Compositional Dependence of the Microphase Separation Transition in Styrene−Butadiene−Styrene Triblock Copolymer/Polystyrene Blends

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ABSTRACT: The change in the microphase separation transition (MST) temperature of a styrene−butadiene−styrene (SBS) triblock copolymer induced by the addition of polystyrene (PS) was investigated by small-angle X-ray scattering. It was found that the transition temperature was determined from the molecular weight (M_H) of the added PS in relation to that of the corresponding blocks (M_A) in the copolymer. The MST temperature decreased with added PS if $M_H/M_A < 1/4$, while it increased with added PS when $M_H/M_A > 1/4$. Analysis of the theoretical expression based on the random phase approximation showed exactly the same tendency of change in the transition temperatures as that observed experimentally. The interaction parameter, χ_{SB}, obtained by nonlinear fitting of the scattering profiles of SBS/PS blends in the disordered state, was found to be a function of temperature and composition. Composition fluctuations were found to exist in SBS/PS blends, increasing with increasing addition of PS but diminishing with increasing molecular weight of the added PS.

Introduction

The broad range of present and potential applications of block copolymers has led to numerous studies of their structures and properties.[1,2] The majority of previous work has focused on characterization of block copolymers and their blends in the strong segregation limit, where microphase separation into well-ordered microdomain morphologies is observed. Only recently, there has been considerable interests in the thermodynamics of block copolymers in the weak segregation limit, where the materials undergo a transition from the well-ordered microphase-separated state to a so-called disordered phase.

The transition from the ordered to the disordered state has been described by a variety of theories.[3−7] Leibler[3] developed a mean-field theory to describe transitions in block copolymers. It predicts that, at compositions other than 0.5, a first-order transition occurs from the homogeneous disordered state to the ordered state, following the sequence of body-centered-cubic, hexagonal, and lamellar mesophase as χN increases, where χ is the interaction parameter and N is the degree of polymerization. At the composition $f = 0.5$, diblock copolymers undergo a second-order transition from the disordered state to the ordered lamellar morphology at $(\chi N)_S = 10.495$ in the limit of infinite molecular weight. Leibler's theory was latter developed by Fredrickson and Helfand[4] and Muthukumar[5] by taking account of the composition fluctuations. The new theories exhibit finite copolymer composition ranges in which the mesophase can be obtained directly from the disordered state by increasing χN. Hashimoto et al.[6] and Mayes and Olvera de la Cruz[7] extended the theory to triblock copolymers and other copolymers of various architectures. According to Hashimoto et al.,[6] the compositional dependence of the spinodal curve for triblock copolymers is asymmetric about $f = 0.5$, but it is symmetric for diblock copolymers. Owing to the asymmetry, the difference of the spinodal microphase separation temperature between ABA and A−(1/2)B is larger for A-rich copolymer ($f > 0.5$) than for A-poor copolymer. One can then expect that the effect of adding homopolymer A to ABA may differ from that of adding homopolymer A to A−(1/2)B. So, it is of great interest to investigate the phase behavior of ABA/A blends theoretically and experimentally.

The molecular weight of the homopolymer was found to be of great influence on the microphase separation transition (MST) in diblock copolymer/homopolymer blends. Whitmore and Noolandi[8] predicted theoretically that the microphase separation temperature decreased with increasing homopolymer content if $M_H/M_A \leq 0.5$ and increased with increasing homopolymer contents if $M_H/M_A > 0.5$ for the symmetric diblock copolymer/homopolymer (AB/A) blends, where M_H and M_A are the molecular weights of the homopolymer A and the corresponding block A in the approximation theory for the AB/A system. Owens et al. obtained similar results theoretically by extending the random phase approximation (RPA) method to AB/A systems and demonstrated experimentally that the microphase separation temperature may be depressed or elevated by changing the molecular weight of the added homopolymer. However, the critical homopolymer molecular weight was found to be substantially lower than the theoretically predicted value of $M_A/2$ for the AB/A blends.[9]

Microphase separation in block copolymers and block copolymer/homopolymer blends is usually investigated by scattering and/or rheological experiments. Small-angle X-ray scattering (SAXS) studies on the MST in styrene−butadiene diblock copolymer and its blends with polystyrene and polybutadiene were first conducted by Roe et al.[10−12] A number of researchers have recently investigated transitions in other block copolymers.[13−19] Both the results of SAXS and those obtained from rheological transition[20,21] were found to be in qualitative agreement with the prediction of Leibler's theory. However, most of the investigations were restricted to neat block copolymers,[10,13−18] and only a few exceptions concerned the effect of added homopolymers on the MST

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in diblock copolymer/homopolymer blends.[9,11,12] As for triblock copolymer, the effect of the added homopolymers on the transition remains unexplored.

The present paper describes the results of small-angle X-ray scattering investigation of the microphase separation transition in blends of styrene−butadiene−styrene triblock copolymer and polystyrene, focusing on the effects of composition and molecular weight of added polystyrene on the transition. The experimental scattering profiles are compared quantitatively to the predictions of Leibler's theory to estimate the stability limit and the vales of the χ parameters. The composition fluctuations near the MST are discussed in terms of composition and molecular weight of added polystyrene.

Prediction from RPA Theory

When the method of random phase approximation is applied to polymer systems consisting of two monomeric species, A and B, the structure factor, $S(q)$, predicted from the theory is related to the absolute small-angle scattering intensity, $I(q)$, observed experimentally and expressed by

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

where ρ_{eA} and ρ_{eB} are the electron densities for polymers A and B, 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 two-component system in the homogeneous region of the phase diagram can be calculated as[3]

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

where χ is the Flory interaction parameter, and $F(q)$ can be expressed as

$$F(q) = \frac{S_{AA}(q) + 2S_{AB}(q) + S_{BB}(q)}{S_{AA}(q)S_{BB}(q) - S_{AB}^{\;2}(q)} \qquad (3)$$

$S_{ij}(q)$ is the Fourier transform of the correlation function between species i and j in the hypothetical case where there is no interaction between different molecules.

The system considered here is a mixture of homopolymer A and triblock copolymer ABA. If the volume fraction of the homopolymer in the mixture is ϕ_H, and the composition of the block copolymer is represented by the volume fraction f_1, f_2, f_3 of A and B in the molecule, one then has[6]

$$S_{AA} = (1 - \phi_H)N_C[g(f_1,N_C) + g(f_2,N_C) + g(f_3,N_C) + g(1,N_C) - g(1 - f_3,N_C) - g(1 - f_1,N_C)] + \phi_H N_H g(1,N_H) \qquad (4)$$

$$S_{BB} = (1 - \phi_H)N_C g(f_2,N_C) \qquad (5)$$

$$S_{AB} = {}^1/_2(1 - \phi_H)N_C[g(1 - f_1,N_C) + g(1 - f_3,N_C) - g(f_1,N_C) - g(f_3,N_C) - 2g(f_2,N_C)] \qquad (6)$$

where N_C and N_H are the degrees of polymerization of block copolymer and homopolymer, respectively, and $g(f_i,N_i)$ is the Debye function,

$$g(f_i,N_i) = \frac{2}{x^2}[(f_i x_i - 1) + \exp(-f_i x_i)] \qquad (7)$$

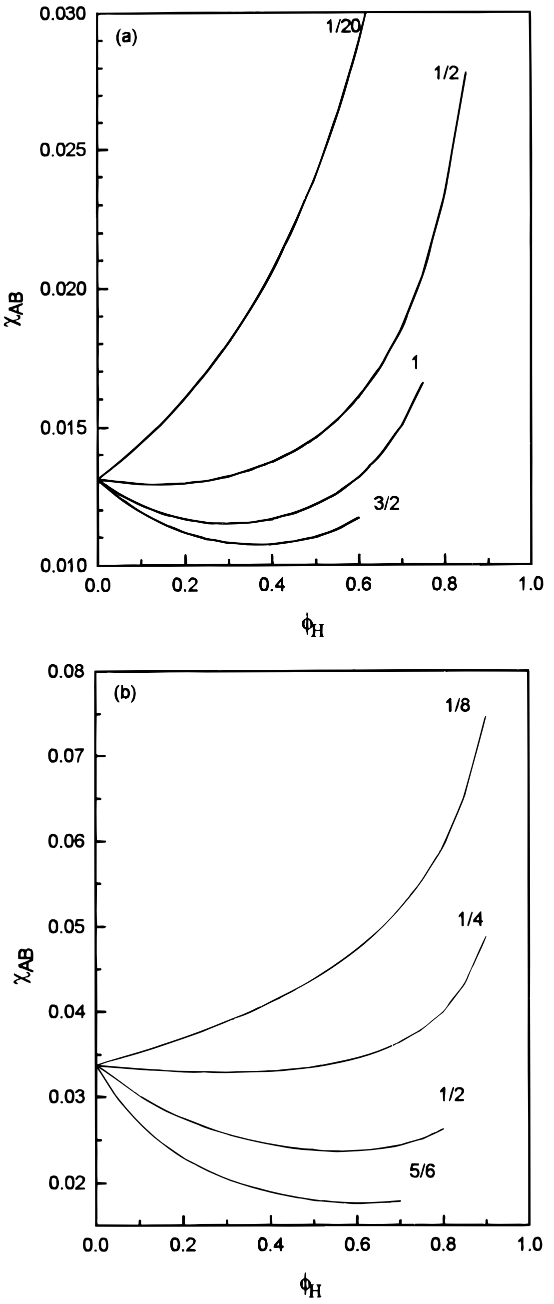

Figure 1. (a) Plots of $(\chi_{AB})_S$ vs ϕ_H in AB/A blends, where $N_C = 800$, $f_1 = f_2 = 0.5$. (b) Plots of $(\chi_{AB})_S$ vs ϕ_H in ABA/A blends, where $N_C = 800$, $f_1 = f_3 = 0.15$.

with $x_i = q^2N_i^2a_i^2/6$, and a_i is the statistic segment length for monomer i.

Substituting eqs 2−7 into eq 1, one then obtains the expression of $I(q)$ as a function of χ. By nonlinear fitting of the SAXS profiles in the disordered state, we obtain the temperature dependence of χ. Furthermore, from eq 2, one can find that there are values of χ at which $S(q)^{-1} = 0$. At $q \neq 0$, the χ parameter that satisfies $S(q)^{-1} = 0$ describes the stability limit of the microphase separation. Thus, we can obtain the spinodal curves of microphase transition in given systems on the basis of this consideration. The values of χ that satisfy $S(q)^{-1} = 0$ are hereafter denoted as $(\chi_{AB})_S$ throughout this article.

The theoretical spinodal temperatures versus volume fraction of the added homopolymer obtained from eqs 2−7 are presented in Figure 1a for a symmetric diblock copolymer blended with homopolymer of varying mo-

Table 1. Characteristics of Homopolystyrene

designation	source	GPC M_w	M_w/M_n
PS5h	Nanjin University	500	1.04
PS3k	Jilin University	3000	1.05
PS5k	Nanjin University	5000	1.05

lecular weights. The homopolymer molecular weights are presented as ratios of M_H to M_A. The spinodal temperature is shown to decrease with increasing homopolymer content for low molecular weight homopolymers. At a homopolymer weight of one-half the corresponding block molecular weight, the spinodal temperature keeps almost constant up to 20 wt % homopolymer and then decreases with further addition of homopolymer. For homopolymer with molecular weight higher than one-half the corresponding block molecular weight, the spinodal temperature increases with the addition of homopolymer and decreases with further addition of the homopolymer as ϕ_H exceeds a critical value. The critical homopolymer content, $(\phi_H)_C$, is seen to decrease with increasing homopolymer molecular weights. In the theoretical calculations performed by Noolandi and Owens, a critical homopolymer molecular weight, $(M_H)_C$, was also observed and agreed well with the result presented here. However, as the ϕ_H involved in their calculations was relatively small (less than 0.3), the critical content $(\phi_H)_C$ for the blends containing high molecular weight homopolymers was not observed. From the theoretical calculations, it is obvious that there is a critical homopolymer molecular weight for a given diblock copolymer. The spinodal temperature decreases with ϕ_H as $M_H \leq (M_H)_C$ and increases with ϕ_H as $M_H \geq (M_H)_C$ over the range of $0 < \phi_H < (\phi_H)_C$, while it decreases with ϕ_H when $\phi_H > (\phi_H)_C$. Similar conclusions can be obtained for triblock copolymer/homopolymer blends, as shown in Figure b, where $N_C = 800$, $f_1 = f_3 = 0.15$. The homopolymer molecular weights are presented as the ratios of M_H to M_A. The critical homopolymer molecular weight is found to be one-fourth the corresponding block molecular weight in ABA. Also, there is a critical homopolymer content for the blends containing high molecular weight homopolymers, and it decreases with increasing M_H.

The homopolymer molecular weight effect on the microphase separation in diblock copolymer/homopolymer blends has been investigated experimentally by Roe[10,11] and Owens et al.[9] The experimental results obtained by Owens et al. agreed qualitatively with the theoretical predictions. The critical molecular weight was found to be substantially lower than the predicted $0.5M_A$. However, the critical content $(\phi_H)_C$ was not observed, since the ϕ_H involved in their experiment was less than 0.15. In the next section, we will provide experimental verification of the theoretical results described above, aiming to explore to the homopolymer molecular weight effect on the microphase separation in triblock copolymer/homopolymer blends.

Experimental Section

Materials. The styrene–butadiene–styrene (SBS) triblock copolymer used here is a commercial product purchased from Aldrich Chemical Co. The copolymer contains 28% polystyrene by weight and has number-average and weight-average molecular weights of 70 000 and 100 000, respectively, as determined by GPC. The butadiene block consists of 74% 1,2-, 15% *trans*-1,4-, and 21% *cis*-1,4-polybutadiene (PB). The characteristics of homopolystyrene (PS), obtained from various sources, are listed in Table 1.

Preparation. SBS and blends of SBS/PS at the desired composition were first dissolved in toluene to form a 3 wt % polymer solution. The solutions were stirred at room temperature for 2 days to make them homogeneous. They were then cast onto PTFE dishes, and the solvent was allowed to evaporate slowly over about 1 week. Films, 1 mm thick, obtained in this way were further dried in a vacuum oven at 80 °C for 1 week to remove the residential solvent. The films were then subjected to small-angle X-ray scattering experiments.

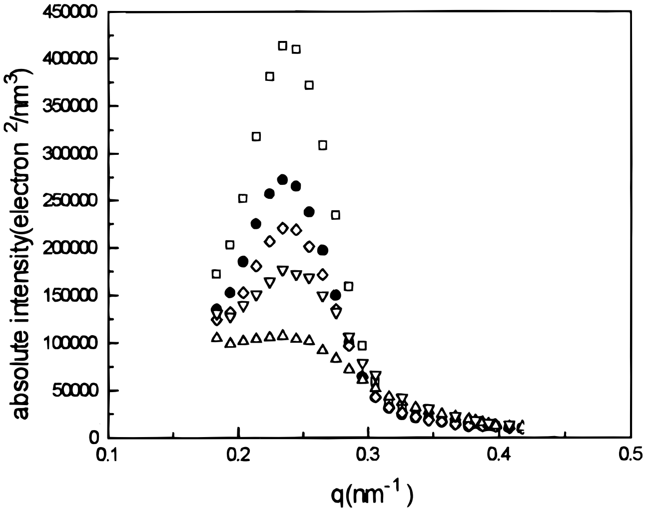

Figure 2. Small-angle X-ray scattering profiles for SBS/PS5h blends at 20 °C (□), 80 °C (●) 110 °C (◇), 180 °C (▽), and 250 °C (△).

Measurements. Small angle x-ray scattering analysis was performed in the Kratky Compact SAXS system, which was equipped with a stationary anode, copper target X-ray tube (wavelength, 1.54 Å). The temperature of the sample was regulated within about ±1 °C up to 300 °C by a hitter. The measured intensity was corrected for background scattering and desmeared with a method proposed by Strobl.[22] A moving slit device was used to measure the absolute intensity.

Results and Discussion

Microphase Separation Transition. The intensity data obtained with SBS/PS5h blend containing 25 wt % PS5h at temperatures between 20 °C and 250 °C are shown in Figure 2. The scattered intensity, $I(q)$, is plotted in absolute units of electron^2/nm^3 as a function of the scattering vector, q. SAXS data taken at selected temperatures are shown, omitting some scattering curves for clarity. The scattered intensity at the peak, $I(q^*)$, increases steadily as the temperature is lowered. Similar behavior is observed for other samples. This agrees well with the results reported by other researchers[3−11] and can be explained as the transition from the ordered microphase-separated state to the homogeneous disordered state. The transition was found to be reversible after the scattering measurements at 250 °C, as indicated in the scattering profiles of neat SBS shown in Figure 3. In Figure 3, the solid circles represent intensity data measured at 60 °C before higher temperature measurements, and the open circles represent intensity data measured at 60 °C after measurements between 60 °C and 250 °C. One can find only a slight depression of the scattering intensity after the higher temperature measurements.

Methods to determine the microphase separation temperatures from scattering results are based on the theory proposed by Leibler. The first method is based on the assumption that the interaction parameter χ is of the form

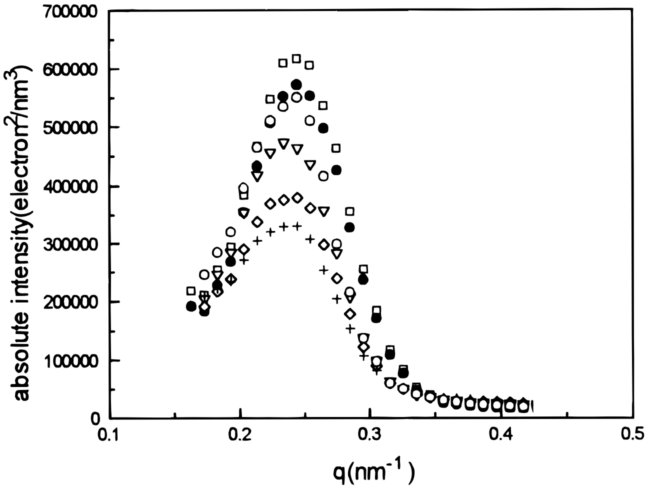

Figure 3. Small-angle X-ray scattering profiles for neat SBS at 20 °C (□), 60 °C (●), 160 °C (▽), 180 °C (◇), 250 °C (+), and 60 °C (○) after the 20–250 °C measurements.

$$\chi(T) = \chi_0 + \chi_b/T \tag{8}$$

where χ_0 and χ_b refer to entropic and enthalpic contributions to χ, and T is the absolute temperature. By substituting the expression into Leibler's structure factor, a linear decrease of $1/I(q^*)$ with $1/T$ is thus predicted for the disordered state, and the deviation from linearity is associated with the onset of the microphase separation, while the spinodal microphase separation temperature is taken as the intersection of the extrapolated line with the x-axis. Some reports[4,5] support this method, while some[6,7] do not agree with it. A critical problem is whether the composition fluctuations are important for the scattering experiments near the MST. The other method is based on the prediction of Leibler's theory that the correlation length, L_c ($L_c = 2\pi/q^*$), within the disordered state is constant. A plot of the domain spacing as a function of temperature defines the MST at which the spacing becomes constant. However, this analysis is confounded by the broadening of the first-order peak over the MST, which causes inaccuracy in determining the correlation length. In our studies, the correlation length L_c in SBS/PS blends decreases slightly with increasing temperature, as shown in Figure 2. However, the correlation length for the neat triblock copolymer remains almost constant. This may be attributed to the nonequilibrium effect. A constant L_c has been observed in neat diblock copolymers[23] and blends of diblock copolymer with high molecular weight homopolymers,[9] which has been attributed to the nonequilibrium effect in the sample. A third theory-independent method for determining the MST is based on the analysis of the width of the main scattering peak. The MST temperature was determined by plotting the peak half-width versus temperature. The temperature at which the largest rate of change in the peak half-width is observed is taken as the MST temperature. Winey et al. found that the MST temperatures determined this way were in good agreement with the rheological studies,[16] which had been proved to be able to ascertain the MST within ±1 °C.[17] However, the transition temperature determined in this way is the microphase separation temperature rather than the spinodal temperature and cannot be compared with the theoretical results.

In the analysis of our experimental results, we used the first method for the analysis of the microphase separation temperatures, since the analysis based on the correlation length for our results produced ambiguous transition temperatures and the half-width analysis only gives the microphase separation temperatures. However, as the composition fluctuation occurs near the MST in diblock copolymers, it should also occur in triblock copolymers and triblock copolymer/homopolymer blends. The composition fluctuations cause a nonlinear relationship between $I(q^*)^{-1}$ and T^{-1} in the disordered state, making the precise evaluation of the spinodal temperature difficult. Nevertheless, since the present work is focused on the molecular weight and composition dependence of spinodal temperatures in triblock copolymer/homopolymer blends rather than quantitative determination of the temperatures, the entire plots of $I(q^*)^{-1}$ vs T^{-1} instead of the extrapolated spinodal temperature should emphasize the overall trends. Figure 4 is the plot of $I(q^*)^{-1}$ vs T^{-1} for SBS/PS5h blends of various weight fractions of PS5h, where $I(q^*)^{-1}$ is in arbitrary units, and T is the absolute temperature. Obviously, with the addition of the homopolymer, the data for the blends are shifted to higher values of T^{-1}. The shifts become more pronounced as the amount of PS5h increases in the blends, demonstrating that the respective spinodal temperatures are depressed as compared to that of neat SBS and decrease with increasing PS5h content in the blends. The onset where $I(q^*)^{-1}$ deviates from linearity is shifted to higher values of T^{-1}, suggesting that the microphase separation temperatures also decrease with increasing PS5h content for SBS/PS5h blends.

A completely different phenomenon is observed in Figure 5, where $I(q^*)^{-1}$ vs T^{-1} is plotted for SBS/PS3k blends. The data for all the blends in the disordered state are shifted to lower values of T^{-1} as compared to those of the neat SBS, suggesting that the respective spinodal temperatures are elevated as compared to that of SBS. The shifts increase with increasing PS3k content in the blends, demonstrating that the spinodal temperatures increase with increasing PS3k content in the blends. The onset where $I(q^*)^{-1}$ deviates from linearity is shifted to lower values of T^{-1}, too, indicating that the order–disorder transition temperatures increase with the addition of PS3k. Similar observations are obtained for SBS/PS5k blends, suggesting that the spinodal and order–disorder transition temperatures increase with increasing PS5k content in the blends.

Theoretically, there exists a critical homopolymer molecular weight, above which the microphase separation temperature increases with the addition of homopolymer, and below which the spinodal temperature decreases with the addition of homopolymer. The experimental observations shown in Figures 4 and 5 agree qualitatively with the theoretical predictions. However, the critical molecular weight is found to be much lower than the predicted value $M_A/4$, as no decrease of the spinodal temperature is observed in SBS/PS3k blends, where the molecular weight of the homopolymer is less than one-fourth the molecular weight of the PS block in the copolymer. The critical content, which has been predicted to exist in higher molecular weight homopolymer/triblock copolymer blends, has not been observed experimentally in SBS/PS3k and SBS/PS5k blends. This may be due to the fact that the amount of homopolymer added to the triblock copolymer is substantially lower than the expected critical content. However, a separate study on the transitions in SBS/poly(vinyl methyl ether) blends did reveal the existence

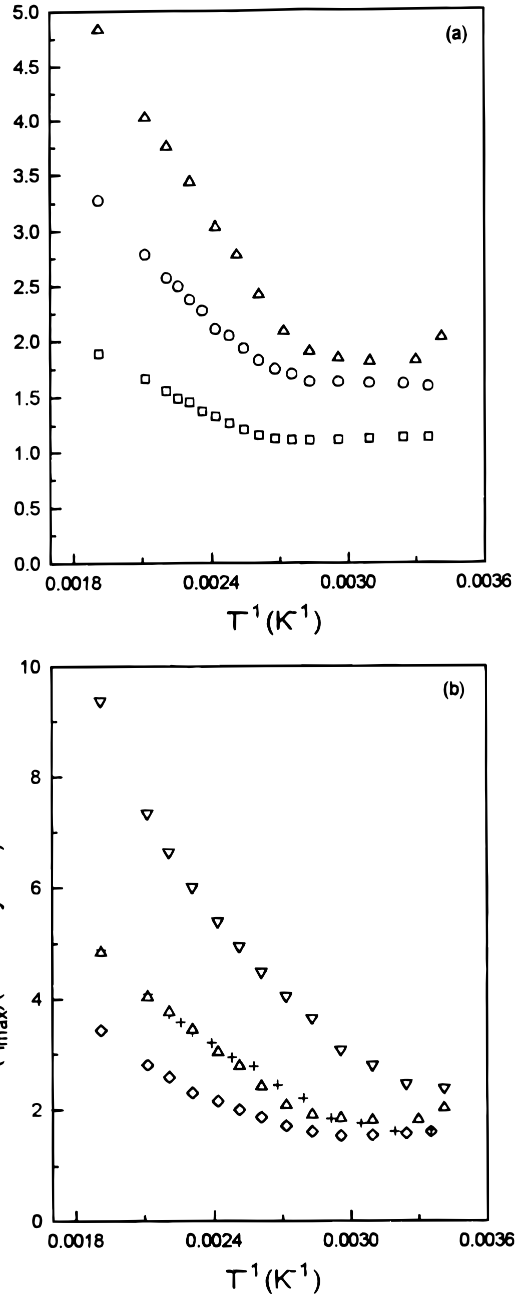

Figure 4. Plots of the reciprocal of observed peak intensity $I(q^*)$ against $1/T$, obtained with neat SBS and five mixtures containing various amounts of polystyrene of M_w 500: (△) SBS, (□) 5 wt %, (○) 10 wt %, (◇) 15 wt %, (+) 20 wt %, and (▽) 25 wt %.

of the critical content in the blends. The results for this system will be discussed elsewhere.

Composition Fluctuations near MST. Composition fluctuations near the microphase separation transition have been found to be important in diblock copolymers and were demonstrated theoretically by Fredrickson and Helfand[4] and experimentally by Bates et al.[17] After including the effect of composition fluctuations, Fredrickson and Helfand predicted a weak first-order character at $f = 0.5$ for diblock copolymers, and the microphase separation occurred at

$$(\chi N)_S = 10.495 + 41.022 N^{-1/3} \qquad (9)$$

Obviously, the fluctuation corrections diminish with increasing N, and in the limit $N \rightarrow \infty$, Leibler's theory is exactly recovered. Recently, Muthukumar performed a similar analysis using a density functional approach that addressed the effect of composition fluctuations on the entire block copolymer phase diagram.[5] According to Bates et al.,[17] such a correction caused a nonlinear relationship between $I(q^*)^{-1}$ and T^{-1} in the disordered state.

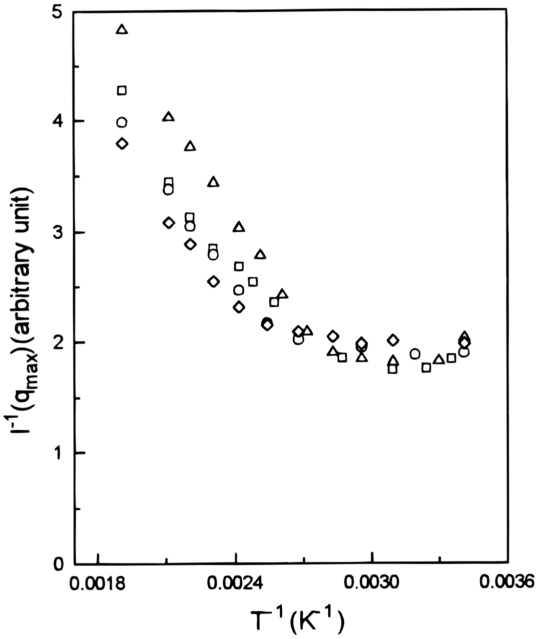

Figure 5. Plots of the reciprocal of observed peak intensity $I(q^*)$ against $1/T$, obtained with neat SBS and three mixtures containing various amounts of polystyrene of M_w 3000. The symbols have the same meaning as those in Figure 4.

From Figure 4, it is clear that composition fluctuations exist in triblock copolymer/homopolymer blends. The shape of the entire $I(q^*)^{-1}$ vs T^{-1} plot changes tremendously with the addition of homopolymers. For the blend containing 5 wt % PS5h, the plot of $I(q^*)^{-1}$ vs T^{-1} at high temperatures resembles fairly well a linear relationship. Deviation from linearity gets pronounced as more PS5h is added. For the blend containing 25 wt % PS5h, there is no linear portion over the entire investigated temperature range. Thus, with the increasing fractions of small molecular weight homopolystyrene in the blends, the composition fluctuations become stronger.

However, the deviation for SBS/PS3k blends is relatively minor as compared with that of SBS/PS5h blends. Figure 6 is the plot of $I(q^*)^{-1}$ vs T^{-1} for the SBS/PS5h and SBS/PS3k blends containing 15 wt % homopolystyrene, where the spheres and diamonds are the experimental data, and the lines are the linear fit of the data. In the two blends, the weight fraction of the added homopolystyrene is the same; only the molecular weight of the added polystyrene changes. For the blend of SBS/PS5h, the linear fit deviates from the curve obtained by nonlinear fitting of the experimental data in the disordered state. As for the SBS/PS3k blend, a fairly good linear relationship is observed. Thus, the composition fluctuations in the triblock copolymer/homopolymer blends depend on the molecular weight of the added homopolymer.

Clearly, composition fluctuation exists in block copolymer/homopolymer blends. It depends not only on the molecular weight of block copolymers but also on the molecular weight and composition of the added homopolymers. The fluctuations get stronger as the

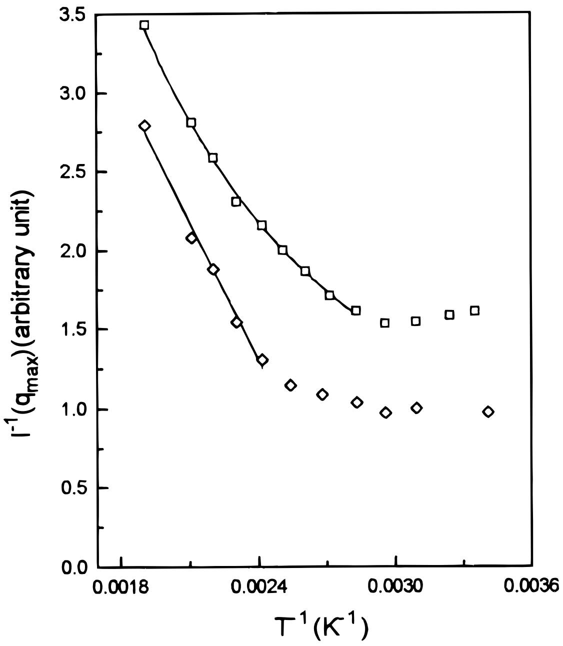

Figure 6. Plots of the reciprocal of observed peak intensity $I(q^*)$ against $1/T$, obtained with (□) SBS/PS5h and (◇) SBS/PS3k blends containing 15 wt % polystyrene, where T is the absolute temperature. To avoid crowding the plot, $1/I(q^*)$ points for SBS/PS3k were shifted downward along the y-axis by 1.0 unit.

composition of the added homopolymer increases and diminish when the molecular weight of the added homopolymer increases. As suggested by Fredrickson and Helfand, composition fluctuations diminish in the limit $N \to \infty$. Therefore, the above conclusions concerning the composition fluctuations in triblock copolymer/homopolymer blends seem reasonable.

Composition fluctuations in the disordered state make the precise determination of the spinodal temperatures difficult. It is necessary to develop a fluctuation-corrected theory for the triblock copolymer/homopolymer blends. Unfortunately, to our best knowledge, theories including composition fluctuation corrections for triblock copolymers and block copolymer/homopolymer blends are not available presently. However, since the entire plots of $I(q^*)^{-1}$ vs T^{-1} still represent the overall trends of the order–disorder transition, the MST investigations described above will still give faithful results.

It should be noted that, although the fluctuation corrections have not been taken into account in the theoretical analysis section, the theoretical analysis still gives reasonable results and agrees qualitatively with the experimental data. However, the theoretically determined critical molecular weight is much higher than that observed experimentally. One can expect that the theoretical result will get closer to the experimental one if the fluctuation corrections are made.

Temperature and Composition Dependence of χ Parameter. From Figure 4, it is clear that the slopes of the linear portions are different for blends containing different weight fractions of PS5h. For the blend containing 5 wt % PS5h, the linear portions have a slope less than that for the neat SBS. With the increase of PS5h in the blend, the slope for the linear portion increases. When the blend contains more than 20 wt % PS5h, the slope of the linear portion gets larger than that of SBS. It implies that the interaction parameter, χ_{AB}, has a different temperature dependence in blends containing different weight fractions of PS5h. However, the slopes of the linear portions of all the plots above the order–disorder transition temperature are similar for SBS/PS3k blends, as shown in Figure 5, which suggests that χ_{AB} has the same temperature dependence in the SBS/PS3k blends as in the neat SBS. From the results shown in Figures 4 and 5, it seems that the temperature dependence of χ_{AB} in SBS/PS blends can vary with the composition and molecular weight of the added homopolymer.

Table 2. Physical Parameters Adopted for Scattering Calculations[a]

specimen	ρ_{PS}, mol/m^3	ρ_{PB}, mol/m^3	N_{PS}	N_{PB}	b_{PS}, Å	b_{PB}, Å
SBS	10 100	16 400	257	1276	6.8	5.3

As indicated in the Prediction from RPA Theory section, under the RPA approximation, the scattering intensity is related to the structure factor by eq 1. By substituting eqs 2–7 into eq 1, one can find that the scattering intensity is a function of χ_{AB}. Thus, one can obtain the χ parameter at different temperatures by fitting of the SAXS profiles at the disordered state. As polydispersity has been shown to have an important effect on the expression of $F(q)$,[24,25] and the molecular weight distribution of the triblock copolymer used here is rather wide, the polydispersity effect is taken into account according to the procedure of Bates and Hartney.[26,27] $F(q)$ for SBS/PS5h blends was calculated from the known physical parameters, as shown in Table 2. However, it should be noted that the theoretical development employed here is based on the assumption that the Kuhn statistical segment lengths are 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 assumptions hold often for the block copolymer/homopolymer blends, where the molecular weight of the added homopolymer is relatively high. As for blends containing relatively low molecular weight homopolymers, the interaction parameter between the homopolymer and its unlike block is no longer equal to χ_{AB}, and the interaction parameter between the homopolymer and its like block will be not zero. The latter has been proved experimentally by Nakajima and Hamada[28] and Prime and Wunderlich[29] and will be the reason that the temperature dependence of χ_{AB} is affected by the molecular weight of the added homopolymers, as shown in Figure 4. In Owens's study, where the added PS had molecular weight larger than 1200, the authors found that χ_{AB} for the blends of HBS/PS had the same temperature dependence as the neat HBS diblock copolymer. In the SBS/PS3k blends, we also observed that χ_{AB} had the same temperature dependence as neat SBS. Thus, it seems that there is a critical homopolymer molecular weight above which χ_{AB} values for blends have the same temperature dependence as neat block copolymer. Combining the results of Owens with ours, the critical molecular weight for the added homopolymer seems to be less than 1200.

Although the assumptions may not apply for the SBS/PS5h blends for the reason indicated above, it is worthwhile to calculate the temperature and composition dependences in the blends on the basis of the theory proposed in the Predictions from RPA Theory section. We believe that the qualitative features of the dependence of χ_{AB} should be observable in a precise theoretical treatment. Figure 7 shows the scattering profiles of the SBS/PS5h blend containing 25 wt % PS5h at selected

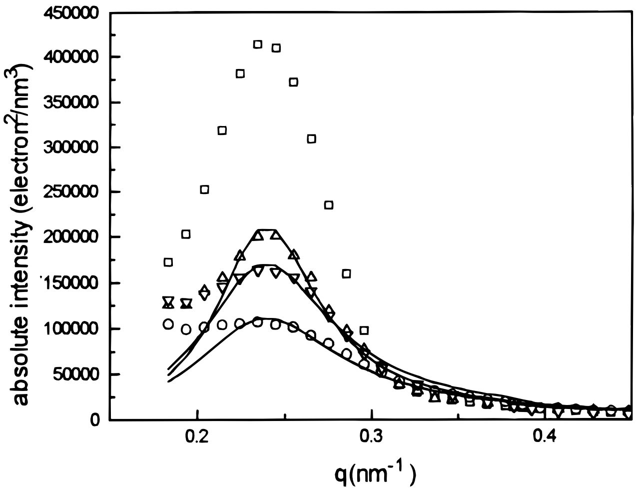

Figure 7. Scattering intensity observed at various temperatures for SBS/PS5h blends containing 25 wt % polystyrene of M_w 500. The solid curves are calculated from eqs 1−8, with the χ values adjusted to give the best fit to the peak intensity: 20 °C (□), 125 °C (△), 200 °C (▽), and 250 °C (○).

temperatures, where the symbols represent scattering intensities at different temperatures, and the solid lines are calculated from the theoretical eqs 1−7, with χ_{AB} adjusted to give the best fit to the peak intensity. There are three points worthy of noting in Figure 7: (1) The angle of maximum intensity, q^*, shows good agreement between the observed and the calculated intensity curves. (2) The degree of the fit for the data at 125 °C is different from that at higher temperatures. There is a deviation at angles larger than q^*, irrespective of the fact that the temperature is above the MST temperature. This can be ascribed to the chain stretching already in the disordered state when the temperature gets closer to the MST.[30] The stretching results in a change of the conformation from Gaussian. Since mean-field theory is based on the assumption that the conformation of block copolymers within the disordered state is Gaussian, the pretransitional stretching implies that the RPA theory is quantitatively invalid near the transition, even in the limit $N \rightarrow \infty$. (3) The observed intensity at angles smaller than q^* fits poorly with the calculated one. This may be attributed to the effect of composition fluctuations, which accounts for the deviation of the mean-field theory prediction from the experiment data,[17] and was found to existed even at temperatures much higher than the MST temperature.[23] The deviation of the fit at angles smaller than q^* can also result from the formation of the mesophase at temperatures near to the microphase separation temperature[11] or the macrophase separation at temperatures near to the spinodal of the macrophase separation. However, as no macrophase separation has been detected in this study, and the data used for the fit are within the disordered state, it seems that the deviation of the fit should be attributed to the composition fluctuation effect.

Table 3. Experimental Interaction Parameter Components for SBS/PS5h Blends

ϕ	χ_0	χ_b	$\chi_{(298\ K)}$
0.250[a]	0.01902	0.8603	0.02191
0.315	0.02156	0.433	0.02301
0.350	0.02229	0.573	0.02482
0.384	0.02249	0.954	0.02566
0.419	0.02311	1.165	0.02711

[a] Neat triblock copolymer SBS.

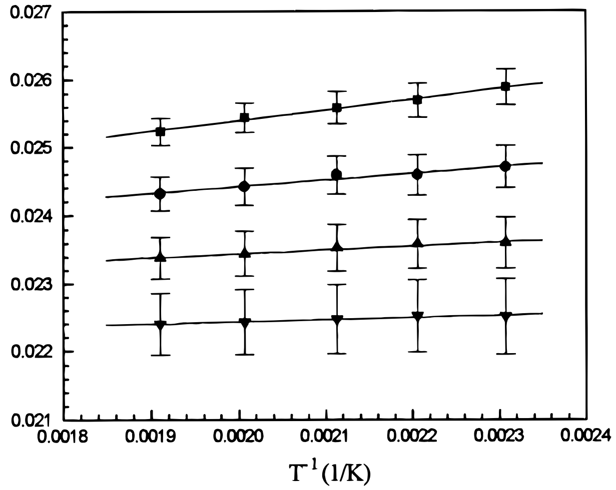

Figure 8. Experimental χ values for SBS/PS5h blends containing various weight fractions of polystyrene, plotted with $1/T$, where T is the absolute temperature: (■) 25 wt %, (●) 20 wt %, (▲) 15 wt %, and (▼) 10 wt %.

The χ_{AB} parameter for SBS/PS5h blends containing various weight fractions of PS5h, obtained by the theoretical fitting of the experimental intensity profiles, is displayed in Figure 8 as a function of reciprocal temperature. In the interval of temperatures studied, the χ parameter is a linear function of $1/T$ for blends containing various weight fractions of PS5h. However, with the change of the weight fraction of PS5h, the slope of the line changes, suggesting that the variation of χ with T depends on the composition of the blends. By fitting the experimental χ values with eq 8, χ_0 and χ_b can be determined. In Table 3, χ_0 and χ_b for neat SBS and SBS/PS5h containing various weight fractions of PS5h are listed. From Table 3, one finds that, with the increase of PS5h in the blends, χ_{AB} changes more pronouncedly with temperature. The value of the temperature-independent component χ_0 increases with increasing added homopolymers. This may be expected due to the entropic contributions of the added low molecular weight PS5h. χ_{AB} values for SBS and SBS/PS5h blends at 298 K are also included in Table 3 to illustrate the composition dependence. The value of χ_{AB} increases with the addition of PS5h, which can be understood considering that the miscibility between SBS and PS5h gets poor with increasing addition of PS. Furthermore, the values of χ_{AB} are much smaller than those reported by Hashimoto et al.,[13] Owens et al.,[14] and Howel and Ruland et al.,[31] who obtained the χ_{AB} parameter between polystyrene and polybutadiene from SB diblock copolymers. This discrepancy may be attributed to the difference in architecture between diblock and triblock copolymers. Hashimoto et al. have found that the value of the χ parameter of a six-arm star block copolymer is half that of its parent diblock copolymer.[13] Furthermore, the microstructure of PB block affects the PS−PB χ parameter. Experimental data suggest that the PS−PB interactions are more favorable for the 1,2 microstructure compared to the mixed microstructure. The value of the χ parameter for SB containing 95% 1,2 microstructure is 0.0629 at 298 K.[14] Based on these considerations, the χ value for SBS should be much smaller than 0.0629. Therefore, the values of χ listed in Table 3 seem to be reasonable.

In Figure 9, the χ_{AB} values for SBS/PS5h blends are replotted versus ϕ, the volume fraction of polystyrene in the blends. In the investigated region, χ_{AB} varies

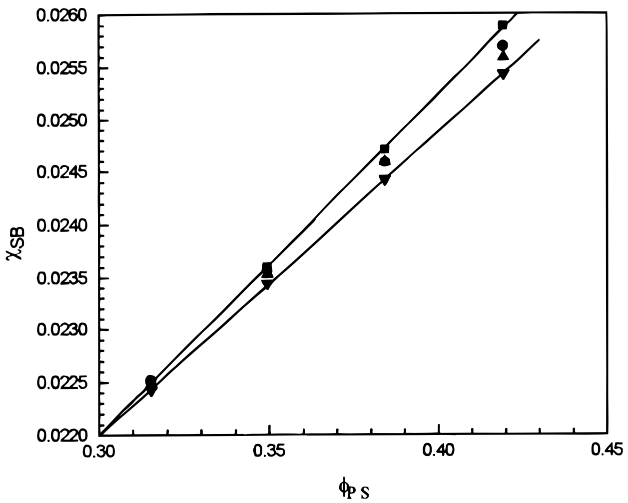

Figure 9. Experimental χ values for SBS/PS5h blends at various temperatures, plotted with the volume fraction of polystyrene in the blends: (■) 25 wt %, (●) 20 wt %, (▲) 5 wt %, and (▼) 10 wt %.

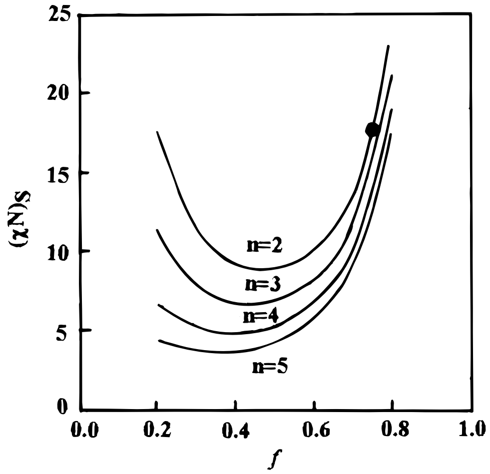

Figure 10. Comparison of spinodal condition for SBS (14 000−72 000−14 000) triblock copolymer with the theoretical predictions of Mayes and Olvera de la Cruz.[7]

linearly with ϕ, and the slope changes slightly as the temperature changes from 160 °C to 250 °C.

It is thus clear that the interaction parameter χ_{AB} is a function of temperature and composition. At given temperatures, χ_{AB} is a linear function of the composition, while at a defined composition, χ_{AB} is a linear function of the reciprocal temperature. The variation of χ_{AB} with T depends on ϕ, and the variation of χ_{AB} with ϕ depends on T. Therefore, it is worthwhile to obtain an empirical expression of χ_{AB} based on the assumption that

$$\chi_{AB}(T,\phi) = A + B\phi + C/T \qquad (10)$$

From the experimental χ_{AB} values of SBS/PS5h blends, we got

$$\chi_{AB}(T,\phi) = 0.01067 + 0.031\phi + 0.889/T \qquad (11)$$

where T is the absolute temperature and ϕ is the volume fraction of polystyrene in the blends.

The theory of Mayes and Olvera de la Cruz[7] predicts the spinodal condition as a function of copolymer architecture and interaction energy. The theoretical $(\chi N_0)_S$ at the spinodal is presented in Figure 10 for star copolymers with n arms of composition f and polymerization index N_0. The SBS(14 000−72 000−14 000) triblock copolymer has $n = 2$ arms and a fractional butadiene composition of $f = 0.75$. The theoretically predicted value for $(\chi N_0)_S$ is 17.5, as shown in Figure 10. Experimentally, the temperature dependence of χ for SBS can be obtained by a regression to the χ values determined in the nonlinear fitting of the experimental data, as stated previously and listed in Table 3. This procedure yields χ at the spinodal of 0.0216 and a $(\chi N_0)_S$ value of 17.3, which is in good agreement with the theoretical prediction. Koberstein et al. have also found an excellent agreement between the experimental result and the theoretical prediction in their study of the MST of a SEBS triblock copolymer.[15] In view of this, the χ values listed in Table 3 are faithful, though they are much smaller than those reported for SB diblock copolymers.

Conclusion

Using small-angle X-ray scattering technique, we studied the order−disorder transition in SBS/PS blends. It was found that the variation of MST temperature with composition depends on the ratio of the molecular weight of added homopolymer to that of the corresponded blocks in the copolymer. In SBS/PS blends, it was determined by the ratio of PS molecular weight to that of the PS blocks in SBS. This has been also demonstrated by theoretical calculations based on the random phase approximation theory. As suggested by the calculated results, for ABA/A systems, there exist a critical molecular weight and volume fraction of the added homopolymer. The spinodal temperature will decrease with ϕ_H as $M_H \le (M_H)_C$ and increase with ϕ_H as $M_H \ge (M_H)_C$ in the interval $0 < \phi_H < (\phi_H)_C$ and decrease with ϕ_H in the interval $\phi_H > (\phi_H)_C$. The microphase transition temperature will decrease with increasing added homopolymer if $N_H/N_A < 1/4$, and it will increase with increasing added homopolymer when $N_H/N_A > 1/4$. After fitting the scattering profiles with theoretical ones, we found that the interaction parameter was a function of temperature and composition, and that it varies with the molecular weight of the added homopolymer. The value of $(\chi N_0)_S$ for SBS found at the spinodal compares favorably with the theoretical prediction by Mayes and Olvera de la Cruz for star block copolymers with $n = 2$ arms.[7] Composition fluctuations were found to exist in SBS/PS blends, which increase with the increasing addition PS and decrease with the increasing molecular weight of added PS.

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