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NMR Investigation of the Order–Disorder and Rheological Transitions in Styrene–Isoprene Diblock Copolymers

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ABSTRACT: ^{13}C NMR spectroscopy was used to investigate the physical basis of the rheological thermal transition (T_{rheo}) in symmetric poly(styrene-b-isoprene) (SI) diblock copolymers. Among the studied samples, those with $M_n = (3-32) \times 10^3$, which all exhibited two glass transition features ($T_{g,I}$ and $T_{g,S}$) in their DSC curves, had T_{rheo} values ranging from −10 °C to 205 °C. The NMR line width data related to the styrene units in the bulk materials show that a strong segregation behavior persists over a wide range of temperature above T_{rheo}. For $M_n > 1.2 \times 10^4$, the rheological transition coincides with the last trace of ordering (extinction of the lamellar grain diffraction), but in the disordered state the materials contain polystyrene (PS) block heterogeneities large enough to exhibit NMR features comparable to those of homo-PS samples having the same T_g as $T_{g,S}$. Over this range, T_{rheo} increases in the same ratio as $M_n^{0.35}$. An analysis of this relationship suggests an order–disorder transition governed by an energy barrier related to the interface tension in the ordered state. For $M_n < 1.2 \times 10^4$, T_{rheo} no longer corresponds to an order–disorder transition because vitrification of the PS block heterogeneities occurs before a lamellar ordering can take place in the materials.

Introduction

Since the report by Chung and Gale[1] in 1976 on the occurrence of a melt rheological transition in a styrene–butadiene–styrene (SBS) triblock copolymer, the so-called order–disorder transition (ODT) in amorphous block copolymers has been investigated by several workers.[2–14] The formation of ordered microphases in these materials indicates that the excess free energy of mixing of the unlike blocks is unfavorable to miscibility. In terms of the Flory–Huggins formalism, this situation corresponds to a positive value of the interaction parameter χ between the unlike components. It is fully documented that χ usually decreases with increasing temperature and that ordered specimens with lamellar, cylindrical, or spherical morphology transform into disordered melts at T_{ODT}. Until recently, the ODT process was essentially considered as a microphase separation transition (MST). This view, which had been reinforced by the RPA (random phase approximation) theory of Leibler,[15] acted as a premise in more recent development of the RPA theory.[16,17] However, Fredrickson and Helfand[17] brought out fluctuation corrections to Leibler's theory, and in a subsequent work by Bates *et al.*,[12] the terminology MST was no longer used because strong fluctuations in composition were shown to persist over a wide range of temperature above T_{ODT}.

Experimentally, T_{ODT} in block copolymers is currently investigated by means of dynamical rheometry,[1–6,12,14] and by small-angle X-ray and neutron scattering (SAXS and SANS).[6–14] Among these techniques, only rheometry has provided unambiguous evidence for a phenomenon that corresponds to a sharp phase transition. However, this phenomenon, which is an abrupt decrease in the isochronal shear moduli, vanishes above a critical frequency (ω_c) of the shear strain. As shown by Bates *et al.*,[5,12] for $\omega \ll \omega_c$ and $T \gg T_{rheo}$ (the rheological transition temperature), the materials exhibit a Newtonian behavior similar to that of homopolymer melts. This rheological transition is unique since the SAXS and SANS data reported for most of the specimens did not show evidence for a marked discontinuity over the range near T_{rheo}.

The scattering behavior of block copolymers is not a simple matter. Due to the so-called correlation hole effect,[18] that is, the local fluctuations in composition resulting from the sequential distribution of the unlike monomers, these materials are expected to yield a scattering peak even under their homogeneous form. According to Leibler's theory,[15] the reciprocal intensity of this peak should decrease linearly with χ (or $1/T$). Thus, until recently, T_{ODT} was assumed to correspond to the onset of this linear relationship.[6,9–11] As pointed out by Bates *et al.*,[12] in view of the stronger fluctuations in composition, this approach may lead to a large overestimation of T_{ODT}. In earlier studies,[7,8] T_{ODT} was defined on the basis of the extinction of the higher than the first-order reflections associated with the ordered morphology. Such a method is also questionable because, as T_{ODT} is approached, a progressive broadening of the microphase interface may take place in the ordered material.[19] This may cause a severe damping of the higher order reflections.

Among the previous works on the compositional features of block copolymers near T_{ODT}, a special attention should be paid to the dielectric study performed by Quan *et al.*[19] on a series of (1,4-PB)–(1,2-PB) (PB = polybutadiene) symmetric diblock copolymers. In this study, the temperature dependence of the dielectric loss of a low molecular weight sample ($M_n = 2.5 \times 10^4$), which was defined as a disordered material by rheology, exhibited relaxation features similar to those of an ordered sample of higher molecular weight ($M_n = 8.4 \times 10^4$). These relaxation features were interpreted as an evidence for local heterogeneities in the disordered state large enough to exhibit an apparent glass transition. Furthermore, a quantitative analysis of the data showed that the fraction of the polymer partitioned into the high-T_g region decreased from 71 to 55% with increasing M_n over the range $(2.5–8.4) \times 10^4$.

These findings by Quan *et al.*[19] call for further investigation based on experimental techniques more appropriate to study the compositional features of block copolymers above T_{ODT}. In the present work, such an investigation was performed by means of ^{13}C NMR spectroscopy on a series of eight styrene–isoprene (SI) symmetric diblock copolymers, $M_n = (2.7–95) \times 10^3$, that exhibited two glass transition features ($T_{g,I}$ and $T_{g,S}$) in their DSC curves.[20,21] For that purpose, the spectral line widths of the styrene units in the bulk materials were measured over the range $50 < T < 150$ °C. One of these

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samples ($M_n = 1.1 \times 10^4$) was the same as that used in a previous SAXS investigation by Owens *et al.*[11] As reported by these authors, a plot as a function of $1/T$ of the reciprocal intensity of the single SAXS peak recorded for this sample yielded a T_{ODT} apparent value of 93 °C. In a more recent work by Stühn *et al.*,[14] a symmetric SI sample of higher molecular weight ($M_n = 1.57 \times 10^4$) was reported to exhibit its rheological transition at 89 °C. Note that this value of T_{rheo} was consistent with the value of T_{ODT} determined from the extinction of the second-order SAXS reflection recorded for this specimen. The present study involves samples having a wide range of T_{rheo}. Also examined are a series of polystyrene (PS) samples having a range of T_g comparable to that of $T_{g,S}$. The NMR spectra were recorded at a ^{13}C Larmor frequency of 100.6 MHz by using the conventional, high-resolution technique.

The line width data analysis is presented in the first section of this paper. It shows that contrary to the (1,4-PB)–(1,2-PB) diblock system studied by Quan *et al.*,[19] the present SI system, which involves a 10 times greater interaction parameter χ, exhibits a strong segregation behavior above T_{ODT}. In view of this feature, the relationship between T_{ODT} and T_{rheo} was examined in more detail through the molecular weight dependence of T_{rheo}. This analysis, which is presented in the second section of this paper, suggests a correlation between T_{ODT} and an energy barrier related to the interface tension.

Experimental Section

Materials. The SI samples were prepared by anionic polymerization by using *sec*-butyllithium as initiator and benzene as solvent. As determined from the methyl resonances in 100.6 MHz proton-decoupled ^{13}C NMR spectra measured on the bulk at 100 °C, the microstructure of the polyisoprene blocks was 71% cis-1,4, 22% trans-1,4, and 7% 3,4. In order to avoid oxidative degradation of these blocks, all the samples were stored at −20 °C in vacuum-sealed tubes. The polystyrene samples were standard materials of low polydispersity. Number-average molecular weights, M_n, were determined by either membrane osmometry in toluene or vapor pressure osmometry in benzene. Polydispersity indexes, M_w/M_n, were characterized by size exclusion chromatography in toluene by using a series of three Ultrastyragel columns calibrated with polystyrene standards. This method also provided quantitative data concerning the good stability of the materials over the years of their various studies.[20,21] Glass transition temperatures, T_g, were measured at a heating rate of 40 °C/min with a model DSC-4 Perkin-Elmer calorimeter flushed with dry helium. Specimens were annealed at 125 °C many days prior to the DSC measurements, and values of T_g were read at half-height of the transitions.

^{13}C NMR Measurements. The ^{13}C NMR spectra (100.6 MHz) were recorded under scalar decoupling with a Model WH-400 Bruker spectrometer. The rigid samples were heat molded into the form of annular cylinders and slipped into 10-mm diameter (Wilmad 513-7PPM) tubes. The viscous or rubbery samples were allowed to flow into the bottom of the tubes by their heating in an oil bath. In both cases, a vacuum-sealed 5-mm diameter (Wilmad 528-PP) tube containing ethylene glycol-d_2 (Aldrich) was inserted concentrically in the 10-mm tubes. This external reference provided deuterium lock for field stability. The rigid materials were further heated for a period of 1 h at 150 °C and slowly cooled to room temperature. All the spectra were recorded under the same instrumental adjustments. The temperature of the probe was controlled by a Model B-ST Bruker unit calibrated with a copper-constantan digital thermometer. At each temperature, the materials were thermally equilibrated for 0.5 h before data collection. Measurements made on different days were reproducible.

T_{rheo} Characterization. The flow behavior of the SI samples was monitored by visual inspection of specimens (0.5 g) of irregular shape placed on a glass plate in 55-mm diameter vacuum ampules, at a temperature 10 °C lower than $T_{g,S}$. By using a Model 3111 Instron environmental chamber, the ampules were heated by step increases of 5 °C at intervals of 1 h and a photography was taken at the end of each step. The T_{rheo} feature was defined as the temperature corresponding to the step at which the specimens commenced to deform under gravity. In each case, the next steps produced an accelerated flow of the specimen, indicating a sharp change in the rheological properties. By means of this qualitative approach, which is based on a method previously tested by Bates *et al.*,[22] T_{rheo} could be estimated with an accuracy of ±5 °C.

Table 1. Styrene Weight Fractions (w_S), Number-Average Molecular Weights (M_n), Polydispersity Indexes (M_w/M_n), Glass Transition Temperatures ($T_{g,S}$ and $T_{g,I}$), and Rheological Transition Temperatures (T_{rheo}) of the SI Samples. Included are M_n, M_w/M_n, and T_g of the Homo-PS Samples

sample	w_S, %	$10^{-3}M_n$	M_w/M_n	$T_{g,S}$, °C	$T_{g,I}$, °C	T_{rheo}, °C
SI-3k	51	2.7	1.05	−23	−46	−10
SI-5k	51	4.85	1.03	3	−49	10
SI-8k	50	8.2	1.02	31	−54	35
SI-11k	50	11.0	1.04	59	−57	60
SI-13k	50	12.6	1.04	65	−58	75
SI-18k	51	18.2	1.07	80	−58	125
SI-32k	49	31.7	1.05	93	−60	205
SI-95k	48	94.7	1.09	104	−60	–
PS-700		0.70	1.11	7		
PS-1k		0.98	1.09	33		
PS-2k		1.79	1.05	67		
PS-4k		3.57	1.04	89		
PS-100k		99.5	1.08	107		

Results and Discussion

(a) Line Width Data Analysis. The detail concerning the molecular features and the physical properties of the polymer samples used in this study is given in Table 1. As shown in a previous work,[21] high-resolution, conventional ^{13}C NMR spectroscopy is particularly well suited to investigate the phase behavior of styrene–isoprene block copolymers. The styrene units in these polymers exhibit aromatic and aliphatic resonances that can be easily distinguished from those of the isoprene units. Figure 1 shows the aromatic region of ^{13}C NMR spectra recorded at different temperatures on samples SI-3k, SI-5k, and SI-13k. For the sake of comparison, spectra recorded under the same conditions on sample PS-2k are shown in Figure 2. The analysis of these spectra will focus on the aromatic resonance at 128 ppm. This resonance arises from the ortho and meta carbons in the benzene ring of the PS units. It is the strongest resonance associated with these units. The other resonances, including those of the cis-1,4, trans-1,4 and 3,4 units of the polyisoprene (PI) blocks, are defined in the legend of Figure 1.

Inspection of Figure 1 shows that the onsets of the PS block resonances occur at temperatures well above the values of $T_{g,S}$ listed in Table 1. These resonances begin to build up near 50 °C for sample SI-3k ($T_{g,S} = -23$ °C), near 65 °C for sample SI-5k ($T_{g,S} = 3$ °C), and near 100 °C for sample SI-13k ($T_{g,S} = 65$ °C). The absence of any residual aromatic resonance in the spectra recorded below these temperatures (see spectrum of sample SI-3k at 40 °C on Figure 1), together with the high resolution of the PI block resonances, provides a strong basis to argue that the values of $T_{g,S}$ and $T_{g,I}$ listed in Table 1 correspond to pure PS and pure PI heterogeneities, respectively. In turn, if this argument is correct, the extensive lowering of $T_{g,S}$ with decreasing molecular weight is necessarily due to an exchange of kinetic energy through the chemical junctions at the boundary of these heterogeneities. A comparison with $T_{g,PS}$ and $T_{g,PI}$ of the corresponding homopolymers (with the same molecular weights as the PS and PI blocks) was reported in the previous work.[21] This effect was shown

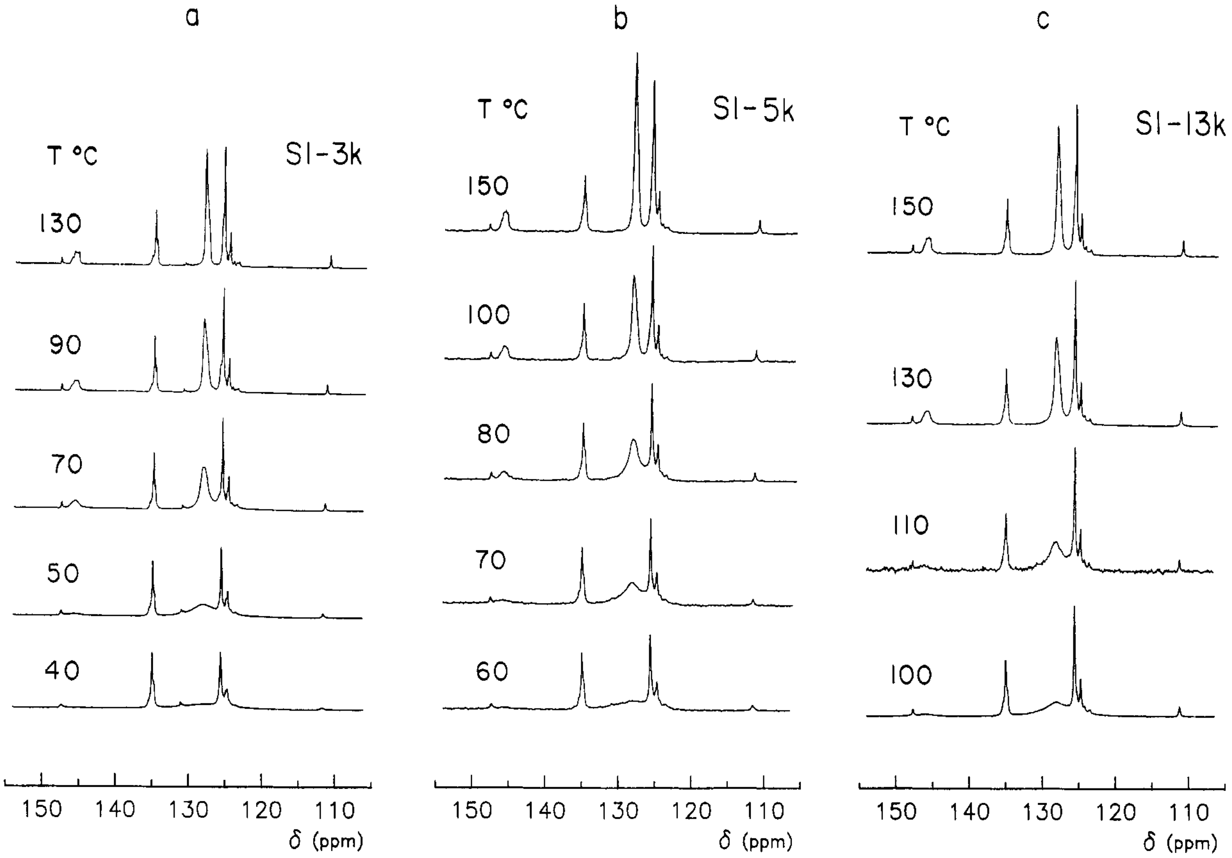

Figure 1. Aromatic–olefinic region of scalar-decoupled ^{13}C NMR spectra recorded at various temperatures on samples SI-3k (a), SI-5k (b), and SI-13k (c). The PS block aromatic resonances are located at 126 ppm (para carbons), 128 ppm (ortho and meta carbons), and 146 ppm (quaternary carbons). The olefinic PI block resonances are located at 112 ppm (3,4 units), 125 ppm (trans-1,4 units), 126 ppm (cis-1,4 units), 135 ppm (trans- and cis-1,4 units), and 148 ppm (3,4 units).

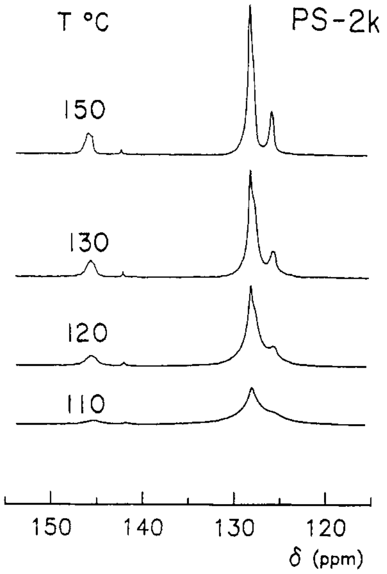

Figure 2. Aromatic region of scalar-decoupled ^{13}C NMR spectra recorded at various temperatures on sample PS-2k. Peak assignments are given in the legend of Figure 1.

to contribute to decrease $T_{g,S}$ with respect to $T_{g,PS}$ and to increase $T_{g,I}$ with respect to $T_{g,PI}$.

The onset of the PS aliphatic resonances (not shown) occurred at a higher temperature than the aromatic resonances. This difference reflects a feature inherent to the physical basis of the present technique. The NMR line of a given ^{13}C nucleus becomes observable when both the ^{13}C–^{1}H dipole–dipole interactions and the chemical shift anisotropy resulting from the uneven electron density around this nucleus are averaged over a range of orientations through molecular motion.[23] The temperature corresponding to the onset of the NMR lines (thereafter denoted as T_{NMR}) is thus closely related to the dynamics and the structure of the chemical groups bearing the ^{13}C nuclei. It also depends on instrumental features such as the spectrometer sensitivity and the static field homogeneity. For instance, measurements made on samples SI-5k and SI-8k with a spectrometer working at a ^{13}C Larmor frequency of 20.1 MHz (instead of 100.6 MHz) yielded T_{NMR} values 20–25 °C higher than the present values. Since T_{NMR} and line widths above T_{NMR} depend on the spectrometer features in addition to the local dynamics of the material, they are difficult to interpret in terms of a quantitative, physical model. Nevertheless, even in the absence of such a model, interesting information can be obtained through quantitative comparisons made with spectra recorded under the same instrumental conditions.

Figure 3 shows the temperature dependence of the line width at half height ($W_{1/2}$) of the 128 ppm resonance recorded on each of the SI samples listed in Table 1. Over the range of the study ($T_{NMR} < T < 150$ °C), each plot exhibits a gradual change with increasing temperature. This, with the absence of any perceptible change in the line widths of the PI resonances (see Figure 1), indicates that there is no sharp compositional transition above T_{NMR}. However, a comparison with the $W_{1/2}$ data obtained for the homo-PS samples (Figure 4) reveals two distinct features associated with the presence of the PI blocks in the SI materials. First, the PS resonances of the SI samples exhibit a more gradual narrowing with increasing temperature than the homo-PS samples. Second, at the highest temperature of the study (150 °C), these resonances are systematically narrower than those of homo-PS specimens of comparable T_g. At first glance, these two

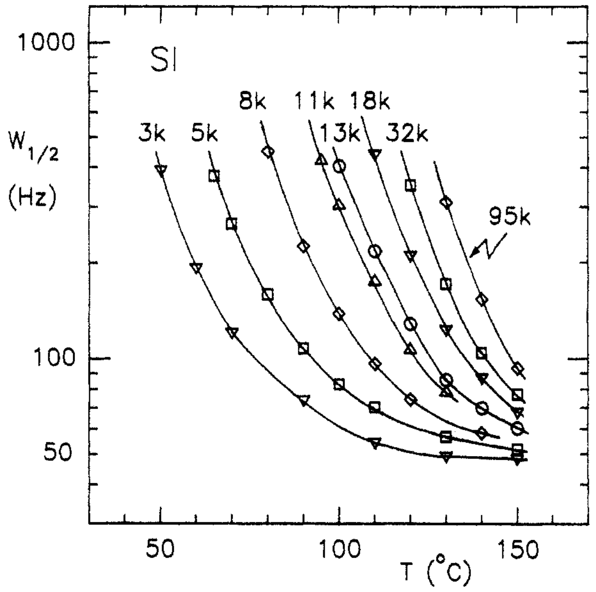

Figure 3. Temperature dependence of the line width at half height ($W_{1/2}$ in hertz) of the 128-ppm aromatic resonance recorded on the SI samples described in Table 1.

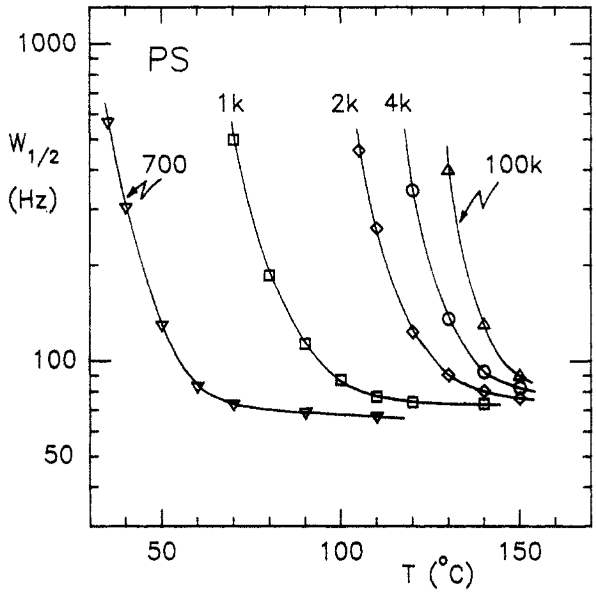

Figure 4. Temperature dependence of the line width at half height ($W_{1/2}$ in hertz) of the 128-ppm aromatic resonance recorded on the homo-PS samples described in Table 1.

features, which are clearly apparent for the low molecular weight SI samples, suggest either a progressive mixing of the unlike components or a greater exchange of kinetic energy between the unlike heterogeneities with increasing temperature.

The $W_{1/2}$ data in Figures 3 and 4 allow a quantitative comparison on a T_g basis. Such a comparison is depicted in Figure 5, where $T(W_{1/2} = 400$ Hz), which essentially corresponds to $T_{\rm NMR}$, and $T(W_{1/2} = 90$ Hz), which corresponds to the highest temperatures yielding a narrow line of common breadth (90 Hz) for all samples, are plotted as a function of $T_{g,S}$ (or $T_{g,PS}$). It may be seen that for $T_{g,S} > 50$ °C, approximately, the relationships related to the SI samples are essentially superimposed on those of the homo-PS samples. Below this limit, however, the latter relationships decrease abruptly with decreasing $T_{g,PS}$. This feature, which is due to the presence of long-range motion (diffusion and tumbling) in the homo-PS oligomeric materials, imposes a severe limitation to the present comparison. Nevertheless, as judged from the common behavior observed for $T_{g,S} > 50$ °C, local mobility associated with the PS chains in the SI samples with $M_n > 1 \times 10^4$ is roughly the same as in homo-PS samples of comparable T_g. From this feature, it may be argued that over the range from $T_{\rm NMR}$ to $T(W_{1/2} = 90$ Hz), there is no apparent mixing of the unlike components in the $M_n > 1 \times 10^4$ SI samples. This feature contrasts with the extensive mixing reported by Quan *et al.*[19] for (1,4-PB)–(1,2-PB) symmetric diblock copolymers of comparable molecular weights. It is due to the greater magnitude of the interaction parameter χ of the present system. As reported by independent groups, at 90 °C the value of χ related to the SI symmetric system[11] is an order of magnitude greater than that of the (1,4-PB)–(1,2-PB) symmetric system[10] (0.078 compared to 0.0083).

Among the present materials, sample SI-13k was the lowest molecular weight sample yielding SAXS unambiguous evidence of a lamellar morphology at room temperature.[21] Samples SI-11k, SI-8k, SI-5k, and SI-3k all exhibited a single SAXS reflection which markedly decreased in intensity and increased in breadth with decreasing M_n. However, down to sample SI-5k, the Bragg spacing (d) of this reflection was shown to fit the same relationship as that ($d_L = 0.0205\ M_n^{0.69}$ nm) established for the lamellar spacings of the higher molecular weight materials.[21] Only sample SI-3k ($d = 5.4$ nm) displayed a discrepancy (+11%) with respect to this relationship. The NMR data (Figure 1) indicate that these low molecular weight, disordered materials remain strongly segregated over a wide range above room temperature.

The absence of ordering at room temperature in sample SI-11k ($T_{g,S} = 59$ °C) is due to the vitrification of the PS heterogeneities at a temperature higher than $T_{\rm ODT}$. This statement is at variance with a recent argument by Stühn[13] that $T_{g,S}$ would be concomitant with the microphase separation transition in comparable low molecular weight materials, including a symmetric SI sample identical to sample SI-11k. As deduced from the present NMR investigation, sample SI-11k already consists of PS and PI heterogeneities at temperatures well above its value of $T_{g,S}$. Therefore, it is clear that the PS heterogeneities undergo vitrification before ordering can take place in this sample.

Although no attempts were made to record SAXS patterns above room temperature on the present SI samples, it is rational to consider that the lamellar morphology observed for sample SI-13k ($d_L = 13.3$ nm)[21] should persist up to its value of $T_{g,S}$ (65 °C). As quoted in Introduction, in another work by Stühn *et al.*,[14] a symmetric SI sample of higher molecular weight ($M_n = 1.57 \times 10^4$) was reported to exhibit a lamellar morphology ($d_L = 16.2$ nm) up to 89 °C. This limit is positively higher than the value of $T_{g,S}$ (72 °C) expected for this sample on the basis of the molecular weight dependence of $T_{g,S}$ (Figure 6). On the other hand, it is positively lower than the value of $T_{\rm NMR}$ (104 °C) expected on the basis of the $T(W_{1/2} = 400$ MHz) vs $T_{g,S}$ relationship depicted in Figure 5. These low molecular weight SI samples are particularly interesting because they become disordered over a range of temperature well below the limit of 150 °C of the present NMR study. Under the assumption that a mixing of the unlike components accounted for the already quoted difference between the extreme narrowing limits of the homo-PS and the PS-block resonances at elevated temperatures, this mixing would be a gradual function of the temperature as in any binary system involving a liquid–liquid equilibrium.

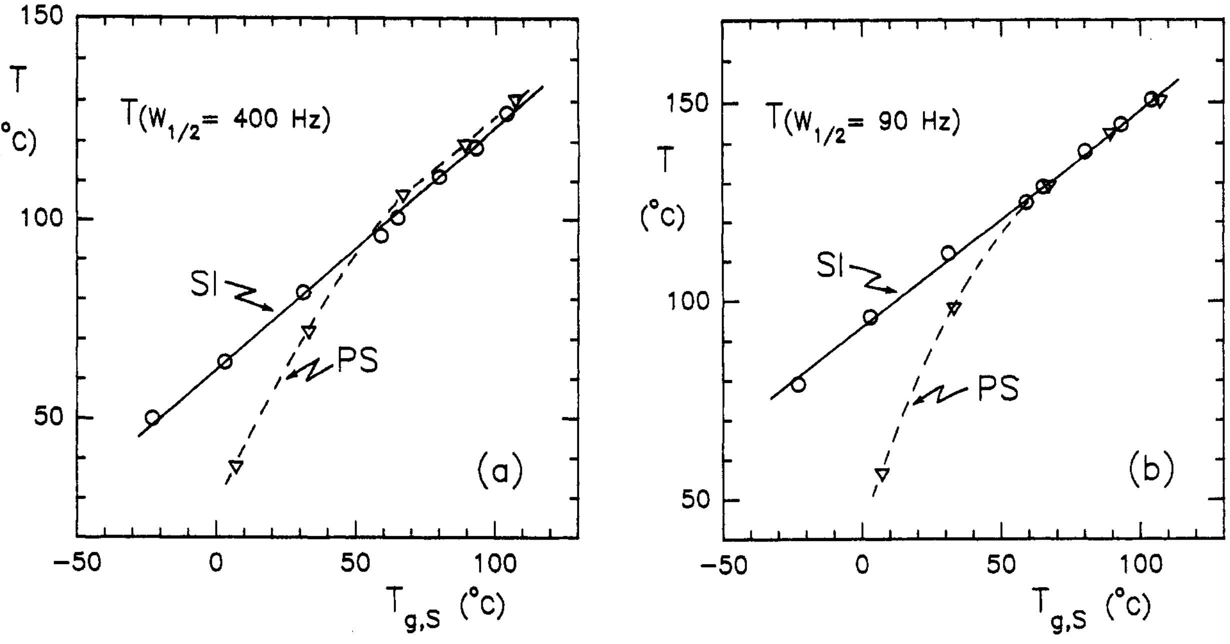

Figure 5. Plots of the temperatures $T(W_{1/2} = 400$ Hz) (a) and $T(W_{1/2} = 90$ Hz) (b) corresponding to line widths of 400 and 90 Hz, respectively, as a function of $T_{g,S}$ (solid line, SI samples) or $T_{g,PS}$ (broken line, homo-PS samples). Constructed from the $W_{1/2}$ data depicted in Figures 3 and 4, and the T_g data listed in Table 1, respectively.

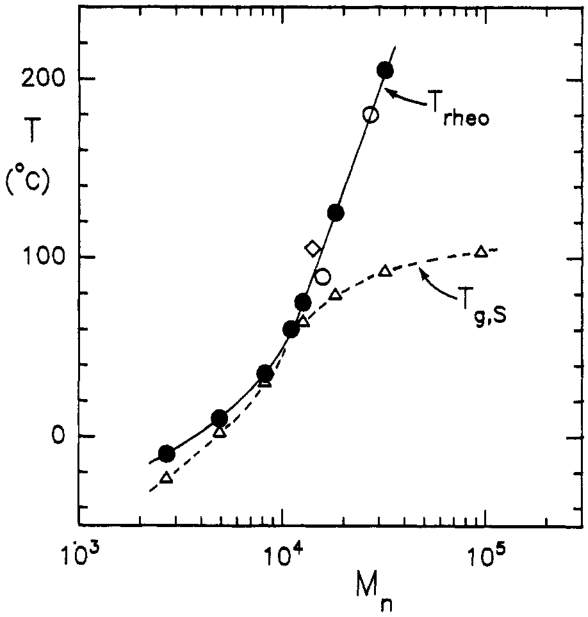

Figure 6. Molecular weight dependences of T_{rheo} (solid line) and $T_{g,S}$ (broken line) for the SI samples studied in this work. Included are the data (open circles) reported by Stühn *et al.*[14] ($T_{ODT} = T_{rheo} = 89$ °C) and Hadziioannou and Skoulios[8] ($T_{ODT} = 180$ °C) for symmetric SI samples with $M_n = 1.57 \times 10^4$ and $M_n = 2.7 \times 10^4$, respectively. Also, plotted on a half-M_n basis (open diamond), is the value of T_{rheo} (105 °C) reported by Han *et al.*[6] for a symmetric SIS ($M_n = 2.8 \times 10^4$, $w_S = 0.52$) triblock copolymer.

In view of these considerations, it is clear that there is no apparent relationship between T_{ODT} and the miscibility behavior of the unlike blocks in materials such as sample SI-13k and the $M_n = 1.57 \times 10^4$ sample studied by Stühn et al.[14] Unfortunately, with increasing molecular weight above this range T_{ODT} rapidly exceeds the limit of 150 °C of the present study. In a SAXS study reported by Hadziioannou and Skoulios,[8] a shear-oriented, symmetric SI specimen with $M_n = 2.7 \times 10^4$ exhibited a lamellar morphology ($d_L = 20 \pm 1$ nm) up to 180 °C. In the same study, shear-oriented specimens of higher molecular weights ($5.1 \times 10^4 < M_n < 9.8 \times 10^4$) exhibited a marked increase in lamellar spacing over the range 210–250 °C. Since this feature was described as a time-dependent, irreversible transformation, it probably resulted from thermal degradation. Thus, SI materials with M_n greater than 5×10^4 should have T_{ODT} values higher than 250 °C.

(b) T_{ODT} and the Rheological Transition. A T_{rheo} feature was observed for all the SI samples studied in this work except sample SI-95k. This feature was evidenced by the occurrence of a gravity-driven viscous flow above a certain temperature when specimens of irregular shape were heated under vacuum. As previously reported by Bates *et al.*,[22] this visual, very simple approach allows a reliable estimation of T_{rheo}. Sample SI-95k was heated up to 325 °C. The specimen, which became slightly discolored, did not exhibit any change in shape over a standing of 5 h at this temperature. Figure 6 shows plots of T_{rheo} and $T_{g,S}$ as a function of log M_n for the other samples. It may be seen that with increasing M_n up to 1.2×10^4, approximately, T_{rheo} roughly coincides with $T_{g,S}$. Above this limit, however, it exhibits an abrupt rise to reach the value of 205 °C for $M_n = 3.2 \times 10^4$. The latter relationship is in agreement with both the T_{rheo} (or T_{ODT}) value of 89 °C ($M_n = 1.57 \times 10^4$) reported by Stühn *et al.*[14] and the T_{ODT} value of 180 °C ($M_n = 2.7 \times 10^4$) reported by Hadziioannou and Skoulios.[8] Furthermore, on a half-M_n basis it also fits the T_{rheo} value of 105 °C reported by Han *et al.*[6] for a $M_n = 2.8 \times 10^4$ symmetric SIS triblock copolymer containing 52% by weight of styrene units.

From the relationships in Figure 6, it is clear that T_{rheo} is governed by two distinct processes depending on the molecular weight of the SI samples. For $M_n < 1.2 \times 10^4$, viscous flow occurs at a temperature just above the glass transition temperature $T_{g,S}$ of the PS heterogeneities. In this region, the sharp change in the rheological properties is definitely not associated with a T_{ODT} process. On the other hand, for $M_n > 1.2 \times 10^4$, that is, in the region where ordering is possible because T_{ODT} is higher than $T_{g,S}$ the rheological transition coincides with T_{ODT}. This latter feature is positively corroborated by the SAXS data of Stühn *et al.*[14] and Hadziioannou and Skoulios.[8]

Over the range where the rheological transition is governed by $T_{g,S}$, the molecular weights of the individual blocks are lower than the critical molecular weights for chain entanglement of the corresponding homopolymers (1.8×10^4 for homo-PS, and 6×10^3 for homo-PI).[24] Therefore, at $T > T_{\rm rheo}$ (or $T > T_{\rm g,S}$) over this range, both the PS and the PI heterogeneities can undergo relatively fast rearrangements through thermally activated jumps of the individual blocks. Since these jumps do not yield an extensive mixing of the unlike blocks, they probably involve a small fraction of the blocks at any one time. It may be argued that the same dynamical features apply to the samples with $M_{\rm n}$ greater than 1.2×10^4. At $T > T_{\rm rheo}$ (or $T > T_{\rm ODT}$), these samples are well above the terminal zone for the viscoelastic properties of either homo-PS or homo-PI of comparable molecular weights. They probably consist of fluid heterogeneities of irregular shape submitted to continuous rearrangements upon thermal agitation. On this basis, $T_{\rm rheo}$ of the ordered specimens would correspond to the energy barrier above which the interface tension, which is among the main driving forces for ordering, is overwhelmed by kinetic effects.

If this hypothesis is correct, the marked increase of $T_{\rm rheo}$ or $T_{\rm ODT}$ with increasing $M_{\rm n}$ would mainly result from the stabilization of the lamellar arrangement due to the decrease in the specific surface with increasing $d_{\rm L}$. On a molecular basis, however, the interface energy increases with increasing $M_{\rm n}$. For a perfectly symmetric diblock copolymer, its magnitude per molecule (or kinetic body) is given by[16]

$$E = \frac{2\gamma N}{n^* d_{\rm L}} \tag{1}$$

where γ is the interface tension, N is the degree of polymerization, and n^* is the number of monomer units per unit volume.

By taking into consideration the molecular weight dependence of $d_{\rm L}$ quoted in the foregoing section, and by replacing the ratio N/n^* by the equivalent ratio $M_{\rm n}/(N_{\rm A}\rho)$, where ρ is the mass density and $N_{\rm A}$ is the Avogadro number, eq 1 may be written as follows:

$$E = 1.38 \times 10^{-15}(\gamma/\rho)M_{\rm n}^{\;0.31} \tag{2}$$

where the quantities γ, ρ, and $M_{\rm n}$ are in SI units.

In turn, according to the data depicted in Figure 6, over the range above $M_{\rm n} = 1.2 \times 10^4$ the molecular weight dependence of $T_{\rm rheo}$ (in kelvin) can be expressed by the relationship

$$T_{\rm rheo} = 143M_{\rm n}^{\;0.35} \tag{3}$$

where $M_{\rm n}$ is in the same units as in eq 2.

The fact that eq 3 essentially yields the same $^1/_3$ power dependence on $M_{\rm n}$, as eq 2 appears to confirm that $T_{\rm rheo}$ is associated with an interface effect. Furthermore, by taking into account the actual values of $M_{\rm n}$ of samples SI-13k, SI-18k, and SI-32k, together with their values of ρ at $T_{\rm rheo}$ (0.95, 0.92, and 0.88 g/cm^3, respectively, as estimated from the volumic properties of homo-PS and homo-PI), the ratio of eq 2 to eq 3 leads to the relationship

$$\frac{E}{kT_{\rm rheo}} = (680 \pm 10)\gamma \tag{4}$$

where k is the Boltzmann constant.

To our knowledge, no measurements of γ were reported for the (homo-PS)–(homo-PI) system. However, Helfand and Wasserman[25] estimated its value ca. 3.1 mN/m at 90 °C by means of a theoretical equation derived by Helfand and Sapse.[26] For the same system, this equation predicts a small decrease of γ with increasing temperature (less than 3% over the range 70–205 °C of the present study). Also note that the estimated value of 3 mN/m appears to be realistic when compared to the experimental data reported for other nonmiscible homopolymer pairs.[26] When applied to eq 4, it yields a value of 2 for the ratio $E/kT_{\rm rheo}$. Such an order of magnitude for this ratio is fully consistent with the hypothesis of an order–disorder transition governed by an energy barrier related to the interface tension.

Concluding Remarks

In agreement with the dielectric study of Quan *et al.*[19] on (1,4-PB)–(1,2-PB) symmetric diblock copolymers, the present NMR study shows that large heterogeneities persist above the order–disorder transition in symmetric SI materials. However, due to its greater interaction parameter χ, a strong segregation behavior is observed in the disordered state of the present system. In view of this feature, one is forced to conclude that, although ODT is a true phase transition because it involves two states of different symmetry, it is not a microphase separation transition. Its physical basis must lie in other factors susceptible to induce disordering. Among these factors, there is the dynamical interactions between the unlike blocks. These interactions, which take place through the chemical junctions at the microphase boundary, may cause a disruption of the lamellae. Such a disruption, which is accompanied by an increase in the specific interface, is necessarily an entropy-driven process. It would result from jumps of the individual blocks from a microdomain to another microdomain. As suggested by the molecular weight dependence of $T_{\rm rheo}$, at the initial stage of the transition, the rate of these jumps is governed by an energy barrier related to the interface energy, per molecule, in the lamellar material. Since γ mainly depends on the interaction parameter χ, that is, on the repulsion between the unlike blocks, $T_{\rm ODT}$ is expected to increase with increasing χ. Thus, it is unnecessary to evoke miscibility at $T_{\rm ODT}$ to predict that a homopolymer pair with a high value of χ will yield corresponding block copolymers with high values of $T_{\rm ODT}$.

Although this interpretation of the order–disorder transition in terms of a dynamical process is entirely speculative, it would account for most of the reported features concerning the rheological properties of symmetric diblock copolymers. It is fully consistent with the fact that the rheological transition vanished above a critical frequency of the shear strain in dynamical measurements. Over the range where the average jump rate is much slower than the deformation rate, that is, for high shear frequencies, the material should behave as a static microcomposite. In this situation, the interface tension in the disordered, segregated material acts against the deformation. On the other hand, for an average jump rate much faster than the deformation rate, that is, for low shear frequencies, there is a complete relaxation of this effect and the material responds as a homogeneous melt. In agreement with the rheological data reported by Bates *et al.*,[12] this latter situation is expected to occur only over a range of temperature well above $T_{\rm rheo}$.

A last point concerns the abrupt rheological transition observed for block copolymers with cylindrical and lamellar morphologies (rheological data reported by Han *et al.*[6] show that this feature does not apply to SIS ordered block copolymers with a spherical morphology). A tentative interpretation of this rheological behavior may be made in terms of a percolation threshold associated with the random disruption of the extended microdomains characteristic of the cylindrical and lamellar morphologies. In the ordered state, these materials consist of randomly oriented grains containing a large number of cylinders or lamellae. Their viscous flow must be hindered by the cooperative reaction of the individual microdomains to the shear stress.[27] This includes orientation and shear deformation of the entire grains. By postulating that the thermal disruption of the microdomains occurs at random locations within the grains, a critical concentration of these locations must exist at which the microdomains no longer react cooperatively. Thus, over the range near this concentration, the low-frequency shear moduli should change abruptly.

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