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Effect of Neutral Solvent on the Phase Behavior of Polystyrene-*block*-Poly(*n*-butyl methacrylate) Copolymers

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Abstract: The effects of a neutral solvent of dioctyl phthalate (DOP) on the phase behavior of symmetric polystyrene-*block*-poly(*n*-butyl methacrylate) copolymers (PS-*b*-PnBMA) were assessed herein. Closed-loop phase behavior with a lower disorder-to-order transition (LDOT) and an upper order-to-disorder transition (UODT) was observed for PS-*b*-PnBMA/DOP solution when the quantity of DOP was carefully controlled. When the molecular weight of PS-*b*-PnBMA became larger, the LDOT did not appreciably change at smaller quantities of DOP. With larger quantities of DOP, the reduction in the UODT is greater than the increase in the LDOT. This behavior is discussed in accordance with a molecular theory predicated on a compressible random-phase approximation.

Keywords: block copolymer, closed-loop type phase behavior, neutral solvent.

Introduction

Block copolymers have drawn much attention because they show a rich variety of spatially periodic nano structures due to their ability of self-assembly.[1-3] Among these various block copolymers, the phase behavior of weakly interacting block copolymers with the lower disorder-to-order transition (LDOT) has been an interesting subject both experimentally[4-21] and theoretically.[22-26] To explain this kind of phase behavior, two important parameters, the difference in compressibility (the free volume effect) and specific interactions between dissimilar monomers, should be taken into account in addition to the translational entropic contribution and unfavorable interaction that determine the phase behavior of the order-to-disorder transition behavior observed in most block copolymers.[27]

One of the most interesting phase behaviors in the weakly interacting block copolymers would be the immiscibility loop (or closed-loop), which was observed for polystyrene-*block*-poly(*n*-pentyl methacrylate) copolymer (PS-*b*-PnPMA)[11-17] and some polymer blends.[20,21] Recently, we showed that polystyrene-*block*-poly(*n*-butyl methacrylate) copolymer (PS-*b*-PnBMA) solutions exhibited the immiscibility loop phase behavior when the solvent power was judiciously controlled by using the mixture of a neutral solvent of dioctyl phthalate (DOP) and a PnBMA-selective solvent of hexadecane, even though the upper order-to-disorder transition (UODT) was not detected within the experimentally accessible temperature range for neat PS-*b*-PnBMA.[18] At a given amount of hexadecane in PS-*b*-PnBMA solution (85/15 (wt/wt) PS-*b*-PnBMA/hexadecane), the increase of the DOP content from 2.7 to 3.9 wt% increased the LDOT, but decreased the UODT.[18] Since it is expected that PS-*b*-PnBMA/DOP solution should become disordered state at higher amounts of DOP, it is possible for one to have in principle a closed-loop type phase behavior even when DOP alone is used. The use of a single neutral solvent instead of mixed solvents would be very effective means to experimentally determine the closed-loops of PS-*b*-PnBMAs with various molecular weights and to investigate the effect of hydrostatic pressure on the closed-loop type phase behavior.

In this study, we changed very carefully the amount of DOP in the PS-*b*-PnBMA/DOP solution. It was found that within limited amounts of DOP, the solution indeed exhibited the immiscibility loop (or closed-loop) with both LDOT and UODT in the experimentally accessible temperature range. We also found that the immiscibility loop size depends greatly on the molecular weight of PS-*b*-PnBMA. The effect

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*Corresponding Author. E-mail: jkkim@postech.ac.kr of the pressure on the LDOT and UODT of the solution was studied, and discussed by using a molecular theory based on a compressible random-phase approximation[10,26,28] including the free volume effect and specific directional interaction as well as the unfavorable contact interaction and configurational entropy.

Experimental

Symmetric PS-*b*-PnBMAs used in this study were synthesized by sequential anionic polymerization.[9,10] The molecular characteristics and transition temperatures of three different PS-*b*-PnBMAs are shown in Table I. DOP was purchased from Aldrich Chem. Co. It was reported that DOP is a neutral solvent for PS and PnBMA blocks.[29] The PS-*b*-PnBMA/DOP solutions with various amounts of DOP were prepared by using methylene chloride as a cosolvent. The cosolvent was removed under a gentle flow of nitrogen and then completely removed under mild vacuum. This is verified that the weight of the sample became constant with time. Due to the high boiling point (384 °C) of DOP, its evaporation below 300 °C was negligible. This is also confirmed that the phase behavior of PS-*b*-PnBMA/DOP mixture was not changed with repeat heating and cooling experiments. It is noted that a small amount of DOP can significantly change the phase behavior, as shown in ref. 17.

Small angle X-ray scattering (SAXS) experiments were performed on Beamlines 4C1 and 4C2 at the Pohang Light Source (Korea).[30] A 2-D CCD camera (Princeton Instruments Inc.SCX-TE/CCD-1242) was used to collect the scattered X-rays. Sample with thickness of 1.0 mm was prepared by compression-molding at 50 °C, followed by annealing at 90 °C for 1 h.

Polarized optical microscopy (POM) measurements were performed with polarized light microscopy (Zeiss Co.). Due to the non-selective nature of DOP and the symmetric composition of PS-*b*-PnBMA, the solutions in the ordered state exhibited lamellar microdomains. The transitions between nonbirefringence and birefringence could be considered as the order-to-disorder (or disorder-to-order) transition of the solutions.[31,32] Depolarization of transmitted light (static birefringence) was used to distinguish the birefringent and nonbirefringent states of block copolymers. Vertically polarized light from an HeNe laser passes through the sample and a horizontal analyzing polarizer onto a photodiode. Samples with a thickness of 0.5-2.0 mm were subjected to a slow increasing temperature rate (1 °C min^{-1}). To avoid thermal degradation, all the samples were heated only up to 300 °C.

Table I. Molecular Characteristics and Transition Temperatures of Various Block Copolymers Employed in This Study

Sample Code	M_w	M_w/M_n	f_{PS}	LDOT[a]	LDOT[b]	UODT[b]
PS-*b*-PnBMA-L	69,900	1.05	0.5	132 °C	143 °C	678 °C
PS-*b*-PnBMA-M	67,000	1.04	0.5	147 °C	160 °C	600 °C
PS-*b*-PnBMA-S	60,300	1.05	0.5	193 °C	237 °C	385 °C

[a]Measured values. [b]Predicted values based on a compressible random phase approximation.[10,28]

Samples for the measurement of the static birefringence at higher hydrostatic pressures were melt-pressed into 1.5 mm thick and 1 mm diameter disks. Silicone oil was used as the pressurizing fluid, with an encapsulated O-ring gasket separating the sample disk from the fluid. The temperature was controlled with the error of ± 0.1 °C, and heating rate was 1 °C min^{-1} under a predetermined pressure.

Results and Discussion

Figure 1 shows the temperature dependence of depolarized light intensity for PS-*b*-PnBMA-M/DOP solutions with various amounts of DOP. The LODT of neat PS-*b*-PnBMA-M was determined to be 147 °C. It is seen that even at the weight fraction of DOP in the solution (w_{DOP}) of 0.135, the depolarized light intensity increases abruptly at 198 °C, and then does not change up to 300 °C. This suggests that this solution exhibits only an LDOT before thermal degradation, similar to neat PS-*b*-PnBMA.[5,6,9,10,18,29,33,34] However, when w_{DOP} increases to 0.145, the depolarized light intensity increases abruptly at 212 °C, and then becomes constant up to 265 °C, finally decreases precipitously at 268 °C. A similar phenomenon has been reported for immiscibility loop (closed-loop) phase behavior as demonstrated in PS-*b*-PnPMA.[11-15] Thus, we conclude that this solution has an LDOT of 212 °C and a UODT of 268 °C. When w_{DOP} becomes 0.155, the solution does not show any transition up to

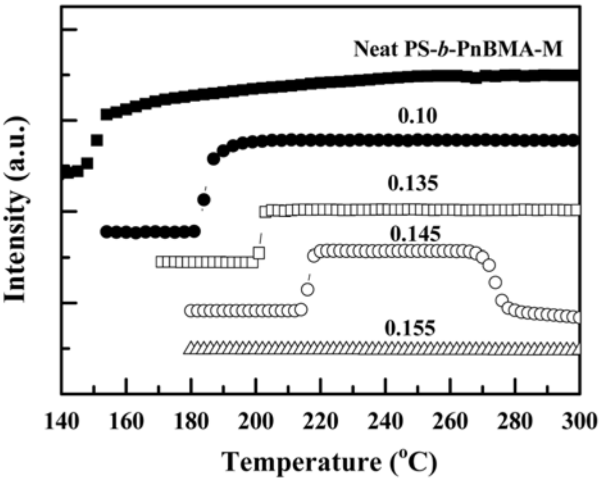

Figure 1. The temperature dependence of depolarized light intensity for PS-*b*-PnBMA-M/DOP solutions with various amounts of DOP. The weight fraction of DOP in the solutions is: 0.1 (●), 0.135 (□), 0.145 (○), and 0.155 (△). For the reference, the depolarized light intensity for neat PS-*b*-PnBMA-M is added.

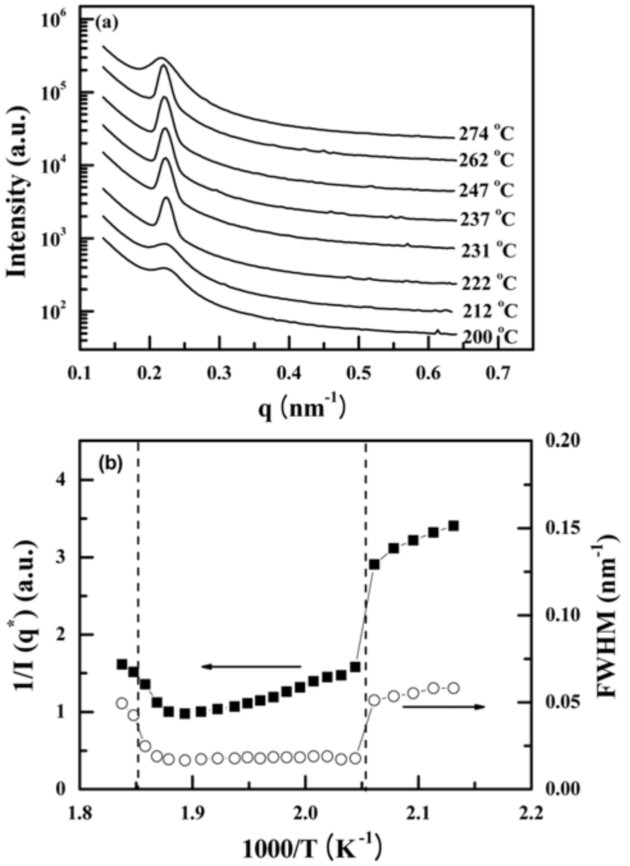

Figure 2. (a) SAXS profiles at various temperatures and (b) plots of $1/I(q_*)$ and FWHM vs. $1/T$ for 85.5/14.5 (wt/wt) PS-*b*-PnBMA-M/DOP solution. All SAXS profiles in part (a) are vertically shifted to avoid the overlap.

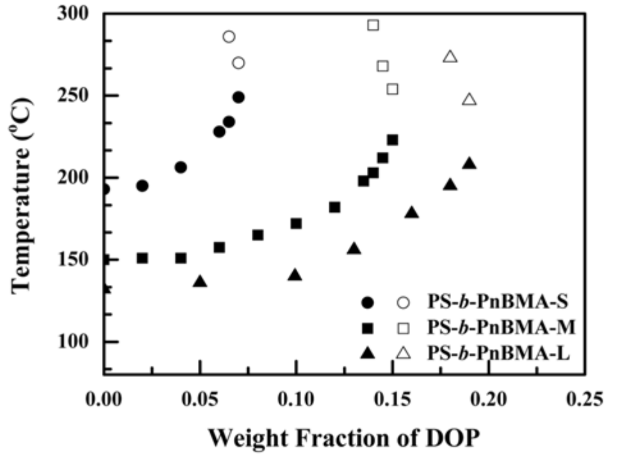

Figure 3. The changes of T_{LDOT} (closed symbols) and T_{UODT} (open symbols) with the amount of DOP of PS-*b*-PnBMA with three different molecular weights: PS-*b*-PnBMA-S (●, ○), PS-*b*-PnBMA-M (■, □), and PS-*b*-PnBMA-L (▲, △).

300 °C, which indicates that the solution becomes disordered in the entire experimentally accessible temperature range. From Figure 1, we conclude that with the addition of DOP into PS-*b*-PnBMA, the LDOT of PS-*b*-PnBMA/DOP solution increases, whereas the UODT decreases. Thus, the closed-loop phase behavior is observed for PS-*b*-PnBMA/DOP solution, as long as w_{DOP} is controlled very carefully within 0.135-0.155.

Figure 2(a) shows the SAXS profiles at various temperatures for the PS-*b*-PnBMA-M/DOP (85.5/14.5 wt/wt) solution. The first order peak ($q^* = 0.21$ nm^{-1}) is very sharp and intense between 213-268 °C, while the peak is broad at temperatures lower than 213 °C as well as higher than 268 °C. Figure 2(b) shows plots of the inverse intensity ($1/I(q^*)$) and full width at half maximum (FWHM) of the first order peak versus the inverse absolute temperature ($1/T$), from which the LDOT and UODT are determined to be 213 and 268 °C, respectively. It should be noted that no higher ordered peak was observed in the ordered state because of the smaller contrast in the electron density between the PS and PnBMA blocks.[9,10] The transition temperatures obtained from SAXS measurements are essentially the same as those obtained by static birefringence.

Figure 3 shows changes of the LDOT and UODT of PS-*b*-PnBMA with three different molecular weights as a function of the amount of DOP. It is seen that the LDOT of PS-*b*-PnBMA-M changes a little, if any, at w_{DOP} less than ~0.06, and the range of w_{DOP} where the LDOT changes a little increases with increasing molecular weight. This would be consistent with the result given in ref. 29 that the LDOT of PS-*b*-PnBMA/DOP solution changed very little with the amount of DOP. However, with increasing the amount of DOP, the LDOT increased very rapidly, and the solution became disordered state at higher amounts of DOP. The UODT for PS-*b*-PnBMA-M was first observed within experimentally accessible temperature range when w_{DOP} is 0.14. With further increase in w_{DOP} to 0.15, the solution became disordered. The above observations suggest that neat PS-*b*-PnBMA should in principle have a closed loop phase behavior with the UODT much higher than 300 °C. Interestingly, with increasing amount of DOP the decrease in the UODT is much larger than the increase in the LDOT, even though the range of the weight fraction of DOP exhibiting a closed-loop is very limited (less than 2 wt%).

It is reported that the immiscible loop in weakly interacting block copolymers resulted from the competing contributions of the free volume effect, nonspecific interactions, and specific interactions between dissimilar monomers to the free energy of mixing.[25,26] Using a Hartree (fluctuation correction) analysis based on a compressible random-phase approximation (RPA), Cho predicted the immiscible closed-loop in PS-*b*-PnPMA with the Flory interaction parameter divided into χ_{comp} and χ_{app} ($\Delta\varepsilon$, $\delta\varepsilon$) as:[26]

$$\chi = \chi_{comp} + \chi_{app}\,(\Delta\varepsilon,\ \delta\varepsilon) \tag{1}$$

where χ_{comp} characterizes the compressibility difference between the block components relative to the bulk modulus of the block copolymer[35] and χ_{app} ($\Delta\varepsilon$, $\delta\varepsilon$) indicates the exchange energy density, where $\Delta\varepsilon$ is the exchange energy of nonspecific pair interactions between dissimilar monomers and $\delta\varepsilon$ is the energy increment due to the specific cross-contact interactions.

DOP is a neutral solvent[29] and equally partitions into both the block domains in PS-*b*-PnBMA, indicating that the difference in the compressibility between both block domains would be little changed by the addition of DOP. Thus, the change of the LDOT with the addition of DOP depends mainly on the change in χ_{app} ($\Delta\varepsilon$, $\delta\varepsilon$). It is noted that DOP screens both unfavorable interactions from $\Delta\varepsilon$ and the weak favorable interactions due to $\delta\varepsilon$. Since the screened unfavorable interactions enhance the miscibility,[36-38] while the screened favorable interactions hamper the miscibility, both competing contributions did not much change the LDOT. With the addition of DOP, however, the combinatorial entropy should increase, resulting in the slight increase of the LDOT. But, a small contribution of free energy gain has a very large effect on the LDOT when the amount of DOP approaches the threshold concentration above which the solution becomes disordered. On the other hand, at higher temperature, combinatorial entropy would be dominant; thus the decrease in the UODT would be very large. According to the compressible Hartree calculations,[10,28] the predicted LDOT and UODT are 237 and 385 °C for PS-*b*-PnBMA-S, 160 and 600 °C for PS-*b*-PnBMA-M, and 143 and 678 °C for PS-*b*-PnBMA-L (shown in Table I). This indicates that the change of the UODT by molecular weight is much larger than that of the LDOT, and would be consistent with the experimental result given in Figure 3.

If the change of the LDOT with the addition of DOP is small at small amounts of DOP, we consider that the change of the LDOT with hydrostatic pressure (P) would be similar. Namely, dT_{LDOT}/dP of PS-*b*-PnBMA/DOP solution having small amounts of DOP would be similar to that of neat PS-*b*-PnBMA, while dT_{LDOT}/dP of PS-*b*-PnBMA/DOP solution having near the threshold weight fraction of DOP becomes much larger than that of neat PS-*b*-PnBMA. Figure 4(a) shows the changes of the LDOT and UODT for the 85.5/14.5 (wt/wt) PS-*b*-PnBMA-M/DOP solution under various P. The LDOT increases but the UODT decreases with the values of dT_{LDOT}/dP and dT_{UODT}/dP having +622 and -624 °C/kbar, respectively. The value of dT_{LDOT}/dP is ~ five times larger than that (135 °C/kbar) for neat PS-*b*-PnBMA-M. Figure 4(b) shows the change of dT_{LDOT}/dP for PS-*b*-PnBMA-M/DOP and PS-*b*-PnBMA-M/DOP solutions, from which dT_{LDOT}/dP does not change much at small amounts of DOP, but it increases dramatically near the threshold weight fraction of DOP. This behavior is very similar to the change of the LDOT with amounts of DOP at ambient pressure, as shown in Figure 3.

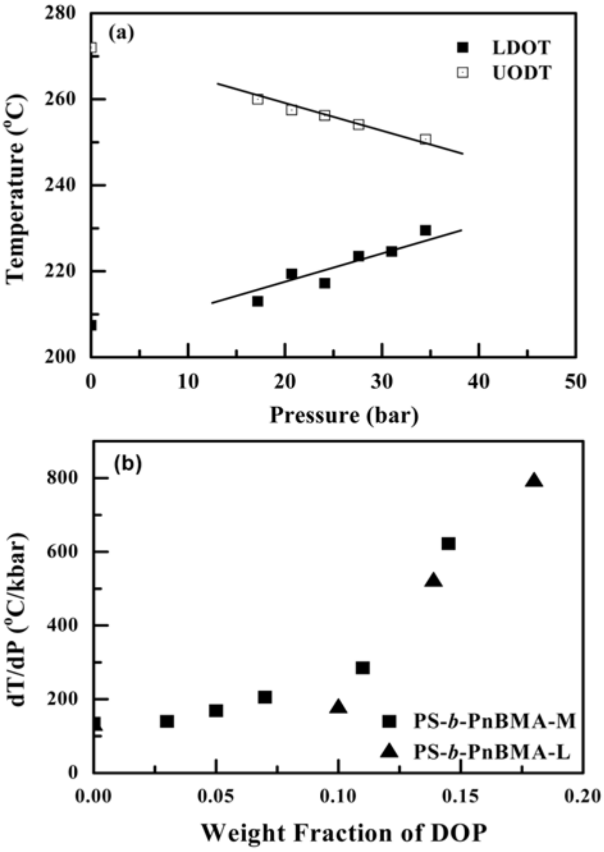

Figure 4. (a) The changes of T_{LDOT} (closed symbols) and T_{UODT} (open symbols) with P for the 85.5/14.5 (wt/wt) PS-*b*-PnBMA-M/DOP solution. (b) Plot of dT_{LDOT}/dP versus weight fraction of DOP for PS-*b*-PnBMA-M (■) and PS-*b*-PnBMA-L (▲).

The effects of molecular weight and hydrostatic pressure on the ordering transition temperatures can be explained by the change of $N\chi$ with temperature. Here, N is the total segments of the block chain. Figure 5 shows the theoretically predicted $N\chi$ for PS-*b*-PnBMA-S and PS-*b*-PnBMA-M from a Hartree (fluctuation correction) theory based on a compressible random-phase approximation. The detailed calculation procedures were given previously[26,28] and the requisite molecular parameters are as follows: for theoretical monomer diameters, $\sigma_{PS} = \sigma_{PnBMA} = 4.04$ Å; for self-interactions, $\varepsilon_{PS}/k = 410.7$ K, $\varepsilon_{PnBMA}/k = 373.8$ K; for theoretical chain size N, $(N\pi\sigma^3/6M)_{PS} = 0.41857$ cm^3/g, $(N\pi\sigma^3/6M)_{PnBMA} = 0.42042$ cm^3/g; for cross-interaction, $\varepsilon_{12}^{ns} = 0.97713(\varepsilon_{PnBMAPS})^{1/2}$ and $\delta\varepsilon/k = 98$ K, where k denotes the Boltzmann constant and M molecular weight. The given ε_{12}^{ns} yields $\Delta\varepsilon/k = 18.790$. It is seen in Figure 5 that with increasing temperature $N\chi$ first increases, characterizing the LDOT. But, it reaches a maximum near 300 °C, and decreases at higher temperatures. This implies that the UODT would be in principle observed at higher temperatures, even though the thermal degradation prohibits seeing

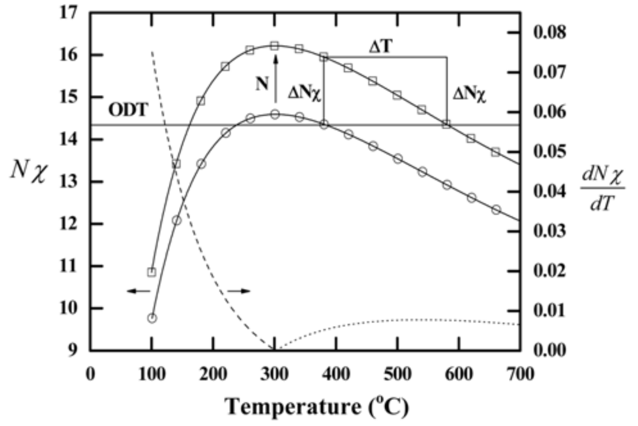

Figure 5. The changes of $N\chi$ with temperature for PS-*b*-PnBMA-S (○) and PS-*b*-PnBMA-M (☐). The solid line is the $N\chi$ (= 14.336) at the ODT of PS-*b*-PnBMA-S. The change of $dN\chi/dT$ with temperature for PS-*b*-PnBMA-S is also added. The long-dashed line in $dN\chi/dT$ represents positive values, while the dotted line represents negative values.

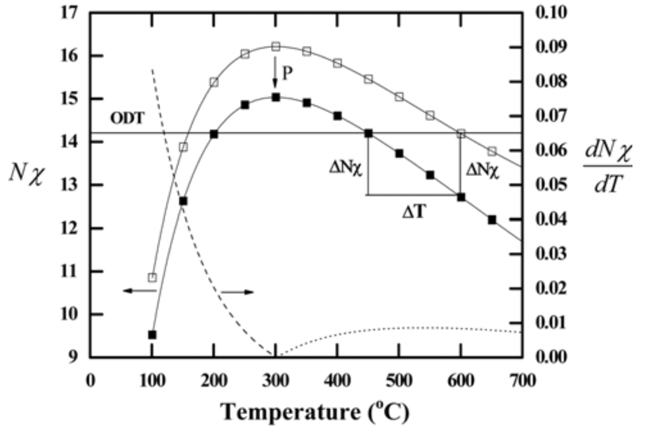

Figure 6. The change of $N\chi$ for PS-*b*-PnBMA-M with temperature at two pressures (MPa) (0.1 (☐) and 50 MPa (■)). The solid line is the $N\chi$ (= 14.204) at the ODT of PS-*b*-PnBMA-M. The change $dN\chi/dT$ with temperature for PS-*b*-PnBMA-M at 0.1 MPa is also added. The long-dashed line in $dN\chi/dT$ represents positive values, while the dotted line represents negative values.

the UODT in the experimentally accessible temperature regions. It is noted that LDOT and UODT are determined by two temperatures where predicted $N\chi$ becomes the same as that at ODT ($(N\chi)_{ODT}$). The predicted values of $(N\chi)_{ODT}$ of PS-*b*-PnBMA-S and PS-*b*-PnBMA-M are 14.336 and 14.204, respectively. This small change in $(N\chi)_{ODT}$ between two block copolymers is attributed to a Hartree correction of the fluctuation, that is, $(N\chi)_{ODT} \sim N^{-1/3}$.[26,39]

If the chain size (N) increases, $N\chi$ increases by $\Delta N\chi$. The new ODT upon increase of N should be changed by ΔT. Furthermore, since the fluctuation effect decreases new ODT by $\Delta(N^{(-1/3)})$, this additional effect changes by δT, which is, of course, a minor correction to ΔT. It can be seen in Figure 5 that the value of $d(N\chi)/dT$ at lower temperatures is much larger than the absolute value of $d(N\chi)/dT$ at higher temperatures. For instance, the values of $d(N\chi)/dT$ for PS-*b*-PnBMA-S are 0.0264, 0.0050, 0.00002, -0.0031, and -0.0067 at 177, 258, 301, 342, and 427 °C, respectively. Therefore, the change of $N\chi$ would not drastically change the LDOT, whereas UODT can change greatly due to the much smaller value of $d(N\chi)/dT$. Around the maximum of $N\chi$, the slope $d(N\chi)/dT$ approaches zero. In this situation, only a slight change in $N\chi$ makes enormous changes in ΔT; thus LDOT and UODT changed significantly. Adding a neutral solvent is equivalent to reducing the overall value of $N\chi$, which is caused mainly by the screening effect of χ_{app} ($\Delta\varepsilon$, $\delta\varepsilon$). Therefore, when DOP weight fraction approaches its threshold value, $N\chi$ becomes flattened and thus ΔT rapidly increases. This prediction is consistent with results given in Figure 3.

We found that the contribution of χ_{comp} to the total χ for PS-*b*-PnBMA is ~30%.[28] Thus, the hydrostatic pressure greatly affects χ_{comp} to reduce N because of the increased bulk modulus upon pressurization, as shown in Figure 6. The reduction of $N\chi$ by $\Delta N\chi$ arising from the increased P lowers the ODT by ΔT. Because of the smaller $d(N\chi)/dT$ at higher temperatures compared with that at lower temperatures, the reduced $\Delta N\chi$ results in a small change in LDOT compared with UODT. Unfortunately, this prediction could not be verified experimentally because the UODT could not be observed within experimentally accessible temperature range at lower amounts of DOP. However, as the amount of DOP approaches the threshold weight fraction, the change of LDOT by pressure is very large compared with that at smaller amounts of DOP. Also, near the threshold weight fraction of DOP, the change of both LDOT and UODT by the pressure would be very large, consistent with the results given in Figure 4.

Conclusions

The effect of DOP on the phase behavior of PS-*b*-PnBMA was investigated. The existence of a UODT of PS-*b*-PnBMA above the degradation temperature was confirmed. When both the molecular weights of PS-*b*-PnBMA and DOP concentration were carefully controlled, the closed-loop phase behavior was observed within the experimentally accessible temperature range. With increasing the amount of DOP, the LDOT does not change much at small amounts of DOP, but it increases dramatically near the threshold amount of DOP. Also, near the threshold amount of DOP, the UODT decreases significantly. The change of the LDOT with the amount of DOP is similar to the change of dT_{LDOT}/dP. These results were satisfactorily explained by using a molecular theory based on a compressible random-phase approximation.

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