Unusual Sensitivity of Closed-Loop Phase Behavior to Chain Size and Distribution

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ABSTRACT: An anionically polymerized polystyrene-*block*-poly(*n*-pentyl methacrylate) (PS-*b*-PnPMA) was fractionated by interaction chromatography (IC), and the closed-loop phase behavior of the mother block copolymer and its fractions with different chemical compositions was investigated by depolarized light scattering and polarized optical microscopy. With increasing elution time the average chain size (or the average molecular weight) of the block copolymer decreased slightly, and the average chemical composition changed steadily from a PS volume fraction of 0.583 to 0.403, thereby producing five fractions collected over the different ranges of elution time. This is caused by the difference of relative interaction strength between the stationary phase and the PnPMA chains of PS-*b*-PnPMA, in which PnPMA chains tend to be adsorbed onto the stationary phase while PS chains behave oppositely. Over the range of accessible temperatures studied (110−250 °C) a variety of phase transitions were observed, including fully ordered state, a closed-loop (consisting of the lower disorder-to-order transition and upper order-to-disorder transition), and fully disordered state. The original, unfractionated block copolymer was disordered over the entire temperature range. The variety of observed phase transitions obtained from the fractionated block copolymers is assumed to be governed by the sensitivity of the closed-loop phase behavior to average chain size, average chemical composition, and the compositional broadness.

Introduction

Block copolymers have drawn attention due to their ability to self-assemble into nanostructures, showing the rich array of microdomains whose morphologies depend on the relative chain sizes of the block components.[1,2] To take advantage of these properties, it is necessary to fully understand the phase behavior of block copolymers as well as polymer blends, and this has been the subject of extensive theoretical and experimental treatments.[3−33] In general, two types of phase transitions are observed upon heating block copolymers: an upper order-to-disorder transition (UODT)[2−6] and a lower disorder-to-order transition (LDOT),[7−18] which are analogous to the upper critical solution transition (UCST) and lower critical solution transition (LCST), respectively, found in polymer blends.[19−26] In the case of UODT, the entropy increases and segmental interactions decrease as temperature increases, resulting in a transition from a microphase-separated to a phase-mixed (or disordered) state at higher temperature. In contrast, the LDOT is characterized by an increase in entropy through a negative volume change on mixing. This behavior has been successfully described by equation-of-state (EOS) arguments that incorporate the difference in the thermal expansion coefficients of the two components, causing an increasing difference in the pure component volumes.[8,20−24] Many theories based on the equations of state and lattice cluster concept with structured monomers[7,9,25] have been used to describe LCST and LDOT behavior. A compressible, regular solution theory has also been proposed to depict the complex phase behaviors in reasonable agreement with the experimental results.[10,26]

Recently, it has been reported that both polystyrene-*block*-poly(*n*-pentyl methacrylate) copolymer (PS-*b*-PnPMA) and polymer mixture (PS/PnPMA) showed two transitions: a LDOT at lower temperature and a UODT at higher temperature, which is referred to as closed-loop phase behavior.[27−33] This phase behavior is caused by the delicate balance between the weak intermolecular interaction and the entropy by disparity in the compressibility as well as by the chain conformation. With increasing temperature, the compressibility difference would gain more entropy due to the increased volume when they microphase-separate, which induces a LDOT at relatively lower temperature. The combinatorial entropy of mixing at higher temperature would eventually drive PS-*b*-PnPMA into the phase-mixed state by prevailing over the compressibility difference and unfavorable interactions from dissimilar monomer segments, resulting in a UODT. It should be pointed out that these weak interactions arise from dipole of phenyl ring and the induced dipole of the polar ester group of *n*-pentyl methacrylates.[32,33] In addition, this behavior was more recently elucidated by the compressible random phase approximation (RPA) theory suggested by Cho.[11,12] Such an observation leads to the possibility of the existence of closed-loop phase behavior in other systems such as PS/Poly(vinyl methyl ether), yet it has not been observed

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due to the limitation of the experimentally accessible temperature window between the glass transition (T_g) and thermal decomposition temperature (T_d).

Particularly, the closed-loop phase behavior verified in PS-*b*-PnPMA was found to be significantly dependent on the average chain size; thus, the closed-loop was subsequently observed within narrow range of molecular weight.[27,28] However, it is difficult to investigate how small changes both in the chain size and chemical composition have influence on the closed-loop phase transition because there has still been the synthetic difficulty in anionic polymerization to delicately control them. The interaction chromatography (IC) technique, nevertheless, uniquely provides us with fractionation to separate a mother block copolymer into the different chain sizes (or molecular weights) and chemical compositions by virtue of the difference of interaction strength between one component of the block copolymer and stationary phase.[34−38]

In this study, the phase transitions for a unfractionated mother PS-*b*-PnPMA and five fractions (sequentially denoted as Fm, F1, F2, F3, F4, and F5) separated by using IC were investigated by depolarized light scattering measurement and polarized optical microscopy to elucidate the sensitivity of closed-loop phase behavior to the average chain size, average chemical composition, and the compositional broadness.

Experimental Section

PS-*b*-PnPMA was synthesized by the sequential, anionic polymerization of styrene and *n*-pentyl methacrylate in tetrahydrofuran at −78 °C under purified argon using *sec*-butyllithium as an initiator. The weight- and number-average molecular weights (M_w and M_n) and polydispersity (M_w/M_n) were measured by size-exclusion chromatography (SEC) with the multiangle laser light scattering (MALLS), yielding more exact and typically smaller polydispersity value comparing with that value obtained from standard calibration method due to the band broadening effect in SEC.[39,40] For the fractionation of PS-*b*-PnPMA, a high-performance liquid chromatography (HPLC) system was used, which consists of a solvent delivery pump (Polymer Lab. LC 1150), a six-port sample injector (Rheodyne, 7125) equipped with a 100 μL injection loop, and a variable wavelength UV/vis absorption detector (Spectra-Series, UV 100). For the reversed phase liquid chromatography (RPLC) separation of the PS-*b*-PnPMA, a C_{18} (octadecylsilane) column (70 × 22 mm i.d.) and CH_2Cl_2/CH_3CN eluent (62/38, v/v) were used as the stationary phase and the mobile phase, respectively. The sample concentration was 150 mg/mL, and the flow rate of the mobile phase was 1.2 mL/min. The temperature of the column was set to 34 °C by circulating fluid from a programmable bath/circulator through a homemade column jacket. The chromatograms were recorded with a UV absorption detector operating at a wavelength of 260 nm.

The mother PS-*b*-PnPMA (denoted as Fm) was fractionated into five fractions by using this IC technique. The PS volume fraction (Φ_{PS}) in the mother and five fractions of PS-*b*-PnPMA was determined by ^{1}H nuclear magnetic resonance (^{1}H NMR) with mass densities of two components (1.05 and 1.03 g/cm^3 for PS and PnPMA, respectively). The molecular characteristics for the samples are given in Table 1.

The transition temperatures for the mother and five fractions of the PS-*b*-PnPMA were measured by depolarized light scattering and polarized optical microscopy. The samples were prepared by compression-molding at 110 °C and then placed between two cover glasses in the heating cell, followed by thermal annealing at 110 °C for 24 h to thermally equilibrate. Measurements were performed using a polarized beam from a He−Ne laser at a wavelength of 632.8 nm. The detector intensity at photodiode through A/D converter is recorded as a function of temperature at the heating rate of 0.3 °C /min from 110 to 250 °C under nitrogen flow, which is as slow as accessible to thermally quasi-equilibrated condition for the samples. In addition, equilibrium experiment by temperature increment showed the similar results for PS-*b*-PnPMA elsewhere.[41]

Table 1. Molecular Characteristics of the Fractions Used in This Study

sample code	M_w[a]	M_w/M_n[a]	Φ_{PS}[b]	state[c]
Fm	53 700	1.01	0.466	disordered
F1	62 400	1.02	0.583	ordered
F2	57 200	1.01	0.526	ordered
F3	53 500	1.01	0.480	LDOT at ~170 °C UODT at ~200 °C
F4	52 900	1.01	0.441	disordered
F5	52 600	1.01	0.403	disordered

[a] Weight- and number-average molecular weights (M_w and M_n) and polydispersity (M_w/M_n) measured by size-exclusion chromatography with multiangle laser light scattering (SEC-MALLS). [b] Volume fraction of PS measured by ^{1}H nuclear magnetic resonance (NMR) with mass densities of two components (1.05 and 1.03 g/cm^3 for PS and PnPMA, respectively). [c] Observed phase states over the entire temperature range.

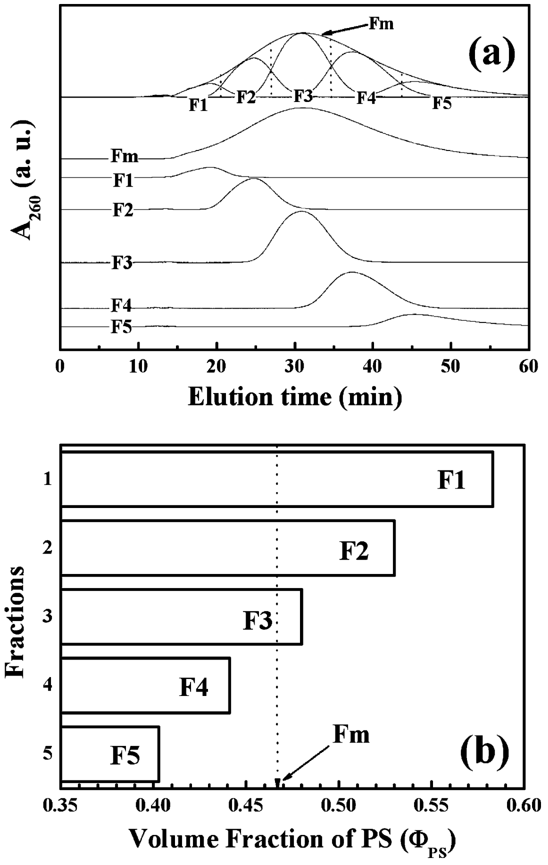

Figure 1. (a) Isothermal IC chromatograms for the mother PS-*b*-PnPMA (Fm) and the fractions. The fractions were collected at the elution time interval indicated with dashed lines. Only the uncoupled PS homopolymer (eluted before 11 min of elution time) was removed for Fm. (b) The volume fraction of PS (Φ_{PS}) for each fraction.

An Advanced Rheometric Expansion System (Rheometrics Co.) with 25 mm diameter parallel plates was used to determine the shear modulus (G' (Pa), G'' (Pa)) of the mother PS-*b*-PnPMA (Fm) from 110 to 250 °C at a heating rate of 0.3 °C/min under nitrogen flow. A strain amplitude of 0.05 and angular frequency of 0.1 rad/s, which lie in linear viscoelasticity, were used.

Results and Discussion

Figure 1a shows the chromatograms in isothermal IC, detected at a wavelength of 260 nm, as a function of elution time for homopolymer-free mother PS-*b*-PnPMA (Fm) and five fractions of PS-*b*-PnPMA (F1, F2, F3, F4, and F5) obtained by the sequential fractionation from Fm. Fm shows the broader

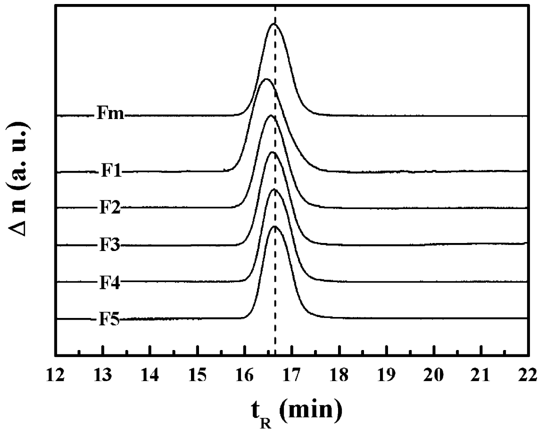

Figure 2. SEC chromatograms detected by refractive index for each fraction. Dashed line corresponds to M_p (peak molecular weight) of the mother PS-*b*-PnPMA (Fm) for comparison.

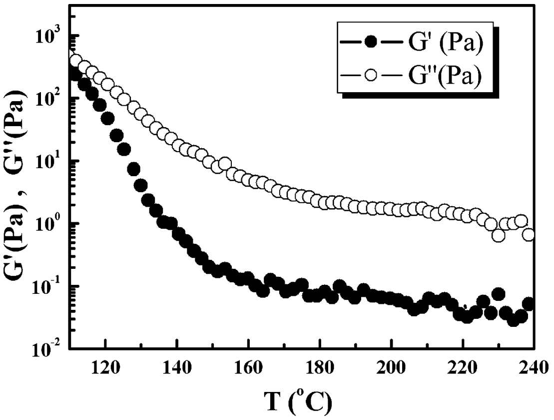

Figure 3. Temperature dependence of the storage (G' (Pa)) and loss (G'' (Pa)) modulus for the mother PS-*b*-PnPMA (Fm). Parallel plates with 25 mm diameter were set to a strain amplitude of 0.05, angular frequency of 0.1 rad/s, and at a heating rate of 0.3 °C/min.

distribution as a statistically averaged summation of whole fractionated samples with no homopolymer. It should be noted that although uncoupled PS homopolymer was successfully removed in Fm in this study, there may be as much as 5 wt % of uncoupled PS homopolymers in PS-based block copolymers, which can be sensitively detected in the interaction chromatogram. This is due to impurities such as water or oxygen that act as terminating agents for the active anions during polymerization, described elsewhere.[34] When Fm was put through to RPLC separation at 34 °C (elution after solvent peak position of 13 min), it was completely resolved and separated into five fractions (F1, F2, F3, F4, and F5) having different chain sizes of PnPMA in the PS-*b*-PnPMA, as shown in Figure 1a. The dashed lines illustrate the time zones over which each fraction was collected, resulting in the corresponding fractionated samples. The narrow distribution of each fraction is shown in the chromatogram series given in Figure 1a.

Isothermal IC separation of PS-*b*-PnPMA is effective since it allows us to fractionate Fm by the differences in the interaction strengths of the PnPMA chains with the stationary phase, which have stronger interaction than PS chains in the IC regime. As a result, the interaction strength depends on the chain size of the PnPMA block in PS-*b*-PnPMA. Additionally, the chain size of PS in PS-*b*-PnPMA influences the elution position of the block copolymer, since the eluent used in this experiment is also good solvent for PS in the SEC regime and it partially prevents interaction of PnPMA chains with the stationary phase.[35] Thus, fractions having relatively longer PnPMA chains will be eluted out at delayed times due to stronger interactions with the stationary phase, while PS-*b*-PnPMA having shorter PnPMA chains experience at shorter elution time, despite weak interactions that might exist between the PS chains and the stationary phase. In this way, Fm was fractionated into the different average chain sizes (or average molecular weights) and the different chemical compositions as given in Figure 1b. It is seen that Φ_{PS} in F1 is the largest (0.583) and gradually decreases with increasing the elution time down to 0.403 in F5. The resolved individual fractions were collected again and their absolute molecular weights were determined by SEC-MALLS separately, based on the method reported previously.[36]

Figure 2 displays the chromatograms of SEC for Fm and five fractions separated by RPLC. It is seen that all samples show a narrow single peak, although the block copolymers are composed of the different PnPMA chain size in PS-*b*-PnPMA. As a result, the total hydrodynamic volume of the fractions, as an average chain size estimated by peak times (deviation from the dashed line), decreased from F1 to F2 but remained similar to Fm for F3, F4, and F5, in accordance with the average molecular weights of these three fractions. The variation of the average molecular weight and chemical composition with elution time in the IC can be explained by the attractive interaction strength of the PnPMA block proportional to the PnPMA chain size and the screening of the attractive interaction by the PS block increasing with the PS chain size, where PS block is not interactive with the stationary phase and uncoupled PS homopolymer elutes by the SEC mechanism. Consequently, the fraction having the shortest PnPMA block and the longest PS block length (F1) elutes first and vice versa. The fractions with higher molecular weight are also excluded from the pores of the column packing materials, which keep them from the effective interaction. This screening and exclusion effects are more significant for the fractions with longer PS block and higher molecular weight which seems to result in a relatively large variation for early eluting fractions in the molecular weight and chemical composition.

The temperature dependence on shear storage and loss moduli (G' (Pa), G'' (Pa)) for Fm is shown in Figure 3. With increasing temperature G' and G'' decrease rapidly past the glass transition temperature (T_g) and then begin to deviate out of the torque regime at temperatures greater than ~180 °C. This is a characteristic of homogeneous block copolymers melt as indicative of the disordered state. If the materials were ordered G' and G'' would be much higher due to the flow resistance caused by the microphase separation of block copolymers. The disordered state in Fm was again verified over this temperature range using depolarized light scattering, as shown in Figure 4. Since the amount of all the fractions was limited, the phase behavior of each fraction could be only measured by depolarized light scattering and confirmed by polarized optical microscopy provided that they form the lamella or cylinder microdomain in the ordered state.

For these morphologies the existence of static birefringence should correspond to the ordered state, whereas total extinction indicates the disordered state for the block copolymers in this range of chemical composition.[42−44] These are summarized in Table 1.

Figure 4 shows depolarized light intensity as a function of temperature for Fm and all fractions studied. All data were taken at 0.1 °C intervals from 110 to 250 °C at a heating rate of 0.3 °C/min, chosen to lie between the glass transition (T_g ~ 100 °C) of PS and degradation temperature (T_d ~ 250 °C). Over the entire temperature range, depolarized light intensity was not

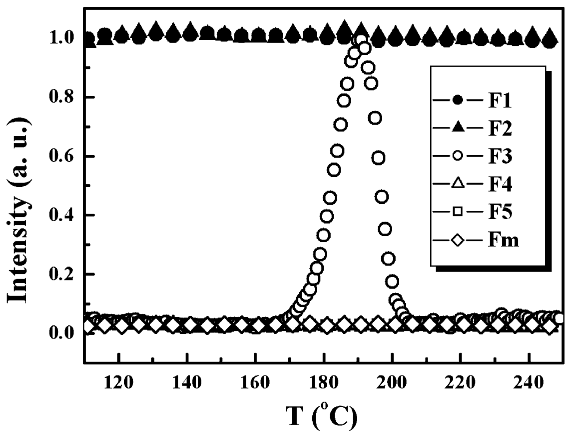

Figure 4. Depolarized light scattering intensity for fractions as a function of temperature from 110 to 250 °C at a heating rate of 0.3 °C/min.

observed for Fm, indicating that it is in the disordered state, consistent with the rheological measurement. For F1 and F2, however, depolarized light intensity remained very high, which is a characteristic of the ordered state.[42−44] F1, taken at earliest elution time, has the highest average molecular weight (M_w, 62 400 g/mol) and F2 has higher M_w (57 200 g/mol) than that of Fm (53 700 g/mol). The ordered state is present over the entire experimentally accessible temperature range in both F1 and F2, presumably accounted for by larger M_w, despite symmetry effects that can result in the disordered state in the weak segregation regime.

Interestingly, depolarized light intensity for F3 begins to increase at 170 °C with increasing temperature and then reaches a maximum, followed by a rapid decrease at nearly 200 °C to zero, where it remains with further increasing temperature up to 250 °C. The abrupt increase and decrease in the intensity correspond to LDOT and UODT, respectively, characterized as a closed-loop phase transition. Whereas Fm showed a fully disordered state, in which M_w and chemical composition were similar to those of F3. It should be emphasized that compositional distribution has an influence on the dramatic difference in the phase transition between Fm and F3 due to the delicate energetic variations between two block components for PS-*b*-PnPMA. This effect would require a detailed theoretical evaluation for the closed-loop phase behavior, incorporating a parameter for compositional distribution into the interaction parameter, which is beyond the scope of this report. Consequently, the closed-loop phase transition was only observed for F3, which has a very narrow compositional distribution. In the case of F4 and F5, which have much longer PnPMA chains of PS-*b*-PnPMA and similar molecular weight as F3, the total extinction indicates the disordered state of the block copolymers. This can be presumably attributed to more asymmetric chemical compositions, leading to the disordered regime out of the phase boundary.

The transition temperatures are confirmed with polarized optical microscopy (POM). For reproducibility, all experiments were performed from 110 to 250 °C at a heating rate of 0.3 °C/min, chosen to coincide with the in-situ depolarized light scattering measurements. The POM images at selected temperatures display visual states of the fractions with increasing temperature. In F1 and F2, as an example, the birefringence from the grain anisotropy of microdomains remains over the entire temperature range, indicative of the ordered state of the block copolymers. F3, however, shows the different images depending on temperature, consistent with the depolarized light scattering results as shown in Figure 5. With increasing temperature, dark images representing the disordered state are observed up to 169 °C, birefringence from 170 to 202 °C, and dark images again at higher temperature, which is another identification of the closed-loop phase transition for F3. The POM observations were consistent with the results from depolarized light scattering over the experimentally accessible temperature range within experimental error range (±1 °C).

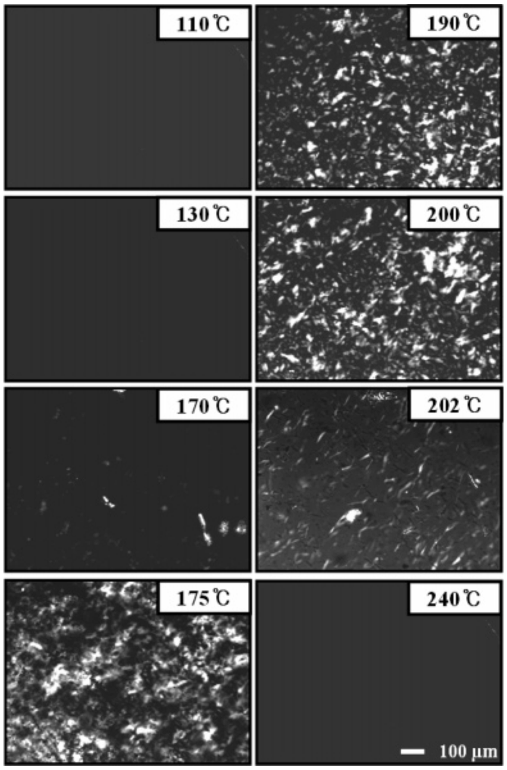

Figure 5. Polarized optical microscopy (POM) images for F3 as taken during 0.1 °C interval from 110 to 250 °C at a heating rate of 0.3 °C/min.

According to the governing rule for the general phase behavior of the block copolymers, the compositional asymmetry increases the χN for microphase separation, where χ and N are the interaction parameter between two block components and the average chain size, respectively.[3] This simple approach could be used in this study to rationalize the various phase transitions for the mother and five fractions because the microphase separation at the different chemical composition demands for the different average chain size on the basis of the same χ. In addition, the phase transition of PS-*b*-PnPMA was also affected by the compositional broadness, leading to the closed-loop phase transition for F3 exclusively. Thus, the disordered mother PS-*b*-PnPMA (Fm) in a vicinity of phase boundary taken as a model system was successfully fractionated into five fractions using IC technology depending on the chain size of the PnPMA block in PS-*b*-PnPMA, caused by the attractive interaction of the PnPMA chains with stationary phase. The results presented in this study indicate the simple approach to investigate the sensitivity of the closed-loop phase behavior to average chain size, average chemical composition, and the compositional broadness.

In summary, the closed-loop phase behavior for the mother and fractionated PS-*b*-PnPMAs, prepared by IC, was investigated. The mother PS-*b*-PnPMA (Fm) was successfully fractionated into five fractions by collecting at different elution times. With increasing elution time, the average chain size of the block copolymer decreased slightly, and the average chemical composition changed steadily from a PS volume fraction of 0.583 to 0.403. Compared with the disordered state for Fm over the entire temperature range, the ordered state was obtained for F1 and F2 dominantly due to the increased average chain sizes, and the disordered state was observed in F4 and F5 due to more asymmetric chemical compositions at nearly same average chain sizes with Fm. However, the fraction taken at intermediate elution time (F3), having a similar molecular weight and chemical composition as Fm, possessed a closed-loop phase transition, implying the significant sensitivity of the closed-loop phase behavior on the broadness of the compositional distribution. We conclude that the closed-loop phase transition of PS-*b*-PnPMA is very sensitive to average chain size (or average molecular weight), average chemical composition, and compositional broadness presumably due to the delicate energetic variations between two block components in the PS-*b*-PnPMA.

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