Viscoelastic Behavior of a Homogeneous Polystyrene-*block*-Polyisoprene-*block*-Polystyrene Copolymer

Chang Dae Han,* Deog Man Baek, and Jin Kon Kim

Department of Chemical Engineering, Polytechnic University, Brooklyn, New York 11201

Takeji Hashimoto* and Shigeru Okamoto

Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

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ABSTRACT: A polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) copolymer having block molecular weights of 3900S–93300I–3900S was synthesized via anionic polymerization, and its linear dynamic viscoelastic properties (dynamic storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, as functions of angular frequency ω) were measured at various temperatures, using a cone-and-plate rheometer. Plots of log G' versus log G'' were found to be independent of temperature in the range from 50 to 150 °C, leading us to conclude that the block copolymer had *no* microdomain structure at $T \geq 50$ °C. Independent study by small-angle X-ray scattering confirmed that the SIS block copolymer indeed had *no* microdomain structure (i.e., homogeneous) at $T \geq 30$ °C.

1. Introduction

It is a well-established fact today that the formation of a microdomain structure of polystyrene in a polydiene-based block copolymer depends, among other factors, upon the molecular weight of the polystyrene block, total molecular weight, and thermodynamic compatibility between the constituent blocks. By applying the "confined chain" theory to a polystyrene-*block*-polyisoprene (SI) copolymer, Meier[1] concluded that a microdomain structure may be formed when the molecular weight of the polystyrene block becomes about 5000 or larger. On the other hand, due to very good thermodynamic compatibility between polystyrene (PS) and poly(α-methylstyrene) (PαMS), it has been reported in the literature[2,3] that *no* microdomain structure will form in PS-*b*-PαMS, PS-*b*-PαMS-*b*-PS, or PαMS-*b*-PS-*b*-PαMS copolymer even when the molecular weights of the constituent blocks become as large as about 2×10^5. It is also well established that the specific morphology of microdomains (spheres, cylinders, or lamellae) that may be formed in a polydiene-based block copolymer depends on the weight (or volume) fraction of polystyrene, f, in the block copolymer. Using transmission electron microscopy, several research groups[4–7] observed that polydiene-based block copolymers have spherical microdomains for values of f less than about 0.25, cylindrical microdomains for values of f between about 0.25 and 0.4, and lamellar microdomains for values of f between 0.4 and 0.5. These experimental findings have been found to be in reasonable agreement with theoretical predictions.[1,8,9]

In the past, a number of research groups[10–19] have reported experimental studies on the rheological behavior of microphase-separated polystyrene-based block copolymers in the flow regime. But no rheological measurements of homogeneous polydiene-based block copolymers have been reported, except in 1975 when Hansen and Shen[3] reported measurements of stress relaxation in extension for *homogeneous* PS–PαMS–PS and PαMS–PS–PαMS block copolymers.

Very recently we synthesized, via anionic polymerization, a polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) copolymer having block molecular weights of 3900S–93300I–3900S and then measured its dynamic viscoelastic properties at temperatures from 50 to 150 °C. In this paper we shall present experimental results showing that this block copolymer is homogeneous at temperatures above room temperature, as determined by dynamic viscoelastic measurement and small-angle X-ray scattering, respectively.

2. Experimental Section

Materials. A polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) copolymer, which has block molecular weights of 3900S–93300I–3900S, hereafter referred to as SIS-D, was synthesized via anionic polymerization. In the polymerization, *sec*-butyllithium was used as initiator to first polymerize styrene monomer anionically, and then this "living" polystyrene was used to initiate isoprene monomer to form a living polystyrene-*block*-polyisoprene (SI) copolymer. The latter was reacted with the stoichiometric amount of 1,2-dibromoethane to couple the SI diblock copolymers into linear SIS triblock copolymers.

The gel permeation chromatograms of this block copolymer indicated that there were some uncoupled diblocks, which was estimated to be about 20 wt %, and a very small amount of dead homopolymer polystyrene, which was determined to be less than 1 wt %. Nuclear magnetic resonance (NMR) spectroscopic analysis indicated that the polyisoprene consisted of about 6 wt % of 3,4-polyisoprene, about 94 wt % of 1,4-polyisoprene, and no detectable amount of 1,2-polyisoprene in the SIS block copolymer.

Homopolymer polystyrene having a molecular weight of 1000 (PS1000) was synthesized via anionic polymerization, and this was mixed with the SIS-D to prepare binary mixtures, using solvent casting. These mixtures were later used to measure dynamic viscoelastic properties.

Sample Preparation. Samples for viscoelastic measurements were prepared by first dissolving a predetermined amount of block copolymer in toluene (10 wt % of solid in solution) in the presence of an antioxidant (Irganox 1010, Ciba-Geigy Group) and then slowly evaporating the toluene. The evaporation of toluene was carried out initially in open air at room temperature for 1 week and then in a vacuum oven at 40 °C for 3 days. The last trace of solvent was removed by drying the samples in a vacuum oven at elevated temperature by gradually raising the oven temperature up to 110 °C. The drying of the samples was continued, until there was no further change in weight. Finally, the samples were annealed at 130 °C for 10 h.

Measurement of Dynamic Viscoelastic Properties. A Model R16 Weissenberg rheogoniometer (Sangamo Control Inc.) in the cone-and-plate mode (25-mm-diameter plate and 4° cone angle with a 160-μm gap) was used to measure the dynamic storage

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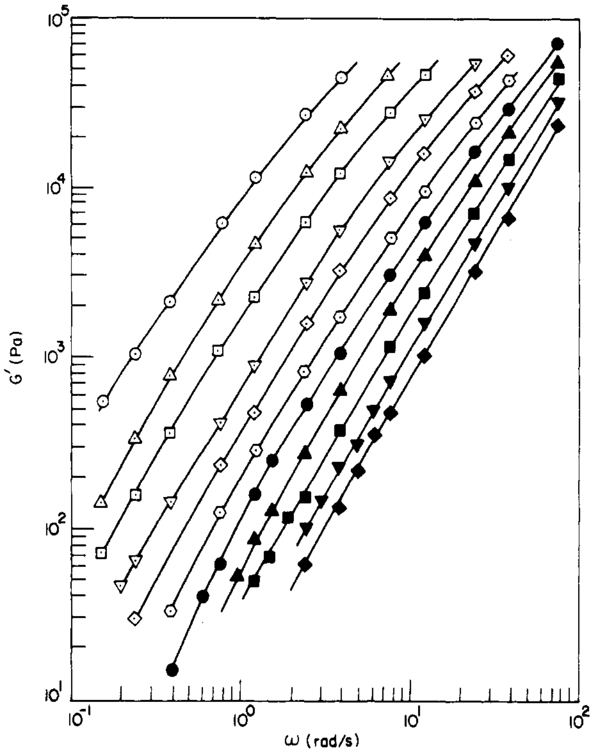

Figure 1. Plots of log G' versus log ω for SIS-D at various temperatures (°C): (⊙) 50; (△) 60; (⊡) 70; (▽) 80; (◇) 90; (⊙) 100; (●) 110; (▲) 120; (■) 130; (▼) 140; (◆) 150.

and loss moduli, $G'(\omega)$ and $G''(\omega)$, as functions of frequency (ω) at various temperatures, for the SIS-D triblock copolymer and mixtures of SIS-D and polystyrene homopolymer. Data acquisition was accomplished with the aid of a microcomputer interfaced with the rheometer. The temperature control was satisfactory within ±1 °C. In the rheological measurements a fixed strain was used at a given temperature. Specifically, the strain was varied from 0.03 to 0.3% depending on temperature, so that measurements were taken well within the linear viscoelastic range for the block copolymer investigated. All experiments were conducted with a nitrogen blanket in order to avoid oxidative degradation of the samples.

Small-Angle X-ray Scattering. Small-angle X-ray scattering (SAXS) experiments were conducted with an apparatus, described in detail elsewhere,[20] that consists of a 12-kW rotating-anode X-ray generator, a graphite crystal for incident-beam monochromatization, a 1.5-m camera, and a one-dimensional, position-sensitive, proportional counter. A Cu Kα line (λ = 0.154 nm) was used. The SAXS profiles were corrected for absorption, air scattering, background scattering arising from thermal diffuse scattering, and slit-height and slit-width smearings.[21] The absolute SAXS intensity was obtained by using the nickel-foil method.[22]

The SAXS profiles were measured in situ as a function of temperature using the temperature enclosure as described elsewhere.[23] Samples annealed at 130 °C for 10 h were used as starting specimens. The SAXS profile at each temperature was obtained for a 3-h exposure to the incident X-ray beam on the sample preheated at the same temperature for 0.5 h in order to ensure thermal equilibration.

3. Results and Discussion

Linear Dynamic Viscoelastic Properties. Figure 1 gives plots of log G' versus log ω, and Figure 2 gives plots of log G'' versus log ω, for the SIS-D triblock copolymer at 11 different temperatures ranging from 50 to 150 °C. It can be seen in these figures that at a given angular frequency ω, both G' and G'' decrease with increasing temperature. However, plots of log G' versus log G'' given in Figure 3, which were obtained by cross-plotting Figures 1 and 2, show a correlation that becomes virtually independent of temperature. Earlier Han and coworkers[17-19] reported that plots of log G' versus log G'' for block copolymers having microdomain structure exhibit temperature dependency and suggested that such plots be used to determine the temperature at which the order–disorder transition (also referred to as the microphase-separation transition) takes place in a given block copolymer. According to this criterion, it can be concluded from Figure 3 that SIS-D is *homogeneous* in the temperature range from 50 to 150 °C.

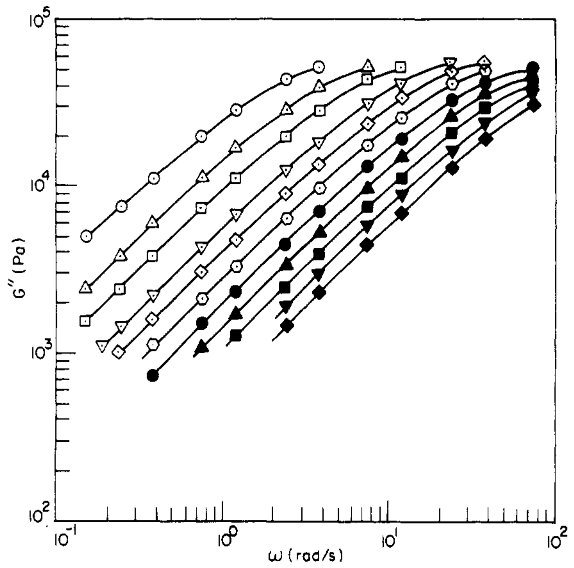

Figure 2. Plots of log G'' versus log ω for SIS-D at various temperatures. Symbols are the same as in Figure 1.

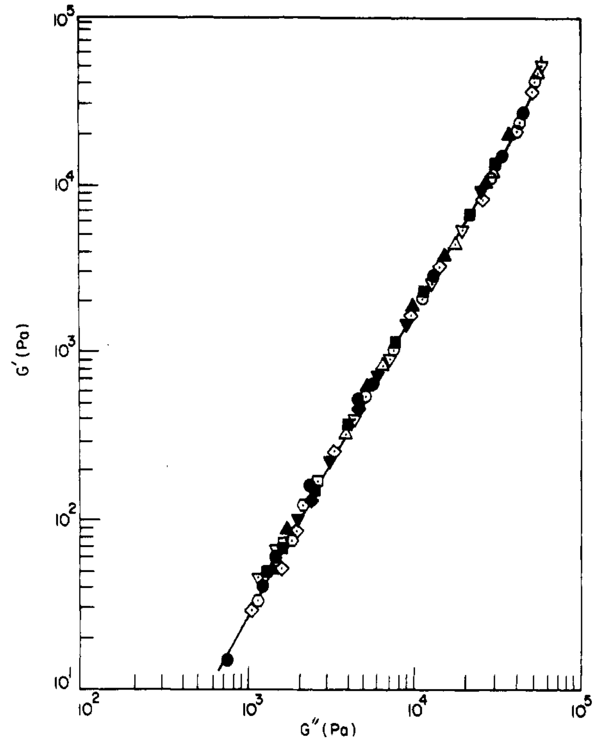

Figure 3. Plots of log G' versus log G'' for SIS-D at various temperatures. Symbols are the same as in Figure 1.

Figure 4 gives plots of log η' versus log ω for SIS-D at 11 different temperatures ranging from 50 to 150 °C. Note that the values of $\eta'(\omega)$ in Figure 4 were determined by using the relationship, $\eta'(\omega) = G''(\omega)/\omega$. It can be seen in Figure 4 that, in the temperature range tested, SIS-D

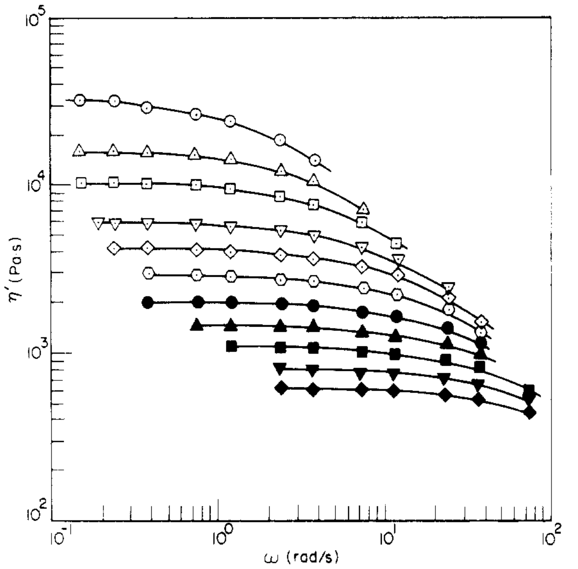

Figure 4. Plots of log η' versus log ω for SIS-D at various temperatures. Symbols are the same as in Figure 1.

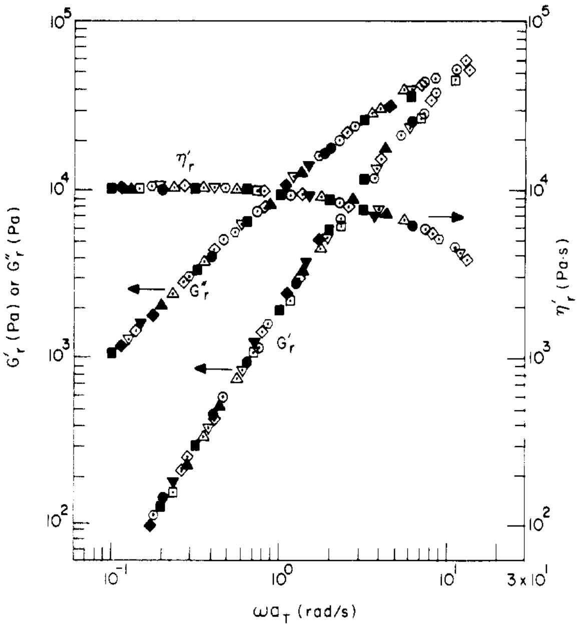

Figure 5. Plots of reduced dynamic moduli, G'_r and G''_r, and reduced dynamic viscosity, η'_r, versus ωa_T for SIS-D, in which a_T is a shift factor and the reference temperature used is 70 °C. Symbols are the same as in Figure 1.

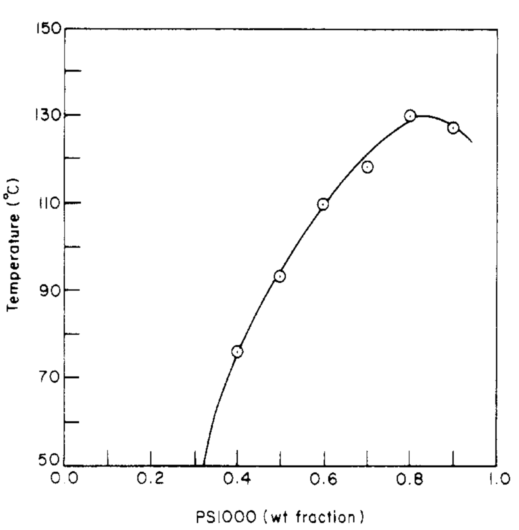

Figure 6. Phase diagram for mixtures of SIS-D and a monodisperse polystyrene having a molecular weight of 1000.

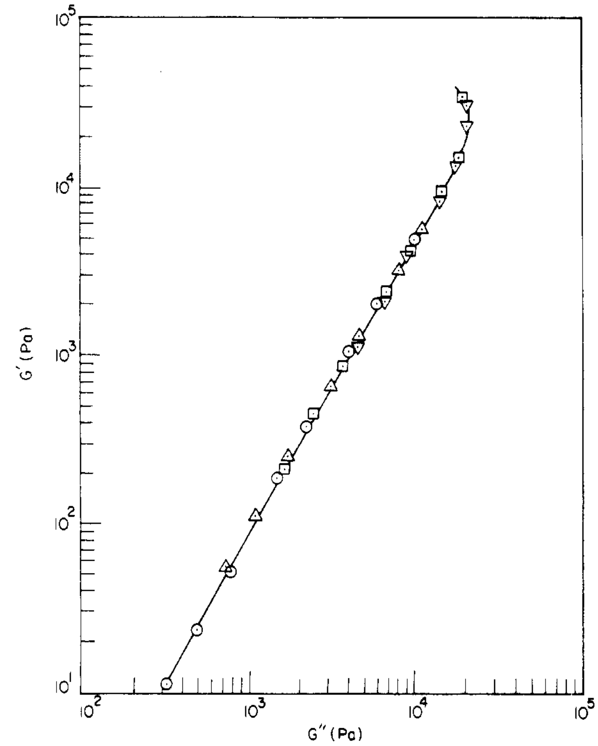

Figure 7. Plots of log G' versus log G'' for the 70/30 SIS-D–PS1000 mixture at various temperatures (°C): (▽) 40; (⊡) 50; (△) 60; (⊙) 70.

exhibits Newtonian behavior at small values of ω. In previous papers[17-19] it was shown that block copolymers having microdomain structure do not exhibit Newtonian behavior. Thus, Figure 4 may be regarded as another manifestation that SIS-D has no microdomains at $T \geq 50$ °C.

In dealing with flexible homopolymers, frequency–temperature superposition has been extensively used to obtain temperature-independent master curves by shifting values of dynamic moduli, G' and G'', along the frequency ω axis.[24] In such an attempt, one chooses a particular temperature as a reference temperature and shifts the values of G' and G'' obtained at all other temperatures to the corresponding values at the reference temperature. Figure 5 gives plots of reduced dynamic moduli, G'_r and G''_r, and reduced dynamic viscosity η'_r, versus ωa_T for the SIS-D, which were prepared with the data given in Figures 1, 2, and 4. Note in Figure 5 that G'_r, G''_r, and η'_r are defined by $G'T_0\rho_0/T\rho$, $G''T_0\rho_0/T\rho$, and $\eta'T_0\rho_0/a_TT\rho$, respectively, where T_0 is the reference temperature, ρ_0 and ρ are the densities at temperatures T_0 and T, respectively, and a_T is a shift factor, which was obtained with 70 °C as the reference temperature. It can be seen in Figure 5 that temperature–frequency superposition gives rise to temperature-independent correlations for the SIS-D, supporting the claim made above in reference to Figure 3 that the block copolymer, SIS-D, is *homogeneous* in the temperature range from 50 to 150 °C.

Figure 6 gives a phase diagram for binary mixtures of SIS-D and a homopolymer polystyrene having a molecular weight of 1000 (PS1000), which was synthesized via anionic polymerization in our laboratory. The phase diagram given in Figure 6 was constructed with turbidity measurements, using light scattering. It can be seen in Figure 6 that the SIS-D–PS1000 mixtures containing less than 30 wt % PS1000 form a single phase at temperatures above 50 °C.

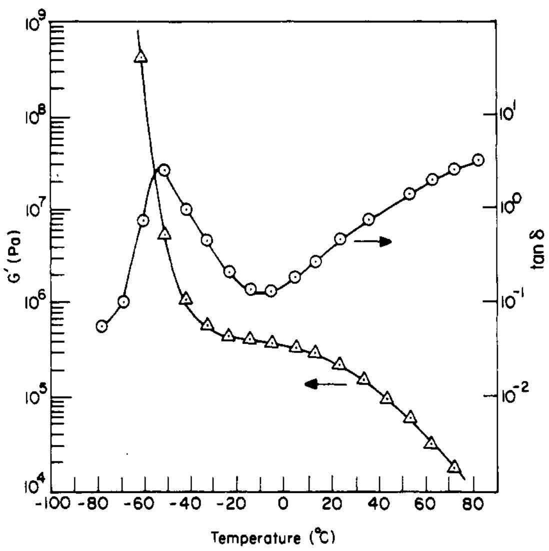

Figure 8. Plots of log G' versus temperature, and tan δ versus temperature, for SIS-D at ω = 10 rad/s.

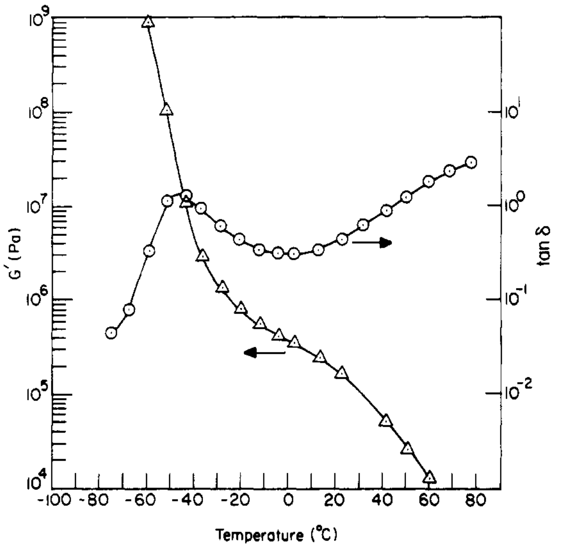

Figure 9. Plots of log G' versus temperature, and tan δ versus temperature, for the 70/30 SIS-D–PS1000 mixture at ω = 10 rad/s.

Figure 7 gives plots of log G' versus log G'' at 40, 50, 60, and 70 °C for a mixture consisting of 70 wt % SIS-D and 30 wt % PS1000 (hereafter referred to as 70/30 SIS-D–PS1000). On the basis of the observation that Figure 7 shows temperature independency, it can be concluded that the 70/30 SIS-D–PS1000 mixture is in the *homogeneous* state at the temperatures investigated, which is consistent with the phase diagram in Figure 6.

Plateau Modulus of SIS-D Block Copolymer. The results of the temperature sweep of the storage modulus (G') and the loss tangent (tan δ) at a fixed angular frequency of 10 rad/s are given in Figure 8 for SIS-D and in Figure 9 for the 70/30 SIS-D–PS1000 mixture. Since a clear plateau region in Figures 8 and 9, respectively, is not observed, we have used the procedure suggested by Kraus and Rollmann[25] that the plateau modulus G°_{N} be approximated by the G' value at the minimum value of tan δ; i.e., $G^{\circ}_{N} \approx G'(\tan \delta_{\min})$. We obtain from Figures 8 and 9 that $G^{\circ}_{N} = 3.6 \times 10^5$ Pa for both SIS-D and the 70/30 SIS-D–PS1000 mixture. It is of great interest to observe that the addition of PS1000 by 30 wt % to the block copolymer SIS-D did not change its plateau modulus.

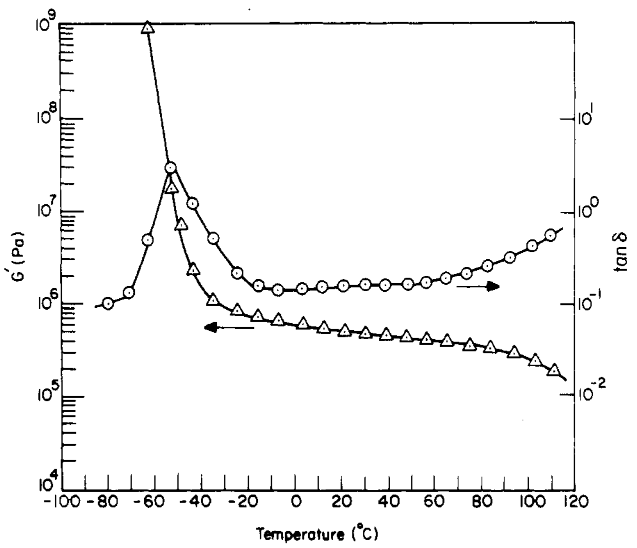

Figure 10. Plots of log G' versus temperature, and tan δ versus temperature, for Kraton 1107 at ω = 10 rad/s.

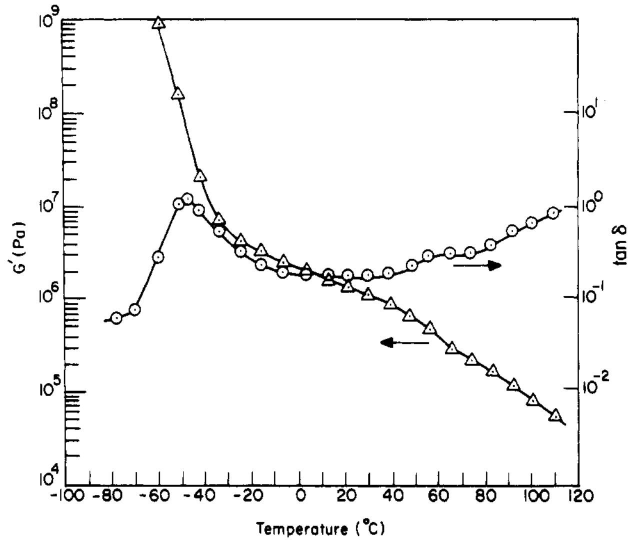

Figure 11. Plots of log G' versus temperature, and tan δ versus temperature, for the 70/30 Kraton 1107–PS1000 mixture at ω = 10 rad/s.

The results of the temperature sweep of G' and tan δ at a fixed angular frequency of 10 rad/s are given in Figure 10 for a commercial SIS triblock copolymer (Kraton 1107, Shell Development Co.) and in Figure 11 for a 70/30 Kraton 1107–PS1000 mixture. Note that Kraton 1107 has block molecular weights 10000S–120000I–10000S and spherical microdomains.[18] We observe from Figure 10 that $G^{\circ}_{N} = 6.7 \times 10^5$ Pa for Kraton 1107 and from Figure 11 that $G^{\circ}_{N} = 1.4 \times 10^6$ Pa for the 70/30 Kraton 1107–PS1000 mixture. In other words, the addition of PS1000 by 30 wt % to Kraton 1107 doubled the plateau modulus of Kraton 1107. In a previous paper,[26] Han et al. showed that when the molecular weight of an added end-block-associating resin was sufficiently low, the resin associated with the polystyrene microdomains of Kraton 1107, increasing the plateau modulus of Kraton 1107. Recognizing the fact that the molecular weight of added PS1000 is about one-tenth of the molecular weight of the polystyrene block in the Kraton 1107, we speculate that most of the added PS1000 in the 70/30 Kraton 1107–PS1000 mixture has associated with (or solubilized in) the polystyrene microdomains of the Kraton 1107 and increased its domain size,[27,28] thus contributing to an increase in the plateau modulus of the Kraton 1107. Along this line of

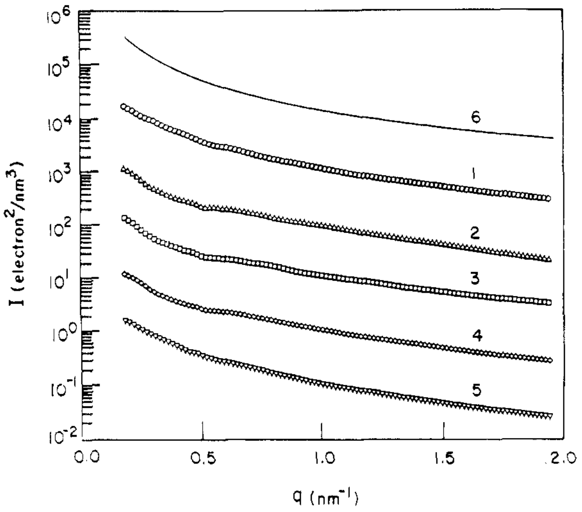

Figure 12. Plots of the logarithm of SAXS intensity I versus q for SIS-D obtained at various temperatures: curve 1 obtained at 30 °C; curve 2 obtained at 40 °C; curve 3 obtained at 50 °C; curve 4 obtained at 60 °C; and curve 5 obtained at 30 °C after a series of measurements at various temperatures. Curves (i + 1), where i runs from 1 to 4, were shifted downward by 1 decade, relative to the curve numbered i, in order to avoid overlaps, in which curve 1 was not shifted. Curve 6 represents the q^{-2} dependency of the intensity I in an arbitrary unit.

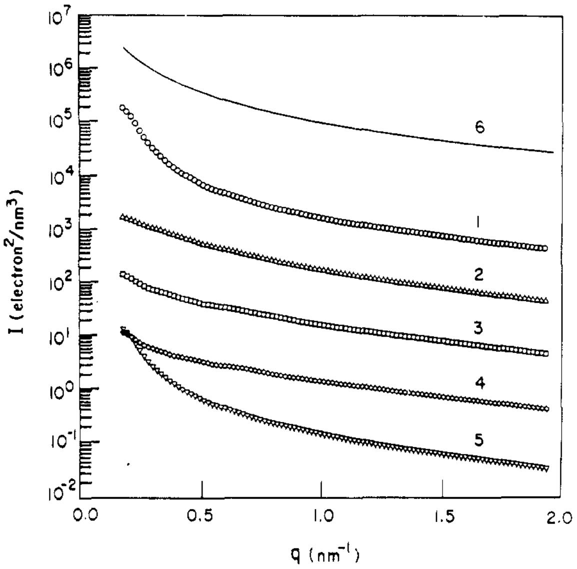

Figure 13. Plots of the logarithm of SAXS intensity I versus q for the 70/30 SIS-D–PS1000 mixture at various temperatures: curve 1 obtained at 30 °C; curve 2 obtained at 60 °C; curve 3 obtained at 90 °C; curve 4 obtained at 120 °C; and curve 5 obtained at 30 °C after a series of measurements at various temperatures. The curves 2–5 were shifted in the same way as in Figure 12, and curve 6 represents the q^{-2} dependency of the intensity I in an arbitrary unit.

thought, we would expect an increase in the plateau modulus of SIS-D when PS1000 was added by 30 wt % to SIS-D, if it had microdomains. The fact that no increase in the plateau modulus was observed in the 70/30 SIS-D–PS1000 mixture leads us to conclude, once again, that SIS-D has *no* microdomains (i.e., homogeneous).

Small-Angle X-ray Scattering of the Block Copolymer SIS-D and Its Mixture with a Homopolymer. Plots of scattering intensity I versus the magnitude of the wave vector, q, at various temperatures are given in Figure 12 for SIS-D and in Figure 13 for the 70/30 SIS-D–PS1000 mixture. Note that no scattering peak is observed in these figures, although there should be one in pure block copolymers in the disordered state.[29] This may be due to the fact that SIS-D is a mixture consisting of SIS triblock copolymer, SI diblock copolymer, and homopolymer polystyrene as described in section 2 (Materials), having a high polydispersity.[30–35] However, if SIS-D is in the single-phase state and homogeneous (i.e., in the disordered state[29]), the scattered intensity $I(q)$ for SIS-D can be represented by

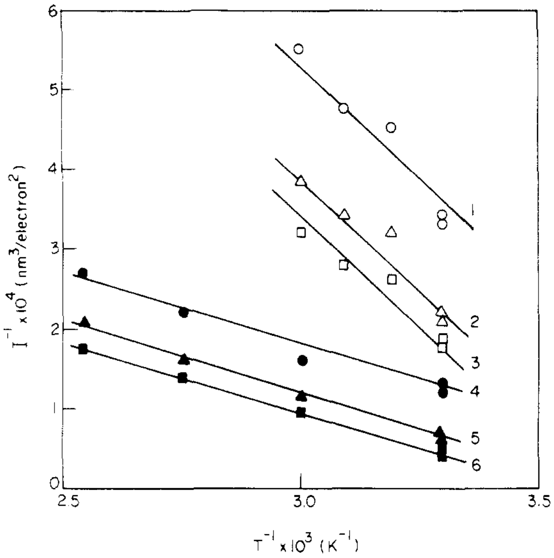

Figure 14. Plots of the reciprocal of the SAXS intensity I^{-1} versus the reciprocal of the absolute temperature T^{-1} for SIS-D (curves 1–3) and for the 70/30 SIS-D–PS1000 mixture (curves 4–6) at different values of q: q = 0.495 nm^{-1} for curves 1 and 4; q = 0.39 nm^{-1} for curves 2 and 5; q = 0.35 nm^{-1} for curves 3 and 6.

$$I(q)^{-1} \sim [F(q) - 2\chi] \qquad (1)$$

where q is the magnitude of the scattering vector, $q = (4\pi/\lambda) \sin(\theta/2)$, in which λ and θ are the wavelength and the scattering angle in the medium, respectively, χ is the Flory interaction parameter per segment base between polystyrene and polyisoprene, and $F(q)$ depends on the Fourier transform of the density–density correlation functions between two segments (e.g., styrene and styrene, styrene and isoprene, and isoprene and isoprene). Equation 1 with an appropriately modified expression for $F(q)$ applies also for the 70/30 SIS-D–PS1000 mixture if it is homogeneous. If the two systems, SIS-D and the SIS-D–PS1000 mixture, are homogeneous, then the scattered intensity, $I(q)$, at given values of q should decrease with increasing temperature (T) as χ decreases with increasing T, following the relationship[36–38]

$$\chi = A + B/T \qquad (2)$$

where A and B are constants. If this is the case, $I(q)^{-1}$ should linearly decrease with increasing T^{-1}; i.e.

$$I(q)^{-1} \sim \{[F(q) - 2A] - 2B/T\} \qquad (3)$$

Figure 14 gives plots of the reciprocal of the scattering intensity (I^{-1}) versus the reciprocal of the absolute temperature (T^{-1}) for SIS-D and the 70/30 SIS-D–PS1000 mixture. The results support eq 3 with positive values of B. Thus, it can be concluded from Figure 14 that both SIS-D and the 70/30 SIS-D–PS1000 mixture are *homogeneous* at $T \geq 30$ °C, supporting the same conclusion drawn above from the dynamic viscoelastic measurements.

It is worth mentioning the following two features of the scattering given in Figures 12–14 for the homogeneous block copolymer SIS-D and its mixture with homopolymer PS1000. (1) It can be seen in Figures 12 and 13 that, for large values of q, the dependence of $I(q)$ on q (curves 1-5) may be described by q^{-2} as represented by curve 6. This is typical of the scattering due to the thermal concentration fluctuations in the homogeneous melts at $q > 1/R_g \approx 0.1$ nm^{-1}, in which R_g is the radius of gyration of the block copolymer. (2) It can be seen in Figure 14 that, at a given temperature, the scattering intensity, $I(q)$, for the SIS-D–PS1000 mixture is higher than that for the pure block copolymer SIS-D. This indicates that the addition of a homopolymer enhances the thermal concentration fluctuations of a block copolymer in the homogeneous state. Notice in Figure 14 that the slopes of the straight lines are constant, independent of q, for both SIS-D and the SIS-D–PS1000 mixture and that the slope for SIS-D is greater than that for the SIS-D–PS1000 mixture, suggesting that, according to eq 3, the value of B for SIS-D is larger than that for the SIS-D–PS1000 mixture. This implies that the value of the effective χ for a block copolymer/homopolymer mixture is different from the value of χ for a block copolymer itself, consistent with the earlier findings.[39,40]

4. Concluding Remarks

In this study we have shown that the triblock copolymer SIS-D having the block molecular weights 3900S–93300I–3900S is *homogeneous* above room temperature, as determined by plots of log G' versus log G''. The homogeneity of this block copolymer was evidenced further by observing that the plateau modulus of the block copolymer remained the same when a homopolymer polystyrene having the molecular weight of 1000 was added by 30 wt %. This was contrasted with the situation where the plateau modulus of a microphase-separated SIS triblock copolymer having block molecular weights 10000S–120000I–10000S was almost doubled when the same homopolymer polystyrene was added by 30 wt %. Independent measurements by small-angle X-ray scattering confirmed the conclusion drawn from the rheological measurements, that the block copolymer SIS-D is indeed *homogeneous*.

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