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Effect of Microdomain Structure on the Order–Disorder Transition Temperature of Polystyrene-*block*-Polyisoprene-*block*-Polystyrene Copolymers

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

Department of Chemical Engineering and Polymer Research Institute, Polytechnic University, Brooklyn, New York 11201.

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ABSTRACT: The effect of microdomain structure on the order–disorder transition temperature (T_r) of polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) copolymers was investigated. For the study, we synthesized, via anionic polymerization, three SIS block copolymers with lamellar, cylindrical, and spherical microdomain structures. The SIS block copolymers were determined to have the following segment molecular weights: (a) 7400S-99000I-7400S for sample A, (b) 5850S-27300I-5850S for sample B, and (c) 7300S-13400I-7300S for sample C. Transmission electron microscopy has identified that sample A has a *spherical* microdomain structure, sample B has a *cylindrical* microdomain structure, and sample C has a *lamellar* microdomain structure. Using logarithmic plots of the storage modulus G' versus the loss modulus G'', obtained by dynamic viscoelastic measurements with a Model R16 Weissenberg rheogoniometer, we found that sample A has a T_r of 180 °C, sample B has a T_r of 90 °C, and sample C has a T_r of 105 °C. The T_r of sample A was also determined by small-angle X-ray scattering by Professor T. Hashimoto at Kyoto University and was found to be about 180 °C, which is in remarkably good agreement with that determined by the log G' versus log G'' plots. Also, we found that the plot of log G' versus temperature at an angular frequency of 0.15 rad/s shows an abrupt decrease in G' at about 105 °C for sample C, but *no* such trend was observed for samples A and B. This observation was confirmed by independent measurements with a Rheometrics dynamic spectrometer, i.e., by temperature scans of storage modulus G' at angular frequencies of 0.15 and 0.05 rad/s. This had led us to conclude that temperature scans of G' do not allow us to determine the T_r of samples A and B, whereas log G' versus log G'' plots do. Finally, the values of T_r determined from log G' versus log G'' plots for each of the SIS block copolymers are compared with theoretical predictions by the currently held theories of Helfand–Wasserman and Leibler. It is found that the accuracy of the theoretical predictions of T_r depends very much on the accuracy of the temperature dependency of the interaction parameter χ for a given polymer pair.

1. Introduction

In the past, a number of research groups have investigated, both theoretically and experimentally, the order–disorder transition (also referred to as the microphase-separation transition) behavior of block copolymers. The order–disorder transition temperature (T_r) of a block copolymer is defined by the temperature at which the microdomain structure in a block copolymer disappears completely as the temperature is raised or by the threshold temperature at which the microdomain structure begins to appear when the temperature of a block copolymer in the homogeneous state is lowered.

Theoretically, there are two approaches, thus far developed, that lead to predictions of the T_r of a block copolymer. Helfand and Wasserman[1-3] have formulated a statistical thermodynamic theory to predict the free-energy density and domain size of diblock or triblock copolymer systems. Using this theory, one can predict the T_r of a block copolymer from the temperature at which the difference in free-energy density of the block copolymer between the state with a microdomain structure and the state with a homogeneous phase becomes zero. Leibler[4] has also developed a statistical thermodynamic theory that allows one to determine the spinodal decomposition temperature (T_s) for microphase separation, as well as the T_r, of diblock copolymers and has shown that the microdomain structure (lamellar, cylindrical, or spherical) of the ordered phase influences the value of T_r. It should be mentioned that Helfand–Wasserman's theory is only valid for a strong segregation limit, i.e., for the formation and dissolution of a fully developed domain system, whereas Leibler's theory is valid for a weak segregation limit, i.e., at the onset conditions of domain formation or for the final step of the domain dissolution. Very recently, by including composition fluctuations, which were neglected in Leibler's analysis, Fredrickson and Helfand[5] have improved Leibler's analysis to predict the T_r of diblock copolymers with finite molecular weight. Note that Leibler's analysis is based on a mean-field theory that is rigorous for infinitely large molecular weight.

Leibler[4] suggested that the scattering of electromagnetic radiation be used to investigate the microphase-separation transition of block copolymers. Leibler's theory seems to have encouraged some investigators[6-10] to use small-angle X-ray scattering and others[11] to use small-angle neutron scattering to investigate the order–disorder transition behavior of block copolymers.

Rheological techniques have also been used to study the order–disorder transition behavior of block copolymers. Some investigators[12] regarded the temperature at which Newtonian viscosity is first observed, when the temperature of a block copolymer with microdomain structure is increased, as the T_r of the block copolymer, and others[13-16] regarded the temperature at which the dynamic storage modulus $G'(\omega)$ drops abruptly, when the temperature of a block copolymer is increased, as the T_r of the block copolymer. Very recently, Han and co-workers[17,18] have proposed the use of logarithmic plots of the dynamic storage modulus $G'(\omega)$ versus the dynamic loss modulus $G''(\omega)$ to determine the T_r of block copolymers; specifically, the T_r of a block copolymer can be determined by the temperature at which log G' versus log G'' plots cease to vary with temperature as the temperature of the block copolymer is increased.

It is a well-established fact that in polystyrene-*block*-polybutadiene (SB), polystyrene-*block*-polyisoprene (SI),

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Table I
Summary of Segment Molecular Weights of the SIS Block Copolymers Investigated

sample	segment molec wt × 10^{-3}	polystyrene, wt %	total molec wt × 10^{-4}
A	7.40S-99.0I-7.40S	13	11.4
B	5.85S-27.3I-5.85S	30	3.9
C	7.30S-13.4I-7.30S	52	2.8

polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS), or polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) copolymers, the morphology (lamellae, cylinders, or spheres) of the microdomain structure depends on the weight fraction (or volume fraction) of the polystyrene phase, f. Specifically, it has been observed[19-22] by transmission electron microscopy that block copolymers have *spherical* microdomain structures for values of f less than about 0.25, *cylindrical* microdomain structures for values of f between about 0.25 and 0.4, and *lamellar* microdomain structures for values of f between 0.4 and 0.5. Such experimental observations are in good agreement with theoretical predictions.[23,24]

As part of a continuing effort to enhance our understanding of the order–disorder transition behavior of block copolymers, very recently we have synthesized three SIS block copolymers, via anionic polymerization, with spherical, cylindrical, and lamellar microdomain structures and determined the T_r's of these block copolymers, using logarithmic plots of the storage modulus G' versus the loss modulus G''. An attempt was also made to determine the T_r's of these block copolymers, using plots of log G' versus temperature that were prepared with experimental data obtained under isothermal conditions at various angular frequencies with a Model R16 Weissenberg rheogoniometer. Also, using a Rheometrics dynamic spectrometer, data on temperature scans of the storage modulus at a fixed angular frequency were obtained. In this paper we will first report on the experimental results for the T_r's of the block copolymers investigated and then compare them with theoretical predictions on the basis of the currently held theories of Helfand–Wasserman[1-3] and Leibler.[4]

2. Experimental Section

Materials. Three polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) copolymers having different block length ratios were synthesized via anionic polymerization. Table I gives a summary of the segment molecular weights of each of the block copolymers synthesized. In the polymerization, *sec*-butyllithium was used as the initiator to first polymerize styrene monomer anionically and then to copolymerize isoprene monomer with this "living" polystyrene to form polystyrene-*block*-polyisoprene (SI) copolymer. The latter was then reacted with a stoichiometric amount of 1,2-dibromoethane to couple the SI diblock copolymers into linear SIS triblock copolymers.

The segment molecular weights of the block copolymers synthesized were determined by measuring the molecular weight of polystyrene precursor by using gel permeation chromatography (GPC) and the weight fraction of polystyrene block by using nuclear magnetic resonance (NMR) spectroscopy. NMR spectroscopic analysis indicated that the polyisoprene consisted of about 6 wt % 3,4-polyisoprene, about 94 wt % 1,4-polyisoprene, and no detectable amount of 1,2-polyisoprene in the SIS block copolymers.

Sample Preparation. Samples for viscoelastic measurements were prepared by first dissolving a predetermined amount of block copolymer into toluene in the presence of an antioxidant (IRGANOX 1010, Ciba-Geigy Group) and then slowly evaporating the solvent. The evaporation of toluene was carried out initially in open air at room temperature for a week and then in a vacuum oven at 40 °C for 3 days. The last trace of toluene 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.

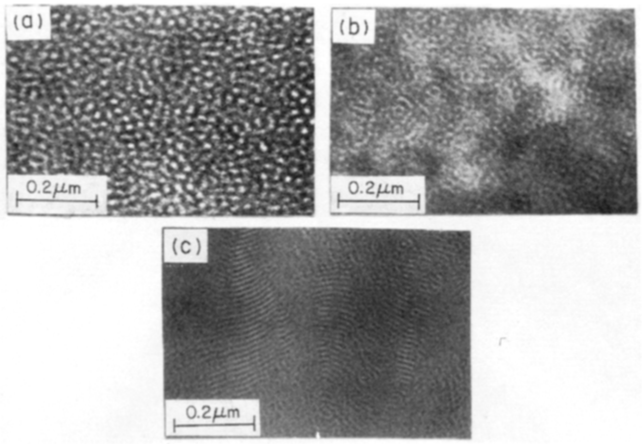

Figure 1. TEM photomicrographs of (a) sample A, (b) sample B, and (c) sample C.

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 and loss moduli, $G'(\omega)$ and $G''(\omega)$, as functions of angular frequency (ω) at various temperatures, for each of the block copolymer samples. The ranges of temperatures investigated varied from sample to sample, depending upon the particular value of the T_r for each sample. Data acquisition was accomplished with the aid of a microcomputer interfaced with the rheometer. The temperature control was satisfactory to within ±1 °C. In the oscillatory measurements a fixed strain of 0.003, which was well within the linear viscoelastic range of the materials investigated, was used. All experiments were conducted in the presence of nitrogen in order to preclude oxidative degradation of the samples.

The measurements taken by the procedures described above also allowed us to investigate how the values of G' vary with temperature at various angular frequencies. In order to take oscillatory measurements at angular frequencies lower than 0.15 rad/s, a Rheometrics dynamic spectrometer (RDS-7700) in the parallel-plate mode (50-mm plates with a 2-mm gap) was used. Temperature scans were made for each of the three block copolymer samples at fixed values of $\omega = 0.05$ and 0.15 rad/s, and the values of G' were recorded as a function of temperature. The value of $\omega = 0.15$ rad/s was chosen in order to check the results obtained with the Weissenberg rheogoniometer, and the value of $\omega = 0.05$ rad/s was chosen to investigate whether or not the temperature scans of G' obtained at this angular frequency might be different from those obtained at $\omega = 0.15$ rad/s. In the use of the Rheometrics dynamic spectrometer, the value of strain, 0.005, was used. It was determined that these values of strain were well within the linear viscoelastic range of the materials investigated.

3. Experimental Results

Microdomain Structure of the Block Copolymer Samples. Figure 1 gives transmission electron microscopy (TEM) photomicrographs for the three SIS block copolymer samples investigated. Note that the light areas represent the polystyrene microdomains, while the dark areas represent the polyisoprene phase stained with osmium tetroxide. It can be seen in Figure 1 that sample A has spherical microdomain structures, sample B has cylindrical microdomain structures, and sample C has lamellar microdomain structures. We believe that imperfect lamellar microdomain structures observed in Figure 1c are due to the rate at which the solvent evaporated

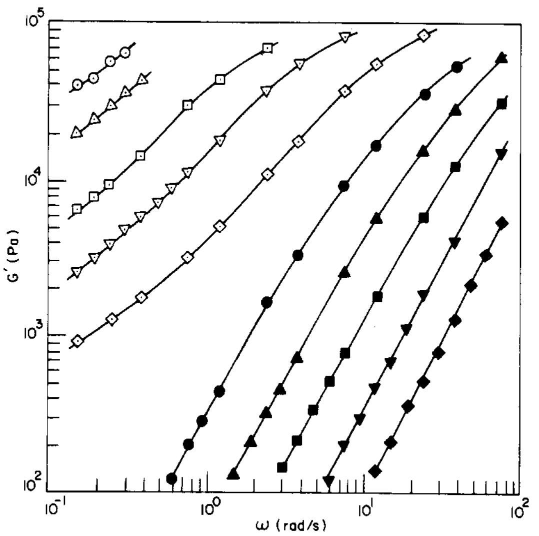

Figure 2. log G' versus log ω plots for sample C at various temperatures (°C): (⊙) 80; (△) 85; (⊡) 90; (▽) 95; (◇) 100; (●) 105; (▲) 110; (■) 115; (▼) 120; (◆) 130.

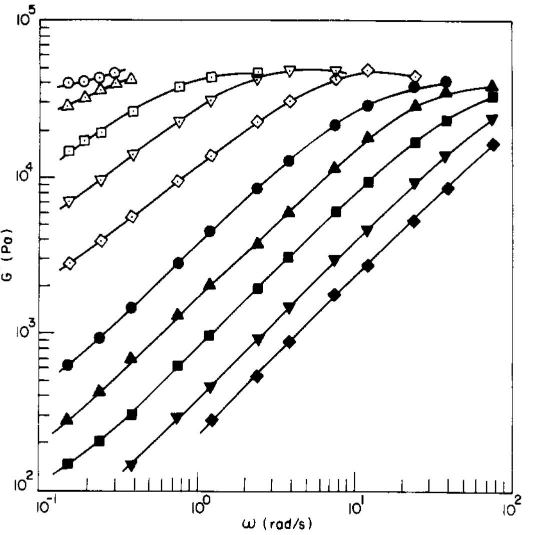

Figure 3. log G'' versus log ω plots for sample C at various temperatures. Symbols are the same as in Figure 2.

during sample preparation. These TEM photomicrographs confirm theoretical predictions for the formation of different microdomain structures based on the amount of polystyrene phase in a given SIS block copolymer.[23,24] (Refer to Table I for the composition and segment molecular weights of the block copolymers.)

Dynamic Viscoelastic Mesurements of the Block Copolymer Samples. Figure 2 gives log G' versus log ω plots, and Figure 3 gives log G'' versus log ω plots, for sample C having lamellar microdomain structures at ten different temperatures: 80, 85, 90, 95, 100, 105, 110, 115, 120, and 130 °C. It can be seen in Figure 2 that at temperatures of 100 °C and below, the shape of the log G' versus log ω curves looks very similar to those often observed for cross-linked polymers or polymers with high concentrations of particulates and that at temperatures of 105 °C and above, the shape of the log G' versus log ω curves looks very similar to those usually observed for homopolymers or random copolymers in the molten state. Note in Figure 2 that there is a rather noticeable change in the shape of the log G' versus log ω curve as the temperature is increased from 100 to 105 °C.

Figure 4 gives log G' versus log G'' plots for sample C, which was obtained from cross-plots of Figures 2 and 3.

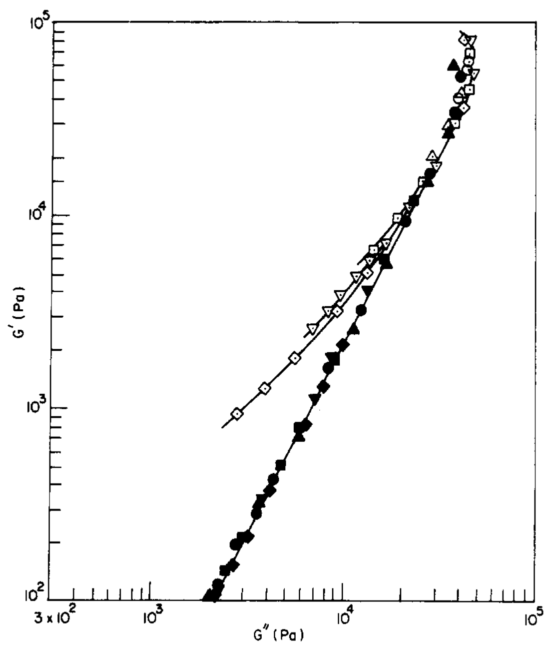

Figure 4. log G' versus log G'' plots for sample C at various temperatures. Symbols are the same as in Figure 2.

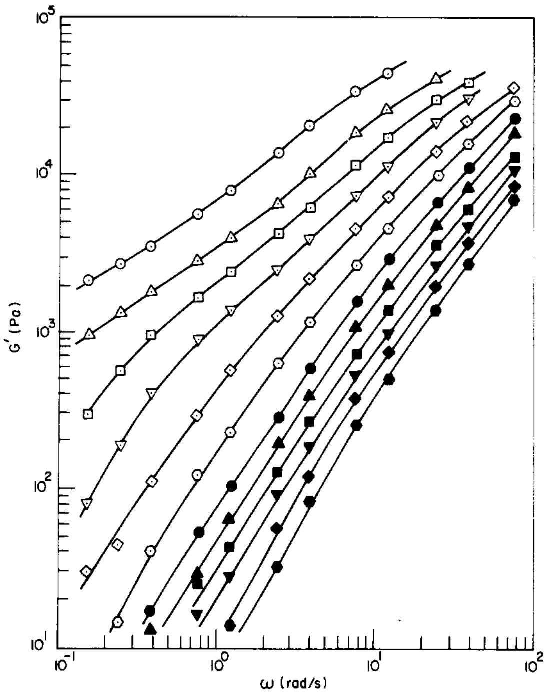

Figure 5. log G' versus log ω plots for sample A at various temperatures (°C): (⊙) 120; (△) 130; (⊡) 140; (▽) 150; (◇) 160; (◎) 170; (●) 180; (▲) 190; (■) 200; (▼) 210; (◆) 220; (●) 230.

It can be seen in Figure 4 that log G' versus log G'' plots show temperature dependence at temperatures of 100 °C and below, show a significant change as the temperature is increased from 100 to 105 °C, and then remain constant at temperatures of 105 °C and above. According to the criterion suggested in our previous papers,[17,18] it can be concluded from Figure 4 that the T_r of sample C is about 105 °C.

Figure 5 gives log G' versus log ω plots, and Figure 6 gives log G'' versus log ω plots, for sample A having spherical microdomain structures at 12 different temperatures: 120, 130, 140, 150, 160, 170, 180, 190, 200, 210, 220, and 230 °C. It can be seen in Figure 5 that values of G' decrease gradually with increasing temperature from 120

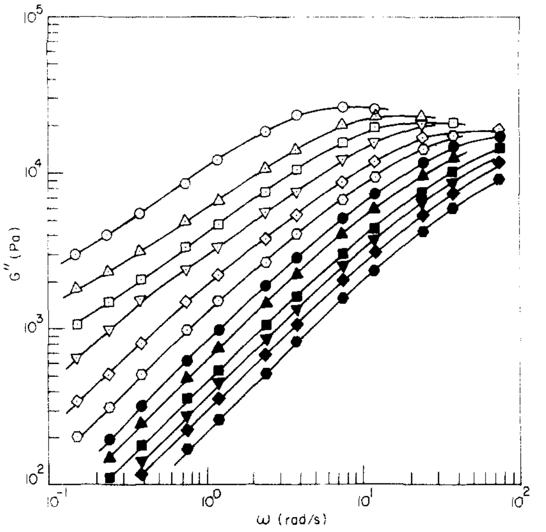

Figure 6. log G'' versus log ω plots for sample A at various temperatures. Symbols are the same as in Figure 5.

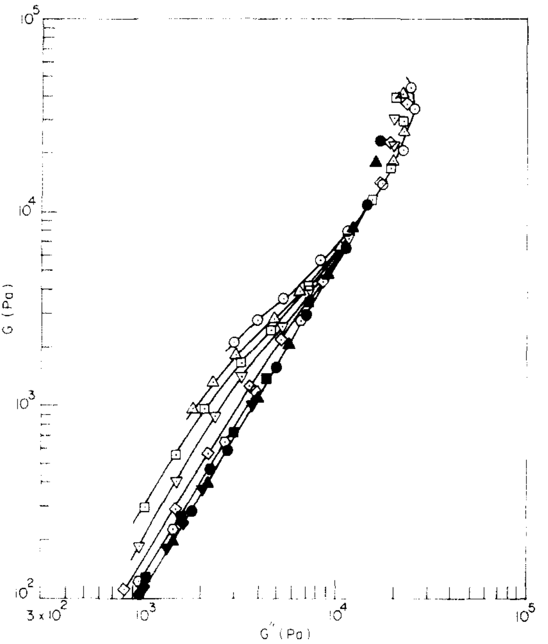

Figure 7. log G' versus log G'' plots for sample A at various temperatures. Symbols are the same as in Figure 5.

to 230 °C and that the slope of log G' versus log ω plots increases gradually with increasing temperature from 120 to about 180 °C *and then remains constant at temperatures of* 180 °C and above. In other words, in Figure 5 there is no evidence of an abrupt change in the slope of the log G' versus log ω curves for sample A, which is quite different from that observed for sample C in Figure 2.

From cross-plots of the data from Figures 5 and 6, log G' versus log G'' plots were prepared and are given in Figure 7. It can be seen in Figure 7 that at a fixed value of G'', G' decreases *gradually* as the temperature is increased from 120 to 180 °C and then remains constant, independent of temperature at temperatures of 180 °C and above. In other words, 180 °C is the lowest temperature at which log G' versus log G'' plots for sample A cease to vary with temperature. According to the criterion suggested in our previous papers,[17,18] we can conclude from Figure 7 that the T_r of sample A is about 180 °C.

Figure 8 shows log G' versus log G'' plots for sample B having cylindrical microdomain structures at different temperatures. It can be seen in Figure 8 that log G' versus log G'' plots show a gradual change in the shape of the curve until the temperature is increased to 90 °C, behavior very similar to that shown in Figure 7 for sample A. We conclude from Figure 8 that the T_r of sample B is about 90 °C.

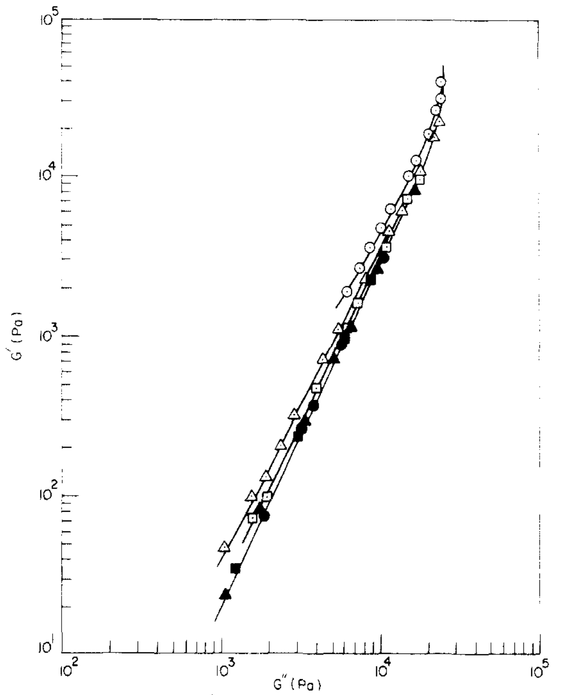

Figure 8. log G' versus log G'' plots for sample B at various temperatures (°C): (⊙) 70; (△) 80; (⊡) 85; (●) 90; (▲) 95; (■) 100.

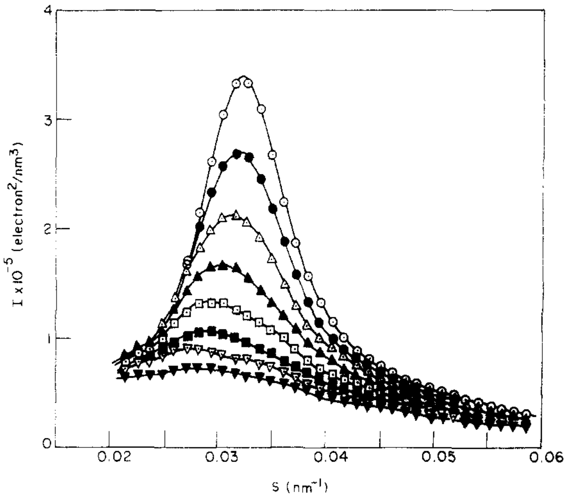

Figure 9. SAXS intensity profiles for sample A at various temperatures (°C): (⊙) 140; (●) 150; (△) 160; (▲) 170; (⊡) 180; (■) 190; (▽) 200; (▼) 210. The data were obtained during the cooling process.[25]

4. Discussion

Comparison of the T_r Determined from log G' versus log G'' Plots with That Determined from Small-Angle X-ray Scattering. Independent of the present study, the value of the T_r for sample A was determined by small-angle X-ray scattering (SAXS) in Professor T. Hashimoto's laboratory at Kyoto University. Figure 9 gives SAXS intensity profiles for sample A at various temperatures, in which $s = (2/\lambda)\sin\theta$ is the scattering vector. Here, 2θ and λ are the scattering angle and the

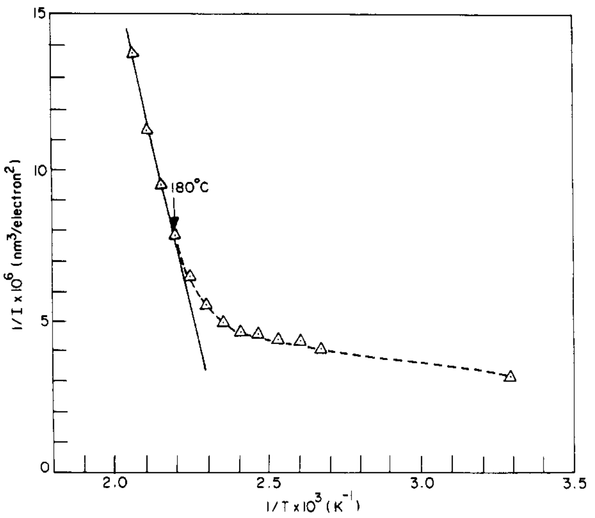

Figure 10. Plots of reciprocal SAXS intensity versus reciprocal absolute temperature for sample A at $s = 2.825 \times 10^{-2}$ nm^{-1}.[25]

wavelength of the X-rays, respectively. For all purposes, the peak positions appearing in Figure 9 can be regarded as being independent of temperature within the limits of experimental accuracy. The details of the interpretation of Figure 9 are given elsewhere.[25]

Figure 10 gives plots of the reciprocal of the SAXS intensity ($1/I$) versus the reciprocal of absolute temperature ($1/T$). According to Leibler,[4] $1/I$ should be a linear function of the interaction parameter χ.[26] If χ is assumed to be proportional to $1/T$

$$\chi = A + B/T \qquad (1)$$

where A and B are constants, Leibler's theory predicts that in the *disordered* state of a block copolymer, the plot of $1/I$ versus $1/T$ should be a straight line, i.e.

$$1/I = F(x)/N - 2A - 2B/T \qquad (2)$$

where $F(x)$ is given by eq IV-6 in Leibler's paper[4] and is independent of temperature and N is the polymerization index of the block copolymer.

It can be seen in Figure 10 that by applying the criterion given by eq 2, the T_r of this particular SIS block copolymer, as determined by SAXS, is about 180 °C, which is in remarkably good agreement with the value determined from the log G' versus log G'' plots, shown in Figure 7. It should be pointed out, however, that the value of T_r for sample A determined by the log G' versus log G'' plots is accurate to within 10 °C. The results of SAXS performed by both heating and cooling the sample indicate that the T_r of the block copolymer lies somewhere between 170 and 180 °C.[25] It is encouraging to observe that the two vastly different types of experimental techniques gave rise to *virtually* the same value of T_r for the block copolymer investigated.

It is of interest to note that the experimental efforts required to determine the T_r of block copolymers from dynamic viscoelastic measurements are quite small compared with those from SAXS. However, SAXS can provide additional important information (e.g., the dimensions of microdomains, kinetics of microphase separation, etc.),[27-30] which dynamic viscoelastic measurements cannot.

Comparison of Experimental Results with Theoretical Predictions. We used both Helfand–Wasserman's[1-3] and Leibler's theory[4] to predict the phase transition temperatures, namely, the spinodal temperature (T_s) and/or order–disorder transition temperature (T_r), of the three block copolymers investigated. The readers may refer to our previous paper[18] for a brief summary of these theories and the computational procedures used to generate the results presented below. In order to carry out the computations, a number of molecular and thermodynamic parameters are needed, namely, (1) the interaction parameter χ or α, which is defined by $\alpha = \chi/V_{\text{ref}}$, where V_{ref} is the reference volume; (2) polymerization index N, which is needed in Leibler's theory; (3) the reference volume V_{ref}, which is needed when information on χ is available; and (4) the Kuhn statistical lengths b_k, which are needed in Helfand–Wasserman's theory. In the numerical computations, we have used the following values for b_k: (1) $b_{\text{PS}} = 0.68$ nm for polystyrene and (2) $b_{\text{PI}} = 0.59$ nm for polyisoprene.[31]

We have used the following three expressions for the interaction parameter χ or α for the polystyrene–polyisoprene pair:

$$\alpha = -0.0009 + 0.75/T \qquad (3)$$

which was reported by Rounds[32] who used turbidity curves

$$\alpha = -0.00118 + 0.839/T \qquad (4)$$

which was obtained in our laboratory using turbidity curves,[33] and

$$\chi = -0.0937 + 66/T \qquad (5)$$

which was reported by Mori et al.[34] who used SAXS. Note in eq 3 and 4 that α is expressed in moles per centimeter cubed and T is the absolute temperature. In applying Leibler's theory, one needs information on χN, and not on χ and N separately. When using eq 3 or 4, we have determined values of χN from the following expression:

$$\chi N = \alpha[\bar{M}_{\text{w,PS}} v_{\text{PS}} + \bar{M}_{\text{w,PI}} v_{\text{PI}}] \qquad (6)$$

where $\bar{M}_{\text{w,PS}}$ and $\bar{M}_{\text{w,PI}}$ are the molecular weights and v_{PS} and v_{PI} are the specific volumes of the polystyrene and polyisoprene phases, respectively. However, when using eq 5, one needs information on the polymerization index N, so that values of χN could be determined. In determining values of N, we have used

$$N = [\bar{M}_{\text{w,PS}} v_{\text{PS}} + \bar{M}_{\text{w,PI}} v_{\text{PI}}]/V_{\text{ref}} \qquad (7)$$

and we have calculated values of V_{ref} from $V_{\text{ref}} = [\text{M}_s]v_{\text{PS}}$, where $[\text{M}_s]$ is the molecular weight of styrene monomer.

In determining the specific volumes, we have used the following expressions:

$$v_{\text{PS}} = 0.9199 + 5.098 \times 10^{-4}(T - 273) + 2.354 \times 10^{-7}(T - 273)^2 + [32.46 + 0.1017(T - 273)]/\bar{M}_{\text{w,PS}} \qquad (8)$$

for polystyrene[35] and

$$v_{\text{PI}} = 1.0771 + 7.22 \times 10^{-4}(T - 273) + 2.46 \times 10^{-7}(T - 273)^2 \qquad (9)$$

for polyisoprene.[18] Note in eq 8 and 9 that v_{PS} and v_{PI} are expressed in centimeters cubed per gram and T is the absolute temperature.

The calculated values of the transition temperatures for the three SIS block copolymers investigated are summarized in Table II, together with the experimental results. Note that Leibler's theory[4] allowed for the calculation of both T_s and T_r. According to Leibler's theory, the microdomain structure of the ordered phase influences the value of T_r; also, a transition from the disordered phase to the lamellar structure passes through the spherical and then cylindrical structure when the tempera-

Table II
Summary of Theoretically Predicted Transition Temperatures for the Three Block Copolymers

interactn param	Helfand–Wasserman's theory for triblock T_r, °C	Leibler's theory			
		diblock		triblock	
		T_s, °C	T_r, °C	T_s, °C	T_r, °C
		Sample A[a]			
eq 3	159	138	149	143	154
eq 4	141	124	133	128	137
eq 5	90	75	83	79	87
		Sample B[b]			
eq 3	120	184	190 (181)[d]	199	205 (196)[d]
eq 4	109	161	166 (159)[d]	173	178 (171)[d]
eq 5	60	108	113 (106)[d]	120	125 (118)[d]
		Sample C[c]			
eq 3	139	207	207 (205)[e]	240	240 (238)[e]
eq 4	125	179	180 (178)[e]	205	206 (204)[e]
eq 5	74	125	125 (124)[e]	150	150 (149)[e]

[a] The experimentally determined value of T_r for sample A is 180 °C. [b] The experimentally determined value of T_r for sample B is 90 °C. [c] The experimentally determined value of T_r for sample C is 105 °C. [d] The value inside the parentheses represents the transition temperature from the disordered phase, passing through the spherical structure, to the cylindrical microdomain structure. [e] The value inside the parentheses represents the transition temperature from the disordered phase, passing through the spherical and then cylindrical structure, to the lamellar microdomain structure.

ture is decreased from a very high value. Therefore, the values of T_r predicted from Leibler's theory, given in Table II, are those for the microphase separation transition (MST) temperature from the disordered phase to the spherical microdomain structure (also often referred to as the body-centered-cubic (bcc) mesophase). Note that, according to Leibler's theory, the value of T_r is always larger than that of T_s, although the differences between the two are negligibly small for the lamellar microdomain structure (see Table II). Also given in Table II are (a) the predicted values of T_r, going from the spherical to cylindrical microdomain structure for sample B, and (b) the predicted values of T_r, going from the spherical, passing through the cylindrical microdomain structure, to the lamellar microdomain structure for sample C.[36]

It should be pointed out in reference to Table II that for comparison purposes, T_r and T_s for the diblock were obtained by dividing the molecular weight of the midblock in half, and in application of Leibler's theory, T_r for the triblock was obtained by the following expression:

$$T_r(\text{triblock}) = T_s(\text{triblock}) - T_s(\text{diblock}) + T_r(\text{diblock}) \quad (10)$$

It should be mentioned that Leibler's theory was developed for diblock copolymers and thus it does not allow one to directly compute values of T_r for triblock copolymers, whereas Helfand–Wasserman's theory allows us to directly calculate values of T_r for triblock copolymers. Inherent in eq 10 is the assumption that the difference in T_s between diblock and triblock copolymers is the same as the difference in T_r between diblock and triblock copolymers, which is yet to be proven theoretically.

The following observations can be made in Table II: (1) Different expressions for the interaction parameter χ predict different values of T_r for block copolymers. (2) Both Helfand–Wasserman's and Leibler's theories predict about the same values of T_r for sample A having spherical microdomain structures. (3) Helfand–Wasserman's theory predicts a value of T_r for sample B having cylindrical microdomain structures, much closer to the experimental value than Leibler's theory does. (4) Helfand–Wasserman's theory predicts a value of T_r for sample C having lamellar microdomain structures, much closer to the experimental value than Leibler's theory does.

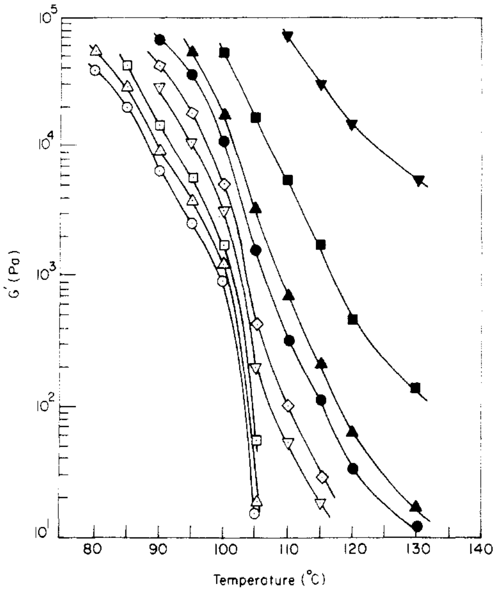

Figure 11. log G' versus temperature plots for sample C at various angular frequencies (rad/s): (⊙) 0.15; (◭) 0.24; (⊡) 0.38; (▽) 0.75; (◇) 1.2; (●) 2.4; (▲) 3.8; (■) 12; (▼) 75. The data were obtained under isothermal conditions at various angular frequencies.

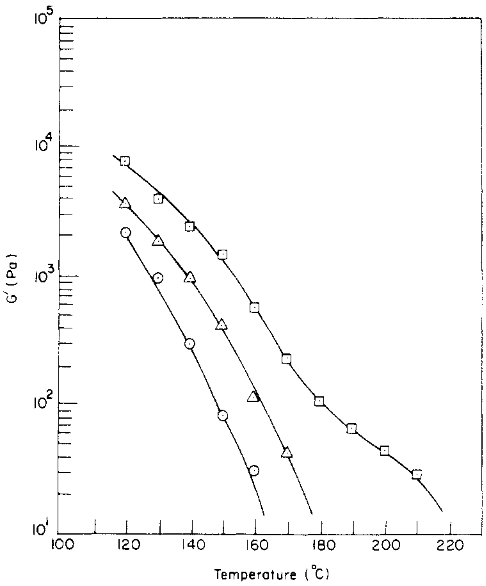

Figure 12. log G' versus temperature plots for sample A at various angular frequenices (rad/s): (⊙) 0.15; (◭) 0.38; (⊡) 1.2. The data were obtained under isothermal conditions at various angular frequencies.

Temperature Scan of the Storage Modulus of the SIS Block Copolymers. In view of the fact that previous investigators[14–16] have advocated the use of log G' versus temperature plots to determine the T_r of block copolymers, we have also prepared such plots, using the same experimental data presented in Figures 2–8. The results are given in Figure 11 for sample C having *lamellar* microdomain structures, in Figure 12 for sample A having *spherical* microdomain structures, and in Figure 13 for sample B having *cylindrical* microdomain struc-

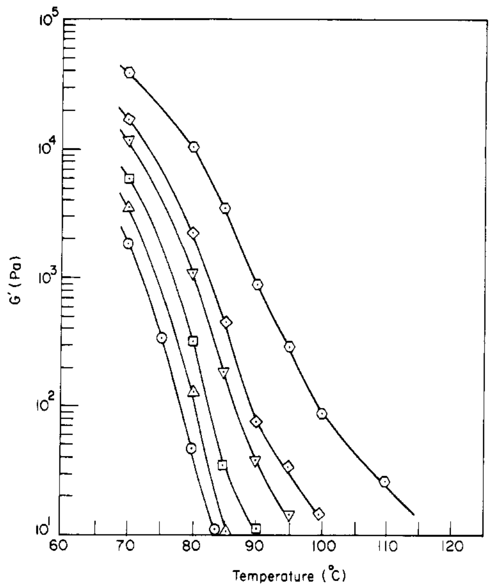

Figure 13. log G' versus temperature plots for sample B at various angular frequencies (rad/s): (⊙) 0.15; (▲) 0.24; (⊡) 0.38; (▼) 0.75; (◇) 1.2; (⊙) 3.8. The data were obtained under isothermal conditions at various angular frequencies.

tures. Note that these data were obtained under isothermal conditions at various angular frequencies, using a Model R16 Weissenberg rheogoniometer. It can be seen in Figure 11 that for sample C the value of G' decreases *abruptly* at a temperature of about 105 °C. But such behavior is not observed for sample A (see Figure 12) or for sample B (see Figure 13). We are well aware of the fact that the dynamic viscoelastic properties of block copolymers are very sensitive to the angular frequency applied and, therefore, it is highly desirable to apply an angular frequency as low as practically possible, approaching the limiting value *zero*, if one wishes to accurately determine the T_r of a block copolymer from the variation of G' with temperature.

It occurred to us that $\omega = 0.15$ rad/s might not have been low enough for us to observe an abrupt change in the value of G' over the temperature range investigated, for samples A and B. For this reason, additional experiments were conducted of temperature scans of storage modulus G', using a Rheometrics dynamic spectrometer. In this experiment, we first used $\omega = 0.15$ rad/s in order to check whether or not our earlier data, obtained with the Weissenberg rheogoniometer, were reproducible, insofar as determining the T_r of the block copolymers is concerned, and then $\omega = 0.05$ rad/s was used in order to observe if additional information could be obtained. The results of the temperature scans of G' are given in Figure 14 for sample C, in Figure 15 for sample A, and in Figure 16 for sample B.

It can be seen in Figure 14 that for sample C having lamellar microdomain structures, a sharp decrease in G' occurs at a temperature of about 105 °C, and this value is in complete agreement with that obtained from Figure 11. Since the value of $\omega = 0.15$ rad/s, used for the temperature scanning experiments, reproduced the result (i.e., an abrupt decrease in G' at about 105 °C) obtained from the isothermal experiments, we did not proceed to use lower values of ω. It is very important to point out that the value of about 105 °C is in complete agreement with the value of T_r determined from the log G' versus log G'' plots, shown in Figure 4.

On the other hand, the results of temperature scans of G' for samples A and B (see Figures 15 and 16) do *not* show any abrupt change in G' over the temperature range investigated at a value of $\omega = 0.05$ rad/s, which was found to be as low as practically achievable, in producing physically meaningful data. We found that the values of G' lower than about 10 Pa were not reliable and, therefore, no need was felt to proceed with values of ω lower than 0.05 rad/s.

The results presented above suggest that the determination of the T_r of the SIS block copolymers having *spherical* and/or *cylindrical* microdomain structures (i.e., block copolymers having relatively low amounts of polystyrene microdomains) may not be possible, in practice, from log G' versus temperature plots, since an abrupt decrease in G' is very difficult, if not impossible, to discern at the lowest angular frequency that a presently available rheological instrument can provide. However, the use of log G' versus log G'' plots (see Figures 4, 7, and 8) allows us to determine the T_r of the SIS block copolymers, including one that contains about 13 wt % polystyrene (i.e., sample A in the present study).

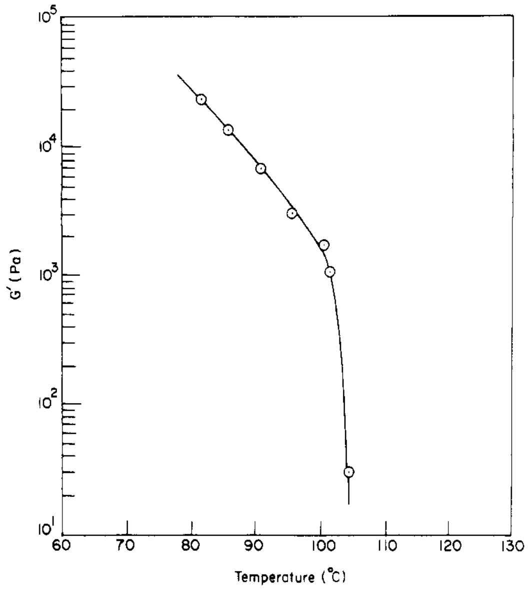

Figure 14. Temperature scans of the storage modulus for sample C at an angular frequency of 0.15 rad/s.

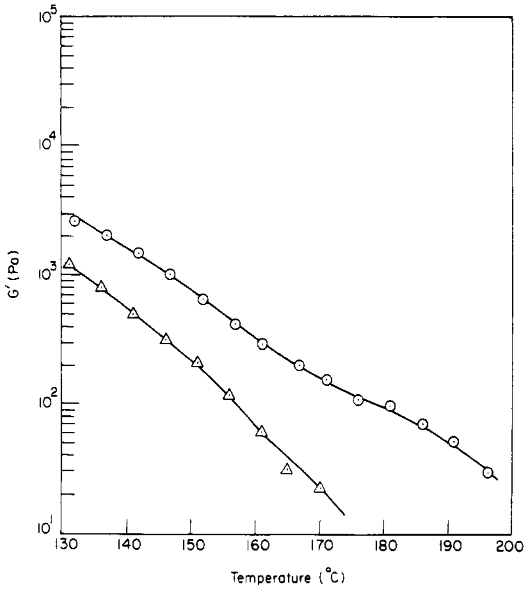

Figure 15. Temperature scans of the storage modulus for sample A at angular frequencies of (⊙) 0.15 rad/s and (▲) 0.05 rad/s.

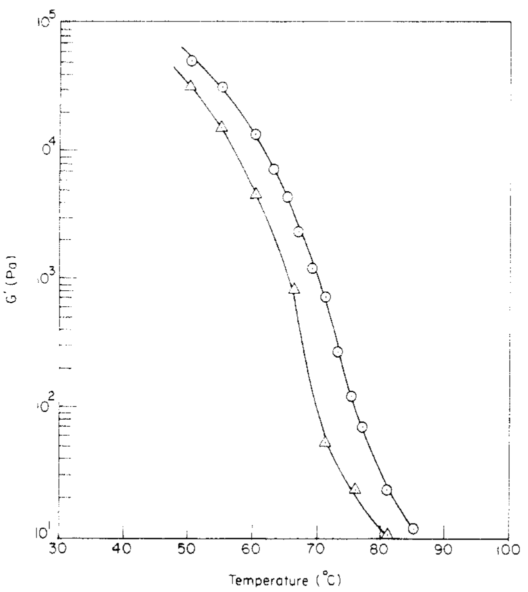

Figure 16. Temperature scans of the storage modulus for sample B at angular frequencies of (⊙) 0.15 rad/s and (▲) 0.05 rad/s.

Composition Fluctuations near a Transition Temperature. Statistical mechanical theories discuss order parameter fluctuations near the critical temperature of a binary mixture of small molecules,[37-40] of a binary mixture of homopolymers,[41,42] and of a homogeneous diblock copolymer.[43,44] Of particular relevance here is the study of Fredrickson and Helfand,[5] who included composition fluctuations in the microphase separation transition in a diblock copolymer. They concluded that the transition temperature with composition fluctuations will be lower than that obtained by Leibler's theory[4] and that the transition temperature will decrease as the molecular weight is decreased.

Having synthesized 1,4-polybutadiene-*block*-1,2-polybutadiene (BB) copolymers, Bates[16] investigated the order–disorder transition behavior of these block copolymers by taking dynamic viscoelastic measurements. The following observations can be made from Bates' study: (1) In the temperature scanning experiment performed on a BB block copolymer (designated as BB6, which had 38 wt % 1,4-polybutadiene) at various angular frequencies, an abrupt decrease in the storage modulus G' occurred at a temperature of about 108 °C at ω = 0.1 and 0.01 rad/s (see Figure 3 of ref 16). On the basis of this observation, Bates concluded that the T_r of this block copolymer is 108 °C. (2) Plots of log G' versus log $a_T\omega$, where a_T is a shift factor, for the BB6 block copolymer show two branches (see Figure 9 of ref 16), the lower branch (passing through the data points obtained at 87 °C) has the slope of 0.5 and the upper branch (passing through the data points obtained at 148 °C) has the slope of 2. Bates interpreted the lower branch as representing the microphase-separated state and the upper branch as representing the homogeneous state. Having observed from log G' versus log $a_T\omega$ plots that values of G' at 108 °C lie between the lower and upper branches, Bates concluded that composition fluctuations occur between 108 and 148 °C.

More recently, Bates[45,46] synthesized poly(ethylene-propylene)-*block*-poly(ethylethylene) (PEP–PEE) copolymers and investigated the order–disorder transition behavior of these block copolymers, by both SANS and dynamic viscoelastic measurements. For a PEP–PEE diblock copolymer with the overall molecular weight $\bar{M}_w$ = 57 500, $\bar{M}_w/\bar{M}_n$ = 1.05, and the volume fraction of PEP f = 0.55, using temperature scans of the storage modulus Bates observed that an abrupt decrease in G' occurred at a temperature of about 125 °C and identified this temperature as the T_r of this block copolymer. On the basis of the results of SANS experiments, Bates concluded that the PEP–PEE block copolymer undergoes very large composition fluctuations (in the temperature range ≥50 °C above its T_r, 125 °C).

On the other hand, the experimental results for the three SIS block copolymers investigated in the present study do *not* show trends similar to those observed by Bates, in the following aspects: (1) Samples A and B do not show an abrupt decrease in G' over the temperature range investigated (see Figures 15 and 16), while the log G' versus log G'' plots cease to vary with temperature at about 180 °C for sample A and at about 90 °C for sample B (see Figures 7 and 8). An independent study by SAXS showed that sample A has T_r of about 180 °C. Therefore, we can conclude that composition fluctuations for sample A near its T_r are negligibly small, and the same conclusion can be drawn for sample B. (2) Sample C shows an abrupt decrease in G' at a temperature of about 105 °C, which is in excellent agreement with that determined from log G' versus log G'' plots. This leads us to conclude that composition fluctuations of sample C near its T_r are negligibly small.

In discussing the composition fluctuations near the MST temperature of block copolymers, Onuki[47] derived the following expression:

$$\epsilon \simeq (4/3^{1/2})[f(1-f)]^{3/2}N(\mathrm{d}\chi/\mathrm{d}T)_c(T_c - T) \qquad (11)$$

where ϵ is assumed to be greater than zero but much less than 1 (i.e., $0 < \epsilon \ll 1$), f is the block copolymer composition, N is the polymerization index, $(\mathrm{d}\chi/\mathrm{d}T)_c$ is the derivative of the interaction parameter χ with respect to temperature at the critical point, and T_c is the critical temperature (which is the same as T_r in our notation). Note that the value of ϵ in eq 11 becomes very small at temperatures near the critical point (i.e., as T approaches T_c) and thus values of ϵ may be used to describe the extent of the composition fluctuations. When eq 1 (see, also eq 3–5) is substituted into eq 11, we obtain

$$\epsilon \simeq (4/3^{1/2})[f(1-f)]^{3/2}N(B/T_c^{\,2})(T - T_c) \qquad (12)$$

Let us now use eq 12 to explain why the SIS block copolymers used in the present study show negligibly small composition fluctuations, compared to the very large composition fluctuations reported by Bates[45] in his BB block copolymers, near the critical point of the respective block copolymers. For this purpose, we use the expressions

$$\chi = 6.79 \times 10^{-3} + 0.561/T \qquad (13)$$

for the 1,4-polybutadiene/1,2-polybutadiene pair[11] and

$$\chi = (-0.0009 + 0.75/T)V_{\mathrm{ref}} \qquad (14)$$

for the polystyrene/polyisoprene pair (see eq 3), where V_{ref} is the reference volume defined by $[\mathrm{M_s}]v_{\mathrm{PS}}$, $[\mathrm{M_s}]$ being the molecular weight of styrene monomer and v_{PS} being the specific volume of polystyrene. Note that the magnitude of $[\mathrm{M_s}]v_{\mathrm{PS}}$ is about 100. In order for Bates' BB block copolymer and our sample C to have the same value of ϵ, the following relationship must be satisfied:

$$(T - T_c)_{\mathrm{SIS}} = 0.052(T - T_c)_{\mathrm{BB}} \qquad (15)$$

Note that both our sample C and Bates' BB block copolymer have the lamellar microdomain structure. Equation 15 indicates that in order for our sample C to have the same extent of composition fluctuations as Bates' block copolymer, the value of $(T - T_c)$ for our sample C would have to be 5% of that for Bates' BB block copolymer. To be more specific, composition fluctuations of our sample C would occur within 2 °C (i.e., $T - T_c = 2$ °C) of T_c, in order to observe the same extent of composition fluctuations as that for the Bates' BB block copolymer in the temperature range from 108 to 148 °C (i.e., $T - T_c = 40$ °C). We conclude, therefore, that the SIS block copolymers used in the present study have very small composition fluctuations near the T_r, while Bates' BB block copolymers had very large composition fluctuations, because the temperature coefficient of χ (i.e., B in eq 1) for the SIS block copolymer is very large, compared to that for Bates' BB block copolymer.

We can think of other possible reasons for the differences observed between Bates' and our studies. First, the segment molecular weight of polystyrene in the SIS block copolymers used in our study (see Table I) is much less than the entanglement molecular weight $M_e = 18\,000$ of polystyrene. On the other hand, the segment molecular weights of the BB diblock copolymer and of the PEP–PEE diblock copolymers used in Bates' study[45,46] are much greater than the entanglement molecular weights of the respective constituent components in each block copolymer. We speculate that when the segment molecular weights in a block copolymer are much less than the entanglement molecular weights of the corresponding components, such a block copolymer, when subjected to temperatures near its transition temperature, may not exhibit measurable amounts of composition fluctuations. It seems appropriate to mention at this juncture a recent experimental study of Kopf et al.[48] who investigated the contour length fluctuation mechanism in SIS block copolymers using ^{13}C NMR. They used an SIS block copolymer that had a total weight-average molecular weight $\bar{M}_w = 110\,000$ with a ratio $\bar{M}_w/\bar{M}_n = 1.09$ and the molecular weight $\bar{M}_w = 1000$ for the polystyrene end blocks. They found that the polystyrene end blocks, whose molecular weight is much less than the entanglement molecular weight ($M_e = 18\,000$), obey Rouse-like chain dynamics although they are connected to an entangled polyisoprene midblock.

Second, the composition of the block copolymer (or block length ratio) appears to play an important role in exhibiting an abrupt decrease (or a sudden change) in storage modulus at some critical temperature. Note that sample C has about 52 wt % polystyrene, whereas sample A has about 13 wt % polystyrene and sample B has about 30 wt % polystyrene. However, the total molecular weight of sample A is much greater than that of samples C and B (see Table I). Our study showed that sample C exhibits a sudden change in storage modulus at a temperature of about 105 °C, whereas samples A and B do not. Since the modulus of polystyrene is much greater than that of polyisoprene at temperatures near the T_r, we believe that the greater the amount of polystyrene in an SIS block copolymer, the more likely it is that the block copolymer, when heated, will exhibit a sudden change in the storage modulus at a certain critical temperature. The observation that the total molecular weight of the block copolymer appears to be less important than the block length ratio, in exhibiting a sudden change in storage modulus at some critical temperature, can best be demonstrated by a comparison of the variations of storage modulus with temperature for two SIS block copolymers, which have the same block length ratio but different total molecular weights.

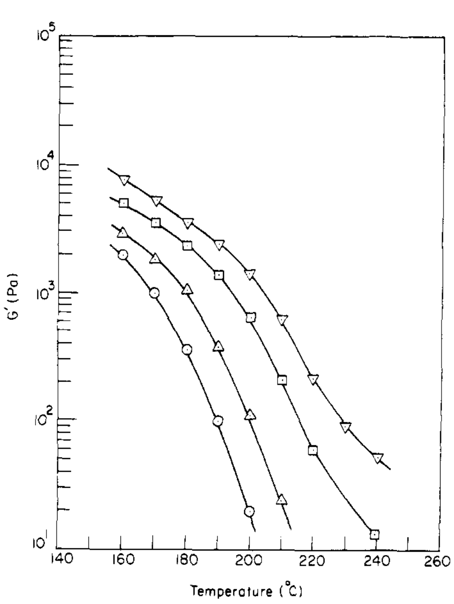

Figure 17. log G' versus temperature plots for KRATON 1107 at various angular frequencies (rad/s): (⊙) 0.15; (▲) 0.38; (⊡) 1.2; (▼) 2.4.

In a previous paper[18] we reported that the T_r of a commercially available SIS block copolymer (KRATON 1107, Shell Development Co.), which has the segment molecular weights 10000S-120000I-10000S, the total weight-average molecular weight $\bar{M}_w = 140\,000$, and about 14 wt % polystyrene, is about 230 °C (see Figure 9 of ref 18). Note that this copolymer has almost the same block length ratio as sample A investigated in the present study, but a larger total molecular weight (see Table I). Figure 17 gives plots of log G' versus temperature for the KRATON 1107. It can be seen in Figure 17 that KRATON 1107 does *not* exhibit a sudden change in G' over the temperature range investigated. The shape of the curves in Figure 17 for KRATON 1107 is very similar to that in Figure 12 for sample A. Note further that the segment molecular weight ($\bar{M}_w = 10\,000$) of polystyrene in KRATON 1107 is much less than its entanglement molecular weight ($M_e = 18\,000$). One may then suggest that an SIS block copolymer be synthesized, which has the segment molecular weight of polystyrene much greater than 18 000. If such an SIS block copolymer is indeed available, however, one will encounter a practical difficulty with experimentally determining its T_r, because the block copolymer will have a T_r above 300 °C, at which point the block copolymer will undergo thermal degradation.

Third, it is possible that the extent of composition fluctuations in a triblock copolymer can be different from that in a diblock copolymer. This is pure speculation at present, and experimental investigation is worth pursuing in the future. It should be pointed out that theoretical studies reported thus far on critical fluctuations have only dealt with diblock copolymers.[5,43,44]

5. Concluding Remarks

In the present study, we have synthesized three SIS block copolymers having spherical, cylindrical, and lamellar microdomain structures and observed that the morphological state of the microdomain structure (or block length ratio) in the SIS block copolymers has a pronounced effect on how the order–disorder transition takes place, as the temperature is increased from the ordered state or is decreased from the disordered state. The results of the present study show that, within the uncertainties involved with measurements, log G' versus log G'' plots give rise to information on the order–disorder transition temperature (T_r) of the SIS block copolymers, even in the situations where plots of storage modulus versus temperature cannot provide such information. The experimentally determined values of T_r are compared with theoretical predictions based on the currently held theories of Helfand–Wasserman[1-3] and Leibler.[4] We have found that the accuracy of the theoretical predictions of T_r depends very much on the accuracy of the temperature dependency of the interaction parameter χ for the polymer pair.

The value of T_r for an SIS block copolymer having *spherical* microdomain structures (referred to as sample A in this paper), which was determined from log G' versus log G'' plots, has been found to be in remarkably good agreement with that determined by small-angle X-ray scattering. We have found that this block copolymer does not exhibit a sudden change in storage modulus over the temperature range investigated, when the sample is measured at an angular frequency as low as 0.05 rad/s. On the other hand, an SIS block copolymer having *lamellar* microdomain structures (referred to as sample C in this paper) *shows* a sudden change in the storage modulus at a temperature of about 105 °C, as the sample is measured and at an angular frequency of 0.15 rad/s. This temperature is in excellent agreement with that determined from log G' versus log G'' plots. On the basis of observations made above, we can conclude that the temperature scans of the storage modulus can provide information on the T_r of an SIS block copolymer only when its block length ratio is greater than some critical value.

We believe from the present study that significant (or measurable) composition fluctuations near a transition temperature of a block copolymer may occur when the segment molecular weights exceed entanglement molecular weights of the constituent components. However, this hypothesis must be tested in the future by synthesizing block copolymers such that they have segment molecular weights above and below the entanglement molecular weights of the constituent components.

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Registry No. (S)(I) (block copolymer), 105729-79-1.