Microphase Separation Transition of a Triblock Copolymer

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ABSTRACT: Small-angle X-ray scattering experiments were used to characterize the microphase separation transition (MST) of a poly(styrene-*b*-ethylenebutene-*b*-styrene) triblock copolymer with a total molecular weight 21 400 and containing 28.5 wt % of styrene. The scattering profiles observed in the homogeneous phase are compared to the predictions of Olvera de la Cruz and Sanchez for an $(AB)_n$ star block copolymer with $n = 2$ arms. The experimental data are found to differ from these predictions in two respects: (1) The dominant wavelength of the concentration fluctuations is found to be temperature dependent in the disordered state; (2) the magnitude of this length exceeds the theoretical prediction. The experimental scattering profiles can be reproduced acceptably by empirically adjusting the value of N_o, the number of monomers in each arm, assumed in the calculation. The resultant interaction parameters obtained by this procedure lead to a spinodal value for $(\chi N_o)_s$ of ca. 14.9, in reasonable agreement with the prediction of ca. 15.0. Pressure-volume-temperature measurements indicate that the MST does not involve a significant change in volume.

Introduction

The microphase separation transition (MST) in block copolymers involves the dissociation of the ordered microdomain structure to form a disordered, so-called homogeneous phase. The MST behavior of diblock copolymers and their binary blends with the corresponding homopolymers has been the subject of many investigations, both experimental and theoretical, as discussed in two previous publications.[1,2] Several experimental investigations have also provided evidence for order-disorder phenomena in triblock copolymer systems. Early rheological studies[3,4] documented a transition in the temperature dependence of the dynamic viscosity and attributed the phenomena to the dissociation of microdomain structure. Rheological methods have also been applied to characterize the order-disorder transition in blends of a triblock copolymer and a low molecular weight midblock associating resin.[5] The results showed that the MST temperature was depressed upon addition of the low molecular weight resin, in qualitative agreement with experimental results and theoretical predictions on diblock copolymer blend systems. The small-angle X-ray scattering technique was used by Roe et al.[6] to study the MST behavior of the same triblock copolymer as was used in the early rheological investigations. The scattering behavior observed was qualitatively consistent with the predictions for diblock copolymers. More recently, a theory of the microphase separation transition in star and graft copolymers has been proposed by Olvera de la Cruz and Sanchez.[7] Triblock copolymers are a special case of n-arm star diblock copolymers (each arm is a diblock copolymer containing N_o segments with volume fraction, f, of the core monomer where $n = 2$). The overall character of the MST for these triblock copolymers is predicted to be qualitatively similar to that of diblock copolymers; however, there are some notable differences: the transition for n-arm diblocks is first order for all compositions; for $f = 0.5$, $(\chi N_o)_s$ at the transition temperature equals 8.86, where χ is the usual interaction parameter; and the phase diagram is asymmetric due to differences in the configurational constraints inherent to the midblock and end-block sequences. While the order-disorder transitions for starblock copolymer solutions have been studied,[8] the quantitative nature of these predictions has not yet been examined in detail for neat copolymers.

Small-angle X-ray scattering (SAXS) and pressure-volume-temperature (P-V-T) measurements are used in this investigation to examine the microphase transition temperature of a poly(styrene-*b*-ethylenebutene-*b*-styrene) triblock copolymer. These copolymers are nearly symmetric in terms of the equivalence of statistical segment lengths for the two species. The experimental results obtained by these analyses are compared with the predictions of the Olvera de la Cruz and Sanchez theory.

Experimental Section

The poly(styrene-*b*-ethylenebutene-*b*-styrene) triblock copolymer studied was supplied by the Shell Development Co. The midblock contains 37.5% of the 1,2-addition product. The copolymer, designated SEBS (3600-14400-3400), has a number-average molecular weight of 30 800, a weight average molecular weight of 33 500, and a polydispersity index 1.09 as characterized by GPC analysis with a polystyrene calibration. After differences were corrected for in hydrodynamic volumes, the midblock molecular weight is determined to be 14 400 and the end-block molecular weights are 3600 and 3400, respectively. The

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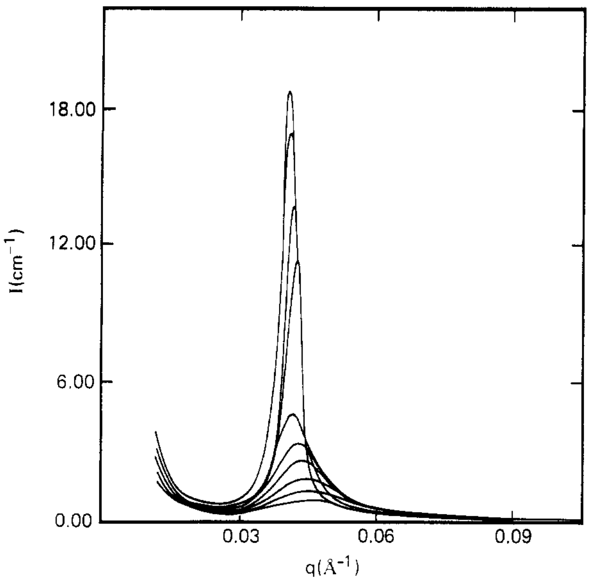

Figure 1. Temperature dependence (heating cycle) of absolute intensity profiles for SEBS (3600–14400–3400). Beginning from the weakest scattering profile the temperatures corresponding to the profiles are 229.3, 204.0, 182.1, 160.7, 146.0, 136.0, 130.0, 120.0, 110.5, and 100.5 °C, respectively.

weight fraction of polystyrene determined by an independent method is 0.31. The error in the composition determination is estimated at 10% while that in the molecular weight characterization is on the order of 5%.[9]

Small-angle X-ray scattering (SAXS) measurements were carried out on beam line I-4 at the Stanford Synchrotron Radiation Laboratory. Specimens of ca. 30 mg were mounted into disklike cells with Kapton windows. Temperature control was accomplished with a Mettler FP80/82 hot stage. Experimental scattering profiles were corrected for specimen adsorption, detector dark current, and parasitic scattering and were calibrated with standard scatterers to obtain absolute intensity units. The details of these procedures are provided elsewhere.[1,2,10,11]

The room-temperature densities of the polymers were measured using an autopycnometer (Micromeritics) at atmospheric pressure. Changes in density as a function of temperature and pressure were measured using a P-V-T apparatus, which has been fully described elsewhere.[12] In the isobaric mode, the pressure is held constant while the temperature is changed by ca. 2 °C increments. The absolute accuracy of the device is $(1-2) \times 10^{-3}$ cm^3/g, and volume changes as small as $(1-2) \times 10^{-4}$ cm^3/g can be resolved.

In fitting the scattering curves, we have used a polystyrene fraction of 0.715 as a volume fraction of ethylenebutene in each arm of the copolymer and have assumed values of 0.71 nm for the statistical segment length of polystyrene (calculated from the tabulated characteristic ratio[13]) and 0.76 nm for the ethylenebutene of mixed microstructure (calculated from reported values of 0.88[14] and 0.56 nm[15] for 1,4- and 1,2-hydrogenated butadiene, respectively). From the point of view of statistical segment length, this copolymer is thus nearly symmetric.

Scattering Theory

The theory for scattering from triblock copolymers in the disordered or homogeneous state (i.e., above the MST temperature) is similar to that of homogenous diblock copolymers. That is, a maximum in the scattering profile persists above the MST due to correlation hole effects associated with concentration fluctuations. The static structure factor has the form[7]

$$S(q)^{-1} = \frac{Q(q) - 2\chi}{N_o} \tag{1}$$

where q is the magnitude of the scattering vector. It is related to the scattering angle, 2θ, and the wavelength λ by $q = (4\pi/\lambda) \sin \theta$. For a triblock copolymer (equivalent to an $[AB]_n$ star block copolymer where $n = 2$), N_o refers to the polymerization index of each arm, χ is the interaction parameter, and $Q(q)$ is a function that depends specifically on the copolymer architecture. The structure factor has a maximum at a critical scattering vector q^*, determined by the equation $\partial Q/\partial q = 0$. At the spinodal temperature, $S(q^*)$ becomes infinite and $\chi = \chi_s = Q(q^*)2N_o$. If χ is of the form $\chi = A - B/T$ where A and B are constants and T is the temperature, the spinodal temperature may be determined from a plot of $S(q^*)^{-1}$ vs T^{-1}. Above the MST temperature, this plot will be linear. The extrapolation of the linear regime to $S(q^*)^{-1} = 0$ provides an estimate of the spinodal temperature, and the departure of the experimental data from the high-temperature linear dependence yields an estimate of the MST temperature.[1,2,6]

In the homogenous state, $S(q)$ for an $[AB]_2$ star (triblock) copolymer is described by the equations[7]

$$\begin{aligned} S(q)^{-1} = {} & \{D_f + D_{1-f} + [F_f^2 + F_{1-f}^2 \exp(-2fx_o)] + \\ & 2F_fF_{1-f}[1 + \exp(-fx_o)]\}/\{N_o\{D_fD_{1-f} + [D_{1-f}F_f^2 + D_fF_{1-f}^2 \times \\ & \exp(-2fx_o)] - (F_fF_{1-f})^2[1 + 2\exp(-fx_o)]\}\} - 2\chi \end{aligned} \tag{2}$$

$$D_\alpha = \alpha^2 D(\alpha x_o) \qquad \alpha = f, 1-f \tag{3}$$

$$D(\mu) = (2/\mu^2)[\mu + e^{-\mu} - 1] \tag{4}$$

$$F_\alpha = 1 - e^{-\alpha x_o} \qquad \alpha = f, 1-f \tag{5}$$

$$x_o = N_o q^2 l^2/6 \tag{6}$$

where l is the statistical segment length and f is the volume fraction of A monomers (i.e., midblock species) in each arm of the 2-arm star diblock copolymer. (Note: each arm is half of the triblock copolymer.) An essentially identical set of scattering relations can be derived from the more general theory proposed by Benoit and Hadziioannou.[16] Polydispersity corrections may also be implemented using their approach but are not applied in the present work.

In addition to the structure factor represented by eq 1, the total scattering intensity, $I(q)$, also contains a contribution due to thermal density and concentration fluctuations. This contribution can be assumed to be a constant independent of q and can be estimated from a plot of $I(q)\,q^4$ vs q^4 as proposed by Bonart and Müller.[17]

Results and Discussion

Small-angle X-ray scattering profiles for the SEBS (3600–14400–3400) copolymer during the heating cycle are shown in Figure 1. The behavior upon cooling (not shown) is completely reversible. The curves are all characterized by a single scattering maximum at a critical scattering vector, q^*. The intensity of the maximum decreases in magnitude and becomes broader with increase in temperature. The reversibility in temperature dependence is emphasized by the critical reciprocal intensity plot shown in Figure 2. The linear region is indicative of the homogeneous state for the block copolymer, and the extrapolation of this line to infinite intensity (i.e., $I(q^*)^{-1} = 0$) provides an estimate of the spinodal temperature as ca. 174 °C. The deviation of the linear extrapolation from the experimental curve occurs at approximately 197 °C, suggesting that this is the microphase separation transition temperature. The data indicate that the transition to the homogeneous phase is quite broad,

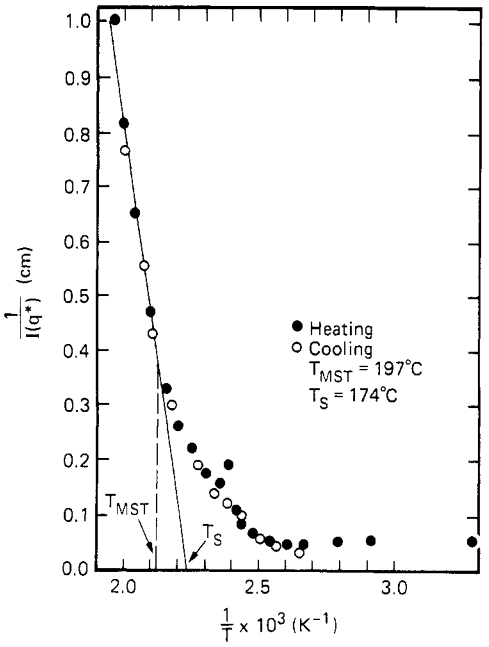

Figure 2. Critical intensity plot for the determination of the spinodal and MST temperatures: (●) heating; (○) cooling. T_{MST} is approximated at 197 °C, and T_s is extrapolated to a temperature of 174 °C.

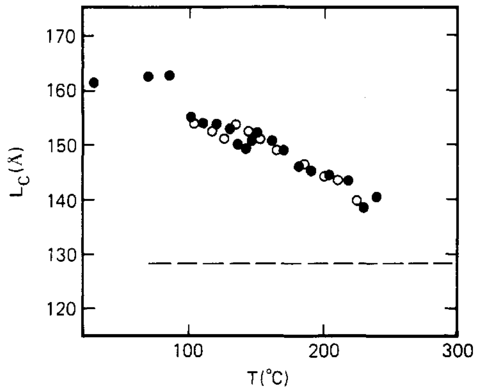

Figure 3. Temperature dependence of the dominant fluctuation wavelength for SEBS (3600–14400–3400): (●) heating; (○) cooling. The dashed line is the theoretically predicted value of 127 Å.

and thus the precision in the estimates of the two transition temperatures is not well characterized.

The dominant wavelength for the concentration fluctuations, L_c, can be determined from the critical scattering vector through the relation

$$L_c = 2\pi/q^* \qquad (7)$$

These are shown in Figure 3 as a function of temperature. L_c decreases monotonically over the entire range of temperatures studied. The theory for homogeneous block copolymers predicts that above the transition temperature, L_c should reach a constant value. For the copolymer studied, eq 2–6 predict a value of L_c = 127 Å, somewhat smaller than the experimental data. There is no clear transition to a constant L_c in the neighborhood of the apparent spinodal temperature of 174 °C.

The lack of a temperature regime above the MST, wherein L_c attains a constant value, might be attributable to several factors. Fluctuation effects have been shown theoretically to influence the behavior of diblock copolymers in this regime.[18] Fluctuation effects should be stronger in triblocks since the interactions between one end block and the midblock are coupled to those between the other end block and the midblock by virture of the covalent bands connecting the unlike sequences. The transition from the extended configuration of these triblocks in the ordered state[15] to the Gaussian configuration postulated for the disordered triblock therefore would be broadened, such that there may still be a significant temperature dependence of the concentration fluctuations (and thus L_c) in the disordered state. Alternatively, transitions between different ordered mesophase geometries (e.g., cylindrical, lamellar, and spherical) are expected near the MST.[19] The quantitative interpretation of our results would require some revision if our experimental conditions incorporate the possibility of crossing one of these phase lines. The present data are insufficient to detect a transition in mesophase geometry, since we detect only a single scattering maximum. Further experimentation would be necessary to investigate either of these factors and their influence on L_c above the MST temperature.

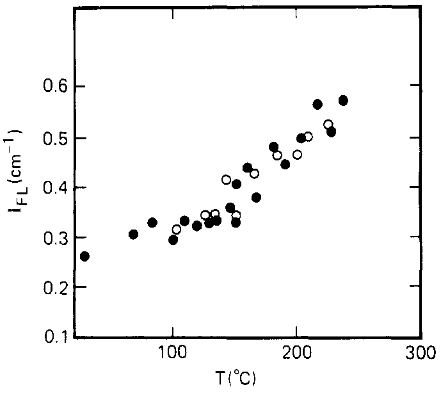

Figure 4. Temperature dependence of fluctuation scattering, I_{FL}, from SEBS (3600–14400–3400): (●) heating; (○) cooling.

The scattering contributions due to local electron density fluctuations are plotted in Figure 4. These contributions may arise either from thermal density fluctuations or concentration fluctuations associated with molecular level intermixing of the two copolymer sequences. The fluctuation scattering is relatively constant up to ca. 140 °C. Above this temperature, an increase in the temperature dependence of the fluctuation scattering is observed.

The temperature dependence of the block copolymer density was measured to ascertain whether this transition could be attributed to mass density changes. Isobaric (P = 50 MPa) specific volume temperature data for SEBS (3600–14400–3400) are shown in Figure 5. No transitions in specific volume are apparent in the region near 140 °C, where the transition in the fluctuation scattering was observed, or at higher temperatures corresponding to the MST and spinodal temperatures determined from Figure 2. It is evident from this data that little if any volume change accompanies the transition from the ordered to the disordered state for this copolymer. In addition, it is apparent that the transition in fluctuation scattering is not associated with density effects and thus is most likely the result of an increase in concentration fluctuations.

An increase in concentration fluctuations at temperatures slightly below the spinodal is expected if the microphase-temperature diagram is considered. The compositions of the coexisting microphases approach each other near the MST temperature indicative of an increase in partial intermixing of the two block copolymer species. This process necessarily involves an increase in con-

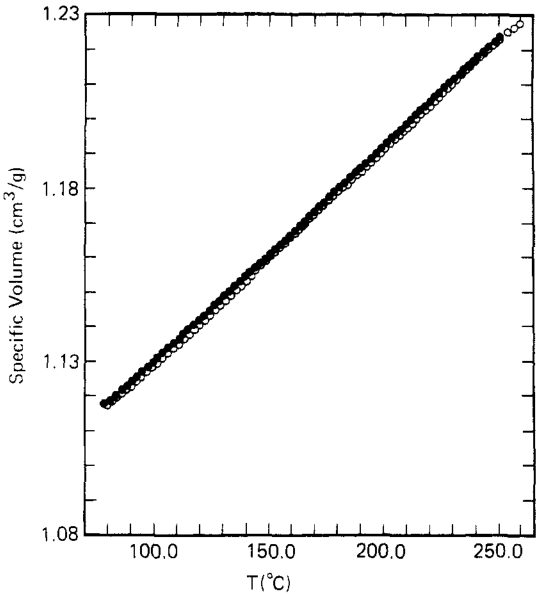

Figure 5. Isobaric (50 MPa) specific volume temperature data for SEBS (3600–14400–3400): (●) heating; (○) cooling.

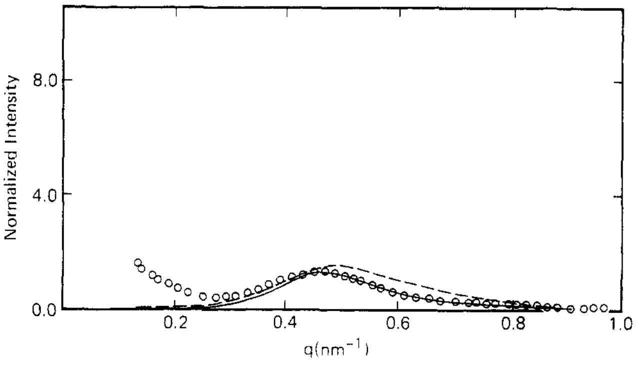

Figure 6. Comparison of theoretical and experimental (○) scattering profiles for SEBS (3600–14400–3400) at 205 °C. The dashed line is the theoretical prediction, and the solid line denotes the theory including a 15% empirical adjustment (increase of N_o).

centration fluctuations as seen in the fluctuation scattering (Figure 4) and is also consistent with the rapidly decreasing magnitude of the scattered intensity in this same temperature range (see Figure 2). These latter data exhibit a diminution in the peak intensity at ca. 140 °C (i.e., $1/T \simeq 0.0024$) attributable to the decrease in contrast resulting from partial microphase mixing.

In the temperature range above the apparent spinodal temperature, the scattering profile for the homogeneous triblock copolymers is predicted to follow eq 1–6. Regression of these equations upon the experimental scattering profiles can be used to estimate the interaction parameter. A comparison between the predicted and experimental profiles for SEBS (3600–14400–3400) at 205 °C appears in Figure 6. The predicted dominant wavelength (i.e., the position of the maximum) does not correspond to that observed experimentally; however, the shapes of the profiles are similar. The theoretical profile can be brought into close agreement with experiment by empirically adjusting (i.e., increasing by 15%) the number of monomers in each arm, N_o, used in the calculation. This is equivalent to adjusting the effective copolymer chain dimensions. The experimental parameters (e.g., molecular weight, composition, segment lengths) are subject to a number of experimental errors that may influence the comparisons of the observed scattering profiles with the theory. In addition, the effects of polydispersity have not been included in these comparisons. The adjustment factors required to match profiles, however, are larger than can be accounted for by these collective errors. There remains the major discrepancy that L_c has not reached a constant value even in the disordered phase (Figure 3) as is expected from theory. Comparisons for the adjusted and unadjusted theories result in values of 0.081 and 0.090, respectively, for the apparent interaction parameter. A similar comparison for the specimen at 180 °C (Figure 7) requires an empirical adjustment by 25% and leads to an apparent χ value of 0.077. A different adjustment factor is necessary in this case since L_c is temperature dependent. It must be stressed that the observed variation of L_c with temperature above the apparent MST places severe limitations on the precise evaluation of χ. However, outside the maximum error limits, χ for the triblocks can be compared with data obtained for SEB diblock copolymers with a 95% 1,2-ethylenebutene microstructure in[1,10] Figure 8. The data suggest that the S–EB interactions are more favorable for the 1,2 microstructure compared to the mixed microstructure, consistent with the trend we have found for styrene–isoprene copolymers.[1]

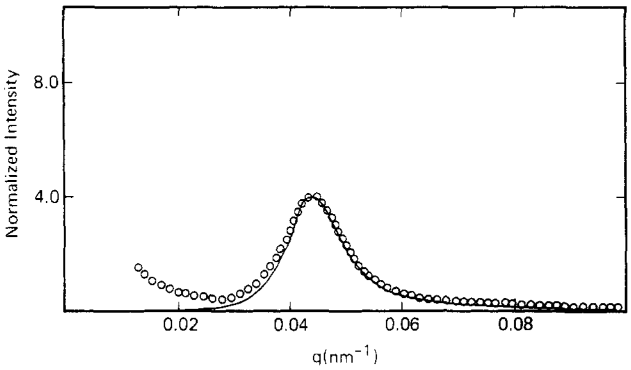

Figure 7. Comparison of experimental (○) and adjusted theoretical (solid line) scattering profiles for SEBS (3600–14400–3400) at 180 °C.

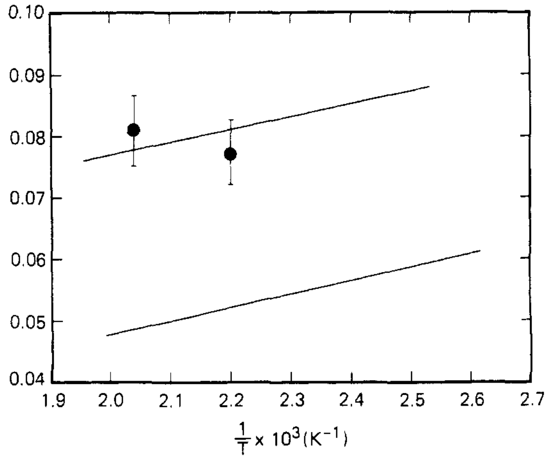

Figure 8. Comparison of interaction parameters determined for SEB diblock[1] (line) and SEBS (3600–14400–3400) triblock copolymers (●).

The theory of Olvera de la Cruz and Sanchez[7] predicts the spinodal condition as a function of copolymer architecture and interaction energy. The theoretical $(\chi N_o)_s$ at the spinodal is plotted in Figure 9 for star block copolymers with n arms of composition f and polymerization index N_o. The SEBS (3600–14400–3400) triblock copolymer has $n = 2$ arms and a fractional ethylenebutene

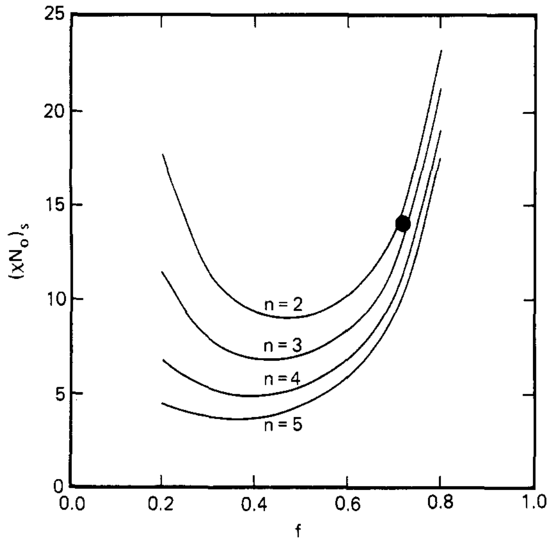

Figure 9. Comparison of spinodal condition for SEBS (3600–14400–3400) triblock copolymer with the predictions of the theory by Olvera de la Cruz and Sanchez.[7]

composition of $f = 0.715$. The theoretically predicted value for $(\chi N_0)_s$ is 15.0 as shown by the calculated MST's in Figure 9. Experimentally, as stated previously, it is difficult to quantitatively assess the temperature dependence of χ. Assuming the same temperature dependence of χ in the triblock copolymers as in the diblock copolymers studied previously,[1] a regression to the χ values found in this study (see Figure 8) yields χ at the spinodal of 0.082 and a $(\chi N_0)_s$ value of 14.9 in good agreement with theory.

Summary

The microphase separation transition for neat poly(styrene-*b*-ethylenebutene-*b*-styrene) triblock copolymers has been characterized by small-angle X-ray scattering experiments. The value of $(\chi N_0)_s$ found at the spinodal compares favorably with the theoretical prediction by Olvera de la Cruz and Sanchez[7] for star block copolymers with $n = 2$ arms. Measurement of the absolute scattered intensity and magnitude of the fluctuation scattering indicate that partial microphase intermixing occurs in the ordered microphases as the spinodal temperature is approached. Above the apparent spinodal temperature, the wavelength of the dominant concentration fluctuation (indicated by the position of the maximum in scattered intensity) continues to decrease with increase in temperature, contrary to the theoretical prediction. For this reason, quantitative comparison of the scattering profile with theory requires a temperature-dependent empirical adjustment of the effective molecular size in order to match peak positions. At the temperatures studied, the experimental and theoretical profiles compare well when properly adjusted. Interaction parameters obtained through the profile regressions suggest that ethylenebutene with a predominant 1,2 microstructure has a more favorable interaction with styrene than does a mixed microstructure.

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Registry No. (S)(E)(B) (block copolymer), 106108-28-5.