

Baroplastic behavior of miscible block copolymer blends



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ABSTRACT

Pressure dependence of various phase transitions for the miscible block copolymer (BCP) blends was evaluated by depolarized light scattering (DPLS) and small-angle neutron scattering (SANS) measurements, in which the blends consist of a polystyrene-*b*-poly(*n*-butyl methacrylate) (PS-*b*-PnBMA) and a deuterated polystyrene-*b*-poly(*n*-hexyl methacrylate) (dPS-*b*-PnHMA). Excellent baroplasticity was observed in nearly symmetric blends of PS-*b*-PnBMA/dPS-*b*-PnHMA, leading to the most outstanding pressure coefficients, $|dT/dP|$, in a closed-loop type phase behavior between a lower disorder-to-order transition (LDOT) and an order-to-disorder transition (ODT) type phase behavior. Together with the estimated pressure coefficients based on the values of enthalpic and volumetric changes at phase transitions, we demonstrate that the entropic compressibility for the miscible BCP blends is a baroplastic indicator, which was characterized by the negative volume change on mixing (ΔV_{mix}) at transitions.

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1. Introduction

Polymer baroplasticity is a desirable property for the recycling and regenerating material industries, since it allows the polymers to flow at relatively mild pressure [1–13]. Particularly in baroplastic block copolymers (BCPs), the compressibility issue pertaining to the enhanced miscibility with pressure has been an attractive topic, because an ordered state of baroplastic BCPs becomes a phase-mixed (or disordered) phase between the two dissimilar blocks upon pressurizing [9–14]. This is in contrast to the incompressibility that was dictated by enthalpic effect arising from the increased unfavorable contacts between the two blocks by increasing pressure [2,15–18].

Since a new finding of a lower disorder-to-order transition (LDOT) by Russell and coworkers in a weakly-interacting BCP that microphase-separates upon heating [19], many efforts have been contributed to the compressible (or baroplastic) behavior of BCPs [9–14,20]. Mayes and coworkers demonstrated that the LDOT of polystyrene-*b*-poly(*n*-butyl methacrylate) (PS-*b*-PnBMA) was elevated with increasing pressure, indicating the enhanced miscibility between the two blocks [3,9–11].

A LDOT of BCPs is analogous to a lower critical solution transition (LCST) in the binary homopolymer blends that macrophase-separate upon heating [21–24]. Above all, a remarkable baroplasticity with large magnitude in pressure coefficients ($|dT/dP| = 725 \text{ }^\circ\text{C/kbar}$) was found in both a LDOT and an upper order-to-disorder transition (UODT) of a closed-loop-type polystyrene-*b*-poly(*n*-pentyl methacrylate) (PS-*b*-PnPeMA), which was reported by Kim and coworkers [12]. These LDOT and UODT in weakly-interacting BCPs are not caused by the specific interaction but attributed to the dominant entropic origin arising from the growing disparity in thermal compressibility (or expansion) between the two blocks [11,25]. In fact, Freed and coworkers firstly predicted a baroplastic closed-loop in polystyrene-*b*-poly(vinyl methyl ether) (PS-*b*-PVME) using lattice cluster theory (LCT) [26], and Cho and coworkers have intensively developed an off-lattice equation-of-state (EOS) model for the compressibility effect in BCPs and blends [20,27–29]. Intriguingly, an order-to-disorder transition (ODT) in polystyrene-*b*-poly(*n*-hexyl methacrylate) (PS-*b*-PnHMA) exhibited a weak baroplasticity, where the ODT decreases with increasing pressure [1,15–17]. Therefore, the pressure-enhanced miscibility between the two blocks in these BCP analogues was correlated to the compressible nature in packing efficiency when the microphase-separated state of BCPs became intimately phase-mixed (or disordered).

Recently, a series of phase behaviors were observed in the miscible BCP blends consisting of a PS-*b*-PnBMA and a PS-*b*-

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PnHMA; this result showed a LDOT to a closed-loop, further to an ODT type phase behaviors, as the blend composition varied from PS-*b*-PnBMA to PS-*b*-PnHMA, leaving behind homework on pressure dependence of various phase behaviors [30]. In the present study, we utilized the BCP blends of PS-*b*-PnBMA/dPS-*b*-PnHMA, where a selectively deuterated BCP was exploited to enlarge the neutron contrast. To elucidate the origin and difference in baroplasticity due to the characteristic phase behaviors of weakly interacting BCP blends, the pressure dependence of transition temperatures was investigated. Depolarized light scattering (DPLS) and small-angle neutron scattering (SANS) measurements were used to evaluate the effect of hydrostatic pressure on phase transitions of PS-*b*-PnBMA/dPS-*b*-PnHMA blends. Together, with the estimated pressure coefficients based on the values of enthalpic and volumetric changes at phase transitions, the composition-dependent baroplastic behavior for the miscible BCP blends is discussed.

2. Experimental

Two symmetric PS-*b*-PnBMA and dPS-*b*-PnHMA were synthesized via sequential, living anionic polymerization of (d)styrene and *n*-alkyl methacrylates in tetrahydrofuran (THF) at $-78\text{ }^{\circ}\text{C}$ under purified argon environment; these reactions were performed in the presence of LiCl (high purity, Aldrich) using *sec*-butyllithium (1.3 M, Aldrich) as an initiator. The (d)PS volume fraction of BCPs was determined to be 0.500 by nuclear magnetic resonance (NMR) measurements based on the mass densities of the components (1.05, 1.13, 1.05, and 1.01 g/cm³ for PS, dPS, PnBMA, and PnHMA, respectively) [14]. The number-average molecular weight (M_n) and dispersity (\bar{D}) were measured to be 69,000 g/mol and 1.03 for PS-*b*-PnBMA, and 46,000 g/mol and 1.04 for dPS-*b*-PnHMA, respectively. Polymer solutions in benzene (5 wt % in solution) from the binary blends of PS-*b*-PnBMA/dPS-*b*-PnHMA were freeze-dried under vacuum for 24 h to remove the solvent at room temperature immediately after quenching them in liquid nitrogen. The samples were sequentially annealed at a target temperature (120 $^{\circ}\text{C}$) above the glass transition temperature (T_g) of the (d)PS block ($\sim 100\text{ }^{\circ}\text{C}$) longer than 24 h for an equilibrium.

Small-angle neutron scattering (SANS) experiments were performed in the 18-m SANS beamline at the HANARO (Korea) with a wavelength (λ) of 8.28 Å and $\Delta\lambda/\lambda = 0.12$. The experimental conditions were set up in a circular beam with a diameter of 6 mm, a sample thickness of 1.5 mm, and a sample-to-detector distance of 6 m. The scattered intensities for 15-min exposure time were collected on a 2-D area detector and then azimuthally averaged. The pressure-dependent SANS profiles were obtained by varying pressure at a constant temperature from 160 to 265 $^{\circ}\text{C}$. A homemade pressure cell with sapphire windows was designed for pressure experiments that were controlled by a media of silicone oil.

Depolarized light scattering (DPLS) was also used to determine pressure-dependent phase transitions of BCP blends, where a polarized He–Ne laser beam at a wavelength of 632.8 nm was set to pass through the sample and analyzer onto a photodiode sensor. The intensity at photodiode was recorded (through A/D converter) as a function of temperature at a heating rate of 0.7 $^{\circ}\text{C}/\text{min}$ from 120 to 280 $^{\circ}\text{C}$ at ambient condition; this experiment was performed under nitrogen flow to avoid thermal degradation of the polymer samples. The pressure-dependent DPLS intensity was also measured at a constant temperature from 150 to 270 $^{\circ}\text{C}$.

Transmission electron microscopy (TEM; JEM-2010, JEOL) was operated at an accelerating voltage of 200 kV to observe the morphology. Ultrathin specimens were prepared at $-25\text{ }^{\circ}\text{C}$ using a cryo-ultramicrotome (CRX-PTXL, RMC) with a diamond knife,

where the (d)PS block in the films was selectively stained with RuO₄ at room temperature to enhance the electron density contrast between two phases. Differential scanning calorimetry (DSC; PerkinElmer Diamond DSC) was scanned at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ from 80 to 280 $^{\circ}\text{C}$, where a relatively large amount ($>20\text{ mg}$) of samples was loaded in order to amplify the signal-to-noise in thermograms. The DSC data were obtained during the first heating run immediately after thermal annealing at 120 $^{\circ}\text{C}$ for 24 h under vacuum. The film thickness was measured by *in-situ* spectroscopic ellipsometry (SEMG-1000, Nanoview Co.) under vacuum, which was operated at an incidence angle of 70 $^{\circ}$ by a halogen light with broad wavelength (λ) ranging from 350 to 850 nm (or 1.5–3.5 eV). Two ellipsometric angles (Ψ and δ) related to the film thickness were continuously monitored during heating at a heating rate of 5 $^{\circ}\text{C}/\text{min}$.

3. Results and discussion

A series of phase transitions of PS-*b*-PnBMA/dPS-*b*-PnHMA blends were reproduced in virtue of an exceptionally miscible phase between the PnBMA and PnHMA blocks. It should be noted that we exploited a selectively deuterated dPS-*b*-PnHMA rather than PS-*b*-PnHMA. Fig. 1 shows a composition-dependent phase transition diagram for PS-*b*-PnBMA/dPS-*b*-PnHMA blends as a function of weight fraction (f) of dPS-*b*-PnHMA. All transition temperatures were measured by the DPLS measurements (Fig. S1), while a LDOT and an UODT of closed-loop were confirmed by SANS and TEM measurements (Fig. S2). The sequential and continuous phase transitions from a LDOT to a closed-loop, further to an ODT were entirely generated as the blend composition varied from PS-*b*-PnBMA ($f = 0$) to dPS-*b*-PnHMA ($f = 1$); this was slightly shifted to higher temperature in comparison to that for (non-deuterated) PS-*b*-PnBMA/PS-*b*-PnHMA blends presented in prior study, while the three phase transitions still remained along composition [30].

Fig. 2a shows SANS intensity profiles for PS-*b*-PnBMA/dPS-*b*-PnHMA blend with $f = 0.54$ as a function of the scattering vector (q), where the sample was subjected to pressurizing and depressurizing in a pressure cell at a constant temperature of 220 $^{\circ}\text{C}$. Here, $q = (4\pi/\lambda)\sin\theta$, and 2θ and λ are the scattering angle and wavelength of the neutron beam, respectively. The primary peak at 6.9 bar due to an ordered state of lamellar morphology weakened

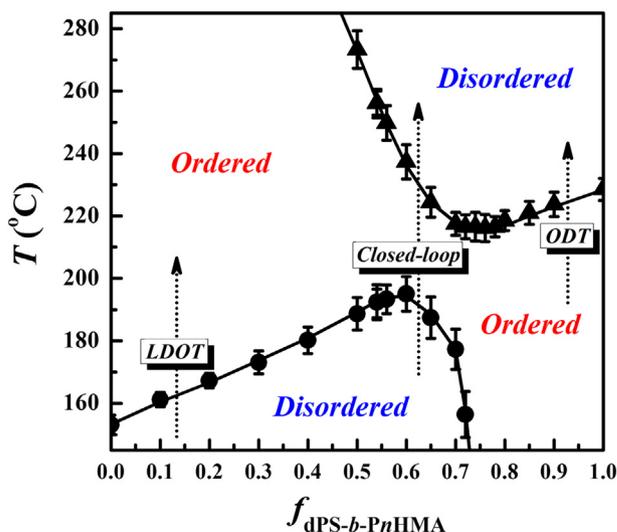


Fig. 1. Phase transition diagram for PS-*b*-PnBMA/dPS-*b*-PnHMA blends as a function of weight fraction (f) of dPS-*b*-PnHMA.

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