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Investigation of the Microphase Separation Transition in Low Molecular Weight Diblock Copolymers

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ABSTRACT: The microphase separation transition in three diblock copolymer systems is studied by differential scanning calorimetry and small-angle X-ray scattering analyses. The experimental absolute scattered intensity profiles for a symmetric poly(styrene-*block*-isoprene) in the homogeneous state compare quantitatively to the theoretical predictions of Leibler. The scattering profiles for homogeneous poly(styrene-*block*-1,2-butadiene) and poly(styrene-*block*-butene) copolymers exhibit a mismatch in the critical scattering vector, q^*, compared to the theoretical prediction. These two diblock copolymers are asymmetric as a result of a dissimilarity in the statistical segment lengths of the two components. The theoretical scattering profiles may be brought in agreement with experiment by empirically adjusting the copolymer chain dimensions assumed in the calculation. These comparisons are used to evaluate the interaction parameters and their temperature dependence for the three copolymer systems. In all three systems, the observed conditions for the apparent spinodal are found to be in good agreement with the predictions of Leibler's theory.

Introduction

The broad range of present and potential applications of block copolymers has led to numerous studies of their structure and properties.[1,2] The majority of previous work has focused on characterization of block copolymers in the strong segregation limit where microphase separation into well-ordered microdomain geometries is observed. More recently, there has been considerable interest in the thermodynamics of block copolymers in the weak segregation limit. Under these conditions, the materials undergo a microphase separation transition (MST) at which point the spatially ordered microdomains spontaneously disorder to form a so-called homogeneous phase.

The microphase separation transition has been treated by Leibler[3] in a theory based upon the consideration of concentration fluctuations within the homogeneous state. The theory utilizes the formalism of de Gennes' random phase approximation (RPA).[4] A mean-field approach that considers polymer/polymer interactions is used to calculate an order parameter for the system as the MST is approached by the homogeneous diblock copolymer. The theory predicts a first-order transition similar in many respects to a liquid–solid transition.

The theory of Leibler also provides a calculation of the small-angle X-ray (SAXS) and neutron-scattering (SANS) functions for homogeneous diblock copolymers. A strong dependence of the scattering curve on the Flory interaction parameter, χ, is predicted, and the use of the theory to determine the χ parameter from experimental scattering is proposed. The calculation of scattering curves for homogeneous diblock copolymers has been extended to include the effects of polydispersity[5,6] and composition fluctuations.[7]

Small-angle scattering measurements on block copolymers in the disordered state have been reported in the literature for a variety of systems. Roe et al.[8] report qualitative agreement with Leibler's theory for SAXS data from a styrene–butadiene diblock copolymer. Qualitative agreement between Leibler theory and SAXS data has been found for styrene–isoprene[9] and styrene–butadiene[10] diblock copolymers and has subsequently been used to determine the χ parameter and its temperature dependence. SANS data for a set of 1,2-butadiene–1,4-butadiene diblock copolymers[11] covering a range of compositions and molecular weights were also found in agreement with the predictions of Leibler's theory.

In addition to determining the χ parameter for the 1,2-PB–1,4-PB system, Bates[12] reports a rheological transition in the diblock copolymers corresponding to the MST. A rheological transition corresponding to the MST has been reported by several other investigators.[13-17] At low frequencies, a transition in the dynamic viscosity is observed as the temperature of the system is increased through the MST region. At temperatures below the MST

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Table I
Specimen Characteristics

designation	material	wt fract polystyrene	diene microstructure	osmometry M_n	GPC M_w/M_n	LS M_w
SI-2	poly(styrene-*b*-isoprene)	0.50	93% 1,2; 7% 3,4 addition	11000	1.05	
BS-5	poly(styrene-*b*-1,2-butadiene)	0.49	95% 1,2 addition	18600	1.06	
HBS-5	poly(styrene-*b*-butene)	0.48	95% 1,2 addition[a]	19800	1.08	22400

[a] Hydrogenated form of BS-5.

temperature, complex non-Newtonian behavior is normally observed, but above the MST temperature, the system becomes Newtonian. Kinetic theories have recently been developed that treat this viscoelastic behavior.[18,19]

The present paper describes the results of a synchrotron small-angle X-ray scattering investigation of three chemically different diblock copolymers in the vicinity of the microphase separation transition. The experimental scattering profiles are compared quantitatively to the predictions of Leibler to estimate values for the χ parameters and their temperature dependencies.

Experimental Section

Synthesis. The diblock copolymers examined were prepared by anionic polymerization. A styrene–isoprene diblock copolymer (SI-2) was kindly supplied by J. Prud'homme. The synthesis and characterization have been described elsewhere.[20] A styrene–butadiene diblock copolymer (BS-5) was synthesized in benzene under an inert atmosphere of argon, with *n*-butyllithium as the initiator. A polar modifier, 1,2-dipiperidinoethane, was added to control the microstructure of the butadiene polymerization. Under similar reaction conditions, the percentage of 1,2 addition has been reported as high as 99%.[21,22] The reaction of styrene was allowed to go to completion, after which the butadiene monomer was added. The butadiene was allowed to react overnight before methanol was added to terminate the polymerization. The copolymer was then precipitated from solution and dried for several days in a vacuum oven.

The HBS-5 copolymer was prepared by hydrogenating the polybutadiene sequence of the BS-5 diblock copolymer. A homogeneous-phase hydrogenation reaction was carried out in a Parr bomb reactor. The BS-5 copolymer was dissolved in cyclohexane (2% solution) and introduced into the reactor. The cobalt salt/*n*-butyllithium coordination complex was then added to catalyze the hydrogenation.[23] The solution in the reactor was prssurized to 60 psi with hydrogen, heated to 60 °C, and allowed to react with agitation for 4 h. Following the hydrogenation reation, the HBS-5 copolymer was precipitated from solution and dried in a vacuum oven for several days.

Characterization. The composition and microstructure of the BS-5 and HBS-5 copolymers were determined from analysis of ultraviolet (UV) and H NMR spectra. The molecular weight distributions were evaluated by combining high-pressure size-exclusion chromatography (HPSEC), membrane osmometry, and low-angle light scattering. Details of these experimental procedures are given elsewhere.[24]

The weight fraction of polystyrene in the HBS-5 block copolymer was determined from UV spectra taken on dilute tetrahydrofuran solutions. Four polystyrene homopolymer solutions were measured to establish a calibration curve for the absorption peak at 259 nm (a wavelength selectively absorbed by the phenyl ring of the polystyrene). The HBS-5 was found to contain 48% polystyrene by weight, which is in accord with the styrene to butadiene monomer ratio used in the polymerization.

The H NMR spectra of BS-5 and HBS-5 were obtained with a 250-MHz Bruker instrument using deuterated chloroform as the solvent. From the BS-5 spectrum, the weight fraction of polystyrene was calculated to be 49% and the precentage of 1,2 addition in the polybutadiene block was found to be 95%. From the HBS-5 spectrum, the extent of hydrogenation of the vinyl unsaturations was greater than 99% as evidenced by the disappearance of the peaks between 4 and 6 ppm.

The number average molecular weights, M_n, were determined from membrane osmometry measurements on toluene solutions at 30 °C using a Knauer osmometer. For each copolymer, five concentrations were measured with each measurement being repeated three times. M_n's of 18600 and 19800 were found for the BS-5 and HBS-5, respectively. The measured increase in M_n from BS-5 to HBS-5 is partially a result of the added hydrogens from the hydrogenation reaction.

The molecular weight distributions of the diblocks were measured by HPSEC on a system composed of a Beckman 100A solvent pump and an Altex 157 differential refractive index detector. For the SI-2 and BS-5 diblocks, the measurements were made in toluene using a pair of 60-cm Polymer Laboratory Gel (10-μm mix) columns. Tetrahydrofuran was used as a solvent for the HBS-5 with use of a pair of Du Pont Zorbax Bimodal columns. The HPSEC data showed that the diblock copolymers had narrow molecular weight distributions and were essentially free of homopolymer fractions. The polydispersity factors calculated for SI-2, BS-5, and HBS-5 are 1.05, 1.06, and 1.08, respectively.

The weight-average molecular weight, M_w, of the HBS-5 diblock was measured by static light scattering,[25] using the theory of Bushuk and Benoit[26] as an additional check. The light-scattering measurements were made in cyclohexane and referenced to the scattered intensity of pure benzene. When coupled with refractive index measurements, the light scattering measurements yielded M_w of 22400 for the HBS-5 diblock.[27] Within experimental uncertainty, this value is consistent with the membrane osmometry and HPSEC data. The composition and molecular weight data for the three diblock copolymers are summarized in Table I.

Thermal Analysis. Differential scanning calorimetry (DSC) was used to investigate the glass transition temperatures (T_g's) of the three diblock copolymers. The DSC measurements were made on a Perkin-Elmer DSC-4. The block temperature was maintained near −70 °C with a circulating Freon coolant, and a constant flow of helium was used for heat transfer from the block to the sample pans. The temperature and enthalpy scales were calibrated with the melting of indium. Approximately 30 mg of polymer were loaded into aluminum sample pans for each measurement.

DSC measurements were taken during both the first and second heatings. The first heating was from −50 to 150 °C at a rate of 20 °C/min. The samples were held at 150 °C for 5 min before being cooled back to −50 °C at a rate of 10 °C/min. The second heating was from −50 to 150 °C at 40 °C/min. The faster heating rate was used to enhance the T_g measurement.

Small-Angle X-ray Scattering. The small-angle X-ray scattering (SAXS) experiments were performed at the Stanford Synchrotron Radiation Laboratory. Details of the beam line and data acquisition system are fully described elsewhere.[28] A focused, monochromatic incident beam (λ = 1.429 Å) is obtained by reflection off a Si(111) monochromator–mirror assembly. The detector is a 1024-channel photodiode array cooled to ca. −80 °C. Scintillation counters placed before and after the specimen stage were used to monitor the specimen adsorption and the incident beam intensity. Specimens were mounted in 2 mm × 5 mm diameter aluminum sample cells fitted with Kapton windows. The temperature was controlled with a Mettler FP80/82 thermal microscopy stage. A schematic diagram of the scattering apparatus is shown in Figure 1. SAXS data were taken at temperatures ranging from 20 to 150 °C for SI-2 and BS-5 (up to 200 °C for HBS-5). The SAXS data taken after heating the samples up to a fixed temperature were identical with data taken after the samples were cooled to the same temperature. Since no hysteresis was found, all reported data correspond to data taken after the sample was heated to temperature. Approximately 1 min was allowed for the samples to equilibrate thermally.

The scattering profiles were corrected for specimen adsorption and parasitic and background scattering and were smoothed and desmeared as necessary. The corrected data were normalized

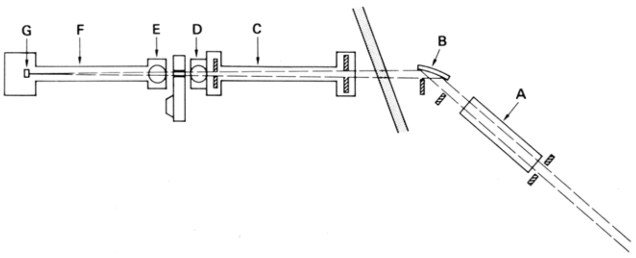

Figure 1. Top view of the small-angle X-ray scattering facility on Beamline I-4 at the Stanford Synchrotron Radiation Laboratory. The components labeled are as follows: (A) 0.5-m Pt-coated mirror; (B) Si monochromator; (C) He-filled beam path; (D) incident beam monitor; (E) transmitted beam monitor; (F) vacuum flight path; (G) photodiode detector. The cross-hatched rectangles shown in the figure are adjustable slits that serve to collimate the incident beam and reduce parasitic scattering. The dashed line is an approximate representation of the beam path. The Mettler hot stage is shown in place in this diagram. The stippled area is the hutch wall where a pneumatically driven lead stopped is raised to allow passage of the beam into the experimental station.

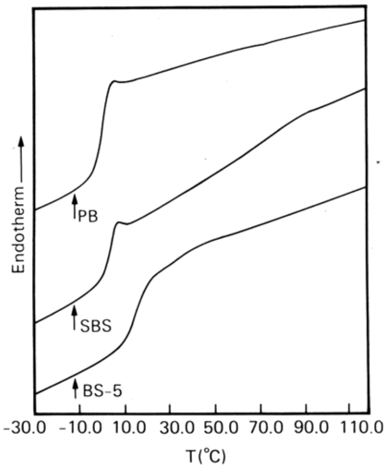

Figure 2. DSC thermograms for the BS-5 block copolymer (BS-5), a polybutadiene homopolymer (PB), and a higher molecular weight poly(styrene-*block*-butadiene-*block*-styrene) triblock copolymer (SBS).

according to incident beam intensity and thickness and were converted to absolute intensity units by using silica sols as a primary standard[29] and a semicrystalline polyethylene specimen as a secondary standard.

Results

DSC Results. Published DSC data from the SI-2 diblock[20] show two distinct glass transition temperatures (T_g). The presence of two T_g's in a diblock copolymer is characteristic of microphase separation, whereas a single T_g would imply a homogeneous system.[31-33] The DSC data from the second heating run of the BS-5 and HBS-5 diblock copolymers are presented in Figures 2 and 3, respectively. Plotted with the BS-5 DSC data for reference are data from a polybutadiene homopolymer with similar microstructure (PB) and data from a triblock copolymer of much higher molecular weight (SBS). Shown with the HBS-5 DSC data are those for HPB and S-HPB-S, which are the hydrogenated forms of PB and SBS.

As seen in Figure 2, the BS-5 diblock copolymer appears to have two T_g's in close proximity to each other. This is in contrast to the well-separated T_g's seen in the SBS data. The onset temperature for the T_g of the PB homopolymer was measured as −3 °C, which is comparable to the literature value of −4 °C.[34] For the SBS, an onset temperature of 1 °C was measured, and for the BS-5, the onset temperature was 10 °C. The T_g's from the polystyrene block of the SBS and BS-5 are not well defined but can be seen to occur over vastly different temperature ranges. From the SBS data, this T_g occurs within the 60–90 °C range, whereas from the BS-5 data, the range is 25–55 °C.

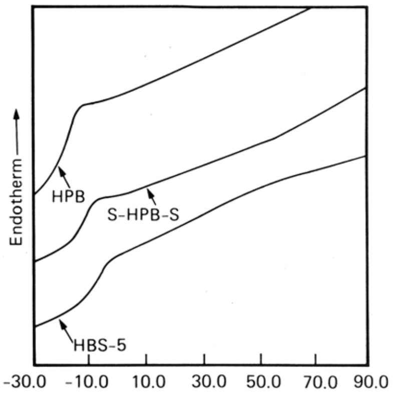

Figure 3. DSC thermograms for the HBS-5 block copolymer (HBS-5), a hydrogenated butadiene homopolymer (HPB) and a poly(styrene-*block*-hydrogenated butadiene-*block*-styrene) triblock copolymer (S-HPB-S).

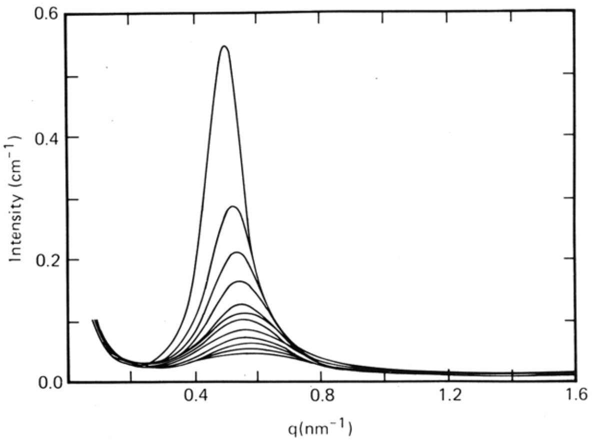

Figure 4. Temperature dependence of absolute SAXS profiles for the SI-2 copolymer. Temperatures from top to bottom are 40, 50, 60, 70, 80, 89, 99, 109, 119, 130, 140, and 150 °C.

Depression of the polystyrene T_g was observed by Morese-Seguela et al.[20] for low molecular weight SI diblock copolymers. They proposed that this behavior was the result of a dynamic coupling between the rubbery and glassy blocks due to the covalent bond joining them. That is, the movement of the rubbery chains was thought to induce motion in the chemically linked polystyrene blocks, thereby lowering the effective polystyrene T_g.

This explanation does not account for the observed T_g behavior of BS-5. This becomes evident upon examination of the DSC results for HBS-5 shown in Figure 3. HBS-5 has an identical chain length as BS-5, but the hydrogenated rubber has a lower T_g than the butadiene precursor. On the basis of the dynamic arguments, one might expect more efficient motional coupling in HBS-5 leading to a larger decrease in the polystyrene T_g. The observed behavior is contrary to this expectation, however.

The onset temperature for the low-temperature T_g for the HPB, S-HPB-S, and HBS-5 polymers are −22, −17, and −15 °C, respectively. The high-temperature T_g's from the S-HPB-S and HBS-5 block copolymers are broad transitions, occurring over the ranges of 55–85 and 30–70 °C, respectively. The polystyrene T_g for HBS-5 is depressed from that of polystyrene homopolymer, perhaps due to the effects of dynamic coupling; however, it is significantly higher than the value for BS-5. In addition, the low-temperature T_g for BS-5 is elevated compared to that of the homopolymer PB. Coupled with the X-ray scattering results that follow, the DSC data for BS-5 provide strong evidence for significant microphase mixing in this material even at room temperature.

SAXS Results. The corrected SAXS data for the SI-2 diblock copolymer is shown in Figure 4. The scattered intensity, $I(q)$, is plotted in absolute units of cm^{-1} as a function of the scattering vector, q, which is given by $(4\pi/\lambda)\sin(\epsilon/2)$, where λ is the wavelength and ϵ is the scattering angle. SAXS data taken at selected temperatures are shown, omitting some scattering profiles for clarity. Similar behavior is observed for the BS-5 and HBS-5 copolymers. Structure factors for HBS-5 were also determined by small-angle neutron scattering (SANS). The normalized SANS data are essentially superposable with the SAXS data, emphasizing the precision of the absolute intensity calibrations and reproducibility of the results.[30]

For each of the three diblock copolymers, the scattered intensity at the peak, $I(q^*)$, decreases with increasing temperature. If a diblock is in the microphase-separated state at room temperature (as suggested by the DSC results from the SI-2 and HBS-5), the magnitude of $I(q^*)$ is inversely related to the degree of microphase mixing. The peak intensity of the BS-5 at room temperature is significantly less than either the SI-2 or HBS-5 peak intensities; an indication that BS-5 is already partially microphase mixed at room temperature. Thus, both the SAXS and DSC results are consistent with a partially microphase-mixed BS-5 and microphase-separated SI-2 and HBS-5 at room temperature.

Analysis

The structure factor, $S(q)$, predicted from theory is related to the absolute small-angle scattering observed experimentally, $I(q)$. For the SAXS data, $S(q)$ and $I(q)$ are related by

$$I(q) = VN_A i_e(\rho_{e1} - \rho_{e2})^2 S(q) \qquad (1)$$

where ρ_{e1} and ρ_{e2} are the electron densities for polymers 1 and 2, respectively. V denotes the average segmental volume, N_A is Avogadro's number, and i_e is the Thomson scattering factor.

The structure factor for a diblock copolymer in the homogeneous region of the phase diagram can be calculated as[3]

$$S(q) = [F(q) - 2\chi]^{-1} \qquad (2)$$

Here χ is the Flory interaction parameter and $F(q)$ is a known function of the chain architecture of the diblock copolymer. The χ parameter is the only temperature-dependent term on the right-hand side of (2) and is assumed to be of the form

$$\chi = \chi_S + \chi_H/T \qquad (3)$$

where χ_S and χ_H refer to entropic and enthalpic contributions to χ, respectively. By combination of (2) and (3), the reciprocal structure factor is seen to be proportional to reciprocal temperature:

$$S(q)^{-1} = F(q) - 2\chi_s - 2\chi_H/T \qquad (4)$$

This predicted proportionality has been demonstrated experimentally and used to identify the transition from microphase-separated to homogeneous states.[8-10]

Plots of reciprocal peak intensity versus reciprocal temperature for SI-2, BS-5, and HBS-5 are presented in Figures 5–7. Each plot shows the predicted linearity at the higher temperatures characteristic of homogeneous diblock copolymers. It should be emphasized that this behavior is fully reversible upon heating and cooling (see, e.g., Figure 7), in contrast to earlier works. Following Roe et al.[8] the MST temperature is taken to be the temperature at which the data first break away from the line drawn through the high-temperature data. The spinodal temperature is found by extending the line to the x axis (corresponding to infinite intensity). The MST temperatures and spinodal temperatures for each of the three diblocks are given in Table II. Transitions in the scattering fluctuation backgrounds and scattering invariants are also observed to occur in the vicinity of the MST temperature.[24]

At temperatures above the MST, the diblock copolymers are in the homogeneous region of the phase diagram so that the measured small-angle scattering structure factors can

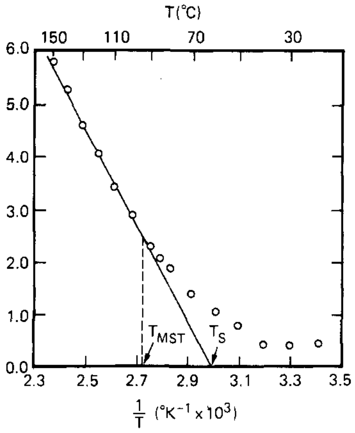

Figure 5. Determination of the apparent MST (T_{MST}) and spinodal (T_S) temperatures for the SI-2 copolymer.

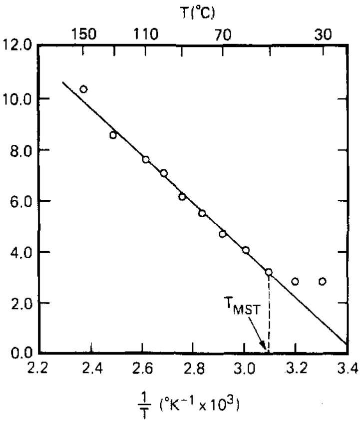

Figure 6. Reciprocal intensity plot for BS-5.

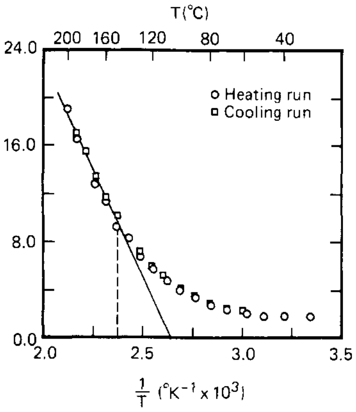

Figure 7. Reciprocal intensity plot for HBS-5 illustrating thermal reversibility and determination of apparent MST and spinodal temperatures.

Table II
Microphase Separation Transition and Spinodal Temperatures

specimen	MST, °C	spinodal, °C
SI-2	93	63
BS-5	50	19
HBS-5	150	104

be compared to theoretical calculations. As can be seen from (1) and (2), a comparison to theory requires both $F(q)$ and χ for a given block copolymer, as well as knowledge of the electron densities of the two constituents. Because the value of χ is not known generally, it is left as an adjustable parameter. It has been shown that the theoretical fits to data are very sensitive to the values of the χ parameter. The small-angle scattering from single-phase diblock copolymers can, therefore, be used to obtain precise experimental values of χ.[11,12] Temperature-dependent electron densities were calculated from data on the temperature dependence of the constituent specific volumes.

The function $F(q)$ can be calculated from the chemical architecture of the diblock copolymer. In terms of single-chain scattering functions of noninteracting chains, the random phase approximation[4] (RPA) yields

$$F(q) = \frac{P_{AA}(q) + 2P_{AB}(q) + P_{BB}(q)}{P_{AA}(q)\,P_{BB}(q) - [P_{AB}(q)]^2} \tag{5}$$

where $P_{ij}(q)$ is the scattering function for pair correlations between i and j type segments where both segments are on the same polymer chain. Since the $P_{ij}(q)$ functions are for noninteracting chains, they can be easily calculated by using Gaussian chain statistics. For an ideal, monodisperse diblock copolymer, the evaluation of (5) is simple and has been demonstrated in the literature. Polydispersity has been shown to be an important effect,[5,6] and, therefore, the molecular weight distribution of the diblock copolymer must be taken into account.

The calculation of $F(q)$ for polydisperse diblock copolymers requires that $P_{ij}(q)$ in (5) represent an average over the entire distribution of diblock chains in the system. The molecular weight distribution of the diblock copolymer must be known to calculate the averages. Following the procedure of Bates and Hartney,[11,35] a few simplifying assumptions are made. First, the molecular weight distribution of each block is assumed to be given by a Shulz–Zimm distribution. Second, the polydispersity factors for each block are assumed to be the same and are calculated to give the measured polydispersity factor for the overall diblock. Finally, the molecular weight distributions of the blocks are taken to be independent of each other. These assumptions allow $F(q)$ to be calculated from measurable parameters. The use of a Schulz–Zimm distribution yields integral equations that are analytically soluble.[5] Details for the calculation of $F(q)$ in the case of diblocks with low polydispersity are available.[24,35] The resultant formulas are rather lengthy and will not be reproduced here.

$F(q)$ for the SI-2 was calculated from the known physical parameters of the diblock copolymer. The physical parameters adopted for this calculation are presented in Table IV. This copolymer is nearly symmetric as judged by the similarity in statistical segment lengths for the two blocks. Comparisons of theoretical scattering profiles to the data were made by adjusting χ to minimize the sum of squared residuals between theoretical and experimental curves over the scattering vector range 0.4–1.6 nm^{-1}. The resulting theoretical profiles are compared with the experimental absolute intensity data in Figure 8. The only adjustable parameter used in generating the theoretical curves was the χ parameter. The temperature dependence of the contrast term was calculated from known expressions for the specific volume. As can be seen, excellent agreement with the experimental profiles was obtained for temperatures exceeding the apparent MST temperature. The values of χ obtained by this procedure are displayed in Figure 9 as a function of reciprocal temperature. These values correspond well to the functional form represented by (3), justifying the use of the I^{-1} versus T^{-1} plot for the determination of the MST and spinodal temperatures.

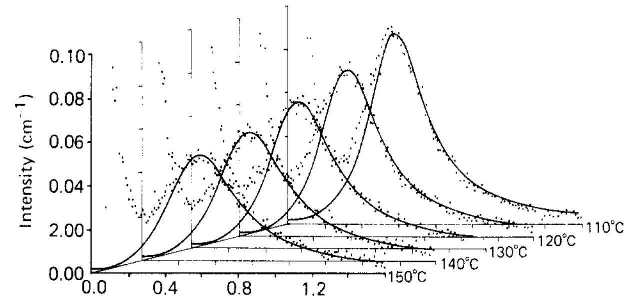

Figure 8. Comparison of theoretical (solid line) and experimental (points) absolute scattered intensity profiles for the SI-2 copolymer in the homogeneous phase.

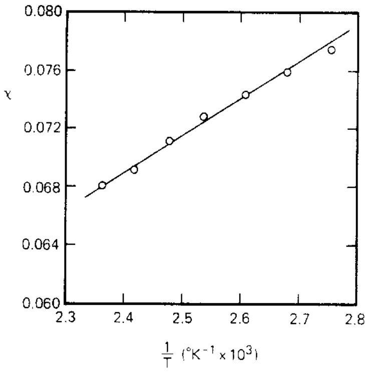

Figure 9. Experimental χ values for the SI-2 copolymer.

$F(q)$ for the BS-5 was calculated from the measured physical parameters (see the Appendix) of the diblock as described above. For this material, however, a significant mismatch is observed between the scattering vectors at which the peak intensity (q^*) occurs. The χ parameter has no effect on q^* so that its adjustment could not bring the theory into agreement with the data. The value of q^* is determined primarily by the radius of gyration (R_g) of the diblock copolymer, which is a function of the molecular weight and the statistical segment length assumed in the calculation. Theoretical profiles could be brought into agreement with experiment by empirical adjustment of the chain dimensions (i.e., M_w) as shown in Figure 10. The best agreement was found for an M_w of 13000. When this value was assumed, theory and experiment were in quantitative accord for data at all temperatures. In contrast to SI-2, BS-5 is decidedly asymmetric in that the two statistical segment lengths differ markedly above 50 °C. Comparisons with the experimental profiles are presented in Figure 11, and the associated χ values are shown in Figure 12 as a function of the inverse temperature. As for the SI-2 data, a linear relationship represented by (3) is obtained.

The calculation of $F(q)$ calculated for HBS-5 (based on the measured physical parameters in the Appendix) also results in a mismatch in q^* when compared to the SAXS data. $F(q)$ for the BS-5 and HBS-5 should be nearly identical (neglecting the minor change in Kuhn segment

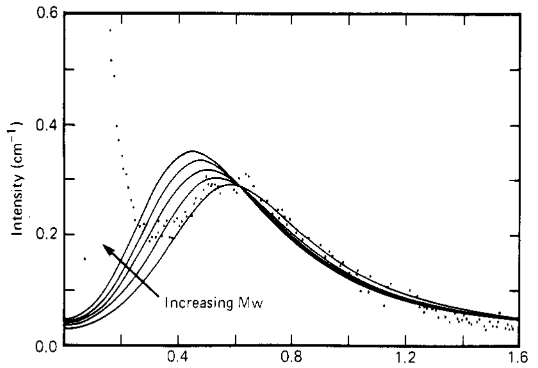

Figure 10. Effect of molecular weight on the comparison between experimental (points) and theoretical (lines) absolute intensity profiles for the BS-5 copolymer. The theoretical molecular weights are 12 000, 14 000, 16 000, 18 000 and 20 000.

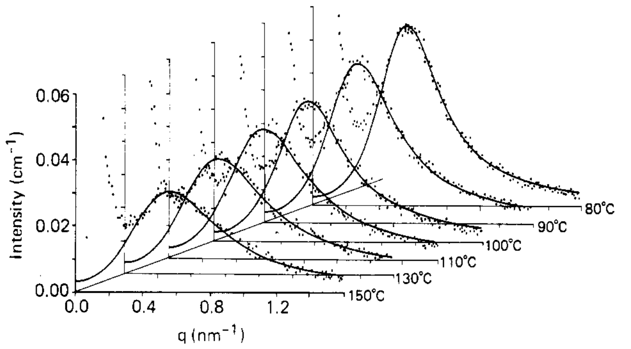

Figure 11. Comparison of experimental (points) and theoretical (lines) absolute intensity profiles for the BS-5 copolymer. Theoretical profiles were generated using the empirically adjusted molecular weight of 13 000.

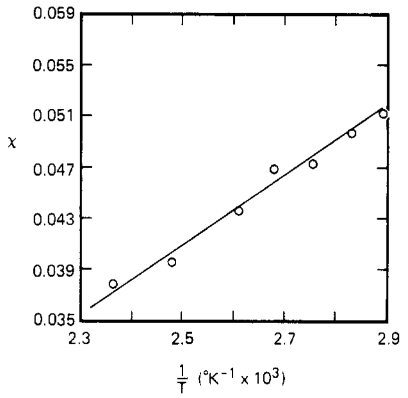

Figure 12. Experimental χ values for the BS-5 copolymer.

length due to the hydrogenation[34]) and, indeed, $F(q)$ found for BS-5 generates theoretical profiles that correspond well with the HBS-5 data. The close agreement with the HBS-5 SAXS data at several temperatures is illustrated in Figure 13. The χ parameters obtained from these comparisons are shown in Figure 14. As can be seen from the figure, a linear relation between χ and T^{-1} is again obtained.

Discussion

On the basis of the observation of two T_g's in the DSC results, the three diblock copolymers are found to be microphase separated at room temperature. The relatively intense peaks in the SAXS data at room temperature provide additional evidence for microphase separation. As temperature is increased, the SAXS peak decreases in intensity, eventually displaying the behavior predicted for homogeneous diblock copolymers. Because the three diblock copolymers are microphase separated at room temperature and are homogeneous at elevated temperatures, the MST phenomena can be investigated by slowly increasing the temperature in these systems.

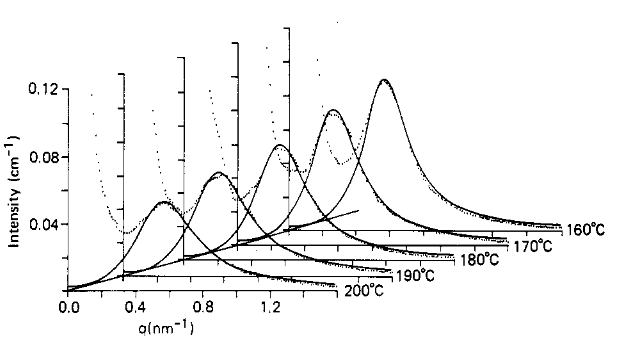

Figure 13. Comparison of experimental (points) and theoretical (lines) absolute intensity profiles for the HBS-5 copolymer. Theoretical profiles were generated by using the empirically adjusted molecular weight.

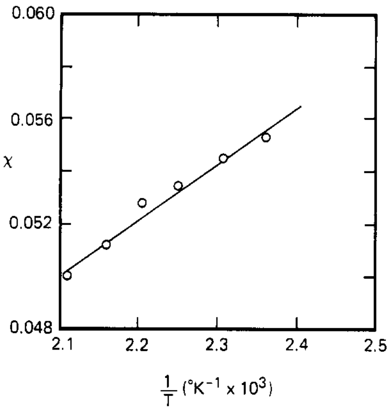

Figure 14. Experimental χ values for the HBS-5 copolymer.

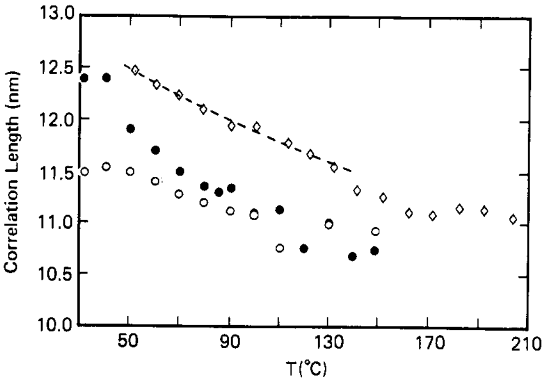

Figure 15. Experimental correlation lengths for the SI-2 (filled circles), the BS-5 (open circles), and the HBS-5 (diamonds) copolymer. The dashed line indicates a best fit to a $T^{-1/3}$ dependence on temperature for the HBS-5 copolymer.

In addition to the decrease in peak intensity observed with increasing temperature, the peak location, q^*, is seen to shift to higher scattering vectors. This trend is followed by plotting the correlation length, L_c ($L_c = 2\pi/q^*$), as a function of temperature. At temperatures below the MST, the correlation length is predicted to scale with $[T^{-1/3}]$[36] or as $[\chi^{1/6}]$.[37] At temperatures above the MST, Leibler's theory predicts that the correlation length is constant, independent of temperature. The predicted transition in the temperature dependence of the correlation length has been used to determine the MST temperature.[36]

In Figure 15, the measured correlation lengths for each of the three diblock copolymers are plotted versus temperature. For the SI-2 copolymer, L_c appears to decrease with increasing temperature over the entire temperature

Table III
Experimental Interaction Parameter Components for Diblock Copolymers

sample	χ_S	χ_H, K^{-1}	χ (298 K)
SI-2	0.0090	25	0.0858
SI[a]	−0.0937	66	0.1278
SI[b]	−0.0419	39	0.0874
BS[c]	−0.027	28	0.0670
BS-5	−0.021	25	0.0629
HBS-5	0.0057	21	0.0726

[a] For 1,2- and 3.4-isoprene.[9] [b] For 1,4-isoprene.[38] [c] For an unspecified butadiene microstructure.[10]

range, even above the MST. Although L_c is not constant at temperatures above the MST as predicted, it does appear to be approaching a limiting value. From the BS-5 correlation length data, a gradual decrease of L_c with increasing temperature is observed. Again, L_c appears to be reaching a limiting value. For HBS-5, L_c decreases steadily over the 50–150 °C range, following closely the predicted $T^{-1/3}$ dependence (valid in the ordered regime) denoted by the dashed line in Figure 15. The correlation length is essentially constant over the 160–200 °C range (i.e., for disordered copolymers) as predicted by theory (MST is 150 °C).

A decrease in the correlation length for diblock copolymers at temperatures above the MST has also been observed in other homogeneous diblock copolymer systems[10,12] and has been explained[12] in terms of non-Gaussian chain statistics. In microphase-separated diblock copolymers, with a lamellar morphology L_c has been found to scale as $N^{2/3}$, whereas in homogeneous diblocks, the Gaussian chain statistics adopted in the theory imply $N^{1/2}$ scaling. Near the MST, a transition from non-Gaussian to Gaussian statistics must occur.

As evidenced by the shift in q^* and the gradual decrease in the intensity of the SAXS peak, the MST is not a sharp transition for our systems. The MST is preceded by phase mixing which decreases the SAXS contrast between phases and results in lower scattered intensities. As an example, DSC and SAXS data for the BS-5 system showed that it is partially phase mixed at room temperature. The low-temperature T_g of BS-5 is shifted 14 °C above the T_g of a pure homopolymer, indicative of phase mixing. Although the high-temperature T_g of BS-5 is shifted to lower temperatures, similar shifts are seen in block copolymers in which microphase separation is nearly complete and have been explained by other mechanisms.[20] In comparison to SI-2 and HBS-5, a relatively weak SAXS peak is observed for BS-5 at room temperature, providing additional evidence for partial mixing as the MST is approached.

As phase mixing continues with increasing temperature, the compositions of the two phases approach each other, thus reducing the SAXS contract between phases. At the MST, the microphases disappear, resulting in a homogeneous system. Although the microphases vanish above the MST temperature, a peak remains in the SAXS data due to the presence of correlated concentration fluctuations. This peak has been predicted for homogeneous block copolymers,[3] and the peak intensity is dependent on the χ parameter. By comparison of theoretical SAXS curves to experimental data, χ parameters were obtained for the block copolymer systems for temperatures above their respective MSTs. The results of linear least-squares regressions on the χ data according to (3) are given in Table III.

For the SI-2 diblock copolymer, the theoretical and experimental SAXS curves could be brought into agreement by using only χ as an adjustable parameter. It should be emphasized that previous studies have fit primarily the scattering functions, whereas in this study, we have found quantitative agreement between theory and experiment for SI-2 in terms of both the structure factor and the absolute intensity (including the temperature dependence of specific volume and electron density).

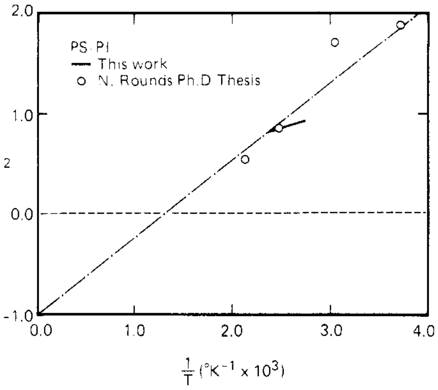

Figure 16. Comparison of experimental interaction energy density, α_{12}, parameters for the SI-2 copolymer (solid line) with corresponding data for a styrene/isoprene blend[38] (circles and dashed-dotted line).

In Figure 16, interaction density parameters ($\alpha_{12} = \chi\rho$) obtained from analysis of the SI-2 data are compared to those obtained by Rounds[39] from analysis of cloud points for the corresponding binary homopolymer mixtures with similar diene microstructure (90% 1,4; 10% 3,4). The overall magnitudes of the respective data are comparable, but the values of the temperature-independent component χ_s in (3) are quite different. This might be expected due to the additional entropic constraints provided by the A–B junction in the block copolymer. Interaction parameters have also been measured for styrene/isoprene (SI) block copolymers with diene microstructures different from that of SI-2. These are shown for comparison in Table III. Adopting a reference temperature of 298 K, these results can be used to illustrate the dependence of styrene/isoprene miscibility on diene microstructure. Specifically, the order of diene miscibility with styrene is found to be (1,2) > (1,4) > (1,2/3,4). The χ values determined for BS-5 agree well with those reported by Hewel and Ruland[10] for a similar copolymer with unspecified diene microstructure. The magnitudes of χ are significantly lower than those obtained for similar homopolymer mixtures containing high 1,4-diene microstructure. From these results it appears that the interactions between styrene and the 1,2-butadiene are stronger than those with 1,4-butadiene, in agreement with what was found for isoprene.

The spinodal for the microphase separation transition of SI-2 is found at a value of $(\chi N)_s = 11.5$, where N is the total number of normalized statistical segments (see the Appendix) in the copolymer. This corresponds well with the value of 11.0 calculated by analysis of the scattering relations including polydispersity effects. A slightly higher theoretical value would result if fluctuations were taken into account.[7] There is some ambiguity in the results for HBS-5 and BS-5 due to the inability of theory to properly predict q^*. When the parameters used in the theory are adjusted so as to obtain a match with the experimental q^*, however, the experimental value of $(\chi N)_s$ is ca. 11.3 for both BS-5 and HBS-5, comparing favorably with the value of 11.1 predicted by the scattering relations for these two copolymers. The adjustment in molecular weight that has been applied is actually an adjustment in the radius of gyration of the block copolymer. In effect, the mismatch in q^* observed for these two copolymers implies that the

Table IV
Physical Parameters Adopted for Scattering Calculations

specimen	ρ_A, mol/m^{3a}	ρ_B, mol/m^3	$N_A{}^a$	N_B	b_B, Å^a	b_B, Å
SI-2	10 100	13 600^b	53	81^b	6.8	6.7^b
BS-5^e	10 100	16 400^b	89	172^c	6.8	5.3^c
HBS-5^f	10 100	15 400^d	96	178^d	6.8	5.0^d

[a] Styrene sequence. [b] Isoprene sequence. [c] 1,2-Butadiene sequence (see ref 40). [d] Butene (hydrogenated 1,2-butadiene) sequence (see ref 40). [e] For empirically adjusted fits values of N_A = 63 and N_B = 121 were used. [f] For empirically adjusted fits values of N_A = 68 and N_B = 126 were used.

treatment of chain statistics inherent to the theory is not fully justified. That is, either the Gaussian chain approximation is not appropriate, or the statistical segment lengths for the copolymer sequences differ from those of the parent homopolymers. An obvious question that arises in examining these results is why deviations from theory are evident for BS-5 and HBS-5 while the experimental data for SI-2 correspond well with the theoretical predictions. The most obvious difference between these materials lies in the apparent symmetry of their molecular properties. The statistical segment lengths for the two sequences in BS-5 and HBS-5 differ considerably, whereas they are nearly identical for SI-2 (see Table IV). Further calculations are necessary to examine the possibility that this asymmetry is responsible for the discrepancy between theory and experiment.

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Appendix

Determination of Physical Parameters. The parameters used in the calculation of theoretical scattering profiles were normalized to constant monomer volume according to the following relations:

average monomer density

$$\rho^* = (\rho_A \rho_B)^{1/2} \tag{A.1}$$

Statistical segment length

$$b^*_i = b_i(\rho_i/\rho^*)^{1/2} \tag{A.2}$$

Polymerization index

$$N^*_i = N_i(b_i/b^*_i)^2 \tag{A.3}$$

The parameters used in these relations are given in Table IV.

Registry No. (S)(I) (block copolymer), 105729-79-1; (B)(S) (block copolymer), 106107-54-4.

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