

Compositional Dependence of the Order-Disorder Transition in Diblock Copolymers

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ABSTRACT: The bulk morphologies and microphase separation behavior were studied in seven low molecular weight poly(styrene-co-isoprene) diblock copolymers with polystyrene volume fractions ranging from 0.21 to 0.76. Their order-disorder transitions (ODT) were investigated using small-angle X-ray scattering and rheological measurements as a function of the degree of polymerization (N), composition, and temperature. The resultant χN versus composition plot has been compared with theories for the ODT in diblock copolymers. Near compositions of 50 vol %, our experiments agree with the fluctuation theories of both Fredrickson-Helfand and Muthukumar. At other compositions the critical χN for the ODT is smaller than that predicted by the available theories. This discrepancy increases as the copolymer composition deviates further from 50 vol %. In addition, transitions from one ordered morphology to another, order-order transitions, exhibit only a slight dependence on the composition.

Introduction

The tendency of diblock copolymers to self-assemble into periodic morphologies depends upon the composition, molecular weight, and monomer-monomer interactions. The transition from the ordered to the disordered state has been described by a variety of theories,¹⁻⁸ two of which will be summarized here. Leibler developed a mean-field theory to describe the order-disorder transition and determine the relevant parameters to be f , the copolymer composition, and χN , the product of the interaction parameter and the degree of polymerization of the copolymer.¹ This approach predicts that, at compositions other than 0.5, a first-order transition occurs from the homogeneous disordered state into the ordered state and follows the sequence of body-centered-cubic, hexagonal, and lamellar mesophases as χN increases. As the composition nears 0.5, the mesophases occur in close succession. At $f = 0.5$, diblock copolymers undergo a second-order transition from the disordered state into the ordered lamellar morphology at $(\chi N)_{\text{ODT}} = 10.495$ in the limit of infinite molecular weight. Fredrickson and Helfand modified Leibler's treatment of the ODT to include the effect of composition fluctuations.² This has the effect of increasing $(\chi N)_{\text{ODT}}$ and predicting a first-order transition at $f = 0.5$. Recently, Muthukumar performed a similar analysis using a density functional approach which addressed the effect of composition fluctuations on the entire block copolymer phase diagram.⁸ In contrast to Leibler's

results, these newer theories involving fluctuations exhibit finite copolymer composition ranges in which each mesophase can be obtained directly from the disordered state by increasing χN . Furthermore, the critical χN values are somewhat higher than Leibler's prediction and depend on the degree of polymerization of the copolymer. Both the Leibler and the fluctuation theories predict transitions between different ordered morphologies with increasing χN .

Because the interaction parameter is temperature dependent, the ODT in diblock copolymers has been investigated as a function of temperature using both scattering techniques and rheological measurements.⁹⁻²¹ Previous studies of the ODT have focused primarily on copolymer compositions near 0.5. Within this paper we present complimentary small-angle X-ray scattering (SAXS), transmission electron microscopy (TEM), and rheological results from seven low molecular weight poly(styrene-co-1,4-isoprene) diblock copolymers. Because our experiments encompass copolymer compositions between 0.21 and 0.76 and χN values between approximately 10 and 28, we are able to develop an experimental diblock copolymer morphology diagram near the ODT.

Experimental Methods

Materials and Sample Preparations. The poly(styrene-co-isoprene) diblock copolymers listed in Table 1 were prepared via anionic polymerization using high-vacuum techniques which have been described previously by Morton and Fetters.²² The polymerizations were carried out at 30 °C in benzene with a sec-

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Table 1. Poly(styrene-*co*-isoprene) Diblock Copolymers

sample designation	PS volume fraction	$M_n (\times 10^{-3})$	N
SI 5/15	0.21	20.5	270
SI 6/8	0.38	14.3	180
SI 7/8	0.41	15.0	190
SI 8/5	0.60	12.8	150
SI 12/6	0.62	17.7	200
SI 21/10	0.64	31.4	350
SI 18/4	0.76	22.2	240

butyllithium initiator. After the minority (first) component was completely reacted, an aliquot was removed for analysis and the monomer for the second block was added. Molecular weight distributions were determined by size-exclusion chromatography (SEC) using a Waters 150C calibrated with polystyrene standards. The polydispersities of the first block and the entire diblock were less than 1.05 for all of the samples. Block copolymer compositions and the microstructure of the polyisoprene blocks were determined with a 400-MHz ^1H NMR spectrometer to an accuracy of 1 mol %. The PI microstructure is approximately 94% 1,4 addition (*cis* and *trans*) and 6% 3,4 addition.

The total molecular weight and degree of polymerization were calculated from the measured molecular weight of the minority component and composition. Volume fractions were calculated by assuming that the densities of the PS blocks and PI blocks of the copolymer are the same as the pure homopolymers. Specific volumes as a function of temperature for homopolystyrene and homopolyisoprene were obtained by a quadratic fit to PVT data provided by Dr. D. Walsh of DuPont²³ and used to calculate the volume fractions from the NMR mole fractions. Over the range of temperatures studied, assuming pure phases the polystyrene volume fractions of the copolymers were found to change by less than 1%. The poly(styrene-*co*-isoprene) diblock copolymers are identified as SI *a/b*, where *a* and *b* refer to the block molecular weights given in kilograms per mole.

The casting protocol for the block copolymers was designed to reproducibly prepare bulk samples near thermodynamic equilibrium. Toluene, an approximately nonpreferential solvent, was used as a casting solvent in order to avoid preferential swelling of either phase during the casting process, which can lead to the trapping of nonequilibrium morphologies. After casting, two different annealing procedures were used: the "quench" method and the "at-temperature" method. For the quench method, cast samples were annealed in a vacuum oven at a fixed temperature for 1 week. Immediately upon removal from the vacuum oven the polymers were quenched into liquid nitrogen to maintain the morphology characteristic of the annealing temperature. Portions of these samples were then examined at room temperature with SAXS and TEM. For the at-temperature method, portions of cast samples were molded either into the sample cell for the SAXS apparatus or into a disk for the rheometer where subsequent experiments were performed at a range of temperatures.

Small-Angle X-ray Scattering. Both quenched and at-temperature samples were studied with small-angle X-ray scattering (SAXS) using Kratky slit collimation, a sealed tube X-ray source with a copper anode, and a nickel filter to reduce the Cu K β component. The scattered intensities were collected by a Braun one-dimensional position-sensitive detector placed ~50 cm from the sample and were corrected for detector wire sensitivity, parasitic scattering, and thermal fluctuation scattering. The angular calibration of the SAXS system was accomplished with a duck tendon sample having a repeat distance of 640 Å and 9 orders of reflection. Data for some samples were also corrected for the slit-smearing effect of the Kratky camera with a modified version of the FFSAXS5 desmearing program by Vonk.^{24,25}

For the at-temperature method, samples were pressed into a sample holder which was held under vacuum during the SAXS experiments. Samples were annealed at selected temperatures for between 2 and 24 h to equilibrate. No measurable change was observed for SAXS patterns collected beginning either 2 or 24 h after a temperature increase. Our data collection times ranged from 3 to 8 h. At the conclusion of each temperature scan, SEC was performed and compared with that of the

unannealed polymer. Discrepancies in the SEC traces indicate molecular weight changes, as was observed in a few cases corresponding to vacuum leaks and excessively long times at elevated temperatures. Data from samples which exhibited molecular weight changes were discarded.

Transmission Electron Microscopy. Quenched samples were directly examined with TEM to identify the morphology. Thin sections (approximately 500 Å) were microtomed from a bulk sample using a diamond knife. The thin sections were cut at -110 °C, floated off the knife edge onto *n*-propanol, and collected onto electron microscope grids. To enhance mass-thickness contrast, the thin sections were exposed to OsO₄ vapors for 4–6 h to selectively stain the isoprene phase. The sections were examined in the bright-field mode using a JEOL 100CX transmission electron microscope at 100 kV.

Rheological Measurements. Dynamic mechanical experiments were used to determine the order-disorder transition by measuring the elastic and loss moduli as a function of temperature and frequency. Samples for the rheometer were shaped into 25 mm disks in a vacuum hot press using various conditions of time, temperature, and pressure depending on the composition of the copolymer. The frequency dependencies of the shear elastic modulus (G') and the shear loss modulus (G'') were measured during isothermal frequency sweeps using the parallel plate geometry of a Rheometrics RDS. Following each set of isothermal frequency sweeps, the temperature was increased manually and held at the new temperature for typically 10 min before performing frequency sweeps. A range of strain amplitudes was used (1–20%) in order to provide suitable torque values to determine the isothermal frequency dependence. No hysteresis effects were observed between data collected upon heating and data collected upon cooling the sample. As with the at-temperature SAXS experiments, heat-treated samples were evaluated using SEC and the molecular weight was found to be unchanged from the initial SEC results. Master curves were constructed from the isothermal frequency sweeps using the principles of time-temperature superposition.

Calculations for Comparison with Theories. Theoretical calculations predict the stable diblock morphologies as a function of χN and copolymer composition. The following calculations were made to account for the simplifying theoretical assumptions in order to compare our experimental data with the theoretical phase diagrams. We assume a composition and molecular weight independent interaction parameter, $\chi(T)$, for the poly(styrene-*co*-isoprene) diblock copolymers, $\chi(T) = 0.0419 + 38.5/T$ (K). Hashimoto et al.²⁶ determined this χ parameter using Leibler's mean-field treatment of the ODT for a SI diblock copolymer with a total molecular weight of 33 000, a PS weight fraction of 0.30, and a polyisoprene microstructure comparable to that of our samples. The degree of polymerization, N , was readily calculated from the molecular weights. While the mole fraction, f_A , is the composition variable in the theories, we employ the volume fraction, ϕ_A , of the A block in our diblock copolymers. The volume fractions, as mentioned above, were assumed to remain constant even as the sample approached the disordered state. In the well-segregated, ordered state the microdomains are essentially pure and the interfaces sharp, so that the volume fraction of the A domains is approximately equal to the volume fraction of the A component. Near the order-disorder transitions, the volume fraction of domains may no longer equal the volume fraction of components as A chains may dissolve into B domains and/or vice versa. This type of mixing is probably more important for low molecular weight samples far from 50/50 composition. This uncertainty is noted but is not incorporated into our experimental phase diagrams.

Determination of the ODT by SAXS

Figure 1 shows the SAXS pattern for SI 5/15 in the ordered state at 90 °C and in the disordered state at 120 °C. As expected for a diblock copolymer with 21 vol % polystyrene, the ordered morphology is cylinders on a hexagonal lattice as evidenced by the ratios of the peak scattering vectors: 1.00, 0.56, 0.50 (1, 1/ $\sqrt{3}$, 1/2). The first peak (d_{10}) corresponds to a spacing of 220 Å, which indicates a lattice parameter or intercylinder distance of

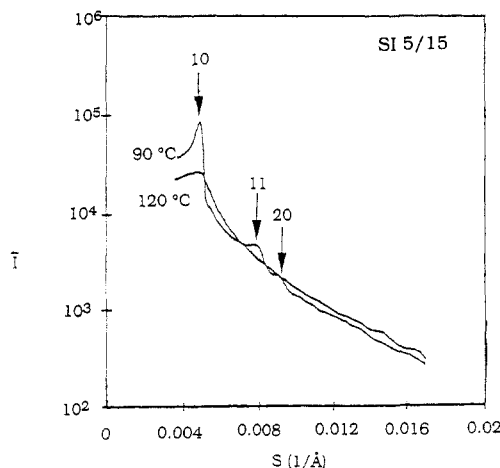


Figure 1. Slit-smear SAXS intensities for SI 5/15 at 90 and 120 °C. The material has an ordered, hexagonal morphology at 90 °C and a disordered, phase-mixed morphology at 120 °C. Numbers above the arrows indicate the indices of the hexagonal lattice corresponding to the observed reflections.

~250 Å. These morphology assignments for SI 5/15 were confirmed by direct observation via TEM of quenched samples from 80 °C (cylinders) and 115 °C (homogeneous). Figure 1 shows that scattering patterns from disordered and ordered block copolymers are sufficiently different to provide a means for measuring the ODT. Below we present two existing methods for determining the ODT from scattering results and introduce a third method of peak shape analysis which we feel is most appropriate for determining the ODT's of our low molecular weight diblock copolymers.

Previous investigators using scattering results have defined the ODT temperature as the temperature at which data when plotted as $1/I_m$ versus $1/T$ first deviates from linearity upon decreasing temperature;^{14,16} I_m is the maximum peak intensity and T is the absolute temperature. This analysis is based on substituting $\chi(T) = A + B/T$ into Leibler's structure factor¹ for the disordered state. A linear decrease of $1/I_m$ with $1/T$ is thus predicted for the disordered state, and deviation from linearity is associated with the onset of macrophase separation. Although some reports^{14,16} have supported Leibler's theory, this approach is problematic for our samples for two reasons: linearity is poorly defined, even at high temperatures, in that the scattering data gradually depart from any imposed linearity at high temperature and Leibler's theory neglects effects due to composition fluctuations which is strictly applicable only to polymers of infinite molecular weight. Fredrickson and Helfand's fluctuation corrections to Leibler's ODT theory for finite molecular weight polymers introduce nonlinear terms in temperature into the expression for the structure factor.² Fluctuation effects have been found to be important for scattering experiments near the ODT by Bates et al.¹⁵ Attempts to use the $1/I_m$ versus $1/T$ analysis method for our low molecular weight SI diblock copolymers produced ambiguous ODT temperatures, because the transition from linear to nonlinear behavior was continuous.

Often the above method is supplemented with a plot of the domain spacing as a function of temperature in which the ODT is defined as the temperature at which the spacing becomes constant. This analysis is also based on Leibler's mean-field theory which predicts a constant correlation length within the disordered state. Researchers have found the correlation length to decrease slightly with increasing temperature and have not observed an abrupt transition in the correlation length as a function of temperature.¹⁷ Similarly, the correlation length analysis for our SI diblock

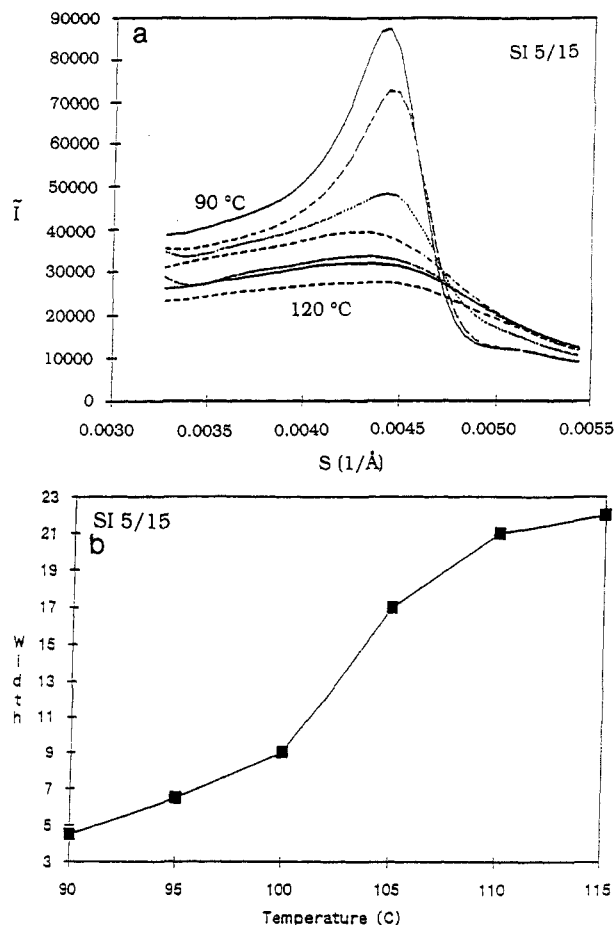


Figure 2. (a) Main SAXS scattering peak of SI 5/15 at various temperatures: 90, 95, 100, 105, 110, 115, and 120 °C from the top of the figure to the bottom. A reduced range of S is shown to expand the area of interest. (b) Peak half-width (in arbitrary units) of the main scattering peak as a function of temperature for SI 5/15. The ODT temperature is taken as the temperature having the largest rate of increase, 100–105 °C.

copolymers produced ambiguous ODT temperatures.

A third method to determine the ODT temperature from scattering data is based on a qualitative observation first made by Roe et al. and involves evaluation of the *shape* of the scattering patterns.²⁷ Roe et al. noted that, as the temperature of a lamellar diblock copolymer increased, the second and higher order peaks disappeared, the intensity of the main peak decreased, and the main peak broadened. We developed a simple analysis method based on the width of the main scattering peak to estimate the ODT temperature. An example of our method using SI 5/15 is given next.

Figure 2a shows the main scattering peak for SI 5/15 at temperatures between 90 and 120 °C. As the temperature increases from 95 to 105 °C, the intensity of the main peak decreases by ~50% and the top portion of the main interference peak broadens significantly. These observations suggest that the sample has changed from an ordered, microdomain material to a disordered, homogeneous material. The ODT temperature was determined by plotting the peak half-width versus temperature. The peak half-width is preferred over the peak full-width due to the asymmetrical shape of the main peak, partially caused by Kratky slit-smearing, and was measured to the right of the peak maximum (that is, toward increased scattering vector). To bias the upper portion of the peak, where most of the shape change occurs, the half-width was measured at 80% of the peak maximum. The peak half-widths, in arbitrary units, are plotted as a function of temperature, and the temperature at which the largest rate of change in the peak half-width is observed is taken

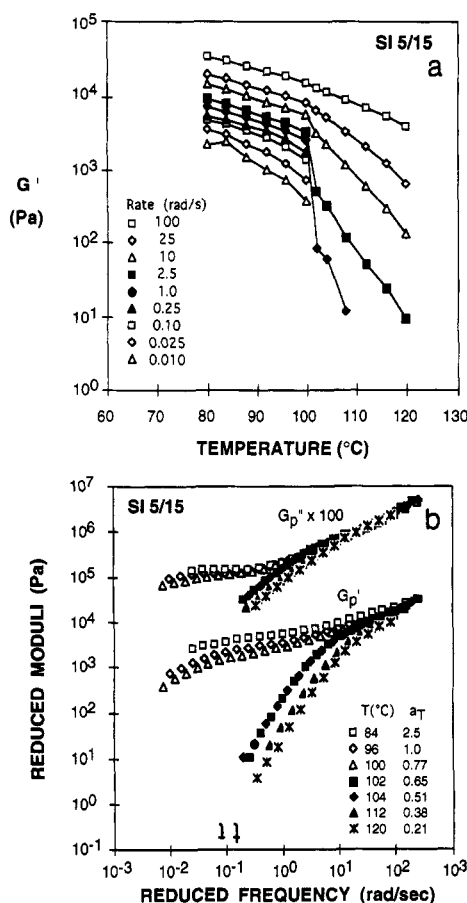


Figure 3. Rheological measurements for SI 5/15 between 80 and 120 °C. (a) Dynamic storage modulus at various frequencies as a function of temperature as measured upon heating. (b) Master curve shows the reduced moduli, G_p' and G_p'' , as a function of frequency; the reference temperature is 96 °C. The discontinuities in both plots indicate the order-disorder transition temperature to lie between 100 and 102 °C.

as the ODT temperature. Figure 2b displays the peak half-widths for SI 5/15 over the temperature range 90–120 °C and indicates an ODT temperature between 100 and 105 °C.

The peak half-width is relatively constant in the ordered state, because the nature of the microphase separation is not changing significantly in this temperature range. However, as the ODT is approached, thermally induced composition fluctuations grow as the respective blocks mix into the opposite phase and the junctions between blocks delocalize from the interface region. The advantage of our peak shape analysis to determine the ODT temperature in block copolymers is that the method is theory independent.

Determination of the ODT by Rheological Measurements

Passing through the order-disorder transition dramatically changes the viscoelastic properties of high molecular weight block copolymers near the ODT.^{9–13,15,16,18–21} These characteristic features were also observed in our case of low molecular weight diblock copolymer as discussed in detail here for one example, SI 5/15.

Figure 3a shows the temperature dependence of the shear storage modulus, G' , for a wide range of frequencies for sample SI 5/15 between 80 and 120 °C. A discontinuity is observed in G' between 100 and 102 °C, which is more pronounced at intermediate frequencies. At lower frequencies, G' could not be measured reliably above 100 °C, because the torque values were too low (<1 g-cm) as compared to the sensitivity of the torque transducer.

Table 2. Summary of Microdomain Structures and Order-Disorder Transition Temperatures

sample designation	morphology (SAXS/TEM)	D (Å) ^a (SAXS)	T_{ODT} (°C)		T_g (°C) PS block
			SAXS	RDS	
SI 5/15	PS cylinders	220	100–105	100–102	
SI 6/8	lamellae	170	70–80	≤70 ^b	72
SI 12/6	ordered ^c	170	100–105	92–96	69
SI 18/4	PI cylinders	180	110–115	≤115 ^b	86

^a Spacing of the first peak in the scattering pattern. ^b ODT is not observed by rheological measurements, but an upper limit for the ODT temperature was established by the presence of the disordered state. ^c Insufficient data to assign a specific microdomain geometry.

Microphase separated domains at temperatures below the ODT temperature behave as physical cross-links to hinder molecular motion, while the disordered state at temperatures above the ODT temperature has significantly enhanced mobility. Consequently, the pronounced decrease of G' at 101 ± 1 °C indicates the order-disorder transition.

Another indication of the ODT is the frequency dependence of the reduced moduli which changes from nonterminal, solidlike behavior in the ordered state ($G_p' \sim \omega^{0.4-0.5}$ and $G_p'' \sim \omega^{0.4-0.5}$) to near-terminal, liquidlike behavior in the disordered state ($G_p' \sim \omega^2$ and $G_p'' \sim \omega^1$). The two frequency dependencies are illustrated as distinct branches in the low-frequency portion of a master curve. The master curve for SI 5/15 shown in Figure 3b exhibits a sharp transition and clearly identifies the ODT temperature between 100 and 102 °C. In the microphase separated state ($T \leq 100$ °C) the frequency dependencies are $G_p' \sim \omega^{0.6}$ and $G_p'' \sim \omega^{0.2}$, and in the disordered state ($T \geq 102$ °C) the frequency dependencies are $G_p' \sim \omega^{1.8}$ and $G_p'' \sim \omega^{1.0}$. The sharpness of this transition also confirms that the SI 5/15 diblock copolymer has a narrow molecular weight distribution, since Almdal et al. recently demonstrated that increased polydispersity smears the transition between solidlike and liquidlike behavior.²⁸ Subsequent rheological results will be presented as master curves.

Results

We now present the order-disorder transition temperatures for each sample separately; see Table 2 for a summary. SAXS, TEM, and rheological results for SI 5/15, with $\phi_{PS} = 0.21$ are consistent in indicating an order-disorder transition from cylinders ordered on a hexagonal lattice to the mixed disordered state at 101 ± 1 °C. For this sample, the dynamic mechanical measurements provide a greater degree of accuracy, because smaller temperature steps were taken.

Sample SI 6/8 ($\phi_{PS} = 0.38$) has a lamellar morphology in the ordered state as determined by TEM. SAXS results at 65 and 70 °C also indicate a lamellar morphology by exhibiting a higher order interference peak occurring at a ratio of 0.5 to the first. A lamellar spacing of 170 Å was determined from the SAXS results. The peak shape analysis, as described above, of the scattering patterns indicates a disordering transition between 70 and 80 °C. Rheological results for SI 6/8 are shown in Figure 4, but the ODT is not evident. Isothermal frequency sweeps were taken between 55 and 100 °C and were compiled onto the master curve with a reference temperature of 70 °C by implementing shift factors between 0.0025 and 410. (In contrast, the shift factors ranged from 0.21 to 4.0 for SI 5/15 in the temperature range of 80–100 °C.) The 5 order of magnitude spread in the shift factors for SI 6/8 is due to the proximity of the glass transition temperature of the PS block, 72 °C, which was determined by

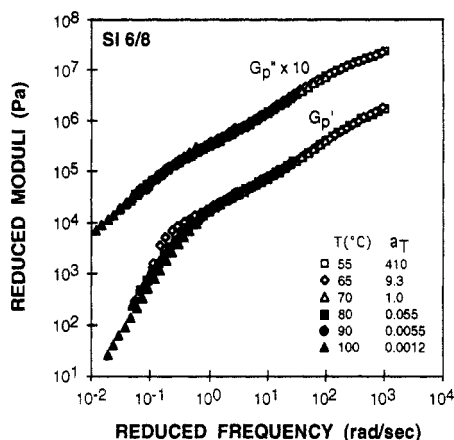


Figure 4. Master curve for SI 6/8 between 55 and 100 °C. The reference temperature is 70 °C. The ODT temperature is not apparent from these data but is apparently lower than 70 °C for which the data exhibit terminal-like behavior.

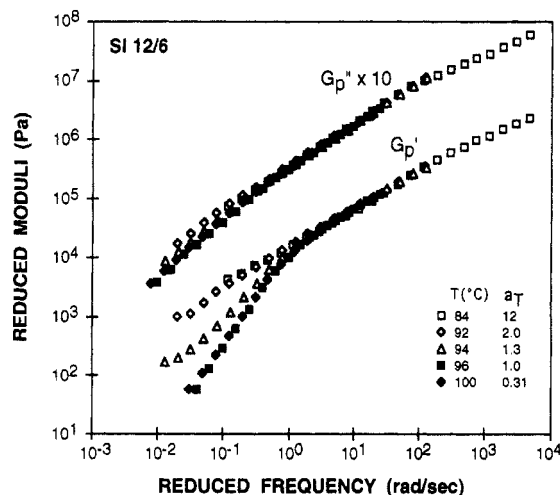


Figure 5. Master curve for SI 12/6 between 84 and 100 °C. The reference temperature is 96 °C. The ODT temperature is between 92 and 96 °C as evidenced by the slope change in G_p' at low frequency. No slope change is observed in G_p'' .

differential scanning calorimetry. Consequently, moduli at low frequency could not be reliably measured for low temperatures, especially at temperatures below the ODT. Low-frequency data for 70 °C clearly exhibit terminal-like behavior ($G_p' \sim \omega^{1.9}$) indicative of the disordered state, while insufficient data are available at lower temperatures to determine the slope. Therefore, we conclude from the dynamic mechanical measurements of SI 6/8 that the ODT temperature is less than ~ 70 °C.

TEM images for a sample of SI 12/6 ($\phi_{PS} = 0.62$) annealed at 80 °C, only 10 °C above the glass transition of the PS block, and quenched show a microphase-separated morphology but lack sufficient order for determination of the type of morphology. SAXS results from SI 12/6 show an ordered state at temperatures ≤ 100 °C, though due to insufficient regularity in the sample there are no higher order peaks to identify the morphology type. The SAXS peak shape analysis identifies the ODT temperature to be between 100 and 105 °C. For SI 12/6 the reduced shear loss modulus, G_p'' , does not display branching at low frequencies, while the shear storage modulus, G_p' , does display branching which identifies the ODT temperature to be between 92 and 96 °C (Figure 5). The absence of the ODT in the G_p'' data is consistent with the branch point or critical reduced frequency being an order of magnitude lower for G_p'' than for G_p' .¹³ As described previously for SI 6/8, lower frequency data could not be obtained for this sample. Unlike the previous two

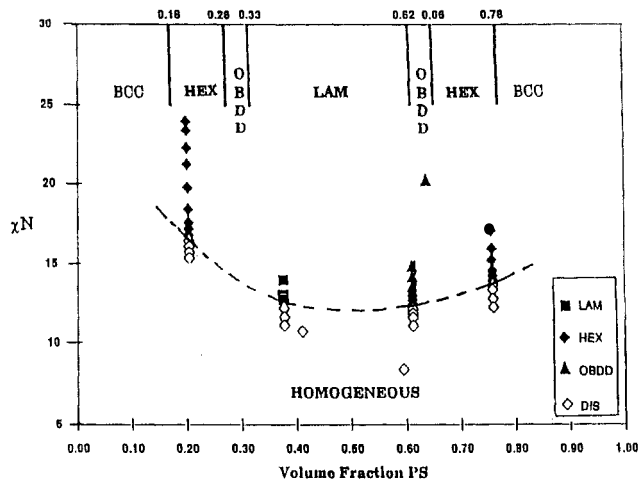


Figure 6. Experimentally determined morphology diagram. Dashed line indicates the order-disorder transition. At high χN values the boundaries between morphologies, as determined elsewhere,²⁹ are approximately independent of composition and indicated here by vertical lines. The ordered morphologies are designated by capital letters: BCC, spherical domains on a body-centered cubic lattice; HEX, cylindrical domains on a hexagonal lattice; OBDD, the ordered bicontinuous double diamond morphology; LAM, lamellae. Results from this study are indicated by the symbols. Open diamonds represent the disordered morphology, while filled symbols (squares, diamonds, triangles) indicate the ordered morphologies (LAM, HEX, OBDD).

samples, measured ODT temperatures from SAXS and rheological measurements disagree by ~ 10 °C for SI 12/6.

Cylinders on a hexagonal lattice are observed via TEM in a sample of SI 18/4 quenched from 80 °C which has a PS volume fraction of 0.76. SAXS experiments confirm this morphology in SI 18/4 by detecting the appropriate higher order peaks at temperatures up to 110 °C. SAXS results indicate that increasing the temperature to 115 °C produces a disordered state. The peak half-width of the main peak undergoes a pronounced increase at the ODT temperature which appears to be between 110 and 115 °C. Dynamic mechanical measurements between 90 and 130 °C are inconclusive for SI 18/4, because low-frequency data were unattainable due to large shift factors and low moduli (that is, low torque levels). From the limited low reduced frequency data available, the disordered state appears to exist at temperatures greater than 115 °C, which is consistent with the SAXS results.

Three additional samples were studied at only one annealing temperature. SI 21/10 exhibited the OBDD morphology as determined by TEM and SAXS ($D = 235$ Å, $a_{OBDD} = 330$ Å) when prepared by the quenching method from an annealing temperature of 115 °C. Both SI 7/8 and SI 8/5 were in the disordered state for the annealing temperature of 115 °C. These single-temperature results will appear as single points, whereas the temperature-dependent results will appear as a series of points at a fixed composition in the subsequent χN versus ϕ_A plots.

Discussion

Figure 6 displays our experimental results in a χN versus copolymer composition plot. At large χN values, Helfand's strong segregation theory predicts morphologies which are independent of temperature, that is, χ . Previous investigations have generally confirmed this experimentally for poly(styrene-*co*-isoprene) and poly(styrene-*co*-butadiene) diblock copolymers of molecular weights considerably higher than those in this study.²⁹ The experimental values for these boundaries in SI diblock copolymers are shown in Figure 6 as dark vertical lines accompanied by numbers indicating the PS volume fraction at the compositional

boundary and labels indicating the ordered morphology. Each vertical set of points corresponds to a single diblock copolymer of a fixed composition over the experimental range of annealing temperatures resulting in an accessible $\Delta\chi N$ range of approximately 10 for the poly(styrene-co-isoprene) system. Unfilled diamonds represent the homogeneous state and filled symbols indicate ordered states, where the shape of the filled symbols indicates the specific ordered morphology type.

The comparison between our experimental findings and theoretical predictions will be presented in three parts: the χN values at the order-disorder transition, the nature of the order-disorder transition, and the composition dependence of the boundaries between ordered morphologies. The order-disorder transition as a function of volume fraction is represented in Figure 6 by a dashed line. The value of $(\chi N)_{\text{ODT}}$ is ~ 12 at a copolymer composition of 0.5 in our experimental system having a degree of polymerization of $N \cong 200$. This value lies within the predictions of Leibler in the limit of infinite molecular weight, $(\chi N)_{\text{ODT}} = 10.495$, and the fluctuation theories of Fredrickson-Helfand and Muthukumar for $N = 200$, $(\chi N)_{\text{ODT}} = 17.5$, where here N is the total number of statistical segments of the block copolymer. Note also that the theories assume the repeat units of the blocks have equivalent volumes, which may not be the case for styrene and isoprene repeat units.

The $(\chi N)_{\text{ODT}}$ varies strongly with composition in both the Leibler and the fluctuation theories. In contrast, our experimental $(\chi N)_{\text{ODT}}$ curve varies significantly more gently as a function of composition. For example, as the copolymer composition increases from 0.5 to 0.75, Leibler's theory predicts an increase in $(\chi N)_{\text{ODT}}$ from 10.5 to ~ 16 , Fredrickson-Helfand's theory predicts an increase from ~ 12.4 to ~ 22 for $N = 10^4$, and Muthukumar's theory predicts an increase from ~ 10.8 to ~ 17.3 . (Note that these comparisons are very approximate due to the low molecular weight of our samples, $N \sim 10^2$.) Our experimental results show an increase in $(\chi N)_{\text{ODT}}$ from ~ 12 at $f = 0.5$ to ~ 13.5 at $f = 0.75$. Decreasing the copolymer composition from 0.5 to 0.25 is equivalent to an increase from 0.5 to 0.75 in the theories, but our experimental $(\chi N)_{\text{ODT}}$ value at $f = 0.25$ is ~ 15 , which gives a measure of the observed asymmetry in the $(\chi N)_{\text{ODT}}$. The experimentally observed dependence of $(\chi N)_{\text{ODT}}$ on the copolymer composition is significantly weaker than the theoretical predictions. Consequently, in regions of the phase diagram in which the theories predict homogeneous behavior, microphase-separated, ordered morphologies are observed.

The nature of the transition between the homogeneous and microphase-separated morphologies indicates the importance of fluctuations. In the absence of fluctuations, Leibler's result predicts a series of order-order transitions at fixed composition near the ODT temperature. In contrast, the Fredrickson-Helfand and the Muthukumar theories which include the effects of fluctuations predict ranges in compositions for direct transitions between the homogeneous state and any of the ordered states, thus consistent with our experimental results. As expected, the phase transitions studied in these low molecular weight ($N \sim 10^2$) diblock copolymers are influenced by fluctuations.

Extension of the theories by Leibler and Fredrickson-Helfand to within the ordered state predicts order-order transitions away from the order-disorder transition which are strongly dependent on the copolymer composition. By way of illustration consider the Fredrickson-Helfand predictions for the lamellar morphology. The composition range of lamellae is 0.38–0.62 at $\chi N = 15$, which enlarges

to 0.27–0.73 upon increasing χN to 30.⁸ These predictions are in contrast to the observed boundaries at large χN between ordered morphologies which are nearly composition independent. We note that the self-consistent mean-field theory by Vavasour and Whitmore⁶ and the recent density functional theory of Lescanec and Muthukumar⁷ predict less compositional dependence on the boundaries between the ordered morphologies. For example, lamellae are predicted to exist in the range $0.36 < f < 0.64$ for $\chi N > 30$ in these theories in reasonable agreement with the experimentally observed strong segregation limits for the PS/PI system. However, in these treatments the nature of the ODT transition is similar to that described by Leibler's theory and is inconsistent with our experimental results. Our experimental results indicate boundaries between ordered morphologies are less dependent of composition than predicted by Leibler or Fredrickson-Helfand theories in this χN regime. As above the density functional theory of Muthukumar^{7,8} is in better agreement with our findings and captures the effect of compositional fluctuations on the ODT as well as the strong segregation limits for the various microphases studied.

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