Macromolecules **2004,** *37,* 215−225

Molecular Weight Dependence of Zero-Shear Viscosity of Block Copolymers in the Disordered State

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Received December 30, 2002; Revised Manuscript Received October 20, 2003

ABSTRACT: The molecular weight dependence of zero-shear viscosity (η_0) of polystyrene-*block*-polyisoprene (SI diblock) copolymer in the disordered state was investigated. For the investigation, a series of lamella-forming, nearly monodisperse SI diblock copolymers were synthesized via sequential anionic polymerization, and order−disorder transition temperatures (T_{ODT}) of the block copolymers were determined from isochronal dynamic temperature sweep experiments at an angular frequency (ω) of 0.01 rad/s and also from dynamic frequency sweep experiments over a wide range of temperatures. The η_0 of the SI diblock copolymers in the disordered state (at $T > T_{\mathrm{ODT}}$) was determined from $\eta_{0,\mathrm{r}} = \lim_{\omega\to0}[|\eta_{\mathrm{r}}^*(\omega)|]$, for which logarithmic plots of reduced complex viscosity $|\eta_{\mathrm{r}}^*(\omega)|$ vs $a_{\mathrm{T}}\omega$ with a_{T} being temperature-dependent shift factor were first prepared, where $|\eta_{\mathrm{r}}^*(\omega)|$ is defined by $|\eta_{\mathrm{r}}^*(\omega)| = |\eta^*(\omega)|(T_{\mathrm{r}}\rho_{\mathrm{r}}/T\rho)/a_{\mathrm{T}}$ in which $|\eta^*(\omega)|$ is the complex viscosity at ω, T is the measurement temperature, T_{r} is a reference temperature defined by $T_{\mathrm{r}} = T_{\mathrm{g,PS}} + 104$ °C with $T_{\mathrm{g,PS}}$ being the glass transition temperature of the polystyrene phase, and ρ and ρ_{r} are the densities at T and T_{r}, respectively. The molecular weight (M) dependence of η_0 for the SI diblock copolymers in the disordered state is found to follow the relationship $\eta_0 \propto M^{1.15\pm0.09}$ for $M < M_{\mathrm{c}}$ and $\eta_0 \propto M^{4.69\pm0.18}$ for $M \geq M_{\mathrm{c}}$, where M_{c} is the viscosity critical molecular weight at which the slope of η_0 vs log M plot changes abruptly. Also investigated, for comparison, was the molecular weight dependence of η_0 for nearly monodisperse homopolystyrenes, which were synthesized via anionic polymerization, and it is found that $\eta_0 \propto M^{1.21\pm0.23}$ for $M < M_{\mathrm{c}}$ and $\eta_0 \propto M^{3.37\pm0.21}$ for $M \geq M_{\mathrm{c}}$, which is in excellent agreement with the literature. Further, the molecular dependence of steady-state recoverable compliance ($J_{\mathrm{e}}^{\mathrm{o}}$) of SI block copolymer in the disordered state was determined from $J_{\mathrm{e}}^{\mathrm{o}} = \lim_{\omega\to0}J'(\omega)$ for which logarithmic plots of dynamic storage compliance $J'(\omega)$ vs $a_{\mathrm{T}}\omega$ were first prepared, where $J'(\omega)$ is defined by $J'(\omega) = G'(\omega)/[(G'(\omega))^2 + (G''(\omega))^2]$. The M dependence of $J_{\mathrm{e}}^{\mathrm{o}}$ for the SI diblock copolymers in the disordered state is found to follow the relationship $J_{\mathrm{e}}^{\mathrm{o}} \propto M^{1.63\pm0.17}$ for $M < M_{\mathrm{c}}$, and $J_{\mathrm{e}}^{\mathrm{o}} \propto M^{5.22\pm0.78}$ for $M \geq M_{\mathrm{c}}$. The much stronger molecular weight dependence of η_0 and $J_{\mathrm{e}}^{\mathrm{o}}$ for the disordered SI diblock copolymers than that for homopolystyrenes observed in this study is attributable to the styrene−isoprene junction effect that originates from the difference in the monomeric friction coefficients between polystyrene and polyisoprene blocks.

Introduction

Today it is well established theoretically that microphase-separated block copolymers undergo, during heating, an order−disorder transition (ODT) at a certain critical temperature, commonly referred to as the ODT temperature (T_{ODT}), which in turn depends on molecular weight, block composition, and segment−segment interaction parameter of the constituent blocks[1−3] and also on conformational asymmetry of the constituent blocks.[4] During the past three decades, numerous investigators have reported on the measurements of T_{ODT} using radiation scattering methods and/or oscillatory shear rheometry. There are too many papers to cite them all here. The readers are referred to a review article.[5]

To date, only a few experimental studies[6,7] have reported on the rheological behavior of microphase-separated block copolymers as affected by the molecular weight and block composition. Owing to the presence of microdomain structures, the rheological behavior of block copolymers in the ordered state (at $T < T_{\mathrm{ODT}}$) is much more complicated than that in the disordered state (at $T \geq T_{\mathrm{ODT}}$). For instance, block copolymers with lamellar or cylindrical microdomains exhibit shear thinning (“yield behavior”) at very low shear rates in steady-state shear flow,[8] very similar to particulate-filled molten thermoplastics[9] or thermotropic liquid-crystalline polymers with nematic mesophase.[10−13] Under such circumstances the determination of zero-shear viscosity (η_0) of microphase-separated block copolymers is practically very difficult, if not impossible. Interestingly, very recently Sebastian et al.[14] reported that sphere-forming block copolymers exhibited extremely large values (10^7−10^8 Pa s) of η_0 at extremely low shear rates (10^{-8} s^{-1}) or at very low shear stresses (<100 Pa), followed by a sudden drop in shear viscosity (almost 4 orders of magnitude) when shear stress was increased to 200 Pa entering a weakly shear-thinning regime.

From a theoretical point of view, there are two features that distinguish the dynamics of a block copolymer chain from the dynamics of a chain in a mixture of two homopolymers. One is the connectivity of the blocks, and the other is a position-dependent external potential. When dealing with the dynamics of a microphase-separated block copolymer, one must include microdomain structures (lamellae, cylinders, gyroids, or spheres) in the formulation of system equations. Until now no comprehensive molecular theory exists, which enables us to predict the rheological behavior of microphase-separated block copolymers although in the past some attempts were made in that direction.[15−17] Certainly, a theoretical treatment of the dynamics of disordered (homogeneous) block copolymers would be much easier than a theoretical treatment of the dynamics of microphase-separated block copolymers. Even so, there has been no theoretical study reported

10.1021/ma021792f CCC: $27.50

in the literature since the seminal studies published in 1975 by four research groups.[18−21]

In 1975, Stockmayer and Kennedy[18] investigated the chain dynamics of homogeneous Rouse chains of AB-type diblock or ABA-type triblock copolymers by modifying the bead−spring model of Rouse for linear flexible homopolymers.[22] They considered the continuous limit of the bead−spring Rouse model and calculated the spectrum of relaxation time ($\tau_{p,block}$) of the block copolymer in terms of the terminal relaxation times for the Rouse chains for the A and B blocks. Once the values of $\tau_{p,block}$ are determined, one can calculate linear dynamic viscoelastic properties of unentangled, homogeneous block copolymers.

However, the fundamental question must first be answered before considering the chain dynamics of homogeneous Rouse chains of AB-type diblock or ABA-type triblock copolymers. Should a homogeneous AB-type diblock copolymer, for instance, be regarded as being unentangled chains as long as the molecular weight of each block is lower than its entanglement molecular weight even when the combined molecular weight is higher than the entanglement molecular weight of one of the two blocks? The above question can be rephrased as follows. Can a homogeneous AB-type diblock copolymer be regarded as being entangled chains if the combined molecular weight of both blocks is higher than the entanglement molecular weight of one of the blocks even when the molecular weight of each block is lower than its entanglement molecular weight? The next question is, how can one define (or determine) the entanglement molecular weight of a homogeneous AB-type diblock copolymer or ABA-type triblock copolymer when information on the entanglement molecular weights of the constituent blocks is available?

Although the rheological behavior of homogeneous block copolymers is perceived to be much less complicated than that of microphase-separated block copolymers, only a small number of experimental studies[23−26] have reported on the rheological behavior of homogeneous block copolymers. In addition to the questions posed above, there are still more fundamental issues that need to be addressed for a better understanding of the rheological behavior of homogeneous block copolymers. One such question is, will the molecular weight (M) dependence of η_0 of disordered block copolymers be the same as the well-established relationship for ordinary flexible polymers? Until now there is no evidence, experimental or theoretical, suggesting that the well-established relationship for ordinary flexible homopolymers,[27] $\eta_0 \propto M^{1.0}$ for $M < M_c$ and $\eta_0 \propto M^{3.4}$ for $M \geq M_c$ with M_c being the viscosity critical molecular weight, also holds for homogeneous block copolymers.

In this study, we carried out an experimental investigation to address some of the questions posed above. For the study, we synthesized, via sequential anionic polymerization, a series of low-molecular-weight lamella-forming, nearly symmetric polystyrene-*block*-polyisoprene (SI diblock) copolymers and then investigated the molecular dependence of η_0 in the disordered state, i.e., at $T > T_{ODT}$. For this, we first determined the T_{ODT} of each block copolymer by conducting both isochronal dynamic temperature sweep experiments and dynamic frequency sweep experiments at various temperatures. We applied time−temperature superposition to the dynamic frequency sweep data taken only at temperatures above T_{ODT} and then determined the molecular weight dependence of η_0 of the SI diblock copolymers in the disordered state (at $T > T_{ODT}$). For comparison, we also synthesized, via anionic polymerization, a series of homopolystyrenes (hPS) and investigated the molecular weight (M) dependence of η_0. We have confirmed that $\eta_0 \propto M^{3.4}$ holds for the hPSs having M greater than a critical value. On the other hand, we have found that the molecular weight dependence of η_0 for SI diblock copolymers in the disordered state is much stronger than 3.4 power for M greater than a critical value. In this paper we present the highlights of our findings.

Experimental Section

Synthesis of Polymers and Characterization. Eight lamella-forming, nearly symmetric low-molecular-weight SI diblock copolymers with molecular weight varying from 8×10^3 to 2.1×10^4 were synthesized, via sequential anionic polymerization, using the standard procedures with *sec*-butyllithium as initiator and cyclohexane as solvent. Also, we synthesized, via anionic polymerization, eight hPS with molecular weight varying from 10^4 to 10^5. The molecular weights of all polymers were determined using two different methods: light scattering and membrane osmometry. Light scattering measurements were conducted on a Wyatt Technology apparatus (model DAWN EOS), which enabled us to obtain, via a Zimm plot, weight-average molecular weight (M_w). Membrane osmometry measurements were conducted on a Jupiter Instruments unit (model 231), which enabled us to determine number-average molecular weight (M_n). In the membrane osmometry measurements two different membranes of cellulose acetate were used: one (molecular weight cutoff 10K, P/N 239006) for samples having molecular weights between ca. 10^4 and 2×10^4 and another (molecular weight cutoff 20K, P/N 239007) for samples having molecular weights higher than ca. 2×10^4. Polymer samples were dissolved in toluene for membrane osmometry measurements, and polymer samples were dissolved in tetrahydrofuran for light scattering measurements. The polydispersity index of each polymer was determined using gel permeation chromatography (GPC) (Waters). The microstructures of polyisoprene block and the compositions of the SI diblock copolymers were determined using proton nuclear magnetic resonance (^{1}H NMR) spectroscopy (Varian Gemini-200, 200 MHz). We found that the polyisoprene block has the microstructures consisting of 6% 3,4-addition, 26% trans-1,4-addition, and 68% cis-1,4-addition. Table 1 gives a summary of the molecular characteristics and block compositions of eight SI diblock copolymers, and Table 2 gives a summary of the molecular characteristics of eight hPSs synthesized in the present study.

Differential Scanning Calorimetry (DSC). We determined glass transition temperature of the eight SI diblock copolymers and also eight hPSs synthesized in this study using DSC (TA Instrument). For SI diblock copolymers we used a heating rate of 20 °C/min. We have found that the use of a heating rate lower than 20 °C/min for SI diblock copolymers did not allow us to discern the endothermic peak of the hPS phase in the SI block copolymers. This apparently was the reason why, earlier, other investigators[28,29] used a heating rate of 40 °C/min to determine the glass transition temperature of the PS phase in their SI diblock copolymers. The values of the glass transition temperatures of the PS block ($T_{g,PS}$) and PI block ($T_{g,PI}$) in the eight SI diblock copolymers determined in this study are summarized in Table 1. In Table 1 we observe that values of $T_{g,PI}$ remain more or less constant while values of $T_{g,PS}$ increase with increasing molecular weight. We determined, via DSC, the glass transition temperature (T_g) of eight hPSs at three different heating rates: 5, 10, and 20 °C/min, the results of which are summarized in Table 2. Notice in Table 2 that the value of T_g for hPS depends on the heating rate employed, specifically the values of T_g obtained at a heating rate of 5 °C/min are considerably lower than those obtained at 20 °C/min. Notice in Table 1 that the $T_{g,PS}$ of an SI diblock

Table 1. Molecular Characteristics, Glass Transition Temperature, and Order−Disorder Transition Temperature of the SI Diblock Copolymers Synthesized in This Study

sample code	M_w (LS)^a (g/mol)	M_n (OS)^b (g/mol)	PDI^c (GPC)	$w_{PS}{}^d$	$f_{PS}{}^e$	$M_{w,PS}{}^f$ (g/mol)	$M_{w,PI}{}^g$ (g/mol)	$T_{g,PS}{}^h$ (°C)	$T_{g,PI}{}^i$ (°C)	$T_r{}^j$ (°C)	T_{ODT} (°C)
SI-1	0.79×10^4	0.81×10^4	1.10	0.55	0.51	4350	3550	33	−57	137	k
SI-2	1.04×10^4	1.04×10^4	1.10	0.53	0.49	5500	4900	44	−60	148	k
SI-3	1.35×10^4	1.25×10^4	1.08	0.53	0.49	7160	6340	55	−62	159	82
SI-4	1.50×10^4	1.43×10^4	1.09	0.54	0.50	8100	6900	62	−61	166	91
SI-5	1.72×10^4	1.61×10^4	1.09	0.55	0.51	9460	7740	67	−62	171	127
SI-6	1.91×10^4	1.87×10^4	1.05	0.55	0.51	10500	8600	76	−60	180	146
SI-7	2.01×10^4	1.88×10^4	1.09	0.54	0.50	10850	9250	74	−62	178	156
SI-8	2.10×10^4	2.34×10^4	1.07	0.51	0.47	10700	10300	82	−60	186	186

[a] Weight-average molecular weight determined using light scattering. [b] Number-average molecular weight determined using membrane osmometry. [c] Polydispersity index (M_w/M_n) determined from gel permeation chromatography. [d] Weight fraction of PS block determined from ^{1}H NMR spectroscopy. [e] Volume fraction of PS block calculated at measured T_{ODT} from $f_{PS} = [M]_S v_{PS}/V_{ref}$, where $[M]_S$ denotes the molecular weight of styrene monomer unit, v_{PS} is the temperature-dependent specific volume in centimeter cubed per gram of polystyrene given by eq 1 in the text, V_{ref} denotes the reference volume defined by $V_{ref} = \{([M]_S v_{PS})([M]_I v_{PI})\}^{1/2}$ with $[M]_I$ being the molecular weight of isoprene monomer unit, and v_{PI} being the temperature-dependent specific volume in centimeter cubed per gram of polyisoprene given by eq 2 in the text. [f] Molecular weight of PS block calculated using the total M_w determined from light scattering. [g] Molecular weight of PI block calculated using the total M_w determined from light scattering. [h] Glass transition temperature of PS block determined using DSC at a heating rate of 20 °C/min. [i] Glass transition temperature of PI block determined using DSC at a heating rate of 20 °C/min. [j] Reference temperature chosen as $T_r = T_{g,PS} + 104$ °C, which was used to obtain a shift factor for each block copolymer. [k] Disordered.

Table 2. Molecular Characteristics and Glass Transition Temperature of the Homopolystyrenes Synthesized in This Study

sample code	M_w (LS)^a (g/mol)	M_n (OS)^b (g/mol)	PDI^c (GPC)	$T_{g,20}{}^d$ (°C)	$T_{g,10}{}^e$ (°C)	$T_{g,5}{}^f$ (°C)	$T_r{}^g$ (°C)
PS-1	1.02×10^4	0.78×10^4	1.08	91	85	83	162
PS-2	1.83×10^4	1.43×10^4	1.09	99	92	90	169
PS-3	2.94×10^4	1.99×10^4	1.08	106	93	92	171
PS-4	3.48×10^4	2.70×10^4	1.08	107	101	99	178
PS-5	5.71×10^4	4.24×10^4	1.07	108	103	101	180
PS-6	7.97×10^4	6.93×10^4	1.03	109	103	101	180
PS-7	8.98×10^4	7.04×10^4	1.04	109	102	101	180
PS-8	10.52×10^4	7.97×10^4	1.05	109	103	101	180

[a] Determined using light scattering. [b] Determined using membrane osmometry. [c] Determined from gel permeation chromatography. [d] Glass transition temperature determined using DSC at a heating rate of 20 °C/min. [e] Glass transition temperature determined using DSC at a heating rate of 10 °C/min. [f] Glass transition temperature determined using DSC at a heating rate of 5 °C/min. [g] Reference temperature chosen as $T_r = T_{g,5} + 79$ °C.

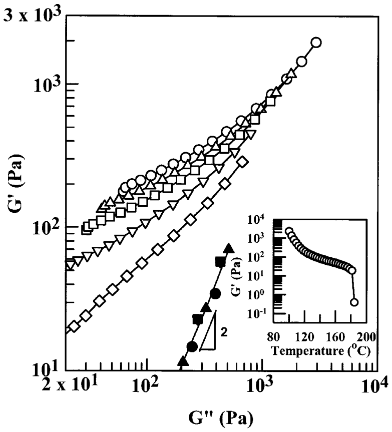

Figure 1. Plots of log G' vs log G'' for SI-8 at various temperatures: (○) 150, (△) 160, (□) 170, (▽) 180, (◇) 183, (●) 186, (▲) 189, and (■) 192 °C. The inset describes variations of G' with temperature during isochronal dynamic temperature sweep experiments of SI-8 at $\omega = 0.01$ rad/s.

copolymer is lower by ca. 20 °C compared to the T_g of hPS with comparable molecular weight (compare the values of $T_{g,PS}$ in Table 1 with the values of T_g in Table 2). This observation is consistent with that made in previous studies.[26,28] Information on the $T_{g,PS}$ of the SI diblock copolymers and the T_g of hPSs will be used to obtain temperature-independent reduced plots for the dynamic moduli and complex viscosity of the respective polymers synthesized in this study.

Sample Preparation. Samples for rheological measurements were prepared by first dissolving a predetermined amount (10 wt %) of SI diblock copolymer or hPS in toluene in the presence of 0.1 wt % 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 $T_{g,PS}$ of each SI diblock copolymer or above the T_g of hPS. 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 °C above the $T_{g,PS}$ of PS block in each SI diblock copolymer or above the T_g of hPS.

Rheological Measurement. An Advanced Rheometric Expansion System (ARES, Rheometric Scientific) was used in the oscillatory mode with parallel plate fixtures (25 mm diameter), i.e., dynamic storage and loss moduli (G' and G'') were measured as functions of angular frequency (ω) ranging from 0.01 to 100 rad/s at various temperatures during heating. The temperature increment in the frequency sweep experiment varied from 3 to 10 °C, and the specimen was kept at a constant temperature for 30−40 min before rheological measurements actually began. Also conducted was the dynamic temperature sweep experiment under isochronal conditions at a fixed angular frequency of 0.01 rad/s. The temperature control was accurate to within ±1 °C, and the strain was varied from 0.03% to 0.3% depending upon the measurement temperature, which was well within the linear viscoelasticity range for the materials investigated. All experiments were conducted under a nitrogen atmosphere to avoid oxidative degradation of the samples.

Results

Determination of the T_{ODT} of the SI Diblock Copolymers Synthesized in This Study. Since the primary objective of the present study was to determine the molecular weight dependence of zero-shear viscosity of SI diblock copolymers in the disordered state, we had to first determine the T_{ODT} of each SI diblock copolymer synthesized in this study. Figure 1 gives plots of log G' vs log G'' for SI-8 at various temperatures ranging from 150 to 192 °C. In Figure 1 we observe that the log G' vs log G'' plot suddenly shifts downward and changes its slope from much less than 2 to virtually 2 as the temperature was increased from 183 to 186 °C and then stays there as the temperature was increased further to 192 °C. Following the rheological criterion of Han and

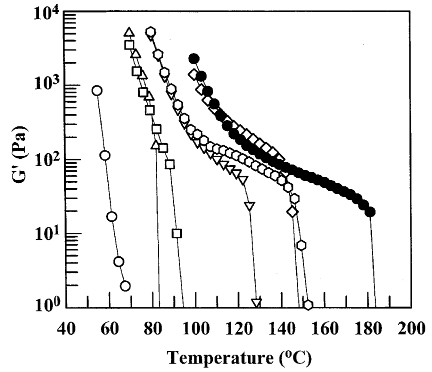

Figure 2. Variations of G' with temperature during isochronal dynamic temperature sweep experiments at $\omega = 0.01$ rad/s for seven SI diblock copolymers synthesized in this study: (○) SI-2, (△) SI-3, (□) SI-4, (▽) SI-5, (◇) SI-6, (⬡) SI-7, and (●) SI-8.

co-workers,[30−32] we determine the T_{ODT} of SI-8 to be about 186 °C. Because of space limitations, the experimental results of the dynamic frequency sweep experiments for other SI diblock copolymers synthesized in this study are not presented here. Also, the results of the isochronal dynamic temperature sweep experiments are given in the inset of Figure 1, in which we observe that G' begins to drop precipitously at about 183 °C. Following the rheological criterion by previous investigators,[33−35] from the inset of Figure 1 we determine the T_{ODT} of SI-8 to be about 183 °C, which is very close to that (186 °C) determined from the log G' vs log G'' plots. Such a good agreement between the two methods for lamella-forming, nearly symmetric block copolymers has been reported previously.[7,36]

Figure 2 presents the results of the isochronal dynamic temperature sweep experiments for seven SI diblock copolymers including SI-8. From Figure 2 we have determined the T_{ODT}s of the SI diblock copolymers except for SI-2, and the results are summarized in Table 1. Notice in Figure 2 that values of G' for SI-2 decrease steadily with increasing temperature from 52 to 68 °C, without going through a temperature at which G' begins to drop precipitously. Therefore, we conclude that SI-2 is virtually homogeneous over the entire range of temperatures investigated. Notice, further, from Table 1 that the $T_{\mathrm{g,PS}}$ of SI-2 is 44 °C, suggesting that the formation of lamellar microdomains in SI-2 would be extremely difficult, if not impossible, at temperatures below 52 °C, because this temperature is very close to $T_{\mathrm{g,PS}}$.

Construction of Reduced Plots for SI Diblock Copolymers in the Disordered State. To obtain temperature-independent reduced plots for complex viscosity $|\eta^*|$, defined by $|\eta^*| = [(G')^2 + (G'')^2]^{1/2}/\omega$, obtained at various temperatures for the eight SI diblock copolymers in the disordered state, we had to obtain a shift factor a_T. For this, log G'' vs log ω plots at various temperatures in the disordered state (at $T > T_{\mathrm{ODT}}$) were first prepared for each SI diblock copolymer. Then, the data at various temperatures were shifted along the ω axis to overlap the log G'' vs log ω plot at a reference temperature $T_r = T_{\mathrm{g,PS}} + 104$ °C with $T_{\mathrm{g,PS}}$ being the glass transition temperature of PS block in the respective SI diblock copolymer (see Table 1 for the values of $T_{\mathrm{g,PS}}$). We chose such a high temperature as reference temperature (T_r) in order to minimize the free volume effect and also to be above the T_{ODT} of each block copolymer. The amount of shift made along the ω axis, commonly referred to as the "shift factor a_T", is plotted against temperature, as given in Figure 3, for the eight SI diblock copolymers in the disordered state (at $T > T_{\mathrm{ODT}}$). A question may be raised as to whether the choice of $T_r = T_{\mathrm{g,PS}} + 104$ °C (i.e., at an equal distance from the $T_{\mathrm{g,PS}}$ of the respective SI diblock copolymer, commonly referred to as an iso-monomeric-friction (iso-zeta) state) to calculate a_T may be justified for SI diblock copolymers in the disordered state, unless the monomeric friction coefficients for PS and PI blocks are the same in the iso-zeta state. Here we neglect a minor correction for a molecular weight dependence difference in the thermal expansion coefficient. To pursue this matter, we have carried out the following analysis.

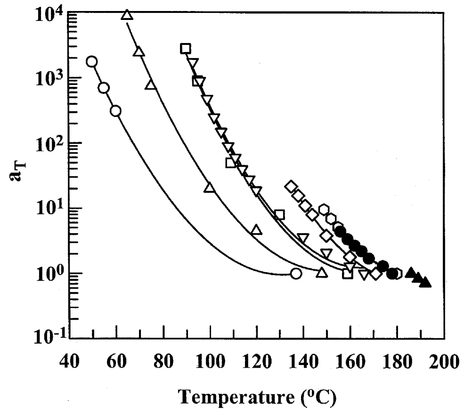

Figure 3. Plots of log a_T vs temperature for eight SI diblock copolymers synthesized in this study: (○) SI-1, (△) SI-2, (□) SI-3, (▽) SI-4, (◇) SI-5, (⬡) SI-6, (●) SI-7, and (▲) SI-8 with $T_r = T_{\mathrm{g,PS}} + 104$ °C as reference temperature.

First, we calculated the monomeric friction coefficients for PS and PI, $\zeta_{0,\mathrm{PS}}$ and $\zeta_{0,\mathrm{PI}}$, using the following expressions:

(i) For $\zeta_{0,\mathrm{PS}}$[37]

$$\log \zeta_{0,\mathrm{PS}} = 3.0 + \frac{13.7(T - T_{\mathrm{g,PS}})}{T - T_{\mathrm{g,PS}} + 48} \tag{1}$$

(ii) For $\zeta_{0,\mathrm{PI}}$[38,39]

$$\log \zeta_{0,\mathrm{PI}} = \log \zeta_{00} + \frac{C_1^{\mathrm{g}} C_2^{\mathrm{g}}}{C_2^{\mathrm{g}} + T - T_{\mathrm{g,PI}}} \tag{2}$$

with $\zeta_{00} = -1.04$ dyn s/cm, $C_1^{\mathrm{g}} = 13.5 \pm 0.2$, and $C_2^{\mathrm{g}} = 45 \pm 3$ K. Note that $\zeta_{0,\mathrm{PS}}$ and $\zeta_{0,\mathrm{PI}}$ have the units of dyn s/cm. Figure 4 describes variations of $\zeta_{0,\mathrm{PS}}$ and $\zeta_{0,\mathrm{PI}}$ with reference temperature $T_r = T_g + 104$ °C. The numerical values of T_r, $T_r - T_{\mathrm{g,PS}}$, $T_r - T_{\mathrm{g,PI}}$, log $\zeta_{0,\mathrm{PS}}$, and log $\zeta_{0,\mathrm{PI}}$, which were used to construct Figure 4, are given in Table 3. In Figure 4 we observe that values of log $\zeta_{0,\mathrm{PS}}$ remain constant, while values of log $\zeta_{0,\mathrm{PI}}$ decrease somewhat, with increasing T_r. Note that in the present study T_r was chosen to have an equal distance (104 °C) from the $T_{\mathrm{g,PS}}$ of each SI diblock copolymer, while the value of $T_{\mathrm{g,PS}}$ increases from 33 °C for SI-1 to 82 °C for SI-8 (see Table 3). Thus, the decreasing trend of log $\zeta_{0,\mathrm{PI}}$ with increasing T_r, observed from Figure 4, is due the fact that values of $T_{\mathrm{g,PI}}$ are more or less constant in all eight SI diblock copolymers (see Table 3), and thus values of $T_r - T_{\mathrm{g,PI}}$ increase from 194 °C for SI-1 to 246 °C for SI-8. The difference between log $\zeta_{0,\mathrm{PS}}$ and log $\zeta_{0,\mathrm{PI}}$ in Figure 4 will remain constant only if $T_{\mathrm{g,PS}}$ and $T_{\mathrm{g,PI}}$ have the same molecular weight dependence, which is

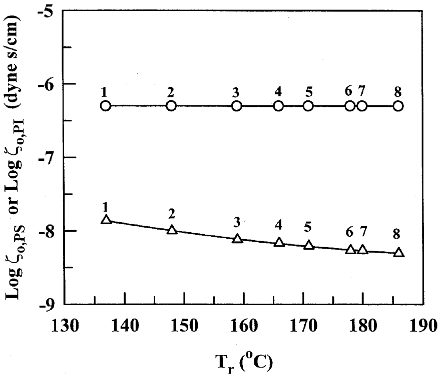

Figure 4. Plots of log $\zeta_{0,PS}$ vs T_r for polystyrene (○) and plots of log $\zeta_{0,PI}$ vs T_r for polyisoprene (△) in eight disordered SI diblock copolymers: (1) SI-1, (2) SI-2, (3) SI-3, (4) SI-4, (5) SI-5, (6) SI-6, (7) SI-7, and (8) SI-8, where $T_r = T_{g,PS} + 104$ °C.

Table 3. Monomeric Friction Coefficients of Polystyrene and Polyisoprene at Various Temperatures for the SI Diblock Copolymers Synthesized in This Study

sample code	T_r (°C)	$T_{g,PS}$ (°C)	$T_{g,PI}$ (°C)	$T_r - T_{g,PS}$ (°C)	$T_r - T_{g,PI}$ (°C)	log $\zeta_{0,PS}$	log $\zeta_{0,PI}$
SI-1	137	33	−57	104	194	−6.30	−7.87
SI-2	148	44	−60	104	208	−6.30	−8.00
SI-3	159	55	−62	104	221	−6.30	−8.12
SI-4	166	62	−61	104	227	−6.30	−8.17
SI-5	171	67	−62	104	233	−6.30	−8.21
SI-6	180	76	−60	104	240	−6.30	−8.27
SI-7	178	74	−62	104	240	−6.30	−8.27
SI-8	186	82	−60	104	246	−6.30	−8.31

Table 4. WLF Parameters for the SI Diblock Copolymers Synthesized in This Study

sample code	T_r (°C)[a]	C_1	C_2 (°C)
SI-1	137	2.46	152.96
SI-2	148	2.47	135.36
SI-3	159	3.11	132.87
SI-4	166	2.11	120.60
SI-5	171	1.59	77.86
SI-6	180	1.60	81.57
SI-7	178	1.47	71.81
SI-8	186	0.93	32.08

[a] $T_r = T_{g,PS} + 104$ °C.

not the case here. Thus, we conclude from Figure 4 that, rigorously speaking, an iso-zeta state is not achieved by simply reducing the linear dynamic viscoelastic data at $T_r = T_{g,PS} + 104$ °C for the eight SI diblock copolymers in the disordered state to compare the molecular dependence of viscosity.

Next, we carried out an analysis of the temperature-dependent shift factor a_T for the eight SI diblock copolymers, given in Figure 3, using the Williams−Landel−Ferry (WLF) analysis commonly made for homopolymers.[40] For the analysis we used the WLF expression

$$\log a_T = \frac{-C_1(T - T_r)}{C_2 + (T - T_r)} \tag{3}$$

to determine the coefficients C_1 and C_2 for all eight SI diblock copolymers in the disordered state by fitting the experimentally determined a_T (see Figure 3) to eq 3. Table 4 gives values of C_1 and C_2 thus determined for all eight SI diblock copolymers synthesized in this study. Using the values of C_1 and C_2 given in Table 4, we prepared plots of log a_T vs $T - T_r$ with $T_r = T_{g,PS} +$ 104 °C, and they are shown in Figure 5, in which the solid line is drawn to guide the eyes. It should be pointed out that the scatter of the data points in Figure 5 is larger than the scatter usually seen for flexible homopolymers of various molecular weights in the iso-zeta state. This large scatter is indicative of a difference in monomeric frictions of the SI diblock copolymer samples of various molecular weights at T_r. Nevertheless, in Figure 6 we have drawn a solid line through the data points showing a reasonable correlation, suggesting that the viscoelastic coefficients at the glass transition temperature (C_1^g and C_2^g) are the same for all eight SI diblock copolymers in the disordered state. Thus, below we shall assume that $\zeta_{0,PI}$ is approximately the same for all eight SI diblock copolymers although, according to Figure 4, the assumption is not valid in the rigorous sense. This is the basis upon which we shall proceed to further analyze our experimental results in order to determine the molecular weight dependence of zero-shear viscosity of disordered SI diblock copolymers.

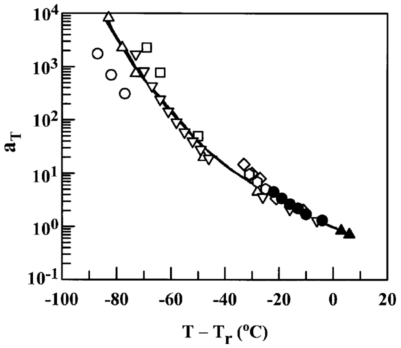

Figure 5. Plots of log a_T vs $T - T_r$ for eight disordered SI diblock copolymers: (○) SI-1, (△) SI-2, (□) SI-3, (▽) SI-4, (◇) SI-5, (⬡) SI-6, (●) SI-7, and (▲) SI-8, where $T_r = T_{g,PS} +$ 104 °C. The solid line is drawn to guide the eyes.

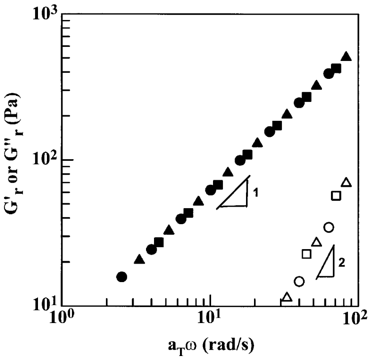

Figure 6. Plots of log G'_r vs log $a_T\omega$ (open symbols) and log G''_r vs log $a_T\omega$ (filled symbols) for SI-8 in the disordered state at various temperatures: (○, ●) 186, (△, ▲) 189, and (□, ■) 192 °C.

To ascertain whether the empirically obtained a_T indeed yields temperature-independent correlation for the dynamic moduli, G' and G'', we prepared reduced plots, log G'_r vs log $a_T\omega$ and log G''_r vs log $a_T\omega$, for all eight SI diblock copolymers synthesized in this study, where G'_r and G''_r are reduced dynamic storage and loss moduli, respectively, defined by $G'_r = G'T_r\rho_r/T\rho$ and $G''_r = G''T_r\rho_r/T\rho$ with ρ being the density at T and ρ_r being the density at T_r. Figure 6 gives log G'_r vs log $a_T\omega$ and log G''_r vs log $a_T\omega$ plots for SI-8 at various temperatures in the disordered state ($T > T_{ODT}$), yielding a temperature-independent correlation. Similar plots (although not presented) were obtained for the other seven

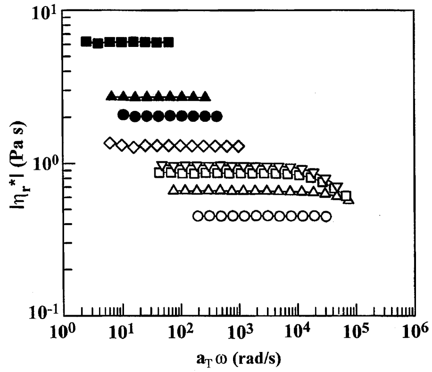

Figure 7. Plots of log $|\eta_r^*|$ vs log $a_T\omega$ for eight SI diblock copolymers synthesized in this study with $T_r = T_{g,PS} + 104$ °C as the reference temperature: (○) SI-1 at 50, 55, 60, and 137 °C; (△) SI-2 at 65, 70, 75, and 148 °C; (□) SI-3 at 86, 90, 95, and 159 °C; (▽) SI-4 at 93, 96, 99, and 166 °C; (◇) SI-5 at 132, 135, 138, and 171 °C; (●) SI-6 at 149, 152, 155, and 180 °C; (▲) SI-7 at 156, 159, 162, and 178 °C; (■) SI-8 at 186, 189, and 192 °C. There are too much data points to use different symbols indicating the data points obtained at different temperatures. Therefore, we have decided to use only one symbol for all the temperatures in each polymer sample.

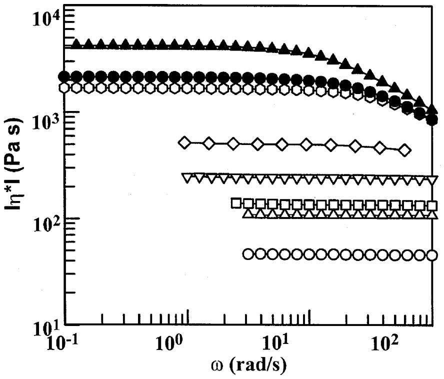

Figure 8. Plots of log $|\eta^*|$ vs log ω for eight homopolystyrenes synthesized in this study with $T_r = T_{g,5} + 79$ °C as the reference temperature: (○) PS-1 at 162 °C, (△) PS-2 at 169 °C, (□) PS-3 at 171 °C, (▽) PS-4 at 178 °C, (◇) PS-5 at 180 °C, (⬡) PS-6 at 180 °C, (●) PS-7 at 180 °C, and (▲) PS-8 at 180 °C.

SI diblock copolymers synthesized in this study. In constructing Figure 6, the following expressions for the specific volume (v) in the units of cm^3/g were used:

$$v_{PS} = 0.9217 + 5.412 \times 10^{-4}(T - 273) + 1.687 \times 10^{-7}(T - 273)^2 \quad (4)$$

for PS[41] and

$$v_{PI} = 1.0771 + 7.22 \times 10^{-4}(T - 273) + 2.46 \times 10^{-7}(T - 273)^2 \quad (5)$$

for PI,[31] in which T is the absolute temperature. The values of v for SI diblock copolymer were calculated from $v = v_{PS}\phi_{PS} + v_{PI}\phi_{PI}$ and thus the density from $\rho = 1/v$, in which ϕ_{PS} and ϕ_{PI} are the volume fractions of PS and PI blocks, respectively. Applying the temperature-dependent shift factor (Figure 3) to log $|\eta^*|$ vs log ω plots for each SI diblock copolymer in the disordered state, we calculated reduced complex viscosity $|\eta_r^*|$ using $|\eta_r^*| = |\eta^*|(T_r\rho_r/T\rho)/a_T$. Figure 7 gives log$|\eta_r^*|$ vs log $a_T\omega$ plots for the eight SI diblock copolymers in the disordered state (at $T > T_{ODT}$). Note in Figure 7 that $|\eta_r^*|$ depends only on molecular weight. Figure 8 gives $|\eta^*|$ vs log ω plots for eight hPSs synthesized in this study, the molecular characteristics of which are summarized in Table 1. In obtaining Figure 8, for each hPS we conducted the dynamic frequency sweep experiments at a temperature that was 79 °C above its T_g. Figure 8 was used to calculate the η_0 of the hPSs using $\eta_0 = \lim_{\omega\to 0}[|\eta^*(\omega)|]$.

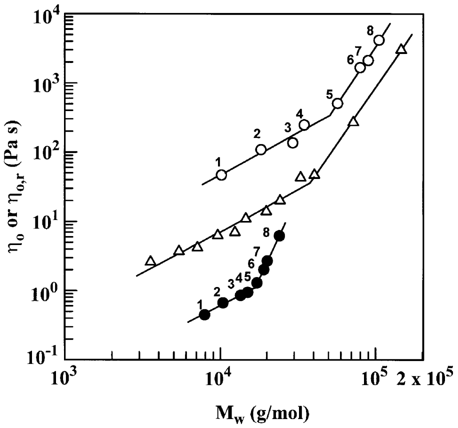

Figure 9. (a) Molecular weight dependence of $\eta_{0,r}$ for eight disordered SI diblock copolymers (●): (1) SI-1, (2) SI-2, (3) SI-3, (4) SI-4, (5) SI-5, (6) SI-6, (7) SI-7, and (8) SI-8, in which the lower slope is 1.15 ± 0.09, the upper slope is 4.69 ± 0.18, and $T_r = T_{g,PS} + 104$ °C. The weight-average molecular weights (M_w) of the SI diblock copolymers are summarized in Table 1. (b) Molecular weight dependence of η_0 for the homopolystyrenes synthesized in this study (○): (1) PS-1, (2) PS-2, (3) PS-3, (4) PS-5, (5) PS-6, (6) PS-6, (7) PS-7, and (8) PS-8, in which the lower slope is 1.21 ± 0.23, the upper slope is 3.37 ± 0.21, and $T_r = T_{g,5} + 79$ °C. The M_w of the homopolystyrenes are summarized Table 2. (c) Molecular weight dependence of η_0 for the homopolystyrenes at 217 °C is based on the experimental data taken from Table 3 of ref 37 (△), in which the lower slope is 1.21 ± 0.23 and the upper slope is 3.28 ± 0.06.

Molecular Weight Dependence of Zero-Shear Viscosity of SI Diblock Copolymers in the Disordered State and Homopolystyrenes. Using Figure 7, we determined reduced zero-shear viscosity ($\eta_{0,r}$) from $\eta_{0,r} = \lim_{\omega\to 0}[|\eta_r^*(\omega)|]$ for each block copolymer in the disordered state (at $T > T_{ODT}$). Figure 9 gives logarithmic plots of η_0 vs weight-average molecular weight (M_w) for all eight SI diblock copolymers synthesized in this study. Also given in Figure 9 are, for comparison, logarithmic plots of η_0 vs M_w for eight hPSs, for which we did not need a shift factor because $T_r = T_g + 79$ °C was used as a reference temperature for all eight hPSs (i.e., at an equal distance from the T_g of each hPS).

In the preparation of Figure 9 we used the values of M_w determined from light scattering for both SI diblock copolymers (Table 1) and hPSs (Table 2). To check the accuracy of the M_w determined in the present study, in Figure 9 we have also prepared logarithmic plots of η_0 vs M_w for 12 hPSs using the experimental data (Table 3) in a paper by Allen and Fox.[37] In Figure 9, the number above each data point refers to the specific polymer whose molecular weight is given in Table 1 for the SI diblock copolymers and in Table 2 for the hPSs. What is of great interest in Figure 9 is that at molecular weights greater than a certain critical value (M_c), commonly referred to as viscosity critical molecular weight, the molecular weight dependence of $\eta_{0,r}$ for the disordered SI diblock copolymers is much stronger than the molecular dependence of η_0 for the hPSs. Applying statistical error analysis[42] to the experimental data given in Figure 9, we have obtained the following relationships: (i) $\eta_{0,\mathrm{r}} \propto M^{1.15\pm0.09}$ for $M < M_\mathrm{c}$ and $\eta_{0,\mathrm{r}} \propto M^{4.69\pm0.18}$ for $M \geq M_\mathrm{c}$ for the disordered SI diblock copolymers synthesized in this study, (ii) $\eta_0 \propto M^{1.21\pm0.23}$ for $M < M_\mathrm{c}$ and $\eta_0 \propto M^{3.37\pm0.21}$ for $M \geq M_\mathrm{c}$ for the hPSs synthesized in this study, and (iii) $\eta_0 \propto M^{1.20\pm0.11}$ for $M < M_\mathrm{c}$ and $\eta_0 \propto M^{3.28\pm0.06}$ for $M \geq M_\mathrm{c}$ for the hPSs reported by Allen and Fox:[37] We wish to mention that we estimated the errors associated with the calculation of a_T and also associated with the calculations of $\eta_{0,\mathrm{r}}$ for the SI diblock copolymers and η_0 for the hPSs synthesized in this study. We have found that the numerical values of the errors for $\eta_{0,\mathrm{r}}$ and η_0 were too small to be discernible on the logarithmic coordinates of Figure 9.

The following observations are worth noting regarding the $\eta_{0,\mathrm{r}}-M$ correlations for SI diblock copolymers and the η_0-M correlations for hPSs given in Figure 9. There is excellent agreement, within experimental uncertainties, in the η_0-M correlations for hPSs between the present study and the study of Allen and Fox[37] that was reported four decades ago. This agreement gives us confidence in our experimental data for molecular weight and rheology measurements. We find that the molecular weight dependence of η_0 or $\eta_{0,\mathrm{r}}$ for $M < M_\mathrm{c}$ is virtually identical for both disordered SI diblock copolymer and hPS, but the molecular weight dependence of η_0 or $\eta_{0,\mathrm{r}}$ for $M \geq M_\mathrm{c}$ is much greater for disordered SI diblock copolymer than for hPS. The observation that $\eta_0 \propto M^{3.37\pm0.21}$ obtained for the hPSs investigated in this study is in good agreement with the well-established relationship in the literature[27,40,43] gives us an assurance that, within experimental uncertainties, the correlation $\eta_{0,\mathrm{r}} \propto M^{4.69\pm0.18}$ obtained from this study on disordered SI diblock copolymers with $M > M_\mathrm{c}$ is real.

Notice in Figure 9 that the value $M_\mathrm{c} \approx 1.7 \times 10^4$ for the disordered SI diblock copolymers is close to the critical viscosity molecular weight of homopolyisoprene (hPI), $M_\mathrm{c,PI} \approx 1.4 \times 10^4$ reported by Raju et al.[44,45] Here we consider that $M_\mathrm{c} \approx 2M_\mathrm{e}$ is valid.[40,43] This observation seems to suggest that a disordered SI diblock copolymer can be regarded as being entangled chains when the combined molecular weight of both blocks exceeds the entanglement molecular weight of polyisoprene (PI) block ($M_\mathrm{c,PI}$). Another interesting observation we can make from Figure 9 is that the viscosity critical molecular weight of polystyrene (PS) ($M_\mathrm{c,PS}$) is about 4×10^4, which is close to the value, 3.6×10^4, reported by Ferry.[40] Again, here we assume that $M_\mathrm{c} \approx 2M_\mathrm{e}$ is valid.[40,43] The above observations bring us to one of the fundamental questions posed in the Introduction section: Can a homogeneous AB-type diblock copolymer be regarded as being entangled chains if the combined molecular weights of both blocks is higher than the entanglement molecular weight of one of the blocks even when the molecular weight of each block is lower than its entanglement molecular weight? According to the information on the molecular weights of PS and PI blocks for the eight SI diblock copolymers summarized in Table 1, the answer to the question posed above is affirmative. Notice in Table 1 that the molecular weights of PS block in all eight SI diblock copolymers are much lower than $M_\mathrm{c,PS}$ (3.6×10^4), and the molecular weights of PI block in all eight SI diblock copolymers are lower than $M_\mathrm{c,PI}$ (1.4×10^4). It is of great interest to observe from Figure 9 and Table 1 that four SI diblock copolymers (SI-5, SI-6, SI-7, and SI-8) having the combined molecular weight higher than $M_\mathrm{c,PI}$ give rise to the relationship $\eta_{0,\mathrm{r}} \propto M^{4.69\pm0.18}$ (thus they are entangled chains), and the other four SI diblock copolymers (SI-1, SI-2, SI-3, and SI-4) having the combined molecular weight lower than $M_\mathrm{c,PI}$ give rise to the relationship $\eta_{0,\mathrm{r}}$ $M^{1.15\pm0.09}$ (thus they are unentangled chains).

Referring to Figure 9, three fundamental questions may be raised. The first question is, why does the η_0 of disordered SI diblock copolymers have much stronger molecular weight dependence than the η_0 of hPSs? The second question is, how can we predict (or estimate) the η_0 of a disordered SI diblock copolymer when information is available on the η_0 of hPS and hPI, respectively, having the same molecular weight as the PS and PI blocks in the SI diblock copolymer? The third question is, how can we predict (or estimate) the M_c (or M_e) of a disordered SI diblock copolymer (or any block copolymers) when information is available on the molecular weights of the constituent blocks? These are not trivial questions. At present we do not have a comprehensive molecular theory that enables us to answer the questions posed. We will have to wait for the development of a molecular theory for the dynamics of block copolymer.

Discussion

Origin of the Stronger Molecular Weight Dependence of Zero-Shear Viscosity of Disordered SI Diblock Copolymers. In the present study, we conducted additional dynamic frequency sweep measurements for the three, among the eight in total, higher molecular weight polymers, SI-6, SI-7, and SI-8 at $T_\mathrm{r} = T_\mathrm{g,PS} + 113$ °C, $T_\mathrm{r} = T_\mathrm{g,PS} + 118$ °C, and $T_\mathrm{r} = T_\mathrm{g,PS} + 123$ °C, respectively. In other words, we varied the experimental temperatures by increasing the distance from $T_\mathrm{g,PS}$. The choice of $T_\mathrm{r} = T_\mathrm{g,PS} + 123$ °C gave us a measurement temperature of 205 °C for SI-8 ($T_\mathrm{g,PS}$ of 82 °C), which had the highest molecular weight among all eight block copolymers employed in this study. We did not choose a higher measurement temperature to avoid the possibility of thermal degradation/cross-linking reactions. The purpose of the additional experiments was twofold. First, in so doing, we did not need to use a shift factor a_T to calculate η_0 from the measurements of G''; i.e., values of η_0 for all three SI diblock copolymers in the disordered state were calculated from $\eta_0 = \lim_{\omega\to0}|\eta^*(\omega)|$. In this way, we were able to assess the validity (or the lack of validity) of using a shift factor a_T to obtain the molecular weight dependence of η_0 summarized in Figure 9. Second, in so doing, we wanted to assess whether the molecular weight dependence of η_0 summarized in Figure 9, which was determined at $T_\mathrm{r} = T_\mathrm{g} + 104$ °C, is valid for higher values of T_r. This is very important in view of the fact from Figure 4 that values of $\zeta_\mathrm{0,PI}$ decrease very slowly with increasing T_r. In other words, we wanted to test the assumption made that values of $\zeta_\mathrm{0,PI}$ are approximately the same for all eight SI diblock copolymers over the range of experimental temperatures employed in this study. That is, we wanted to check whether the difference in the monomeric friction coefficients between the PS and PI blocks were adequately incorporated in a sound comparison of the viscosities of the disordered SI diblock copolymers in the iso-zeta state.

Figure 10 gives log η_0 vs log M_w plots for SI-6, SI-7, and SI-8 at $T_\mathrm{r} = T_\mathrm{g,PS} + 113$ °C, $T_\mathrm{r} = T_\mathrm{g,PS} + 118$ °C,

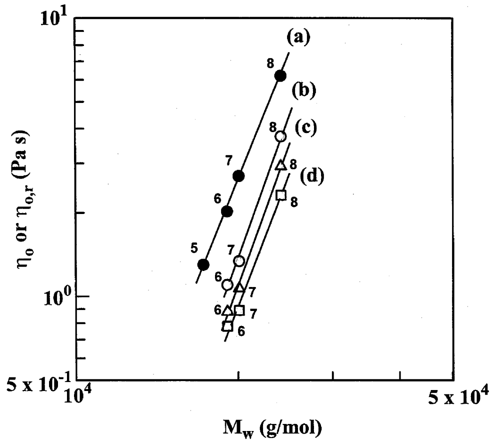

Figure 10. Molecular weight dependence of η_0 for SI-5, SI-6, SI-7, and SI-8 in the disordered state at different values of reduced temperature: (a) a slope of 4.69 ± 0.18 at $T_r = T_{g,PS} + 104$ °C; (b) a slope of 5.38 ± 0.11 at $T_r = T_{g,PS} + 113$ °C; (c) a slope of 5.27 ± 0.24 at $T_r = T_{g,PS} + 123$ °C; and (d) a slope of 4.82 ± 0.24 at $T_r = T_{g,PS} + 123$ °C.

and $T_r = T_{g,PS} + 123$ °C. For comparison, also included in Figure 10 are the experimental data obtained at $T_r = T_{g,PS} + 104$ °C that was used in Figure 9. Applying statistical error analysis[42] to the experimental data given in Figure 10, we have obtained the following values of the exponent in the expression $\eta_0 \propto M^{\alpha}$ for $M \geq M_c$: (i) $\alpha = 5.38 \pm 0.11$ at $T_r = T_{g,PS} + 113$ °C, (ii) $\alpha = 5.27 \pm 0.24$ at $T_r = T_{g,PS} + 118$ °C, and (iii) $\alpha = 4.82 \pm 0.24$ at $T_r = T_{g,PS} + 123$ °C. These values of exponent α are slightly higher than $\alpha = 4.69 \pm 0.18$ at $T_r = T_{g,PS} + 104$ °C summarized in Figure 9.

Thus, we tentatively conclude that within experimental uncertainties the stronger molecular weight dependence of η_0 observed for disordered SI diblock copolymers seems to be real.

We attribute the stronger molecular weight dependence of η_0 for disordered SI diblock copolymers ($\eta_0 \propto M^{4.69\pm0.18}$ for $M > M_c$) observed in this study to the presence of the styrene–isoprene (S–I) junction that originates from the difference in the monomeric friction coefficients between PS and PI blocks. Until now no other experimental data have ever been reported on the molecular weight dependence of η_0 for disordered diblock copolymers, and at present we do not have a molecular theory that is able to predict the molecular weight dependence of η_0 for disordered diblock copolymers. The readers are reminded from Figure 4 that the monomeric friction coefficient of PS is not the same as that of PI in SI diblock copolymers, i.e., $\zeta_{0,PS} > \xi_{0,PI}$. If $\zeta_{0,PS} = \xi_{0,PI}$ was true for SI diblock copolymers, then the dynamics of SI diblock copolymers in the disordered state would be essentially the same as the dynamics of homopolymers and the S–I junction would play little role in the dynamics of disordered SI block copolymers. Under such circumstances, we cannot think of any reason(s) why the molecular weight dependence of η_0 of disordered SI diblock copolymers should be different from that of ordinary flexible polymers.

One plausible explanation for the stronger molecular weight dependence of η_0 observed for disordered SI diblock copolymers, as compared to the molecular weight dependence of ordinary flexible homopolymers, is the potential influence of concentration fluctuations on the rheology of disordered block copolymers. Below we will address this issue separately.

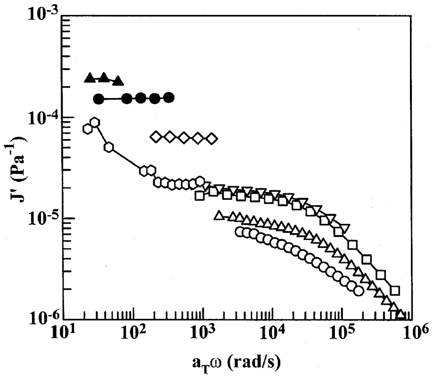

Figure 11. Plots of J' vs log $a_T\omega$ for eight disordered SI diblock copolymers: (○) PS-1, (△) PS-2, (□) PS-3, (▽) PS-4, (◇) PS-5, (⬡) PS-6, (●) PS-7, and (▲) PS-8, in which the shift factor a_T was obtained at $T_r = T_g + 104$ °C as a reference temperature.

Steady-State Recoverable Compliance of Disordered SI Diblock Copolymers. It is well established that steady-state recoverable compliance (J_e^o) of ordinary flexible polymers is very sensitive to the distribution of the slow viscoelastic modes that is strongly affected by molecular weight distribution as well as spatial inhomogeneity.[44,46–48] According to molecular theory,[43] $J_e^o \propto M$ for Rouse chains, and J_e^o is independent of M for entangled flexible homopolymer chains.

In this study, we calculated J_e^o for SI-1, SI-2, and six other SI diblock copolymers (SI-3 through SI-8) in the disordered state (at $T > T_{ODT}$). Specifically, we first calculated the dynamic storage compliance $J'(\omega)$ from

$$J'(\omega) = G'(\omega)/[(G'(\omega))^2 + (G''(\omega))^2] \qquad (6)$$

Figure 11 gives log $J'(\omega)$ vs log $a_T\omega$ plots for eight disordered SI diblock copolymers at $T_r = T_{g,PS} + 104$ °C. Then we calculated J_e^o from

$$J_e^o = \lim_{\omega \to 0} J'(\omega) \qquad (7)$$

Figure 12 describes the molecular weight dependence of J_e^o for the eight SI diblock copolymers. For comparison, also included in Figure 12 is the molecular weight dependence of J_e^o for the eight hPSs synthesized in this study. The following observations are worth noting in Figure 12. The values of J_e^o for hPSs first increase with increasing M ($J_e^o \propto M^{0.82\pm0.15}$) and then tend to level off as M increases further above a certain critical value, which is in general agreement with the literature.[49] Applying statistical error analysis[42] to the experimental data given in Figure 12, we have obtained the following relationship: $J_e^o \propto M^{1.63\pm0.17}$ for $M < M_c$ and $J_e^o \propto M^{5.22\pm0.78}$ for $M \geq M_c$ for disordered SI diblock copolymers; i.e., the molecular weight dependence of J_e^o for disordered SI diblock copolymers is much stronger, particularly for $M \geq M_c$, than that for hPSs. In Figure 12 we observe a very strong M dependence of J_e^o for $M \geq M_c$ in the disordered SI diblock copolymers.

The difference in the monomeric friction coefficients of PS and PI blocks certainly have contributed to an increase in the values of J_e^o of the disordered SI diblock copolymers compared to those of hPS. However, this difference itself would not result in the very strong M dependence of J_e^o of the disordered SI diblock copoly-

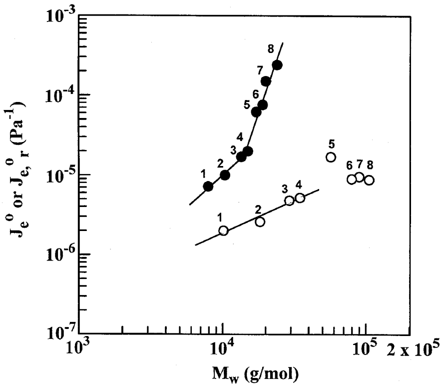

Figure 12. (a) Molecular weight dependence of $J_{e,r}^0$ for eight disordered SI diblock copolymers (●): (1) SI-1, (2) SI-2, (3) SI-3, (4) SI-4, (5) SI-5, (6) SI-6, (7) SI-7, and (8) SI-8, in which the lower slope is 1.63 ± 0.17, the upper slope is 5.22 ± 0.78, and $T_r = T_{g,PS} + 104$ °C. The weight-average molecular weights (M_w) of the SI diblock copolymers are summarized in Table 1. (b) Molecular weight dependence of J_e^0 for the homopolystyrenes synthesized in this study (○): (1) PS-1, (2) PS-2, (3) PS-3, (4) PS-5, (5) PS-6, (6) PS-6, (7) PS-7, and (8) PS-8, in which the lower slope is 0.82 ± 0.15, virtually independent of M_w above a critical molecular weight, and $T_r = T_{g,5} + 79$ °C. The M_w of the homopolystyrenes are summarized Table 2.

mer if the mechanism of the block copolymer motion does not change with M. Thus, the strong M dependence of J_e^0 observed in Figure 12 may be related, at least in part, to the concentration fluctuation (or similar dynamic heterogeneity) with its magnitude at a given T_r changing with M. In the presence of this fluctuation, the styrene−isoprene junction motion can play an important role in enhancing the M dependence of J_e^0. Until now, no other experimental data have ever been reported in the literature on the molecular weight dependence of J_e^0 for disordered diblock copolymers, and at present we do not have a comprehensive theory predicting the molecular weight dependence of J_e^0 for disordered diblock copolymers.

It is worth mentioning that, owing to the very strong M dependence of η_0 and J_e^0 for the disordered SI diblock copolymers observed in Figures 9 and 12, the terminal relaxation time, which is defined by the product of η_0 and J_e^0 for flexible homopolymers,[43] exhibits enormously strong M dependence which may be, at least in part, due to the styrene−isoprene junction motion in the presence of the concentration fluctuation.

Assessment of the Potential Influence of Concentration Fluctuations on the Rheology of Disordered Block Copolymers. The subject of concentration fluctuations in block copolymers has been discussed extensively in the literature by numerous investigators, and there are too many papers to cite them all here. The interested readers are referred to review articles[5,50,51] that describe in general terms the importance of concentration fluctuations in a block copolymer near T_{ODT}.

Restricting our discussion to the possible influence of concentration fluctuations on the rheology of disordered block copolymers, earlier Bates and co-workers[52,53] observed a parallel shift in the log G' vs log $a_T\omega$ plots (or log G' vs log G'' plots) of two nearly symmetric poly(ethylene-*alt*-propylene)-*block*-poly(ethylethylene) (PEP-*block*-PEE) copolymers: PEP−PEE-5 from 124 to 161 °C and PEP−PEE-2 from 96 to 155 °C. They attributed the parallel shift in the log G' vs log $a_T\omega$ plots (or log G' vs log G'' plots) to concentration fluctuations. We are not aware of any theory which predicts that a parallel shift in log G' vs log $a_T\omega$ plots (or log G' vs log G'' plots) of symmetric or nearly symmetric block copolymers signifies the onset of concentration fluctuations. Interestingly, we have not observed a parallel shift in the log G' vs log G'' plots of all six, nearly symmetric SI diblock copolymers (SI-3 through SI-8) investigated in this study (see Figure 1). Therefore, we cannot estimate from the log G' vs log G'' plots the extent of concentration fluctuations on the rheology of the six, nearly symmetric disordered SI diblock copolymers. As a matter of fact, we are not aware of any papers published in the literature, reporting a parallel shift in log G' vs log G'' plots (or log G' vs log G'' plots) for symmetric or nearly symmetric SI diblock copolymers, polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS triblock) copolymers, polystyrene-*block*-polybutadiene (SB diblock) copolymers, or polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS triblock) copolymers. Jin and Lodge[54] reported measurements of the dynamic shear moduli of solutions of three relatively high molecular weight, lamella-forming SI diblock copolymers dissolved in bis(2-ethylhexyl) phthalate (DOP) at various temperatures and observed a marked increase in the fluctuations of dynamic shear moduli as the order−disorder transition was approached. On the basis of these observations, they concluded that concentration fluctuations were present in the solutions of SI diblock copolymers. It is not clear, however, how such an experimental observation made from block copolymer solutions can be used to estimate the extent of concentration fluctuations in disordered SI diblock copolymers in the bulk state. At present we do not have a theoretical basis upon which we can assess (or estimate) quantitatively the extent of concentration fluctuations on the rheology of disordered block copolymers in terms of the block copolymer composition, degree of polymerization, and most importantly the chemical structure of block copolymers.

Table 5. Summary of the Experimental Temperature above the T_{ODT}s of SI-5, SI-6, SI-7, and SI-8 Employed in Figure 10

sample code	measurement temperature T (°C)	T_{ODT} (°C)	$T - T_{ODT}$ (°C)
SI-5	171	127	44
SI-6	180; 189; 194; 199	146	34; 43; 48; 53
SI-7	178; 187; 192; 197	156	22; 31; 38; 41
SI-8	186; 195; 200; 205	186	0; 9; 14; 19

For the reasons of the practical constraint we had on the molecular weight of the SI diblock copolymers investigated in this study, we were forced to take the rheology data for the disordered phase at temperatures not very far above T_{ODT}, and thus there is a possibility that the measured values of η_0 for the disordered SI diblock copolymers summarized above could have been influenced by concentration fluctuations. Table 5 summarizes values of $T - T_{ODT}$ with T being the experimental temperature employed for rheological measurements in the disordered state (at $T > T_{ODT}$) of six SI diblock copolymers (SI-3 through SI-8). Restricting our attention to the four block copolymers (SI-5 through SI-8) that seem to have entangled chains on the basis of Figures 9 and 10, in Table 5 we observe that, except for SI-8 which has the highest molecular weight, the data for the rest of the copolymers were taken at temperatures higher than ca. 30 °C above T_{ODT}. Even for SI-8, the data were taken at temperatures higher than 9 °C above T_{ODT}. Few people doubt the existence of concentration fluctuations in block copolymers near T_{ODT}. A fundamental question that must be answered is, how far above T_{ODT} should rheological measurements be taken in order to avoid the influence of concentration fluctuations on the rheology of disordered block copolymers? We are not aware of the existence of a theory that can answer the question posed above.

Concluding Remarks

In this paper, we have presented the first experimental evidence, to the best of our knowledge, that entangled SI diblock copolymers in the disordered state have a much stronger molecular weight (M) dependence of zero-shear viscosity (η_0) than homopolystyrenes. Namely, the M dependence of η_0 for the SI diblock copolymers in the disordered state follows the relationship $\eta_0 \propto M^{1.15\pm0.09}$ for $M < M_c$ and $\eta_0 \propto M^{4.69\pm0.18}$ for $M \geq M_c$, where M_c is the viscosity critical molecular weight. Also, in this paper we have presented that the M dependence of steady-state recoverable compliance (J_e^o) of SI block copolymer in the disordered state follows the relationship $J_e^o \propto M^{1.63\pm0.17}$ for $M < M_c$ and $J_e^o \propto M^{5.22\pm0.78}$ for $M \geq M_c$. The much stronger molecular weight dependence of η_0 and J_e^o for the disordered SI diblock copolymers than that for homopolystyrenes observed in this study is attributable to the styrene–isoprene junction effect that originates from the difference in the monomeric friction coefficients between polystyrene and polyisoprene blocks. One plausible explanation for the strong molecular weight dependence of η_0 and J_e^o observed for disordered SI diblock copolymers, as compared to the molecular weight dependence of ordinary flexible polymers, is the possible influence of concentration fluctuations on the rheology of disordered block copolymers. Another plausible explanation, perhaps in part, may be due to the fact that an iso-zeta state was not achieved owing to the differences in the monomeric friction coefficients between PS and PI (i.e., $\zeta_{0,PS} \neq \zeta_{0,PI}$) when values of η_0 and J_e^o of the SI diblock copolymers of various molecular weights in the disordered state were compared at $T_r = T_{g,PS} + 104$ °C. We have discussed the potential influence of concentration fluctuations on the rheology of disordered SI diblock copolymers. However, we are of the opinion that concentration fluctuations could not have had such a dramatic influence on the rheology of disordered SI diblock copolymers observed in this study because much of the rheological data were obtained at temperatures ca. 30 °C and higher above the T_{ODT} of the SI diblock copolymers synthesized in this study. What is unknown at the present time is whether the molecular weight dependence of η_0 and J_e^o of disordered SIS triblock copolymers might be the same as that of disordered SI diblock copolymers observed in this study.

At present we do not have theory that can explain the experimental results presented in this paper. We suggest that molecular theory be developed, enabling us to predict (or to estimate), at least in the beginning, the rheological behavior of disordered (or homogeneous) block copolymers in the Rouse regimes as well as in the entangled regime and then later the rheological behavior of microphase-separated block copolymers. Understandably, theoretical development of microphase-separated block copolymers would be very complicated because microdomains (lamellae, cylinders, gyroids, or spheres) must be included in the formulation of a system of equations. The present study indicates that microphase-separated block copolymers will become entangled flexible chains when the temperature is increased above T_{ODT}. This observation suggests that in the theoretical development microphase-separated block copolymers must be treated as entangled chains. Also, we need theory that can guide us to determine whether a block copolymer is entangled when information on the molecular weights of the constituent blocks is available. Further, we need theory that will enable us to predict (or estimate) the entanglement molecular weight of a block copolymer.

The task of predicting the rheological behavior of block copolymers is a real challenge. It is quite astonishing, and at the same time very discouraging, to find that even after more than four decades since the first commercialization of AB-type diblock and ABA-type triblock copolymers, to date there exists no comprehensive molecular theory predicting the rheological behavior of such block copolymers. In recent years, the synthesis of ABC-type triblock copolymer has become very active. It is even more challenging to develop theory that will enable one to predict the rheological behavior of ABC-type triblock copolymers.

Acknowledgment. We acknowledge that anonymous reviewers' constructive comments helped us to improve the original manuscript.

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(39) The authors of ref 38 used the notations C_1^g and C_2^g in eq 2, while the notations C_1 and C_2 are usually used in the WLF equation, eq 3, presented later in this paper. However, eq 2 is not identical to eq 3 even when C_1^g and C_2^g in eq 2 are replaced by C_1 and C_2, respectively. Below, we present the derivation of eq 2. Using the notations C_1^g and C_2^g, the monomeric friction coefficients $\zeta_0(T)$ and $\zeta_0(T_g)$ can be expressed in the form of the WLF equation $\log[\zeta_0(T)/\zeta_0(T_g)] = [-C_1^g(T - T_g)]/[C_2^g + (T - T_g)]$ (8), in which T is the measurement temperature and T_g is the glass transition temperature. With ζ_{00} representing the intrinsic monomeric friction coefficient at $T = T_\infty$, eq 8 can be expressed as $\log[\zeta_{00}/\zeta_0(T_g)] = [-C_1^g(T_\infty - T_g)]/[C_2^g + (T_\infty - T_g)]$ (9), in which $T_\infty \gg T_g$, C_1^g, and C_2^g. Thus eq 9 reduces to $\log[\zeta_{00}/\zeta_0(T_g)] \approx -C_1^g$ (10). Substitution of eq 10 into eq 8 gives eq 2.

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MA021792F