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Order–Disorder Transitions in Mixtures of Homopolymers with Diblock Copolymers

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ABSTRACT: The microphase separation transition (MST) behavior has been characterized by small-angle X-ray scattering analyses for a series of binary blends of a poly(styrene-*block*-hydrogenated butadiene) diblock copolymer with either polystyrene or poly(hydrogenated butadiene) homopolymers. This copolymer is symmetric in many respects; however, the statistical segment lengths of the two components differ markedly. The solubility behavior is asymmetric with respect to homopolymer type, showing significantly lower solubility limits for blends with the latter homopolymer. Experimentally determined apparent spinodal temperatures and correlation lengths exhibit trends with homopolymer molecular weight and content that correspond qualitatively to theoretical predictions derived for perfectly symmetric copolymers. That is, there is a critical homopolymer molecular weight at which the addition of homopolymer has no effect on either the microphase separation transition temperature or the correlation length. For homopolymer molecular weights below this threshold, the MST temperature is depressed, while for higher homopolymer molecular weights, the MST temperature is elevated and the correlation length increases with homopolymer addition. The experimental critical homopolymer molecular weight is found to be substantially lower than the predicted value of $N/4$, where N is the total copolymer molecular weight. The experimental correlation lengths depend approximately linearly on homopolymer composition and molecular weight, as predicted, but the magnitude of the molecular weight dependence is underestimated, leading to a mismatch in the theoretical and experimental correlation lengths. When the theoretical correlation length is adjusted empirically so as to match the experimental value, the entire scattering profile compares well with the predictions for a perfectly symmetric block copolymer. These results provide estimates of the segmental interaction parameters that agree closely with values obtained previously for the neat block copolymer.

Introduction

Blends of block copolymers and homopolymers are becoming an increasingly important class of specialty engineering materials. Small quantities of copolymer containing a rubbery sequence, for example, can be effective in toughening otherwise brittle plastics.[1-4] Small amounts of homopolymers added to a block copolymer matrix, on the other hand, are useful in tailoring properties and sometimes produce synergistic effects on the mechanical properties.[2-7] Finally, block copolymers can serve as efficient interfacial agents when added to binary homopolymer blends[8-10] and be used to control the size and stability of dispersed phase particles.

Experimental[11-14] and theoretical[15-18] investigations of the properties and phase behavior of block copolymer/homopolymer blends have shown them to be rich in complexity. As an example of this complexity, in Figure 1, we represent schematically a phase diagram expected for a blend of a diblock copolymer and a homopolymer based upon the experimental observations of Roe and Zin[19] for a mixture of polystyrene with poly(styrene-*block*-butadiene). The M_1 phase represents a microphase-separated state and L_1 represents a disordered or homogeneous state. As the weight fraction of PS in the blend increases, a solubility limit is reached at which point macrophase separation of the homopolymer into an L_2 phase occurs. Their experimental phase diagram is qualitatively similar to those that have been proposed from theoretical considerations.[17,18]

Whitmore and Noolandi[17] predict that the phase diagram for a given molecular weight copolymer depends strongly on the molecular weight of the added homopolymer. In particular, the slope of the line separating M_1 from L_1 is expected to be a function of the homopolymer to copolymer molecular weight ratio. For low values of this ratio, the slope is calculated to be negative, indicating that the microphase separation transition (MST) temperature decreases with the addition of homopolymer. For large ratio values, the slope is predicted to be positive (as shown in Figure 1), signifying an increase in the MST temperature upon homopolymer addition. The molecular weight M of the homopolymer also affects the solubility of the homopolymer in the block copolymer microdomains. As the homopolymer M approaches that of the similar block of the copolymer, the homopolymer solubility is predicted to fall rapidly. Experimental results for triblock copolymer/homopolymer blends support this qualitative trend.[7] In a previous article,[20] we reported results of an investigation of the microphase separation transition of several diblock copolymers. In the present article we present a study of the effect of homopolymer addition on the MST behavior of one of these copolymers and compare these results to predictions derived from theoretical considerations.

Experimental Section

The poly(hydrogenated butadiene-*block*-styrene) diblock copolymer (HBS-5) was prepared by homogeneous solution catalyzed hydrogenation of poly(butadiene-*block*-styrene) copolymer. Procedures for the synthesis and characterization of the copolymer are reported elsewhere.[7,20] The microstructure of the diene block was determined to be 5% of the 1,4 and 95% of the 1,2 addition

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Table I
Material Characteristics

sample	sample type	M_n	M_w/M_n	wt fract polystyrene	hydrogenated butadiene microstructure	degree of saturation %
HBS-5	poly(styrene-*b*-hydrogenated butadiene) diblock copolymer	19800	1.08	0.48	5% 1,4 95% 1,2	~100
PS 1000	polystyrene homopolymer	1200	1.08	1.00		
PS 2000	polystyrene homopolymer	2200	1.06	1.00		
PS 3000	polystyrene homopolymer	3100	1.05	1.00		
PS 4000	polystyrene homopolymer	3550	1.05	1.00		
PS 8000	polystyrene homopolymer	7600	1.04	1.00		
HPB 3000	hydrogenated polybutadiene homopolymer	2900[a]	1.04[a]	0.00	9% 1,4[a] 91% 1,2	~100
HBB 8000	hydrogenated polybutadiene homopolymer	8090[a]	1.02[a]	0.00	5% 1,4[a] 95% 1,2	~100

[a] Based upon polybutadiene precursor, assuming complete saturation.

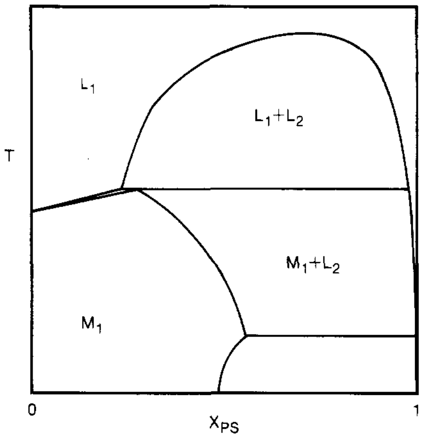

Figure 1. Schematic phase diagram for poly(styrene-*block*-butadiene) blended with polystyrene homopolymer as a function of the weight fraction of polystyrene, X_{PS}, following Roe and Zin.[19] M represents a microphase separated state, L_1 a disordered or homogeneous state, and L_2 a macrophase-separated homopolymer phase.

products. The hydrogenated copolymer contains 48 wt % of styrene, has an overall number-average molecular weight of 19800, a heterogeneity index of 1.08, and a degree of hydrogenation greater than 99%. This block copolymer is asymmetric as a result of the large difference in the statistical segment lengths (0.68 nm for polystyrene and 0.5 nm for the hydrogenated polybutadiene[7]).

Blends of the HBS-5 diblock copolymer with homopolymer were prepared as a function of both concentration and molecular weight of added homopolymer. The polystyrene (PS) homopolymers used in the blend studies were commercially available standards of low polydispersity. The hydrogenated butadiene (HPB) homopolymers were prepared by hydrogenating polybutadiene precursors (ca. 95% 1,2 microstructure) which were synthesized in house. The synthesis and characterization procedures have been previously discussed.[7,20,21] The heterogeneity indexes of the homopolymers were all less than 1.05.

The blend components were mixed in benzene followed by freeze drying. Specimen placques for small-angle X-ray scattering (SAXS) experiments were prepared by compression molding under vacuum at 110 °C. The molded disks were 0.5 in. in diameter with a nominal thickness of 1 mm. Blend compositions were verified by gel permeation chromatography analysis of elution peak areas. Characteristics of the materials employed in this study are listed in Table I.

SAXS experiments were carried out on Beamline I-4 at the Stanford Synchrotron Radiation Laboratory. Samples (~30 mg) were mounted in aluminum cells fitted with Kapton windows. The specimen temperatures were controlled by a Mettler FP80/FP82 hot stage. Experimental scattering profiles were corrected for the effects of specimen adsorption and thickness, detector dark current, parasitic scattering, and detector smearing (when necessary). Absolute intensities were calculated by comparison with previously calibrated standards. These general procedures and details pertaining to the scattering line are discussed elsewhere.[20-22]

Results and Analysis

SAXS Theory. The small-angle scattering for pure diblock copolymers above the MST temperature (i.e., in the homogeneous state) has been derived by Leibler.[23] General scattering theories for homogeneous mixtures of homopolymers and block copolymers have also been developed.[24-27] The general applicability of these scattering relationships was demonstrated recently by Bates.[28]

The SAXS from a blend of a block copolymer with one of its parent homopolymers may be written

$$I(q) = N_A V i_e (\rho_A - \rho_B)^2 S(q) \tag{1}$$

where V is the average segment volume, i_e is the Thompson scattering factor, ρ_i is the electron density of species i, N_A is Avogadro's number, and q is the magnitude of the scattering vector. In the homogeneous state, the scattering function is of the general form

$$S(q) = [F(q) - 2\chi_{AB}]^{-1} \tag{2}$$

where χ_{AB} is the segmental interaction parameter and $F(q)$ is the structure factor for a pure diblock copolymer in the homogeneous phase. It is given by

$$F(q) = \frac{P_{AA}(q) + 2P_{AB}(q) + P_{BB}(q)}{P_{AA}(q)\,P_{BB}(q) - [P_{AB}(q)]^2} \tag{3}$$

where $P_{ij}(q)$ are intramolecular single-chain scattering functions.[20,21] For the case of a homopolymer (A)/diblock copolymer (AB) blend, these three functions in (3) are modified as

$$P_{AA}(q)_{\text{blend}} = \phi_A P_{AA}(q)_{\text{homopolymer}} + (1 - \phi_A) P_{AA}(q)_{\text{diblock}} \tag{4a}$$

$$P_{BB}(q)_{\text{blend}} = (1 - \phi_A) P_{BB}(q)_{\text{diblock}} \tag{4b}$$

$$P_{AB}(q)_{\text{blend}} = (1 - \phi_A) P_{AB}(q)_{\text{diblock}} \tag{4c}$$

where ϕ_A is the volume fraction of added homopolymer (A). In application of relations (1)–(4) to model experimental data, corrections for polydispersity were applied assuming a Schulz–Zimm distribution.[21,29,30]

These scattering equations also provide a framework for the prediction of the theoretical MST temperatures (i.e., the spinodals) as a function of blend composition and constituent molecular weights. Since the molecular weights, compositions, and polydispersities of the specimens are known, there will be a critical scattering vector q^*, defined by a maximum in $F(q)$, and a value of χ_{AB}, at the spinodal temperature, where eq 2 becomes infinite. Although theoretical predictions for blend spinodals could also be obtained by applications of thermodynamic theories,[15-18] there are certain advantages to the approach

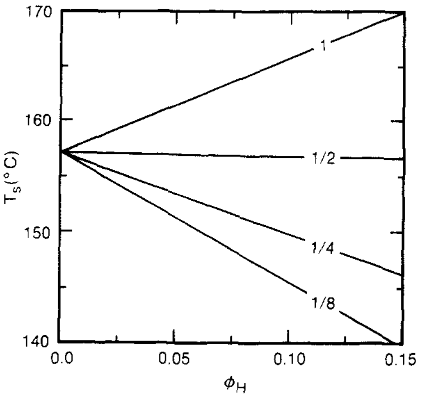

Figure 2. Theoretical spinodal temperatures for fully symmetric diblock copolymer/homopolymer blends as a function of the volume fraction of added homopolymer, ϕ_H. The numbers on each line correspond to ratios of the added homopolymer molecular weight to that of the corresponding block in the copolymer. Consequently, the homopolymer molecular weight decreases as one proceeds clockwise through the diagrams.

adopted here, namely, the consistency with our analysis of scattering functions and the straightforward nature of the calculations, including the effects of polydispersity.

The theoretical spinodal temperatures versus volume fraction of added homopolymer obtained from (2)–(4) are presented in Figure 2 for a hypothetical diblock copolymer blended with homopolymer of varying molecular weights. The homopolymer molecular weights are presented as fractions of the corresponding block molecular weight. The spinodal temperature is seen to decrease with the addition of the low molecular weight homopolymers. At a homopolymer weight of one-half the block molecular weight, the spinodal temperature is unchanged upon addition of homopolymer. This critical molecular weight ratio is identical with the value calculated by Whitmore and Noolandi[17] for perfectly symmetric copolymers using their statistical thermodynamic theory. Higher molecular weight homopolymers cause the spinodal temperatures to increase. Thus, the spinodal temperature for diblock/homopolymer blends is predicted to decrease for low molecular weight homopolymers and increase for high molecular weight homopolymers.

From the critical scattering vector, a correlation length, L_c can be calculated as follows:

$$L_c = 2\pi/q^* \qquad (5)$$

The L_c values predicted for diblock/homopolymer blends from eq 2–4 are presented in Figure 3. L_c is predicted to increase with added homopolymer at a rate that is determined by the molecular weight of the homopolymer. The larger the molecular weight of the added homopolymer, the faster the rate of increase of L_c.

The theoretical development employed to make these predictions applies to perfectly symmetric copolymers. That is the degrees of polymerization, Kuhn statistical segment lengths, and molecular weights must be equal for the two blocks. In addition, the interaction parameter between the two blocks must be equal to that between the homopolymer and its unlike block, and the interaction parameter between the homopolymer and its like block must be zero. These limitations must be kept in mind for any quantitative comparison between theory and experiment that may follow.

SAXS Results from Diblock Copolymer/Homopolymer Blends

Blends of the HBS-5 diblock with PS and with HPB were investigated with SAXS to probe the effect of the added homopolymer on the MST. Compositions of 5, 10, and 15 wt % homopolymer were prepared for a set of different molecular weight homopolymers.

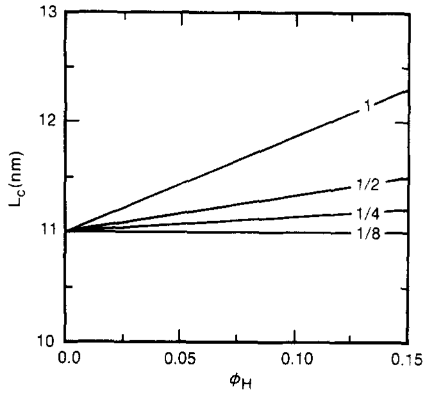

Figure 3. Theoretical correlation lengths, L_c, as a function of the volume fraction of added homopolymer, ϕ_H, for diblock copolymer/homopolymer mixtures. The numbers on each line correspond to ratios of the molecular weights of the homopolymer to that of the corresponding block in the copolymer. The homopolymer molecular weight decreases as one proceeds in a clockwise manner through the diagram.

The majority of PS/HBS-5 blends are optically clear at room temperature. However, a few of the blends appear cloudy for the higher molecular weight PS homopolymers. The opacities of the HPB/HBS-5 blend are greater than that of pure HBS-5 and increase with increase in HPB concentration. Optical clarity is an indication that the homopolymer is completely dissolved within the block copolymer microdomains, whereas opacity suggests the presence of homopolymer-rich macrophases, i.e., region $M_1 + L_2$ in Figure 1. Roe and Zin,[19] for example, have used cloud point measurements to determine the $M_1 + L_2$ coexistence curve of diblock/homopolymer blends.

The opacity observed in the blends containing the higher molecular weight PS homopolymer is understandable because the solubility of a homopolymer in a diblock copolymer is theoretically predicted to decrease with increasing molecular weight and volume fraction of the homopolymer.[17] Such solubility behavior was observed in blends of PS homopolymer with PS–PB diblock.[19] The cloudiness observed in the HPB/HBS-5 blends is puzzling, however, since the solubility of HPB is not expected to be different from the solubility of the PS homopolymer due to the structural symmetry of HBS-5 (i.e., equal block lengths). The asymmetric solubility behavior may reflect the dissimilarity of statistical segment lengths or may be due to slight differences in microstructure between the hydrogenated diene homopolymer and its like copolymer block which would lead to a finite interaction parameter and decrease their mutual compatibility. The presence of macrophases does not affect our ability to monitor the MST and determine the correlation length, but it does rule out the possibility of quantitatively modeling the intensity function given by (1)–(4) since we have not determined the volume fraction of homopolymer dissolved within the homogeneous phase.

Correlation Lengths. The correlation length corresponding to the maximum in the SAXS profile for homogeneous diblock copolymer/homopolymer blends is predicted to be a function of the molecular weight and volume fraction of the added homopolymer but independent of temperature. Experimental correlation lengths for the 5% PS blends are presented in Figure 4. The effect of the molecular weight of the added homopolymer at constant composition is seen to be significant, particularly at the higher molecular weights. The data for the PS

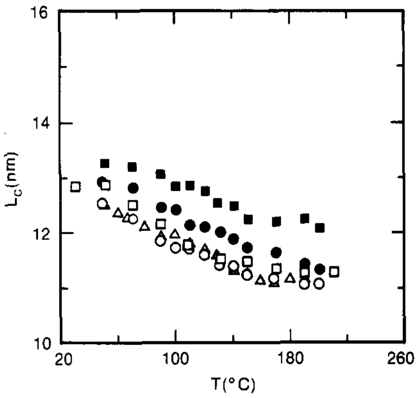

Figure 4. Temperature dependence of correlation lengths for HBS-5 blends containing 5% bwt PS: neat HBS-5 (triangles); PS 1000 (open circles); PS 2000 (open squares); PS 4000 (filled circles); PS 8000 (filled squares).

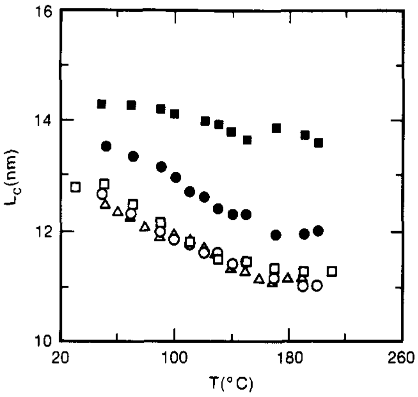

Figure 5. Temperature dependence of correlation lengths for HBS-5 blends containing 10% bwt PS: neat HBS-5 (triangles); PS 1000 (open circles); PS 2000 (open squares); PS 4000 (filled circles); PS 8000 (filled squares).

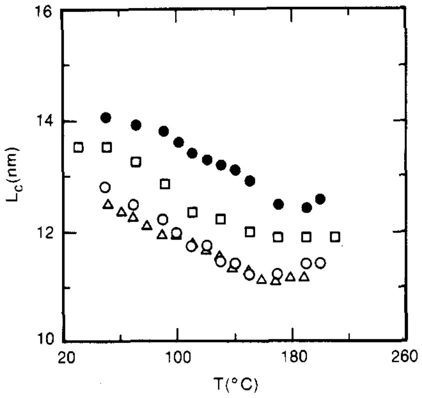

Figure 6. Temperature dependence of correlation lengths for HBS-5 blends containing 15% bwt PS: neat HBS-5 (triangles); PS 1000 (open circles); PS 2000 (open squares); PS 4000 (filled circles).

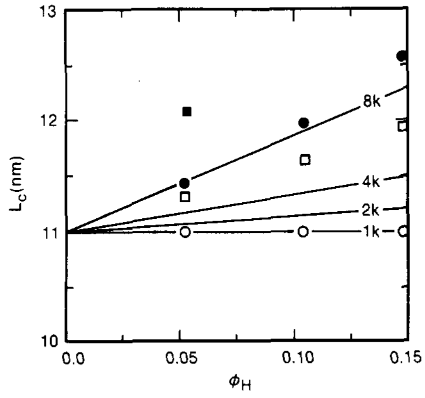

Figure 7. Comparison of theoretical (lines) and experimental correlation lengths for HBS-5/PS blends: PS 1000 (open circles); PS 2000 (open squares); PS 4000 (filled circles); PS 8000 (filled square).

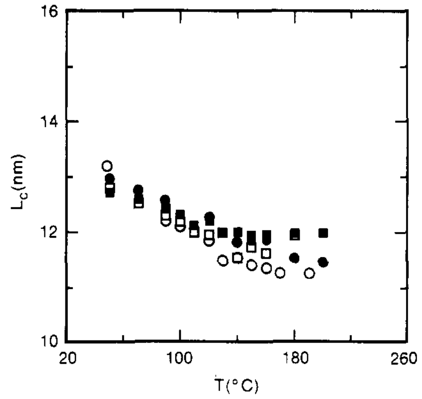

Figure 8. Temperature dependence of correlation lengths for HBS-5/HPB blends: 5% HPB 3000 (open circles); 10% HPB 3000 (filled circles); 5% HPB 8000 (open squares); 10% HPB 8000 (filled squares).

1000 blend is identical with that of the pure HBS-5 over the entire temperature range, reaching a constant value characteristic of the homogeneous state at temperatures above 140 °C. Correlation lengths for the PS 2000 blend are larger than those of pure HBS-5 and appear to level off at high temperatures. The PS 4000 and PS 8000 blends show an increase in L_c with increasing molecular weight. Thus, the experimental correlation lengths from the PS 2000, PS 4000, and PS 8000 blends increase with increasing molecular weight.

The 10% PS blends display a similar trend as seen in Figure 5. Again, the PS 1000 blend values are coincident with the pure HBS-5 values over the entire temperature range. Correlation lengths for the PS 2000, PS 4000, and PS 8000 blends increase with increasing molecular weight of the added homopolymer. The increases in L_c are almost twice as large for the 10% series as for the 5% series.

Correlation length data for the 15% PS blends are presented in Figure 6. The PS 8000 data are not included because the sample exhibits macroscopic phase separation. The PS 1000 data indicate that the correlation length is unchanged from that of the HBS-5 diblock copolymer. The correlation lengths for the other blends increase with increasing molecular weight of the homopolymer additive.

In a previous article,[20] the theoretical correlation length for pure HBS-5 assuming perfect symmetry was found to exceed that determined experimentally. Theoretical correlation lengths for the PS/HBS-5 blends were calculated from (2)–(5) by using the empirically adjusted block copolymer molecular weight, which provided a match between the theoretical and experimental value of L_c for HBS-5 in the preceding paper. These theoretical values and the corresponding experimental values are given in Figure 7. The experimental values plotted are the high-temperature limiting values taken from Figures 4–6.

The experimental data qualitatively reflect the trends predicted by theory. That is, there is a critical homopolymer molecular weight for which the correlation length is independent of homopolymer content, the increase in correlation lengths for larger homopolymers is essentially linear in homopolymer content, and the correlation length increases with molecular weight for fixed homopolymer fraction. Quantitatively, however, the theory for symmetric copolymers underestimates the magnitude of the molecular weight dependence of the correlation length for all blends

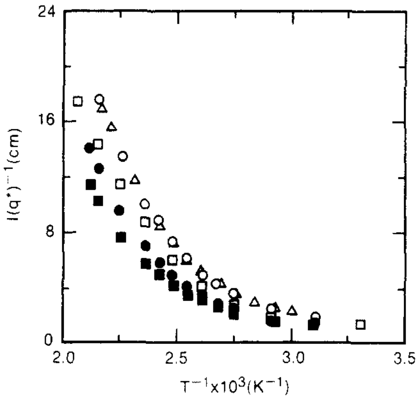

Figure 9. Dependence of inverse peak intensity on inverse temperature for blends of HBS-5 containing 5% bwt PS: neat HBS-5 (triangles); PS 1000 (open circles); PS 2000 (open squares); PS 4000 (filled circles); PS 8000 (filled squares).

other than those containing the M_w 1000 homopolymer.

The temperature dependence of the correlation length for the HPB/HBS-5 blends is presented in Figure 8. The low-temperature data for 5% and 10% HPB 3000 and HPB 8000 blends do not display the strong molecular weight or composition dependence shown by the PS blends. The L_c values are nearly the same for the four HPB blends, supporting the premise that the HPB blends contain macrophases of pure homopolymer. If, at a certain temperature, for example, the solubility of HPB 3000 in the HBS-5 microdomains were 4%, then the 5% and the 10% HPB blends would have identical saturated microdomain structures containing identical amounts of dissolved HPB but differing amounts of HPB in the macrophases. This would account for the similarity in SAXS data and the observed increase in opacity at higher homopolymer concentrations. As the temperature of the blend is increased, the homopolymer solubility in the diblock microdomains is expected to increase, which provides an explanation for the high-temperature data observed in the HPB blends. At high temperatures, the L_c values are found to separate from one another with the 10% HPB 8000 blend having the highest values and the 5% HPB 3000 blend having the lowest values. This trend is consistent with the results found for the PS/HBS-5 blends. Thus, the correlation length data for the HPB/HBS-5 blends support the existence of a room-temperature morphology comprised of HPB-rich macrophases in a matrix of HPB-saturated block copolymer microdomains (i.e., region $M_1 + L_2$ in Figure 1).

Spinodal Temperatures. The spinodal temperatures of the diblock/homopolymer blends are determined from plots of reciprocal peak intensity versus reciprocal temperature as was done for the pure diblock systems.[20] For many of the blend systems investigated, the high-temperature linear region in these plots is ill-defined, making precise evaluation of the spinodal temperature difficult since it is determined by the extrapolation of this linear region to the abscissa. Consequently, the entire plots are shown rather than an extrapolated spinodal temperature so as to emphasize the overall trends. Plots for HBS-5 blended with 5% PS of various molecular weights are shown in Figure 9. The presentation of data at constant composition illustrates the effect of homopolymer molecular weight on the spinodal temperatures of the blends.

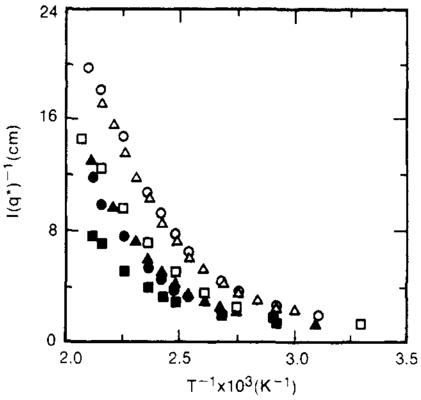

Figure 10. Dependence of inverse peak intensity on inverse temperature for blends of HBS-5 containing 10% bwt PS: neat HBS-5 (open triangles); PS 1000 (open circles); PS 2000 (open squares); PS 3000 (filled triangles); PS 4000 (filled circles); PS 8000 (filled squares).

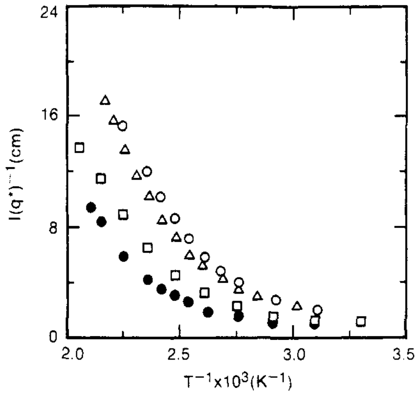

Figure 11. Dependence of inverse peak intensity on inverse temperature for blends of HBS-5 containing 15% bwt PS: neat HBS-5 (triangles); PS 1000 (open circles); PS 2000 (open squares); PS 4000 (filled circles).

The data from the PS 1000 blend can be superposed on the pure HBS-5 diblock data to within experimental errors, indicating that the spinodal temperature is identical with that of the pure diblock. The data for the PS 4000 and PS 8000 blends, on the other hand, are shifted to lower values of T^{-1}, demonstrating that the respective spinodal temperatures are elevated compared to that of HBS-5. The slopes of the linear portions of these plots (i.e., above the MST) are all similar, implying that χ_{AB} has the same temperature dependence in the blends as in the neat HBS-5 copolymer.

The 10% PS blend data are presented in Figure 10. The data for the PS 1000 blend now fall slightly above (lower intensity) the corresponding HBS-5 points at the higher temperatures, indicating a spinodal temperature lower than that of pure HBS-5. The PS 2000, PS 3000, PS 4000, and PS 8000 blends all have spinodal temperatures greater than that of HBS-5, and these temperatures increase with increasing PS molecular weight. The estimates of spinodals from these blends are made assuming that a limiting slope equal to that of the pure HBS-5 is approached. Qualitatively, the molecular weight trends observed in the spinodal temperatures are correct; however, the lack of a true linear regime limits the precision to which the spinodal temperature could be determined.

Data from the 15% PS blend series are shown in Figure 11. The decrease in the spinodal temperature of the PS 1000 15% blend is even more pronounced than that observed for the 10% blend. The data from the PS 2000 and PS 4000 blends are indicative of spinodal temperatures greater than that of pure HBS-5 and are consistent with the molecular weight trend observed for the other blend compositions.

Theoretically, there is a critical homopolymer molecular weight for which the MST is independent of homopolymer content. This critical molecular weight is predicted by

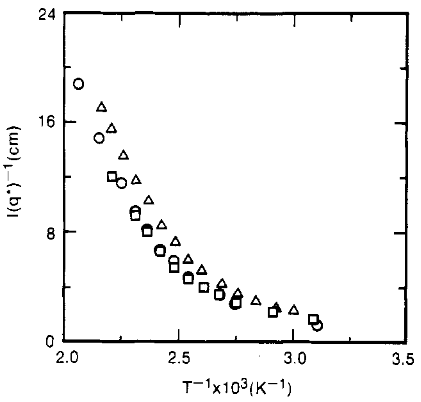

Figure 12. Dependence of inverse peak intensity on inverse temperature for blends of HBS-5 containing 5% bwt HPB: neat HBS-5 (triangles); HPB 3000 (open circles); HPB 8000 (open squares).

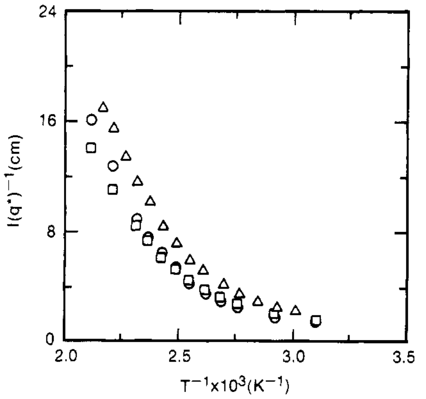

Figure 13. Dependence of inverse peak intensity on inverse temperature for blends of HBS-5 containing 10% bwt neat HBS-5 (triangles); HPB 3000 (open circles); HPB 8000 (open squares).

Whitmore and Noolandi[2] to be one-fourth of the total copolymer length for fully symmetric copolymers or roughly one-half the block length from our scattering calculations. Addition of homopolymers with molecular weights less than this critical molecular weight is predicted to depress the MST, while addition of homopolymers with molecular weights greater than the critical molecular weight is predicted to elevate the MST. The data for PS/HBS-5 blends qualitatively support these trends. The PS 1000 homopolymer is observed to lower the spinodal temperature from the pure diblock value while the PS 2000, PS 4000, and PS 8000 blends are observed to increase the spinodal temperature. The critical PS homopolymer molecular weight is therefore between 1000 and 2000.

Quantitative determination of the experimental critical molecular weight ratio is complicated by the mismatch between the experimental and predicted L_c. In the case of the experimentally determined diblock molecular weight (19 800), the critical homopolymer molecular weight is predicted to be ca. 5000. The adjusted diblock molecular weight (13 000) yields a critical molecular weight of ca. 3000. Even with the adjusted molecular weight, the predicted critical molecular weight for symmetric copolymers exceeds substantially the observed critical PS molecular weight of 1000–2000.

The MST behavior of blends of HBS-5 with HPB homopolymers (at concentrations of 5% and 10%; for molecular weights of 3000 and 8000) was also investigated. As was pointed out earlier, these blends were found to be opaque at room temperature, suggesting macrophase separation. Although the data[21] (Figures 12 and 13) are only qualitative, the results are consistent with what might be expected for a transition from region ($M_1 + L_2$) to region ($L_1 + L_2$) in the phase diagram (Figure 1). That is, the spinodal temperatures of the blends are somewhat higher than that of the neat copolymer, appear to be independent of homopolymer composition, and are only weakly dependent on homopolymer molecular weight.

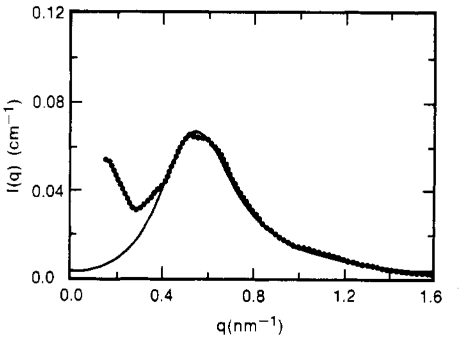

Figure 14. Comparison of experimental (points) and theoretical (line) scattering profiles for an HBS-5 blend with 5% bwt PS 3000 at 200 °C.

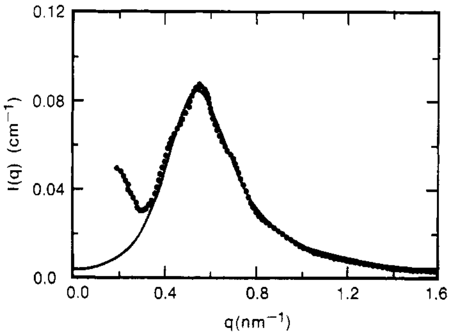

Figure 15. Comparison of experimental (points) and theoretical (line) scattering profiles for an HBS-5 blend with 5% bwt PS 3000 at 180 °C.

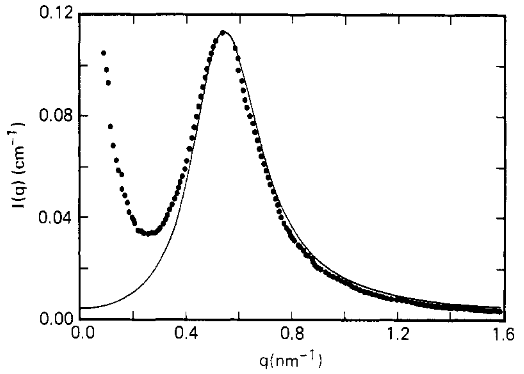

Figure 16. Comparison of experimental (points) and theoretical (line) scattering profiles for an HBS-5 blend with 5% bwt PS 3000 at 160 °C.

Comparison of Theoretical and Experimental SAXS Profiles. Theoretical SAXS profiles for symmetric homogeneous diblock copolymer/homopolymer blends can be calculated by using eq 1–4. The procedure for fitting the theoretical curves to experimental data has been detailed for the pure diblock copolymers in the preceding paper,[20] and a similar procedure[21] including polydispersity corrections is followed for the mixtures. To accomplish these regressions, we employ the same adjusted molecular weight that was used previously for neat HBS-5 and also adjust the molecular weight of the homopolymer to achieve a match of the experimental q^*. Examples are given in Figures 14–16 for 5% blends of PS 3000 at 200, 180, and 160 °C, respectively. In affecting these fits we have set the copolymer M_w at 13 000 and the homopolymer M_w at

Table II
Comparison of Experimental Interaction Parameters for Blends of HBS-5 with 5% bwt PS 3000 and for Neat HBS-5[20]

temp, °C	blend	neat HBS-5
200	0.0508	0.0500
180	0.0523	0.0528
160	0.0538	0.0545

8000 so as to match the experimental L_c. As can be seen from these figures, the scattering profiles can be acceptably reproduced by using this procedure. The values of χ_{AB} furnished by these comparisons correspond closely to those values obtained by analysis of the neat copolymer[20] as shown in Table II.

Summary

The order–disorder transition behavior of binary mixtures of a diblock copolymer with its parent homopolymers has been characterized by small-angle X-ray scattering analyses. The solubility behavior is found to be asymmetric, differing significantly for the two homopolymers, even though the diblock copolymer contains essentially equal fractions of the two constituent species (i.e., hydrogenated 1,2-butadiene and styrene). At equal homopolymer molecular weights, polystyrene homopolymers appear to be soluble in the copolymer microdomains at homopolymer contents up to 15%, while there is evidence for macroscopic phase separation of the hydrogenated butadiene homopolymer at contents as low as 5%.

Experimental trends in the MST temperature qualitatively support the predictions of Whitmore and Noolandi for perfectly symmetric copolymers and those of the scattering theory (eq 1–4). That is, there is a critical homopolymer molecular weight below which addition of small amounts of homopolymer depresses the MST temperature of the neat block copolymer. The addition of homopolymer with a molecular weight exceeding the critical molecular weight has the effect of increasing the MST temperature. However, the experimentally determined critical molecular weight is considerably lower than that predicted by theory (i.e., one-half of the corresponding copolymer sequence length).

Experimental correlation lengths also correspond qualitatively with the theoretical predictions. For low ratios of the homopolymer to copolymer molecular weight, the correlation lengths are essentially independent of homopolymer molecular weight. The correlation length is otherwise approximately linear in the fraction of homopolymer and the homopolymer molecular weight. For all mixtures, the magnitudes of the predicted correlation lengths were significantly lower than the experimental values.

Upon adjustment of the apparent molecular weight of the homopolymer so as to effect a match of the experimental and theoretical correlation lengths, the complete absolute scattering intensity profiles compare well with those derived from the symmetric theory. The regression results of these comparisons provide estimates of the segmental interaction parameters as a function of temperature that correspond closely with those values determined from analysis of the neat block copolymer.

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References and Notes

(1) Kawai, H.; Hashimoto, T.; Miyoshi, K.; Uno, K.; Fujimura, M. *J. Macromol. Sci.-Phys.* **1980**, *B17* (3), 427.

(2) Korata, T.; Miki, T.; Arai, K. J. *J. Macromol. Sci.-Phys.* **1980**, *B17* (2), 303.

(3) Riess, G.; Schilienger, M.; Marti, S. *J. Macromol. Sci.-Phys.* **1980**, *B17* (2), 355.

(4) Aggarwal, S. L.; Livigni, R. A. *Polym. Eng. Sci.* **1977**, *17* (8), 498.

(5) Selb, J.; Marie, P.; Rameau, A.; Duplessix, R.; Gallot, Y. *Polym. Bull.* **1983**, *10*, 444.

(6) Molau, G. E. *Colloidal and Morphological Behavior of Block and Graft Copolymers*; Aggarwal, S. L., Ed.; Plenum Press: New York, 1970.

(7) Quan, X. S. Ph.D. Dissertation, Princeton University, 1986.

(8) Jerome, R.; Teyssie, P. *J. Polym. Sci., Polym. Lett. Ed.* **1986**, *24*, 25.

(9) Ouhadi, T.; Fayt, R.; Jerome, R.; Teyssie, P. *J. Appl. Polym. Sci.* **1986**, *32*, 5647.

(10) Anastasiadis, S. H. Ph.D. Dissertation, Princeton University, 1988.

(11) Riess, G.; Periard, J.; Banderet, A. In ref 6.

(12) Inoue, T.; Soen, T.; Hashimoto, T.; Kawai, H. *J. Polym. Sci. A-2* **1969**, *7*, 1283. Inoue, T.; Soen, T.; Hashimoto, T.; Kawai, H. *Macromolecules* **1970**, *3*, 87.

(13) Fayt, R.; Jerome, R.; Teyssie, Ph. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1269. Fayt, R.; Jerome, R.; Teyssie, Ph. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 2209.

(14) Rigby, D.; Li Lin, J.; Roe, R. *Macromolecules* **1985**, *18*, 2269.

(15) Leibler, L. *Makromol. Chem. Rapid Commun.* **1981**, *2*, 393.

(16) Noolandi, J.; Hong, K. *Macromolecules* **1982**, *15*, 482.

(17) Whitmore, M. D.; Noolandi, J. *Macromolecules* **1985**, *18*, 2486.

(18) Whitmore, M. D.; Noolandi, J. *Polym. Commun.* **1985**, *26*, 267.

(19) Zin, W. C.; Roe, R. *Macromolecules* **1984**, *178* 183. Roe, R. J.; Zin, W. C. *Macromolecules* **1984**, *17*, 189.

(20) Owens, J. N.; Gancarz, I.; Koberstein, J. T.; Russell, T. P. *Macromolecules*, preceding article in this issue.

(21) Owens, J. N. Ph.D. Dissertation, Princeton University, 1986.

(22) Stephenson, G. B. Ph.D. Dissertation, Stanford University, 1982.

(23) Leibler, L. *Macromolecules* **1980**, *13*, 1602.

(24) Benmouna, M.; Benoit, H. *J. Polym. Sci. Phys. Ed.* **1983**, *21*, 1227.

(25) Benoit, H.; Picot, C.; Benmouna, M. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1545.

(26) Benoit, H.; Wu, W.; Benmouna, M.; Mozer, B.; Bauer, B.; Lapp, A. *Macromolecules* **1985**, *18*, 986.

(27) Olvera de la Cruz, M.; Sanchez, I. C. *Macromolecules* **1987**, *20*, 440.

(28) Bates, F. S. *Macromolecules* **1987**, *20*, 2221.

(29) Bates, F. S.; Hartney, M. A. *Macromolecules* **1985**, *18*, 2478.

(30) Bates, F. S.; Hartney, M. A. *Macromolecules* **1986**, *19*, 2892.