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Transition of Linear Polymer Dimension from Θ to Collapsed Regime. Intrinsic Viscosity

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ABSTRACT: Intrinsic viscosity $[\eta]$ of polystyrene in cyclohexane from the Θ temperature to the collapsed regime has been measured by using a novel precision capillary viscometer which has a time resolution of ±0.001 s. The temperature (T) dependence of $[\eta]$ can be represented by a master curve in a $\alpha_\eta^3|\tau|M_w^{1/2}$ ($g^{1/2}$ $mol^{-1/2}$) vs $|\tau|M_w^{1/2}$ ($g^{1/2}$ $mol^{-1/2}$) plot, where α_η [$\equiv([\eta(T)]/[\eta(\theta)])^{1/3}$] is the expansion factor and τ [$\equiv(T-\Theta)/T$] is the reduced temperature. A comparison of the plateau value for the scaled expansion factors $\alpha^3|\tau|M_w^{1/2}$ in the collapsed regime based on the radius of gyration R_g with $\alpha_s = R_g(T)/R_g(\Theta)$, the hydrodynamic radius R_h with $\alpha_h = R_h(T)/R_h(\Theta)$, and the intrinsic viscosity shows $\alpha_h^3:\alpha_\eta^3:\alpha_s^3 = 2.14 \pm 0.19:1.2 \pm 0.1:1$, in fairly good agreement with the blob theory prediction of 2.08:1.28:1 with $\alpha_\eta^3 = \alpha_s^2\alpha_h$ and a plateau value of 24.1 ± 3% for $\alpha_\eta^3|\tau|M_w^{1/2}$.

I. Introduction

Recent light-scattering studies on the transition of linear polymer dimension from the Θ temperature to the collapsed regime have shown our successes in being able to reach the collapsed state: (1) based on the static radius of gyration R_g by using high molecular weight fractions of polystyrene with (a) M_w ranging from 4×10^6 to 20×10^6 g/mol in cyclohexane,[1] below the upper Θ temperature (Θ_U = 35 °C), and (b) M_w ranging from 2×10^6 to 8.6×10^6 g/mol in methyl acetate,[2] both below the upper Θ temperature (Θ_U = 43 °C) and above the lower Θ temperature (Θ_L = 114 °C); (2) based on the hydrodynamic radius R_h by using a specially fractionated high molecular weight polystyrene with $M_w = 4.83 \times 10^7$ g/mol and $M_w/M_n \lesssim 1.03$ at a concentration $C \approx 3 \times 10^{-8}$ g/mL in cyclohexane.[3] Results of polymer coil-to-globule transition have also been reviewed[4] and its relationship to critical phenomena reexamined[5] on the basis of an extended universal coexistence curve for polymer solutions[6] as originally proposed by Sanchez.[7] In this paper, we report intrinsic viscosity measurements of polystyrene in cyclohexane using a new precision capillary viscometer[8] which has a time resolution of ±0.001 s. The purpose of the present study is twofold. We want (1) to check the intrinsic viscosity results of Perzynski et al.[9] in the collapsed regime and (2) to compare the plateau value for the scaled expansion factor $\alpha^3|\tau|M_w^{1/2}$ in the collapsed regime based on the radius of gyration R_g with $\alpha_s = R_g(T)/R_g(\Theta)$, the hydrodynamic radius R_h with $\alpha_h = R_h(T)/R_h(\Theta)$, and the intrinsic viscosity $[\eta]$ with $\alpha_\eta^3 = [\eta(T)]/[\eta(\Theta)]$. Perzynski et al. have already observed that $[\eta]$ scaled with $|\tau|M_w^{1/2}$ where M_w and τ [$\equiv(T-\Theta)/T$] are the weight-average molecular weight and the reduced temperature, respectively. However, a plateau value of $\alpha_\eta^3|\tau|M_w^{1/2} \simeq 27$ $g^{1/2}$ $mol^{-1/2}$ starting at $|\tau|M_w^{1/2} \gtrsim 40$ $g^{1/2}$ $mol^{-1/2}$ appeared to show much larger than usual experimental error limits. With the higher time resolution of our viscometer, we could reduce the polymer concentration further and test possible phase separation effects in the very immediate neighborhood of the coexistence curve. As polydispersity has been shown to play a major role in our experiments[3-5,10] and the amount of specially fractionated polystyrene[3] ($M_w = 4.83 \times 10^7$; $M_w/M_n \le 1.03$) was insufficient for viscosity studies, we selected the highest molecular weight fraction ($M_w = 8.6 \times 10^6$ g/mol; $M_w/M_n \simeq 1.26$) polystyrene which we used successfully to reach the collapsed regime based on the radius of gyration in two different solvents[1,2] as our polystyrene sample for the intrinsic viscosity experiment. It should be noted that a polydispersity index ($\equiv M_w/M_n$) of ≤1.03 for an ultrahigh molecular weight polystyrene sample represented a polymer fraction which could not be obtained by standard analytic means. It took us close to a year to finally obtain quantities of a few milligrams. Thus, we did not want to repeat the effort for the viscosity experiment. On the other hand, $M_w/M_n \simeq 1.26$ for the 8.6×10^6 g/mol polystyrene sample is somewhat broad. Then, we would expect phase separation before we reach the coexistence (COEX) curve based on more monodisperse polystyrene samples.

In the literature, only few experiments[1-3,5,9,11] have successfully reached the collapsed regime based on static and hydrodynamic properties of polymer solutions, exclusively using polystyrene as the polymer and mostly using cyclohexane as the solvent. The experimental difficulties encountered could mainly be attributed as due to polymer polydispersity for high molecular weight polystyrene samples. With the exception of the 8.6×10^6 g/mol polystyrene sample purchased from Toyo Soda, almost none exist with narrow enough molecular weight distributions commercially. Now as we have established an extended universal coexistence (COEX) curve for polystyrene in cyclohexane[6] with

$$\psi_C - \psi_D = (0.595 \pm 0.001)X^{0.327} - (0.425 \pm 0.001)X^{0.827} \tag{1}$$

$$\psi_{SD} - \psi_C = (0.595 \pm 0.001)X^{0.327} + (0.018 \pm 0.004)X^{0.827} \tag{2}$$

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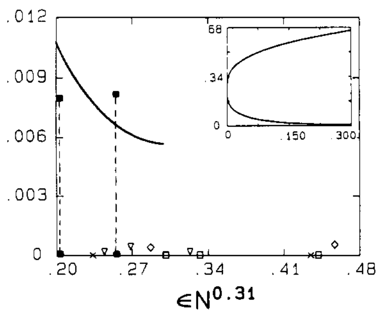

Figure 1. Plot of extended universal coexistence (COEX) curve by means of eq 1 and 2. ψ_D vs X with inset denoting the complete coexistence curve in a plot of ψ vs X. $X = \epsilon N^{0.31}$ with $\epsilon = (T_C - T)/T_C$ and T_C and N are the critical solution temperature and the degree of polymerization, respectively. Symbols denote thermodynamic states of polystyrene in cyclohexane as reached by some of the experiments: solid squares, ref 9; inverted hollow triangles, ref 1, crosses, ref 3; hollow squares, present work; hollow diamonds, ref 11.

where ψ [$= \phi/[\phi + R(1 - \phi)]$] is a dimensionless variable with ϕ being the volume fraction and $R = (1 - 1/\psi_C)/(1 - 1/\phi_C)$. SD, D, and C subscripts denote polymer-rich semidilute, polymer-poor dilute phases, and critical behavior, respectively. $\psi_C = 0.250 \pm 0.003$; $X = \epsilon N^{0.31}$ with ϵ [$= (T_C - T)/T_C$] and N being the reduced critical temperature and the degree of polymerization, respectively. The deviation from the law of rectilinear diameter in the symmetrized COEX curve has the form

$$\frac{\psi_{SD} + \psi_D}{2} = \psi_C + (0.222 \pm 0.005)X^{0.827} \qquad (3)$$

Equations 1–3 are valid for $X \leq 0.306$ and $\psi_D \gtrsim 5.65 \times 10^{-3}$. Figure 1 shows a plot of ψ_D vs X for polystyrene in cyclohexane and the temperature/concentration ranges covered by some of the previous reports[1-3,9,11] as well as the present study. With eq 1 (and Figure 1) as our guideline, we now have a better understanding in our experiments when we try to approach the collapsed regime. Unfortunately, the validity of eq 1 is limited to $X \leq 0.306$. For $X > 0.306$, we can only estimate whether phase separation imposes a serious problem in our measurements. With our precision viscometer[8] and a high molecular weight polystyrene sample ($M_w = 8.6 \times 10^6$ g/mol) which was capable of reaching the collapsed state based on the static radius of gyration, we undertake the viscosity experiments from Θ to collapsed regime for polystyrene in cyclohexane.

II. Intrinsic Viscosity

The intrinsic viscosity is defined by

$$[\eta] = \lim_{C \to 0} (\eta_{sp}/C) \qquad (4)$$

where the specific viscosity $\eta_{sp} = (\eta - \eta_0)/\eta_0$ with η and η_0 being the polymer solution viscosity and the solvent viscosity, respectively, and C is the polymer concentration. At finite concentrations in the dilute solution regime

$$\eta_{sp}/C = [\eta](1 + k_H[\eta]C) \qquad (5)$$

where k_H is the Huggins interaction coefficient. In our case, as C ($\lesssim 4 \times 10^{-6}$ g/mL) is very near infinite dilution (i.e., $k_H[\eta]C \ll 1$), $[\eta] \simeq \eta_{sp}/C$).

On the basis of the temperature blob theory,[12,13] we have, in the collapsed regime

$$\alpha_s = 1.161(N/N_C)^{-1/6} \qquad (6)$$

$$\alpha_h = 1.481(N/N_C)^{-1/6} \qquad (7)$$

Table I
Intrinsic Viscosity of Polystyrene ($M_w = 8.6 \times 10^6$ g/mol) in Cyclohexane Using Capillary Viscometers with Different Shear Rates and Concentrations

viscometer type	Cannon 75	Cannon 25
concn[a] (g/mL)	3.834×10^{-6}	3.234×10^{-4}
T (°C)	34.413, 32.556	34.413, 32.467
η_{sp}/C[b] (mL/g)	237, 175	236, 175

[a] Concentrations are sufficiently dilute so that $k_H[\eta]C \ll 1$ and $[\eta] = \eta_{sp}/C$. [b] $[\eta]$ has a precision of $\sim\pm1\%$.

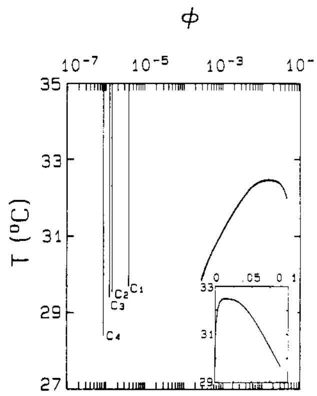

Figure 2. Schematic representation of the thermodynamic states of viscosity measurements reported in the present work. The solid COEX curve was constructed on the basis of eq 1 and 2 using $M_w = 8.6 \times 10^6$ g/mol. $C_1 = 3.834 \times 10^{-6}$ g/mL; $C_2 = 1.327 \times 10^{-6}$ g/mL; $C_3 = 1.235 \times 10^{-6}$ g/mL; $C_4 = 7.492 \times 10^{-7}$ g/mL. It should be noted that we have tried to reach the lowest temperature at each concentration before anomalous behavior (probably due to the onset of critical-point/phase separation phenomena) occurs.

where (N/N_C) is the reduced blob parameter and has been discussed in ref 1 and 2. For α_η, the value is between α_s and α_h.

III. Experimental Methods

The polymer solution used for viscosity measurements was prepared according to the same procedure which has been described elsewhere for light-scattering studies.[1,2]

We used a precision capillary viscometer[8] which has a time resolution of ±0.001 s. The viscometer (Cannon 75) was immersed in a constant temperature bath controlled to ±0.001 °C. In our present viscosity studies, the time precision over repeated viscosity measurements of very dilute polymer solutions agreed to better than ±0.001 s, often reaching ±0.0002 s and in the worst case to ±0.002 s. The precision of our viscosity measurements depended upon the polymer concentration since the specific viscosity measured the difference in viscosity between the polymer solution and the solvent. As the flow time was of the order of 250 s, the precision of $[\eta]$ varied in the range of 1, 2.6, 4.5, and 5% for concentrations of 3.834×10^{-6}, 1.327×10^{-6}, 1.235×10^{-6}, and 7.492×10^{-7} g/mL, respectively. In terms of overlap concentrations, the concentrations correspond to C/C^* values in the range of 2.8×10^{-4} to 5.5×10^{-5} where C^* (g/mL) was taken to be $40/M_w^{1/2}$ with M_w expressed in g/mol.

In order to ascertain the shear rate dependence of our viscosity data measured mainly using the Cannon 75 capillary viscometer, we used another viscometer (Cannon 25) with a different shear-rate rating. The usual parameter for representing the shear rate effect to the viscosity is the reduced shear rate β defined by $M[\eta]\eta_0 G/RT$ with $G = 4v/(\pi a^3 t)$. The quantities v, a, and t denote flow volume, radius of capillary, and flow time, respectively. For the two viscometers, β = 0.088 and 1.4 for Cannon 75 and 25 viscometers, respectively. Our viscosity measurements were performed with $\beta \lesssim 0.1$, and the tests showed same viscosities using the two different viscometers as listed in Table I. Thus, the effect due to finite shear rates could be ignored under our experimental conditions by using the Cannon 75 capillary viscometer.

Table II
Specific Viscosities of Polystyrene (M_w = 8.6 × 10^6 g/mol in Cyclohexane) from Θ Temperature (35 °C) to the Collapsed Regime

identificatn no.[a]	temp[b] (°C)	$10^4\eta_{sp}$	α_η^3	$\tau M_w^{1/2}$	$\alpha_\eta^3\tau M_w^{1/2}$[c]
C_1 = 3.834 × 10^{-6} (g/mL); Denoted by Hollow Squares in Figure 3					
1	35.000	9.968	1.000	0	0
2	34.413	9.100	0.9128	5.597	5.110
3	33.504	7.151	0.7174	14.31	10.26
4	32.556	6.697	0.6719	23.44	15.75
5	31.485	6.409	0.6430	33.80	21.73
6	30.583	5.387	0.5404	42.14	22.77
7	30.334	5.452	0.5469	45.09	24.66(*)
8	29.422	5.329	0.5346	54.063	28.90
9	29.704	4.835	0.4850	51.28	24.87(*)
10	30.835	5.928	0.5947	40.16	23.88
C_2 = 1.327 × 10^{-6} (g/mL); Denoted by Hollow Diamonds in Figure 3					
1	35.000	3.450	1.000	0	0
2	32.555	2.130	0.6174	23.45	14.48
3	30.835	1.941	0.5626	40.16	22.59
4	29.708	1.633	0.4733	51.24	24.25(*)
5	29.422	1.389	0.4026	54.06	21.76
6	29.089	1.956	0.5570	57.35	32.51
7	29.540	1.529	0.4432	52.89	23.44(*)
8	30.334	1.744	0.5052	45.09	22.78(*)
C_3 = 1.235 × 10^{-6} (g/mL); Denoted by Filled Circles in Figure 3					
1	29.707	1.468	0.4569	51.25	23.42
2	29.415	1.354	0.4215	54.12	22.81
3	29.235	1.205	0.3753	55.91	20.98
C_4 = 7.492 × 10^{-7} (g/mL); Denoted by Inverted Hollow Triangles in Figure 3					
1	35.002	1.798	1.000	0	0
2	33.597	1.572	0.8743	13.41	11.72
3	33.037	1.440	0.8009	18.80	15.06
4	32.370	1.362	0.7575	25.24	19.12
5	31.481	1.245	0.6924	33.88	23.46
6	30.893	1.106	0.6151	39.61	24.37
7	29.761	0.8517	0.4737	50.72	24.03*
8	28.966	0.7413	0.4123	58.57	24.15*
9	28.417	0.6915	0.3846	64.02	24.62*
10	29.457	0.8064	0.4485	53.72	24.09*

[a] The identification number denotes the measurement sequence. See discussion for details. [b] Temperature has a relative precision of 0.001 °C. [c] The overall precision of our experimental values is between 1 and 5% depending on concentration used. We have not taken into account the uncertainties in the absolute determination of M_w. We have defined τ as $(T - \Theta)/T$ in order to compare with the results in ref 9. In fact, the alternative definition $\tau = 1 - T/\Theta$ appears to be more reasonable.

IV. Results and Discussion

The thermodynamic states of our polystyrene solutions are presented schematically in Figure 2, in which the coexistence curve was computed based on eq 1 and 2. Table II lists the numerical values with identification numbers denoting the sequence of our viscosity measurements. We have noted that deviations from the plateau value of $\alpha_\eta^3|\tau|M_w^{1/2}$, as shown in Figure 3, are closely related to critical-point behavior. For examples, as we approach the collapsed regime at C = 3.834 × 10^{-6} g/mL, marked deviation from the plateau value occurred as the temperature was lowered from 30.334 (number 7) to 29.422 °C (number 8). The value could be retrieved if we increased the temperature to 29.704 °C (number 9). At a lower concentration (C = 1.327 × 10^{-6} g/mL), we could retain a constant plateau value to a slightly lower temperature (at 29.540 °C with 7 as the identification number). Finally, at C = 7.492 × 10^{-7} g/mL, the plateau value remained constant at temperatures less than 29 °C as listed in Table II.

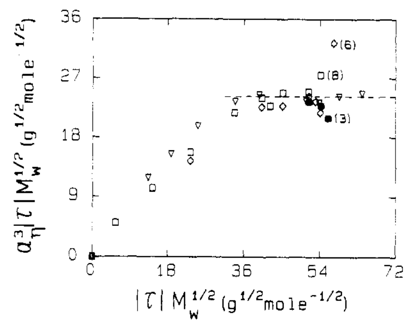

Figure 3. Plot of scaled expansion factor $\alpha_\eta^3|\tau|M_w^{1/2}$ of intrinsic viscosity as a function of scaled reduced temperature $|\tau|M_w^{1/2}$. $\alpha_\eta|\tau|M_w^{1/2}$ at the asymptotic plateau region is 24.2 ± 0.5 g$^{1/2}$ mol$^{-1/2}$. See Table II and text for discussions on the data fluctuations in the plateau region. Hollow squares denote C_1 = 3.834 × 10^{-6} g/mL; hollow diamonds denote C_2 = 1.327 × 10^{-6} g/mL; filled squares denote C_3 = 1.235 × 10^{-6} g/mL; inverted hollow triangles denote C_4 = 7.492 × 10^{-7} g/mL. Fluctuations of data at the plateau value can be interpreted as due to the onset of critical-point/phase separation behavior. For examples, at C_1 and 29.422 °C, an apparent plateau value of 28.90 g$^{1/2}$ mol$^{-1/2}$ (as listed in Table II under C_1 with identification number 8) was observed. The "anomaly" could be removed either by increasing the temperature to 29.704 °C or by decreasing the concentration to 7.492 × 10^{-7} g/mL which yielded a plateau value of 24.15 at 28.966 °C. Symbols with (#) denote those measurements where critical-point/phase separation behavior could occur.

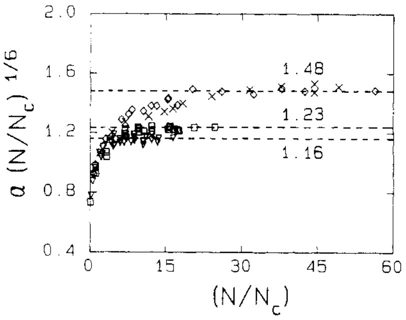

Figure 4. Universal plot of reduced hydrodynamic size (α_h), viscosity size (α_η), and static size (α_s) vs reduced blob parameter (N/N_C). The asymptotic values reached by α_h, α_η, and α_s have ratios of 2.14 ± 0.19:1.2 ± 0.1:1. In our experiments, $\alpha_\eta^3 \simeq \alpha_s^2\alpha_h$. Hollow inverted triangles denote R_g data from ref 1; crosses denote R_h data from ref 3; hollow diamonds denote sedimentation data from ref 11; hollow squares denote viscosity data from present work.

Our viscosity data are in essential agreement with those reported by Perzynski et al.[9] However, we determined an average plateau value of 24.1 ± 3% (g$^{1/2}$ mol$^{-1/2}$) instead of 27. On the basis of our extended universal coexistence curve for polystyrene in cyclohexane, some of the viscosity data reported by Perzynski et al.[9] could have crossed the COEX curve. Our results showed smaller fluctuations since we were able to distinguish those data points in the very immediate neighborhood of the coexistence curve. Furthermore, our precision in flow time measurements was about a factor of 10 better than that reported previously.[9] On the other hand, the magnitude of the expansion factor depends on the normalization factor, i.e., the value at Θ temperature. Thus, for the two sets of experiments (present work and ref 9), a discrepancy in the magnitude of α_η of at least a few percent is to be expected. The collapsed regime started at about $\tau M_w^{1/2} \sim 40$ g$^{1/2}$/mol$^{1/2}$, and we were able to reach $\tau M_w^{1/2} \sim 65$ with the polymer chain contracted to 73% of the unperturbed theta state. We used the experimental values (denoted by an asterisk (*) in Table II) at $\tau M_w^{1/2} > 42$ g$^{1/2}$/mol$^{1/2}$ to compute the average plateau value.

Figure 4 shows a universal plot of reduced expansion factor $\alpha(N/N_C)^{1/6}$ vs reduced blob size (N/N_C). The experimental data for light scattering studies yielded α_s and α_h and were transferred from Figure 14 of ref 1 and Figure 6 of ref 11, respectively, and α_h in the collapsed regime also from Figure 2 of ref 3. In Figure 4, an experimental ratio of $\alpha_h^3:\alpha_\eta^3:\alpha_s^3 = 2.14 \pm 0.19:1.2 \pm 0.1:1$ was obtained. We noted that $\alpha_h\alpha_s^2$ as $\alpha_\eta^3/\alpha_s^2\alpha_h = 24.1/25.6 \simeq 1$, while if we take an average of the two data sets (present work and ref 9) $(\alpha_\eta^3|\tau|M_w^{1/2})_{\mathrm{plateau}} = 25.6$, we have $\alpha_\eta^3/\alpha_s^2\alpha_h \simeq 25.6/25.6 = 1$ or $\alpha_\eta^3 = \alpha_s^2\alpha_h$. It should be noted that there is one true value for α_η and we should not really add the two data sets. By averaging the two data sets, we merely point out that the expansion factors contain fairly large experimental uncertainties.

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Registry No. Polystyrene, 9003-53-6; cyclohexane, 110-82-7.

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Determination of the Order–Disorder Transition Temperature of Block Copolymers

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ABSTRACT: The order–disorder transition temperature (T_r) of two commercial block copolymers, a polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) (Kraton 1102, Shell Development Co.) and a polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) (Kraton 1107, Shell Development Co.), was determined, by using a rheological technique recently suggested by Han and Kim. The rheological technique calls for measurements of dynamic viscoelastic properties, namely, storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ as a function of angular frequency (ω) under isothermal conditions. It has been observed that log G' versus log G'' plots for the block copolymers investigated vary with temperature up to a certain critical value and then become *virtually* independent of temperature as the temperature increases further. Therefore the critical temperature at which log G' versus log G'' plots cease to vary with temperature is regarded as T_r. Our experimental results indicate that, to within ±10 °C, the T_r of Kraton 1102 is 220 °C and the T_r of Kraton 1107 is 230 °C. The currently held theories of Helfand–Wasserman and Leibler were used to predict the T_r's of the block copolymers investigated. It has been found that the accuracy of the theoretical predictions of T_r depends very much on the accuracy of the temperature dependency of both the interaction parameter and the specific volumes of the constituent components in a block copolymer.

Introduction

It is a well-established fact today that diene-based block copolymers, such as polystyrene-*block*-polybutadiene (SB), polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS), and polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS), have an ordered microdomain structure in the form of spheres, cylinders, or lamellae, depending upon the proportions of the constituent components.[1,2] However, as the temperature is raised above a certain critical value, the microdomain structure disappears completely, giving rise to a disordered homogeneous phase. The temperature at which the microdomain structure completely disappears is referred to as the order–disorder transition (also referred to as the microphase separation transition (MST)) temperature (T_r). In recent years, several research groups[3-12] have investigated the order–disorder transition behavior of block copolymers. Some investigators[3-5] conducted theoretical studies while others[6-12] carried out experimental studies.

Leibler[4] has developed a theory, suggesting that small-angle X-ray or neutron scattering techniques be used to investigate the order–disorder transition behavior of block copolymers. Apparently, Leibler's theory has encouraged some investigators[8-11] to use small-angle X-ray scattering (SAXS) and others[12] to use small-angle neutron scattering (SANS) to investigate the order–disorder transition behavior of diene-based block copolymers. They reported that the maximum scattered intensity present at room temperature persists well above the glass transition temperature of the polystyrene domains but disappears at a critical temperature at which the block polymer is believed to become a homogeneous phase.

In the past, the rheological behavior of SB, SBS, and SIS block copolymers at temperatures above the glass transition temperature of the styrene domains was studied extensively by a number of investigators.[13-17] By applying frequency–temperature superposition to their dynamic viscoelastic data, some investigators[13,14] have reported that logarithmic plots of dynamic viscosity (η') versus angular frequency (ω) or logarithmic plots of dynamic storage modulus (G') versus ω for an SB, SBS, or SIS block copolymer show an abrupt change over a narrow temperature

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