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Closed-Loop Phase Behavior for Weakly Interacting Block Copolymers

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ABSTRACT: Polystyrene-*block*-poly(*n*-butyl methacrylate) copolymer (PS-*b*-PnBMA) exhibits only a lower disorder-to-order transition (LDOT), not a closed-loop phase behavior, within an experimentally accessible temperature range. But, when mixed solvents of di-*n*-octyl phthalate and hexadecane were added to PS-*b*-PnBMA, this mixture exhibited the upper order-to-disorder transition (UODT) below the degradation temperature as well as an LDOT above the glass transition temperatures of both blocks; thus, a close-loop phase behavior was observed. These results suggest that the closed-loop phase behavior may be a general phenomenon for weakly interacting polystyrene-*block*-poly(*n*-alkyl methacrylate) copolymers with LDOT.

1. Introduction

Closed-loop (or immiscibility loop) phase behavior is a rarely observed but, nonetheless, very interesting phenomenon. This has been observed in some small molecule mixtures,[1−3] mixtures of ionic molecules,[4] polymer blends,[5,6] and certain polymer solutions with strong interactions such as hydrogen bonding.[7,8] Furthermore, it has also been observed for liquid crystals[9,10] and protein denaturation.[11,12] In protein/water systems, protein folding related to the phase-separated state was observed within an immiscibility loop. The closed-loop phase behavior was recently found for a weakly interacting polymer system of polystyrene-*block*-poly(*n*-pentyl methacrylate) copolymer (PS-*b*-PnPMA), exhibiting both a lower disorder-to-order transition (LDOT) at a low temperature and an upper order-to-disorder transition (UODT) at a high temperature.[13−19] However, when the carbon number of the alkyl group is slightly changed, PS-*block*-poly(*n*-alkyl methacrylate) copolymers with $n = 2$ (ethyl), 3 (propyl), and 4 (butyl) exhibited only LDOT, not a closed loop, within an experimentally accessible temperature range.[20−22]

For weakly interacting polymer systems, the origin of the LDOT (or lower critical solution transition (LCST)) might be twofold.[7] The first is a free volume effect arising from the difference in compressibilities of the two components (or the equation-of state variables). In this situation, with increasing temperature the degree of phase separation increases because of the increased free volume effect. The second is related to the directional entropy. At lower temperatures, there are weak interactions and the free energy gain, though small, can surpass the directional entropic loss due to the special positioning of two dissimilar chains. With increasing temperature the directional entropic loss becomes large, which results in the LDOT (or LCST). At higher temperatures, unless the translational (or combinatorial) entropy of mixing prevails over the free volume effect and unfavorable interactions between dissimilar monomers, the homogeneous state might not be expected (see Figure 1a) because the weak interaction becomes negligible at higher temperature. On the other hand, closed-loop phase behavior has been theoretically predicted for polymer systems.[23−26] In particular, Dudowicz and Freed[25] predicted the existence of a closed-loop phase behavior in PS-*b*-poly(vinyl methyl ether) copolymer. They suggested that the UODT may exist above the degradation temperature (T_d) for weakly interacting polymer systems with the LDOT, which is the case depicted in Figure 1b.[25] The experimental proof of this premise is, however, not simple due to the temperature limit set by degradation. The appearance of the homogeneous state at higher temperatures has been the key issue in understanding the complete closed-loop phase behavior of weakly interacting block copolymers (or polymer blends).

To verify experimentally the phase diagram given in Figure 1b, the UODT must be shifted below the degradation temperature (T_d), while the LDOT must be kept higher than the glass transition temperature (T_g) of both blocks. It is well-known that the order/disorder transitions of a block copolymer can be changed by static pressure (p), absorption of compressive solvents, and solvents with high boiling points. However, the first two methods are not suitable to depress the UODT to an experimentally accessible temperature, since the decrease rate of UODT with p is very similar to the increase in the LODT with p.[16] So, when the midpoint of a close loop is above T_d, the UODT is never shifted to a temperature lower than T_d, while keeping the LDOT higher than T_g. Also, the absorption of compressive solvents such as supercritical CO_2 depressed the LDOT greatly but the ODT of some block copolymers slightly;[27] thus, their UODTs might still be above T_d. If the UODT is

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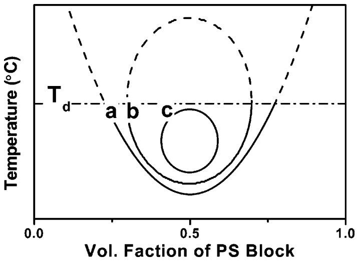

Figure 1. Various phase behaviors of weakly interacting block copolymers: (a) the LDOT is induced by a free volume effect, where a reentrant homogeneous phase might not be expected even at higher temperatures; (b) the LDOT is induced by the combination of the free volume effect and directional entropy, where a UODT might exist above the degradation temperature (T_d); (c) the closed-loop phase behavior with LDOT $> T_g$ and UODT $< T_d$.

greatly reduced, while the LDOT is not changed much, which is the case of Figure 1c, a closed-loop phase behavior is seen at an experimentally accessible temperature.

In this study, we show experimentally that when mixed solvents of di-*n*-octyl phthalate and hexadecane were added to PS-*b*-PnBMA, this mixture exhibited the UODT occurring below the degradation temperature as well as the LDOT occurring at temperatures above the T_gs of both blocks; thus, a close-loop phase behavior was observed. These results would be applicable to all the weakly interacting polystyrene-*block*-poly(*n*-alkyl methacrylate) copolymers with an LDOT.

2. Experimental Section

A symmetric PS-*b*-PnBMA copolymer was prepared by successive addition of styrene and *n*-butyl methacrylate monomers at −78 °C in tetrahydrofuran under an argon environment by using *sec*-BuLi as an initiator.[28] The number-average molecular weights (M_n) and the polydispersity index were 71 600 and 1.05, respectively, measured by size exclusion chromatography combined with a multiangle laser light scattering. The PS block composition was 0.5, determined by nuclear magnetic resonance. It is known that PS-*b*-PnBMA exhibits the phase behavior with LDOT.[20−22,28] The solvents of di-*n*-octyl phthalate (DOP) and hexadecane ($C_{16}H_{34}$) were purchased from Aldrich Chemical Co. The block copolymer/solvent mixtures were prepared using methylene chloride (CH_2Cl_2) as a cosolvent. The CH_2Cl_2 was removed first under a gentle flow of nitrogen and then under mild vacuum until a constant weight was achieved.

SAXS experiments were performed on Beamlines 4C1 and 4C2 at the Pohang Light Source (Korea), where a W/B4C double multilayer monochromatic delivered monochromatic X-rays on the samples with a wavelength of 0.1608 nm.[29] A 2-D CCD camera (Princeton Instruments Inc. SCX-TE/CCD-1242) was used to collect the scattered X-rays. Samples (thickness 1.0 mm) were prepared by compression-molding at 50 °C and subject to a constant heat rate of 1.0 °C min^{-1}.

Depolarized transmitted light (static birefringence)[30] was used to determine the ordered transition of neat PS-*b*-PnBMA and PS-*b*-PnBMA/solvent mixtures. Vertically polarized light from a HeNe laser passes through the sample and a horizontal analyzing polarizer onto a photodiode. Samples with a thickness of 1.0 mm and a diameter of 5 mm were covered by two glass disks and then subjected to a slowly increasing temperature rate (1.0 °C min^{-1}).

The turbidity points (T_b) of PS/$C_{16}H_{34}$ and PnBMA/$C_{16}H_{34}$ blends were measured by optical microscopy (OM, Axioplan, Zeiss Co.) using a heating block blanketed in nitrogen. The number-average molecular weights (M_n) and the polydispersity indices of PS and PnBMA homopolymers were 19 000 and 1.05 and 22 000 and 1.04, respectively. The blends were prepared using methylene chloride (CH_2Cl_2) as a cosolvent and then removing the cosolvent until a constant weight was achieved. The turbidity point was first estimated by the threshold temperature, above which phase-separated structures were not observed under the OM with a magnification of 400× upon heating at a rate of 1 °C/min. Once T_b of a specimen was estimated, the exact T_b was determined by OM with a stepwise change of 1 °C near the T_b; thus, the maximum error in T_b would be less than ±1 °C.

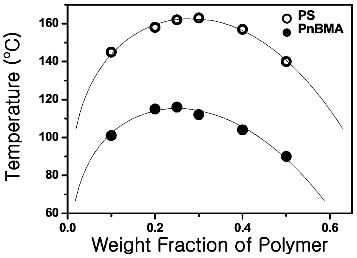

Figure 2. Turbidity curves for PS/$C_{16}H_{34}$ and PnBMA/$C_{16}H_{34}$ solutions. Solid lines are drawn based on the Flory−Huggins lattice theory with eq 1a and eq 1b, respectively.

3. Results and Discussion

Figure 2 gives turbidity curves for PS/$C_{16}H_{34}$ and PnBMA/$C_{16}H_{34}$ solutions. Using the turbidity point measurement together with the Flory−Huggins theory, we obtained the interaction parameter α (in mol/cm^3) for these two blend systems:

$$\alpha_{PS/C_{16}H_{34}} = 0.958 \times 10^{-3} + (0.705 + 0.336\phi_{PS})/T \tag{1a}$$

$$\alpha_{PnBMA/C_{16}H_{34}} = 0.985 \times 10^{-3} + (0.599 + 0.269\phi_{PnBMA})/T \tag{1b}$$

where ϕ_{PS} is the volume fraction of PS in PS/$C_{16}H_{34}$ solution, ϕ_{PnBMA} is the volume fraction of PnBMA in PnBMA/$C_{16}H_{34}$ solution, and T is the absolute temperature. The solid lines in Figure 2 are the binodal curves calculated from the Flory−Huggins theory with the aid of eq 1. In calculating the binodal curves, we used the specific volumes (in cm^3/g) of PS (0.952), PnBMA (0.957), and $C_{16}H_{34}$ (1.294). The predicted bimodal curves are in good agreement with measured turbidity curves. It is seen in Figure 2 that the upper critical solution transition of PnBMA/$C_{16}H_{34}$ solution was 110 °C, 50 °C lower than that of PS/$C_{16}H_{34}$ solution, even though the molecular weight (22 000) of PnBMA is slightly larger than that (19 000) of PS. From this result as well as the comparison of eq 1a with eq 1b, we consider that $C_{16}H_{34}$ is a slightly more selective solvent for PnBMA block than for PS block. However, we could not observe any turbidity above 50 °C for the PS-*b*-PnBMA/$C_{16}H_{34}$ mixture, even if the weight fraction of $C_{16}H_{34}$ in the mixture was increased to 0.2. On the other hand, DOP acts as a nonselective solvent for both PS and PnBMA blocks,[27] since both PS and PnBMA homopolymers are completely miscible with DOP.

Figure 3 shows static birefringence of neat PS-*b*-PnBMA. Since the volume fraction of PS in the copolymer is 0.5 and the microdomains are lamellar, the transition between nonbirefringence and birefringence can be considered as the lower disorder-to-order transition (LDOT).[30] It is clear that the copolymer exhibited the LDOT at 147 ± 1 °C, and a disordered state was not achieved up to 300 °C (close to the degradation temperature).

Figure 4 shows the temperature dependence of depolarized light intensity for (a) 85/15/2.7 (w/w/w) PS-*b*-PnBMA/$C_{16}H_{34}$/DOP and (b) 85/15/3.9 (w/w/w) PS-*b*-PnBMA/$C_{16}H_{34}$/DOP mixtures. Because of the nature of lamellar microdomain, a birefringence is only observed in the ordered phase.[30] Therefore, the abrupt increase in the intensity signifies an LDOT, whereas

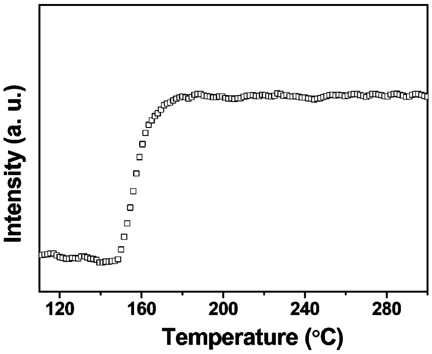

Figure 3. Temperature dependence of depolarized light intensity for neat PS-*b*-PnBMA employed in this study.

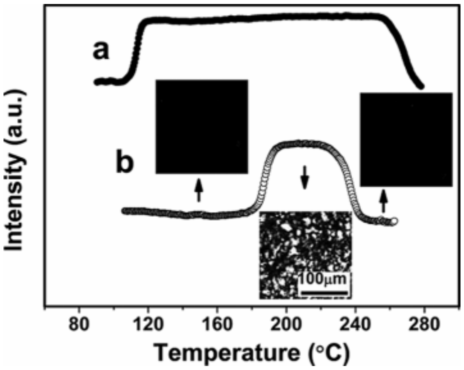

Figure 4. Temperature dependence of depolarized light intensity for two mixtures: (a) 85/15/2.9 (w/w/w) PS-*b*-PnBMA/$C_{16}H_{34}$/DOP mixture and (b) 85/15/3.9 (w/w/w) PS-*b*-PnBMA/$C_{16}H_{34}$/DOP mixture. The inset gives POM images at 140, 220, and 250 °C. The curve (a) was vertically shifted to avoid overlap.

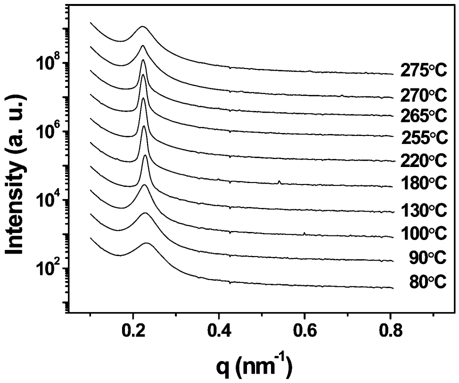

Figure 5. SAXS profiles at various temperatures for 85/15/2.7 (w/w/w) PS-*b*-PnBMA/$C_{16}H_{34}$/DOP mixture.

the abrupt decrease signifies a UODT. This is the experimental proof that both mixtures showed the closed-loop phase behavior.

Figure 5 gives SAXS profiles $I(q)$ vs q ($q = (4\pi/\lambda)\sin\theta$, where 2θ is the scattering angle and λ is the wavelength) at various temperatures for the 85/15/2.7 (w/w/w) PS-*b*-PnBMA/$C_{16}H_{34}$/DOP mixture. To avoid overlap, the SAXS profiles are shifted vertically by a factor of 5. In Figure 5 it is seen that the first-order peak is sharper at temperatures between 100 and 265 °C and broader at all other temperatures. We could not observe higher order peaks even though the expose time was increased to 30 min. This is due to small difference in the electron densities between PS and PnBMA blocks. The ordered state in all mixtures exhibits lamellar microdomain due to the symmetric volume fraction of PS-*b*-PnBMA.

Figure 6 gives the plots of the inverse of the SAXS intensity ($1/I(q_{\max})$) and the full width at half-maximum (fwhm) of the first-order peak vs the inverse of the temperature ($1/T$) for 85/15/2.7 (w/w/w) PS-*b*-PnBMA/$C_{16}H_{34}$/DOP mixture. A rapid decrease in $1/I(q_{\max})$ and fwhm at 100 °C corresponds to the LDOT, and a rapid increase in $1/I(q_{\max})$ and fwhm at 265 °C corresponds to the UODT. These two temperatures are essentially the same as those obtained from Figure 4.

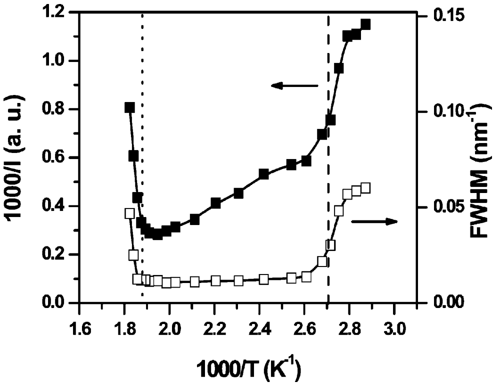

Figure 6. Plots of $1/I(q^*)$ (filled symbol) and fwhm (open symbol) vs $1/T$ for 85/15/2.7 (w/w/w) PS-*b*-PnBMA/$C_{16}H_{34}$/DOP mixture.

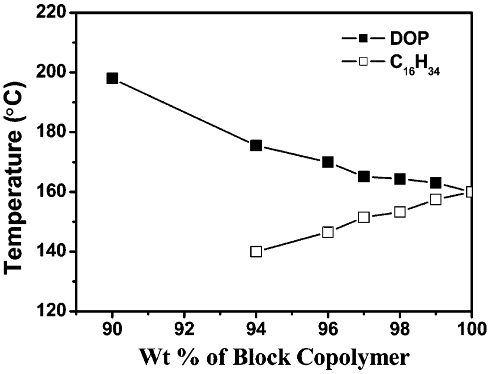

Figure 7. Change of the LDOT of PS-*b*-PnBMA/DOP mixture (■) and PS-*b*-PnBMA/ $C_{16}H_{34}$ mixture (□) as a function of weight fraction of the block copolymer.

The reason why the closed-loop phase behavior of a block copolymer with a LDOT was observed by adding mixed solvents can be qualitatively explained by using the total Gibbs free energy of mixing (ΔG_m), which consists of three terms (ΔG_m^0, ΔG_{FV}, and ΔG_{SI}). Here, ΔG_m^0, ΔG_{FV}, and ΔG_{SI} are the conventionally defined Flory–Huggins free energy of mixing expressed by $\Delta G_m^0 = \Delta H_m^0 - T\Delta S_m^0$, the free volume contribution term, and the specific favorable interaction contribution term, respectively.[1,26] It is noted that the source of the weak interactions in PS-*b*-PnBMA has not been studied yet. However, we previously showed, via Fourier transformed infrared spectroscopy, that PS-*b*-PnPMA ($n = 5$) has a weak interaction arising from the dipoles of the PS block and induced dipoles of the PnPMA block.[32] We assume that a similar type of a weak interaction exists in PS-*b*-PnBMA.

When a nonselective solvent, such as DOP, is added to PS-*b*-PnBMA, as shown in Figure 7, the increasing LDOT suggests the increasing miscibility between PS and PnBMA, thus the decreasing total Gibbs free energy of mixing (ΔG_m). Here the positive ΔG_m^0 term should become smaller due to screening unfavorable interactions by the solvent along with an increase in ΔS_m^0 in the presence of the solvent.[31] Although the screening effect by the solvent decreases the favorable specific interaction term (ΔG_{SI}), this term contributes less than the decrease in ΔG_m^0. Also, ΔG_{FV} does not change much because the disparity of thermal expansion coefficients (α) between PS

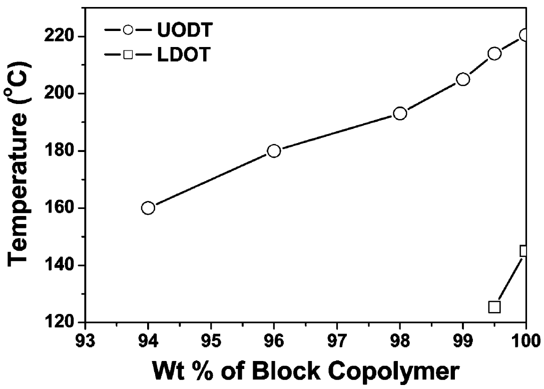

Figure 8. Changes of the LODT (□) and UODT (○) of the PS-*b*-PnPMA ($n = 5$)/$C_{16}H_{34}$ mixture as a function of weight fraction of the block copolymer.

and PnBMA would not change due to the approximately equal partitioning of the neutral solvent into each block. Therefore, the total Gibbs free energy of mixing (ΔG_m) decreases, producing the elevated LDOT and the depressed UODT.

On the other hand, when a selective solvent of $C_{16}H_{34}$ is added, the decreasing LDOT shown in Figure 7 indicates a stabilization of the ordered phase. Here, we must first consider the free volume contribution (corresponding to the term ΔG_{FV}). In the literature, the values of thermal expansion coefficient (α) for PS, PnBMA, and $C_{16}H_{34}$ at temperatures higher than their respective T_gs are 5.6×10^{-4}, 6.7×10^{-4}, and 10.4×10^{-4} (1/K), respectively.[33] Since the solvent of $C_{16}H_{34}$ partitions more selectively into the PnBMA block than the PS block, the difference in α between PS and PnBMA in the mixture increases, which increases the free-volume disparity. This effect stabilizes the ordered state near the LDOT. Also, favorable directional interactions (corresponding to the term ΔG_{SI}) are screened by selective solvents, analogous to the "$\Delta\chi$" effect in PS/poly(vinyl methyl ether) (PVME) blends;[34−36] thus, the phase-separated (or ordered) state is stabilized. In PS/PVME blends, the LCST decreased with addition of the highly selective solvents.[36] This is because the contribution of the increase in ΔS_m^0 (thus decreasing free energy of the mixing) with the addition of a solvent would be smaller than the free volume effect as well as the screening effect of the favorable interaction. Combining these factors, $C_{16}H_{34}$ should decrease the LODT of PS-*b*-PnBMA.

However, the UODT of PS-*b*-PnBMA at various amounts of $C_{16}H_{34}$ was not observed at an experimentally accessible temperature, as shown in Figure 7. To compare the effect of $C_{16}H_{34}$ on both the LDOT and UODT, we employed PS-*b*-PnPMA ($n = 5$) exhibiting both LDOT and UODT at experimentally accessible temperatures. The changes of the LDOT and UODT of PS-*b*-PnPMA/$C_{16}H_{34}$ mixtures with the addition of $C_{16}H_{34}$ are given in Figure 8. It is seen in Figure 8 that the addition of $C_{16}H_{34}$, which is a selective solvent for PnPMA block compared with PS block, decreases both the UODT and the LODT of PS-*b*-PnPMA. When the amount of $C_{16}H_{34}$ is 1 wt %, the LDOT is lower than 120 °C, which is the lower limit to measure the LODT due to proximity to the T_g of PS block. At a given amount of $C_{16}H_{34}$, the decrease of the UODT of PS-*b*-PnPMA/$C_{16}H_{34}$ mixture is smaller than the decrease of the LDOT of the same mixture. Here the decreasing UODT suggests that the decrease in ΔG_m^0 due to the large values of ($-T\Delta S_m$) should overcome over free energy penalty driven by ΔG_{FV} as well as the screening effect. Similarly, it is also expected that the addition of $C_{16}H_{34}$ decreases the UODT of PS-*b*-PnBMA. The decrease of the UODT would smaller than the decrease of the LDOT. According to the experimental results as well as the above-mentioned total Gibbs free energy of mixing containing four different contributions, the change in the LDOT is more sensitive to the solvent selectivity. Addition of a solvent decreases the UODT, but it decreases or increases the LDOT depending on the solvent selectivity. When the selectivity of a solvent is delicately controlled by using two solvents, here $C_{16}H_{34}$ and DOP, the LDOT can be kept slightly changed while the UODT shifts below T_d; thus, a closed-loop phase behavior can be observed within experimentally accessible temperature range ($T_g < T < T_d$).

In conclusion, we introduced a simple, but powerful, method to prove experimentally the existence of an UODT above the degradation temperature for PS-*b*-PnBMA by using mixed solvents of $C_{16}H_{34}$ and DOP. Together with the ODT observed previously below the LDOT,[28] this helps to construct the complete phase behavior for PS-*b*-PnBMA. Also, this leads us to conclude that the series of PS-*b*-poly(*n*-alkyl methacrylate) copolymers with $n = 2-4$ would exhibit a closed-loop phase behavior once a proper solvent (or solvent mixture) is used. The experimental results shown here indicate that it is possible to predict quantitatively (not phenomenologically) a closed-loop phase behavior in weakly interacting polymer systems by modifying the Flory−Huggins theory taking into account the directional entropy (or enthalpy) and the free volume effect.

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