



# Multiple phase transitions in block copolymer blends and pressure effects on these transitions



Yonghoon Lee<sup>a</sup>, Seongjun Jo<sup>a</sup>, Wooseop Lee<sup>a</sup>, Hoyeon Lee<sup>a</sup>, Young Soo Han<sup>b</sup>,  
Du Yeol Ryu<sup>a,\*</sup>

<sup>a</sup> Department of Chemical and Biomolecular Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 03722, South Korea

<sup>b</sup> Neutron Science Division, Research Reactor Utilization Department, Korea Atomic Energy Research Institute, Daejeon 34057, South Korea

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## ABSTRACT

We sought to identify an evident enthalpic-driven transition below an entropic-driven closed-loop phase transition by studying the phase behavior in miscible binary block copolymer (BCP) blends of a polystyrene-*b*-poly (*n*-butyl methacrylate) (PS-*b*-PnBMA) and a deuterated polystyrene-*b*-poly (*n*-hexyl methacrylate) (*d*PS-*b*-PnHMA), using small-angle x-ray scattering (SAXS) and depolarized light scattering (DPLS). Intriguingly, an order-to-disorder transition (ODT) below the closed-loop transition consisting of a lower disorder-to-order transition (LDOT) and an upper order-to-disorder transition (UODT) was observed in the BCP blends of an asymmetric (PS-rich) PS-*b*-PnBMA and a symmetric *d*PS-*b*-PnHMA. Multiple phase transitions, previously undiscovered in BCP system, were attributed to a delicate balance in the free energy of the dispersive intermolecular interactions, the entropic compressibility, and the combinatorial entropy of mixing at an experimental temperature range between the glass transition temperature ( $T_g$ ) and degradation temperature ( $T_d$ ). We also characterized the effects of hydrostatic pressure on the transition temperatures to determine the thermodynamic origins of each phase transition.

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## 1. Introduction

Multicomponent polymer systems have been studied experimentally and theoretically in an effort to meet the increasing application demands for the system compatibility and material performance [1–5]. Upon heating, the entropy of mixing in a binary polymer system contributes strongly to the free energy, and it overcomes the unfavorable (dispersive intermolecular) interactions between dissimilar components, leading to a transition from a phase-separated to a phase-mixed state [1–6]. This behavior is referred to as the upper critical solution transition (UCST) and the order-to-disorder transition (ODT) in a binary polymer blend and block copolymer (BCP), respectively [4–8]. In contrast with these transitions, increasing the temperature from a phase-mixed state can lead to a phase-separated state, which undergoes a lower critical solution transition (LCST) and a lower disorder-to-order transition (LDOT) in certain polymer blends and BCPs,

respectively [3,8–12]. LCST behavior is typically observed in polymer solutions of poly (ethylene oxide)/water, which is driven by directional interactions such as strong hydrogen-bonding that weakens as the temperature increases [13,14]. However, the LDOT in a weakly interacting (no specific interactions) BCP was first observed by Russell and coworkers in polystyrene-*b*-poly (*n*-butyl methacrylate) (PS-*b*-PnBMA) [10]; this behavior could be understood in terms of equations-of-state (EOS) arguments that incorporated differences in thermal compressibility (or expansion) between the components, resulting in a positive volume change upon demixing at higher temperatures [1–3,15]. Experimental studies of weakly interacting LDOT-type BCPs have focused on a small number of well-defined systems such as polystyrene-*b*-poly (alkyl methacrylate) copolymers [7–9,16–18].

Moreover, Kim, Russell and coworkers reported a unique closed-loop phase transition that exhibits a LDOT and an upper order-to-disorder transition (UODT) upon heating in polystyrene-*b*-poly (*n*-pentyl methacrylate) (PS-*b*-PnPeMA) [19]. They suggested the possible existence of an ODT below the closed-loop transition, although an ODT at lower temperature was not detected explicitly due to the proximity to the glass transition temperature of the PS

\* Corresponding author.

E-mail address: [dyryu@yonsei.ac.kr](mailto:dyryu@yonsei.ac.kr) (D.Y. Ryu).

block. Likewise, no evidence has yet been secured to support a phase diagram comprising an ODT below the closed-loop transition due to limits on the accessible temperature range toward ODT at lower temperature.

The effects of hydrostatic pressure on a phase transition is an essential parameter for understanding the characteristic phase behaviors of the polymer blends and BCPs, because the pressure is closely associated with the thermodynamic balance between enthalpic and entropic contributions to the free energy on mixing [7,9,18–33]. Multi-component baroplastic polymers that exhibit a large magnitude of pressure coefficient ( $|dT/dP|$ ) would be desirable in regenerating polymer product, because their eco-friendly manufacturing processes require low energy consumption at lower temperatures and/or milder pressures [19]. Particularly in the LDOT-type and closed-loop-type BCPs, the phase transitions were so sensitive to pressure that an ordered state between the two dissimilar blocks could become disordered (intimately mixed) state simply upon application of a mild pressure [7,25,34]. The most remarkable responses to pressure have been observed in closed-loop-type PS-*b*-PnPeMA ( $|dT/dP| = 725$  °C/kbar) and miscible BCP blends of PS-*b*-PnBMA/deuterated PS-*b*-poly (*n*-hexyl methacrylate) (*d*PS-*b*-PnHMA) ( $|dT/dP| \sim 800$  °C/kbar), which was caused by the entropic compressibility arising from large differences in thermal expansion between the two components [25,33].

In this study, we investigated the phase behavior in miscible binary BCP blends of weakly interacting PS-*b*-PnBMA/*d*PS-*b*-PnHMA to seek an explicit ODT below the closed-loop phase transition. For this purpose, the asymmetric (PS-rich) disordered PS-*b*-PnBMA was blended with a symmetric ordered *d*PS-*b*-PnHMA. The composition-dependent phase transitions were identified using small-angle x-ray scattering (SAXS) and depolarized light scattering (DPLS) to obtain a new phase diagram. Intriguingly, multiple phase transitions, like an ODT to a LDOT and an UODT (in the closed-loop transition) upon heating, were achieved in specific BCP blend compositions at an experimentally observable temperature range between  $T_g$  and  $T_d$ . We also evaluated the effects of hydrostatic pressure on each transition to rationalize the thermodynamic origins of the phase transitions.

## 2. Experimental

An asymmetric PS-*b*-PnBMA and a symmetric *d*PS-*b*-PnHMA were synthesized by sequential, living anionic polymerization of (*d*) styrene and *n*-alkyl methacrylates in tetrahydrofuran (THF) at  $-78$  °C under a purified argon environment [35]. The (*d*)PS volume fractions evaluated by nuclear magnetic resonance (NMR) measurements were controlled to be 0.500 and 0.713 for PS-*b*-PnBMA and *d*PS-*b*-PnHMA, respectively, based on the mass densities of the components (1.05, 1.13, 1.053, and 1.01 g/cm<sup>3</sup> for PS, *d*PS, PnBMA, and PnHMA, respectively) [27]. The number-average molecular weight ( $M_n$ ) and dispersity ( $\bar{D}$ ) were measured to be 62 470 g/mol and 1.08 for PS-*b*-PnBMA, and 48 900 g/mol and 1.01 for *d*PS-*b*-PnHMA, respectively, as listed on Table 1. Binary blends of PS-*b*-PnBMA/*d*PS-*b*-PnHMA were prepared in benzene solution (5 wt%) and freeze-dried under vacuum for 24 h to remove the

solvent at room temperature immediately after quenching the solutions in liquid nitrogen. The samples were sequentially annealed at a target temperature of 120 °C, which was above the glass transition temperature ( $T_g$ ) of the (*d*)PS block ( $\sim 100$  °C) over more than 24 h to reach equilibrium.

Synchrotron small-angle x-ray scattering (SAXS) experiments were carried out at the 4C and 9A beamlines of the Pohang Light Source (PLS), Korea. The wavelength ( $\lambda$ ) of the x-ray beam was 1.175 Å, and the energy resolution ( $\Delta E/E$ ) was  $2 \times 10^{-4}$ . A 2-D Mar CCD camera (Rayonix LLC., Marccd-165) was used to collect the scattered intensities. The experimental conditions were set up in a typical beam size of  $0.8 \times 0.8$  mm<sup>2</sup>, a sample thickness of 1.5 mm, a sample-to-detector distance of 4 m, and exposure times of 20–40 s. Depolarized light scattering (DPLS) experiments were used to determine the transition temperatures of the BCP blends, such that a polarized He-Ne laser beam at  $\lambda = 632.8$  nm was directed to pass through the sample and analyzer onto a photodiode sensor. The intensity perceived at the photodiode was recorded (through an A/D converter) as a function of temperature during heating from 120 to 260 °C at a heating rate of 0.5 °C/min under ambient condition. This experiment was performed under nitrogen flow to avoid thermal degradation of the polymer samples. A homemade pressure cell was installed in the sample stage to measure the pressure-dependent DPLS intensity. The hydrostatic pressure was controlled using silicone oil within sapphire windows. The pressure was applied stepwise to the sample at the target temperatures during heating, and the pressure was returned to 6.9 bar after each step to maintain the sample dimension.

Transmission electron microscopy (TEM; JEM-2010, JEOL) images were collected at an accelerating voltage of 200 kV to observe the morphology. Ultrathin specimens were prepared at  $-25$  °C using a cryo-ultramicrotome (CRX-PTXL, RMC) with a diamond knife, where the (*d*)PS block in the films was selectively stained with RuO<sub>4</sub> at room temperature to enhance the electron density contrast between the two phases.

## 3. Results and discussion

Prior studies reported that the existence of a miscible phase between the PnBMA and PnHMA blocks enabled the binary BCP blends of symmetric PS-*b*-PnBMA/symmetric PS-*b*-PnHMA to produce a variety of phase behaviors, from LDOT-to ODT-type upon heating, as the blend composition was varied from PS-*b*-PnBMA to PS-*b*-PnHMA [30]. A closed-loop phase transition consisting of a LDOT and an UODT was reproduced at nearly symmetric blend compositions. Although an order-to-disorder transition observed in symmetric PS-*b*-PnHMA was presumed to be UODT-like in the BCP blends, no evidence was found for the existence of an enthalpic-driven ODT at lower temperature. We therefore exploited compositionally distinct BCP blends of an asymmetric (PS-rich) disordered PS-*b*-PnBMA and a symmetric ordered *d*PS-*b*-PnHMA in search of other transitions below the closed-loop transition. Here, a deuterated BCP was selected to elevate the electron density contrast between the two phases in case of BCP blends.

Fig. 1a shows the SAXS intensity profiles of PS-*b*-PnBMA and

**Table 1**  
Sample characteristics used in this study.

BCPs	$M_n$ (g/mol)	$\bar{D}$ ( $M_w/M_n$ )	$\phi_{(d)PS}^a$	Remark
PS- <i>b</i> -PnBMA	62 470	1.08	0.713	Entirely disordered
<i>d</i> PS- <i>b</i> -PnHMA	48 900	1.01	0.500	Lamellar morphology (over the entire temperature range)

<sup>a</sup> Volume fractions of (*d*)PS were calculated with mass densities of the components (1.13, 1.05, 1.053, and 1.006 g/cm<sup>3</sup> for *d*PS, PS, PnBMA, and PnHMA, respectively) using <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR).

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