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Effect of Volume Fraction on the Order–Disorder Transition in Low Molecular Weight Polystyrene-*block*-Polyisoprene Copolymers. 1. Order–Disorder Transition Temperature Determined by Rheological Measurements

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ABSTRACT: Low molecular weight polystyrene-*block*-polyisoprene (SI diblock) copolymers having a wide range of compositions were synthesized via anionic polymerization, and the order–disorder transition temperatures (T_{ODT}) of the block copolymers were determined using dynamic viscoelastic measurements. We have shown that logarithmic plots of dynamic storage modulus (G') versus dynamic loss modulus (G'') are very effective to determine the T_{ODT}s of the block copolymers. The experimentally determined $\mathrm{T_{ODT}}$s are compared with the predictions made from currently held theories. We point out that the reliability of the predicted T_{ODT} of a block copolymer depends, among many factors, on the accuracy of the expression for the Flory–Huggins interaction parameter χ. We observed that the SI diblock copolymers having a low volume fraction of polystyrene or polyisoprene block (e.g., less than about 0.2) exhibited "liquidlike" rheological behavior at temperatures below their T_{ODT}s, for instance at temperatures as low as about 30 °C below the T_{ODT}. We attribute this observation to the existence of defects in the long-range spatial order of microdomains (grain-boundary defects) which are continuous in three-dimensional space. Using the Onuki analysis that the extent of composition fluctuations of a block copolymer near the critical temperature, at a given temperature difference $\Delta T = T - T_c$ from the critical temperature T_c, is determined very much by the temperature dependence of the Flory–Huggins interaction parameter χ, we have shown that the extent of composition fluctuations for SI diblock copolymers in the disordered state near the critical temperature is very small. Specifically, we have shown that for the same extent of composition fluctuations ϵ, defined by $\epsilon = 2\,(1 - \chi/\chi_c)$, where χ_c is the value of χ at the critical point, a temperature difference ΔT of 1 °C for an SI diblock copolymer corresponds to ca. 20 °C for a 1,2-polybutadiene-*block*-1,4-polybutadiene copolymer. This difference in ΔT between the two block copolymer systems is attributed to the difference in the temperature coefficient B appearing in the expression, $\chi = A + B/T$. Using the Onuki analysis, we have shown further that the extent of composition fluctuations in the disordered state near the critical temperature varies *little* with block copolymer composition.

Background

It is well established today that by choosing the molecular weight and block length ratio judiciously, one can synthesize block copolymers that have the ordered microdomain structure in the form of spheres, cylinders, lamellae, or ordered bicontinuous microdomains.[1–6] However, as the temperature is raised above a certain critical value, the microdomain structure disappears completely, giving rise to a disordered (homogeneous) phase. Such a phenomenon is referred to as the order–disorder transition (ODT). In the past, a number of research groups have investigated the ODT of block copolymers; some research groups[7,8] conducted theoretical studies while others[9–34] carried out experimental studies.

Using a random phase approximation, Leibler[8] formulated a statistical thermodynamic theory, suggesting that small-angle X-ray scattering (SAXS) or small-angle neutron scattering (SANS) be used to investigate the ODT of block copolymers. Several research groups[9–22,33,34] have used SAXS or SANS to investigate the ODT of block copolymers and reported that the scattering maximum present at room temperature persists well above the glass transition temperature of the microdomain phase. They further determined the spinodal temperature (T_s) for microphase separation and/or the order–disorder transition temperature (T_{ODT}) at which a block copolymer attains the homogeneous phase (or disordered state).

It should be mentioned that the Leibler theory is valid only for infinite molecular weight of diblock copolymer. Using the Hartree approximation for a finite-sized diblock copolymer, Fredrickson and Helfand[35] took into account composition fluctuations and improved the Landau-type mean-field prediction, yielding

$$(\chi N)_t = 10.495 + 41.022 N^{-1/3} \qquad (1)$$

for *symmetric* monodisperse diblock copolymers with equal block lengths (i.e., f = 0.5) and, also, equal statistical lengths, with $(\chi N)_t$ referring to the location

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of the transition induced by composition fluctuations. Note that the derivation of eq 1 includes the effect of composition fluctuations of the ODT, which was neglected in Leibler's final equation, $(\chi N)_t = 10.495$, although the importance of this effect was pointed out by Leibler. In view of the fact that χ is inversely proportional to temperature, it can be seen in eq 1 that the presence of the second term $41.022N^{-1/3}$ will lower the predicted value of the transition temperature below the value based on the first term alone.

For *asymmetric* polydisperse block copolymers with unequal block lengths (i.e., $f \neq 0.5$) and, also, unequal statistical lengths, we must use, in place of eq 1, the general expression[36]

$$(\chi N)_{\mathrm{t}} = (\chi N)_{\mathrm{s}} - (1/2)c^2\tau^*(d\lambda)^{2/3}\tilde{N}^{-1/3} \qquad (2)$$

where $(\chi N)_s$ is the value of χN at the spinodal point, $\tilde{N}$ is the *reduced* degree of polymerization defined by $\tilde{N} = N[(b^6/v^2)_A(b^6/v^2)_B]^{1/2}$ in which b is the Kuhn statistical length, the subscripts A and B refer to blocks A and B, respectively, in an AB-type diblock copolymer, and v is the statistical segment volume, and c is defined by

$$c = \left[\frac{x}{3}\frac{\partial^2 F(x,f)}{\partial x^2}\right]^{1/2}_{x=x^*} \qquad (3)$$

where $F(x,f)$ is defined by[8]

$$F(x,f) = \frac{g_1(1,\mathrm{x})}{g_1(f,x)g_1(1-f,x) - {}^1\!/_4[g_1(1,x) - g_1(f,x) - g_1(1-f,x)]^2} \qquad (4)$$

in which $g_1(f,x)$ is the Debye function, and d is given by[8]

$$d = 3x^*/2\pi \qquad (5)$$

where x^* denotes the value of x at $q = q^*$, defined by $x = q^2Nb^2/6$, with q being the scattering vector and q^* being the value of q at the maximum scattering intensity. τ^* appearing in eq 2 is a dimensionless parameter defined by[36] $\tau^* = \tau(d\lambda)^{-2/3}\tilde{N}^{1/3}$, where τ is defined by[35] $\tau = [F(x,f) - 2\chi N]/c^2$. Note that τ^* is a constant (-2.0308) for lamellar microdomains but varies with f and $\tilde{N}$ for spherical and cylindrical microdomains, respectively. Note further that τ and λ are related to the Leibler coefficients α_n and β_n,[8] which can be evaluated once the morphology of the microdomains (spheres, cylinders, or lamellae) is specified. It should be mentioned that the Fredrickson–Helfand analysis is valid only for $\tilde{N} \geq 10^4$. It should also be mentioned that by including higher-order harmonics to the Fredrickson–Helfand analysis, Barrat and Fredrickson[37] predicted the values of $(\chi N)_t$ to be greater than those predicted from the Leibler analysis[8] but less than those predicted from the Fredrickson–Helfand analysis.[35]

Recently, using self-consistent mean-field theory, Vavasour and Whitmore[38] and Matsen and Schick[39] carried out numerical computations for diblock copolymers and obtained an equilibrium phase diagram which is somewhat similar to that of Leibler but shows that lamellar microdomains can be obtained without having to pass through spherical microdomains first as the value of χN is increased (i.e., either by increasing the molecular weight of the block copolymer or by cooling the block copolymer from the disordered state).

In the use of rheological methods, some investigators[23-28] determined the T_{ODT} of a block copolymer by observing the temperature at which the dynamic storage modulus drops precipitously or by observing the temperature at which the Newtonian viscosity is first observed as the temperature is increased. Han and coworkers[29-32] have suggested that the threshold temperature at which logarithmic plots of dynamic storage modulus (G') versus dynamic loss modulus (G'') become independent of temperature be used to determine the T_{ODT} of a block copolymer as the temperature is increased. The rationale behind the use of log G' versus log G'' plots lies in that such plots in the *terminal region* are expected to have the slope of 2 when an SI diblock copolymer is in the *disordered(homogeneous)* state.

It should be pointed out that regardless of whether a homopolymer is *entangled* or *unentangled*, the slope of log G' versus log G'' plots in the *terminal region* must be 2, i.e. (i) For *entangled* homopolymers in the terminal region, we have[40]

$$\log G' = 2 \log G'' + \log(6M_e/5\varrho RT) \qquad (6)$$

(ii) For *unentangled* homopolymers in the terminal region, we have[41]

$$\log G' = 2 \log G'' + \log(2M/5\varrho RT) \qquad (7)$$

where M_e is the entanglement molecular weight, ϱ is the density, R is the universal gas constant, T is the absolute temperature, and M is the molecular weight. Note in eq 7 that plots of log G' versus log G'' for *unentangled* homopolymers depend on molecular weight M. The fact that even *unentangled* homopolymers must have the slope of 2 in the *terminal region* of log G' versus log G'' plots is important to remember, because some of the low molecular weight SI diblock copolymers synthesized in this study may be regarded as being *unentangled.*

There remains, however, an important question as to how one can determine *unambiguously*, via rheological measurement the T_{ODT} of asymmetric polystyrene-*block*-polyisoprene (SI diblock) copolymer having "low molecular weight". Here a "low molecular weight" SI diblock copolymer is referred to one which has the T_{ODT} relatively close to the glass transition temperature ($T_{\mathrm{g,PS}}$) of the polystyrene (PS) microphase in the block copolymer. We have found that "low molecular weight" SI diblock copolymer undergoes a unique ordering process, giving rise to very subtle microdomain morphology. We are of the opinion that "low molecular weight" SI diblock copolymers must be treated differently from "high molecular weight" SI diblock copolymers that have the T_{ODT} well above the $T_{\mathrm{g,PS}}$ of the polystyrene microphase (e.g., $T_{\mathrm{ODT}} > T_{\mathrm{g,PS}} + 60$ °C) when investigating their ordering processes. In an effort to find a resolution to the question posed above, we recently synthesized via anionic polymerization a series of low molecular weight SI diblock copolymers having a wide range of block compositions and then determined the T_{ODT}s of the block copolymers using various rheological methods. In this paper we shall report the highlights of our findings.

The organization of this paper is as follows. First we will present the experimentally determined T_{ODT}s of seven low molecular weight SI diblock copolymers, which were synthesized in this study, using four different rheological methods, namely, (i) plots of G' versus temperature obtained from temperature sweep experiments at low angular frequencies (ω), (ii) plots of log G' versus log ω and log G'' versus log ω from frequency sweep experiments at various temperatures, (iii) plots of log G' versus log G'', and (iv) plots of log $|\eta^*|$ versus log ω, with $|\eta^*|$ being the absolute value of the complex viscosity. We will then show that plots of log G'' versus log G'' have an advantage over the other methods in determining the T_{ODT} of low molecular weight SI diblock copolymers with a wide range of compositions. Next, we will first compare the values of T_{ODT} determined in the present study with the predictions made with the Helfand–Wasserman theory[7] and, also, the Leibler theory[8] with varous modifications[35,36] including composition fluctuations and then compare the values of T_{ODT} determined in the present study with those reported in the literature. Finally, we will show that the extent of composition fluctuations, which scales with ϵ defined by $\epsilon = 2(1 - \chi/\chi_c)$, where χ_c is the Flory–Huggins interaction parameter χ at the critical point, at a given $\Delta T = |T - T_c|$ near the critical temperature T_c is very small for SI diblock copolymers as compared to that for 1,2-polybutadiene-*block*-1,4-polybutadiene (1,2-PB-*block*-1,4-PB) copolymers or poly(ethylenepropylene)-*block*-poly(ethylethylene) (PEP-*block*-PEE) copolymers. We will explain the difference in the magnitude of ϵ between SI diblock copolymers and 1,2-PB-*block*-1,4-PB or PEP-*block*-PEE copolymers by showing that the magnitude of ϵ at a given ΔT near the T_c is very sensitive to the temperature coefficient B in the expression $\chi = A + B/T$; namely, the larger the value of B, the smaller the value of ϵ at a given ΔT near the T_c.

Experimental Section

Materials. A series of SI diblock copolymers were synthesized via anionic polymerization using an inert gas, stirred-tank reactor system. Before beginning polymerization, the reactor system was evacuated and then purged with purified argon gas. The inhibitor in styrene monomer (99% purity) was removed by passing it through an inhibitor removal column (DTR-7, Scientific Polymer Products Inc.) using a dropping funnel, after which the styrene was poured into a bottle which contained molecular sieves of 40 nm. A few days before polymerization, the styrene monomer was distilled in the presence of CaH_2 at 30 °C, and the middle fraction was received via a two-way Teflon stopcock into a flask, where dibutylmagnesium (1.0 M solution in heptane, Aldrich Chemical Co.) had been added. Just before polymerization, the styrene monomer containing dibutylmagnesium was distilled again, and the middle fraction of styrene monomer was received directly into the dropping funnel. Isoprene monomer received from the Goodyear Tire and Rubber Co. was purified by using essentially the same procedures, except that the isoprene monomer was distilled under an argon atmosphere under a slightly positive pressure (ca. 14 kPa), whereas styrene monomer was distilled under vacuum.

In the polymerization, the reactor was first thoroughly washed with purified THF, then evacuated using high vacuum for 12 h, and finally heated with a heat gun. Cyclohexane was used as the solvent, and *sec*-butyllithium was used as initiator to first polymerize at 35 °C the isoprene monomer anionically, which lasted about 4 h, and then to copolymerize styrene monomer with this "living" polyisoprene at 45 °C to form SI diblock copolymer, which lasted about 2 h. Upon completion of the copolymerization reaction, a small amount of degassed methanol was injected into the reactor using a hypodermic syringe to deactivate anions in the reactor, at which point the color of the solution in the reactor changed from yellowish-red to white. Then the reactor temperature was lowered to room temperature, and the solution in the reactor was precipitated by addition of an excess amount of methanol. The precipitated polymer was filtered and dried for 2 days at room temperature under vacuum and finally dried at 90 °C for 12 h under vacuum.

Table 1. Molecular Characteristics of the SI Diblock Copolymers Synthesized in This Study

sample code	M_w(PS-*b*-PI)	M_w/M_n	wt % PS	f[a]	N[b]	$T_{g,PS}$[c]
SI-Q	5930-*b*-22070	1.06	21.2	0.186	348	55
SI-Z	6500-*b*-12800	1.09	33.6	0.303	235	63
SI-S	7200-*b*-10400	1.06	40.9	0.372	212	63
SI-X	8950-*b*-8950	1.07	50.0	0.461	213	66
SI-R	8200-*b*-6800	1.07	54.5	0.508	177	65
SI-O	20800-*b*-5600	1.06	78.8	0.760	300	85
SI-L	34200-*b*-6800	1.05	83.3	0.811	462	94

[a] f is the volume fraction of PS block in the SI diblock copolymer at 25 °C. [b] N is the total number of statistical segments at 25 °C, defined by $N = (M_{w,PS}v_{PS} + M_{w,PI}v_{PI})/V_{ref}$, where $M_{w,PS}$ and $M_{w,PI}$ are the molecular weights of the PS and PI blocks, respectively, in the SI diblock copolymer, v_{PS} and v_{PI} are the specific volumes of PS and PI, respectively, and V_{ref} is the molar volume of a reference component, which in this case is defined by $[(M_S v_{PS})(M_I v_{PI})]^{1/2}$, where M_S and M_I are the molecular weights of the styrene and isoprene monomer units, respectively. [c] After the specimens were aged for 8 months.

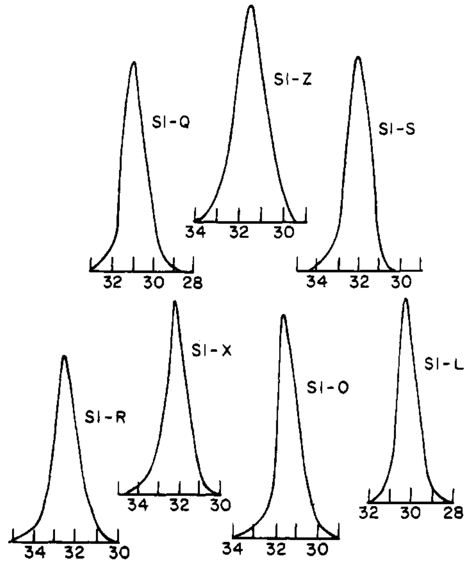

Figure 1. GPC chromatograms for the seven SI diblock copolymers synthesized in this study.

Table 1 gives a summary of the molecular characteristics for the seven SI block copolymers that we synthesized. The number-average molecular weight was determined via membrane osmometry, the polydispersity (M_w/M_n) via gel permeation chromatography (GPC), and the weight fraction of the polystyrene phase by ultraviolet spectroscopy at a wavelength of 254 nm. Figure 1 gives the GPC chromatograms for the seven SI diblock copolymers synthesized in this study. Nuclear magnetic resonance spectroscopy indicated that the microstructure of polyisoprene had 94 wt% 1,4-linkage, 6 wt% 3,4-linkage, and no detectable amount of 1,2-linkage in the SI diblock copolymers.

Sample Preparation. Samples were prepared by first dissolving a predetermined amount of SI diblock copolymer (10 wt %) in toluene in the presence of an antioxidant (Irganox 1010, Ciba-Geigy Group) and then slowly evaporating the solvent. The evaporation of the solvent 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 in a vacuum oven at an elevated temperature by gradually raising the oven temperature to 10 °C above the glass transition temperature of the polystyrene phase ($T_{g,PS}$) in each block copolymer. The drying of the samples was continued until there was *no* further change in weight. Finally, the samples were annealed for 10 h at a temperature about 20 °C above the $T_{g,PS}$ in each block copolymer.

Rheological Measurements. 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 between the cone tip and the plate) 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 the SI diblock copolymers synthesized in this study. Data acquisition was accomplished with the aid of a microcomputer interfaced with the rheometer. The temperature control was accurate to 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 the measurement temperature, which was well within the linear viscoelastic range of the materials investigated. All experiments were conducted under a nitrogen atmosphere to avoid oxidative degradation of the samples. Also used was a Rheometrics mechanical spectrometer (Model, RMS-800) to conduct temperature sweep experiments of G' for the seven SI diblock copolymers at low angular frequencies of 0.01 and 0.5 rad/s, respectively, in order to investigate whether or not the value of G' decreases precipitously at a certain critical temperature.

Transmission Electron Microscopy (TEM). The as-cast films which were prepared by the slow solvent evaporation process and by the drying process described above were subjected to TEM observation for morphological investigation. Since the exact T_{ODT} of each sample was not well established *a priori* and could be very low for these low molecular weight SI diblock copolymers, the as-cast films were not annealed deliberately. Effects of annealing on the morphology of these block copolymers will be reported in a future publication. The ultrathin sections of ca. 50-nm thickness were obtained by microtoming at −85 °C with a Reichert-Jung Ultracut E together with a cryogenic unit FC 4E and a diamond knife, and they were picked up on 400-mesh copper grids and then stained by exposure to osmium tetroxide vapor for a few hours. Electron microscopic observation was made with a Hitachi H-600 transmission microscope operated at 100 kV.

Results

Microdomain Structure of the SI Diblock Copolymers Synthesized. Figure 2 gives micrographs taken by TEM, describing the microdomain structures of the SI diblock copolymers synthesized in this study. We have found that the micrographs taken of the SI diblock copolymers do *not* show very distinct microdomain structures such as spheres, cylinders, lamellae, or ordered bicontinuous microdomains, usually observed in high molecular weight SI diblock copolymers. A detailed discussion about the origin(s) of the seemingly complex morphological states of the low molecular weight SI diblock copolymers is outside the scope of this paper and, thus, below we shall describe very briefly the highlights of the microdomain structure of each SI diblock copolymer synthesized in this study. (i) SI-Z has PS cylinders in the matrix of PI. (ii) SI-S has bicontinuous microdomains with a considerable distortion having the appearance locally of lamellar catenoids. (iii) SI-X has lamellae in most areas, but in some areas it has imperfect lamellae having the appearance of a distorted, chaotic microdomain morphology. (iv) SI-R shows the coexistence of well-developed lamellae and a bicontinuous microdomain. (v) SI-O has PI cylinders in the matrix of PS. (vi) SI-L has PI cylinders in the matrix of PS. Although, owing to the space limitation here, the micrograph of SI-Q is not given in Figure 2, we found that it has PS cylinders in the matrix of PI. The results of TEM presented above were confirmed by independent SAXS measurements, which will be presented in a future publication.

We have experienced some difficulties in obtaining clear micrographs of the SI diblock copolymers (with the exception of SI-X) synthesized in this study. This is attributable to the fact that, as will be shown below, these low molecular weight SI diblock copolymers (especially SI-Q, SI-S, SI-Z, and SI-R) have T_{ODT}s not much higher than (within ca. 40 °C of) the glass transition temperature ($T_{\mathrm{g,PS}}$) of the polystyrene (PS) microdomains in the respective block copolymers (see Table 1 for the $T_{\mathrm{g,PS}}$s of the block copolymers). This suggests to us that the ordering process would occur extremely slowly and thus the annealing conditions employed to prepare the specimens for rheological measurements, the results of which will be presented below, would have changed *little* the state of order found in as-cast specimens. This indeed was confirmed by time-resolved SAXS experiments. Specifically, (a) an SI-Z specimen (having $T_{\mathrm{ODT}} \cong 90$ °C) quenched from a disordered state to 85 °C revealed that ordering took place very slowly over 10 h; (b) the slow cooling of an SI-Q specimen (having $T_{\mathrm{ODT}} \cong 95$ °C) from 100 to 80 °C at a rate of ca. 5 °C/h and the slow cooling of an SI-Z specimen from 120 to 85 °C at a rate of 9 °C/h, respectively, gave no ordering at all but generated a frozen disordered state. Further discussion of the effect of thermal history (i.e., the effect of annealing) on the microdomain morphology of low molecular weight SI diblock copolymers is beyond the main theme of this paper and such results will be presented in a future publication. Although the T_{ODT}s for SI-O (having $T_{\mathrm{ODT}} \cong 130$ °C) and SI-L (having $T_{\mathrm{ODT}} \cong 170$ °C) are substantially higher than the $T_{\mathrm{g,PS}}$s of the respective block copolymers, ordering in these block copolymers would presumably take place via nucleation and growth and hence is expected to be very slow. It should be remembered that in these two block copolymers the polyisoprene (PI) blocks form microdomains in the matrix of the PS phase and that the volume fractions of the PS phase in SI-O and SI-L are 0.760 and 0.811, respectively (see Table 1). Judging from the slow ordering process taking place in these SI diblock copolymers, the micrographs shown in Figure 2 may not necessarily represent equilibrium morphologies. Here we merely show typical microdomain morphologies of the specimens subjected to the rheological investigation reported below.

Another compelling reason why we have presented the micrographs shown in Figure 2 lies in that such information is needed to predict the T_{ODT} of a block copolymer when using the Helfand–Wasserman theory[7] or the Leibler theory.[8] Below we will compare experimentally determined T_{ODT}s with predictions from the Helfand–Wasserman theory and the Leibler theory, respectively.

Determination of T_{ODT} for SI Diblock Copolymers from the Temperature Sweep of G' at Low Angular Frequencies. By conducting temperature sweep experiments at low angular frequencies for block copolymers, it has been reported[22–28] that G' decreases precipitously at or near a certain critical temperature and thus suggested that such a temperature be regarded as the T_{ODT} of a block copolymer. In the present study, using a Rheometrics mechanical spectrometer we carried out temperature sweep experiments at two angular frequencies, $\omega = 0.5$ and 0.01 rad/s. In those experiments, the temperature was increased stepwise, 3 °C in each step, by waiting for 3 min before measurements were taken at a fixed angular frequency ω. All the experimental results reported below were obtained during heating.

Figures 3–9 give plots of G' versus temperature for the seven SI diblock copolymers synthesized in this

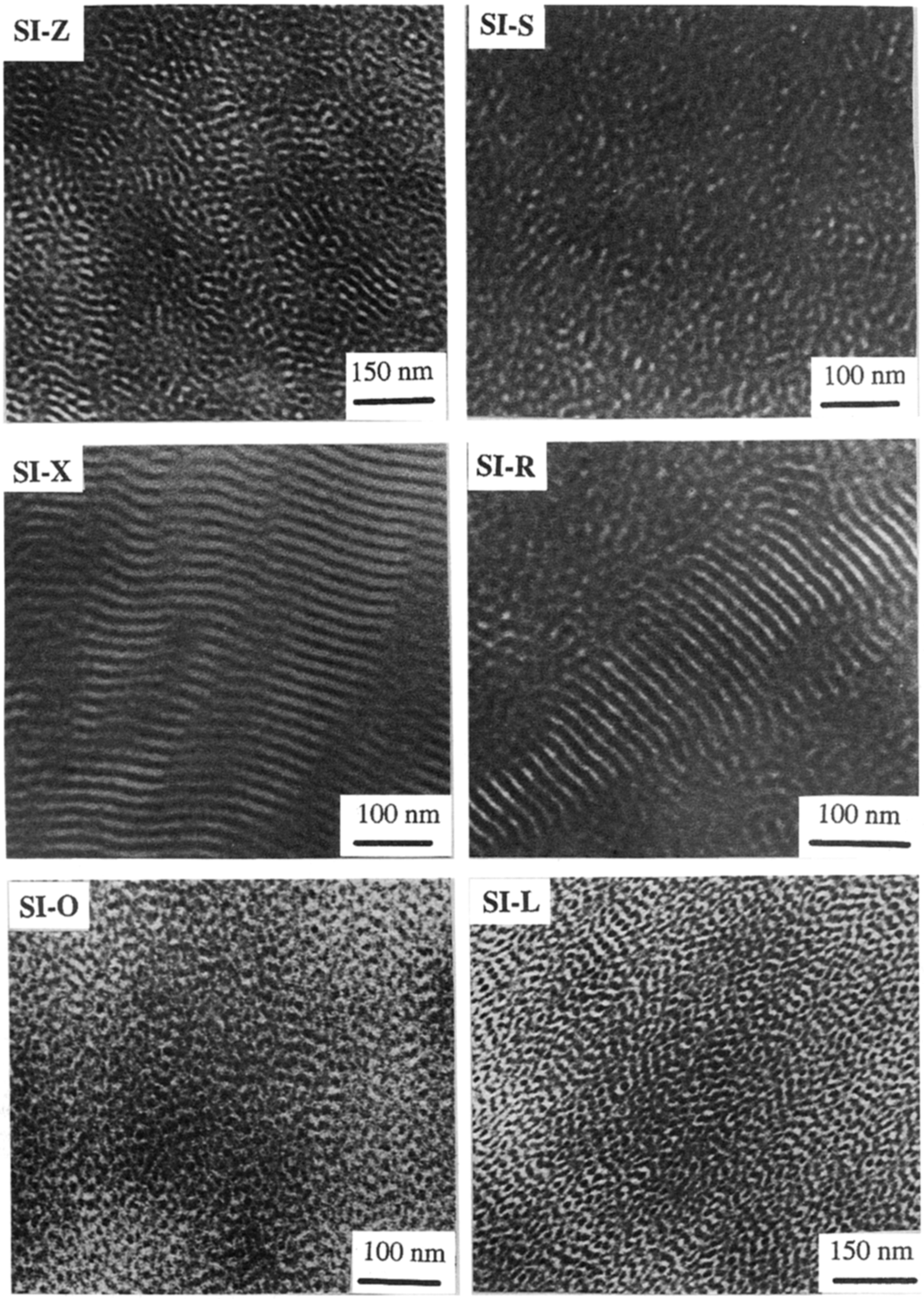

Figure 2. Transmission electron micrographs for the SI diblock copolymers synthesized in this study.

study. The following observations are worth noting in Figures 3–9. For SI-R (Figure 3) and SI-X (Figure 4), which have lamellar microdomains (see Figure 2), a precipitous drop in G' is observed at or near a certain critical temperature, and we tentatively conclude that the T_{ODT} for SI-R is ca. 95 °C and the T_{ODT} for SI-X is ca. 115 °C. In view of the fact that in the present study the temperature was increased with an increment of 3 °C, a much more precise determination of T_{ODT} was not possible. Nevertheless, Figures 3 and 4 demonstrate clearly that the storage modulus G' of an SI diblock copolymer decreases very abruptly at or near a certain critical temperature, suggesting that the ordered microdomains in an SI diblock copolymer disappear, giving rise to a disordered (i.e., homogeneous) state. On the other hand, in Figure 5 it is not easy to find a temperature at which the value of G' for the block copolymer SI-S drops precipitously. However, in Figure 5 we observe a large change in the slope of the plot at a temperature near 82 °C and, thus, we draw a line, admittedly arguable, through the data points as a visual aid. We tentatively conclude that the T_{ODT} for SI-S is ca. 82 °C. Similarly, in Figure 6 we observe that the plot of G' versus temperature for the block copolymer SI-Z shows a large change in the slope at a temperature near ca. 87 °C. Again, we draw a line,

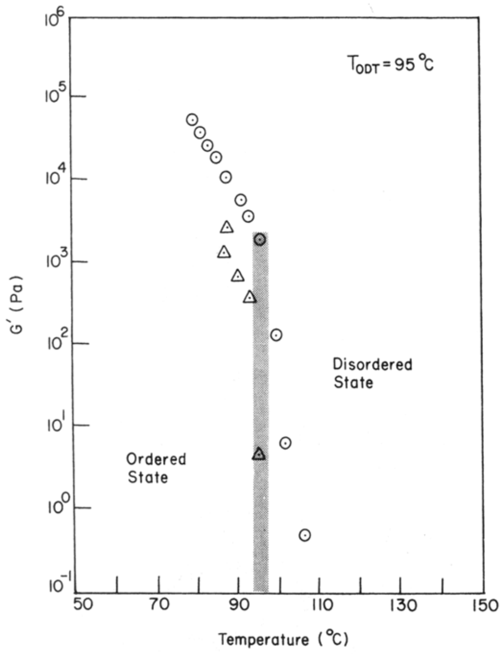

Figure 3. Variations of G' with temperature obtained at ω = 0.5 rad/s (⊙) and at ω = 0.01 rad/s (▵) for SI-R. The T_{ODT} for this block copolymer is determined to be ca. 95 °C, as determined by a sudden drop in G'.

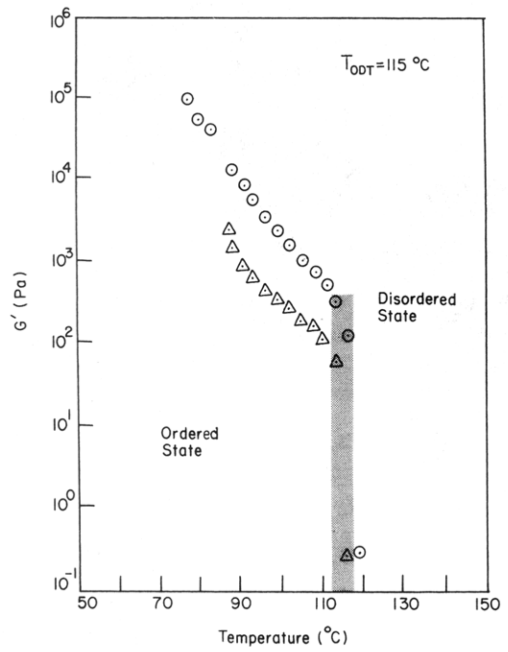

Figure 4. Variations of G' with temperature obtained at ω = 0.5 rad/s (⊙) and at ω = 0.01 rad/s (▵) for SI-X. The T_{ODT} for this block copolymer is determined to be ca. 115 °C, as determined by a sudden drop in G'.

admittedly arguable, through the data points as a visual aid. Thus we tentatively conclude that the T_{ODT} for SI–Z is ca. 87 °C. It should be remembered that SI-S has a volume fraction (*f*) of PS block of 0.372 and it has PS cylindrical microdomains in the PI matrix (see Figure 2). A comparison of Figures 3 and 4 with Figures 5 and 6 seems to indicate that the use of plots of G' versus temperature became *increasingly difficult* to determine the T_{ODT}s of the low molecular weight SI diblock copolymers as the value of f decreased from ca. 0.5.

Interestingly enough, in Figures 7–9 for the block copolymer SI-Q having cylindrical microdomains of PS in the PI matrix and for the block copolymers SI-O and SI-L having cylindrical microdomains of PI in the PS matrix, we do *not* observe an abrupt drop in storage modulus G' at or near a certain critical temperature. We thus conclude that it is *not* possible for us to determine the T_{ODT}s of these three SI diblock copolymers using information given in Figures 7–9. The possible reason(s) for the absence of a precipitous drop in G' at or near a certain critical temperature for SI-Q, SI-O, and SI-L will be given below after other types of rheological correlations are presented. It should be mentioned that previously Han and co-workers[31] made similar observations for polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS triblock) copolymers having *spherical* or *cylindrical* microdomains. We thus conclude that temperature sweep experiments in oscillatory shear flow mode are *not* effective to determine the T_{ODT} of the highly asymmetric, low molecular weight SI diblock

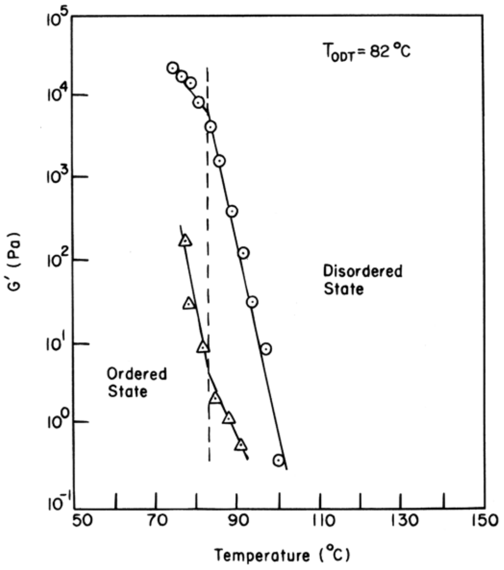

Figure 5. Variations of G' with temperature obtained at ω = 0.5 rad/s (⊙) and at ω = 0.01 rad/s (▵) for SI-S. No sudden drop in G' is discernible and thus it is *not* possible to determine the T_{ODT} of this block copolymer from this plot.

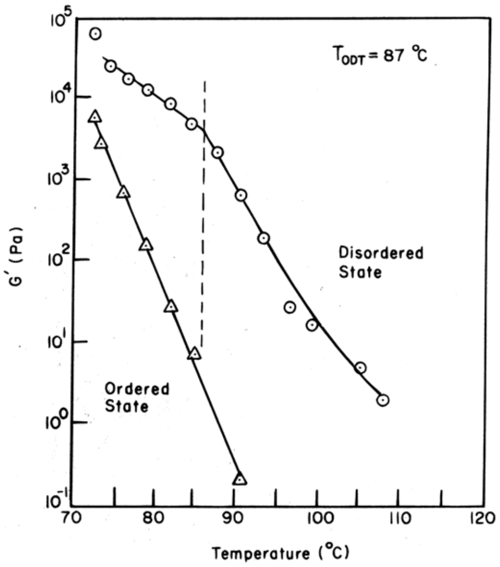

Figure 6. Variations of G' with temperature obtained at ω = 0.5 rad/s (⊙) and at ω = 0.01 rad/s (▵) for SI-Z. No sudden drop in G' is discernible and thus it is *not* possible to determine the T_{ODT} of this block copolymer from this plot.

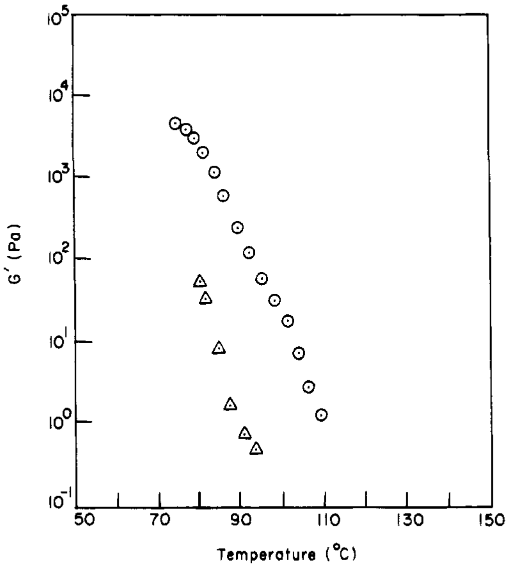

Figure 7. Variations of G' with temperature obtained at ω = 0.5 rad/s (⊙) and at ω = 0.01 rad/s (△) for SI-Q. No sudden drop in G' is discernible and thus it is *not* possible to determine the T_{ODT} of this block copolymer from this plot.

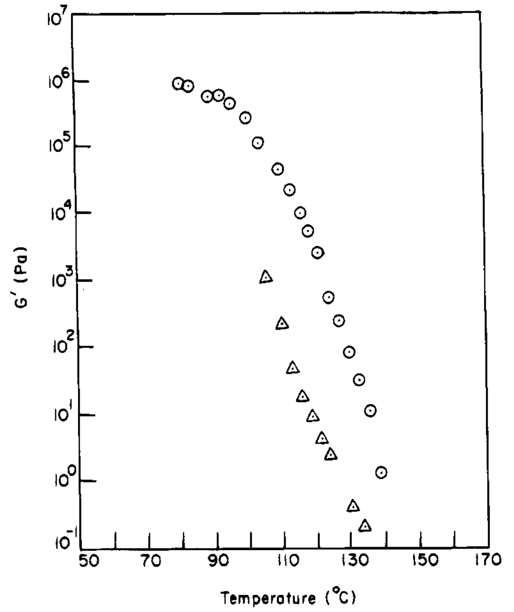

Figure 8. Variations of G' with temperature obtained at ω = 0.5 rad/s (⊙) and at ω = 0.01 rad/s (△) for SI-O. No sudden drop in G' is discernible and thus it is *not* possible to determine the T_{ODT} of this block copolymer from this plot.

copolymers (i.e., SI block copolymers having a value of f far away from 0.5) synthesized in this study.

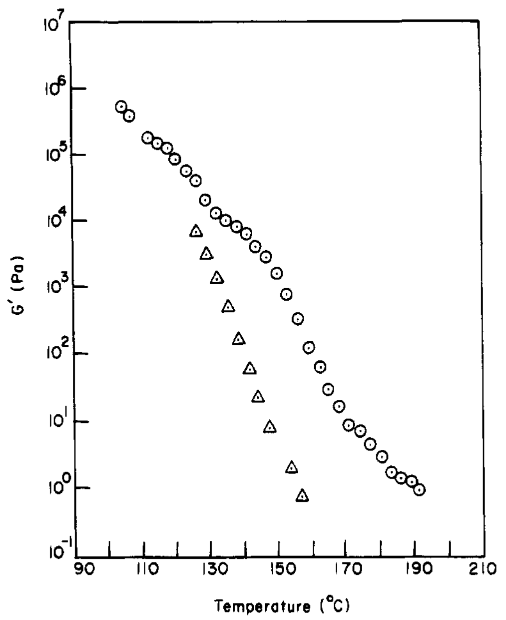

Figure 9. Variations of G' with temperature obtained at ω = 0.5 rad/s (⊙) and at ω = 0.01 rad/s (△) for SI-L. No sudden drop in G' is discernible and thus it is *not* possible to determine the T_{ODT} of this block copolymer from this plot.

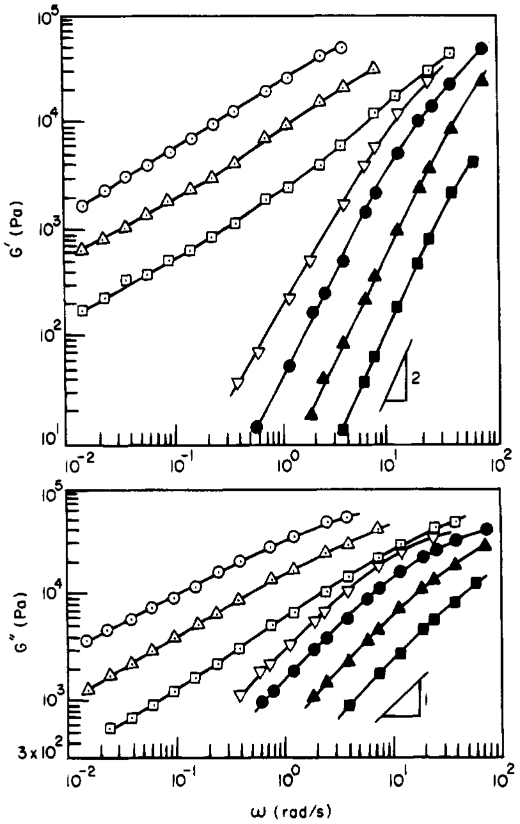

Figure 10. Plots of log G' versus log ω and log G'' versus log ω for SI-R at various temperatures: (⊙) 85 °C; (△) 90 °C; (⊡) 95 °C; (▽) 97 °C; (●) 100 °C; (▲) 105 °C; (■) 110 °C.

Determination of T_{ODT} for SI Diblock Copolymers Using Plots of log G' versus log ω. Below we present the experimental results of oscillatory shear flow measurements at various temperatures for the seven SI diblock copolymers synthesized in this study and then discuss their ODT. Figure 10 gives plots of log G' versus log ω and log G'' versus log ω for SI-R (f = 0.508) at temperatures of 85, 90, 95, 97, 100, 105, and 110 °C. The following observations are worth noting in the *terminal zone* of Figure 10: (1) at temperatures of 95 °C and below, the slope of the plots of log G' versus log ω and log G'' versus log ω is *about* 0.5. (2) At temperatures of 100 °C and above, the slope of the plots of log G' versus log ω is *about* 2, and the slope of the plots of log G'' versus log ω is *about* 1, typically observed for flexible homopolymers or random copolymers. Figure 10 suggests that the block copolymer SI-R reached the disordered state at temperatures of 100 °C and higher. (3) A sudden displacement is observed at 97 °C in the plots of log G' versus log ω, but *no* such sudden displacement is observed in the plots of log G'' versus log ω. This observation seems to indicate that G', which describes the elastic property, is much more sensitive to a change in phase morphology of the block copolymer

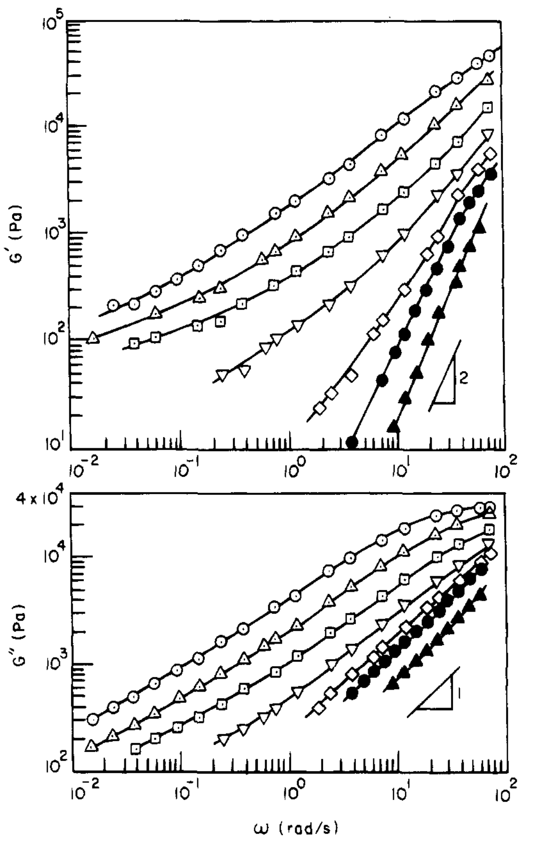

Figure 11. Plots of log G' versus log ω and log G'' versus log ω for SI-X at various temperatures: (⊙) 100 °C; (△) 105 °C; (⊡) 110 °C; (▽) 115 °C; (◇) 117 °C; (●) 120 °C; (▲) 125 °C.

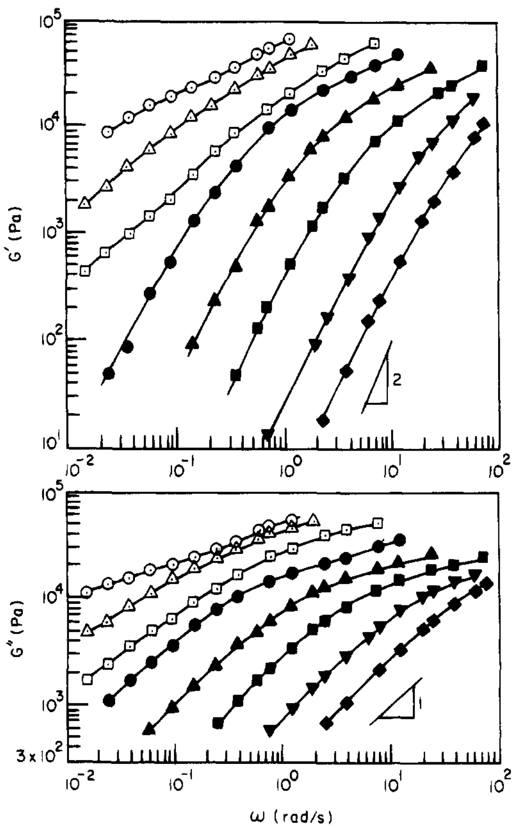

Figure 12. Plots of log G' versus log ω and log G'' versus log ω for SI-S at various temperatures: (⊙) 70 °C; (△) 72 °C; (⊡) 75 °C; (●) 80 °C; (▲) 85 °C; (■) 90 °C; (▼) 95 °C; (◆) 100 °C.

at a certain critical temperature than G'', which describes the viscous property.[26,29,30] Note that the temperature (97 °C) at which the sudden displacement of the log G' versus log ω plot occurred in Figure 10 is very close to 95 °C at which the value of G' dropped abruptly in Figure 3.

Figure 11 gives plots of log G' versus log ω and log G'' versus log ω for SI-X ($f = 0.461$) at temperatures of 100, 105, 110, 115, 117, 120, and 125 °C, showing that there is a rather *gradual decrease* in G' as the temperature increased from 100 to 115 °C and then a larger decrease in G' as the temperature increased further to 117 °C. But the slope of the plot of log G' versus log ω becomes 2 at temperatures of 120 °C and higher. We can thus tentatively conclude from Figure 11 that the T_{ODT} of SI-X is ca. 120 °C. This value is reasonably close to that obtained from the plot of G' versus temperature (see Figure 4). It should be noted in Figure 11 that as the temperature increased from 100 to 125 °C, the shape of the log G'' versus log ω plots changes very mildly, as compared to the shape of the log G' versus log ω plots.

Figure 12 gives plots of log G' versus log ω and log G'' versus log ω for SI-S ($f = 0.372$) at temperatures of 70, 72, 75, 80, 85, 90, 95, and 100 °C, showing that there is a rather *abrupt de*crease in G' as the temperature increased from 75 to 80 °C, at which the slope of the log G' versus log ω plots becomes 2. Notice in Figure 12 that there is hardly any discernible change in the shape of the log G'' versus log ω plots as the temperature increased from 75 to 80 °C. This reinforces, once again, the point made above that the dynamic loss modulus G'' is much less sensitive to a change in phase morphology of the block copolymer, as compared to the dynamic storage modulus G'. We can thus tentatively conclude from Figure 12 that the T_{ODT} of SI-S is ca. 80 °C. This value is very close to that obtained from the plots of G' versus temperature (see Figure 5).

As the volume fraction (f) of PS microdomains in the SI diblock copolymer is decreased to 0.303 (SI-Z) and further to 0.186 (SI-Q), as can be seen in Figures 13 and 14, we find it *increasingly difficult* to discern the temperature dependence of the shape of the log G' versus log ω plots. Specifically, we find from Figure 14 that over the entire range of temperatures investigated ranging from 75 to 120 °C, plots of log G' versus log ω for the block copolymer SI-Q exhibit the slope of 2 and plots of log G'' versus log ω exhibit the slope of 1, typically observed in flexible homopolymers in the molten state. That is, SI-Q exhibits "liquidlike" behavior over the entire range of temperatures investigated from 75 to 120 °C, and thus we conclude that it is *not* possible for us to determine the T_{ODT} of this block copolymer using log G' versus log ω plots. The same conclusion can be drawn from Figure 15 for the block copolymer SI-O and from Figure 16 for the block copolymer SI-L, both having PI cylindrical microdomains in the PS matrix (see Figure 2). It appears that the determination of T_{ODT}, via log G' versus log ω plots, of low molecular weight SI diblock copolymers becomes increasingly difficult as the volume fraction of microdomains moves farther away from 0.5 (i.e., as a block copolymer becomes highly asymmetric).

It should be mentioned that the conclusions drawn from Figures 13–16 about the *absence* of a sudden displacement in the plot of log G' versus log ω with a slope approaching 2 at or near a certain critical temperature are entirely consistent with the conclusions drawn from Figures 7–9 about the *absence* of a precipitous drop in G' at or near a certain critical temperature. Below we shall offer an explanation for this after

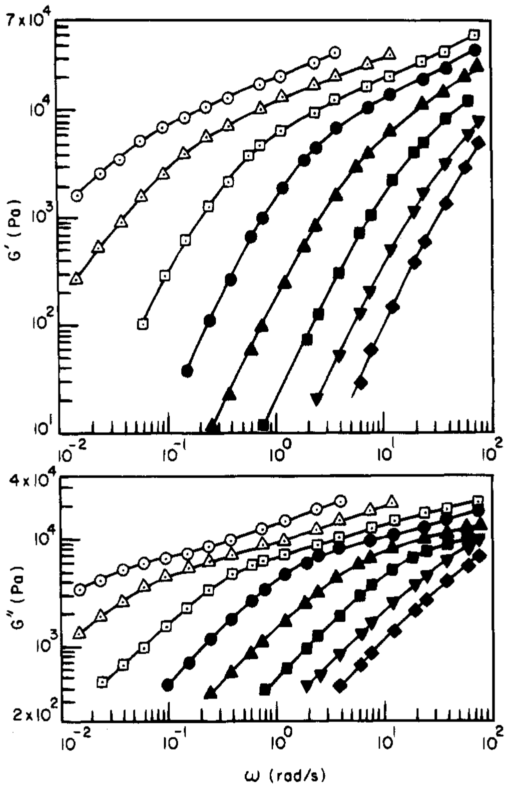

Figure 13. Plots of log G' versus log ω and log G'' versus log ω for SI-Z at various temperatures: (⊙) 75 °C; (△) 80 °C; (⊡) 85 °C; (●) 90 °C; (▲) 95 °C; (■) 100 °C; (▼) 105 °C; (◆) 110 °C.

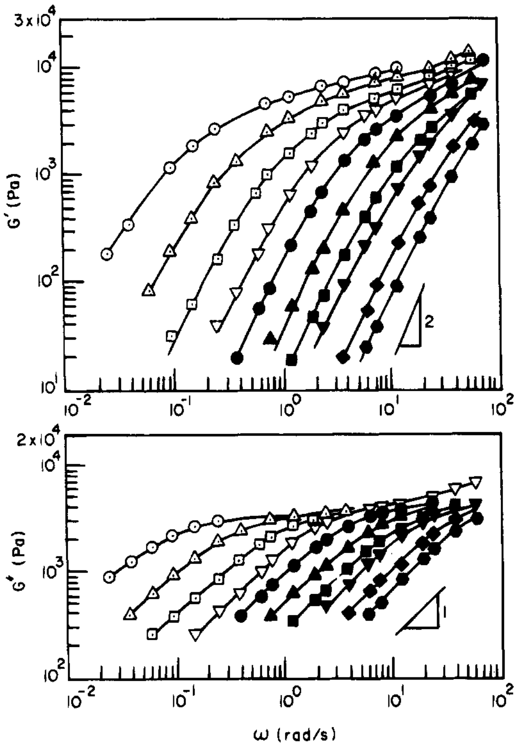

Figure 14. Plots of log G' versus log ω and log G'' versus log ω for SI-Q at various temperatures: (⊙) 75 °C; (△) 80 °C; (⊡) 85 °C; (▽) 90 °C; (●) 95 °C; (▲) 100 °C; (■) 105 °C; (▼) 110 °C; (◆) 115 °C; (⬣) 120 °C.

presenting other ways of interpreting the oscillatory shear flow experiments.

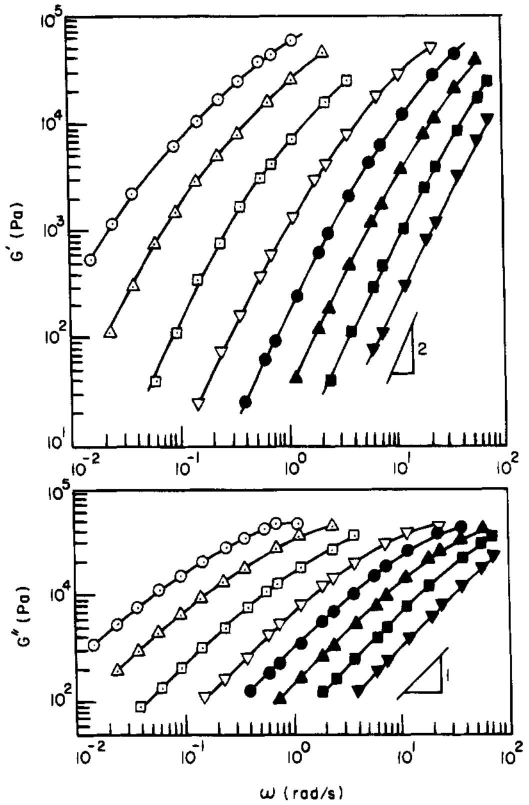

Figure 15. Plots of log G' versus log ω and log G'' versus log ω for SI-O at various temperatures: (⊙) 110 °C; (△) 115 °C; (⊡) 120 °C; (▽) 125 °C; (●) 130 °C; (▲) 135 °C; (■) 140 °C; (▼) 145 °C.

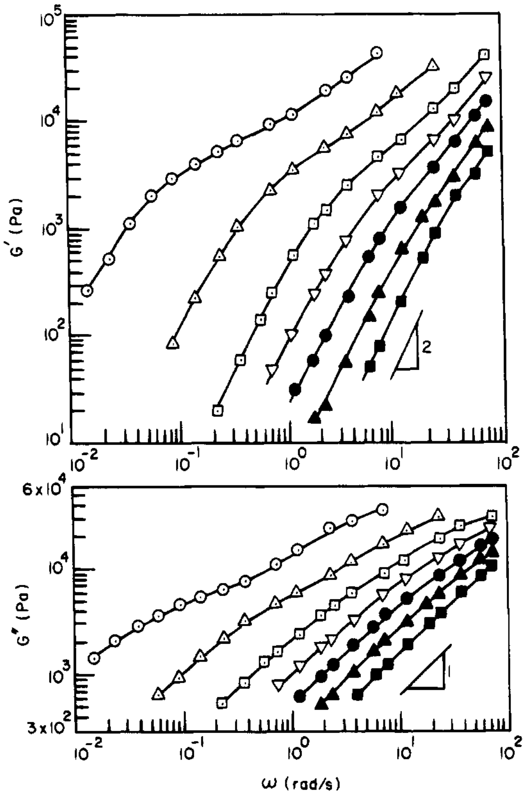

Figure 16. Plots of log G' versus log ω and log G'' versus log ω for SI-L at various temperatures: (⊙) 140 °C; (△) 150 °C; (⊡) 160 °C; (▽) 165 °C; (●) 170 °C; (▲) 175 °C; (■) 180 °C.

Determination of T_{ODT} for SI Diblock Copolymers Using Plots of log G' versus log G''. Using the rheological data presented in Figures 10–16, below we present plots of log G' versus log G'' for the seven SI diblock copolymers synthesized in this study. Figure 17 gives log G' versus log G'' plots for the block

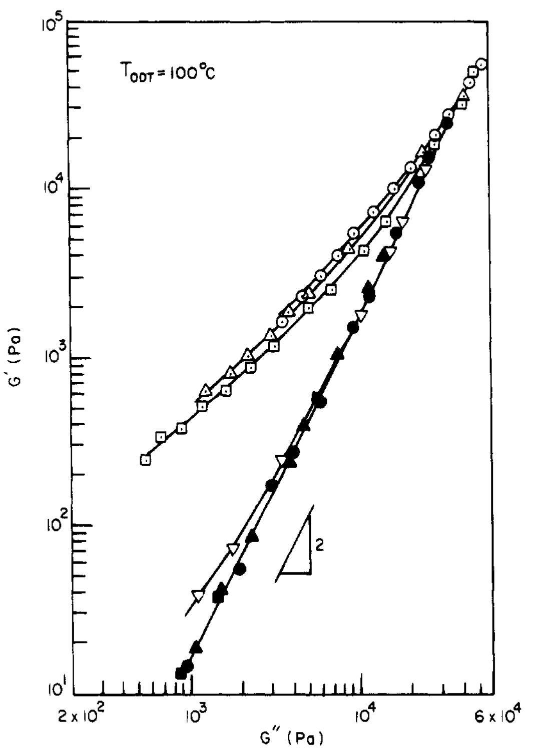

Figure 17. Plots of log G' versus log G'' for SI-R at various temperatures: (⊙) 85 °C; (△) 90 °C; (⊡) 95 °C; (▽) 97 °C; (●) 100 °C; (▲) 105 °C; (■) 110 °C. The T_{ODT} of this block copolymer is determined to be ca. 100 °C, which is the lowest temperature at and above which the plots become independent of temperature.

copolymer SI-R at temperatures of 85, 90, 95, 97, 100, 105, and 110 °C. It can be seen in Figure 17 that plots of log G' versus log G'' become virtually independent of temperature at 100 °C and higher. It is of particular interest to note in Figure 17 that as the temperature is increased from 95 to 97 °C, a large displacement is seen in the log G' versus log G'' plot, still maintaining a slight curvature, while at temperatures of 100 °C and above, the slope of the log G' versus log G'' plots is *about* 2, a value which is typical for flexible homopolymers or random copolymers in the *terminal* zone. Following the criterion suggested by Han and co-workers,[29–31] we thus conclude that the T_{ODT} for SI–R is ca. 100 °C. This value is about 5 °C higher than the one determined from the plot of G' versus temperature, given in Figure 3. It should be remembered that the temperature sweep experiment, the results of which are displayed in Figure 3, was conducted with an increment of 3 °C, and thus it is difficult to claim high accuracy for the T_{ODT} in such an experiment. It is fair to state that the agreement in T_{ODT} between the two types of experiments is reasonable.

Figure 18 gives plots of log G' versus log G'' for the block copolymer SI-X at temperatures of 100, 105, 110, 115, 117, 120, and 125 °C. It is of interest to observe in Figure 18 that the slope of the log G' versus log G'' plots increases gradually as the temperature is increased from 100 to 120 °C, at which the slope becomes *about* 2, leading us to conclude that the T_{ODT} of SI-X is ca. 120 °C.

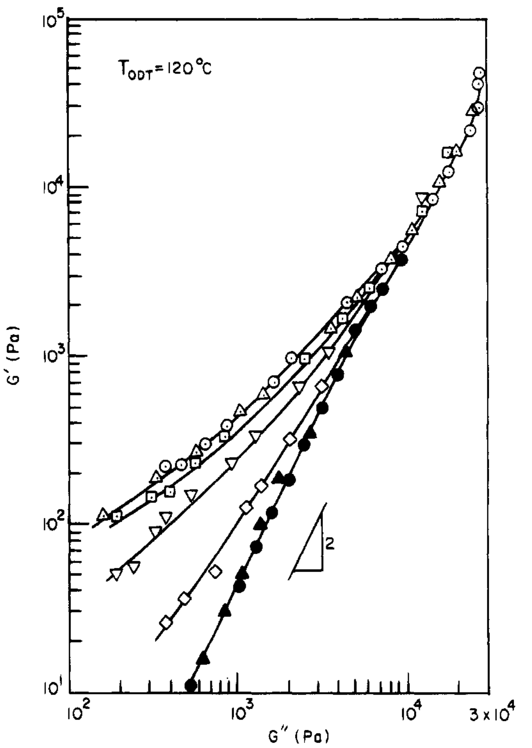

Figure 18. Plots of log G' versus log G'' for SI-X at various temperatures: (⊙) 100 °C; (△) 105 °C; (⊡) 110 °C; (▽) 115 °C; (◇) 117 °C; (●) 120 °C; (▲) 125 °C. The T_{ODT} of this block copolymer is determined to be ca. 120 °C.

A comparison of Figure 17 for SI-R with Figure 18 for SI-X shows the distinct difference as described above. It should be noted that according to Figure 2 both SI-R and SI-X have lamellar microdomains. Note that (i) at room temperature SI-R has $f = 0.508$ and SI-X has $f = 0.461$, (ii) at the critical temperature (i.e., at the respective T_{ODT}s) SI-R has $f = 0.505$ and SI-X has $f = 0.458$, and (iii) the molecular weight of SI-X is slightly higher (ca. 10%) than that of SI-R. Whether or not the subtle difference observed in the temperature dependence of the log G' versus log G'' plots between SI-R and SI-X before attaining the disordered state (compare Figure 17 with Figure 18) may be attributable to the difference in the value of f and/or N will be discussed later after more experimental results are presented for other SI diblock copolymers synthesized in this study.

Figure 19 gives plots of log G' versus log G'' for the block copolymer SI-S at temperatures of 70, 72, 75, 80, 85, 90, 95, and 100 °C, from which we can conclude that the T_{ODT} for SI-S is ca. 80 °C. Owing to the fact that an increment of 5 °C was chosen in the temperature interval between 75 and 80 °C, we have no way of knowing the exact value of T_{ODT} between 75 and 80 °C for SI-S. It is worth pointing out that the value of T_{ODT} = 80 °C is very close to 82 °C, which was determined from the temperature sweep experiment (see Figure 5). It should be remembered from Figure 2 that SI-S has bicontinuous microdomains of PS with a considerable distortion having the appearance locally of lamellar catenoids. Such a unique microdomain structure might be responsible (i) for the somewhat unusual shape of the log G' versus log G'' plots, which show a crossover at a large value of G'' (compare Figure 19 for SI-S with Figure 17 for SI-R and with Figure 18 for SI-X), and (ii) perhaps, also, for the *absence* of a precipitous drop in G' at a certain critical temperature during the temperature sweep experiment (compare Figure 5 for SI-S with Figure 3 for SI-R or with Figure 4 for SI-X).

Figure 20 gives plots of log G' versus log G'' for the block copolymer SI-Z at temperatures of 75, 80, 85, 90, 95, 100, 105, and 110 °C, from which we can conclude

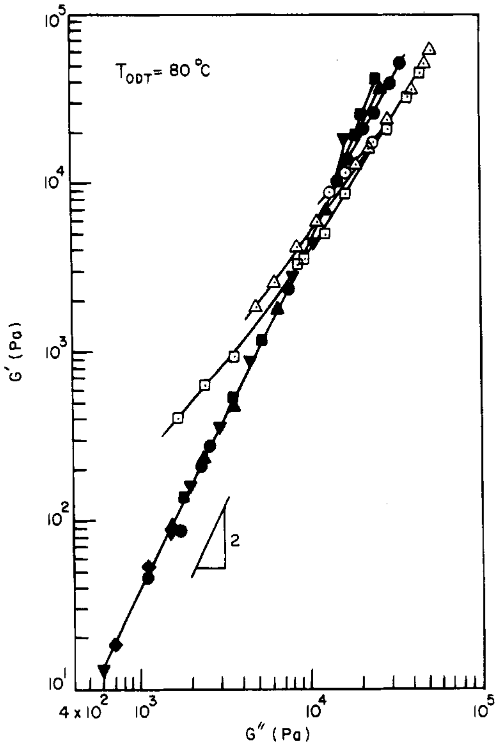

Figure 19. Plots of log G' versus log G'' for SI-S at various temperatures: (⊙) 70 °C; (△) 72 °C; (⊡) 75 °C; (●) 80 °C; (▲) 85 °C; (■) 90 °C; (▼) 95 °C; (◆) 100 °C. The T_{ODT} of this block copolymer is determined to be ca. 80 °C.

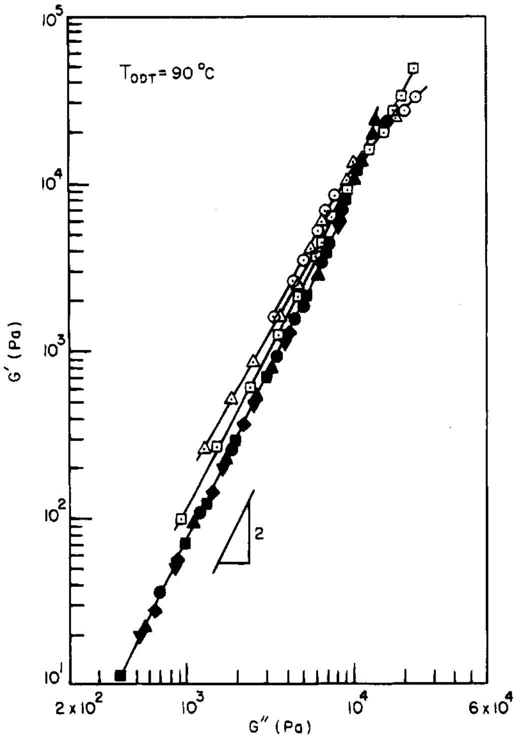

Figure 20. Plots of log G' versus log G'' for SI-Z at various temperatures: (⊙) 75 °C; (△) 80 °C; (⊡) 85 °C; (●) 90 °C; (▲) 95 °C; (■) 100 °C; (▼) 105 °C; (◆) 110 °C. The T_{ODT} of this block copolymer is determined to be ca. 90 °C.

that the T_{ODT} for SI-Z is ca. 90 °C. This value is very close to 87 °C, which was determined from the temperature sweep experiment (see Figure 6). It should be remembered that Si-Z has $f = 0.303$, and it has PS cylindrical microdomains in the PI matrix. Notice in Figure 20, however, that in the *terminal* region there is a rather *gradual* increase in the slope of the log G' versus log G'' plots, giving rise to a constant slope of 2 at temperatures of 90 °C and above. The shape of the log G' versus log G'' plots at temperatures below 90 °C, given in Figure 20, is quite different from that observed in Figure 17 for SI-R, in Figure 18 for SI-X, and in Figure 19 for SI-S. Notice in Figure 20 that the log G' versus log G'' plots begin to be independent of temperature at 90 °C and remain that way as the temperature is increased to 95, 100, 105, and 110 °C.

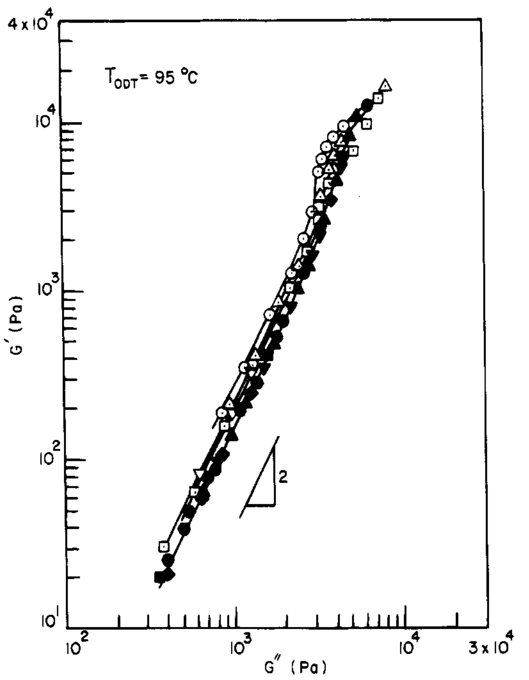

Figure 21. Plots of log G' versus log G'' for SI-Q at various temperatures: (⊙) 75 °C; (△) 80 °C; (⊡) 85 °C; (▽) 90 °C; (●) 95 °C; (▲) 100 °C; (■) 105 °C; (▼) 110 °C; (◆) 115 °C; (●) 120 °C. The T_{ODT} of this block copolymer is determined to be ca. 95 °C.

Figure 21 gives plots of log G' versus log G'' for the block copolymer SI-Q at temperatures of 75, 80, 85, 90, 95, 100, 105, 110, 115, and 120 °C. It can be seen in Figure 21 that plots of log G' versus log G'' have a slope of 2 over the entire range of temperatures investigated. Although in Figure 21 the slopes of the log G' versus log G'' plots are *virtually* indistinguishable for different curves, we observe that the data points lie on a single curve at temperatures of 95 °C and higher. Thus we can conclude from Figure 21 that the T_{ODT} for SI-Q is ca. 95 °C. What is unusual in Figure 21 is that the log G' versus log G'' plots at temperatures 75, 80, 85, and 90 °C have a slope of about 2, but they are displaced upward from the other curve (having filled symbols) on which all the data points at temperatures of 95 °C and higher lie together. Previously, similar observations were noted by Bates,[26] who investigated the ODT of 1,2-PB-*block*-1,4-PB copolymers, and by Rosedale and Bates,[27] who investigated the ODT of PEP-*block*-PEE copolymers. According to them, in the plots of log G' versus log G'', when data points of a block copolymer at temperatures below the *true* T_{ODT} lie on the curve (or curves) parallel to the curve which represents the *true* disordered state (i.e., having the slope of 2), it signifies that there exist composition fluctuations at or near the critical temperature. Such an interpretation is very reasonable in view of the fact that only "liquid-like" materials are expected to have a slope of 2 in the *terminal* region of log G' versus log G'' plots.

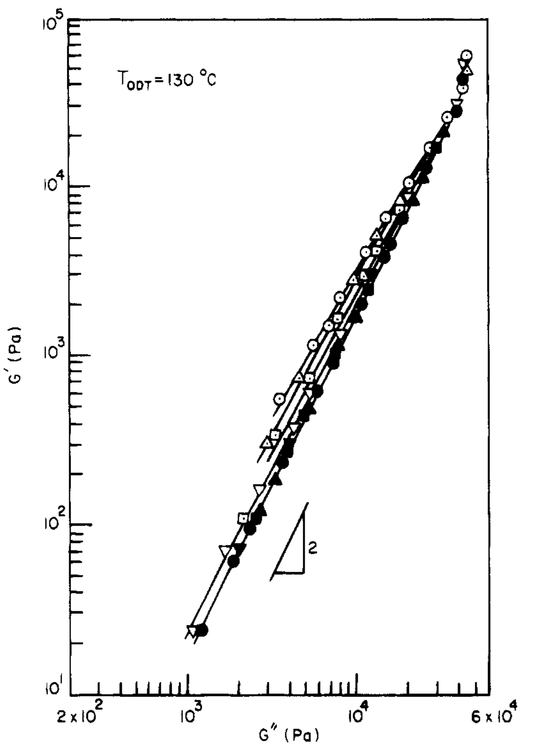

Figure 22. Plots of log G' versus log G'' for SI-O at various temperatures: (⊙) 110 °C; (△) 115 °C; (⊡) 120 °C; (▽) 125 °C; (●) 130 °C; (▲) 135 °C; (■) 140 °C; (▼) 145 °C. The T_{ODT} of this block copolymer is determined to be ca. 130 °C.

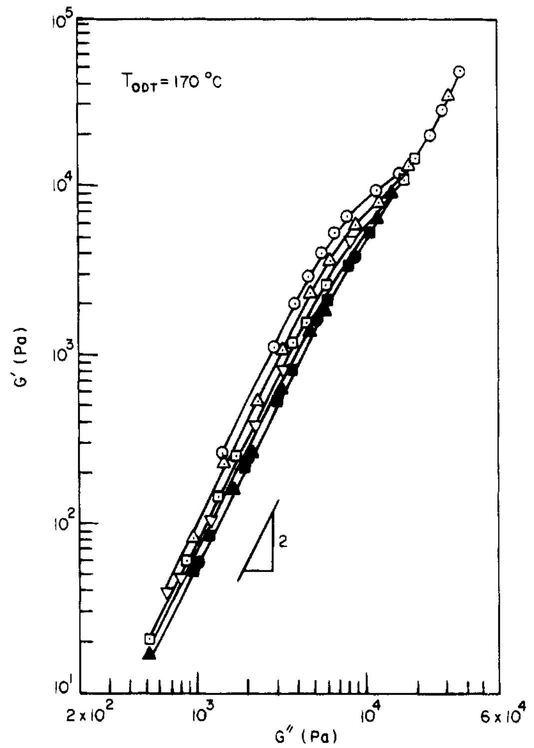

Figure 23. Plots of log G' versus log G'' for SI-L at various temperatures: (⊙) 140 °C; (△) 150 °C; (⊡) 160 °C; (▽) 165 °C; (●) 170 °C; (▲) 175 °C; (■) 180 °C. The T_{ODT} of this block copolymer is determined to be ca. 170 °C.

In reference to Figure 21, one is tempted to ascribe the parallel curves at 75, 80, 85, and 90 °C to composition fluctuations in the disordered state near the T_{ODT}, which in this case is ca. 95 °C, of the block copolymer SI-Q. This interpretation then suggests that the block copolymer SI-Q is in the disordered state at $T \geq 75$ °C and has the effect of composition fluctuations over 20 °C. If this is correct, a serious question can be raised as to why then other SI diblock copolymers (i.e., SI-R, SI-X, and SI-S) investigated in this study do *not* show discernible evidence of composition fluctuations (see Figures 17–19) near T_{ODT}. To resolve this seemingly inconsistent interpretation of the experimental results for the block copolymer SI-Q on the one hand and for other SI diblock copolymers (SI-R, SI-X, and SI-S) on the other hand, we must address the following questions. (1) Is the extent of composition fluctuations of low molecular weight SI diblock copolymers near the critical temperature strongly dependent upon block copolymer composition? (2) To what extent do composition fluctuations of an SI diblock copolymer depend on its molecular weight (or degree of polymerization)? (3) Can there be other explanation(s) as to why the log G' versus log G'' plots in Figure 21 for SI-Q have the slope of 2 at temperatures below its T_{ODT}? Below we shall attempt to answer these questions after presenting the experimental results for two other SI diblock copolymers, SI-O and SI-L.

Figure 22 gives plots of log G' versus log G'' for the block copolymer SI-O at temperatures of 110, 115, 120, 125, 130, 135, 140, and 145 °C, from which we determine the T_{ODT} of SI-O to be ca. 130 °C. Figure 23 gives plots of log G' versus log G'' for the block copolymer SI-L at temperatures of 140, 150, 160, 165, 170, 175, and 180 °C, from which we determine the T_{ODT} of SI-L to be ca. 170 °C. It should be remembered from Figure 2 that both SI-O and SI-L have PI cylindrical microdomains in the PS matrix. It is of interest to observe a similarity in the temperature dependence of the log G' versus log G'' plots at temperatures below the T_{ODT} among SI-Q (Figure 21), SI-O (Figure 22), and SI-L (Figure 23). In other words, for all three block copolymers (SI-Q, SI-O, and SI-L) plots of log G' versus log G'' show the slope of 2 at temperatures of 20–30 °C below the T_{ODT}. There is, also, another common feature in these three SI diblock copolymers, namely, the dispersed microdomains occupy a minor fraction of the whole sample space; specifically, (i) SI-Q has 21.2 wt % of PS cylindrical microdomains in the PI matrix, (ii) SI-O has 21.2 wt % of PI cylindrical microdomains in the PS matrix, and (iii) SI-L has 16.7 wt % of PI cylindrical microdomains in the PS matrix, if we assume complete segregation of each block chain in the respective microdomains.

Determination of T_{ODT} for SI Diblock Copolymers Using Plots of log $|\eta^*|$ versus log ω. Figure 24 gives plots of log $|\eta^*|$ versus log ω for SI-X at various temperatures, where values of $|\eta^*|$ were calculated using the expression $|\eta^*| = [(G'/\omega)^2 + (G''/\omega)^2]^{1/2}$. Similar plots are given in Figure 25 for SI-S, in Figure 26 for SI-Q, and in Figure 27 for SI-L. It can be seen in Figures 24–27 that at temperatures below a certain critical value, plots of log $|\eta^*|$ versus log ω at low values of ω exhibit *yield* behavior, commonly observed in concentrated suspensions or in highly filled molten polymers. Earlier, Chung and Gale[42] reported that plots of log η' versus log ω, where η' is the dynamic viscosity defined by $\eta' = G''(\omega)/\omega$, for a polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS triblock) copolymer exhibited *yield* behavior at temperatures below a certain *critical value*, but Newtonian behavior as the temperature increased above the critical value. They suggested that such behavior may be regarded as an indication of phase transition from an ordered state to the disordered state.

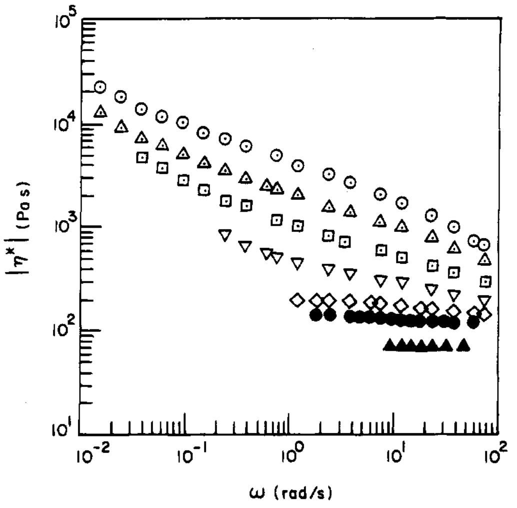

Figure 24. Plots of log $|\eta^*|$ versus log ω for SI-X at various temperatures: (⊙) 100 °C; (△) 105 °C; (⊡) 110 °C; (▽) 115 °C; (◇) 117 °C; (●) 120 °C; (▲) 125 °C.

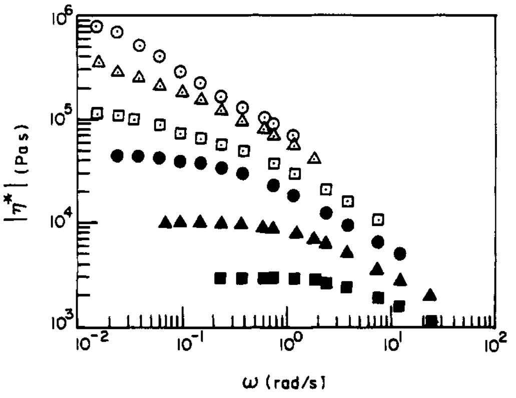

Figure 25. Plots of log $|\eta^*|$ versus log ω for SI-S at various temperatures: (⊙) 70 °C; (△) 72 °C; (⊡) 75 °C; (●) 80 °C; (▲) 85 °C; (■) 90 °C.

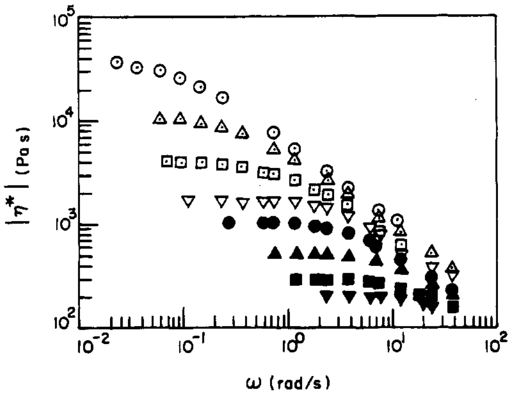

Figure 26. Plots of log $|\eta^*|$ versus log ω for SI-Q at various temperatures: (⊙) 75 °C; (△) 80 °C; (⊡) 85 °C; (▽) 90 °C; (●) 95 °C; (▲) 100 °C; (■) 105 °C; (▼) 110 °C.

By applying this criterion to Figures 24–27, we make the following observations: (i) $T_{\mathrm{ODT}} = 117$ °C for SI-X, (ii) $T_{\mathrm{ODT}} = 75$–80 °C for SI-S, (iii) $T_{\mathrm{ODT}} = 80$ °C for SI-Q, and (iv) $T_{\mathrm{ODT}} = 150$ °C for SI-L.

Let us now compare the values of T_{ODT} determined from the log $|\eta^*|$ versus log ω plots (see Figures 24–27) with those determined from the log G' versus log G'' plots (see Figures 18, 19, 21, and 23). We observe that both types of plots give, within experimental uncertainties, essentially the same value of T_{ODT} for SI-X and SI-S, but the values of T_{ODT} determined from the log $|\eta^*|$ versus log ω plots are 15–20 °C lower than those determined from the log G' versus log G'' plots for SI-Q and SI-L. It should be noted from Table 1 that the volume fractions (f) of these block copolymers are (i) $f = 0.461$ for SI-X, (ii) $f = 0.372$ for SI-S, (iii) $f = 0.186$ for SI-Q, and (iv) $f = 0.811$ for SI-L. We are thus led to conclude that as the volume fraction of PS (or PI) microdomains in an SI diblock copolymer deviates more from 0.5 (i.e., as an SI diblock copolymer becomes highly asymmetric), the values of T_{ODT} determined from log $|\eta^*|$ versus log ω plots become less accurate. This is not surprising in that (a) the values of $|\eta^*|$ are determined from both G' and G'', (b) at a critical temperature the value of G' decreases much more abruptly than the value of G'' in SI-X (see Figure 11) and also in SI-S (see Figure 12), and (c) the values of both G' and G'' decrease gradually with increasing temperature in SI-Q (see Figure 14) and also in SI-L (see Figure 16). It should be remembered from Figures 7 and 9 that there was *no* abrupt change in the value of G' during the temperature sweep experiments for SI-Q and SI-L. Therefore we conclude that use of log $|\eta^*|$ versus log ω plots is *not* effective to determine the T_{ODT} of highly *asymmetric* block copolymers.

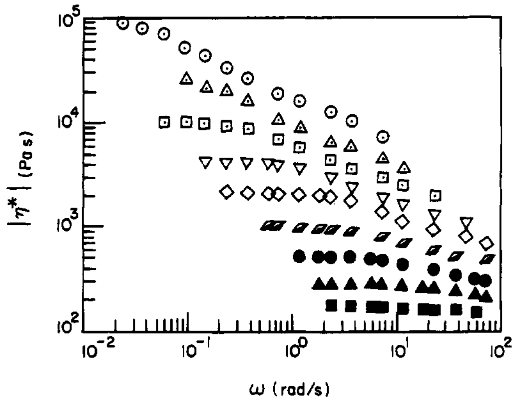

Figure 27. Plots of log $|\eta^*|$ versus log ω for SI-L at various temperatures: (⊙) 140 °C; (△) 145 °C; (⊡) 150 °C; (▽) 155 °C; (◇) 160 °C; (◪) 165 °C; (●) 170 °C; (▲) 175 °C; (■) 180 °C.

It should be pointed out that the use of log η' versus log ω plots would give a far less accurate determination of T_{ODT} than the use of log $|\eta^*|$ versus log ω plots, because (i) $|\eta^*|$ makes use of both G' and G'' while η' makes use of only G'', and (ii) G'' is far less sensitive to temperature than G' is (see Figures 10–16).

Discussion

Failure of Time–Temperature Superposition. Readers might wonder why we have *not* applied time–temperature superposition to the log G' versus log ω plots and log G'' versus log ω plots, given in Figures 10–16, whereas a number of other investigators[22–28,42,43] have applied time–temperature superposition to block copolymers. As pointed out earlier by Tschoegl et al.[44–46] and more recently by Han et al.,[29–31] the use of time–temperature superposition to thermorheologically complex block copolymers is *not* warranted. That is, the choice of a particular temperature in the ordered state (or in the disordered state) as a reference temperature to empirically shift the rheological data of a microphase-separated block copolymer which were obtained at other temperatures is *not* appropriate, because, rheologically speaking, a microphase-separated block copolymer at each temperature must be regarded as being a diffferent material. It should be noted that the solubility between the two blocks in a given block copolymer (e.g., between the PS phase and the PI phase in an SI diblock copolymer) increases with increasing temperature before reaching its T_{ODT}.

As pointed out recently by Han and Kim,[41] log G' versus log G'' plots must first exhibit a temperature independence and then the slope of such plots in the *terminal region* must be 2 (see eqs 1 and 2) before time–temperature superposition is applied to any polymer system. As shown above (see Figures 17–23), to obtain the T_{ODT} of a block copolymer, one can simply prepare log G' versus log G'' plots, without having to manipulate experimentally obtained log G' versus log ω plots and log G'' versus log ω plots to obtain reduced plots. In other words, insofar as determining the T_{ODT} of a block copolymer is concerned, there is no need for one to obtain reduced plots, log G' versus log $a_T\omega$ plots and log G'' versus log $a_T\omega$ plots, by empirically finding a temperature-dependent shift factor a_T with choice of a particular temperature at the ordered state (or at a disordered state) as a reference temperature (i.e., by shifting log G' versus log ω plots and log G'' versus log ω plots with reference to an arbitrarily chosen temperature).

In the literature, log G' versus log G'' plots are often referred to as modified Cole–Cole plots. It should be emphasized that log G' versus log G'' plots for polymeric liquids have *no* relation with an empirical correlation, a Cole–Cole plot, simply because logarithmic coordinates are employed. As shown earlier by Han et al.[40,41] (also see eqs 1 and 2), log G' versus log G'' plots for polymeric liquids have a basis in molecular viscoelasticity theory, and thus the two are *not* related to each other. We might add that log G' versus log G'' plots have also been used very effectively to distinguish between an isotropic state and an anisotropic state in a thermotropic liquid-crystalline polymer and thus to determine the isotropization temperature.[47,48]

Possibility of Having Grain-Boundary Defects Continuous in Three-Dimensional Space in Low Molecular Weight SI Diblock Copolymers with $f < 0.2$ or $f > 0.8$. What seems to be very clear from the observations made above is that as the value of f moves farther away from 0.5, it becomes increasingly difficult for us to discern (a) a precipitous drop in G' at a certain critical temperature, using a temperature sweep experiment, in the plot of G' versus temperature (see Figures 3–9), (b) a sudden displacement at a certain critical temperature, using a frequency sweep experiment, in the log G' versus log ω plot with a slope approaching 2 (see Figures 10–16), and (c) a precipitous displacement at a certain critical temperature, using a frequency sweep experiment, in the plot of log G' versus log G'' with a slope approaching 2 (see Figures 17–23). In this study we have learned that using the first two rheological methods, it was not possible for us to determine the T_{ODT}s of low molecular weight SI diblock copolymers when the weight fraction of one of the microdomains in an SI diblock copolymer, regardless of whether there are PS microdomains in the PI matrix or PI microdomains in the PS matrix, was decreased to about 20 wt % or less. However, using the third rheological method, we were able to determine the T_{ODT}s for the same SI diblock copolymers including those having about 20 wt % or less of microdomains. We found that when the amount of microdomains is about 20 wt % or less, a block copolymer exhibits "liquidlike" rheological behavior at temperatures below its T_{ODT} (i.e., the slope of the log G' versus log G'' plots is *virtually* equal to 2) with a larger storage modulus than at temperatures above its T_{ODT} (i.e., in the disordered state).

We speculate that as the temperature of a microphase-separated low molecular weight SI diblock copolymer approaches its critical temperature T_{ODT} on the low-temperature side, the volume fraction of the grain-boundary region, which contains the microdomains but whose spatial order is destroyed, would increase and the modulus of the ordered regions would decrease, giving rise to decreased modulus levels for G' and G''. If the systems can achieve true thermodynamic equilibrium, they will not have any defects in their spatial order, so that they would exhibit soft solidlike rheological behavior (e.g., $G', G'' \sim \omega^n$, with $n \cong 0.5$). In reality, they may have defectes which are continuous in three-dimensional space, and such defects would control the low-frequency rheological behavior, giving rise to the liquidlike behavior (e.g., $G' \sim \omega^2$ and $G'' \sim \omega$) even though there exist microdomains and hence the systems are in an ordered state. The modulus levels would depend on the volume fraction of defects and moduli of the ordered regions within the grains and of the grain-boundary defects and hence on temperature.

Using SAXS, we confirmed that the "*apparent*" liquidlike behavior at low values of ω, observed in Figures 20–23 for SI-Z, SI-Q, and SI-L, was definitely not due *to the effect of the critical concentration fluctuations* in the disordered state near the ODT, because SAXS taken in situ at $T < T_{\mathrm{ODT}}$ showed the cylindrical microdomains. Moreover, if this is due to the effect of the critical thermal concentrations in the disordered state, the rheological properties should not change with time upon annealing in a particular temperature range where the "*apparent*" liquidlike rheological behavior is observed. However, we found that, upon annealing, the storage modulus G' of a specimen increased and its frequency dependence tended to shift very slowly (over 1–2 weeks) from the liquidlike dependence to the soft solidlike dependence, indicating that the microdomains in the specimen tended to approach a more ordered state. This investigation is in progress and will be reported in a future publication.

Comparison of Experimentally Determined T_{ODT} with Prediction for SI Diblock Copolymers. To predict the T_{ODT} of an SI diblock copolymer using the Helfand–Wasserman theory[7] or the Leibler theory,[8] we must choose a specific expression for the temperature-dependent χ. Below we discuss the sensitivity of the expression for χ to the prediction of T_{ODT}s of SI diblock copolymers. In the literature there are many different expressions for the interaction energy density α, which is expressed in moles per unit volume, or χ for SI diblock copolymers. Note that α and χ are related to each other by $\alpha = \chi/V_{\mathrm{ref}}$, V_{ref} being the molar volume of a reference component. Table 2 gives a summary of the expressions for α or χ for PS/PI pairs in the literature, which were obtained either from cloud-point measurements or from SAXS measurements. Notice in Table 2 that there are considerable differences in the temperature coefficient of χ. It should be pointed out that the reliability of the predicted T_{ODT} of a block copolymer depends, among many factors, on the accuracy of the expression for χ.

Table 3 gives a summary of the experimentally determined values of T_{ODT} and, also, the predicted values of T_{ODT} of the seven SI diblock copolymers synthesized in this study, using both the Leibler theory and the Helfand–Wasserman theory. Note that the

Table 2. Interaction Parameters Reported in the Literature for SI Diblock Copolymers

expression for the interaction parameter	microstructure of isoprene or butadiene	method employed	ref	eq
$\alpha = -0.0009 + 0.75/T^{a}$	86–94% 1,4-linkage and 14–6% 3,4-linkage	turbidity	49	8
or				
$\chi = -0.1035 + 86.21/T$				8a[b]
$\alpha = -0.00118 + 0.839/T^{a}$	94% 1,4-linkage and 6% 3,4-linkage and	turbidity	31	9
or				
$\chi = -0.1356 + 96.44/T$				9a[b]
$\chi = -0.0937 + 60/T$	93% 1,2-linkage and 7% 3,4-linkage	SAXS	15	10
$\chi = -0.0258 + 27.9/T$	93% 1,4-linkage and 7% 3,4-linkage	SAXS	21	11
$\chi = 0.0090 + 25/T$	93% 1,2-linkage and 7% 3,4-linkage	SAXS	17	12
$\chi = -0.079 + 55/T$	unspecified	SAXS	18	13
$\chi = -0.0419 + 38.54/T$	93% 1,4-linkage and 7% 3,4-linkage	SAXS	16	14

[a] α has dimensions of mol/cm^3. [b] χ is related to α by $\chi = \alpha V_{\mathrm{ref}}$, V_{ref} being the molar volume of a reference component, which in this case may be taken to be 114.95 cm^3/mol for the styrene monomer.

Table 3. Comparison of Measured T_{ODT} with Prediction for the SI Diblock Copolymers Synthesized in This Study

				pred T_{ODT} (°C)	
sample code	block mol wt	measd T_{ODT} (°C)	eq employed	H–W theory	Leibler theory
SI-Q	5930PS-*b*-22070PI	95	8	108	149
			9	101	134
			14 and 15	−17	15
			14 and 16	9	42
SI-Z	6500PS-*b*-12800PI	90	8	124	210
			9	113	182
			14 and 15	−6	68
			14 and 16	20	97
SI-S	7200PS-*b*-10400PI	80	8	135	181
			9	122	159
			14 and 15	3	43
			14 and 16	29	71
SI-X	8950PS-*b*-8950PI	120	8	160	254
			9	142	216
			14 and 15	23	111
			14 and 16	51	140
SI-R	8200PS-*b*-6800PI	100	8	118	223
			9	108	192
			14 and 15	−11	78
			14 and 16	15	108
SI-O	20800PS-*b*-5600PI	130	8	136	204
			9	122	177
			14 and 15	2	60
			14 and 16	29	89
SI-L	34200PS-*b*-6800PI	170	8	184	227
			9	161	195
			14 and 15	43	81
			14 and 16	71	111

predicted values of T_{ODT} given in Table 3 are based on the temperature-dependent expressions for χ presented in Table 2. It should be noted, however, that there are theoretical[50,51] and experimental studies[52] reporting that χ depends not only on temperature T but also on composition f and molecular weight M. Further, a small change in χ strongly affects T_{ODT}, because the value of χ at T_{ODT} is a small quantity that is proportional to $1/N$.

It should be mentioned that the Helfand–Wasserman theory requires an expression for α. On the other hand, the Leibler theory requires an expression for χ. This difference is not a trivial matter in the prediction of T_{ODT} because different definitions of V_{ref} can give rise to different values of the predicted T_{ODT} when the Leibler theory is used. Note that the Helfand–Wasserman theory does not require the use of V_{ref}. In predicting T_{ODT} with the Leibler theory, we used the following definitions for V_{ref}:

$$V_{\mathrm{ref}} = [\mathrm{M}]_{\mathrm{S}} v_{\mathrm{PS}} \tag{15}$$

and

$$V_{\mathrm{ref}} = \{([\mathrm{M}]_{\mathrm{S}} v_{\mathrm{PS}})([\mathrm{M}]_{\mathrm{I}} v_{\mathrm{PI}})\}^{1/2} \tag{16}$$

where $[\mathrm{M}]_{\mathrm{S}}$ and $[\mathrm{M}]_{\mathrm{I}}$ are the molecular weights of the styrene and isoprene monomers, respectively, and v_{PS} and v_{PI} are the specific volumes of polystyrene (PS) and polyisoprene (PI), respectively. Presently, there is no theoretical guideline as to which of the two expressions, eq 15 or 16, is more appropriate to use for calculating the values of N although some research groups[7,10,21,22] preferred eq 16 to eq 15. Note that eq 16 has its origin in the incompressibility constraint for the block copolymer melt while eq 15 has its origin in the mean-field concept of Flory.

In the present study the following expressions for the specific volume were used:

$$v_{\mathrm{PS}} = 0.9199 + 5.098 \times 10^{-4}(T - 273) + 2.354 \times 10^{-7}(T - 273)^2 + (32.46 + 0.1017(T - 273))/M_{\mathrm{w,PS}} \tag{17}$$

for PS,[53] where $M_{\mathrm{w,PS}}$ is the molecular weight of PS, and

$$v_{\mathrm{PI}} = 1.0771 + 7.22 \times 10^{-4}(T - 273) + 2.46 \times 10^{-7}(T - 273)^2 \tag{18}$$

for PI.[30] Note in eqs 17 and 18 that v_{PS} and v_{PI} have units of centimeters cubed per gram and T is the absolute temperature.

There are other quantities which have to be either given or defined before calculations for T_{ODT} using the Helfand–Wasserman theory or the Leibler theory. They are (1) the statistical lengths b_{k} (k = PS or PI), which are needed in the Helfand-Wasserman theory, where we have used $b_{\mathrm{PS}} = 0.68$ nm for PS and $b_{\mathrm{PI}} = 0.63$ nm for PI, and (2) the polymerization index N. In the present study, we used the following expression for N:

$$N = [M_{\mathrm{w,PS}} v_{\mathrm{PS}} + M_{\mathrm{w,PI}} v_{\mathrm{PI}}]/V_{\mathrm{ref}} \tag{19}$$

where $M_{\mathrm{w,PS}}$ and $M_{\mathrm{w,PI}}$ are the molecular weights of the PS and PI blocks, respectively, in the SI diblock copolymer. In view of the fact that N is defined by eq 19 and not by a sum of the polymerization indices for the PS and PI blocks, N can be regarded as the total number of statistical segments in an SI diblock copolymer rather than simply the polymerization index. Using v_{PS} and v_{PI} given by eqs 17 and 18, respectively, we can calculate the volume fraction (f) of the PS phase in an SI diblock copolymer from $f = v_{\mathrm{PS}}M_{\mathrm{PS}}/(v_{\mathrm{PS}}M_{\mathrm{PS}} + v_{\mathrm{PI}}M_{\mathrm{PI}})$. It is now clear that f depends on temperature.

Table 4. Summary of Computed $(\chi N)_t$ and Coefficients Associated with Eq 2 for the SI Diblock Copolymers Synthesized in This Study

sample	N^a	f^b	c	τ^*	d	λ	$\tilde{N}^c$	$(\chi N)_s{}^d$	$(\chi N)_t{}^e$	$T_{ODT}{}^f$ (°C)
SI-Q	349	0.184	1.430	−1.640	2.186	681.1	1255	27.8	48.1	−58
SI-Z	236	0.301	1.205	−1.695	1.927	234.3	854	14.6	22.2	11
SI-S	213	0.369	1.143	−1.880	1.856	153.1	781	12.0	17.8	35
SI-X	213	0.458	1.106	−2.031	1.812	110.5	742	10.6	15.3	66
SI-R	177	0.505	1.102	−2.031	1.807	106.2	632	10.5	15.3	28
SI-O	299	0.759	1.294	−1.636	2.031	380.9	1029	19.1	30.5	−6
SI-L	460	0.809	1.409	−1.606	2.163	629.0	1505	26.3	43.4	9

[a] N is the total number of statistical segments at T_{ODT}, defined by eq 19 together with eq 16. [b] f is the volume fraction of the PS phase in each SI diblock copolymer, which was calculated at the measured T_{ODT} using eq 17 for the specific volume of PS and eq 18 for the specific volume of PI. [c] $\tilde{N}$ is the reduced degree of polymerization defined by $\tilde{N} = N(b^6/v^2)_{PS}[(b^6/v^2)_{PI}]^{1/2}$, in which b is the statistical length and v is the statistical segment volume. [d] Based on the Leibler theory.[8] [e] Based on the Burger–Ruland–Semenov analysis.[36] [f] Predicted with composition fluctuations taken into account from the Fredrickson–Helfand theory, together with the finite-size effect and asymmetry due to the Burger–Ruland–Semenov analysis, for which eq 14 (see Table 2) for the temperature dependence of χ was used.

Table 5. Effect of Polydispersity on $(\chi N)_t$ with or without Composition Fluctuations near the Transition Temperature for the SI Diblock Copolymers Synthesized in This Study

sample code	$(\chi N)_{s,m}{}^a$	$(\chi N)_{t,m}{}^b$	$(\chi N)_{t,fm}{}^c$	$(\chi N)_{s,p}{}^d$	$(\chi N)_{t,fp}{}^e$
SI-Q	27.8	28.4	48.1	26.5	46.1
SI-Z	14.6	14.7	22.2	13.6	20.6
SI-S	12.0	12.1	17.8	11.5	17.0
SI-X	10.6	10.9	15.3	10.1	14.5
SI-R	10.5	10.5	15.3	9.9	14.5
SI-O	19.1	19.3	30.3	18.2	29.1
SI-L	26.3	26.8	43.4	25.3	41.9

[a] $(\chi N)_{s,m}$ is the value of χN at the spinodal point, which is predicted by the Leibler theory,[8] for the *monodisperse* SI diblock copolymer. [b] $(\chi N)_{t,m}$ is the value of χN at T_{ODT}, which is predicted by the Leibler theory,[8] for the *monodisperse* SI diblock copolymer. [c] $(\chi N)_{t,fm} = (\chi N)_{s,m} + (\chi N)_{m,fluc}$, where $(\chi N)_{m,fluc}$ is the contribution of the composition fluctuations for the *monodisperse* SI diblock copolymers, which is predicted by the Fredrickson–Helfand theory.[35] [d] $(\chi N)_{s,p}$ is the value of χN at the spinodal point, which is predicted by the analysis of Burger et al.,[36] for the *polydisperse* SI diblock copolymers. [e] $(\chi N)_{t,fp} = (\chi N)_{s,p} + (\chi N)_{p,fluc}$, where $(\chi N)_{p,fluc}$ is the contribution of the composition fluctuations for the *polydisperse* SI diblock copolymers, which is predicted by the analysis of Burger et al.[36]

Therefore we must specify the temperature when mentioning the block copolymer composition in terms of volume fraction. It should be mentioned that in ref 8, f was defined by $f = N_A/(N_A + N_B)$, N_A and N_B being the polymerization indices for blocks A and B, respectively. The two definitions are identical *only when* the densities and monomeric volumes of blocks A and B are the same. Note that the densities and monomeric volumes of the PS and PI blocks in SI diblock copolymers are *not* the same. For details of the computational procedures employed in obtaining the values of T_{ODT} given in Table 3, readers are referred to a paper of Han et al.[30]

The following observations are worth noting in Table 3. (1) The use of eq 8 or 9, which was obtained from turbidity measurements, in the Helfand–Wasserman theory predicts values of T_{ODT} reasonably close (with a few exceptions) to experimental results. (2) The use of eq 14, which was obtained from SAXS measurements, together with eq 16 in the Leibler theory predicts values of T_{ODT} reasonably close (with a few exceptions) to experimental results. Notice in Table 3, as pointed out above, that the predicted values of T_{ODT} from the Leibler theory depend also on the expression for V_{ref} employed, eq 15 or 16. It can thus be concluded from Table 3 that the predicted values of T_{ODT} depend very much on the expressions for α or χ employed. This then raises a serious question as to which expression for α or χ must be used in predicting the T_{ODT} of SI diblock copolymers. As pointed out above, a rigorous determination of T_{ODT} may require an expression for χ which depends not only on temperature T but also on composition f and molecular weight M.

We calculated values of $(\chi N)_t$ and thus predicted the T_{ODT}s for the seven SI diblock copolymers synthesized in this study, using the Fredrickson–Helfand fluctuation theory,[35] together with the Burger–Ruland–Semenov analysis[36] for finite-size effect and asymmetry in a block copolymer. The calculated results are summarized in Table 4, in which the values for T_{ODT} were obtained using the expression for χ described by eq 14 in Table 2. We observe from Table 4 that the inclusion of composition fluctuations *underpredicts* considerably the values of T_{ODT} for the seven SI diblock copolymers, as compared to measured ones (compare the values in the third column of Table 3 with the values in the last column of Table 4). Notice in Table 4 that the difference between prediction and experiment becomes larger as the value of f moves farther away from 0.5. It shouild be remembered that, as pointed out in ref 35, the Fredrickson–Helfand analysis is valid only for $\tilde{N} \geq 10^4$. This means that this theory is *not* useful to assess the extent of composition fluctuations near the transition temperature of block copolymers such as SI or SB diblock copolymers, which invariably have small values of $\tilde{N}$ (e.g., the order of magnitude of 10^3).

Finally, it should be mentioned that both the Helfand–Wasserman and the Leibler theories are based on the assumption that block copolymers are monodisperse. However, several research groups[54–60] have incorporated the polydispersity effect into the Leibler theory, and Burger et al.[36] incorporated the polydispersity effect into the Fredrickson–Helfand analysis.[35] Particularly noteworthy is the experimental study of Tanaka et al.,[60] who, using SAXS measurements, incorporated the polydispersity effect and the asymmetry in block copolymers in the estimation of χ. Table 5 gives a summary of our calculations based on the analysis of Burger et al.[36] Also given in Table 5 are, for comparison, the predictions from the Leibler analysis and also from the Fredrickson–Helfand analysis. It can be seen in Table 5 that (a) the inclusion of composition fluctuations predicts larger values of $(\chi N)_t$ (thus lower values of T_{ODT}) than the Leibler analysis (compare values of $(\chi N)_{t,fm}$ with values of $(\chi N)_{t,m}$) and (b) the inclusion of the polydispersity effect predicts smaller values of $(XN)_t$ (thus higher values of T_{ODT}) than the analysis based on the assumption of monodisperse block copolymers (compare values of $(\chi N)_{t,fp}$ with values of $(\chi N)_{t,fm}$). Thus, the inclusion of the polydispersity effect counterbalances the contributions of composition fluctuations to $(\chi N)_t$, inso-

Table 6. Values of T_{ODT}s for SI Diblock Copolymers Reported in the Literature

ref	sample code	block mol wt	method employed	measd T_{ODT} (°C)
17	SI-2	5775PS-*b*-5775PI	SAXS	93
18	SI 4/11	4100PS-*b*-11230PI	SAXS	65
20	SI 7/8	7400PS-*b*-8300PI	SAXS	89
22	SI 6/8	6000PS-b-8000PI	SAXS	70−80
22	SI 18/4	18000PS-b-4000PI	SAXS	110−115
28	PS−PI-2	9000PS-b-9000PI	rheology	124.9
34	SI(6−13)	5900PS-*b*-12900PI	SANS	91 ± 2

far as predicting the T_{ODT} of a block copolymer is concerned.

Comparison of the Values of T_{ODT} Determined in the Present Study with Those Reported in the Literature. It is very difficult to compare, with great accuracy, the values of T_{ODT} determined at one laboratory with those determined at another laboratory, because (1) invariably different research groups used diblock copolymers having different molecular weights and/or different block length ratios and (2) different research groups might have used different experimental techniques (e.g., SAXS, SANS, or rheology). With this understanding, we nevertheless made an attempt to compare the values of T_{ODT} determined in the present study with those reported in the literature. To facilitate our discussion, we prepared Table 6, which summarizes (i) block molecular weights, (ii) the experimental method employed, (iii) experimentally determined values of T_{ODT}, and (iv) the sources of information.

When comparing Table 6 with Table 3, we make the following observations. (1) T_{ODT} = 124.9 °C for PS−PI-2 in Table 6 is comparable with T_{ODT} = 120 °C for SI-X in Table 3. Note that these SI diblock copolymers have virtually identical molecular weights and identical block compositions. (2) $T_{\mathrm{ODT}} = 91 \pm 2$ °C for SI(6−13) in Table 6 is comparable with T_{ODT} = 90 °C for SI-Z in Table 3. Considering that the block copolymer SI(6−13) has the composition 5900PS-*b*-12900PI while the block copolymer SI-Z has the composition 6500PS-*b*-12800PI and that the former specimen was subjected to SAXS while the latter specimen was subjected to oscillatory shear flow, the experimentally determined values of T_{ODT} for the two block copolymers can be considered to be in good agreement. (3) T_{ODT} = 70−80 °C for SI 6/8 in Table 6 is comparable with T_{ODT} = 80 °C for SI-S in Table 3. Note that these two SI diblock copolymers have slightly different compositions—SI 6/8 has the composition 6000PS-*b*-8000PI while SI-S has the composition 7200PS-*b*-10400PI—and that SI 6/8 was subjected to SAXS whereas SI-S was subjected to oscillatory shear flow. (4) T_{ODT} = 110−115 °C for SI 18/4 in Table 6 is comparable with T_{ODT} = 130 °C for SI-O in Table 3. Note that these two SI diblock copolymers have slightly different compositions—SI 18/4 has the composition 18000PS-*b*-4000PI while SI-O has the composition 20800PS-*b*-5600PI—and that SI 18/4 was subjected to SAXS whereas SI-O was subjected to oscillatory shear flow. It is fair to say that as a whole, the comparison presented above gives credence to the various research groups which reported on the T_{ODT}s of SI diblock copolymers.

Sensitivity of the Temperature Dependence of χ to Composition Fluctuations near the T_{ODT} of a Diblock Copolymer. To estimate the extent of composition fluctuations near the critical temperature of a diblock copolymer, we define a reduced parameters ϵ by

$$\epsilon = 2(1 - \chi/\chi_c) \tag{20}$$

where χ_c is the Flory−Huggins interaction parameter χ at the critical point, and we assume that ϵ is very small, i.e., $0 < \epsilon \ll 1$. In the literature there are many different expressions for χ for SI diblock copolymers (see Table 2).

Note that, according to eq 20, ϵ is proportional to the temperature difference $\Delta T = T - T_c$ from the critical point (T_c) and reflects the extent of composition fluctuations. For illustration, let us assume $\epsilon = 0.01$ and then estimate ΔT for the block copolymer SI-R, which has $f = 0.505$ at T_{ODT} = 100 °C (see Figure 17). According to Leibler,[8] for a symmetric block copolymer ($f = 0.5$), $T_c = T_{\mathrm{ODT}}$; so assuming that T_c = 100 °C for SI-R, from eq 20 and also eq 9a in Table 2 we obtain ΔT = 0.89 °C, which indicates that the temperature difference from T_{ODT} would be less than 1 °C for $\epsilon = 0.01$.

For comparison, let us consider a 1,2-PB-*block*-1,4-PB copolymer, BB6, which, according to Bates and Hartney,[13] has T_{ODT} = 108 °C. The expression for χ for BB6 is given by[13]

$$\chi = 6.79 \times 10^{-3} + 0.561/T \tag{21}$$

For $\epsilon = 0.01$, using eq 21 in eq 20 we obtain ΔT = 10.95 °C for BB6, which indicates that the value of ΔT for BB6 is about 12 times greater than that of SI-R. The above observation indicates that the extent of composition fluctuations at a given ΔT near the T_{ODT} (or T_c) of a block copolymer depends very much on the temperature dependence of χ. The range of *effective temperature* over which the composition fluctuation is important is very different in the two block copolymers: 1 °C away from T_{ODT} in SI diblock copolymer corresponds roughly to about 10 °C in 1,2-PB-*block*-1,4-PB copolymer. Note that this argument is based upon a crude approximation that Si-R has a temperature-dependent χ as described by eq 9a, which was obtained from turbidity measurements for binary mixtures of homopolymers PS and PI. According to the theoretical[50,51] and experimental studies,[52] χ depends not only on temperature T but also on composition f and molecular weight M. Note further that a small change in χ strongly affects T_{ODT}, because the value of χ at T_{ODT} is a small quantity that is proportional to $1/N$, with N being the degree of polymerization. Nevertheless, the argument given above on ΔT with which the composition fluctuation effect is significant may be qualitatively valid.

To facilitate our discussion here, plots of χN versus the reciprocal of absolute temperature ($1/T$) for two pairs of polymers are given schematically in Figure 28, where curve 1 is given to represent the temperature dependence of χN for SI diblock copolymer and curve 2 to represent the temperature dependence of χN for 1,2-PB-*block*-1,4-PB copolymer. The sole purpose of showing this schematic is to indicate the difference in the slope of the respective polymer systems. Notice in Figure 28 a very large difference in the slope of the χN versus $1/T$ plot between the two polymer systems. The qualitative discussion presented above can be explained by the magnitude of ΔT indicated in Figure 28. Since the definition of ϵ given by eq 20 in terms of χ is also valid for χN, the argument presented above in terms of χ should also be valid for χN.

Let us now consider the Onuki analysis,[61] which presents the following analytical expression:

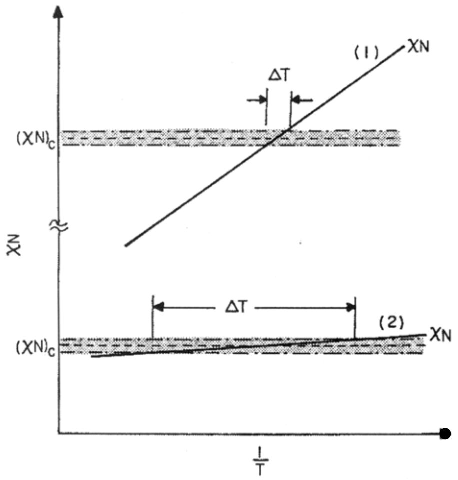

Figure 28. Schematic describing the temperature dependence of χN on the reciprocal of temperature ($1/T$), showing that curve 1, representing SI diblock copolymer, has a very large slope, and curve 2, representing 1,2-PB-*block*-1,4-PB copolymer or PEE-*block*-PEP copolymer, has a very small slope. ΔT shows the temperature difference corresponding to a given $\Delta(\chi N) = |(\chi N)_c - \chi N|$ which determines the extent of the composition fluctuations near the critical temperature.

$$\epsilon \approx \frac{4}{3^{1/2}}[f(1-f)]^{3/2}N\left(\frac{d\chi}{dT}\right)_c(T_c - T) \qquad (22)$$

where ϵ is defined by eq 20, f is the block copolymer composition, N is the degree of polymerization, and $(d\chi/dT)_c$ is the derivative of χ with respect to temperature at the critical point T_c. Readers are referred to ref 61 for the derivation of eq 22. From the various expressions for χ given in Table 2 let us express the temperature dependence of χ in the following general form:

$$\chi = A + B/T \qquad (23)$$

Then use of eq 23 in eq 22 gives

$$\epsilon = \frac{4}{3^{1/2}}[f(1-f)]^{3/2}N\left(\frac{B}{T_c^{\,2}}\right)(T - T_c) \qquad (24)$$

Using the values of f and N given in Table 4 for the seven SI diblock copolymers synthesized in this study, we find that the values of $[f(1-f)]^{3/2}N$ appearing in eq 24 vary *little* (20.30 for SI-Q, 22.77 for SI-Z, 23.92 for SI-S, 26.34 for SI-X, and 22.12 for SI-R), and thus the value of ϵ depends very much on the value of B appearing in eq 23 for a given ΔT. In other words, the slope of the χN versus $1/T$ plot given in Figure 28 plays a predominant role in determining the extent of composition fluctuations of a block copolymer near its critical temperature.

For illustration, let us consider the block copolymer SI-R having $f = 0.505$ and $N = 177$ at the transition temperature and the block copolymer BB6 having $f = 0.38$ and $N = 1396$. Using eqs 9a and 21, respectively, in eq 24, for the same value of ϵ, we obtain the following relationship:

$$(T - T_c)_{\text{SI-R}} = 0.0402(T - T_c)_{\text{BB6}} \qquad (25)$$

indicating that the temperature difference $(T - T_c)$ for BB6 would be about 25 times that for SI-R; i.e., $\Delta T = 1$ °C for SI-R corresponds to $\Delta T = 25$ °C for BB6, as illustrated schematically in Figure 28.

According to Bates et al.,[14] the expression for χ for PEP-*block*-PEE copolymer is given by

$$\chi = 4.44 \times 10^{-4} + 4.69/T \qquad (26)$$

Using eq 26 in eq 24, for the same value of ϵ, we obtain the following relationship:

$$(T - T_c)_{\text{SI-R}} = 0.2439(T - T_c)_{\text{PEP-PEE}} \qquad (27)$$

The above analysis explains why the 1,2-PB-*block*-1,4-PB copolymers employed by Bates and Hartney[13] and the PEP-*block*-PEE copolymers employed by Bates et al.[14] gave rise to *large* fluctuation effects at a given ΔT near the respective T_{ODT}s, whereas the SI diblock copolymers synthesized in this study show, within experimental uncertainties, *indiscernible* fluctuation effects (see Figures 17–19). It can be concluded from the above observations that the *larger* the value of B in eq 23, the *smaller* the composition fluctuations near the critical temperature of a diblock copolymer (see Figure 28) and that fluctuation effects scale with ϵ, which is defined by eq 20.

It should be mentioned that the block copolymer composition f in the seven SI diblock copolymers synthesized in this study does *not* seem to have affected the extent of composition fluctuations at or near their critical temperatures, because the values of $[f(1-f)]^{3/2}N/T_c^{\,2}$ appearing in eq 24 vary *little* as the value of f varies from 0.184 for SI-Q to 0.505 for SI-R. This then supports our view that the "liquidlike" rheological behavior, observed for SI-Q ($f = 0.184$) in Figure 21, at temperatures below its T_{ODT} cannot be ascribed to composition fluctuations, because *no* similar rheological behavior was observed for SI-R ($f = 0.505$) in Figure 17. It has to be ascribed to the grain-boundary defects. Similar conclusions can be drawn for the block copolymers SI-O and SI-L.

Concluding Remarks

In this paper we have shown that plots of log G' versus log G'' are very effective in determining the T_{ODT}s of low molecular weight SI diblock copolymers having a wide range of block length ratios, while plots of log G' versus log ω (obtained from frequency sweep experiments) and plots of G' versus temperature (obtained from temperature sweep experiments) are *not* effective for determining the T_{ODT}s of the low molecular weight SI diblock copolymers having a *low volume fraction* (f) of polystyrene or polyisoprene block (say, $f < 0.2$). The rheological criterion for the onset of the ODT of a block copolymer, i.e., the log G' versus log G'' plot in the disordered state must be independent of temperature and its slope must be equal to 2 in the terminal region, is based on the molecular viscoelasticity theory, eq 6 or 7, depending on whether the block copolymer is entangled or unentangled.

We observed that the SI diblock copolymers having $f \leq$ ca. 0.2 exhibited "liquidlike" rheological behavior at temperatures below their T_{ODT}s, for instance at temperatures as low as about 30 °C below its T_{ODT}. We attribute this observation to the existence of defects in the long-range spatial order of microdomains (the grain-boundary defects) which are continuous in three-dimensional space. Whether this argument is vaild or not must be verified experimentally, and at present research is in progress on this subject.

Using currently held theories, we predicted the T_{ODT} of the seven SI diblock copolymers synthesized in the present study and found that predicted values of T_{ODT} varied considerably, depending on which expression for χ was used. Specifically, we found that the Helfand–Wasserman theory, together with an expression for χ obtained from turbidity measurement (see eq 8 or 9 in Table 2), happens to give a reasonable prediction of T_{ODT} for SI diblock copolymers (see Table 3). It can be argued, however, that the reasonable prediction of T_{ODT} by the Helfand–Wasserman theory, together with an expression for χ obtained from turbidity measurement, may be fortuitous in that the Helfand–Wasserman theory *overpredicts* $(\chi N)_{\mathrm{ODT}}$ while eq 8 or 9 also *overpredicts* χ values. Notice in Table 2 that the temperature coefficient in the expression of χ obtained from turbidity measurements is much larger than that obtained from SAXS measurements.

On the other hand, there are many different expressions for χ obtained from SAXS experiments; namely, the value of the temperature coefficient of χ varies considerably from one expression to another (see Table 2). This can be interpreted as being a situation where the χ values determined from SAXS experiments are very sensitive to molecular weight and block copolymer composition. As a matter of fact, there is experimental evidence suggesting that χ values for SI diblock copolymers also depend on molecular weight, molecular weight distribution, and block copolymer composition.[52] If this is the case, the χ values determined from turbidity measurements for a pair of homopolymers PS and PI may *not* be suitable for accurately predicting the T_{ODT}s of such block copolymers, because turbidity measurement, which relies on the Flory–Huggins theory, does not allow us to obtain an expression for χ which depends on N. In other words, a question remains as to whether it is valid to use the expression for α, which was obtained from turbidity measurements for a pair of homopolymers with the aid of the Flory–Huggins theory, to predict the T_{ODT} of a diblock copolymer.

In the absence of a very accurate expression for χ which includes the dependencies of molecular weight and block copolymer composition, we have found it *practically* very useful to predict the T_{ODT}s of SI diblock copolymers using the Helfand–Wasserman theory together with eq 8 or 9. Specifically, we have found that such an approach predicts, when compared with experimental results, the values of T_{ODT} for SI diblock copolymers with uncertainties to within 20% (see Table 3). However, we feel strongly that it is highly desirable to obtain accurate expressions for χ, which include the effects of molecular weight and block composition, for block copolymers, so that one can use such expressions to predict the T_{ODT}s of block copolymers before synthesis.

Using the Onuki analysis,[61] we have shown that the extent of composition fluctuations of a block copolymer in the disordered state near the critical temperature, at a given temperature difference $\Delta T = T - T_{\mathrm{c}}$ from the critical temperature T_{c}, depends very much on the temperature coefficient B appearing in eq 23 and that the larger the value of B, the smaller the extent of composition fluctuations at a given ΔT. Using this analysis, we have shown that for the same extent of composition fluctuations ϵ, defined by eq 20, a temperature difference ΔT of 1 °C for an SI diblock copolymer (SI-R employed in this study) corresponds to ca. 25 °C for a 1,2-PB-*block*-1,4-PB copolymer (BB6 employed in ref 26). This difference in ΔT is believed to be attributable to the difference in the value of B appearing in eq 23 for the two block copolymer systems; specifically, from the literature we find that the value of B for SI diblock copolymer ranges from 28 to 96, depending on the experimental methods employed (see Table 2), while the value of B for 1,2-PB-*block*-1,4-PB copolymer is reported to be 0.561 (see eq 21) and 4.69 for PEE-*block*-PEP copolymer (see eq 26). Using the Onuki analysis for the seven SI diblock copolymers synthesized in this study, we have concluded that the value of ϵ (i.e., the extent of composition fluctuations near the critical temperature) at a given ΔT varies *little* with block copolymer composition for the seven SI diblock copolymers studied.

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