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Rheology and the Microphase Separation Transition in Styrene–Isoprene Block Copolymers

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ABSTRACT: We have used dynamic oscillatory measurements to locate the temperature of the microphase separation transition ($T_{\rm MST}$) for a series of nearly monodisperse styrene–isoprene diblock (SI) and triblock (SIS) copolymers, all containing 13 wt % styrene and ranging in molecular weight from 48K to 149K. The microphase-separated morphology in all cases is a disordered (liquidlike) arrangement of polystyrene spheres in a polyisoprene matrix, as determined by small-angle X-ray scattering. Values of $T_{\rm MST}$ were obtained from isochronal plots of the storage modulus versus temperature. The marked change in slope at the MST demonstrates that even materials with a disordered microdomain structure can experience significant property changes when the MST is traversed. The diblock and triblock $T_{\rm MST}$ values are consistent with a single $\chi(T)$ relation, indicating that large-scale polymer architecture has little effect on χ.

I. Introduction

Microphase separation in block copolymers is driven by the thermodynamic incompatibility of the block constituents. While the resulting microphase-separated morphology gives rise to useful mechanical properties, it also produces large viscosities and memory effects when it persists into the melt, making processing difficult. The microphase separation transition (MST) divides the microphase-separated and single-phase states, and the transition temperature $T_{\rm MST}$ depends strongly on polymer composition and molecular weight. Rheological measurements[1–8] are useful in locating $T_{\rm MST}$, since the flow properties differ markedly between the single-phase and microphase-separated states. The dynamic storage and loss moduli (G', G'') of block copolymers in the single-phase state (well above $T_{\rm MST}$) resemble those of homopolymers. The moduli are higher in the microphase-separated state (below $T_{\rm MST}$) at low frequencies. As a consequence, isochronal plots of G' vs T at low frequencies often show an abrupt drop or change in slope at the MST.[2,4–8] For some range of temperatures above $T_{\rm MST}$, composition fluctuations may influence the rheological response,[5,7,9,10] leading to deviations from thermorheological simplicity.

Phase diagrams have been calculated for a range of block copolymer architectures. Leibler's mean-field treatment[11] expresses the MST for AB diblock copolymers in terms of the fraction f of A units and the product χN, where χ is the Flory interaction parameter and N is the total number of monomer units in the diblock. Leibler's theory has been extended to more complicated architectures, including multiblock and graft polymers.[12–14] As discussed in detail below, $T_{\rm MST}$ values obtained from rheological measurements can be combined with a suitable theory to provide values of χ for the monomer pair.[15]

Here, we address two issues. First, previous studies showing abrupt drops in G' at the MST have employed materials with ordered microdomains.[2,4–8,16] In those cases, both microphases were also continuous in at least one direction (such as cylinders or lamellae). Here we study materials in which the minority component forms spheres with only a liquidlike ordering.[17] The absence of a microdomain lattice allows us to probe the effect of microphase separation on rheological response without the complications of domain director orientation and anisotropic mechanical properties.[7,16,18] Beyond that, however, we can determine whether the presence of a microdomain lattice is a necessary condition for abrupt rheological changes at $T_{\rm MST}$. Second, there are conflicting reports about whether $\chi(T)$ depends on how the monomers are combined (e.g., as a homopolymer blend or as a diblock or triblock copolymer). From small-angle X-ray scattering (SAXS) measurements above $T_{\rm MST}$, Ijichi *et al.*[19] concluded that $\chi(T)$ for the styrene–isoprene system varies strongly with block architecture, most noticeably between diblocks and triblocks. On the other hand, Gehlsen *et al.*[6] found that the $T_{\rm MST}$ values for diblocks and triblocks of poly(ethylethylene)–poly(ethylene–propylene) were consistent with an architecture-independent $\chi(T)$. We address this question by studying diblock and triblock copolymers of styrene–isoprene with a fixed composition and varying molecular weights.

Table 1. Characteristics of Block Copolymers

material	$10^{-3}M_w$	wt % of styrene	$T_{\rm MST}$ (°C)
D48	48.3	13.2	55 ± 10
D62	62.6	13.0	105 ± 3
D78	78.4	13.5	153 ± 3
D90	90.6	13.1	191 ± 3
T90	90.6	13.0	58 ± 10
T107	106.8	12.2	87 ± 10
T120	120.1	13.3	102 ± 6
T149	149.0	13.0	158 ± 3

II. Experimental Section

Four polystyrene–polyisoprene–polystyrene (SIS) triblock and four polystyrene–polyisoprene (SI) diblock copolymers (Table 1) were synthesized and characterized by DEXCO Polymers for this study. Compositions were determined by ^{1}H nuclear magnetic resonance (NMR), which showed all polymers to contain 13 ± 0.8 wt % styrene and isoprene blocks high in 1,4 addition (7.1 ± 0.3% 3,4 addition). Molecular weights were determined by gel permeation chromatography (GPC) in tetrahydrofuran, calibrated with narrow-distribution polystyrene and polyisoprene standards. The interpolation method of Tung[20] was used to determine the copolymer molecular weights from the measured styrene contents. The GPC measurements also showed the diblocks to be free of triblock and homopolymer; the triblocks were free of diblock and homopolymer but contained traces (<0.6%) of pentablock (SISIS) material. The values of M_w/M_n were less than 1.03 for all the block copolymers. All materials were protected against oxidation at high temperatures with a commercial stabilizer package.

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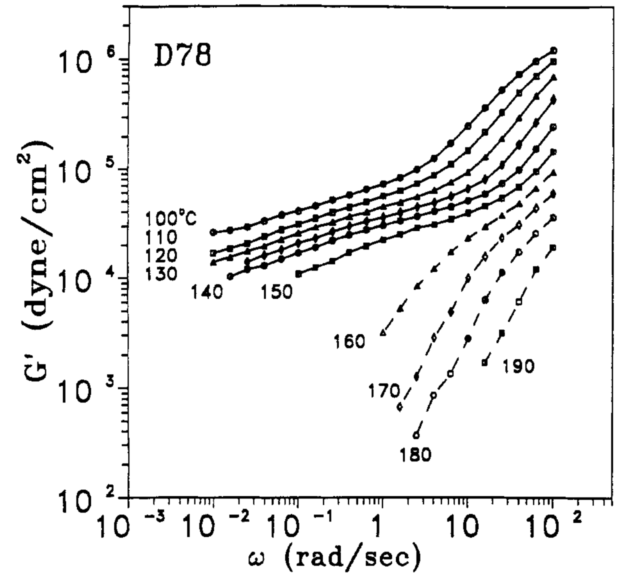

Figure 1. Dynamic storage modulus G' as a function of frequency ω for the diblock D78. Temperatures (°C) are indicated on the curves. Note the abrupt change between 150 and 160 °C, corresponding to the MST.

The letters "D" and "T" in the sample code indicate the architecture (diblock or triblock), while the digits correspond to the total molecular weight of the sample $(\times 10^3)$. SAXS measurements[21] at room temperature show all eight polymers to have a liquidlike packing of spherical microdomains.[17] Due to the very low styrene content $(f = 0.13)$, differential scanning calorimetry measurements were unsuccessful in determining the glass transition temperature of the polystyrene phase, but we estimated it to be less than 70 °C in all eight polymers on the basis of the literature.[22] The triblocks were compression-molded under vacuum at 140 °C, while the diblocks were compression-molded at room temperature. Subsequent tests showed that the rheological results were unaffected by molding history.

A Rheometrics System IV rheometer with 25 mm parallel-plate platens and a 1–2 mm gap was used to measure $G'(\omega)$ and $G''(\omega)$ in the frequency range $0.001 \leq \omega$ (rad/s) ≤ 100 at various temperatures; the gap was corrected for thermal expansion. The samples were tested isothermally (±2 deg) in an environmental chamber flushed with nitrogen. Strain amplitudes up to 15% were used; at $T > T_{\mathrm{MST}}$ the response was linear over this range. At $T < T_{\mathrm{MST}}$ the response was also linear over the range of strain amplitudes used (up to 15%) at high frequencies. However, at low frequencies the linear response window was reduced to about 8% strain. The entire frequency range was utilized whenever possible, but in many cases the lowest usable frequency was limited by a low torque signal, especially at temperatures above T_{MST}. No evidence of molecular weight changes in samples tested at or below 200 °C was found by GPC. Small but detectable amounts of both chain scission and branching were found in samples tested above 200 °C for 2 h or more. This should have no effect on our values of T_{MST}, however, since all are below 200 °C.

III. Results and Discussion

A. MST Determination. The dynamic moduli, $G'(\omega)$ and $G''(\omega)$, showed two distinctly different types of behavior, depending on the temperature; representative data for diblocks are illustrated by the D78 results in Figures 1 and 2. For $\omega < 10$ rad/s, both G' and G'' display very weak frequency dependencies below 150 °C. At 160 °C and above, G' and G'' decay much more rapidly over the same frequency range. The relaxation spectrum evidently contains a long-time component below 150 °C, which vanishes at higher temperatures. Above 160 °C, the moduli approach the limiting low-frequency dependencies characteristic of single-phase homopolymers in the terminal region ($G' \propto \omega^2$ and $G'' \propto \omega$). The change is more distinct in G' because its frequency dependence in the terminal region is stronger.

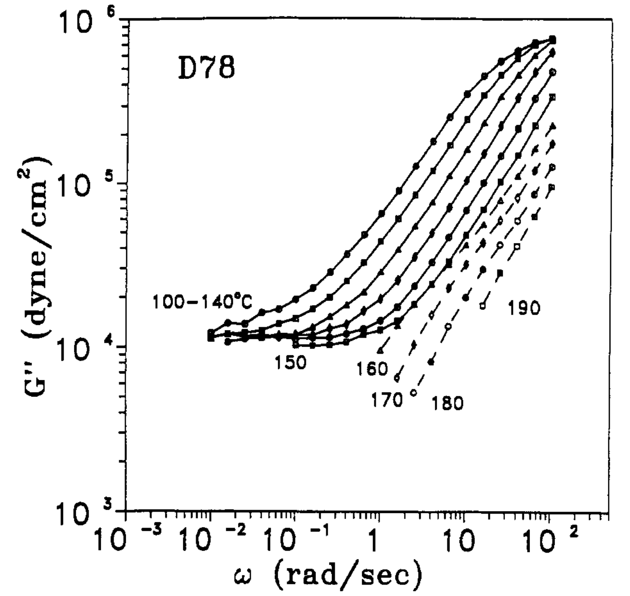

Figure 2. Dynamic loss modulus G'' as a function of frequency ω for the diblock D78. Temperatures (°C) are indicated on the curves. Note the abrupt change between 150 and 160 °C, corresponding to the MST.

The abrupt change in the behavior of G' and G'' has previously been identified[2,4–7,16] with the MST, an assignment we make here as well. In previous work, the materials in question generally exhibited ordered microdomain lattices (lamellae[4–7,18] or cylinders[2,8,16]). In these cases, rearrangement of the lattice structure should correspond to the longest-time component of the relaxation spectrum; the destruction of the lattice at the MST should produce simultaneous drops in both G' and G'' which will be most evident at low frequencies. However, our materials have no lattice, although they are indeed microphase-separated at the lower measurement temperatures. In such cases, the longest relaxation time of the system should correspond to diffusion of the entire polymer chain, which is greatly hindered below T_{MST} by the thermodynamic localization of the block junction point at the domain interface. At the MST, this constraint is relaxed, and the long-time component of the relaxation spectrum vanishes.

The rheological signature of the MST can also be seen in isochronal plots of G' vs T, as shown for several values of ω in Figure 3. There is a distinct change in slope between 150 and 160 °C, especially at frequencies below 10 rad/s. We assigned a T_{MST} of 153 ± 3 °C for D78 from the $\omega = 2.5$ rad/s isochrone, by extrapolating the curve segments below 150 °C and above 160 °C to their intersection. The data in Figures 1–3 clearly show that a microdomain lattice is not required to produce the rheological signature of an MST; it has previously been suggested[23] that this signature would be experimentally unobservable for SI and SIS materials with a spherical microdomain structure.

The plots of G' vs ω and G' vs T for the triblock T149 are shown in Figures 4 and 5, respectively. We observed that when diblocks and triblocks with similar T_{MST} values are compared at the same frequencies, the triblock G' vs T plots exhibited drops that are not as sharp as those of the diblocks. Since the experimental frequency window is set by the rheometer, this made the assignments of T_{MST} for the triblocks slightly more difficult. From the G' vs T isochrone with $\omega = 0.25$ rad/s (Figure 5), we obtained a value of 158 ± 3 °C for T_{MST}.

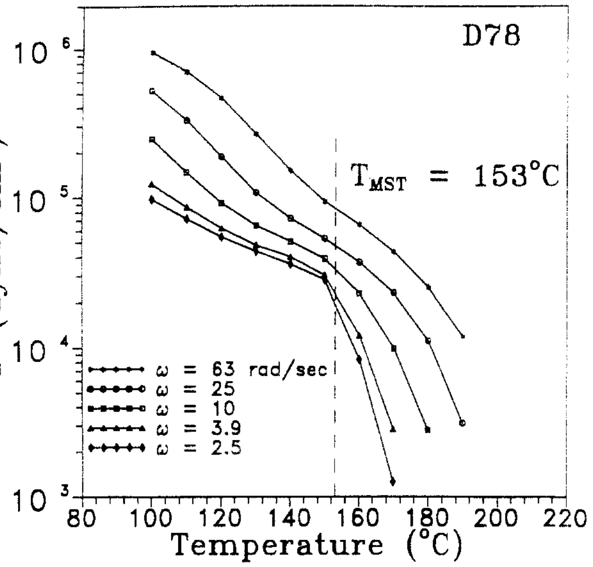

Figure 3. Isochronal plots of G' vs temperature for the diblock D78 for various frequencies. Note the abrupt drop in G' near 150 °C in the ω = 2.5 rad/s curve, corresponding to the MST.

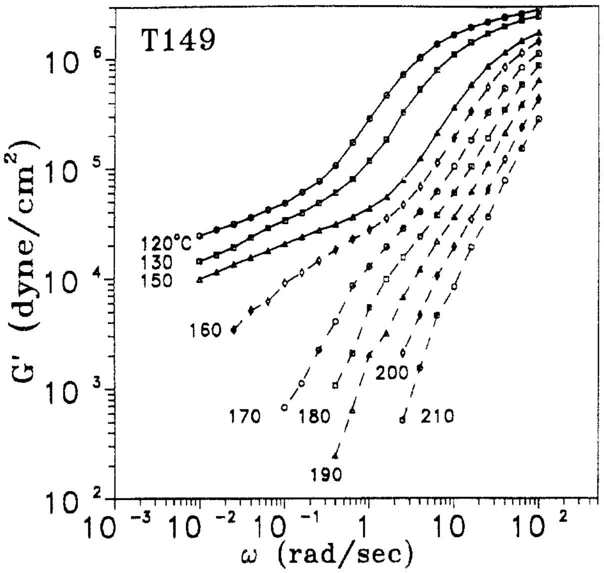

Figure 4. Dynamic storage modulus G' as a function of frequency ω for the triblock T149. Temperatures (°C) are indicated on the curves. Note the abrupt change between 150 and 160 °C, corresponding to the MST.

Han and co-workers[3] have suggested that plots of G' vs G'' depend on temperature below T_{MST}, but not above, and have used such plots to assign values of T_{MST}. Figure 6 shows the D78 data replotted in this manner. The curves show a temperature dependence up to the maximum temperature investigated, implying that T_{MST} exceeds 190 °C by the Han criterion, well beyond the drop observed in G' at 153 °C. As previously noted by Bates and co-workers,[5,7] using G' vs G'' plots to determine T_{MST} can lead to a substantial overestimation. They attributed the temperature dependence of the G' versus G'' plots above T_{MST} to the persistence of composition fluctuations well into the single-phase region. Interestingly, Figure 6 suggests that temperature independence of G' vs G'' is in fact approached, but *below* T_{MST}. This results from the relative temperature and frequency independence at low ω of both G' and G'' below T_{MST}, as shown in Figures 1 and 2.

During the course of determining the T_{MST} values, we found the drop in modulus at T_{MST} was sharp for all diblocks, except for the lowest molecular weight sample (D48). In contrast, the G' vs T curves for the triblocks became smoother as the molecular weight was reduced. This difference is illustrated via the comparison of the G' vs T plots in Figures 7 and 8 for the diblock D62 (T_{MST} = 105 °C) and triblock T120 (T_{MST} = 102 °C), respectively. This effect is due in part to the differences in terminal relaxation times of the diblock and triblock materials in the disordered state (discussed below) and to the fact that the G' vs T plots for the triblocks appear to have a steeper slope below T_{MST} than do the corresponding diblock plots. In samples of lower molecular weight (lower T_{MST}) the temperature window for probing the microphase-separated region was also limited by the proximity of the glass transition temperature of the polystyrene phase. Nevertheless, assignments of T_{MST} were possible for all samples. For T_{MST} determination for both the diblocks and triblocks, we selected the lowest ω for which the

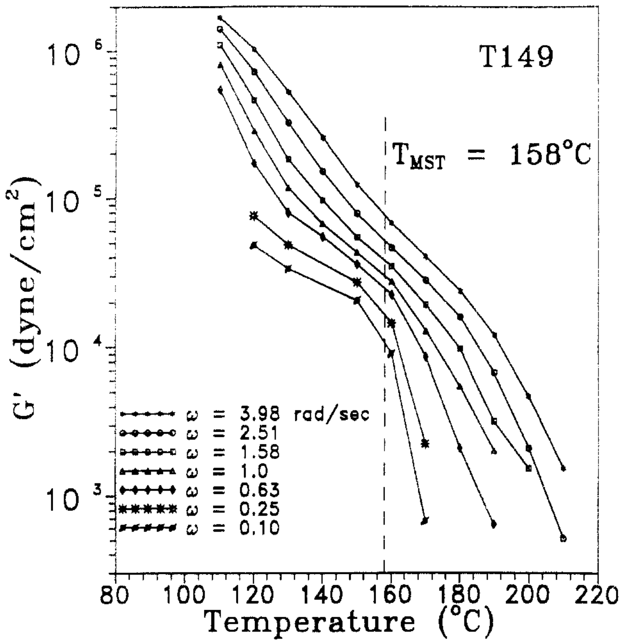

Figure 5. Isochronal plots of G' vs temperature for the triblock T149 for various frequencies. Note the change in slope commencing near 150 °C in the ω = 0.25 rad/s curve, corresponding to the MST.

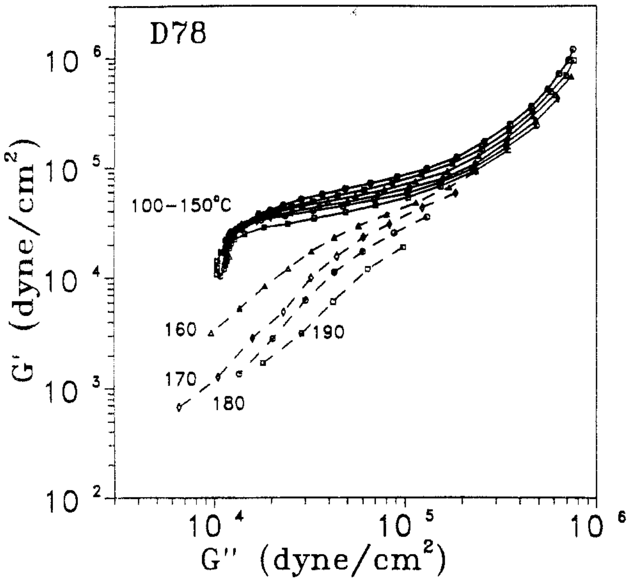

Figure 6. Plots of G' vs G'' for the diblock D78. Temperatures (°C) are indicated on the curves. Note the lack of convergence at high temperatures.

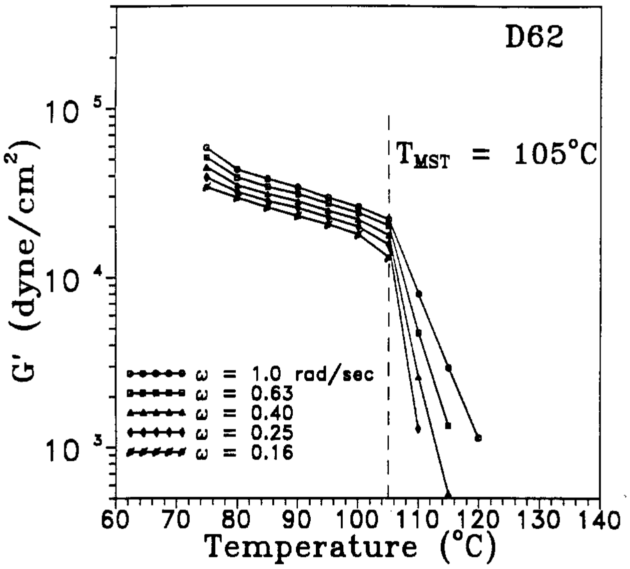

Figure 7. Isochronal plots of G' vs temperature for the diblock D62 for various frequencies. Note the abrupt drop in G' near 105 °C, corresponding to the MST.

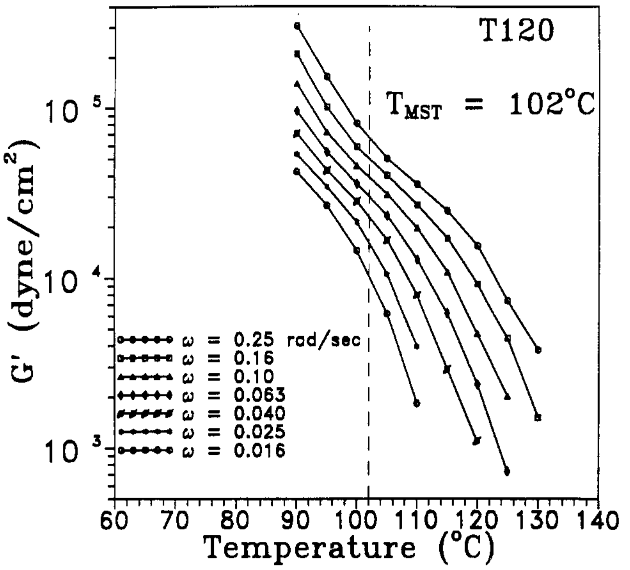

Figure 8. Isochronal plots of G' vs temperature for the triblock T120 for various frequencies. Note the more gradual drop in G' near 102 °C (MST) compared to that observed for the diblock D62 in Figure 7.

experimental torque limits still produced two or more data points above T_{MST}; for the diblocks, $0.16 < \omega < 4$ rad/s, while for the triblocks $0.01 < \omega < 0.2$ rad/s. The values obtained for T_{MST} and our estimates of the uncertainties are given in Table 1.

B. Time–Temperature Superposition. When sufficiently far above the MST, block copolymers often appear to be thermorheologically simple: master curves of G' and G'' can be constructed via frequency–temperature superposition[2,8] at both high and low reduced frequencies. When frequency–temperature superposition is applied to data obtained at temperatures both above and below T_{MST}, all the curves again superpose at high reduced frequencies (in or near the rubbery plateau), but fail to superpose at low reduced frequencies. The data instead form two distinct branches on the master curve, one for temperatures below T_{MST} and one for temperatures well above T_{MST}.

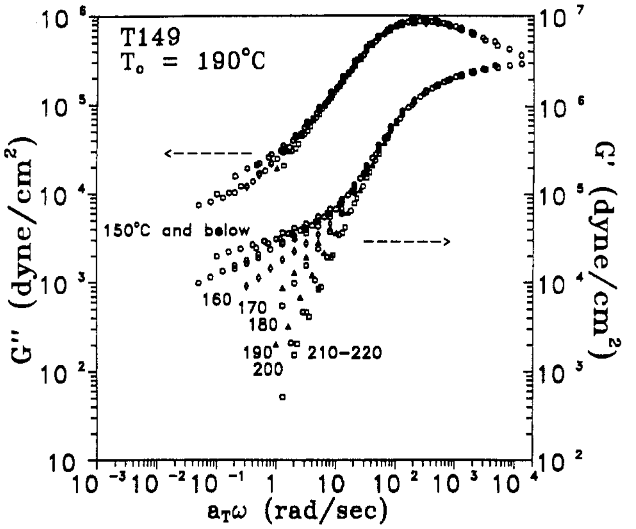

Figure 9. G' and G'' master curves for triblock T149 with a reference temperature of 190 °C. Temperatures (°C) of the original data sets are indicated on the curves.

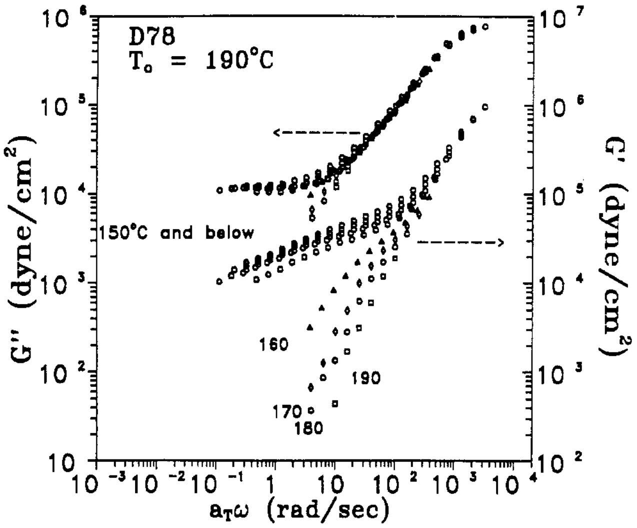

Figure 10. G' and G'' master curves for diblock D78 with a reference temperature of 190 °C. Temperatures (°C) of the original data sets are indicated on the curves.

We constructed master curves for our materials from the dynamic moduli isotherms. The results for T149 and D78 (reference temperature T_o = 190 °C for both) are shown in Figures 9 and 10. In constructing the master curves for T149, we were able to superpose the high ω portions (rubbery plateau) of the isotherms, whose shapes were independent of temperature, with no change in the modulus scale ($b_T = 1$ at all temperatures). The same values of the frequency shift factor a_T satisfied both the G' and G'' master curves. For the case of D78, the absence of a well-defined rubbery plateau at accessible frequencies made construction of the master curves more difficult. No modulus shift was necessary, as evidenced by the good superposition for G'' in and near the rubbery plateau; values of a_T were chosen that best satisfied both G' and G''. The shift factors for the triblock T149 were larger than those for the diblock D78 below T_{MST}; above T_{MST}, the same shift factors could be used for both the diblock and triblock (see Table 2).

For both T149 and D78, the data at 150 °C and below form one segment of the master curve and exhibit a very weak dependence on reduced frequency. For T149, $G' \propto \omega^{0.3}$ and $G'' \propto \omega^{0.4}$, while for D78, $G' \propto \omega^{0.3}$ and $G'' \propto \omega^{0.1}$. These power law exponents are noticeably smaller than the 0.5 value observed for both G' and G'' by Bates and co-workers[4,5] for block copolymers with lamellar microstructures; a review of the literature[2–6,8,24,25] shows that

Table 2. Frequency–Temperature Shift Factors

	$\log a_T$	
T (°C)	T149	D78
110	2.10	1.50
120	1.66	1.30
130	1.30	1.10
140	1.00	0.85
150	0.70	0.67
160	0.55	0.57
170	0.37	0.40
180	0.21	0.20
190	0.00	0.00
200	−0.15	−0.17
210	−0.29	
220	−0.46	

G' exponents ranging from 0.28 to 0.7 have been reported. For our samples, the diblocks showed apparent G' power law exponents between 0.2 and 0.35 below T_{MST}, while the triblocks exhibited values ranging from 0.3 to 0.7. However, the range of ω used to determine these values never exceeded two decades, so it is unclear whether there is in fact a substantial frequency range over which the response truly obeys a power law.

Above 150 °C, the low-frequency data for both T149 and D78 fail to superpose, instead forming a "fan". The highest-temperature data seem to be converging to form a second low-frequency branch on the master curve; however, convergence is not attained for D78, even at 190 °C, which is 30–40 deg above its T_{MST}. Convergence is attained for T149 at 210 °C, more than 50 deg above its T_{MST}. These frequency–temperature results display the same behavior observed by Bates and co-workers,[4,5,7] who attributed the data between the two branches, which spanned roughly 50 deg in their copolymer also, to composition fluctuations in the disordered state near the MST. Composition fluctuations hinder chain diffusion but are damped out as the temperature is raised well above T_{MST}. Even for the symmetric case, the magnitude of the fluctuation contribution to modulus is not quantitatively predicted by existing theories;[9,10] the situation is expected to be even worse for very asymmetric polymers of moderate molecular weight, such as ours, for which the Hartree approximation employed in the theories is poor.[26]

The major difference between the T149 and D78 master curves is that the confluence of the two low-frequency branches occurs at a reduced frequency that is lower by a factor of 16 for T149 than for D78, reflecting the difference in relaxation time τ of the two materials. The zero-shear viscosity, $\eta_0 = \lim_{\omega \to 0} G''/\omega$, for the two block architectures also differs by this same factor of 16 at both 190 and 200 °C. However, on the basis the known molecular weights of D78 and T149, and by assuming that they behave as homopolymers above T_{MST} ($\tau \sim M^{3.4}$), we expect a factor of 9 difference in the relaxation times. The discrepancy between the two (9 vs 16) lies outside the bounds of experimental error and may again reflect the influence of composition fluctuations on τ.

The difference in the sharpness of the drop in the G' vs T isochrones for the diblocks and triblocks with similar T_{MST}, when compared at the same frequency, is a direct consequence of the difference in τ for the two architectures. The more appropriate comparison[6] is one of constant $\omega\tau$, rather than constant ω. Figures 3 and 5 show that G' vs T for D78 at 10 rad/s is very similar to G' vs T for T149 at 0.63 rad/s, which is again consistent with $\tau_{\mathrm{T149}}/\tau_{\mathrm{D78}} \approx 16$. For the triblocks and even some of the diblocks, the experimental limitations on torque and frequency preclude measurements at values of $\omega\tau$ that would make the G' drop more distinct ($\omega\tau \ll 1$ for $T \approx T_{\mathrm{MST}}$).

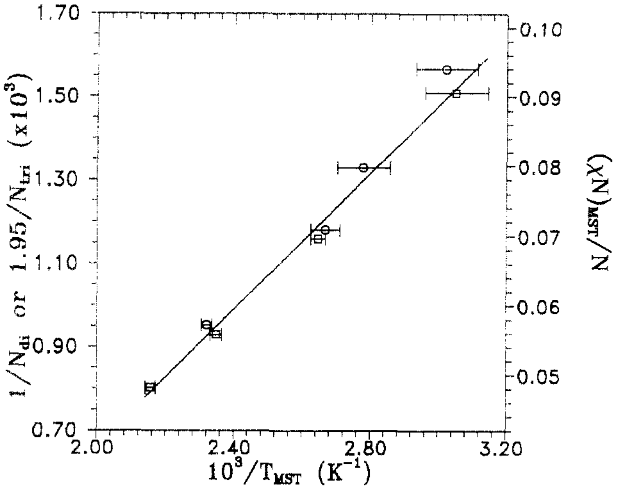

Figure 11. Comparison of diblock (□) and triblock (○) T_{MST} values. The left hand axis shows the reciprocal degree of polymerization N, with the factor of 1.95 coming from mean-field predictions for the spinodal $(\chi N)_{\mathrm{S}}$ for the two architectures with $f = 0.11$. On the right hand axis are given values of $(\chi N)_{\mathrm{MST}}/N$, where 60 and 117 are the values of $(\chi N)_{\mathrm{MST}}$ for the diblocks and triblocks, respectively. Error bars denote uncertainty in the location of T_{MST}. The line is a least-squares fit.

Previous work[6] on lamellar PEP–PEE diblock/triblock mixtures showed that an equally abrupt drop at the MST was observed at a fixed ω for either architecture, or for any mixture of the two, even though the τ values for the diblock and triblock differ substantially. In the case of materials with domain lattices, the destruction of the lattice at T_{MST} can also contribute to the drop in G' and G''. This contribution would likely be similar for the diblock and triblock structures, and if it dominates, equally sharp transitions would be seen for both cases. Morrison[27] has observed a more gradual modulus drop for triblocks than for diblocks in samples with a cylindrical morphology, which may represent an intermediate case.

C. Effect of Molecular Architecture on χ. Having established values of T_{MST} for both diblock and triblock copolymers, we proceed to evaluate whether these values are consistent with a single $\chi(T)$ function or whether molecular architecture exerts an effect on the apparent value of χ. In all theories not incorporating fluctuations, for a given architecture and composition f, the MST is predicted to occur at a fixed value of χN, which we denote $(\chi N)_{\mathrm{MST}}$. Intuitively, the symmetric ABA triblocks studied here should resemble AB diblocks of half the triblock degree of polymerization in their thermodynamics,[28] meaning that $(\chi N)_{\mathrm{MST,tri}}/(\chi N)_{\mathrm{MST,di}} \approx 2$. This approximation improves as the volume fraction of A becomes small, as is the case here. To obtain a more accurate value of this ratio, we calculated the spinodal values, $(\chi N)_{\mathrm{S}}$, for both architectures using the approach of Benoit and Hadziioannou;[13] the spinodal lies close to the MST, so the ratio of the spinodal and MST values for the two architectures should be quite similar. Using the known densities of styrene and isoprene homopolymers,[29,30] a block copolymer containing 13 wt % styrene should have a volume fraction of styrene $f \approx 0.11$ at the melt temperatures of interest; with this volume fraction, $(\chi N)_{\mathrm{S,tri}}/(\chi N)_{\mathrm{S,di}} = 1.95$, very close to the intuitive factor of 2. If $\chi(T)$ were independent of molecular architecture, diblocks with a chain length N_{di} and triblocks with a chain length $N_{\mathrm{tri}} = 1.95N_{\mathrm{di}}$ should thus have identical T_{MST} values.

Figure 11 tests this idea by plotting the reciprocal degree of polymerization (left hand axis) vs reciprocal T_{MST}. We

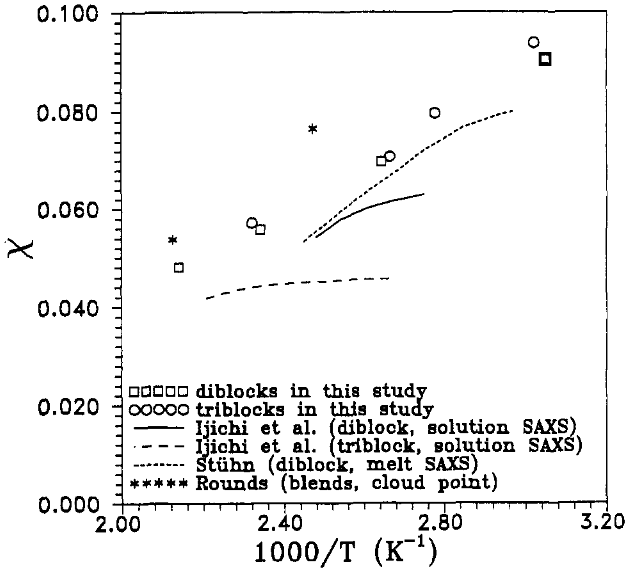

Figure 12. Comparison of χ values obtained from different sources.

have counted each styrene or isoprene unit as one mer in determining N to facilitate comparisons discussed below; note, however, that the choice of repeat unit has no effect on comparison of the two architectures, as the compositions of the diblock and triblock copolymers are identical. Points from diblocks and triblocks fall onto the same curve within experimental error, indicating that these two architectures have indistinguishable $\chi(T)$ functions. Note that the only quantity required for this comparison not directly obtained from experiment is the factor of 1.95, which is not strongly dependent on the theoretical treatment used.

Moreover, the data in Figure 11 appear to form a straight line, consistent with the commonly-used expression

$$\chi(T) = [(\chi N)_{\mathrm{MST}}]/N = A + B/T \qquad (1)$$

We would like to determine actual χ values from our data, to compare with other researchers' χ values, and to compare our $\chi(T)$ expression with that found for styrene/isoprene homopolymer blends. However, this requires a value for $(\chi N)_{\mathrm{MST}}$ in eq 1, and the range of $(\chi N)_{\mathrm{MST}}$ values predicted by various theories is substantial. For diblocks with $f = 0.11$, the Leibler theory predicts $(\chi N)_{\mathrm{MST}} = 60$; more recent self-consistent field theory calculations of Vavasour and Whitmore,[31] assuming no statistical segment length asymmetry, predict $(\chi N)_{\mathrm{MST}} = 43$ for the same case. For consistency, we will take the Leibler value of 60, since we have used the same weak-segregation limit treatment to obtain our value of $(\chi N)_{\mathrm{S,tri}}/(\chi N)_{\mathrm{S,di}}$. However, we take this difference in theoretical estimates of $(\chi N)_{\mathrm{MST}}$ to be a measure of numerical uncertainty in the absolute values of $\chi(T)$. With $(\chi N)_{\mathrm{MST,di}} = 60$, $\chi(T)$ is obtained directly by multiplying the left hand axis values in Figure 11 by 60; these values are given on the right hand axis. The least-squares fit to these data, appropriately weighted by the uncertainty in T_{MST}, is

$$\chi = -0.058 + 48.9/T \qquad (2)$$

Figure 12 compares our χ values with results from others for SI block copolymers and homopolymer blends, including those obtained from SAXS measurements above T_{MST} by Stühn[32] for an undiluted diblock ($f = 0.25$), from SAXS above T_{MST} by Ijichi *et al.*[19] for concentrated solutions (60–80% polymer) of both diblocks and triblocks ($f = 0.3$) in the "neutral" solvent dioctyl phthalate (DOP), and from cloud point measurements by Rounds[33] for undiluted homopolymer blends. Other results for χ obtained from SI block copolymers have been published.[34–38] However, Stühn's work[32] suggests a strong dependence of χ on f for SI block copolymers, so we have used only those for which f corresponds most closely to our polymers. The values from concentrated solutions were converted to those from the undiluted state by the Ijichi *et al.* pseudobinary approximation. All data in Figure 12 were generated with similar (high 1,4) isoprene microstructures, and all use the same definition for N (i.e., each styrene or isoprene unit counts as one mer). Our values and those of Rounds (indicated by symbols in Figure 12) employed different polymers to obtain each data point, while the other data sets (lines in Figure 12) were each obtained from measurements at different temperatures on a single block copolymer.

The magnitudes of χ among the various sets of block copolymer data in Figure 12 agree reasonably well, despite some differences in composition (13–30 wt % S), and all have qualitatively similar temperature dependencies. All the lines, indicating $\chi(T)$ was obtained from SAXS in the disordered state, show notable downward curvature, which is not seen in our data. The recent work of Balsara[39] suggests that such curvature is due to an inadequacy in the random phase approximation used in interpreting the scattering data. We consider the χ values obtained from Rounds' data on homopolymer blends to be in satisfactory agreement with our values. The blend components have low molecular weights (<5 kg/mol), which have been reported[37] to yield somewhat larger values of χ. We conclude that large-scale polymer architecture does not have a substantial effect on χ values for the styrene–isoprene system, whether derived from data on homopolymer blends or from diblocks and triblocks in the low to moderate range of f.

Despite the generally good agreement evident in Figure 12 between the various data sets, values of A and B obtained from fits to eq 2 can vary widely. Ijichi *et al.*[19] found $A = -0.042$ and $B = 38$ for their diblock, in reasonable agreement with our eq 2 but found $A = +0.033$ and $B = 5.0$ for their triblock, leading to the inference that architecture somehow exerts a substantial effect on χ. These differences are probably traceable to the long extrapolation of the data to $1/T = 0$ in the fit. Any uncertainties are accentuated by even subtle curvature in the data and are exacerbated by application of the pseudobinary approximation to diluted systems. Even a small degree of selectivity in the solvent, if temperature-dependent, could substantially affect the apparent temperature dependence of χ. For these reasons, simple comparisons of values of A and B in discussing $\chi(T)$ relations should be viewed with caution.

IV. Conclusions

Rheologically-determined MST temperatures for SI and SIS block copolymers were found to obey a single $\chi(T)$ relation, indicating that large-scale polymer architecture does not have a substantial effect on χ for the styrene–isoprene system. Using $(\chi N)_{\mathrm{MST}}$ predictions from mean-field theory, the T_{MST} temperatures were converted to χ values. These were in reasonable agreement with literature values obtained from small-angle X-ray scattering for block copolymers, and from cloud point measurements on blends of the homopolymers. The MST for the block copolymers was identified with a sudden change in the slope of G' vs T plots obtained at low frequency. The fairly abrupt change in slope observed for our materials, which possess a liquidlike packing of polystyrene spheres in a polyisoprene matrix, indicates that an ordered microdomain lattice is not required for the rheological signature of the MST to be exhibited. Plots of G' vs T near and above T_{MST} are very similar for the two block architectures when a frequency shift is invoked, corresponding to the shift in the terminal relaxation time τ in the disordered state between the two architectures. The observed shift factor observed is larger than predictions based on linear homopolymer behavior, $\tau \sim M^{3.4}$, possibly due to composition fluctuations which perturb the relaxation spectrum of the block copolymers just above the MST.

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