Effects of Molecular Weight and Block Length Ratio on the Rheological Behavior of Low Molecular Weight Polystyrene-*block*-polyisoprene Copolymers in the Disordered State

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ABSTRACT: Effects of molecular weight (M) and block length ratio (ϕ) on the rheological behavior of low molecular weight polystyrene-*block*-polyisoprene (SI diblock) copolymers in the *disordered* state were investigated. Here ϕ is defined by $N_{PS}/(N_{PS} + N_{PI})$, where N_{PS} and N_{PI} are polymerization indices for PS and PI blocks, respectively. For the study, a series of SI diblock copolymers were synthesized via anionic polymerization, and their dynamic storage and loss moduli (G' and G'') were measured as functions of angular frequency at various temperatures. The *disordered* state of each block copolymer was ascertained by observing that plots of log G' versus log G'' were independent of temperature and had a slope of 2 in the *terminal region.* Using log G' versus log G'' plots for the block copolymers in the *disordered* state, we were able to investigate the effects of M and ϕ on their linear viscoelastic properties. We found that the melt elasticity, as judged from the values of G' in the log G' versus log G'' plots, increased with increasing M but decreased with increasing ϕ. Reduced plots for dynamic storage modulus and dynamic viscosity were prepared with reference temperature, which was chosen by two different ways: (1) by choosing the temperature at an equal distance from the glass temperature of component polystyrene in each SI diblock copolymer and (2) by choosing the temperature at an equal distance from the order–disorder transition temperature of each SI diblock copolymer. We point out an urgent need for developing a comprehensive molecular theory predicting the rheological behavior of block copolymers.

Background

The rheological behavior of a block copolymer is controlled by the molecular weight and block length ratio (or block copolymer composition). It is well documented in the literature[1–3] that there exists a threshold molecular weight at and above which microdomains are formed in a block copolymer and that block length ratio determines the type of microdomain structure: spheres, cylinders, lamellae, or ordered bicontinuous microdomains.[4,5] Of particular interest is the possibility that the microdomains in a block copolymer can be made to disappear completely, giving rise to the *disordered* (i.e., *homogeneous*) state, by raising the temperature above a certain critical value, often referred to as the order–disorder transition temperature (T_{ODT}).[2,3] The T_{ODT} of a block copolymer can be determined by using either (a) small-angle X-ray (or neutron) scattering or (b) rheological measurement. It is beyond the scope of this paper to describe in detail how to determine experimentally the T_{ODT} of a block copolymer, and the readers are referred to the recent literature.[6–8] It should be mentioned that the T_{ODT} of a block copolymer depends on both molecular weight and block copolymer composition.[2,3]

It is then not too difficult to imagine that the rheological behavior of a block copolymer with microdomains (i.e., in an ordered state) would be quite different from that without microdomains (i.e., in the disordered state). Therefore, in order to have a better understanding of the rheological behavior of a block copolymer, it is essential for one to have block copolymers which will allow one to measure their rheological properties in the ordered and disordered states, respectively. However, most of the literature has dealt with the rheological properties of block copolymers only in the ordered state. The most prevailing reason for this is that when restricting our attention to styrene-based block copolymers, which are abundantly available commercially, they have sufficiently high molecular weights, giving rise to high T_{ODT}'s (e.g., above 220 °C) which are close to or above their thermal degradation temperature. For this reason, today there exist only a small number of papers which report on the rheological properties of block copolymers in both the ordered and disordered state[8,9] or only in the disordered state.[10,11]

At present there is no comprehensive theory which will enable us to predict the rheological properties of a microphase-separated block copolymer in terms of its molecular parameters. It can be easily surmised that prediction of the rheological properties of a microphase-separated block copolymer is a difficult task, because the type of microdomain structure (spheres, cylinders, lamellae, or ordered bicontinuous microdomains) must be incorporated into the development of a molecular theory. It should be pointed out that spherical microdomains, for instance, having the dimensions of ca. 50 nm in a block copolymer *cannot* be regarded as being equal to particles suspended freely in a liquid, because the microdomains in a block copolymer are attached to the chains of the other block (i.e., they are part of the entire block copolymer chains). In this regard, any attempt to predict the rheological behavior of a microphase-separated block copolymer with a continuum approach is *not* warranged. Accordingly, a molecular approach is most welcome.

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About two decades ago, four research groups[12-16] independently investigated the chain dynamics of *homogeneous*, *unentangled* AB- or ABA-type block copolymers by either modifying or extending the bead–spring model of Rouse[17] and Zimm.[18] Specifically, Stockmayer and Kennedy[12] considered the continuous limit of the bead–spring Rouse model:

$$\frac{\partial x}{\partial t} = \left(\frac{2}{\tau_1 \pi^2}\right)\frac{\partial^2 x}{\partial s^2} \qquad (1)$$

where x denotes the average displacement of a bead, s is a continuous variable that lies between −1 and +1 (i.e., $-1 \le s \le +1$), and τ_1 is the Rouse terminal relaxation time. For eq 1, they obtained the general solutions

$$x_{\mathrm{A}} = \exp(-t/2\tau_{\mathrm{p,block}})(C_{\mathrm{A}} \sin \alpha s + D_{\mathrm{A}} \cos \alpha s) \qquad (2a)$$

$$x_{\mathrm{B}} = \exp(-t/2\tau_{\mathrm{p,block}})(C_{\mathrm{B}} \sin \beta s + D_{\mathrm{B}} \cos \beta s) \qquad (2b)$$

where $\tau_{p,\mathrm{block}}$ is the relaxation time spectrum of the block copolymer given by

(i) for diblock copolymers,

$$\tau_{p,\mathrm{block}} = \tau_{1,\mathrm{A}}^{\mathrm{b}}(\pi/\alpha_p)^2 = \tau_{1,\mathrm{B}}^{\mathrm{b}}(\pi/\beta_p)^2 \qquad p = 2, 4, 6, ... \qquad (3)$$

(ii) for triblock copolymers,

$$\tau_{p,\mathrm{block}} = \tau_{1,\mathrm{A}}^{\mathrm{b}}(\pi/2\alpha_p)^2 = \tau_{1,\mathrm{B}}^{\mathrm{b}}(\pi/2\beta_p)^2 \qquad p = 1, 2, 3, ... \qquad (4)$$

in which $\tau_{1,\mathrm{A}}^{\mathrm{b}}$ and $\tau_{1,\mathrm{B}}^{\mathrm{b}}$ are the terminal relaxation times for components A and B, respectively, in the block copolymer medium, which are defined by

$$\tau_{1,\mathrm{i}}^{\mathrm{b}} = 6\eta_{0,\mathrm{i}}^{\mathrm{b}} M_{\mathrm{i}}^{\mathrm{b}}/\pi^2 \varrho_{\mathrm{i}} RT \qquad \mathrm{i} = \mathrm{A, B} \qquad (5)$$

where $\mathrm{M}_{\mathrm{i}}^{\mathrm{b}}$ is the molecular weight of component i, ϱ_{i} is the density of component i, R is the universal gas constant, T is the absolute temperature, and $\eta_{0,\mathrm{i}}^{\mathrm{b}}$ is the zero-shear viscosity of component i in the block copolymer medium and it is related to the friction coefficient $\zeta_{0,\mathrm{i}}^{\mathrm{b}}$ of component i in the block copolymer medium.

The values of α_p appearing in eqs 3 and 4 can be determined by satisfying the following characteristic equation,

$$\tan[\alpha_p(1-\theta)] = -\lambda\mu \tan \alpha_p\lambda\theta \qquad \text{even modes of } p \qquad (6a)$$

$$\tan[\alpha_p(1-\theta)] = \lambda\mu \cot \alpha_p\lambda\theta \qquad \text{odd modes of } p \qquad (6b)$$

where

$$\lambda = (\tau_{1,\mathrm{B}}^{\mathrm{b}}/\tau_{1,\mathrm{A}}^{\mathrm{b}})^{1/2} \qquad \mu = (b_{\mathrm{A}}/b_{\mathrm{B}})^2 \qquad (7)$$

in which b_{A} and b_{B} are the Kuhn statistical lengths for components A and B, respectively, and θ is the fractional volume of component B. Note that eq 6 was obtained by applying the following boundary conditions to eq 1:

$$K_{\mathrm{A}}\left(\frac{\partial x_{\mathrm{A}}}{\partial s}\right)_{s=\theta} = K_{\mathrm{B}}\left(\frac{\partial x_{\mathrm{B}}}{\partial s}\right)_{s=\theta} \qquad (8a)$$

$$x_{\mathrm{A}}(\theta,t) = x_{\mathrm{B}}(\theta,t) \qquad (8b)$$

$$\left(\frac{\partial x(s,t)}{\partial s}\right)_{s=\pm 1} = 0 \qquad (8c)$$

where $K_{\mathrm{A}} = 3k_{\mathrm{B}}T/b_{\mathrm{A}}^2$ and $K_{\mathrm{B}} = 3k_{\mathrm{B}}T/b_{\mathrm{B}}^2$ with k_{B} being the Boltzmann constant.

Once the values of $\tau_{p,\mathrm{block}}$ are determined (see eqs 3 and 4), one can calculate the linear viscoelastic properties of a block copolymer from the following expression for the reduced complex dynamic modulus $G_{\mathrm{R}}^{*}(\omega)$,

$$G_{\mathrm{R}}^{*}(\omega) = G_{\mathrm{R}}'(\omega) + iG_{\mathrm{R}}''(\omega) \qquad (9)$$

where $G_{\mathrm{R}}'(\omega)$ and $G_{\mathrm{R}}''(\omega)$ are reduced storage and loss moduli, respectively, defined by

$$G_{\mathrm{R}}'(\omega) = \sum_{\mathrm{even}\, p}^{\infty} \frac{(\omega\tau_{p,\mathrm{block}})^2}{1 + (\omega\tau_{p,\mathrm{block}})^2}$$

$$G_{\mathrm{R}}''(\omega) = \sum_{\mathrm{even}\, p}^{\infty} \frac{\omega\tau_{p,\mathrm{block}}}{1 + (\omega\tau_{p,\mathrm{block}})^2} \qquad (10)$$

and the reduced compliance $J_{\mathrm{e,R}}^{0}$ from

$$J_{\mathrm{e,R}}^{0} = \lim_{\omega \to 0} \frac{G_{\mathrm{R}}'(\omega)}{G_{\mathrm{R}}'(\omega)^2 + G_{\mathrm{R}}''(\omega)^2} \qquad (11)$$

Once values of $G_{\mathrm{R}}'(\omega)$ and $G_{\mathrm{R}}''(\omega)$ are available, the storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, can be calculated by

$$G'(\omega) = \frac{\varrho RT}{M}G_{\mathrm{R}}'(\omega) \qquad G''(\omega) = \frac{\varrho RT}{M}G_{\mathrm{R}}''(\omega) \qquad (12)$$

in which $M = M_{\mathrm{A}}^{\mathrm{b}} + M_{\mathrm{B}}^{\mathrm{b}}$ is the molecular weight of block copolymer with $M_{\mathrm{A}}^{\mathrm{b}}$ and $M_{\mathrm{B}}^{\mathrm{b}}$ being the molecular weights of components A and B, respectively, and the steady-state shear compliance J_{e}^{0} can be calculated by

$$J_{\mathrm{e}}^{0} = \lim_{\omega \to 0} \frac{G'(\omega)}{G'(\omega)^2 + G''(\omega)^2} = \frac{M}{\varrho RT}J_{\mathrm{e,R}}^{0} \qquad (13)$$

In the past, some research groups[12,14,15,19] have calculated $G_{\mathrm{R}}'(\omega)$, $G_{\mathrm{R}}''(\omega)$, and $J_{\mathrm{e,R}}^{0}$. However, when investigating the effects of molecular weight and block copolymer composition on the linear viscoelastic properties of a block copolymer, one must calculate $G'(\omega)$ and $G''(\omega)$ from eq 12 and J_{e}^{0} from 13.

In this paper we present our recent experimental results for the linear viscoelastic properties in the *disordered* state of low molecular weight polystyrene-*block*-polyisoprene (SI diblock) copolymers, which were synthesized via anionic polymerization in our laboratory. Here a "low molecular weight" SI diblock copolymer refers to one which has the T_{ODT} relative close to the glass transition temperature of the polystyrene block. The *disordered* state of each block copolymer was ascertained by observing that plots of log G' versus log G'' were independent of temperature and had a slope of 2 in the terminal region. Using log G' versus log G'' plots for the block copolymers in the *disordered* state, we were able to investigate the effects of molecular weight and block copolymer composition on their linear viscoelastic properties. We prepared reduced plots for storage modulus and dynamic viscosity, for which the shift factor was obtained by choosing the reference temperature using two different methods: (1) by choos-

Table 1. Molecular Characteristics and Order–Disorder Transition Temperatures of the SI Diblock Copolymers Synthesized in This Study

sample code	$M^{\mathrm{b}}_{\mathrm{PS}}$	$M^{\mathrm{b}}_{\mathrm{PI}}$	M_w/M_n	N_{PS}	N_{PI}	ϕ^a	T_{ODT} (°C)^b
SI-N	5600	13720	1.05	54	201	0.21	75
SI-T	6200	6200	1.07	60	91	0.40	≤65^c
SI-R	8200	6800	1.07	79	100	0.44	100
SI-M	10320	5160	1.06	99	76	0.57	≤90^d
SI-O	20800	5600	1.06	200	82	0.71	130
SI-L	34200	6800	1.05	328	100	0.77	170

[a] ϕ is the block length ratio defined by $N_{PS}/(N_{PS} + N_{PI})$, where N_{PS} is the polymerization index of the PS block and N_{PI} is the polymerization index of the PI block in a given SI diblock copolymer. [b] The values of the T_{ODT} reported here were determined from log G' versus log G'' plots, following the procedure suggested by Han and co-workers.[8] [c] The lowest possible measurement temperature was 65 °C, at and above which plots of log G' versus log G'' were found to be independent of temperature. [d] The lowest possible measurement temperature was 90 °C, at and above which plots of log G' versus log G'' were found to be independent of temperature.

ing the temperature at an equal distance from the glass transition temperature of component polystyrene (PS) in each SI diblock copolymer and (2) by choosing the temperature at an equal distance from the T_{ODT} of each SI diblock copolymer.

Experimental Section

Materials. Six SI diblock copolymers with various molecular weights and block length ratios were synthesized via anionic polymerization in our laboratory. Table 1 gives a summary of the molecular characteristics of the block copolymers synthesized. For the polymerization, an inert-gas stirred-tank reactor system described in a paper by Kim and Han[11] was employed. The details about the synthesis procedures, including the steps taken to purify the monomers, are described elsewhere.[11] Also given in Table 1 are the experimentally determined T_{ODT}'s for the six SI diblock copolymers synthesized. The details of experimental procedures employed to determine the T_{ODT}'s given in Table 1 are described elsewhere.[8] It should be mentioned that before synthesis, using the Helfand–Wasserman theory,[2] we determined the molecular weight and block length ratio, which would yield a *targeted* T_{ODT}. We found that the predicted T_{ODT}'s from the Helfand–Wasserman theory were within 20% of the measured ones.

Sample Preparation. Samples for rheological measurements 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 solvent was carried out slowly at room temperature for 1 week and then in a vacuum oven at 40 °C for 3 days. The last trace of solvent was removed by drying the samples in a vacuum oven at an elevated temperature by gradually raising the oven temperature to 10 °C above the glass transition temperature of component 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 which is about 20 deg above the glass temperature of the component PS.

Rheological Measurement. 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 temperatures above the T_{ODT} of each block copolymer synthesized in this study (see Table 1 for the T_{ODT}'s of the six SI diblock copolymers). The temperature control was accurate to within ±1 deg. In the rheological measurements a fixed strain was used at a given temperature, to ensure that measurements were taken well within the linear viscoelastic range of the materials investigated. All the rheological measurements were conducted under a nitrogen atmosphere in order to avoid oxidative degradation of the samples.

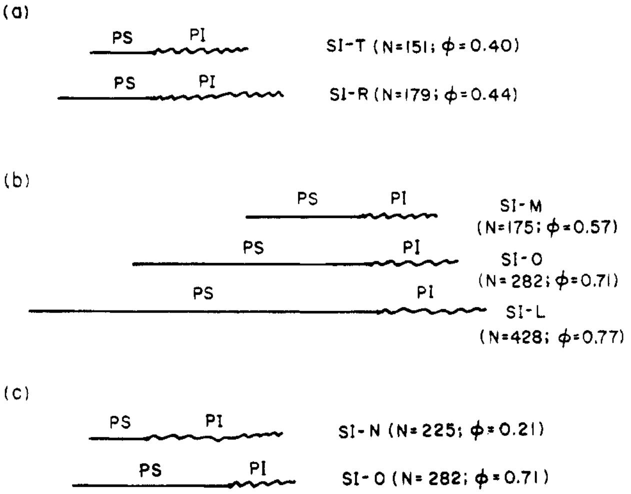

Figure 1. Schematic describing the block lengths for (a) block copolymers SI-T and SI-R, (b) block copolymers SI-M, SI-O, and SI-L, and (c) block copolymers SI-N and SI-O.

Differential Scanning Calorimetry. Glass transition temperatures of the SI diblock copolymers, as well as the glass transition temperature of homopolymer PS, having the M_w ranging from 1000–33 000, were determined by differential scanning calorimetry (DSC) (DuPont 9900). All DSC runs were made under a nitrogen atmosphere with a heating rate of 20 °C/min. The purpose of having measured the glass transition temperature ($T^{\mathrm{h}}_{\mathrm{g,PS}}$) of homopolymer PS was to compare the glass transition temperature ($T^{\mathrm{b}}_{\mathrm{g,PS}}$) of component PS in each SI diblock copolymer.

Results

The main purpose of the present study was to investigate the effects of molecular weight M and block length ratio ϕ on the rheological behavior of low molecular weight SI diblock copolymers. Here ϕ is defined by $N_{PS}/(N_{PS} + N_{PI})$ with N_{PS} and N_{PI} being the polymerization indices of the PS and PI blocks, respectively. It should be pointed out that both PS and PI blocks in each of the six SI diblock copolymers synthesized in this study may be regarded as Rouse chains (see Table 1), because the entanglement molecular weight for homopolymer PS ($M_{e,PS}$) is ca. 18 100[20] and the entanglement molecular weight for homopolymer polyisoprene (PI) ($M_{e,PI}$) is ca. 7000.[21] Note that the critical molecular weight (M_c) is about twice the entanglement molecular weight (M_e), and a criterion that a homopolymer may be regarded as being *entangled* must satisfy the relationship:[20,22] $\eta \sim M_w{}^{3.4}$, which is valid for $M_w > M_c$, where η is viscosity and M_w is molecular weight of the homopolymer. This now poses a very important question as to whether or not an SI diblock copolymer consisting of two Rouse (i.e., unentangled) chains, each having the molecular weight ($M^{\mathrm{b}}_{\mathrm{PS}}$ or $M^{\mathrm{b}}_{\mathrm{PI}}$) almost equal to or slightly less than the corresponding critical molecular weight ($M_{c,PS}$ or $M_{c,PI}$), must be regarded as an unentangled chain. A case in point is block copolymers SI-N and SI-L synthesized in this study (see Table 1). We shall return to this question later in this paper.

In order to investigate the effects of M and ϕ on the rheological behavior of the SI diblock copolymers synthesized in this study, let us consider the following three cases, as shown schematically in Figure 1. In case a, we will examine the effect of M on the rheological behavior of two block copolymers SI-T and SI-R. Note that the length of PS block in SI-R is 1.31 times that in SI-T and the length of PI block in SI-R is 1.1 times that

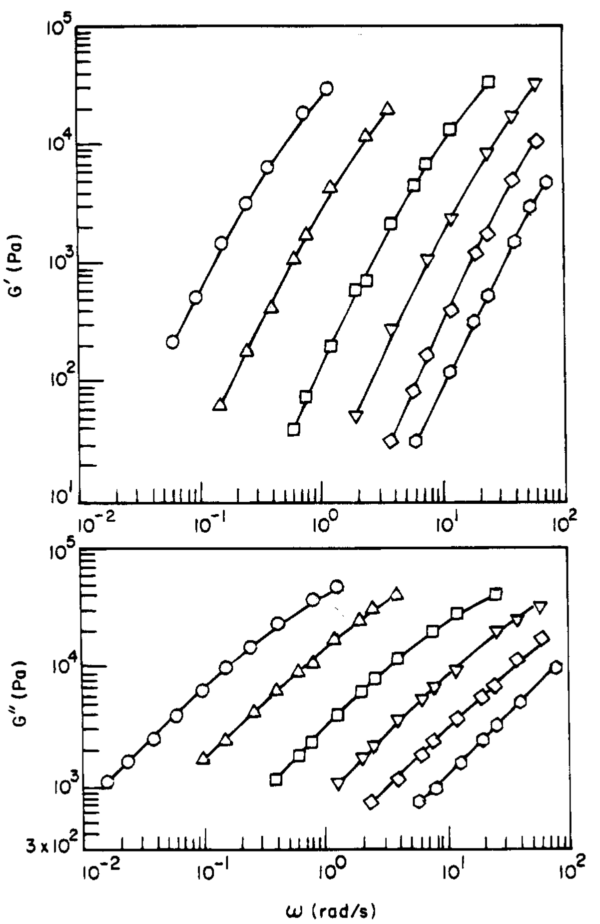

Figure 2. Plots of log G' versus log ω and log G'' versus log ω for the block copolymer SI-T at 65 °C (○), 70 °C (△), 75 °C (□), 80 °C (▽), 85 °C (◇), and 90 °C (○).

in SI-T, but the value of ϕ of the two block copolymers is about the same. In case b, we will examine further the effect of M on the rheological behavior of three block copolymers SI-M, SI-O, and SI-L. Note that the molecular weight of the PI block (M^{b}_{PI}) is increased moderately in going from SI-M to SI-O and to SI-L, but the molecular weight of PS block (M^{b}_{PS}) is doubled in going from SI-M to SI-O and tripled in going from SI-M to SI-L. In other words, the increase of M in the three block copolymers comes primarily from the increase in M^{b}_{PS}. In case c, we will examine the effect of ϕ on the rheological behavior of two block copolymers SI-N and SI-O. Note that while M increases moderately, ϕ increases considerably, in going from SI-N to SI-O, namely, $\phi = 0.21$ for SI-N and $\phi = 0.71$ for SI-O.

Let us now look at representative experimental results obtained in this study. Figure 2 gives plots of log G' versus log ω and log G'' versus log ω for SI-T at various temperatures, and Figure 3 gives similar plots for SI-R at various temperatures. In order to compare the rheological behavior of two polymers which were subjected to a totally different range of temperatures, one commonly applies time–temperature superposition to obtain master (or reduced) plots. As will be shown later in this paper, it is *not* obvious how to assess, using reduced plots, the effects of M and ϕ on the rheological behavior of block copolymers. Therefore, below, we will first employ an alternative method.

Using the data given in Figures 2 and 3, we prepared plots of log G' versus log G'' for SI-R and SI-T, and they are displayed in Figure 4. The *solid lines* in Figure 4 are theoretical predictions, which will be elaborated on later in this paper. If we assume that both SI-R and

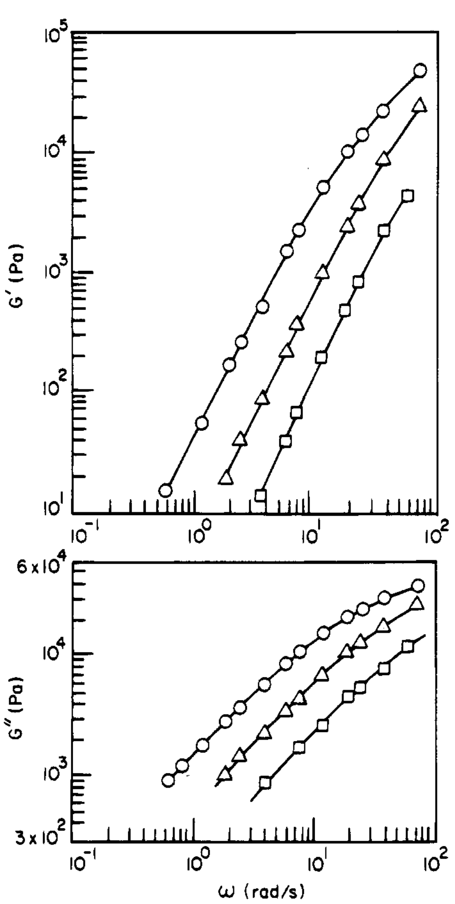

Figure 3. Plots of log G' versus log ω and log G'' versus log ω for the block copolymer SI-R at 100 °C (○), 105 °C (△), and 110 °C (□).

SI-T are unentangled block copolymers, according to Han and Kim[23] we have

$$\log G' = 2 \log G'' + \log(2M/5\varrho RT) \qquad (14)$$

Equation 14 now seems to explain (a) why in Figure 4 log G' versus log G'' plots are *virtually* independent of temperature and (b) why in Figure 4 the log G' versus log G'' plot for SI-R lies slightly above that for SI-T. Note that the M of SI-R is slightly larger than that of SI-T (see Table 1).

However, if an SI block copolymer is assumed to be entangled, we have[24,25]

$$\log G' = 2 \log G'' + \log(6M_{\mathrm{e,block}}/5\varrho RT) \qquad (15)$$

where $M_{\mathrm{e,block}}$ is the entanglement molecular weight of the block copolymer, indicating that log G' versus log G'' plots for an entangled block copolymer are independent of molecular weight and *virtually* independent of temperature over a reasonable range of temperatures. The validity of this prediction is demonstrated in Figure 5, showing that log G' versus log G'' plots for two high molecular weight polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS triblock) copolymers, Kraton 1107 and SIS-A, the molecular characteristics of which are given in Table 2, lie on a single correlation. This indicates that the two block copolymers are indeed entangled because the effect of molecular weight is *not* discernible in Figure 5. This experimental observation is consistent with the prediction by eq 15. Note that these two block copolymers have approximately the same ϕ, but the M of Kraton 1107 is about 1.2 times that of SIS-A (see Table 2).

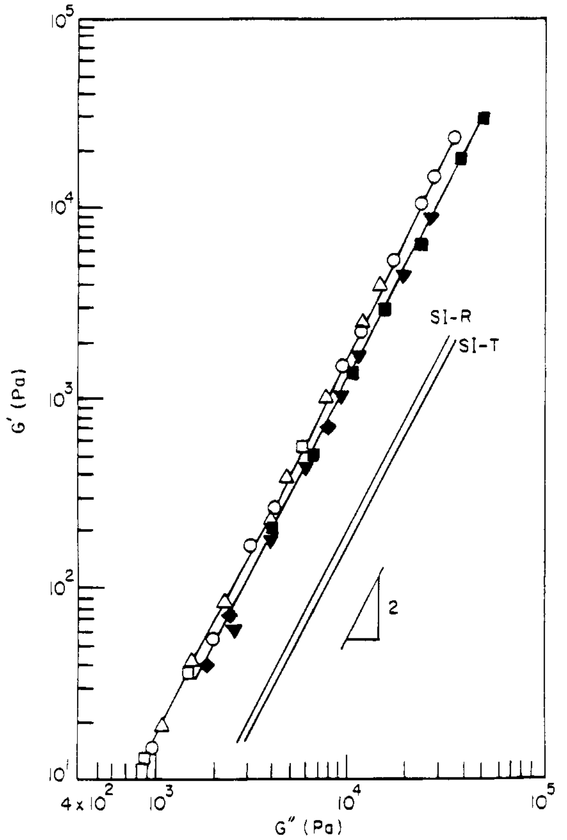

Figure 4. Experimentally obtained plots of log G' versus log G'' for (a) SI-R at 100 °C (○), 105 °C (△), and 110 °C (□) and (b) SI-T at 65 °C (■), 70 °C (▼), and 75 °C (◆). The solid lines are theoretical predictions.

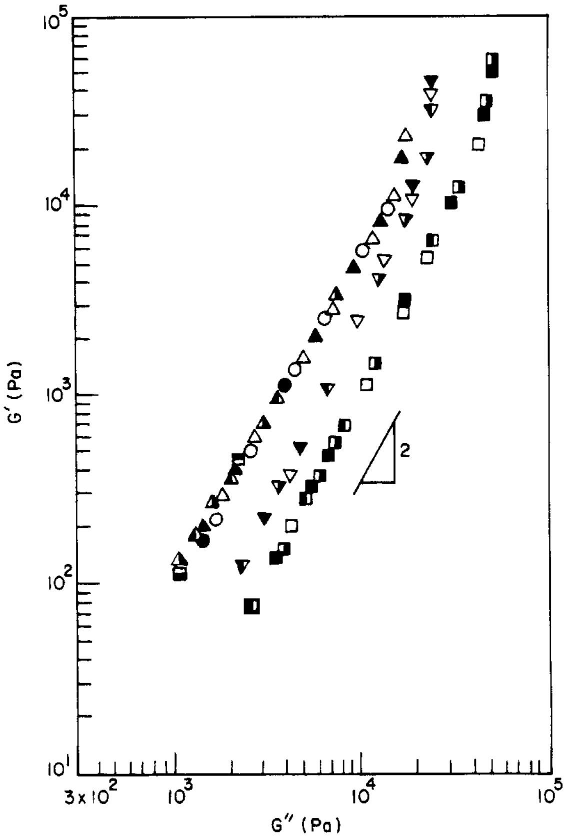

Figure 5. Plots of log G' versus log G'' for (a) Kraton 1107 at 220 °C (○) and 230 °C (●), (b) SIS-A at 180 °C (△), 190 °C (▲), 200 °C (◭), 210 °C (◮), 220 °C (⬒), and 230 °C (⬓), (c) PS having a molecular weight of 2×10^5 at 170 °C (▽), 190 °C (▼), 200 °C (⧩), and 210 °C (⧨), and (d) PI having a molecular weight of 9×10^4 at 30 °C (□), 60 °C (■), 90 °C (◨), and 120 °C (◧).

Table 2. Molecular Characteristics and Order–Disorder Transition Temperatures of Two SIS Triblock Copolymers

sample code	M^b_{PS}	M^b_{PI}	N_{PS}	N_{PI}	ϕ	T_{ODT} (°C)[a]
Kraton 1107	20 000	120.000	169	1762	0.087	220
SIS-A	14 800	99 000	125	1453	0.079	180

[a] Reference 9.

Figure 6 gives plots of log G' versus log G'' for SI-M, SI-O, and SI-L at various temperatures. The *solid lines* in Figure 6 are theoretical predictions, which will be elaborated on later in this paper. If we assume that all three block copolymers in Figure 6 are unentangled chains, using eq 14 we can explain, in terms of M (see Table 1), the relative positions of the log G' versus log G'' plots for the three block copolymers. However, as will be discussed below, SI-L (perhaps, also, SI-O) may *no* longer be regarded as an unentangled block copolymer.

Figure 7 gives plots of log G' versus log G'' for SI-N and SI-O at various temperatures. The *solid lines* in Figure 7 are theoretical predictions, which will be elaborated on later in this paper. It is of interest to observe in Figure 7 that, in spite of the fact that the M of SI-N is less than that of SI-O (see Table 1), the log G' versus log G'' plot for SI-N lies above that for SI-O. There are two factors that might have contributed to this observation: (a) the large difference in ϕ between the two block copolymers, and (b) SI-N may be regarded as an entangled block copolymer, as will be elaborated on below. Note that the log G' versus log G'' plot for an entangled polymer lies above that for an unentangled polymer (compare eq 14 with eq 15).

Discussion

Entanglement Molecular Weight of Low Molecular Weight Diblock Copolymers. What is uncertain to us at this point is how to estimate the entanglement molecular weight of a diblock copolymer ($M_{e,block}$), which consists of two chemically dissimilar chains. In dealing with an AB-type diblock copolymer, four different situations, as schematically given in Figure 8, may arise. It should be pointed out that all the low molecular weight SI diblock copolymers synthesized in this study (see Table 1) belong to case a depicted in Figure 8; i.e., both PS and PI blocks are Rouse chains because the molecular weight of the PS block (M^b_{PS}) in each of these SI diblock copolymers is less than the critical molecular weight for PS ($M_{c,PS}$), which is ca. 36 000, and also, the molecular weight of PI block (M^b_{PI}) in each of these SI diblock copolymers is less than the critical molecular weight for PI ($M_{c,PI}$),·which is ca. 14 000. However, since a diblock copolymer must be regarded as a *single chain*, the following question must be raised: Can we still consider, for instance, the block copolymer SI-N or SI-L to be a Rouse chain? This is a very challenging question to us, because from the point of view of the PI block, the M of SI-N is greater than $M_{c,PI}$, and from the point of the PS block, the M of SI-L is greater than $M_{c,PS}$. Therefore, SI-N and SI-L may be regarded as *entangled* block copolymers.

Let us now return to Figure 5, which compares log G' versus log G'' plots for two entangled SIS triblock copolymers, Kraton 1107 and SIS-A, with those for entangled homopolymers PS and PI. It is of interest to observe in Figure 5 that log G' versus log G'' plots for the two SIS triblock copolymers lie above those for the entangled homopolymers PS and PI. In view of the fact that the M^b_{PI} in the two SIS triblock copolymers (see

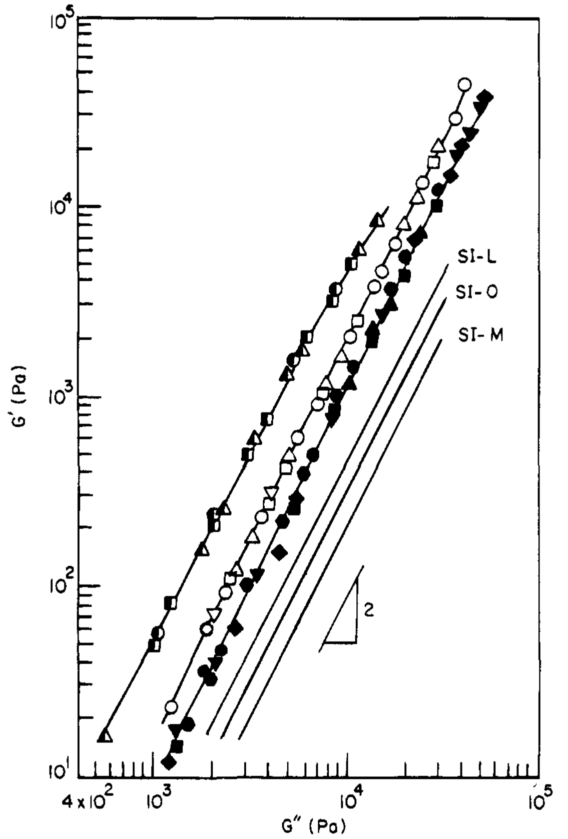

Figure 6. Experimentally obtained plots of log G' versus log G'' for (a) SI-M at 90 °C (▲), 95 °C (■), 100 °C (▼), 105 °C (◆), 110 °C (⬢), and 115 °C (●), (b) SI-O at 130 °C (○), 135 °C (△), 140 °C, (□), and 145 °C (▽), and (c) SI-L at 170 °C (◐), 175 °C (▲), and 180 °C (◧). The solid lines are theoretical predictions.

Table 2) is much greater than the $M_{\mathrm{c,PI}}$, it is reasonable to state that the two SIS triblock copolymers must be regarded as entangled chains. We can then conclude that the entanglement molecular weight of SIS triblock copolymer ($M_{\mathrm{e,SIS}}$) is greater than the entanglement molecular weight of homopolymer PS ($M_{\mathrm{e,PS}}$) since the log G' versus log G'' plots for the two SIS triblock copolymers lie above those for the entangled homopolymer PS.

Figure 9 gives log G' versus log G'' plots for (a) an SIS triblock copolymer, Kraton 1107, (b) two SI diblock copolymers, SI-N and SI-L, (c) an entangled homopolymer, PS, having the molecular weight (M_w) of 2×10^5, and (d) an entangled homopolymer, PI, having $M_w = 9 \times 10^4$. The purpose of this figure is to assess whether or not it is reasonable to consider that indeed SI-N and SI-L are entangled block copolymers. It can be seen in Figure 9 that within experimental uncertainties, the log G' versus log G'' plots for SI-N and SI-L lie very close to the log G' versus log G'' plots for Kraton 1107. This observation seems to reinforce our view that SI-N and SI-L may be regarded as entangled block copolymers.

However, a question remains: How can we prove theoretically that SI-N and SI-L are indeed entangled block copolymers while the constituent PS and PI blocks are unentangled chains? Further, at present there is *no* theoretical guideline as to how we can estimate the $M_{\mathrm{e,block}}$ of an AB-type diblock copolymer in terms of $M_{\mathrm{e,A}}$, $M_{\mathrm{e,B}}$, and ϕ, i.e.,

$$M_{\mathrm{e,block}} = f(M_{\mathrm{e,A}}, M_{\mathrm{e,B}}, \phi) \qquad (16)$$

when the constituent blocks are entangled chains. These questions require the attention of future investigation.

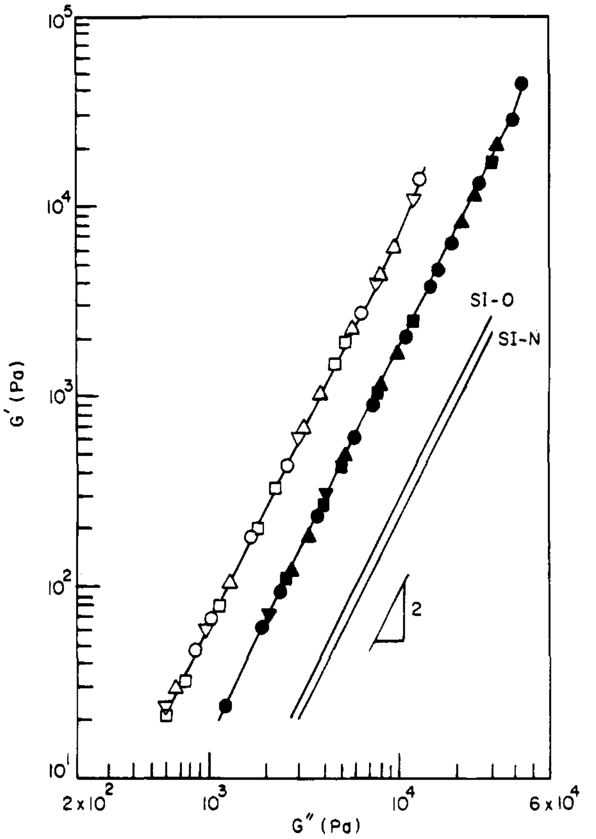

Figure 7. Experimentally obtained plots of log G' versus log G'' for (a) SI-N at 75 °C (○), 80 °C (△), 85 °C (□), and 90 °C (▽) and (b) SI-O at 130 °C (●), 135 °C (▲), 140 °C (■), and 145 °C (▼). The solid lines are theoretical predictions.

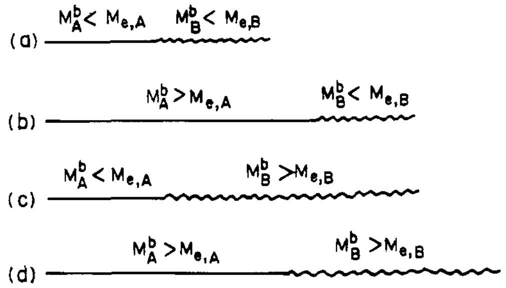

Figure 8. Schematic describing different combinations of block molecular weights in an AB-type diblock copolymer.

Glass Transition Temperature of Low Molecular Weight SI Diblock Copolymers. Table 3 gives a summary of the glass transition temperature ($T_{\mathrm{g,PS}}^{\mathrm{b}}$) of the PS block in each SI diblock copolymer synthesized in this study. As reported earlier by Morese-Seguela et al.,[26] we also found that the value of $T_{\mathrm{g,PS}}^{\mathrm{b}}$ varied with the duration of aging of the sample, and the values of $T_{\mathrm{g,PS}}^{\mathrm{b}}$ given in Table 3 are based on the samples which were aged for over 6 months at room temperature.

Figure 10 gives plots of $T_{\mathrm{g,PS}}^{\mathrm{b}}$ versus $M_{\mathrm{PS}}^{\mathrm{b}}$ in the SI diblock copolymer synthesized in this study. Also given in Figure 10 are, for comparison, the experimental data of Morese-Seguela et al.[26] who, over a decade ago, also reported the $T_{\mathrm{g,PS}}^{\mathrm{b}}$ of low molecular weight SI diblock copolymers. It is very gratifying to observe in Figure 10 that two separate sets of data, which were obtained for a period over a decade apart, agree very well.

Having observed that the values of $T_{\mathrm{g,PS}}^{\mathrm{b}}$ obtained in this study were considerably lower than the values *estimated* for the glass transition temperature ($T_{\mathrm{g,PS}}^{\mathrm{h}}$)

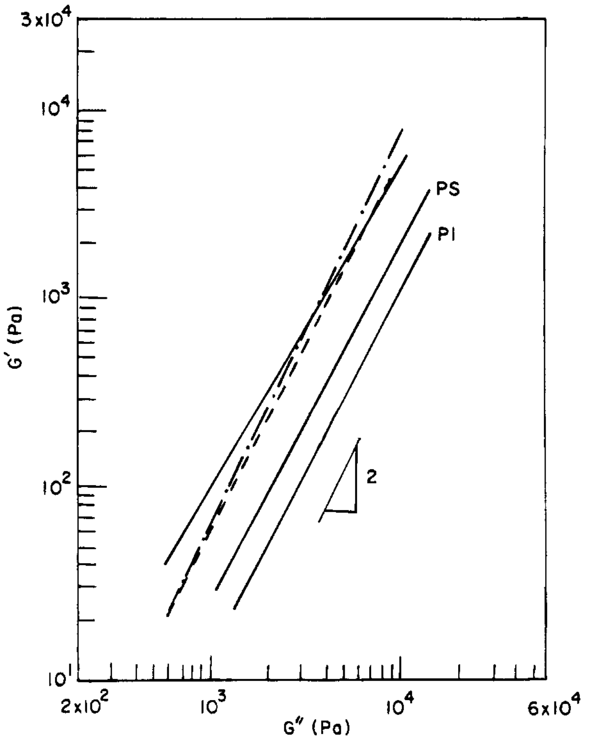

Figure 9. Comparison of the log G' versus log G'' plots for Kraton 1107 (—), SI-N (– · –), and SI-L (- - -) with the log G' versus log G'' plots for the entangled homopolymers PS having $M_w = 2 \times 10^5$ and PI having $M_w = 9 \times 10^4$.

Table 3. Glass Transition Temperature of the Polystyrene Block in the SI Diblock Copolymers Synthesized in This Study

sample code	M^b_{PS}	$T^b_{g,PS}$ (°C)
SI-N	5 600	58
SI-T	6 200	60
SI-R	8 200	65
SI-M	10 300	75
SI-O	20 800	85
SI-L	34 100	94

of homopolymer PS, we decided to measure the $T^h_{g,PS}$ of six homopolymer PSs, which were also synthesized in our laboratory, and the results are summarized in Table 4. Note that the molecular weights of the homopolymer PSs given in Table 4 are comparable with those of the PS block in the SI diblock copolymers given in Table 3. Also given in Figure 10 are plots of $T^h_{g,PS}$ versus M^h_{PS} for homopolymer polystyrene obtained in this study and also from the study of Morese-Seguela et al.[26] It can be seen in Figure 10 that the value of $T^b_{g,PS}$ is lower by as much as ca. 25 deg than the value of $T^h_{g,ps}$. This observation is very important to prepare reduced plots, as will be presented below.

Reduced Plots of log G'_r versus log $a_T\omega$ and log η'_r versus log $a_T\omega$. In the present study, we prepared reduced plots by choosing the reference temperature (T_0) in two different ways, namely (a) by choosing the temperature which is at an *equal* distance from the $T^b_{g,PS}$ in each SI diblock copolymer and (b) by choosing the temperature which is at an equal distance from the T_{ODT} of each SI diblock copolymer.

Let us first look at reduced plots prepared with T_0, which is at an equal distance from the $T^b_{g,PS}$ in each block copolymer. Figure 11 gives plots of log G'_r versus log $a_T\omega$ and log η'_r versus log $a_T\omega$ for SI-R and SI-T, in which a_T was determined with $T_0 = T^b_{g,PS} + 35$ °C for each block copolymer, i.e., $T_0 = 100$ °C for SI-R and $T_0 = 95$ °C for SI-T. Note in Figure 11 that $G'_r = G'\varrho_0 T_0/\varrho T$ and $\eta'_r = \eta'\varrho_0 T_0/a_T\varrho T$, where $\eta'(\omega)$ is the dynamic viscosity defined by $\eta'(\omega) = G''(\omega)/\omega$ and ϱ and ϱ_0 are the densities at measurement temperatures T and T_0, respectively. It should be mentioned that owing to the

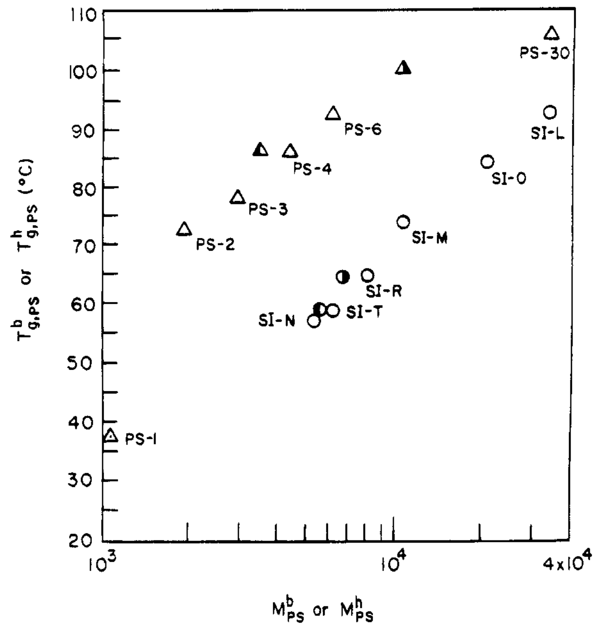

Figure 10. Plots of $T^b_{g,PS}$ versus M^b_{PS} for PS block in SI diblock copolymer: this study (○), SI-1 in ref 26 (◑), and SI-2 in ref 26 (◐). Plots of $T^h_{g,PS}$ versus M^h_{PS} for homopolymer PS: this study (△), PS-1 in ref 26 (▲), and PS-2 in ref 26 (◭).

Table 4. Glass Transition Temperature of the Homopolymer Polystyrenes Synthesized in This Study

sample code	M^h_{PS}	$T^h_{g,PS}$ (°C)
PS-1	1090	37
PS-2	1940	74
PS-3	2920	79
PS-4	4300	87
PS-6	6100	93
PS-30	33000	107

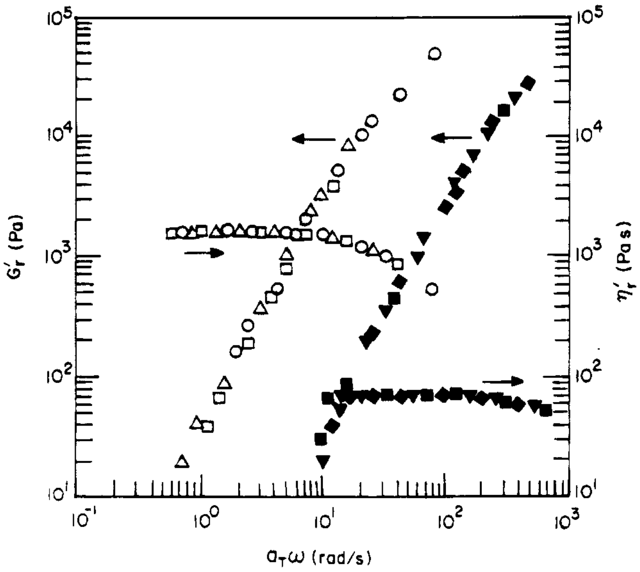

Figure 11. Plots of log G'_r versus log $a_T\omega$ and log η'_r versus log $a_T\omega$ for (a) SI-R at 100 °C (○), 105 °C (△), and 110 °C (□) and (b) SI-T at 65 °C (■), 70 °C (▼), and 75 °C (◆) in the disordered state, using the temperature at an equal distance from the glass transition temperature of the polystyrene block ($T^b_{g,PS} + 35$ °C) in each block copolymer as reference temperature T_0.

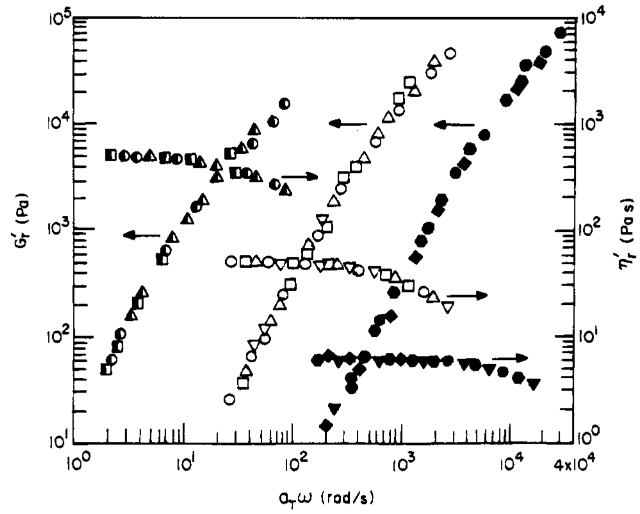

Figure 12. Plots of log G_r' versus log $a_T\omega$ and log η_r' versus log $a_T\omega$ for (a) SI-M at 100 °C (▼), 105 °C (◆), 110 °C (●), and 115 °C (●), (b) SI-O at 130 °C (○), 135 °C (△), 140 °C (□), and 145 °C (▽), and (c) SI-L at 170 °C (◐), 175 °C (▲), and 180 °C (◧) in the disordered state, using the temperature at an equal distance from the glass transition temperature of the polystyrene block ($T^b_{g,PS}$ + 76 °C) in each block copolymer as reference temperature T_0.

fact that the molecular weights of SI-R and SI-T were so low, it was not possible for us to take reliable data for G' and G'' at temperatures far above the $T^b_{g,PS}$ and therefore T_0 could not be chosen at temperatures far above the $T^b_{g,PS}$. What is unusual in Figure 11 is that the values of G_r' and η_r' for SI-R are about 1 order of magnitude larger than those for SI-T, while the molecular weight of SI-R is only about 1.3 times that of SI-T (see Table 1). Such a large difference in G_r' and η_r' cannot be explained solely by the difference in M between the two block copolymers if they are assumed to be *unentangled* chains.

Figure 12 gives plots of log G_r' versus log $a_T\omega$ and log η_r' versus log $a_T\omega$ for SI-M, SI-O, and SI-L, in which a_T was determined with $T_0 = T^b_{g,PS}$ + 76 °C for each block copolymer, i.e., T_0 = 151 °C for SI-M, T_0 = 161 °C for SI-O, and T_0 = 170 °C for SI-L. It can be seen in Figure 12 that the values of η_r' and G_r' increase in going from SI-M to SI-O and to SI-L, the same trend as the increase in M in going from SI-M to SI-O and to SI-L. Again, the observed differences in η_r' and G_r' among the three block copolymers are too large to be accounted for solely by the differences in M if all three block copolymers are assumed to be *unentangled* chains. However, this can be explained, at least in part, if SI-L and SI-O are regarded as being *entangled* block copolymers. More of this will be discussed later in this paper.

Let us now turn to reduced plots prepared with T_0, which is at an equal distance from the T_{ODT} of each block copolymer. Figure 13 gives plots of log G_r' versus log $a_T\omega$ and log η_r' versus log $a_T\omega$ for SI-R and SI-T, in which a_T was determined with $T_0 = T_{ODT}$ + 10 °C for each block copolymer, i.e., T_0 = 110 °C for SI-R and T_0 = 75 °C for SI-T. Again, it should be mentioned that owing to the fact that the M of SI-R and SI-T were so low, it was not possible for us to take reliable data for G' and G'' at temperatures far above the T_{ODT} and therefore T_0 could not be chosen at temperatures far above the T_{ODT}. It can be seen in Figure 13 that at a given value of $a_T\omega$, the values of η_r' and G_r' for SI-T are much larger than those for SI-R, behavior quite the opposite to that shown in Figure 11.

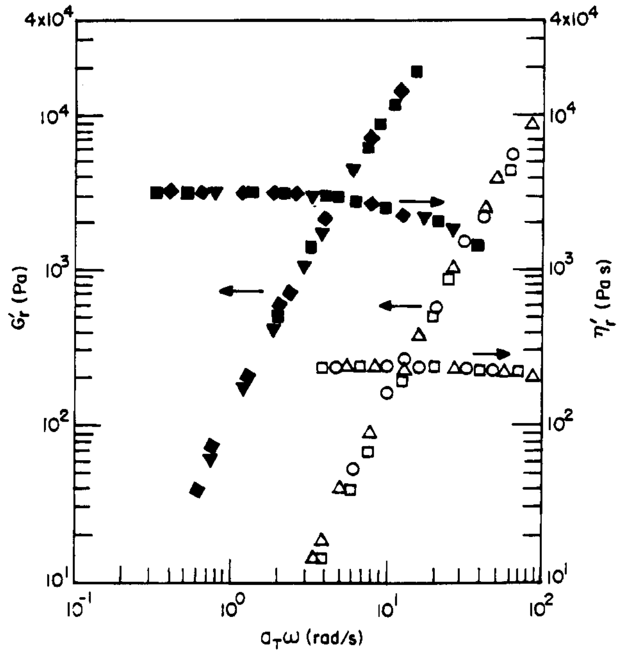

Figure 13. Plots of log G_r' versus log $a_T\omega$ and log η_r' versus log $a_T\omega$ for (a) SI-R at 100 °C (○), 105 °C (△), and 110 °C (□) and (b) SI-T at 65 °C (■), 70 °C (▼), and 75 °C (◆) in the disordered state, using the temperature at an equal distance from the order–disorder transition temperature (T_{ODT} + 10 °C) of each block copolymer as reference temperature T_0.

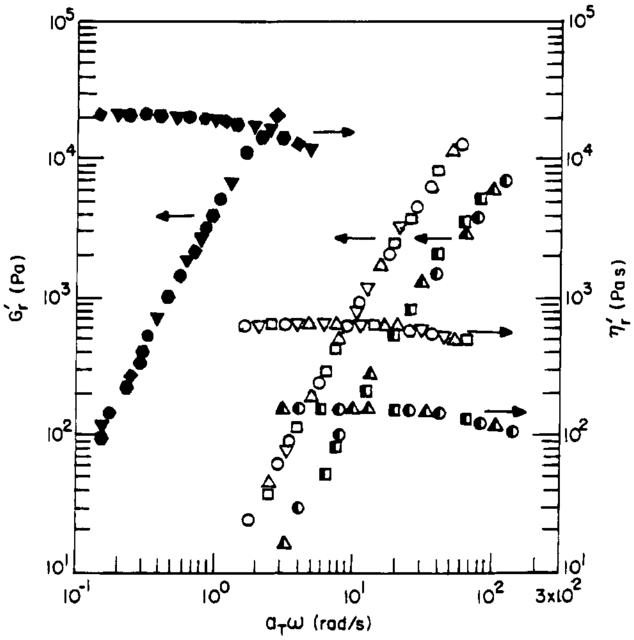

Figure 14. Plots of log G_r' versus log $a_T\omega$ and log η_r' versus log $a_T\omega$ for (a) SI-M at 100 °C (▼), 105 °C (◆), 110 °C (●), and 115 °C (●), (b) SI-O at 130 °C (○), 135 °C (△), 140 °C (□) and 145 °C (▽), and (c) SI-L at 170 °C (◐), 175 °C (▲), and 180 °C (◧) in the disordered state, using the temperature at an equal distance from the order–disorder transition temperature (T_{ODT} + 10 °C) of each block copolymer as reference temperature T_0.

Figure 14 gives plots of log G_r' versus log $a_T\omega$ and log η_r' versus log $a_T\omega$ for SI-M, SI-O, and SI-L, in which a_T was determined with $T_0 = T_{ODT}$ + 10 °C for each block copolymer, i.e., T_0 = 100 °C for SI-M, T_0 = 140 °C for SI-O, and T_0 = 180 °C for SI-L. It can be seen in Figure 14 that at a given value $a_T\omega$, the values of η_r' and G_r' for SI-M are the largest while the values of η_r' and G_r' for SI-L are the smallest, among the three block copolymers. This trend is quite the opposite to that shown in Figure 12.

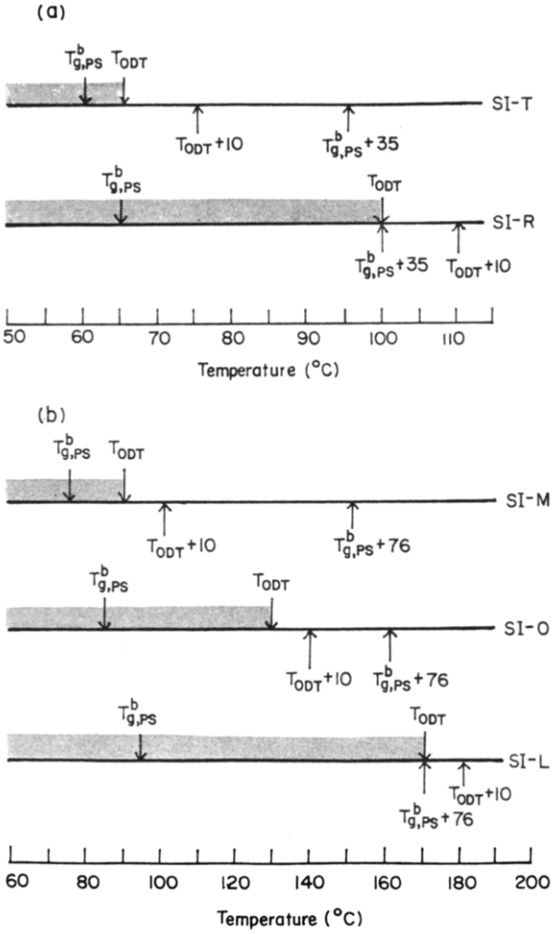

Figure 15. Schematic describing the reference temperatures T_0, which were used to construct reduced plots of log G_r' versus log $a_T\omega$ and log η_r' versus log $a_T\omega$ (a) relative to the $T^b_{g,PS}$ and T_{ODT} of SI-T and SI-R and (b) relative to the $T^b_{g,PS}$ and T_{ODT} of SI-M, SI-O, and SI-L.

In order to help explain the seemingly contradictory correlations given in Figures 11–14, let us look at the schematic given in Figure 15. It seems clear from Figure 15 that the reduced plots are greatly influenced by how far the T_{ODT} is from the $T^b_{g,PS}$ in each block copolymer, because the reference temperature chosen, $T_0 = T_{ODT} + 10$ °C, is very close to the $T^b_{g,PS}$, i.e., the $T_0 = 75$ °C for SI-T is *only* 15 °C above its $T^b_{g,PS}$ while the $T_0 = 110$ °C for SI-R is 45 °C above its $T^b_{g,PS}$, although the values of T_0 chosen lie in the *disordered* state of the respective block copolymers. That is, the closer the T_{ODT} to the $T^b_{g,PS}$, the greater the influence of $T^b_{g,PS}$ on reduced plots. This now explains why in Figure 13 the values of η_r' and G_r' for SI-T are much larger than those for SI-R. The same explanation can be applied to Figure 14, where the values of η_r' and G_r' for SI-M are seen to be much larger than those for SI-O and SI-L because the $T_0 = 100$ °C for SI-M is *only* 25 deg above its $T^b_{g,PS}$, whereas the $T_0 = 140$ °C for SI-O is 55 deg above its $T^b_{g,PS}$, and the $T_0 = 180$ °C for SI-L is 86 deg above its $T^b_{g,PS}$. Thus we can conclude that reduced plots given in Figures 13 and 14 do *not* reflect correctly the effect of M on the rheological behavior of the SI diblock copolymers. If T_{ODT} is to be used as reference temperature to prepare reduced plots for a block copolymer in the *disordered* state, the T_{ODT} must be located very far above its $T^b_{g,PS}$ (e.g., $T_{ODT} > T^b_{g,PS} + 100$ °C).

The choice of T_0 which is at an equal distance from the $T^b_{g,PS}$ in each block copolymer, employed in Figures 11 and 12, is based on the well-known concept of iso-free-volume, which in the past was used to compare the rheological properties of different blend compositions in binary mixtures of amorphous homopolymers.[27,28] However, in the present study we encounter a practical difficulty with this approach, because the $T^b_{g,PS}$ lies in the *ordered* state of the block copolymers investigated. The choice of a temperature above the $T^b_{g,PS}$, which is still in the *ordered* state of a block copolymer, as reference temperature T_0 to obtain reduced plots in the *disordered* state implies that time–temperature superposition is applicable to a block copolymer in both the ordered and disordered states. An objection can be raised to this approach, because the experimental glass transition temperature used to establish the reference temperature is for *microphase-separated* systems and thus is not appropriate for establishing reference temperatures which permit fair comparison of different *homogeneous* (*disordered*) SI diblock copolymers.

It should be mentioned that using log G_r' versus log $a_T\omega$ plots (see Figures 11–14), we have no way of knowing whether a polymer is *entangled* or not. On the other hand, as discussed above, plots of log G' versus log G'' are very effective in making such a determination. This is because log G_r' versus log $a_T\omega$ plots are *dependent* upon M regardless of whether a polymer is entangled or not, whereas log G' versus log G'' plots are *independent* of M if a polymer is *entangled*.

Comparison of Experiment with Theory. We made an attempt to compare experimental results with predictions made from the Stockmayer–Kennedy theory presented above. Using eq 12 we calculated values of $G'(\omega)$ and $G''(\omega)$ with the following procedures. Specifically, using eq 3 we calculated the relaxation time spectra, $\tau_{p,\mathrm{block}}$, for a given SI diblock copolymer, which then enabled us to calculate, with the aid of eq 10, *reduced* storage and loss moduli, $G_R'(\omega)$ and $G_R''(\omega)$. For this, using eq 5 we first calculated the terminal relaxation times $\tau^b_{1,PS}$ and $\tau^b_{1,PI}$ for blocks PS and PI, respectively. This required calculations of $\eta^b_{o,i}$, for which the following expression was used:[20]

$$\eta^b_{o,i} = \zeta^b_{o,i}\varrho_i b_i^{\,2} N_A M^b_i / 36 M_{o,i}^{\,2} \qquad i = \mathrm{PS, PI} \qquad (17)$$

where b_i is the Kuhn statistical length for component i, N_A is Avogadro's number, and $M_{o,i}$ is the monomeric molecular weight of component i.

There is experimental evidence[29–32] indicating that the friction coefficients for the two species in a miscible polymer blend are quite different from the friction coefficients for the corresponding *homopolymers* and they vary with blend composition. On the basis of such experimental observations, it seems reasonable to speculate that the friction coefficients $\zeta^b_{o,i}$ for the two species PS and PI in the block copolymer medium might depend on the friction coefficients $\zeta^h_{o,i}$ for the corresponding *homopolymers* PS and PI, and also on block copolymer composition. However, since *no* such information is available in the literature, in the present study we calculated $\eta^b_{o,PS}$ using the expression:

$$\eta^b_{0,PS} = \zeta^h_{0,PS}\varrho_{PS} b_{PS}^{\,2} N_A M^b_{PS} / 36 M_{0,PS}^{\,2} \qquad (18)$$

in which $\zeta^b_{0,PS} \approx \zeta^h_{0,PS}$ is assumed. Below, we shall discuss the consequence of this assumption after comparing experimental results with predictions.

In calculating $\eta^{b}_{0,PS}$ at various temperatures from eq 18, we used $\zeta^{h}_{0,PS} = 0.1148$ (N s)/m at $T^{b}_{g,ps}$, together with the WLF equation:[20]

$$\log a_{T}(T) = \frac{-13.7(T - T^{b}_{g,PS})}{50.5 + T - T^{b}_{g,PS}} \qquad (19)$$

Note that the values of $T^{b}_{g,ps}$ for the six SI diblock copolymers synthesized in this study are given in Table 3.

In calculating $\eta^{b}_{0,PI}$ at various temperatures, we used the following empirical expression,[33]

$$\eta^{b}_{0,PI} = 3.70 \times 10^{-18} \times \exp(4478/T)(M_{c,PI}/90000)^{3.4}(M^{b}_{PI}/M_{c,PI}) \qquad (20)$$

It should be mentioned that the microstructure (6 wt % 3,4-addition, 26 wt % trans 1,4-addition, and 68 wt % cis 1,4-addition) of the homopolymer PIs were determined, via NMR spectroscopy, to be the same as that of the PI block in the SI diblock copolymers investigated in this study.

The values used for the Kuhn statistical length for styrene and isoprene monomers were: $b_{PS} = 0.68$ nm and $b_{PI} = 0.63$ nm, and the following expressions were used for the temperature dependence of density for PS[34]

$$1/\varrho_{PS} = 0.9199 + 5.098 \times 10^{-4}(T - 273) + 2.354 \times 10^{-7}(T - 273)^{2} + [32.46 + 0.1017(T - 273)]/M^{b}_{PS} \qquad (21)$$

and for PI[8b]

$$1/\varrho_{PI} = 1.0771 + 7.22 \times 10^{-4}(T - 273) + 2.46 \times 10^{-7}(T - 273)^{2} \qquad (22)$$

Let us now return to Figures 4, 6, and 7, in which *solid lines* are predicted log G' versus log G'' plots. It can be seen in these figures that the theory predicts correctly the experimental trend, but the absolute values for the predicted G' are about 1 order of magnitude smaller than the measured ones. Specifically, in reference to Figure 4, the log G' versus log G'' plot for SI-R lies slightly above that for SI-T, which is consistent with experimental results. By calculating $J^{0}_{e,R}$ from eq 11, we obtained 0.41 for SI-R and 0.42 for SI-T. Most interestingly, the values of $J^{0}_{e,R}$ for the two block copolymers are found to be very close to $J^{0}_{e,R} = 0.40$ which is predicted for *homopolymer melts* by the Rouse theory. This observation is in agreement with the earlier findings by Stockmayer and Kennedy[12] and Wang and DiMarzio[15] who reported that the block copolymer structure had *little* influence on the *reduced* storage and loss moduli, $G'_{R}(\omega)$ and $G''_{R}(\omega)$. This is not surprising because, according to eq 10, $G'_{R}(\omega)$ and $G''_{R}(\omega)$ are independent of the total molecular weight of block copolymer. Of course, $G''_{R}(\omega)$ and $G'_{R}(\omega)$ can vary with block length ratio. On the other hand, the storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, defined by eq 12, depend on the total molecular weight of block copolymer. Therefore we conclude that the predicted difference in log G' versus log G'' plots between SI-R and SI-T, displayed in Figure 4, is attributable to the difference in molecular weight between the two block copolymers (see Table 1). The same explanation can be offered to the differences in log G' versus log G'' plots among the three block copolymers, SI-M, SI-O, and SI-L, the predictions of which are displayed in Figure 6.

In reference to Figure 7, we observe that the predicted log G' versus log G'' plot for SI-N lies slightly below that for SI-O, which is opposite to the experimental observation. This discrepancy may be attributable to the assumption made in the calculation that SI-N is an *unentangled* block copolymer, while it could be an *entangled* block copolymer. As discussed above in reference to Figure 9, there is strong experimental evidence, suggesting that SI-N may be regarded as an *entangled* block copolymer. If SI-N is regarded as an entangled block copolymer, the predicted log G' versus log G'' plot for SI-N, given in Figure 7, would lie above that for SI-O.

There are two questions which must be addressed before leaving this section. (1) How much error might have been incurred from the assumption of $\zeta^{b}_{0,PS} \approx \zeta^{h}_{0,PS}$ in calculating from eq 12 the values of $G'(\omega)$ and $G''(\omega)$ for the SI diblock copolymers investigated in this study? (2) Why are the calculated values of $G'(\omega)$ and $G''(\omega)$ for the SI diblock copolymers so much smaller than the experimentally measured ones?

Regarding the first question posed above, using eq 11 we calculated $J^{0}_{e,R}$ for values of λ, defined by eq 7, ranging from $0.01\lambda_0$ to $100\lambda_0$, where $\lambda_0 = (\tau^{h}_{1,PI}/\tau^{h}_{1,PS})^{1/2}$ with $\tau^{h}_{1,PI}$ and $\tau^{h}_{1,PS}$ being the terminal relaxation times for homopolymers PI and PS, respectively. Note that $\lambda/\lambda_0 = (\zeta^{b}_{0,PI}/\zeta^{h}_{0,PI})^{1/2}/(\zeta^{b}_{0,PS}/\zeta^{h}_{0,PS})^{1/2}$. We have learned that the values of $J^{0}_{e,R}$ varied little (within ±10%) as λ/λ_0 varied from 0.01 to 100. Therefore we can conclude from eq 13 that J^{0}_{e} varies *little* with λ/λ_0 ranging from 0.01 to 100. From the relationship of $G'(\omega) = J^{0}_{e}G''(\omega)^{2}$,[20,22] we are led to conclude that the large discrepancy observed in log G' versus log G'' plots between experiment and theory, shown in Figures 4, 6, and 7, cannot be ascribed solely to the errors that might have been incurred from the assumption of $\zeta^{b}_{0,PS} \approx \zeta^{h}_{0,PS}$ and $\zeta^{b}_{0,PI} \approx \zeta^{h}_{0,PI}$ made in estimating $\zeta^{b}_{0,PS}$ and $\zeta^{b}_{0,PI}$ and hence in the calculation of $\eta^{b}_{0,PS}$ from eq 18 and $\eta^{b}_{0,PI}$ from eq 20.

Regarding the second question posed above, we are of the opinion that some of the SI block copolymers, if not all, investigated in this study may be regarded as *entangled* chains. This will then increase considerably the predicted values of $G'(\omega)$ and $G''(\omega)$ over those based on *unentangled* chains. The readers are reminded that the value of $J^{0}_{e,R}$ for entangled chains is about 3 times greater than that for unentangled chains. At present there is *no* comprehensive theory predicting the rheological behavior of *homogeneous*, *entangled* block copolymers. Previously, Kim and Han[11] extended, on an *ad hoc* basis, the Stockmayer–Kennedy theory to interpret their experimental results for the rheological behavior of *homogeneous*, *entangled* polystyrene-*block*-poly(α-methylstyrene) copolymers, by calculating the terminal relaxation times for the two species within the spirit of the tube model.[22] However, we are of the opinion that the inclusion of intermolecular interactions between the species would be very important to the development of a comprehensive molecular theory predicting the rheological behavior of a block copolymer, whether it is entangled or not.

Concluding Remarks

In this paper we have presented experimental results for the linear viscoelastic properties of low molecular weight SI diblock copolymers in the *disordered* state. To the best of our knowledge, such experimental results have never been reported in the literature. We have shown that use of log G' versus log G'' plots is very useful for investigating the effects of molecular weight and block length ratio on the rheological behavior of the SI diblock copolymers synthesized in this study. It should be pointed out that the experimental data reported in this paper are very limited to the range of temperatures covered; namely, most of the data were taken at temperatures *not* far above the T_{ODT} of each block copolymer. The primary reason for this is that, owing to the nature of the low molecular weight of SI diblock copolymers synthesized in this study, the torque that could be recorded reliably during the rheological measurements decreased very rapidly as the temperature was increased farther above the T_{ODT} of each block copolymer.

We suggest that a theory be developed to predict the entanglement molecular weight of a diblock copolymer with information on the entanglement molecular weights of the constituent blocks and block length ratio. We suggest further that a theory be developed to determine whether a diblock copolymer, which consists of two *unentangled* chains, remains as an *unentangled* chain, or may be considered as an *entangled* chain.

The task of predicting the rheological properties of block copolymers is a real challenge not only to rheologists but also to polymer scientists. It is quite astonishing, and at the same time very discouraging, to find that even after more than three decades since the first commercialization of styrene-based diblock and triblock copolymers, today there exists *no* comprehensive theory predicting the rheological properties of such block copolymers. There are two parts in the development of a comprehensive theory predicting the rheological behavior of block copolymers, namely, (a) in the *ordered* state and (b) in the *disordered* state. The former requires specification of the type of microdomain structure (spheres, cylinders, lamellae, or ordered bicontinuous microdomains), and hence it is not a trivial task and yet this must be dealt with. The latter, however, is much less complicated than the former, but we must realize that two flexible chains in a diblock copolymer (and three flexible chains in a triblock copolymer) are connected. A more challenging problem may arise when considering the possibility of having a diblock copolymer which consists of a *flexible* chain on one side and a *rigid rodlike* chain on the other side. As a matter of fact, such diblock copolymers are being synthesized in some research laboratories. The discussion of potential applications of such polymer molecules is beyond the scope of this paper. It seems that this area requires a great deal of attention from polymer scientists in the future.

References and Notes

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