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Tuned phase behavior of weakly interacting polystyrene-*block*-poly(n-pentyl methacrylate) by selective solvent

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ABSTRACT

We investigated, via small angle X-ray scattering, depolarized light scattering, rheometry, and transmission electron microscopy, the phase behavior of the mixture of a symmetric polystyrene-*block*-poly(n-pentyl methacrylate) copolymer (PS-*b*-PnPMA) showing the closed-loop phase behavior and excellent baroplasticity, and dodecanol, a PnPMA-selective solvent. We found that the addition of a selective solvent is simple, but very effective to obtain various microdomains including hexagonally packed cylinders and gyroids. Also, with increasing temperature, the mixtures showed multiple ordered-to-ordered transitions (OOTs) in addition to upper ordered-to-disordered transition (UODT). The first observation of gyroid microdomains in PS-*b*-PnPMA is very important, although they have been widely reported in many block copolymers, for instance, PS-*block*-polyisoprene copolymer (PS-*b*-PI) and PS-*block*-poly(D,L-lactide) copolymer (PS-*b*-PLA). Since the gyroid microdomains of PS-*b*-PnPMA show excellent baroplasticity, external pressure instead of temperature could easily change the microdomains.

1. Introduction

Block copolymers have been studied extensively due to their self-assembled nanostructures which are governed by the degree of segregation (χN), where χ is the Flory–Huggins interaction parameter and N is the degree of polymerization, and volume fraction for one of the blocks (f) [1–6]. While most block copolymers show order-to-disorder transition (ODT) [1–9], some weakly interacting block copolymers exhibit lower disorder-to-order transition (LDOT) [10–13]. We reported that polystyrene-*block*-poly(n-pentyl methacrylate) copolymer (PS-*b*-PnPMA) and its derivatives have the closed-loop phase behavior, combining LDOT at a lower temperature and an upper order-to-disorder transition (UODT) at a higher temperature [13–20]. Since the phase behavior of PS-*b*-PnPMA is greatly changed by pressure [16,20], the transition temperatures of the closed-loop are easily adjusted by pressure. For instance, the closed-loop size was shrunk with increasing external hydrostatic pressure, while it was enlarged with increasing nitrogen or argon gas pressure [20]. Also, we fabricated high density arrays of nano-indentations for phase-change data-storage device using excellent baroplasticity [21].

Among various microdomains observed in block copolymers, gyroid microdomains have received a great attention owing to their 3D periodic bicontinuous network and large surface area. Crossland et al. [22,23] fabricated dye-sensitized solar cell (DSSC) by employing bicontinuous gyroid microdomains of poly(4-fluorostyrene)-*block*-poly(D,L-lactide) (PFS-*b*-PLA), and investigated the photovoltaic performance–morphology relationship. A photovoltaic cell with TiO_2 gyroids gave higher solar cell efficiency than that with wire or particle-shaped TiO_2 [23]. Also, based on the 3D periodic interconnected gyroids of vanadium pentoxide, Scherer et al. [24] fabricated an electrochromic device showing fast switching speed, high coloration contrast and composite coloration efficiency. Accordingly, if such gyroid microdomains are combined with excellent baroplasticity as shown in PS-*b*-PnPMA, they would be employed in future nanotechnology such as superlenses with negative refractive index [25,26] whose refractive index would be precisely controlled by an external pressure instead of temperature.

However, to the best of our knowledge, there has been no report on gyroid microdomains in PS-*b*-PnPMA. This might be due to experimental difficulty in the synthesis of PS-*b*-PnPMA having gyroid microdomains, since they only exist within quite narrow ranges of the total molecular weight and volume fraction. One approach to achieve gyroid microdomains is to add a solvent to PS-

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b-PnPMA, because various microdomains have been observed in block copolymer/solvent mixtures [27–33]. Solvents (*S*) are classified into two categories for A-*b*-B diblock copolymer: neutral solvents ($\chi_{AS} = \chi_{BS}$) and selective solvents ($\chi_{AS} \neq \chi_{BS}$). The neutral solvents, partitioning equally into two block domains, could effectively screen unfavorable contacts between dissimilar monomers, resulting in reducing the interaction parameter of A and B blocks, but the effective volume fraction occupied by one block domains remains nearly constant. On the other hand, the selective solvents, preferentially partitioning into one-block domains, change the block volume fraction obviously. It is noted that the blend consisting of an A-*b*-B and homopolymer A (or B) is similar to the mixture of A-*b*-B with a selective solvent [34,35]. However, macrophase (not microphase) separation could occur for the blend with a large amount of a homopolymer. But, a relatively large volume fraction of a selective solvent can be used without occurrence of the macrophase separation in the mixture. Thus the use of a selective solvent is more appropriate for obtaining gyroid microdomains of PS-*b*-PnPMA compared with the blend of PS-*b*-PnPMA and homopolymer (PS or PnPMA).

In this study, we chose dodecanol as a PnPMA-selective solvent [31] to tune the phase behavior of a symmetric PS-*b*-PnPMA. The phase behavior was studied as functions of temperature and solvent fraction by using small angle X-ray scattering (SAXS), depolarized light scattering, rheometry, and transmission electron microscopy (TEM). By the judicious control of the weight fraction for dodecanol and temperature, we successfully obtained gyroid microdomains of PS-*b*-PnPMA. Also, we found multiple ordered-to-ordered transitions (OOTs) in addition to UODT in the mixtures. Based on these observations, a full phase diagram for PS-*b*-PnPMA/dodecanol mixture was obtained.

2. Experimental section

2.1. Materials and molecular characterization

The PS-*b*-PnPMA used in this study was synthesized by conventional sequential anionic polymerization described in detail elsewhere [13–15]. The number-average molecular weights (M_n) and the polydispersity index (M_w/M_n) were 53,800 and 1.05, respectively, measured by size exclusion chromatography (SEC: Waters) combined with a multi-angle laser light scattering. The PS block volume fraction in the PS-*b*-PnPMA was 0.50 determined by ^{1}H nuclear magnetic resonance (^{1}H NMR: Bruker digital Avance III 400). Dodecanol (the boiling point is 262 °C), was purchased from Sigma–Aldrich and used without further purification. Previously, we reported that PS/dodecanol mixture had upper critical solution transition (UCST) at ~130 °C, while PnPMA/dodecanol mixture did not show any turbidity above room temperature [31]. Thus, dodecanol is a PnPMA-selective solvent because of the possible formation of hydrogen bonding between dodecanol and PnPMA block. The pre-determined amount of PS-*b*-PnPMA and dodecanol was mixed using methylene chloride (CH_2Cl_2) as a co-solvent. The CH_2Cl_2 was removed under a gentle flow of nitrogen first, and then under mild vacuum until a constant weight was achieved. Samples were prepared by compression molding at 50 °C. Molecular characteristics for all the samples employed in this study are given in Table 1.

2.2. Small angle X-ray scattering (SAXS)

SAXS profiles ($I(q)$ vs q ($=(4\pi/\lambda)\sin\theta$); here q and 2θ are the magnitude of scattering vector and scattering angle, respectively) were obtained on beam line 4C at the Pohang Light Source (Korea), where the X-ray wavelength was 0.1115 nm. The scattered X-rays were collected onto a CCD detector (Rayonix SX165, USA). The sample to detector distance was 2.60 m, and the sample thickness and the exposure time were 1.0 mm and 20 s, respectively.

Table 1
Molecular characteristics of all the samples employed in this study.

Sample code	M_n[a]	PDI[a]	f_{PS}[b]	$w_{dodecanol}$[c]	Transition[d]
SnPMA	53,000	1.05	0.50	0	L → D
SnPMA-15				0.15	L → D
SnPMA-21				0.21	C → G → L → D
SnPMA-25				0.25	C → G → D
SnPMA-35				0.35	C → D

[a] Determined by SEC calibrated with PS standards.
[b] Measured by ^{1}H NMR with the known densities for PS (1.05 g/cm^3) [36] and PnPMA (1.03 g/cm^3) [15].
[c] Weight fraction of dodecanol in the mixtures.
[d] L: lamella, C: hexagonally packed cylinder, G: gyroid, and D: disordered state.

2.3. Rheometry

Dynamic rheological measurements were carried out by using an Advanced Rheometrics Expansion System (ARES) with 25 mm parallel plate geometry and a 1 mm gap. Samples were first annealed at 90 °C for 1 h to remove thermal history, and then temperature was increased at a heating rate of 1.0 °C/min. The strain amplitude and the angular frequency were 0.05 and 0.1 rad/s, respectively, which lie within the linear viscoelastic region.

2.4. Depolarized transmitted light scattering

Depolarized transmitted light scattering (static birefringence) experiments were performed at a heating rate of 1.0 °C/min. The samples were sealed between two glass plates with thickness of 0.5 mm. Vertically polarized light from a HeNe laser (632.8 nm) passes through the sample and a horizontal analyzing polarizer onto a photodiode. The absence of birefringence indicated the isotropic states (disordered, sphere and gyroid), while lamellar or cylinder phases showed birefringence. Polarized optical microscopy (POM, Axioplan, Zeiss Co.) with a heating block blanketed in nitrogen was also used to confirm the results of birefringence experiments.

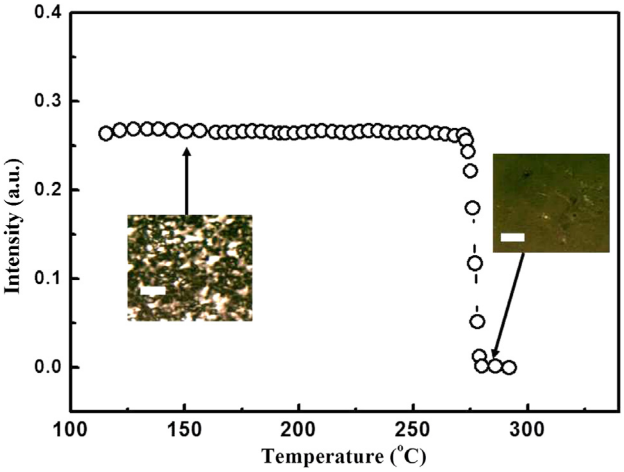

Fig. 1. Temperature dependence of depolarized light scattering intensity for neat SnPMA and two POM images (the scale bar = 40 μm) at 150 °C and at 280 °C.