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Complex Phase Behavior of a Weakly Interacting Binary Polymer Blend

Du Yeol Ryu,[†] Dong Hyun Lee, Jin Jang, and Jin Kon Kim*

National Creative Research Initiative Center for Block Copolymer Self-Assembly and Department of Chemical Engineering, Electronic and Computer Engineering Divisions, Pohang University of Science and Technology, Kyungbuk 790-784, Korea

Kristopher A. Lavery and Thomas P. Russell*

Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003

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The phase behavior of polymer blends has been studied extensively,[1−22] both experimentally and theoretically. Two types of phase transitions have been reported in terms of the temperature dependence of the segmental interaction parameter, χ: the upper critical solution transition (UCST), above which two polymers mix, and the lower critical solution transition (LCST), above which two polymers phase separate. A number of polymer blends, such as polystyrene (PS) and poly(vinyl methyl ether) (PVME),[23−25] exhibit LCST-type behavior. Since the LCST-type phase behavior cannot be explained by Flory's mean field theory alone, equation-of-state theories[9−17] have been developed to include differences in the thermal expansion coefficients of the components and/or specific interactions. The LCST is characterized by a negative volume change on mixing (ΔV_{mix}), resulting in enhanced miscibility with increasing hydrostatic pressure (P).

Recently, we showed that the weakly interacting PS/poly(*n*-pentyl methacrylate) blend exhibits both a UCST and an LCST.[26] On the other hand, PS-*block*-poly(*n*-pentyl methacrylate) copolymers [PS-*b*-PnPMA] exhibit closed-loop phase behavior, where the lower disorder-to-order transition (LDOT) and upper order-to-disorder transition (UODT) curves form the lower and upper bounds of the closed loop.[27−29] With increasing temperature, the copolymer was found to undergo a transition from the disordered to the ordered state at T_{LDOT} and then pass from the ordered state back into the disordered state at T_{UODT}.

The major difference in the phase behavior of PS/PnPMA blends from that of PS-*b*-PnPMA copolymers is the lack of evidence of an upper critical solution transition (u-UCST) above an observed LCST in the blend system, i.e., closed-loop phase behavior. Such phase behavior has not been observed in any polymer/polymer mixture, although the lattice cluster theory which includes the effect of the monomer structure and interaction asymmetry on phase behavior can predict the existence of the closed-loop phase behavior for special polyolefin blends.[13,16] One obvious reason for this is that one or both of the components decompose at temperatures less than the $T_{\mathrm{u-UCST}}$. Alternatively, as noted by Dudowicz and Freed,[15] the $1/N$ contribution to χ for block copolymers, arising from the connectivity of the blocks, becomes important when compared with the corresponding polymer blend. Here, N is the total number of repeat segments in the polymer. As a result, the u-UCST would not be observable, even at very high temperatures.

One means of obtaining access to a u-UCST in PS/PnPMA blends is by use of hydrostatic pressure (P). Previously, it was shown that both the LDOT and UODT of dPS-*b*-PnPMA are quite sensitive to P, where $\mathrm{d}T_{\mathrm{LDOT}}/\mathrm{d}P = 725$ °C/kbar and $\mathrm{d}T_{\mathrm{UODT}}/\mathrm{d}P = -725$ °C/kbar.[30] If the pressure coefficients for the LCST and u-UCST are of similar magnitude to those in the block copolymer system, the mixtures of PS and PnPMA should become increasingly miscible with increasing P, bringing the u-UCST into an experimentally accessible temperature.

Here, we report the complex phase behavior of the weakly interacting deuterated PS (dPS) and PnPMA blend system. It is shown that at higher P this blend exhibits a closed-loop phase behavior. With increasing P, the size of the closed loop decreases and vanishes when $P > 200$ bar. In addition, the UCST was observed to decrease with increasing P. The pressure coefficients of the LCST and the u-UCST in the closed loop are similar in magnitude to those for the LDOT and UODT found in the PS-*b*-PnPMA copolymer. This is the first experimental evidence illustrating the complex phase behavior consisting of a closed loop and a UCST for a weakly interacting polymer/polymer blend system.

The results presented in this study indicate that as long as the free volume effects are significantly suppressed by P, a blend exhibiting an LCST should become homogeneous at higher temperatures since the translational (or combinatorial) entropic contribution can, in principle, prevail over the combination of the repulsive interaction and the negative entropic contributions due to the free volume. The experimental observation of a closed loop, in conjunction with a UCST, for dPS/PnPMA blends is consistent with the result that the segmental interaction parameter χ_{eff}, determined from random phase approximation fits to small-angle neutron scattering data, shows a minimum followed by a maximum and finally a continuous decrease with increasing temperature.

Polystyrene (PS-BH) and dPS were synthesized anionically in tetrahydrofuran (THF) at −78 °C under purified argon using *sec*-BuLi as an initiator. Two PnPMA's (PnPMA-L, PnPMA-M) were synthesized anionically in THF containing excess dried LiCl at −78 °C using an initiator prepared by *sec*-BuLi addition to 1,1-diphenylethylene. The number- and weight-average molecular weights, M_{n} and M_{w} respectively, of all homopolymers used in this study were determined by size exclusion chromatography (SEC) combined with multiangle laser light scattering (MALLS) and are given in Table 1.[26]

Various blend compositions for the turbidity temperature (T_{b}) measurements were prepared by dissolving a predetermined amount of the mixtures in toluene (10 wt %) and slowly evaporating the solvent at room temperature for 12 h. All samples were annealed at 100 °C under vacuum for 1 day. The sample was melt-pressed into a disk with a thickness of 0.5 mm and a

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[†] Present address: Polymer Science and Engineering Department, University of Massachusetts at Amherst.

* To whom correspondence should be addressed. E-mail: jkkim@postech.ac.kr; russell@mail.pse.umass.edu.

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Table 1. Molecular Characteristics of PS, d-PS, and PnPMA Homopolymers Employed in This Study

sample code	M_n	M_w	M_w/M_n
PS-BH	6960	7200	1.04
d-PS	9150	9250	1.02
PnPMA-L	7570	7700	1.02
PnPMA-M	7900	8030	1.02

radius of 14 mm. The specimen was then loaded into the pressure cell and sandwiched between two sapphire windows. The T_b's for the LCST at various P were measured from the sudden increase in light scattering intensity at a scattering angle of 30° upon heating the mixture from 100 °C at a rate of 0.1 °C/min. Once the T_b of a specimen was estimated, the exact T_b was determined by turbidity measurements using a temperature increment by 0.5 °C near the temperature of interest. The specimen was held at each temperature for 1 h for the LCST measurement and for 5 h for the UCST measurement due to the proximity of the glass transition temperature (T_g) of the blend. The maximum error in the values of T_b determined was less than ±0.5 °C.

T_b as a function of P for the u-UCST was obtained as follows. First, a series of blends were prepared in phase-mixed state at higher pressures (>500 bar). The temperature was then raised to ~260 °C while maintaining a high pressure. The pressure was then slowly decreased. At a particular pressure, the temperature was decreased at a rate of 1 °C/h. As soon as the sample became turbid, that temperature was taken as T_b for the u-UCST. The T_b found by observing sample turbidity was the same as that determined by an abrupt increase in the light scattering intensity upon cooling at a given pressure. However, without first establishing a phase-mixed state at a high pressure, a u-UCST could not be obtained clearly upon heating. Once significant phase separation at high temperatures occurred, a perfect phase-mixed state could not be reached, even with the application of a high P. This is due to the long time required for a phase-separated blend to reach an equilibrium phase-mixed state. Therefore, once phase separation occurred near the transition temperature, the transition could be reversible.

SANS experiments were performed at the NIST NG3-SANS beamline with neutrons of a wavelength, λ, of 0.6 nm and a sample to detector distance of 13.1 m. The SANS was collected on a 2D position-sensitive detector and was circularly averaged. The sample, 1.5 mm in thickness, was loaded between two sapphire windows with four Teflon backing rings and two FETFE O-rings on both sides of the sample. Scattering data were collected from 70 to 240 °C in increments of 10 °C. At each temperature a series of pressure measurements were made. SANS curves were found to be identical whether the pressure or temperature was increased or decreased.

Cloud point curves for dPS/PnPMA-M at various P are shown in Figure 1. At ambient P, the blend exhibited both a UCST and an LCST at 71 °C and 133 °C, respectively. The UCST was measurable at temperatures below the T_g (~90 °C) for dPS since the blend T_g in the phase mixed state was lower than T_b, as indicated by the dashed line in Figure 1. Similar phase behavior was observed for the hydrogenated PS/PnPMA blend.[26] At ambient P, only a phase-separated mixture was seen above the LCST with no indication of mixing at higher temperatures. By increasing P, though, the closed-loop-type phase behavior was clearly evident, and the size of the loop decreased significantly with increasing P. Ultimately, at pressures greater than 200 bar, the blends were homogeneous (phase-mixed) over the entire temperature range. This suggests that the entropic penalty arising from the difference in free-volume (or equation-of-state variables) for dPS and PnPMA, the driving force for phase separation, is reduced with increasing P. Thus, at higher T the gain in combinatorial entropy prevails over the above-mentioned entropic penalty. Unfortunately, the turbidity curve for the lower-UCST for dPS/PnPMA-M at higher P could not be detected, even at 50 bar. Thus, the blend is fully phase-mixed up to the T_g (~50 °C) of the homogeneous blend at P > 50 bar.

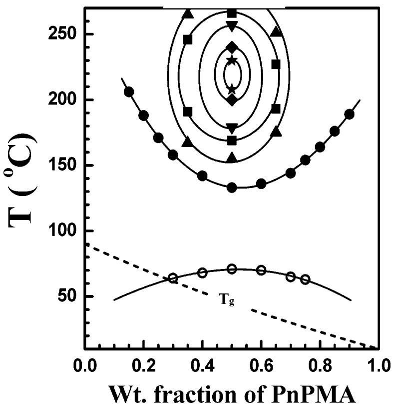

Figure 1. Phase diagrams of dPS/PnPMA-M blends at various P. Open (○) and closed (●) circles represent UCST and LCST, respectively, at ambient P. Closed-loop phase behaviors are observed at higher P (bar): 97 (▲), 117 (■), 138 (▼), 166 (◆), and 186 (★). Dashed curve of $T_{g,\mathrm{blend}}$ is the prediction by the Fox equation at ambient pressure.

This work represents the first experimental evidence that a weakly interacting polymer blend undergoing LCST-type phase behavior can also exhibit a closed-loop-type phase diagram at high pressure. To observe this closed-loop behavior experimentally, the magnitude of $\mathrm{d}T_{\mathrm{LCST}}/\mathrm{d}P$ and $\mathrm{d}T_{\mathrm{u-UCST}}/\mathrm{d}P$ must be sufficiently large to shift the transition temperature (particularly the u-UCST) into an experimentally accessible regime. Previously, we reported that $\mathrm{d}T_{\mathrm{LDOT}}/\mathrm{d}P$ and $\mathrm{d}T_{\mathrm{UODT}}/\mathrm{d}P$ for the dPS−PnPMA block copolymer are ±750 °C /kbar, where the + sign corresponds to the LDOT and the − sign to the UODT.[30] To compare these values with the dPS/PnPMA blend, the pressure dependence of all critical temperatures (LCST, u-UCST) for 50/50 (w/w) dPS/PnPMA-M was measured by turbidity, as summarized in Figure 2. It should be noted that the pressure dependences on the transition temperature might not be a linear relationship. Therefore, the lines drawn in Figure 2 were made in the vicinity of the maximum accessible pressure. $\mathrm{d}T/\mathrm{d}P$ for this blend was found to be very large. For the LCST $\mathrm{d}T/\mathrm{d}P$ = 560 °C/kbar and for the u-UCST $\mathrm{d}T/\mathrm{d}P$ = −540 °C/kbar, which are similar in magnitude to those for the symmetric dPS−PnPMA block copolymer.

The $\mathrm{d}T_{\mathrm{UCST}}/\mathrm{d}P$ for 50/50 (w/w) dPS/PnPMA-M blend could not be measured due to the proximity of the UCST to the T_g (or even below T_g) of the blend. Thus, another blend exhibiting a higher UCST was studied. It was previously shown that a 50/50 (w/w) PS-BH/PnPMA-L blend exhibited a UCST and an LCST at 108 °C and 143 °C, respectively.[26] $\mathrm{d}T_{\mathrm{LCST}}/\mathrm{d}P$ and $\mathrm{d}T_{\mathrm{u-UCST}}/\mathrm{d}P$ for

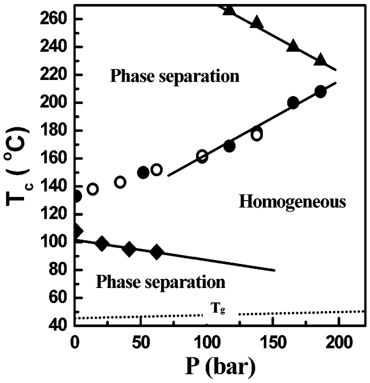

Figure 2. Pressure dependence of T_{LCST} (●) and T_{u-UCST} (▲) measured by turbidity for the 50/50 (w/w) dPS/PnPMA-M blend. Open circles (○) represent spinodal temperatures of the LCST ($T_{sp,LCST}$) obtained from SANS. Closed diamonds (◆) correspond to T_{UCST} measured by turbidity at various P for the 50/50 (w/w) PS-BH/PnPMA-L blend. The T_g of this blend in the homogeneous state is given in the dotted line.[31]

this blend composition were 520 and −560 °C/kbar, respectively, which are close to those of the 50/50 (w/w) dPS/PnPMA-M blend. The UCST for the 50/50 (w/w) PS-BH/PnPMA-L blend was measured up to $P = 60$ bar and are added in Figure 2, from which dT_{UCST}/dP was found to be ∼−120 °C/kbar, ∼25% of that of the u-UCST for this blend. This result is consistent with predictions based on the perturbed hard-sphere-chain (PHSC) equation-of-state arguments of Hino and Prausnitz,[17] where dT_{LCST}/dP and dT_{UCST}/dP for PS/poly(*n*-butyl methacrylate) blend are ∼200 °C/kbar and ∼−40 °C/kbar, respectively. Furthermore, dT_{LDOT}/dP and dT_{ODT}/dP for the PS−PnBMA block copolymer are almost the same as dT_{LCST}/dP and dT_{UCST}/dP for the PS/PnBMA blend.[17] Large values of pressure coefficients have been reported for polymer solutions. For instance, dT_{LCST}/dP and dT_{UCST}/dP are ∼670 °C/kbar and −145 °C/kbar, respectively, for a PS/*tert*-butyl acetate solution, and ∼620 °C/kbar and ∼−240 °C/kbar, respectively, for a PS/diethyl ether solution.[5] Since the absolute magnitude of dT_{LCST}/dP is close to that for dT_{u-UCST}/dP, the reason that the closed-loop phase behavior for PS/PVME blends was not observed can be explained. Despite theoretical predictions that dT_{LCST}/dP for dPS/PVME blends is ∼200 °C/kbar,[10,15] a lower experimental value (∼12 °C/kbar) was found.[33,34] This indicates that thermal degradation would occur before encountering the u-UCST even with high pressure (∼5 kbar).

To understand the complex phase behavior of PS/PnPMA blends (or PS−PnPMA block copolymers), the change of χ with temperature as a function of P was determined. Figure 3 shows the SANS profiles of a 50/50 (w/w) dPS/PnPMA blend at various P at a constant temperature (100 °C). It is noted that this blend composition becomes homogeneous at 100 °C regardless of P, as shown in Figure 1. With increasing P, the SANS intensity ($I(q) = d\Sigma(q)/d\Omega$ in cm^{-1}) at all wavelengths (0.04−0.5 nm^{-1}) decreases, which means that the miscibility of the blend is continuously enhanced with increasing P. This behavior originates from the reduced compressibility effect driven by negative volume change on mixing. The solid curves in Figure 3a are fits by the Ornstein−Zernike equation.[35]

$$I(q) = \frac{I(q{=}0)}{1 + (q\xi)^2} \qquad (1)$$

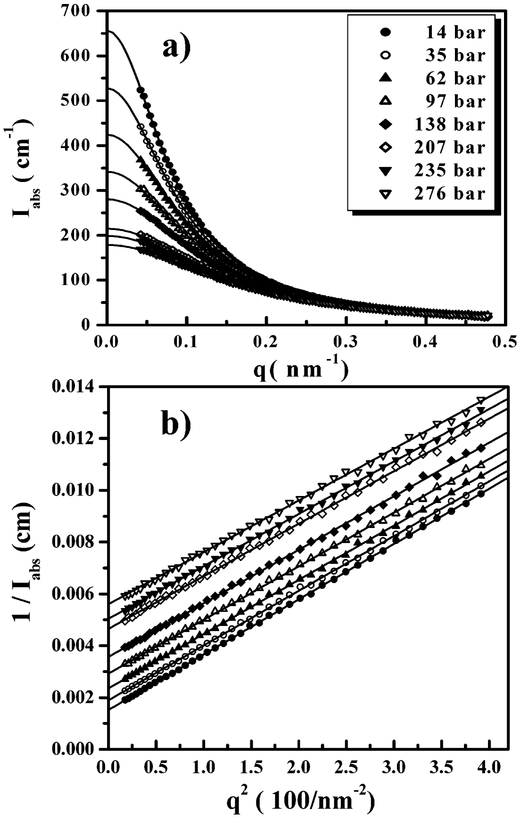

Figure 3. (a) Absolute SANS intensity ($I(q)$) vs q and (b) $[I(q)]^{-1}$ vs q^2 plots in the range of 0.047 nm^{-1} < q < 0.2 nm^{-1} for the 50/50 (w/w) dPS/PnPMA-M blend at 100 °C and various P. The solid curves in (a) are fits by the Orstein−Zenike equation.

where $q = (4\pi/\lambda)\sin(\theta/2)$ is the magnitude of the scattering vector and ξ is the correlation length of fluctuations in the homogeneous regime. From the intercept and the slope in plots of $[I(q)]^{-1}$ vs q^2 plots (0.047 nm^{-1} < q < 0.2 nm^{-1}) at 100 °C at different P, as shown in Figure 3b, $I(0)$ and ξ^2 data were obtained. Even though the PS/PnPMA blend is compressible, the incompressible random phase approximation (IRPA) (eq 1) was used to obtain the χ_{eff}:[35]

$$\frac{d\Sigma(q)}{d\Omega} = v_0\left(\frac{b_1}{v_1} - \frac{b_1}{v_1}\right)^2\left\{\frac{\phi_1}{V_1} + \frac{\phi_2}{V_2} - 2\frac{\chi_{eff}}{v_0}\right\}^{-1} \qquad (2)$$

where b_i, v_i, V_i, and ϕ_i are neutron coherent scattering length, monomeric volume, molar volume, and volume fraction for component i, respectively. v_0 is the reference volume defined as

$$v_0 = (v_{sp,dPS}[M]_{0,dPS}v_{sp,PnPMA}[M]_{0,PnPMA})^{1/2} \qquad (3)$$

where $v_{sp,i}$ and $[M]_{0,i}$ (i = dPS, PnPMA) are the specific volume (cm^3/g) and monomer molecular weight of component i, respectively.

Figure 4 shows the temperature dependence of $I(q{=}0)^{-1}$, $1/\xi^2$, and χ_{eff} for the 50/50 (w/w) dPS/PnPMA blend as a function of P. The value of χ_{eff} at the spinodal points (0.0312) calculated from $\chi_{sp} = (1/2)v_0(\phi_1/V_1 + \phi_2/V_2)$ is added as the dotted line in Figure 4c. Experimentally, the spinodal temperatures (T_{sp}) were evaluated by the extrapolation of $I(q{=}0)^{-1}$ to zero. The estimated values of T_{sp} for the LCST at various P are given as open circles in Figure 2. These are essentially the same as T_b's, since the 50/50 (w/w) dPS/PnPMA

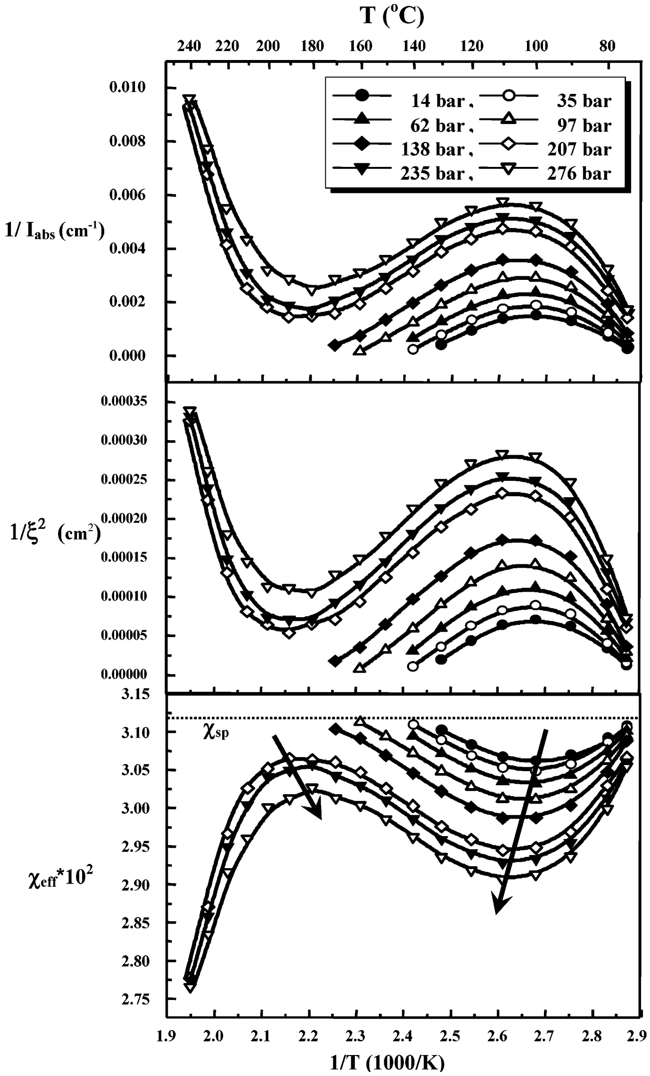

Figure 4. Temperature dependence of (a) $1/I(q=0)$, (b) $1/\xi^2$, and (c) χ for 50/50 (w/w) dPS/PnPMA-M blend at various *P*.

blend is close to the critical composition. Also, the temperature dependence of $1/\xi^2$ is similar to that of $I(q=0)^{-1}$. At lower *P*, with increasing *T* (or decreasing $1/T$), χ_{eff} first decreases, goes through a minimum, and then increases again. This is consistent with a blend having a UCST and LCST.

Interestingly, at higher *P*, χ_{eff} passes through a maximum at higher temperatures and decreases again with increasing temperature. This indicates that the blend exhibits a closed-loop-type phase behavior at higher *P*, which is consistent with results shown in Figure 1. Since the dependence of χ_{eff} on temperature was so complicated, the standard expression of χ ($\chi = -\chi_\sigma + \chi_h/T$) could not be used to fit the experimental data. A simple regular solution theory argument developed by Ruzette et al.[20,21] can be used to predict the T_{UCST}, T_{LCST}, and $T_{\mathrm{u-UCST}}$ for the 50/50 (w/w) dPS/PnPMA-M blend. From these arguments, values of 55 K, 415 K, and 5625 K were calculated, respectively. The thermal expansion coefficient and solubility parameter of dPS were assumed to be the same as those for PS. The predicted T_{LCST} of 415 K is in very good agreement with the experimental value (406 K) given in Figure 1, but the predicted value of the UCST (55 K) is too low in comparison with experimental value of 344 K. However, these arguments cannot be used to predict phase behavior at higher *P*. Thus, while these arguments provide some insight into the phase behavior of the polymer blend, agreement with experiments is not quantitative.

The complex phase behavior of dPS/PnPMA (and PS/PnPMA) can be qualitatively understood by considering three different temperature regimes for $\chi = -\chi_\sigma + \chi_h/T$. (i) At lower temperatures, enthalpy (a positive contribution to the free energy) dominates the combinatorial entropy and the free volume term is negligible. Thus, a UCST is expected since enthalpy steadily decreases with increasing temperature. The χ_h/T (positive) and χ_σ (negative) increase with increasing *P*, but the $\partial|\chi_\sigma|/\partial P > \partial(\chi_h/T)/\partial P$. Thus, χ at a given temperature decreases (miscibility is enhanced) with increasing *P*. This leads to the expectation that ΔV_{mix} at the UCST of a dPS/PnPMA blend is negative, though both enthalpic and entropic effects are important. Similar behavior was reported for poly(ethylmethyl siloxane)/poly(dimethylsiloxane) blends.[8] (ii) At intermediate temperatures, the free volume term prevails over the combinatorial entropy, which induces the LCST. Also, the dependence of χ_h/T with *P* is very small, whereas χ_σ decreases strongly with *P*. Thus, compressibility effects are minimized in this region, which is consistent with previous results for the dPS/PVME blend.[33] (iii) At higher temperatures, translational entropy again prevails over the free volume, which results in the u-UCST. The dependence of χ_σ on *P* seems to be larger than that of χ_h/T. It was also found that $\partial\chi_\sigma/\partial P \gg \partial(\chi_h/T)/\partial P$ at higher temperatures (205−260 °C), as determined by SANS of a lower molecular weight dPS-*b*-PnPMA copolymer that was disordered over the entire temperature regime. Interestingly, it is seen in Figure 4c that with increasing *P*, the temperature (T_{max}) corresponding to the maximum χ decreases, whereas the other temperature (T_{min}) corresponding to the minimum χ increases, as indicated by the arrows. This suggests that the standard expression of $\chi = -\chi_\sigma + \chi_h/T$ might be obtained at high *P* because of the suppressed compressibility difference between each homopolymer. Studies are underway to determine the behavior of χ_{eff} as a function of *T* at very large values of *P*. Very recently, Cho[19,36] theoretically predicted a closed-loop of PS-*b*-PnPMA using the compressible RPA theory with the combination of fluctuation effects and a small, but nonzero, specific interaction between PS and PnPMA.

In summary, a complex phase behavior consisting of a closed-loop plus a separate, lower UCST was observed for the dPS/PnPMA blend system. The pressure dependences of the LCST and u-UCST were found to be similar in magnitude, although opposite in sign. The magnitudes of the pressure coefficients were similar to those found for dPS-*b*-PnPMA copolymers. For the closed-loop phase behavior in systems with no specific interactions and negative volume changes on mixing, increasing pressure enhances the miscibility between PS and PnPMA. For pressures higher than 200 bar, the dPS/PnPMA becomes homogeneous at all temperatures, completely eliminating the closed-loop behavior. Finally, the pressure dependence of the UCST was smaller than that of the LCST or the u-UCST, suggesting that the origin for lower-UCST is different in nature from that for u-UCST.

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