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Effect of solvents on closed-loop phase behavior of block copolymers

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Abstract

We studied the effect of solvent selectivity on the closed-loop phase behavior of a polystyrene-*block*-poly(*n*-pentyl methacrylate) copolymer. It was found that the lower disorder-to-order transition temperature (LDOT) and upper order-to-disorder transition temperature (UODT) consisting of the closed-loop were very sensitive to the selectivity of the solvent. With the addition of very small amounts of non-selective solvents such as di-*n*-octyl phthalate and dimethyl phthalate, the LDOT increased rapidly, whereas the UODT decreased dramatically; thus, the immiscibility loop was shrunk greatly. On the other hand, both the LDOT and UODT decreased with increasing amount of dodecanol, a highly selective solvent to poly(*n*-pentyl methacrylate) block. However, the decrease in the LDOT was greater than that of the UODT, leading to an increased immiscibility loop.

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Keywords: Block copolymer; Closed-loop type phase behavior; Solvent selectivity

1. Introduction

The order-to-disorder transition (ODT) in block copolymers has been extensively studied theoretically and experimentally [1–11]. Most block copolymers self-assemble into periodic nanostructures upon cooling. However, some block copolymers, such as polystyrene-*block*-poly(*n*-butyl methacrylate) copolymer (PS-*b*-P*n*BMA) and polystyrene-*block*-poly (vinyl methyl ether) copolymer (PS-*b*-PVME), were found to undergo a lower disorder-to-order transition (LDOT) upon heating [12–16]. Recently, the closed-loop phase behavior bounded by two transition temperatures, a LDOT at a low temperature and an upper ordered-to-disorder transition (UODT) at a high temperature, was observed in polystyrene-*block*-poly-(*n*-pentyl methacrylate) copolymer (PS-*b*-P*n*PMA) [17–23] and weakly interacting polymer blends [24,25]. The LDOT and UODT of PS-*b*-P*n*PMA could be explained by incorporating the weak interaction, free volume (or equation-of-state effect), and the fluctuation effects into the random phase approximation [26,27].

The effect of various solvents with high boiling points on the transition temperature of block copolymers with ODT has been reported [28–31]. The solvents usually depress the ODT by screening unfavorable segmental interactions between two blocks along with increased combinatorial entropy. Moreover, the change of the ODT depends upon the selectivity of a solvent toward the blocks, since the screening effect changed with solvent selectivity [28]. Some studies have been performed to investigate the effect of solvents on the LDOT of block copolymers [32–35] or the lower critical solution transition (LCST) of polymer blends [36–38].

Since the directional interaction and free volume (or equation-of-states) influence the closed-loop phase behavior, the solvents with various selectivities should also change dramatically the LDOT and UODT. Very recently, we demonstrated that the LDOT of PS-*b*-P*n*BMA increased with the addition of dioctyl phthalate (DOP), a neutral solvent for both PS and P*n*BMA blocks, while it decreased with the addition of hexadecane, a selective solvent to P*n*BMA block [39]. This suggests that the LDOT of a block copolymer in the solution

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depends on the solvent selectivity. However, since only two solvents were used in Ref. [39], the effect of the solvent selectivity on the LDOT is not well understood. Moreover, the effect of the solvent selectivity on the UODT could not be estimated from PS-*b*-P*n*BMA/solvent mixture, since the UODT of PS-*b*-P*n*BMA could not be detected experimentally. Therefore, to understand in detail the effect of the solvent selectivity on the directional interaction and free-volume effect of polymer system, the block copolymer should exhibit both the LDOT and UODT within experimentally accessible temperature range.

PS-*b*-P*n*PMA exhibits both the LODT and UODT (closed-loop phase behavior) within the experimentally accessible temperature range (120–300 °C) when the molecular weight is chosen appropriately [19]. In this situation, the effect of the solvent selectivity on both the LODT and UODT of a block copolymer is easily investigated. In this study, the solvent selectivity was judiciously changed from neutral to highly selective to P*n*PMA block. Interestingly, we found that the closed (or immiscibility) loop of PS-*b*-P*n*PMA disappeared even at very small amount (less than 1.5 vol%) of neutral solvents of DOP and dimethyl phthalate (DMP). We also observed that although both the LDOT and UODT decreased with the addition of hexadecane or dodecanol, the degree of the decrease in the LDOT was larger for a highly P*n*PMA-selective solvent of dodecanol compared with a slightly P*n*PMA-selective solvent of hexadecane. We explained this difference qualitatively by employing the total Gibbs free energy of mixing including the free-volume effect and the specific interaction depending on the solvent selectivity. This would help one to understand in detail the closed-loop phase behavior of a block copolymer.

2. Experimental section

A symmetric PS-*b*-P*n*PMA was synthesized anionically [17,19]. The number-average molecular weight (M_n) and the polydispersity index (M_w/M_n) were 49 900 and 1.02, respectively, measured by size exclusion chromatography combined with multiangle laser light scattering. The volume fraction of PS block (f_{PS}) was 0.5, determined by nuclear magnetic resonance. This block copolymer exhibits both the LDOT (142 °C) and UODT (220 °C). And between LODT and UODT, this block copolymer exhibited lamellar microdomains with a long-spacing of 23 nm [21]. The solvents employed in this study were DOP, DMP, hexadecane ($C_{16}H_{34}$) and dodecanol ($C_{12}H_{25}OH$) with boiling points higher than 260 °C. All were purchased from Aldrich Chem. Co., and used without any further purification. The density at room temperature and the boiling and melting points of the solvents are given in Table 1 [40]. The block copolymer/solvent mixtures were prepared by using methylene chloride (CH_2Cl_2) as a cosolvent. The CH_2Cl_2 was removed under a gentle flow of nitrogen first, then under mild vacuum until a constant weight was achieved.

Rheological measurement of the mixtures was carried out by using an Advanced Rheometrics Expansion System (ARES) with 25 mm parallel plate geometry and 1 mm gap. Samples were first annealed at 120 °C for 1 h to remove thermal history, and then temperature was increased at a heating rate of 0.5 °C min^{-1}. The strain amplitude and the angular frequency were 0.05 and 0.1 rad/s, respectively, which lie within the linear viscoelastic region.

Table 1
Physical properties of solvents employed in this study

Solvent	Density at 25 °C (g cm^{-3})	B.p. (°C)	M.p. (°C)
$C_{16}H_{34}$	0.773	287	18
$C_{12}H_{25}OH$	0.831	262	24
DOP	0.986	384	−46
DMP	1.194	284	5.5

Depolarization of transmitted light (static birefringence) [41,42] was used to determine the LODT and UODT of neat PS-*b*-P*n*PMA and PS-*b*-P*n*PMA/solvent mixtures. Vertically polarized light from a HeNe laser passed 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 (0.5 °C min^{-1}). It is noted that the transition temperatures determined during the first heating are essentially the same as those obtained from the second heating after the cooling; thus the evaporation of all the solvents was negligible.

The microdomain of the mixtures was also obtained with transmission electron microscopy (TEM Hitachi 7600) operating at 100 kV. The samples were ultramicrotomed and stained with RuO_4 vapor.

We observed that PS and P*n*PMA homopolymers are completely soluble in DOP and DMP. Thus, the selectivity of these two solvents to the blocks could be estimated by the magnitude of the second virial coefficient (A_2) determined by using membrane osmosis and light scattering method. However, for DOP/P*n*PMA and DMP/P*n*PMA solutions, we could not obtain A_2 by using light scattering because the refractive index increment with the increasing polymer concentration (dn/dc) was too small to measure. Furthermore, since both DOP and DMP penetrate easily into the membranes used in membrane osmosis, we could not perform this experiment. Thus, the selectivity of DOP and DMP was indirectly estimated by the magnitude of the a in the Mark–Houwink equation $[\eta] = KM^a$ [43]. Here, $[\eta]$ is the intrinsic viscosity, M is the molecular weight, and K and a are the Mark–Houwink constants. The $[\eta]$ was obtained by using an Ubbelohde type viscometer at given temperature controlled with ±0.1 °C.

On the other hand, the selectivity of hexadecane and dodecanol to PS and P*n*PMA blocks was easily judged by the turbidity points (T_b) experiment measured by optical microscopy (OM, Axioplan, Zeiss Co.). The number-average molecular weights (M_n) and the polydispersity indices (PDI) of PS (purchased from Aldrich Chem. Co.) and P*n*PMA (prepared by anionic polymerization in this laboratory) homopolymers were 29 300 and 1.03, and 111 000 and 1.05, respectively. The mixtures of polymers and solvents were prepared by using CH_2Cl_2 as a cosolvent and then removing the cosolvent until a constant weight was achieved. The T_b 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^{-1}. 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.

3. Results and discussion

Fig. 1a gives turbidity curves of PS/$C_{16}H_{34}$ and P*n*PMA/$C_{16}H_{34}$ mixtures, from which the Flory–Huggins interaction parameter (α in mol/cm^3 and given by χ/V_{ref}, in which V_{ref} is the reference monomeric volume) of these two mixtures is given by:

$$\alpha_{\mathrm{PS/C_{16}H_{34}}} = 0.958\times10^{-3} + \left(0.705 + 0.336\phi_{\mathrm{PS}}\right)/T \tag{1a}$$

$$\alpha_{\mathrm{P}n\mathrm{PMA/C_{16}H_{34}}} = 0.819\times10^{-3} + \left(0.588 + 0.319\phi_{\mathrm{P}n\mathrm{PMA}}\right)/T \tag{1b}$$

where ϕ_{PS} is the volume fraction of PS in PS/$C_{16}H_{34}$ solution and $\phi_{\mathrm{P}n\mathrm{PMA}}$ is the volume fraction of P*n*PMA in P*n*PMA/$C_{16}H_{34}$ solution. The solid lines in Fig. 1a are the binodal curves calculated from the Flory–Huggins theory with the aid of Eqs. (1a) and (1b), respectively, where the specific volumes (in cm^3/g) of PS (0.952), P*n*PMA (0.970) and $C_{16}H_{34}$ (1.290) are used. The predicted binodal curves are in good agreement with measured turbidity curves. The UCST of P*n*PMA/$C_{16}H_{34}$ mixture was 70 °C, 90 °C lower than that of PS/$C_{16}H_{34}$ blend, even though the molecular weight (111 000) of P*n*PMA is four times larger than that (29 300) of PS. From Fig. 1 and the comparison of Eq. (1a) with Eq. (1b), we conclude that $C_{16}H_{34}$ is a selective solvent for P*n*PMA block compared with PS block. The temperature dependence of the solubility of polymers could be estimated from the ratio of $\alpha_{\mathrm{PS/C_{16}H_{34}}}/\alpha_{\mathrm{P}n\mathrm{PMA/C_{16}H_{34}}}$. From Eqs. (1a) and (1b), $\alpha_{\mathrm{PS/C_{16}H_{34}}}/\alpha_{\mathrm{P}n\mathrm{PMA/C_{16}H_{34}}}$ at 230 °C is 1.154, which is essentially the same as that (1.153) at 100 °C at given volume fractions of polymers ranging from 0.93 to 0.99. Therefore, we consider that $C_{16}H_{34}$ is a selective solvent for P*n*PMA compared with PS regardless of temperatures.

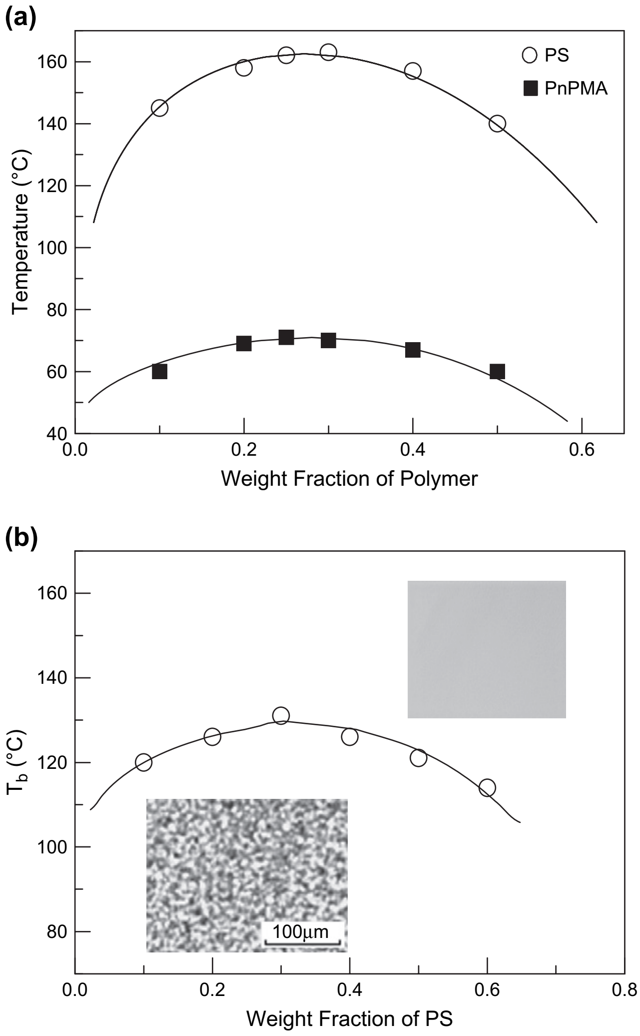

Fig. 1. (a) Turbidity curves of PS/hexadecane mixtures and P*n*PMA/hexadecane mixtures. Solid lines are drawn based on the Flory–Huggins lattice theory with Eqs. (1a) and (1b), respectively. (b) Turbidity curve of PS/dodecanol mixture. Solid line is drawn based on the Flory–Huggins lattice theory with Eq. (2). The insets give OM images in homogeneous and phase-separated states.

Fig. 1b shows the turbidity curve of the PS/$C_{12}H_{25}OH$ mixture with a UCST of ~130 °C. But all compositions of P*n*PMA/$C_{12}H_{25}OH$ mixture did not exhibit any turbidity above room temperature, even though the M_n of P*n*PMA was as large as 111 000. Thus, $C_{12}H_{25}OH$ is considered as a selective solvent to P*n*PMA. Using the turbidity point measurement together with the Flory–Huggins mean field theory, we obtained the interaction parameter α for this mixture:

$$\alpha_{\mathrm{PS/dodecanol}} = -1.49 \times 10^{-3} + \left(1.967 + 0.524\phi_{\mathrm{PS}}\right)/T \qquad (2)$$

where ϕ_{PS} is the volume fraction of PS in PS/$C_{12}H_{25}OH$ mixture. The solid line in Fig. 1b is the binodal curve calculated with the aid of Eq. (2). In calculating the binodal curves, we used the specific volume (1.203 cm^3/g) of $C_{12}H_{25}OH$. The predicted binodal curve is in good agreement with the measured turbidity curve. We further consider that the selective nature of $C_{12}H_{25}OH$ to P*n*PMA block does not change much with temperature.

Now, we test whether DMP and DOP are neutral solvents for both P*n*PMA and PS blocks. Fig. 2a gives the plots of [η] vs M_w for PS/DOP and P*n*PMA/DOP mixtures at two temperatures (62 °C and 110 °C). The Mark–Houwink constants (*a*) for PS and P*n*PMA in DOP at 62 °C are essentially the same (0.56 ± 0.005). Also, the values of *a* for PS and P*n*PMA in DOP at 110 °C are essentially the same (0.64 ± 0.01), even though this value is larger than that at 62 °C. This suggests that the solubility of PS and P*n*PMA in DOP increases with increasing temperature, as expected. But, the DOP remains to be a non-selective (neutral) solvent for both PS and P*n*PMA at a given temperature.

Fig. 2b gives the plots of [η] vs M_w for PS/DMP and P*n*PMA/DMP mixtures at two temperatures (51 °C and 110 °C). The value of *a* (0.48 ± 0.02) for PS in DMP at 51 °C is very similar to that (0.46 ± 0.03) for P*n*PMA. Also, the values of *a* for PS and P*n*PMA in DOP at 110 °C are essentially the same (0.68 ± 0.02). Although the solubility of both PS and P*n*PMA in DMP increases with increasing temperature, DMP remains to be a non-selective (neutral) solvent for both PS and P*n*PMA at a given temperature.

Fig. 3 gives temporal change of storage modulus (G') and depolarizing light intensity of neat PS-*b*-P*n*PMA. Because the microdomains of the block copolymer are lamellar, an abrupt increase in G' and depolarizing light intensity is referred to as the LDOT, whereas a precipitous decrease in G' and depolarizing light intensity is referred to as the UODT [44–47]. From Fig. 3, PS-*b*-P*n*PMA exhibits an LDOT at 142 °C and a UODT at 220 °C, and these two values are consistent with the SAXS results reported previously [21]. Hereafter, the transition temperatures of block copolymer/solvent mixtures were determined by the static birefringence, since all mixtures employed in this study show lamellar microdomains between the LDOT and UODT.

Fig. 4 shows temperature dependence of static birefringence of PS-*b*-P*n*PMA with various amounts of DMP. Interestingly, even if 0.9 vol% of DMP was added to the mixture, the LDOT was increased by 26 °C, while the UODT was decreased by 20 °C. When the amount of DMP was above 1.3 vol%, we could not detect the LDOT and UODT, indicating that this mixture becomes the disordered state. Previously, we reported that the LDOT and UODT changed significantly with static pressure [20]. Thus, the addition of a neutral solvent is another simple but efficient way to change significantly the closed-loop phase behavior of block copolymers. Fig. 5 compares the effect of DOP and DMP on the transition temperatures of PS-*b*-P*n*PMA/solvent mixtures. Within the experimental error, both solvents showed almost the same effect on the LODT and UODT. Since the change of the ODT depends on solvent selectivity [28], both DOP and DMP should have the similar selectivity for both blocks, which was also confirmed by the experimental results.

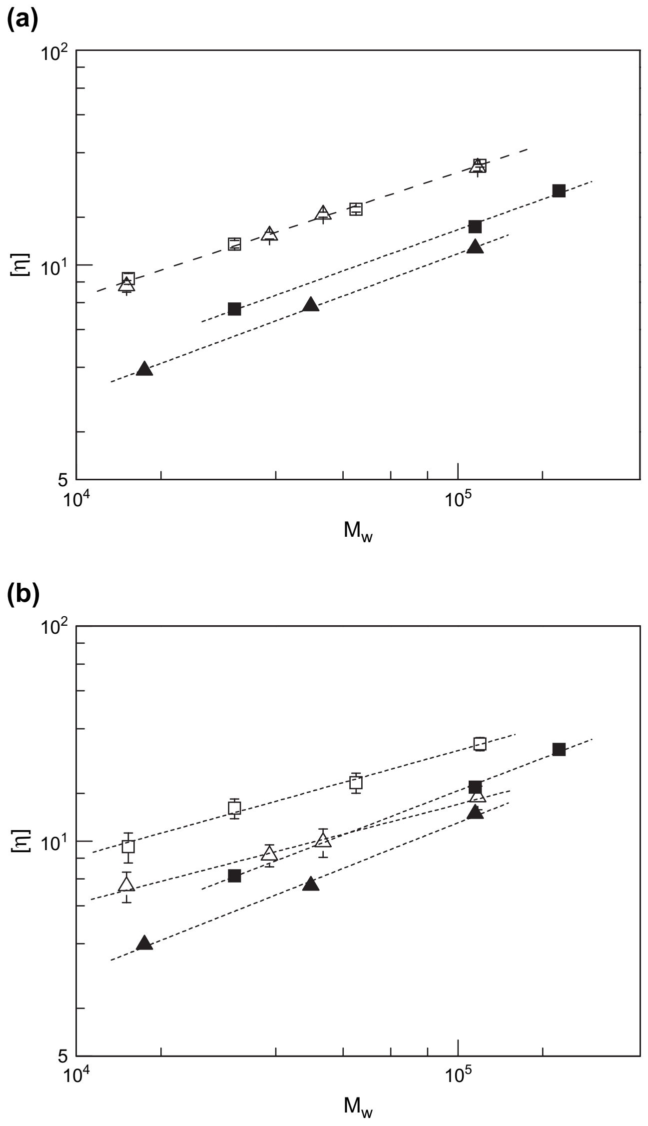

Fig. 2. (a) The plots of [η] vs M_w for PS/DOP (□, ■) and P*n*PMA/DOP (△, ▲) mixtures at two temperatures (62 °C (open symbols) and 110 °C (closed symbols)). (b) The plots of [η] vs M_w for PS/DMP (□, ■) and P*n*PMA/DMP (△, ▲) mixtures at two temperatures (51 °C (open symbols) and 110 °C (closed symbols)).

Figs. 4 and 5 clearly demonstrate that the non-selective solvents destabilized greatly the ordered phase. This is due to the

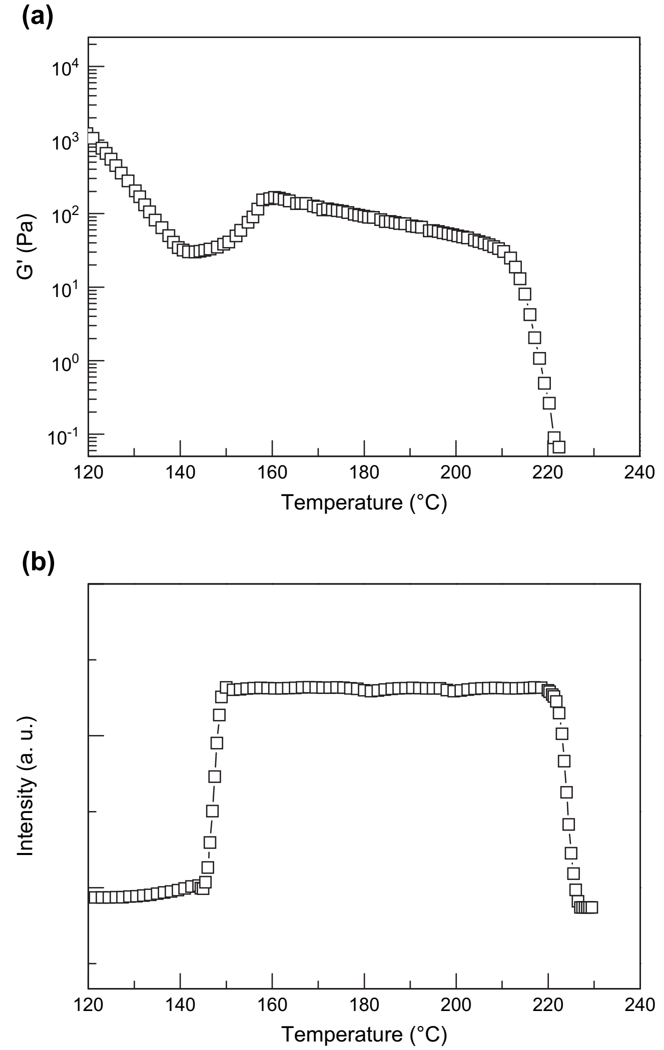

Fig. 3. Temperature dependence of (a) dynamic storage modulus (G') and (b) static birefringence for neat PS-*b*-P*n*PMA.

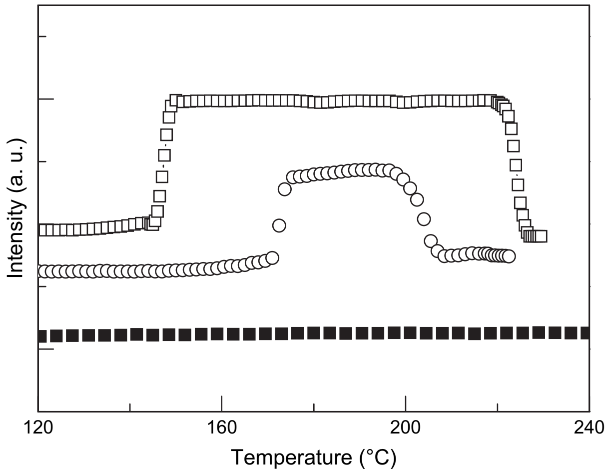

Fig. 4. Temperature dependence of static birefringence of neat PS-*b*-P*n*PMA and two mixtures with DMP: neat PS-*b*-P*n*PMA (□), 99.1/0.9 (v/v) (○), and 98.5/1.5 (v/v) (■) PS-*b*-P*n*PMA/DMP mixtures. The curves were shifted vertically for clarity.

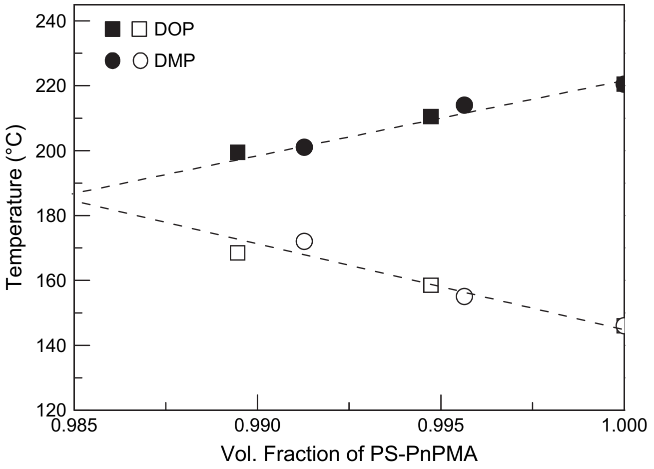

Fig. 5. The changes of LODT (open symbols) and UODT (closed symbols) of PS-*b*-P*n*PMA with the amount of DMP (○, ●) and DOP (□, ■).

screening of unfavorable segmental interactions along with increased combinational entropy in the presence of the solvent. However, for PS-*b*-P*n*PMA, the contributions of two more factors to free energy of mixing should be taken into account: the free-volume effect and the specific favorable interaction. The former arises from the disparity of isothermal compressibility (or thermal expansion coefficient (α_T)) between two block segments (equation-of-state effects) [48–50]. A weak interaction in PS-*b*-P*n*PMA was found via Fourier transformed infrared spectroscopy arising from the dipole of the PS block and induced dipole of the P*n*PMA block [23]. For PS-*b*-P*n*PMA in a neutral solvent, due to the approximately equal partitioning of the neutral solvent into each block, the disparity of α_T between PS and P*n*PMA would not change even though a non-selective solvent is added. Although the screening effect by the solvent slightly decreases the favorable specific interaction, it contributes much less than the screening of unfavorable segmental interactions along with increased combinational entropy. Therefore, the ordered phase in PS-*b*-P*n*PMA destabilizes with the addition of a non-selective solvent.

Fig. 6 shows temperature dependence of static birefringence of PS-*b*-P*n*PMA with various amounts of $C_{16}H_{34}$. The UODT decreased with increasing amount of the solvent, which is similar to the non-selective solvents. However, the LDOT decreased, *not increased*, with increasing amount of $C_{16}H_{34}$, which is quite different behavior compared with DOP (or DMP) solvent. When the amount of $C_{16}H_{34}$ in the mixture was 1.3 vol%, the LDOT was lower than 120 °C, which is the lower limit to measure the LODT due to proximity to the T_g of PS block. Therefore, $C_{16}H_{34}$ stabilizes the ordered phase near LODT, whereas it destabilizes the ordered phase near UODT.

Fig. 7 compares the changes of the LDOT and UODT of PS-*b*-P*n*PMA with two different solvents. It is noted that even when 7.5 vol% $C_{12}H_{25}OH$ was added, the lamellar microdomains were maintained, as shown in the inset of Fig. 7. We found, however, that when the volume fraction of $C_{12}H_{25}OH$ in PS-*b*-P*n*PMA/$C_{12}H_{25}OH$ mixture was higher than 0.2, morphological transformation from lamellar to

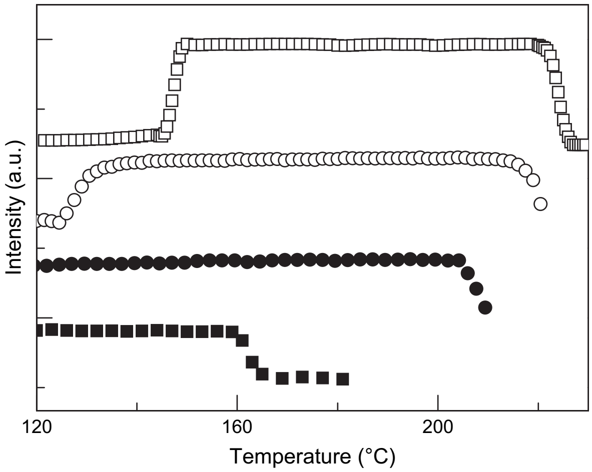

Fig. 6. Temperature dependence of static birefringence of neat PS-*b*-P*n*PMA and three mixtures with hexadecane: neat PS-*b*-P*n*PMA (□), 99.3/0.7 (v/v) (○), 98.7/1.3 (v/v) (●), and 92.1/7.9 (v/v) (■) PS-*b*-P*n*PMA/hexadecane mixtures. The curves were shifted vertically for clarity.

hexagonally packed cylindrical microdomains was observed. Phase behavior of PS-*b*-P*n*PMA/$C_{12}H_{25}OH$ mixture at higher amounts of $C_{12}H_{25}OH$ will be reported in a future publication. It is seen in Fig. 7 that although both the LODT and UODT decrease with increasing amounts of $C_{12}H_{25}OH$ and $C_{16}H_{34}$, the former solvent stabilizes the ordered phase slightly more than the latter does. Furthermore, the change of the LDOT is more sensitive to the selectivity of the solvent compared with the change of the UODT.

The stabilization of the LODT by the addition of a selective solvent to PS-*b*-P*n*PMA is mainly due to the change of the compressibility disparity. It is noted that the preferential partition of a solvent into one block could enhance the phase separation below the LDOT [32], because solvents usually possess higher compressibility than polymers [48,49]. The thermal expansion coefficients (α_T) for PS, P*n*PMA at temperatures higher than their respective T_gs, $C_{16}H_{34}$ and $C_{12}H_{25}OH$ are 5.6×10^{-4}, 7.7×10^{-4}, 10.4×10^{-4} and 8.15×10^{-4} (K^{-1}), respectively [51]. Since both $C_{12}H_{25}OH$ and $C_{16}H_{34}$ partition more selectively into the P*n*PMA block than the PS block, the difference in α_T between PS and P*n*PMA in the mixture increases, thus the free-volume disparity increases. This effect stabilizes the ordered state near the LDOT. Also, because favorable directional interactions are screened by selective solvents, phase-separated (or ordered) state is stabilized. Both contributions to the free energy of mixing could prevail over the screening of unfavorable segmental interactions along with increased combinational entropy in the presence of the solvent mentioned before. Therefore, the LDOT decreased by increasing the P*n*PMA selectivity of solvents.

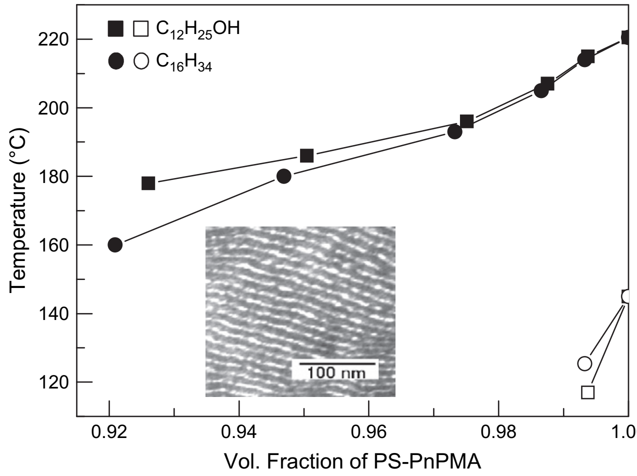

Fig. 7. The changes of LODT (open symbols) and UODT (closed symbols) of PS-*b*-P*n*PMA with the amount of $C_{12}H_{25}OH$ (□, ■) and $C_{16}H_{34}$ (○, ●). The inset gives the TEM image of 92.5/7.5 (v/v) PS-*b*-P*n*PMA/$C_{12}H_{25}OH$ mixture after annealing at 150 °C for 3 h.

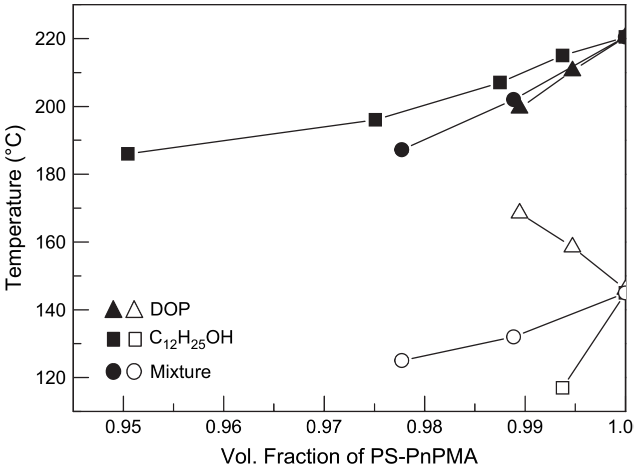

Fig. 8. The changes of LODT (open symbols) and UODT (closed symbols) of PS-*b*-P*n*PMA with DOP (△, ▲), $C_{12}H_{25}OH$ (□, ■) and 65/35 (wt/wt) DOP/dodecanol mixed solvent (○, ●).

However, near the UODT, the large values of combinational entropy may overcome the free energy penalty driven by the free-volume effect as well as the screening effect; a slight decrease in the UODT is expected. Thus, the decrease of the UODT with the addition of a selective solvent to P*n*PMA block was smaller than that with the decrease of the LDOT of PS-*b*-P*n*PMA, consistent with results given in Figs. 6 and 7. Finally, since the LDOT and UODT of PS-*b*-P*n*PMA/solvent mixtures depend upon solvent selectivity, we can easily control the LDOT and UODT by mixing of two solvents. Specifically, when a mixed solvent of DOP and $C_{12}H_{25}OH$ was used, the LODT changed little with amounts of mixed solvent, whereas the UODT decreased steadily, as shown in Fig. 8.

4. Conclusion

We have shown that the solvents significantly affected the closed-loop type phase behavior of PS-*b*-P*n*PMA/solvent mixtures depending on the solvent selectivity. With the addition of non-selective solvents, such as DOP and DMP, the LDOT increased rapidly, whereas the UODT decreased dramatically; thus, the disordered state was easily obtained even at smaller amounts of solvents. On the other hand, both LDOT and UODT decreased with increasing amount of $C_{12}H_{25}OH$, a highly selective solvent to the P*n*PMA block. However, the decrease in LDOT was greater than that of the UODT, leading to an increased immiscibility loop. The free-volume effect arising from the disparity of the thermal expansion coefficients between PS and P*n*PMA phase greatly influences the LDOT.

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