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Phase Behavior of Polystyrene and Poly(*n*-pentyl methacrylate) Blend with Small Amounts of Symmetric Polystyrene-*block*-poly(*n*-pentyl methacrylate) Copolymers

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ABSTRACT: The phase behavior of polystyrene and poly(*n*-pentyl methacrylate) (PS/PnPMA) blends with small amounts of symmetric PS-*block*-PnPMA copolymer (PS-*b*-PnPMA) was studied by turbidity, light scattering, and small-angle neutron scattering (SANS). At ambient pressure, PS/PnPMA with lower molecular weights exhibited both the upper critical solution transition (UCST) and the lower critical solution transition (LCST), and with increasing molecular weights of PS, an hourglass type of phase behavior was observed. When a very small amount (∼0.5 wt %) of symmetric PS-*b*-PnPMA is added to the blend, LCST increases but UCST decreases. This indicates that the miscibility window is expanded, and the PS-*b*-PnPMA acts as an effective compatibilizer in the PS/PnPMA blend. However, when the amount of symmetric PS-*b*-PnPMA is larger than a critical amount which depends on the molecular weight of block copolymers, the turbidity temperatures (T_b) for the LCST are essentially the same regardless of blend compositions. Thus, the turbidity temperature for the LCST of an asymmetric blend composition (for instance, 20/80 (w/w) or 80/20 (w/w) PS/PnPMA blend) with a symmetric PS-*b*-PnPMA was lower than that for another blend without the block copolymer, suggesting that the block copolymer does not act as a compatibilizer for asymmetric blend compositions. This interesting phase behavior was discussed in terms of the segmental interaction parameter (χ) measured by SANS and compared with predictions by the incompressible mean-field theory and the lattice cluster theory.

Introduction

The phase behavior of mixtures consisting of two homopolymers (A/B blend) and a block (A-*b*-B) copolymer has been extensively studied experimentally and theoretically.[1−11] While a full phase diagram for these mixtures can be obtained by self-consistent mean-field theories, the stability limit (or spinodal points) can be easily obtained from incompressible random phase approximation (RPA) theory.

In these mixtures, two types of spinodal points can be considered:[12−15] (i) a spinodal point for macrophase separation $(\chi N)_{\mathrm{s,macro}}$ where the scattering intensity $I(q)$ becomes infinite at $q = q_{\max} = 0$ and (ii) a spinodal point for microphase separation $(\chi N)_{\mathrm{s,micro}}$ where $I(q)$ becomes infinite at $q = q_{\max} \neq 0$. Here, q is a scattering vector and given by $(4\pi/\lambda) \sin \theta$, where 2θ is the scattering angle and λ is the wavelength. χ is Flory's interaction parameter between block components, and N is the total number of statistical segments of the block copolymer. A block copolymer becomes an effective compatibilizer in a polymer blend system with an upper critical solution temperature (UCST) if $\partial(\chi N)_{\mathrm{s,macro}}/\partial\phi_b > 0$, where ϕ_b is the volume fraction of a block copolymer in the mixture and is assumed to be much smaller than 1.[13] As $(\chi N)_{\mathrm{s,macro}}$ increases, the critical (or spinodal) temperature (T_c), above which the mixture becomes homogeneous, decreases for a blend with UCST-type phase diagram. Thus, at a given temperature the increased value of $(\chi N)_{\mathrm{s,macro}}$ means an expanded miscibility window (or better compatibilization) for two incompatible homopolymers.

Dudowicz and Freed[16] have developed the lattice cluster theory (LCT) to predict the phase behavior (thus the compatibilization effect) of an A/B blend in the presence of A-*b*-B. The phase diagram of an A/B blend exhibiting UCST (such as polystyrene [PS]/poly(methyl methacrylate) [PMMA] blend or PS/deuterated PS (dPS) blend) was shifted toward lower temperatures with increasing amounts of A-*b*-B, although the decrease was not large. Accordingly, the miscibility of an A/B blend is enhanced, suggesting that A-*b*-B acts as an effective compatibilizer. Also, the critical composition can move depending upon the volume fraction (f) of one block in the block copolymer.

Some research groups[17−19] showed that the turbidity temperature (T_b) of a polymer blend with UCST-type phase behavior decreases with increasing amount of block copolymer added, although the decrease is not large. According to Jackson et al.,[18] the UCST of a blend consisting of dPS with a weight-average molecular weight (M_w) of 1000 and poly(butadiene) (PB) with $M_w = 5360$ was decreased by as much as ∼15 °C when the amount of symmetric dPS-*b*-PB with M_w of 10 600 added was 8.6 wt %. Furthermore, the critical composition of dPS in the blend was shifted toward smaller value. These results are consistent with the predictions by the LCT theory.[16] Roe and Kuo[19a] found a small decrease (∼2 °C) in T_b for a 80/20 (w/w) PS/PB blend (the number-average molecular weight (M_n) of PS and PB was 1900 and 2650, respectively) when 1 wt % of a symmetric PS-*b*-PB with M_n of 25 000 was added.

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On the other hand, for a blend with LCST such as PS/poly(vinyl methyl ether) (PVME), the LCT theory predicts that the LCST decreases with increasing amount of symmetrical PS-*b*-PVME copolymer.[16] For instance, an addition of 0.03 wt % of PS-*b*-PVME to this blend decreased the LCST by as much as 140 °C. Furthermore, a UCST appeared and increased with increasing amount of PS-*b*-PVME, even though a UCST was not observed for the blend without adding PS-*b*-PVME. However, because of the difficulty in synthesizing high molecular weight PS-*b*-PVME, the prediction by the LCT theory for an LCST blend has not been verified experimentally yet.

Chen et al.[20] studied the compatibilization effect of a PMMA-*block*-poly(vinyl acetate) (PMMA-*b*-PVAc) in a PMMA/PVAc blend exhibiting an LCST. Depending upon the volume fraction of PMMA block in the PMMA-*b*-PVAc, the phase separation kinetics of the PMMA/PVAc blend in the phase-separating regime was either retarded or accelerated. They referred to the former as the compatibilization effect and the latter as the incompatibilization effect, and they tried to explain the behavior qualitatively within the frame of the incompressible RPA theory.[12,13] However, the equilibrium phase diagram of this blend system, including the change of LCST or T_b with the amount of added block copolymer, has not been reported.

It is of interest to compare the LCT results with experimental data for a blend having combinations of UCST and LCST because of the different driving forces present for phase separation. Fortunately, the PS/poly(*n*-pentyl methacrylate) (PnPMA) blend and the dPS/PnPMA blends exhibit this kind of phase behavior at ambient pressure.[21,22] For a lower molecular weight of PS (or PnPMA), the phase behavior is a combination of UCST and LCST, whereas an hourglass type of phase behavior is found for this blend with higher molecular weights.

Here, we investigate the phase behavior of PS/PnPMA blend in the presence of small amounts of symmetric PS-*b*-PnPMA (or dPS-*b*-PnPMA) block copolymer. Even though the symmetric PS-*b*-PnPMA (or dPS-*b*-PnPMA) employed in this study exhibits a closed loop phase behavior,[24−26] it is not likely that these block copolymers themselves self-assemble into lamellar microdomains in the blend because of the small amounts (<5 wt %). We also employed small molecular weight PS-*b*-PnPMA exhibiting disordered state at the entire temperature range to investigate the effect of total block length on the compatibilization and phase behavior of the PS/PnPMA blend. We found that the T_b of the LCST does not change with blend composition when the amount of PS-*b*-PnPMA is larger than a critical amount depending upon the molecular weight of PS-*b*-PnPMA. These results were discussed in terms of χ obtained from SANS and the incompressible RPA.[12−15]

Experimental Section

Homopolymers of PS and dPS were synthesized anionically in tetrahydrofuran (THF) at −78 °C under purified argon using *sec*-BuLi as an initiator, and PnPMAs was synthesized using an initiator prepared by *sec*-BuLi and 1,1-diphenylethylene under dried LiCl, as described previously.[25] Several symmetric PS-*b*-PnPMA and dPS-*b*-PnPMA copolymers were also prepared anionically by sequential addition of PS (or dPS) and PnPMA. The number- and weight-average molecular weights, M_n and M_w, respectively, of all the homopolymers as well as block copolymers used in this study were measured by size exclusion chromatography (SEC) with multiangle laser light scattering (MALLS) and are given in Table 1.

Table 1. Molecular Characteristics of PS, dPS, PnPMA Homopolymers and PS−PnPMA, dPS−PnPMA Block Copolymers Employed in This Study

sample code	M_n	M_w	M_w/M_n[a]
PS-L	6610	6810	1.03
PS-BH[b]	6960		
PS-H	7110	7270	1.02
dPS	9150	9250	1.02
PnPMA-L	7570	7700	1.02
PnPMA-M	7900	8030	1.02
PnPMA-H	8480	8650	1.02
PS-*b*-PnPMA-S[c]	14000	14420	1.03
PS-*b*-PnPMA-L[c]	33000	33990	1.03
PS-*b*-PnPMA-H[c]	52000	53040	1.02
dPS-*b*-PnPMA-M[c]	48000	48960	1.02

[a] Measured by multiangle laser light scattering combined with SEC. [b] PS-BH was prepared by blending of 70 wt % of PS-H and 30 wt % of PS-L. Since the M_w's for PS-H and PS-L differ by only 7.5% and their polydispersities (M_w/M_n) are less than 1.03, M_w/M_n's for PS-BH were also ∼1.03, which can be treated as a homopolymer. [c] The volume fraction of PS and dPS block in all block copolymers was 0.5.

Various blend compositions for the turbidity temperature (T_b) measurements were prepared by dissolving a predetermined amount of the mixtures in toluene (10 wt % in solute) and slowly evaporating solvent over 8 h at room temperature. The sample thickness was ∼10 μm. Each specimen was annealed in the homogeneous state (∼130 °C) for 4 h. The T_b of each blend was determined either by optical microscopy (OM, Axioplan, Zeiss Co.) or by the light scattering (LS) method using a heating stage blanketed in nitrogen. For LS experiment, the T_b for the LCST for a blend was determined by a threshold temperature above which light scattering intensity at 30° increased rapidly upon heating at a rate of 0.1 °C/min from the homogeneous state (at ∼110 °C). The T_b for the UCST was similarly estimated on cooling from a homogeneous state at a rate of 0.1 °C/min. The determination of both LCST and UCST by OM was described in a previous paper.[21] We found that the measured values of T_b by both methods are essentially the same, and the maximum error was ±0.5 °C.

Samples for SANS were prepared by compression-molding plaques at 100 °C followed by annealing at this temperature for 24 h under vacuum. SANS experiments were performed at the Hanaro Reactor (Korea) with a wavelength (λ) of 0.431 nm and $\Delta\lambda/\lambda = 0.12$ at a sample-to-detector distance of 3 m. Scattering intensities were collected on a 2-D area detector and then circularly averaged. The sample thickness was 1.0 mm, and the exposure time was 30 min.

Results and Discussion

Figure 1 shows changes of light scattering intensity with temperature for 50/50 (w/w) PS−BH/PnPMA-L without and with 3 wt % of PS-*b*-PnPMA-H. As previously reported,[21] the PS-BH/PnPMA-L blend without PS-*b*-PnPMA exhibited a combination of LCST (143 °C) and UCST (107 °C). With the addition of PS-*b*-PnPMA-H, the LCST increased, whereas the UCST decreased. These results are not consistent with the LCT theory.[16] The increase in LCST (∼55 °C) at a 3 wt % of PS-*b*-PnPMA-H is larger than the decrease in UCST (∼20 °C). It is consistent with prediction by LCT theory[16] that the change of LCST of a blend at a given amount of a block copolymer is much larger than that of UCST of another blend. The results given in Figure 1 indicate that PS-*b*-PnPMA-H acts as an effective compatibilizer of PS/PnPMA blends, in that miscibility window of this blend becomes wider with increasing amounts of PS-*b*-PnPMA-H. It should be noted that the UCST was measurable at temperatures below the T_g of PS−BH (∼90 °C), since the blend T_g in the homogeneous state

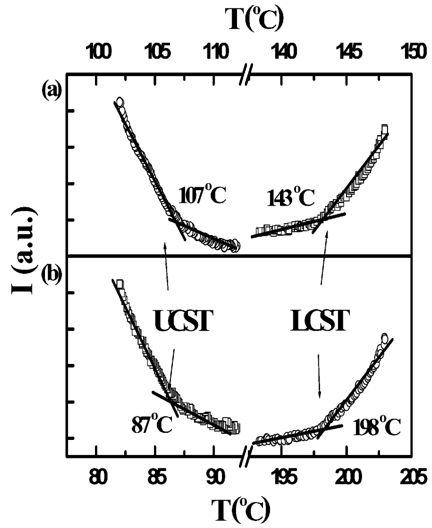

Figure 1. Changes of light scattering intensity with temperature for 50/50 (w/w) PS-BH/PnPMA-L blend without (a) and with 3 wt % of PS-*b*-PnPMA-H (b).

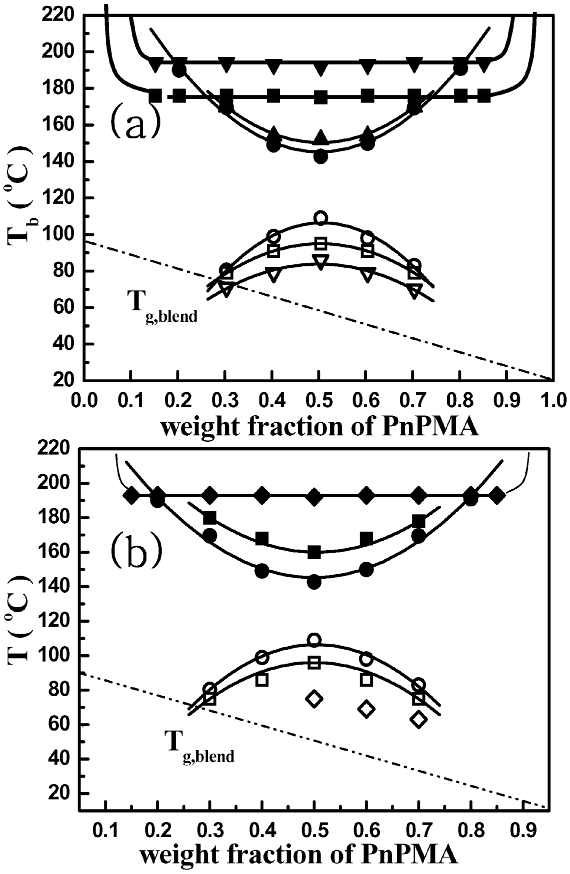

Figure 2. Phase diagrams of PS-BH/PnPMA-L blend with various amounts of PS-*b*-PnPMA-H (a) and PS-*b*-PnPMA-S (b). The amounts of the block copolymer in the mixture are (wt %) (○ and ●) 0, (▲) 0.1, (□ and ■) 0.5, (▽ and ▼) 3, and (◇ and ◆) 5. The open and closed symbols represent the UCST and the LCST of the mixture, respectively. The dashed curve of $T_{g,\mathrm{blend}}$ of the blend is the prediction by the Fox equation.

was lower than the T_b of the UCST, as was previously reported.[21]

On the basis of Figure 1, the phase behavior of PS-BH/PnPMA-L blends with various amounts of PS-*b*-PnPMA-H is shown in Figure 2a. Very interestingly, when the amount of PS-*b*-PnPMA-H is larger than 0.5 wt %, T_bs of LCST curves of blends with $0.15 < w_{\mathrm{PnPMA}} < 0.85$ are essentially the same regardless of w_{PnPMA}. Here, w_{PnPMA} is the weight fraction of PnPMA homopolymer in the PS-BH/PnPMA blend without taking account of the PnPMA block of the copolymer, and it is very similar to the volume fraction (ϕ_{PnPMA}) of PnPMA homopolymer in the blend because of very close densities of PS and PnPMA (1.05 and 1.03 cm^3/g at room temperature). When the w_{PnPMA} lies outside this range, we cannot measure T_b at temperatures below ~270 °C, which is close to the degradation temperature for PnPMA. Since the T_b for the LCST become flat, with increasing amount of PS-*b*-PnPMA-H, the miscibility of highly asymmetric blend compositions (for instance, $w_{\mathrm{PnPMA}} = 0.15$ and $w_{\mathrm{PnPMA}} = 0.85$) decreases, whereas that for symmetric blend compositions increases.

The miscibility change with blend composition has been theoretically predicted by the RPA theory for the A/B/A-*b*-B ternary blend.[13,15] For instance, the phase diagam of mixtures of A/B and symmetric A-*b*-B given in Figure 1b in ref 15 shows that the miscibility of the mixture decreases when the blend composition of homopolymer A (ϕ_A) in the mixture becomes asymmetric ($\phi_A < 0.2$ or $\phi_A > 0.8$). Thus, the results given in Figure 1 are qualitatively consistent with RPA predictions. However, even though predicted curves of $(\chi N)_{s,\mathrm{macro}}$ as a function of ϕ_A become flatter with increasing amounts of A-*b*-B, the complete flatness (namely, the values of $(\chi N)_{s,\mathrm{macro}}$ not changing with ϕ_A) could not be achieved even when the volume fraction of A-*b*-B in the mixture was as large as 0.3.

On the other hand, Figure 2a in this study shows that T_b for the UCST curves decreased gradually with increasing the amount of added PS-*b*-PnPMA-H up to 3 wt %. We could not measure T_b for UCST of asymmetric compositions due to the proximity to the T_g of the blend. Nonetheless, when the amount of PS-PnPMA-H is larger than 0.5 wt %, the change of T_b for the UCST with w_{PnPMA} is quite different from that for the LCST.

Park and Roe[19b] showed that, in order for a PS-*b*-PB to retard the phase separation kinetics for PS/PB blend, the ordered-to-disordered transition temperature of the block copolymer should be larger than the experimental temperature. However, they did not investigate the change of T_b with different molecular weights of PS-*b*-PB since the amount of added block copolymer was very small. To test the effect of molecular weight, we employed PS-*b*-PnPMA-L, which showed phase-mixed state over the entire temperature range. We found that the phase behavior for PS-BH/PnPMA-L in the presence PS-*b*-PnPMA-L was essentially the same as that for the blend with PS-*b*-PnPMA-H. A decrease in M_w from 52 000 (PS-*b*-PnPMA-H) to 33 000 (PS-*b*-PnPMA-L) does not much change the T_b of the blend. This is because M_w of blend components are still small in comparison with PS-*b*-PnPMA-L, which is classified as a wet-brush regime.

Figure 2b shows phase diagrams of PS-BH/PnPMA-L blend with low molecular weight (14 000) PS-*b*-PnPMA-S, whose M_w is very similar to the combined molecular weights of the two homopolymers (PS-BH (6960) and PnPMA-L (7570)). We found that the addition of 3 wt % of PS-*b*-PnPMA-S increased the T_b of the LCST for the entire blend compositions. But, at a higher content (5 wt %) of PS-*b*-PnPMA-S, the T_bs of the LCST are essentially the same for all blend compositions and very similar to the T_bs of the blend with 0.5 wt % of PS-*b*-

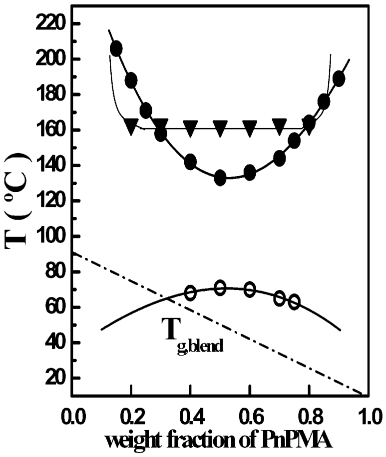

Figure 3. Phase diagram of dPS/PnPMA-M blend without (○ and ●) and with 3 wt % (▼) of dPS-*b*-PnPMA-M.

PnPMA-H. Thus, the ratio of molecular weight of a block copolymer to that of homopolymers (N_C/N_H) affects the phase behavior more than the ability of microdomain formation of a block copolymer at experimental temperatures.

We now consider why the T_bs for the LCST do not depend on w_{PnPMA} when the amount of added symmetric block copolymer is greater than a critical value which depends on the molecular weight of the block copolymer. It might be argued that it is possible to form the micelles of PS-*b*-PnPMA in just one component (or in both components) of the blend near T_b. However, when a 95/5 (w/w) PS-BH/PS-*b*-PnPMA-H mixture and a 95/5 (w/w) PnPMA-L/PS-*b*-PnPMA-H mixture were prepared, we did not observe any increase in the light scattering intensity for these two mixtures up to 240 °C. Since it is possible that micellization could occur without affecting light scattering intensity, we carried out a small-angle X-ray scattering (SAXS) experiment. We could not detect any peak corresponding to a bicontinuous microemulsion or micelles in SAXS profiles for three blend compositions (20/80, 50/50, and 80/20 (w/w) PS-BH/PnPMA-L) with 3 wt % of PS-*b*-PnPMA-H. This suggests that micelle formation of PS-*b*-PnPMA-H in PS-BH/PnPMA-L blends should be hardly expected. It is noted that a square-well type of phase behavior in which the LCST was not changed with blend composition was seen in the poly(ethylene oxide) (PEO)/water mixture. However, in this blend, the change of the strong intermolecular hydrogen bonding occurs near the same temperature regardless of blend compositions.[27] It is considered that the subtle change in free volume (and/or directional entropy) by the addition of the block copolymer might be the main source of the flat phase behavior of the LCST for PS/PnPMA blend.

We employed SANS experiments to obtain the temperature dependence of χ for PS/PnPMA blend in the presence of PS-*b*-PnPMA. The phase diagram of dPS/PnPMA-M blend without and with 3 wt % dPS-*b*-PnPMA-M is shown in Figure 3. Without the block copolymer, the phase behavior was a combination of an LCST at 133 °C and a UCST at 71 °C. At 3 wt % of dPS-*b*-PnPMA-M, the turbidity temperatures for LCST are essentially the same regardless of w_{PnPMA}, which is the same phenomenon observed in the PS/PnPMA blend with 3 wt % of PS-*b*-PnPMA-H.

Figure 4a shows the SANS profiles ($I(q)$ vs q) for 50/50 (w/w) dPS/PnPMA-M blend with 3 wt % of dPS-*b*-PnPMA-M as a function of temperature. It is seen that with increasing temperature the SANS intensity ($I(q)$) at all wavelengths (0.08–0.5 nm^{-1}, although SANS intensities up to 0.3 nm^{-1} are shown in Figure 4a) first decreased, went through a minimum, and then increased again. The absolute SANS scattering intensity, $d\Sigma(q)/d\Omega$, is given by [28]

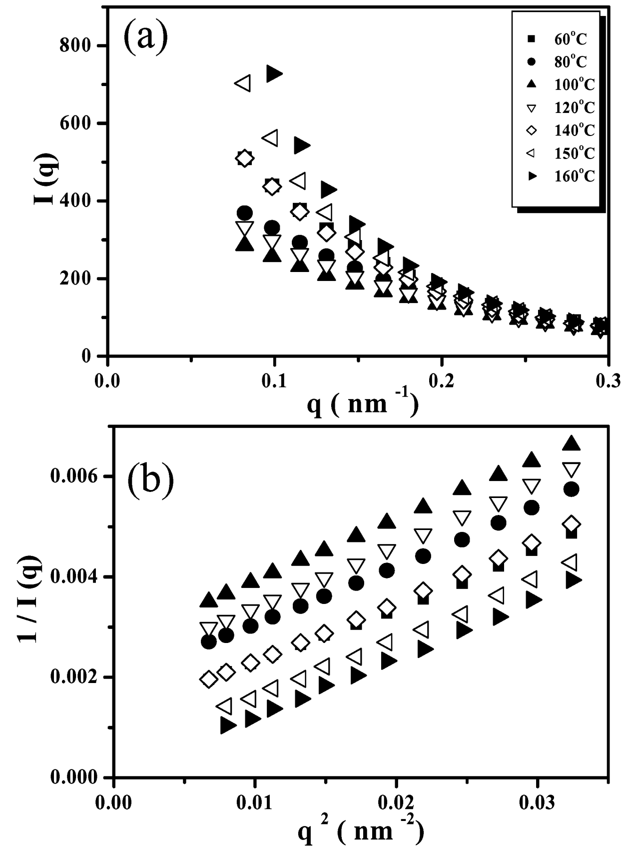

Figure 4. (a) Plots of $I(q)$ vs q and (b) plots of $1/I(q)$ vs q^2 at various temperatures for 50/50 (w/w) dPS/PnPMA-M blend with 3 wt % of dPS-*b*-PnPMA-M.

$$I(q) = \frac{d\sum(q)}{d\Omega} = v_{ref}\left(\frac{b_1}{v_1} - \frac{b_2}{v_2}\right)^2 \tilde{S}(q) \qquad (1)$$

where v_{ref} is the reference volume, b_i the neutron coherent scattering length, v_i the monomeric volume for component i, and $\tilde{S}(q)$ the structure factor. From the incompressible RPA, $\tilde{S}(q)$ for the ternary mixture consisting of A/B blend and A-*b*-B copolymer is given by[12–15]

$$\tilde{S}(q) = 1/[S_2(q)/W_2(q) - 2\chi] \qquad (2)$$

where

$$S_2(q) = S_{AA}(q) + 2S_{AB}(q) + S_{BB}(q) \qquad (3a)$$

$$W_2(q) = S_{AA}(q)S_{BB}(q) - [S_{AB}(q)]^2 \qquad (3b)$$

$$S_{AA}(q) = \phi_C N_C g(f,N_C) + \phi_{HA} N_{HA} g(1,N_{HA}) \qquad (3c)$$

$$S_{BB}(q) = \phi_C N_C g(1-f,N_C) + \phi_{HB} N_{HB} g(1,N_{HB}) \qquad (3d)$$

$$S_{AB}(q) = (1/2)\phi_C N_C[1 - g(f, N_C) - g(1-f,N_C)] \qquad (3e)$$

Here, f is the volume fraction of A block in A-*b*-B. $N_C(\phi_C)$, $N_{HA}(\phi_{HA})$, and $N_{HB}(\phi_{HB})$ are the total number of segments (volume fraction) of A-*b*-B, A, and B homopolymers in the mixtures, respectively. N_C is defined by $(V_{PS} + V_{PnPMA})/v_{ref}$, in which v_{ref} is the reference volume taken as the $(v_{sp,PS}[M]_{0,PS}v_{sp,PnPMA}[M]_{0,PnPMA})^{1/2}$. $v_{sp,i}$ and $[M]_{0,i}$ (i = PS, PnPMA) are the specific volume and monomer molecular weight of component i, respectively. $g(f_i,N_i)$ is the Debye function and given by

$$g(f,N_i) = 2[f x_i + \exp(-f x_i) - 1]/x_i^2 \qquad (4a)$$

$$x_i = (qR_{gi})^2 = q^2 l_i^2 (N_i/6) \qquad (4b)$$

in which R_{gi} and l_i are the radius of gyration and Kuhn length of component i. Notice that in the derivation of eq 2 the χ of dPS and PnPMA segments in the blend is assumed to be the same as that in the block copolymer, even though χ obtained from the blend might not be the same as that obtained from the block copolymer.[29]

For the mixture employed in this study, $I(q=0)$ can be determined using the Ornstein–Zernike equation[28]

$$\frac{d\sum(q)}{d\Omega} = I(q) = I(0)/(1 + (q\xi)^2) \qquad (5)$$

where ξ is the correlation length for the concentration fluctuation. We found that eq 5 is also valid for A/B/(A-*b*-B) mixtures at small q regions, as shown in Figure 4b. Although dPS-*b*-PnPMA-M has a maximum SANS intensity at $q \sim 0.28$ nm^{-1}, SANS intensity for dPS-*b*-PnPMA-M at a given q was negligibly small compared with that for dPS/PnPMA blend at small q ($<\sim 0.16$ nm^{-1}) (see Supporting Information). When the amount of block copolymer is less than 3 wt %, the contribution of dPS-*b*-PnPMA-M at $q < 0.2$ nm^{-1} to SANS intensity was found to be less than a few percent of that of the blend without block copolymer (see Supporting Information). Once $I(0)$ (and thus $\tilde{S}(0)$ from eq 1) is known, χ is given by

$$\tilde{S}(0)^{-1} = \frac{\phi_{HA}V_{HA} + \phi_{HB}V_{HB} + \phi_C V_C}{\phi_{HA}V_{HA}\phi_{HB}V_{HB} + \phi_C V_C[(1-f)^2\phi_{HA}V_{HA} + f^2\phi_{HB}V_{HB}]} - 2\frac{\chi}{v_{ref}} \qquad (6)$$

Figure 5a,b shows plots of $1/I(0)$ and $1/\xi^2$ vs inverse temperature for various blend compositions of dPS/PnPMA-M blend without and with 3 wt % of dPS-*b*-PnPMA-M. For all mixtures, with increasing temperature, the miscibility (or $1/I(0)$ and $1/\xi^2$) first increases and reaches a maximum (near 100 °C) and then decreases. This is consistent with phase behavior of the combination of LCST and UCST for a blend with lower molecular weights and hourglass type of phase behavior for another blend with higher molecular weights. $I(0)$ for 50/50 (w/w) dPS/PnPMA-M blend with 3 wt % of dPS-*b*-PnPMA-M is smaller than that without the block copolymer. Interestingly, $I(0)$ at the entire temperature range for 30/70 (w/w) dPS/PnPMA-M with 3 wt % of dPS-*b*-PnPMA-M is larger than that without the block copolymer, even though the T_b of the LCST for the former mixture (163 °C) is larger than that (~148 °C) of the latter, as shown in Figure 3. Thus, a symmetric block copolymer does not act as an effective compatibilizer for an off-critical blend composition. It was reported that the miscibility of a mixture of low molecular weights with an additive can be enhanced when an additive is soluble in both components, while the miscibility is reduced when another additive is more soluble in one component.[30]

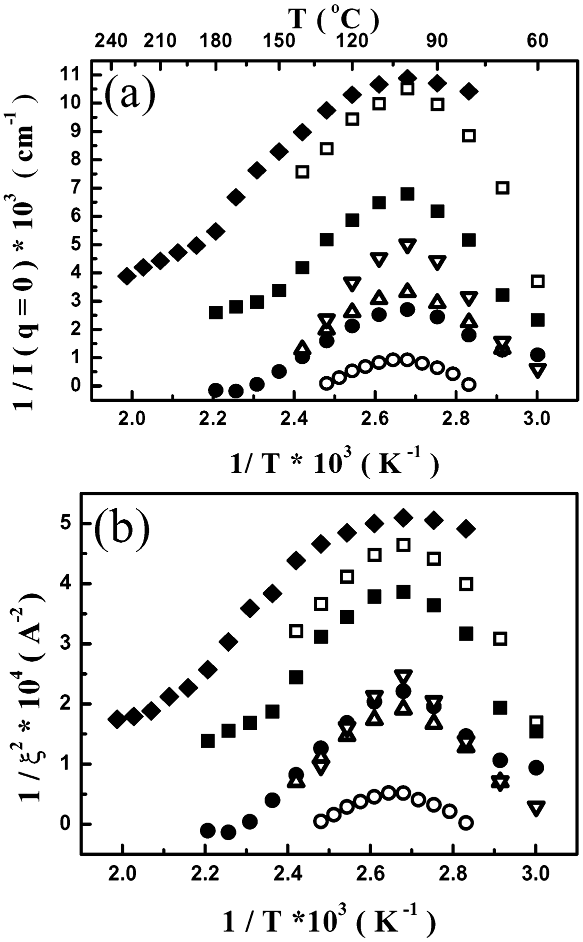

Figure 5. Plots of (a) $1/I(0)$ and (b) $1/\xi^2$ vs $1/T$ for various blend compositions of dPS/PnPMA-M blend without (open symbols) and with 3 wt % of dPS-*b*-PnPMA-M (closed symbols): (○ and ●) 50/50 (w/w) dPS/PnPMA-M; (□ and ■) 30/70 (w/w) dPS/PnPMA-M; (▽) 35/65 (w/w) dPS/PnPMA-M; (△) 65/35 (w/w) dPS/PnPMA-M; (◆) 80/20 (w/w) dPS/PnPMA-M.

Figure 6 shows the temperature dependence of χ obtained from eqs 1 and 6 for various compositions of d-PS/PnPMA-M without and with 3 wt % dPS-*b*-PnPMA-M. The dotted lines in Figure 6 are χ_s obtained from eq 6 with $S^{-1}(0) = 0$ for various mixtures. It is seen in Figure 6 that with increasing T (or decreasing $1/T$) χ for all mixtures first decreases, goes through a minimum, and then increases again. This behavior is observed in lower molecular weight blends with both a LCST and a UCST and in higher molecular weight blends with an hourglass type of phase behavior. When there is no dPS-*b*-PnPMA-M, χ of the off-critical composition (35/65 and 65/35 (w/w) dPS/PnPMA-M) is larger than that of the critical composition, which is commonly seen in polyethylene isotope blends.[31,32]

It is seen that χ obtained from 50/50 (w/w) dPS/PnPMA-M without block copolymer is very similar to that obtained from the same blend with 3 wt % of dPS-*b*-PnPMA-M. The spinodal temperatures (T_s) are usually obtained from a plot of $1/I(0)$ (and $1/\xi^2$) vs $1/T$, since this plot give a linear line. However, $1/I(0)$ vs $1/T$, and thus χ vs $1/T$, plots showed a maximum, as shown in Figure 5; thus, one could not obtain a linear line. Although two separate linear lines at higher and lower

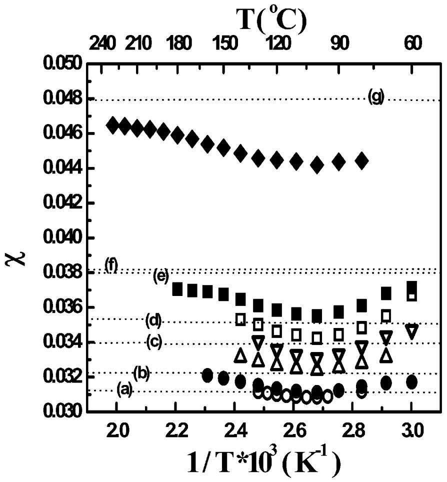

Figure 6. Temperature dependence of χ for various blend compositions of dPS/PnPMA-M blend without and with dPS-*b*-PnPMA-M. The symbols are the same as those in Figure 5. The predicted values of χ at the spinodal points for various blend compositions are also added as lines. (a) 50/50 (w/w) dPS/PnPMA-M (○); (b) 50/50 (w/w) dPS/PnPMA-M with 3 wt % of dPS-*b*-PnPMA-M (●); (c) 65/35 (w/w) dPS/PnPMA-M (△); (d) 35/65 (w/w) dPS/PnPMA-M (▽); (e) 30/70 (w/w) dPS/PnPMA-M (□); (f) 30/70 (w/w) dPS/PnPMA-M with 3 wt % of dPS-*b*-PnPMA-M (■); and (g) 80/20 (w/w) dPS/PnPMA-M with 3 wt % of dPS-*b*-PnPMA-M (◆).

temperature regimes might be obtained for 35/65, 65/35, and 50/50 (w/w) dPS/PnPMA-M blends without dPS-*b*-PnPMA-M as well as 50/50 (w/w) dPS/PnPMA-M blend with 3 wt % of dPS-*b*-PnPMA-M, in this study, two empirical expressions, (i) $\chi = a + b/T + c/T^2$[33] and (ii) $\chi = a' + b'/T + c' \ln T$,[34,35] are used to estimate the T_s. We found that the T_s obtained from two empirical expressions of χ is almost the same as that obtained from the two separate linear lines for the above blends. Since $c > 0$ and $b < 0$ (also, $c' > 0$ and $b' > 0$), this blend exhibits phase behavior of a combination of the LCST and UCST. Using two expressions, the values of T_s for the LCST and UCST are estimated to be 134 and 70 °C, respectively, for 50/50 (w/w) dPS/PnPMA-M, while the LCST for 50/50 (w/w) dPS/PnPMA-M with 3 wt % of dPS-*b*-PnPMA-M is estimated to be 162 °C. These values are almost the same as those measured by the turbidity since this blend composition is close to the critical composition. Furthermore, these values are the same as those obtained from the temperatures where $1/I(0)$ becomes zero. Similarly, we estimated the T_s for the LCST and UCST for 65/35 (w/w) and 35/65 (w/w) dPS/PnPMA-M blends to be 163 and 56 °C for the former and 150 and 56 °C for the latter.

However, the determination of T_s of the LCST for 30/70 (w/w) and 80/20 (w/w) dPS/PnPMA-M with 3 wt % of dPS-*b*-PnPMA-M is not straightforward even though two empirical equations for χ are used. This is because the rate of decrease of $1/I(0)$ or $1/\xi^2$ with increasing temperature at high temperature regions changes dramatically at ~150 °C. $1/I(0)$ at temperatures higher than 150 °C decreases slowly; thus, one might not have a temperature where $1/I(0)$ becomes zero, even at very high temperatures (say 240 °C). It was previously shown that the χ measured by SANS and the mean-field RPA for dPS/PnPMA as well as dPS-*b*-PnPMA does not increase steadily at higher temperature; rather, χ becomes a maximum near ~200 °C.[23,25] Then, the spinodal temperature corresponding to infinite SANS intensity might not exist for asymmetric blend composition, especially in the presence of a small amount of dPS-*b*-PnPMA-M. This result might be consistent with the statement made by Dudowicz and Freed that the critical exponents describing the intensity and scale of the critical fluctuations as well as the shape of the coexistence curve can be changed with the addition of a symmetric diblock copolymer to a polymer blend.[16] Further investigation should be carried out why the spinodal of asymmetric blend composition, especially in the presence of a diblock copolymer could not be measured by SANS.

Conclusion

In this study we have shown that the phase behavior of PS/PnPMA blend was dramatically changed even if small amounts of symmetric PS-*b*-PnPMA were added. When a very small amount (~0.5 wt %) of symmetric PS-*b*-PnPMA is added to the blend, LCST increases but UCST decreases. This indicates that the miscibility window is expanded, and the PS-*b*-PnPMA acts as an effective compatibilizer on PS/PnPMA blend. However, when the amount of symmetric PS-*b*-PnPMA is larger than a critical amount which depends on the molecular weight of the block copolymers, the turbidity temperatures (T_b) for the LCST are essentially the same regardless of blend compositions. Thus, the turbidity temperature for the LCST of an asymmetric blend composition (for instance, 20/80 (w/w) or 80/20 (w/w) PS/PnPMA blend) with a symmetric PS-*b*-PnPMA was smaller than that for another blend without the block copolymer, suggesting that the block copolymer acts as incompatibilizer for asymmetric blend compositions. We found that with increasing T (or decreasing $1/T$) χ first decreases, then goes through a minimum, and then increases again.

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Supporting Information Available: SANS profiles and $N_{cs2}(q)/W_2(q)$ vs q of neat dPS-*b*-PnPMA-M and 30/70 (w/w) dPS/PnPMA-H blend without and with 3 wt % of dPS-*b*-PnPMA-M. This material is available free of charge via the Internet at http://pubs.acs.org.

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