli measured for both undiluted network and network containing unattached species observed at long times. In the present experiments, no equilibium modulus is attained. Accordingly, the contribution of the network to the modulus, $E_2(t)$, is taken as that of the undiluted network, $E_a^0(t)$, reduced by a weighting factor V_2 determined as the ratio $E_2(t)/E_a^0(t)$ observed at long times, where the unattached species is believed to be fully relaxed. The factor V_2 was chosen empirically for each network but it was very close (±0.01) to the value $v_2'^2 = 0.73$ expected for reduction of trapped entanglement strands by volume dilution. Accordingly, the contribution of unattached species to the modulus was calculated as

$$E_1(t) = E_a(t) - V_2E_a^0(t) \qquad (3)$$

Data for $E_1(t)$ at individual temperatures could be superposed closely to give composite curves with shift factors which were the same for all unattached species and are plotted against temperature in Figure 4. They are quite close to values for the pure uncross-linked polybutadienes as calculated from the WLF equation for a polybutadiene with this microstructure[28] (T_0 = 293 K, $c_1^0 = 3.73$, $c_2^0 = 181.5$), also plotted in Figure 4; these latter agree well with the values determined empirically by Graessley and coworkers[20] and Plazek.[25] The composite curves of $E_1(t)$ for the three linear polybutadienes, reduced to 20 °C, are shown in Figure 5. The magnitude of $E_1(t)$ has been increased by the factor $(1 - v_2'^2)^{-1}$ for comparison with the relaxation modulus $E_{11}(t)$ of the pure linear species as will be explained in the Discussion. The modulus falls steeply, decreasing by a factor of about 0.02 in the time range covered.

Similar composite plots for the three star-branched polybutadienes are shown in Figures 6–8. The relaxation of the 4-arm star with M_w = 88 000 is much less, and that of the 3-arm and 4-arm stars with higher molecular weights is very much less, than that of the linear polymers. The latter falls by a factor of about 0.25 in the time range covered.

Stress Relaxation of the Pure Unattached Species. The relaxation modulus $E_{11}(t)$ for each unattached species is plotted in Figures 5–8. As explained in the Experimental Section, only one was measured directly: polymer 813L, measured at -20 °C with stretch ratio λ = 1.08 and reduced to 20 °C by the shift factor shown for polybutadiene with this microstructure in Figure 4. The others were calculated indirectly from data of Graessley and co-workers[20] and Plazek[25] on the same or closely similar polymers.

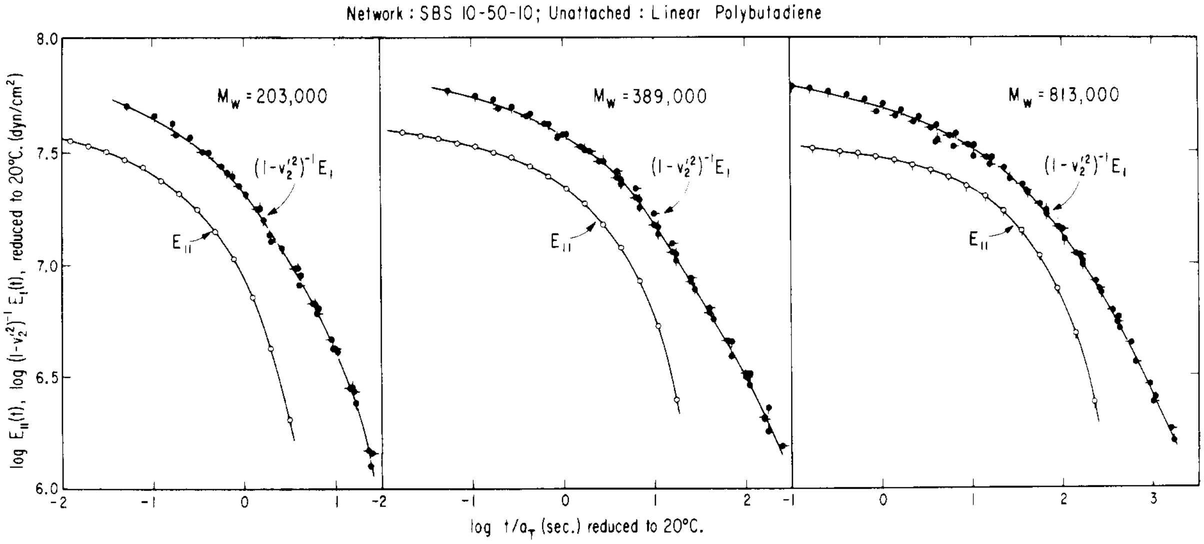

Figure 5. Logarithmic plots of $E_{11}(t)$ and $(1 - v_2'^2)^{-1}E_1(t)$ for three linear polybutadienes, reduced to 20 °C. Key to temperatures same as in Figure 3. For the first two polymers, $E_{11}(t)$ is calculated from data of Graessley.[20,23]

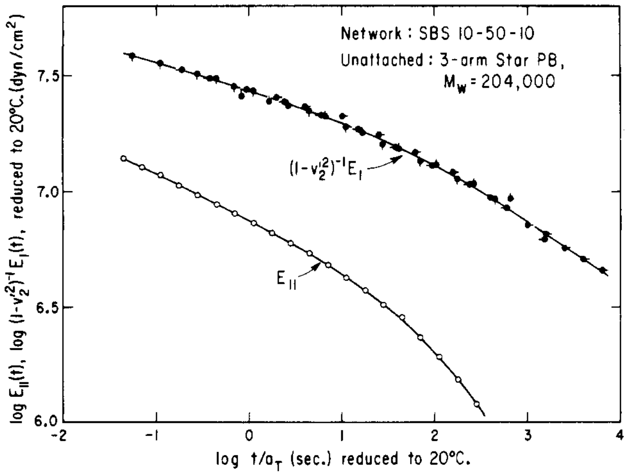

Figure 6. Logarithmic plots of $E_{11}(t)$ and $(1 - v_2'^2)^{-1}E_1(t)$ for 3-arm star polybutadiene, $\bar{M}_w$ = 204 000, reduced to 20 °C. Key to temperatures same as in Figure 3. $E_{11}(t)$ is calculated from data of Plazek.[25]

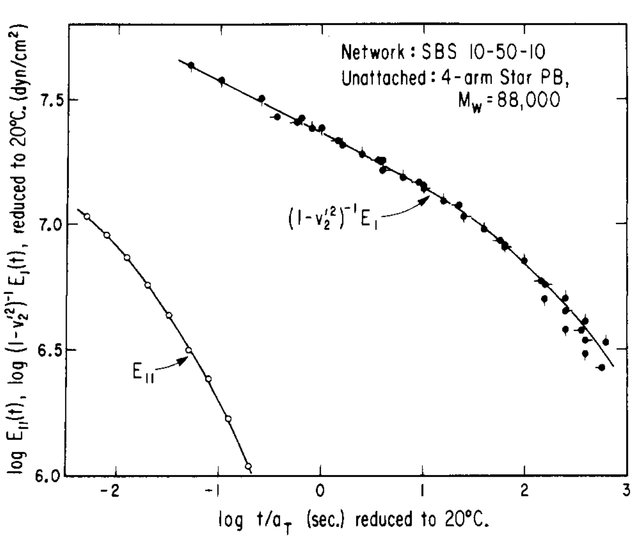

Figure 7. Logarithmic plots of $E_{11}(t)$ and $(1 - v_2'^2)^{-1}E_1(t)$ for 4-arm star polybutadiene, $\bar{M}_w$ = 88 000, reduced to 20 °C. Key to temperatures same as in Figure 3. E_{11} is calculated from data of Graessley.[20,23]

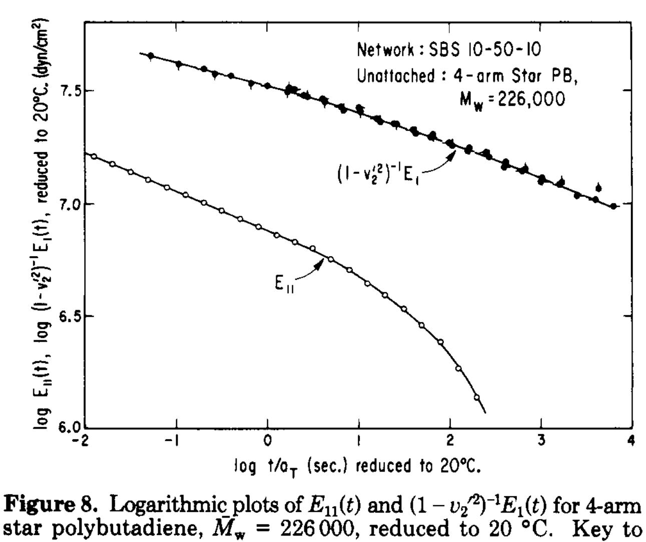

Figure 8. Logarithmic plots of $E_{11}(t)$ and $(1 - v_2'^2)^{-1}E_1(t)$ for 4-arm star polybutadiene, $\bar{M}_w$ = 226 000, reduced to 20 °C. Key to temperatures same as in Figure 3. E_{11} is calculated from data of Graessley.[20,23]

Discussion

Modulus of the Undiluted Network. Although there is no equilibrium modulus for the SBS network in Figure 3, log $E(t)$ is near 8.0 over a considerable range of time scale. This may be compared with a rough calculation on the basis of a trapped entanglement network of the continuous polybutadiene phase modified by the filler effect of the polystyrene domains.[29] The Guth–Smallwood equation[30] with a polystyrene volume fraction of 0.245 would provide a filler enhancement factor of 2.46; with log E_N^0 = 7.54 (in dyn/cm^2) for the plateau modulus of polybutadiene with this microstructure,[20] we obtain log E = 7.93, in reasonable agreement. On the other hand, if there were no trapped entanglements and the network strands were represented by the full length of the polybutadiene blocks, log E would be about 6.4, lower by more than an order of magnitude than the observed level. We conclude, therefore, that the elasticity of the SBS reflects a network of trapped entanglements, although a different opinion has been expressed.[31] Dilution by either oil or unattached species should reduce the density of trapped entanglements by the factor $v_2'^2$, as has been used above. (A slightly different exponent of 2.25 has been reached by alternative reasoning[32] and may agree better with experiment[33] over a large range of v_2', but the difference is negligible here.)

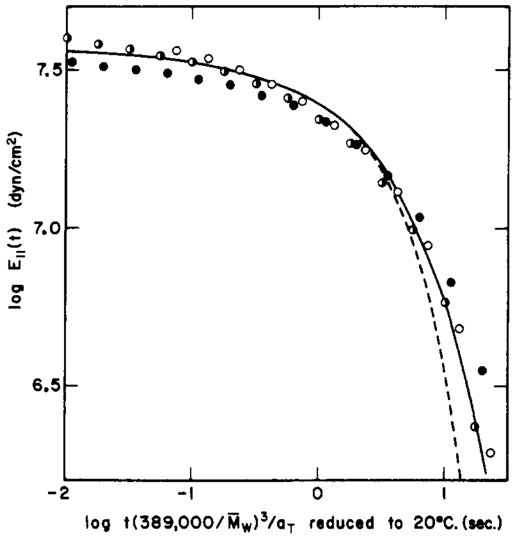

Figure 9. Logarithmic plot of $E_{11}(t)$, interpolated from Figure 5, against $t(389\,000/\bar{M}_w)^3/a_T$. Open circles, M_w = 203 000; half black, 389 000; black, 813 000. Solid curve calculated from Doi–Edwards theory with $\bar{M}_w/\bar{M}_n$ = 1.05, log τ_d = 0.68, and log E_N^0 = 7.57. Dashed curve: Doi–Edwards theory for uniform molecular weight.

Relaxation of Linear Polymers in the Terminal Zone. Since according to the reptation mechanism[7-10] the relaxation times in the terminal zone should be proportional to M^3, the curves of $E_{11}(t)$ for the three linear polymers have been reduced in time scale to that with $\bar{M}_w$ = 389 000 by plotting against log $[t(389\,000/\bar{M}_w)^3/a_T]$ in Figure 9. The coincidence is quite good, although the dynamic data of Graessley and co-workers[20] and the steady-flow viscosity data of Gruver and Kraus[34] together with a plateau modulus independent of molecular weight[20] would be more consistent with an exponent of 3.4. The plateau modulus E_N^0 expected from Graessley's data corresponds to log E_N^0 = 7.54.

In the Doi–Edwards theory,[6,8,9] the relaxation in the terminal zone for uniform molecular weight is given by

$$E(t) = E_N^0 \frac{8}{\pi^2} \sum_{\text{odd } n} \frac{1}{n^2} \exp(-n^2 t/\tau_d) \qquad (4)$$

where τ_d is the disengagement time for escape of the

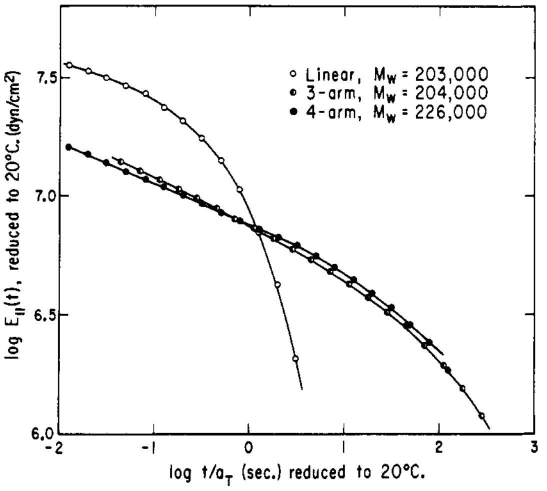

Figure 10. Logarithmic plots of $E_{11}(t)$ against t/a_T reduced to 20 °C, interpolated from Figures 5, 6, and 8, for three polybutadienes of closely similar molecular weights as indicated.

molecule from its virtual tube. This is very close to a single exponential. For a narrow molecular weight distribution, it can be integrated[6] over a Schulz distribution function[35] with the coefficient b determined by the observed $\bar{M}_w/\bar{M}_n$ ratio; for $\bar{M}_w/\bar{M}_n$ = 1.05, b = 19. Curves for $E(t)$ are drawn in Figure 9 for eq 4 and also for $\bar{M}_w/\bar{M}_n$ = 1.05, with the scales arbitrarily adjusted. They differ only slightly and the fit with the latter is quite good. It corresponds to log τ_d = 0.68 for $\bar{M}_n$ = 370 000 ($\bar{M}_n$ because the molecular weight distribution is normalized to $\bar{M}_n$). This may be compared with a calculation from Graessley's application of the Doi–Edwards theory, which can be reformulated as[6]

$$\tau_d = M^3a^2\zeta_0E_N{}^0/3\pi^2M_0{}^2\rho N_0(kT)^2 \qquad (5)$$

where a^2 is the mean-square end-to-end length per monomer unit, ζ_0 the monomeric friction coefficient, M_0 the monomer molecular weight, ρ the density, and N_0 Avogadro's number. For this purpose, a is taken as 6.0 Å and log ζ_0 at 20 °C as −6.65 (reduced from the literature value at 25 °C[36]). The result is log τ_d = 1.27. The origin of the difference is not clear.

Comparison of Linear and Star Polybutadienes, both as Single Components and in the Network. In Figure 10, $E_{11}(t)$ is plotted logarithmically for a linear, a 3-arm star, and a 4-arm star polybutadiene with closely similar molecular weights. The two stars are essentially indistinguishable but relax much more gradually than the linear polymer. Still, a low value for the modulus is eventually reached and there is clearly a mechanism for substantial relaxation even if the reptation process is severely impeded. These curves represent, of course, a restatement of the conclusions of Graessley and co-workers,[20] who pointed out that the star-branched molecules showed no plateau in the storage modulus.

In Figure 11, $(1 - v_2'^2)^{-1}E_1(t)$ is plotted logarithmically for the same three polymers as in Figure 10. The difference between linear and stars is now considerably exaggerated when the relaxation is taking place in a medium of trapped entanglements; the stars relax relatively little.

We turn now to the comparison of each unattached species in the network and in its own environment as portrayed in Figures 5–8. The magnitude of $E_1(t)$ is, of course, affected by its dilution in the network, and it is assumed to be reduced by the factor $1 - v_2'^2$ as in previous work on end-linked networks;[6] this represents the proportion of entanglements in which at least one of the two participating molecules belongs to the unattached species, i.e., untrapped. Accordingly, $(1 - v_2'^2)^{-1}E_1(t)$ is compared with $E_{11}(t)$.

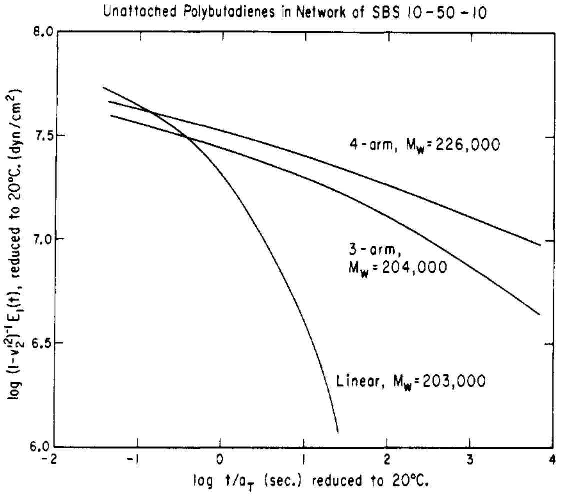

Figure 11. Logarithmic plots of $(1 - v_2'^2)^{-1}E_1(t)$ against t/a_T reduced to 20 °C, interpolated from Figures 5, 6, and 8 as in Figure 10.

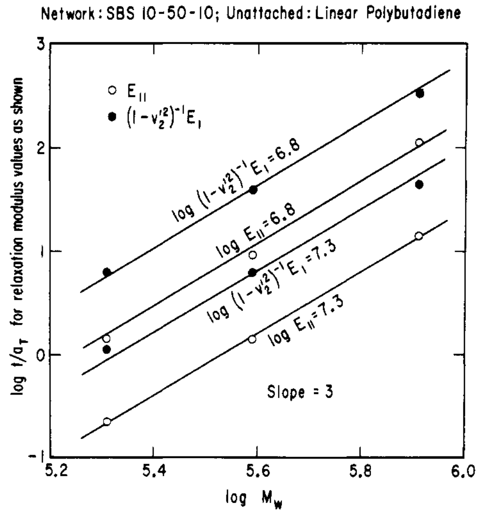

Figure 12. Values of log t/a_T interpolated from Figure 5 corresponding to log $E_{11}(t)$ or log $(1 - v_2'^2)^{-1}E_1(t)$ = 6.8 or 7.3 (units dyn/cm²) plotted against log $\bar{M}_w$ for the three linear polybutadienes. Lines drawn with slope of 3.0.

For the linear polymers, shown in Figure 5, the form of the relaxation is very similar in the two media. Thus the reptation appears to be similar in character whether the entanglements of the medium are trapped or untrapped. The corrected $E_1(t)$ appears to be approaching a plateau value somewhat higher than $E_N{}^0$ of the pure unattached species. The relaxation appears to be slower by about half an order of magnitude in the trapped network than in the unattached species. A similar difference was found for relaxation of linear molecules of narrow molecular weight distribution in end-linked networks.[6] The location of the terminal zone on the time scale is proportional to M^3 for both $E_1(t)$ and $E_{11}(t)$, as shown in Figure 12.

For the star-branched polymers, shown in Figures 6–8, the magnitude of the corrected $E_1(t)$ is close to $E_N{}^0$ at short times and decreases relatively little, so the relaxation is far slower in the trapped network than in the unattached species alone and has a different time dependence. It may be concluded that the suppression of relaxation by branching is much more effective when the ends of the molecules comprising the environment are anchored. Either the suppression of reptation is much more effective when the topological restraints consist of trapped obstacles or else there is a substantial contribution from processes other than reptation, such as tube renewal,[9] when the obstacles are untrapped.

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References and Notes

(1) This work was part of the research program of the Rheology Research Center, University of Wisconsin.
(2) (a) Department of Chemistry, University of Wisconsin. (b) Institute of Polymer Science, The University of Akron.
(3) Kramer, O.; Greco, R.; Neira, R. A.; Ferry, J. D. *J. Polym. Sci., Polym. Phys. Ed.* **1974,** *12,* 2361.
(4) Kramer, O.; Greco, R.; Ferry, J. D.; McDonel, E. T. *J. Polym. Sci., Polym. Phys. Ed.* **1975,** *13,* 1675.
(5) Greco, R.; Taylor, C. R.; Kramer, O.; Ferry, J. D. *J. Polym. Sci., Polym. Phys. Ed.* **1975,** *13,* 1687.
(6) Nelb, G. W.; Pedersen, S.; Taylor, C. R.; Ferry, J. D. *J. Polym. Sci., Polym. Phys. Ed.* **1980,** *18,* 645.
(7) de Gennes, P. G. *J. Chem. Phys.* **1971,** *55,* 572.
(8) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978,** *74,* 1818.
(9) Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1980,** *18,* 27.
(10) Kraus, G.; Gruver, J. T. *J. Polym. Sci., Part A* **1965,** *3,* 105. *J. Appl. Polym. Sci.* **1965,** *9,* 739.
(11) de Gennes, P. G. *J. Phys. (Paris)* **1975,** *36,* 1199.
(12) Toy, L.; Niinomi, M.; Shen, M. *J. Macromol. Sci., Phys.* **1975,** *B11,* 281.
(13) Kraus, G.; Rollmann, K. W. *J. Polym. Sci., Polym. Phys. Ed.* **1977,** *15,* 385.
(14) Morton, M.; Fetters, L. J. *Rubber Revs.* **1975,** *48,* 359.
(15) Bi, L.-K.; Fetters, L. J. *Macromolecules* **1976,** *9,* 732.
(16) Hadjichristidis, N.; Guyot, A.; Fetters, L. J. *Macromolecules* **1978,** *11,* 668.
(17) Ambler, M.; Fetters, L. J.; Kesten, Y. *J. Appl. Polym. Sci.* **1977,** *21,* 2439.
(18) Grubisic, Z.; Rempp, P.; Benoit, H. *J. Polym. Sci., Part B* **1967,** *5,* 753.
(19) Bywater, S.; Worsfold, D. J. *Can. J. Chem.* **1962,** *40,* 1564.
(20) Rochefort, W. E.; Smith, G. G.; Rachapudy, H.; Raju, V. R.; Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1979,** *17,* 1197.
(21) Beecher, J. F.; Marker, L.; Bradford, R. D.; Aggarwal, S. L. *J. Polym. Sci., Part C* **1969,** *26,* 117.
(22) Kan, H.-C. Ph.D. Thesis, University of Wisconsin, 1979.
(23) Graessley, W. W., personal communication.
(24) Schwarzl, F. *Pure Appl. Chem.* **1970,** *23,* 219.
(25) Plazek, D. J., personal communication.
(26) Leaderman, H. In "Rheology"; Eirich, F. R., Ed.; Academic Press: New York, 1958; Vol. II, p 1.
(27) Ferry, J. D. "Viscoelastic Properties of Polymers", 2nd ed.; Wiley: New York, 1970; p 524.
(28) Ferry, J. D. "Viscoelastic Properties of Polymers", 3rd ed.; Wiley: New York, 1980; Table 11-II.
(29) Holden, G.; Bishop, E. T.; Legee, N. R. *J. Polym. Sci., Part C* **1969,** *26,* 37.
(30) Guth, E. *J. Appl. Phys.* **1945,** *16,* 20.
(31) Meier, D. *J. Macromol. Sci., Phys.* **1980,** *B17,* 181.
(32) de Gennes, P. G. *Macromolecules* **1976,** *9,* 594.
(33) Marin, G.; Menezes, E.; Raju, V. R.; Graessley, W. W. *Rheol. Acta,* submitted for publication.
(34) Gruver, J. T.; Kraus, G. *J. Polym. Sci., Part A* **1964,** *2,* 797.
(35) Tung, L. H. In "Polymer Fractionation"; Cantow, M. J. R., Ed.; Academic Press: New York, 1967; p 379.
(36) Reference 28, Table 12-III.

Dielectric Relaxation Studies of Bis[4-(diethylamino)-2-methylphenyl]phenylmethane/ Polycarbonate Solid Solutions. A Correlation of Sub-T_g Relaxations and the Glass Transition Activation Energy

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ABSTRACT: The dielectric relaxation spectra of solid solutions of bis[4-(diethylamino)-2-methylphenyl]-phenylmethane (BDETPM)/polycarbonate (BPAPC) solid solutions have been studied as a function of composition. The T_g of the system is a continuous function of composition and has been interpreted in terms of a free-volume additivity equation. The polymer and monomer exhibit correlated motion at T_g. The activation energies of T_g are Arrhenius activated over the temperature–frequency regime of the experiments. These activation energies show a composition dependence made up of two linear portions which intersect between 20 and 30 wt % BDETPM. This intersection is directly correlatable to the disappearance of the BPAPC β relaxation and indicates a change in the dynamics of the T_g reorientation process with the elimination of the β relaxation. The results are discussed in terms of previously studied small-molecule/polymer solid solutions. It is shown that the sub-T_g relaxations of BPAPC are affected by the addition of BDETPM. The β and γ relaxations are plasticized and decrease in intensity. The β relaxation disappears between 20 and 30 wt % BDETPM, while the γ intensity is a direct function of composition. Little evidence for the β relaxation of BDETPM is observed.

Introduction

The effect of plasticizers on polymer properties is important scientifically as well as industrially. The plasticizer not only can play the role of a softener[1–5] but also can have intrinsic properties that produce other valuable characteristics. An example of this latter effect is the addition of *n*-butyl 4,5,7-trinitrofluorenone-2-carboxylate to polycarbonate[4] (BPAPC). The dopant not only plasticizes the polycarbonate but also is capable of transporting electrons.[6]

The dynamics of many plasticized polymer systems have been well studied.[1–5,7–10] These studies reveal a correlated motion of both components at a mixture's T_g or an un-

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