

Effect of composition of added random copolymer on the phase behavior of block copolymer

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Abstract

Blends of styrene–butadiene diblock copolymer (S–B, 52 wt% styrene content) and styrene–butadiene random copolymer (SBR) of various styrene compositions were studied by small-angle X-ray scattering, light scattering, and transmission electron microscopy. The composition of random copolymer plays an important role in the solubilization of SBR in S–B. The order–disorder transition temperature, T_{ODT} , decreases linearly with the addition of SBR. T_{ODT} decreases as the symmetry in SBR composition increases and shows the highest value in the case of homopolymers. Asymmetric butadiene-rich SBR dissolves mostly into PB microdomain of S–B to increase lamella microdomain spacing, D , and its addition makes the overall microdomains of S and B in the mixture more asymmetrical. Symmetric SBR is localized into the interface of S–B microdomain to reduce unfavorable S–B contact at the interface. The phase diagram for S–B containing asymmetric SBR shows a succession of mixed mesophases of different morphologies from lamellae and cylinder to disordered liquid phases, whereas the phase diagram containing symmetric SBR shows two homogeneous phases and one region of two-phase coexistence, where macroscopically separated phases coexist together.

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1. Introduction

Many studies have investigated the phase behavior in binary mixtures of diblock copolymer and homopolymer [1–14]. Nojima and Roe undertook studies on diblock copolymer (A–B)/homopolymer (A) blend [7], and showed (1) that, when a small amount of A is dissolved into A–B, the spinodal temperature (T_S) is either elevated or lowered according to the molecular weight ratio of A over A–B, (2) so that the magnitude in the change of T_S is higher with larger amounts of added homopolymer. Tanaka and Hashimoto [15] studied order–disorder transition temperature, T_{ODT} , of styrene–isoprene diblock copolymer on addition of polystyrene and DOP (dioctyl phthalate, neutral solvent) in a regime where PS is solubilized in styrene microdomains. Solvent DOP is most effective in lowering T_{ODT} , and the degree of depression is slowed by increasing the molecular weight of PS. This tendency is in good

agreement with that predicted by Noolandi et al. [5]. There have also been some studies [16–20] on block copolymer/block copolymer blends, or block copolymer/random copolymer blends, which are expected to exhibit different phase behavior from diblock copolymer/homopolymer blends.

In addition to the above studies, an extension to diblock copolymer solutions with a neutral (nonselective) solvent has been carried out [21–25]. A theory developed by Whitmore and Noolandi [26] predicted that, if the solvent is a good solvent of roughly equal affinity for both of the blocks, the copolymer solution will display thermodynamics similar to that of the pure melt and there will be a tendency for neutral solvents to accumulate at the microdomain interface to screen unfavorable A–B monomer contacts at the interface. Lodge et al. [25] constructed a phase diagram for styrene–isoprene diblock copolymers by varying the selectivity of added solvents. Each solvent became less selective as T increased, inducing a variety of thermally accessible order–order transitions (OOTs) such as lamella, cylinder, and spherical micelles. The addition of a neutral solvent is analogous to increasing temperature or reducing effective interaction parameters, and the principal interdomain distance decreases as solvent the volume

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fraction increases. In one of our previous studies [18], we constructed a theoretical phase diagram for diblock copolymer (A–B) blends containing random copolymers (ABR) with compositions similar to those of diblock copolymers. The T_{ODT} of block copolymers was lowered by the addition of random copolymers regardless of their molecular weight. It was also found that the fraction of ABR solubilized into the A–B was very limited due to endothermic mixing between ABR and each block of A–B. An experimental study [19,20] on A–B/ABR blends was subsequently carried out, where the composition and molecular weight of ABR were similar to those of A–B. We showed that the T_{ODT} and the interdomain distance (D) almost linearly decreased as the ABR fraction increased within the solubility limit.

In the present study, binary blends containing symmetric diblock copolymer (A–B) and random copolymer (ABR) of various compositions are studied by small angle X-ray scattering (SAXS), light scattering (LS), differential scanning calorimetry (DSC), and transmission electron microscopy (TEM) techniques. AB random copolymer was chosen as the diluent, and the effect of composition of added random copolymer on the phase behavior of A–B is discussed. It is expected that, at temperatures below the T_{ODT} where A–B has a lamellar morphology, ABR will have solubility to A–B depending on the styrene composition of ABR: (1) if added ABR has asymmetric composition, it will dissolve either at the A or B domain of A–B to extend lamella microdomain thickness, and (2) if added ABR has symmetric composition, it will have poor solubility to both A and B domains and may dissolve at the interface of the microdomains to reduce unfavorable interaction between ABR and A-, B-monomers of A–B ($\chi_{\text{ABR/PA}} \approx \chi_{\text{ABR/PB}} \approx 0.5\chi_{\text{A/B}}$). Macroscopic phase separation will occur above the solubility limit of SBR, which will be evidenced by optical turbidity in LS and TEM experiments. Block copolymer-rich mesophase may still reveal a periodic peak profile in SAXS and heat change of microdomain formation in DSC experiments, since this is in a similar state to pure block copolymers. These independent experiments were carried out to give complementary results on the phase behavior of A–B/ABR blends, and an experimental phase diagram will be constructed.

2. Experimental section

2.1. Materials

The information of the copolymers used is listed in Table 1. Styrene–butadiene diblock copolymer (denoted by S–B50) is the same material used in the previous study [19,20], which contains 52 wt% of styrene as determined by the NMR technique, and its M_n and M_w are 25,000 and 26,000, respectively. The blend samples were prepared by first dissolving a predetermined amount of each copolymer in

toluene in the presence of an antioxidant (Irganox 1010, Ciba–Geigy Group) and then by slow evaporation of the solvent at room temperature. To remove the residual solvent, the samples were further dried under a vacuum at about 60 °C for over a day. After complete removal of the solvent, the samples were further annealed at 120 °C for 24 h. The mixture sample was designated by the sample label followed by their weight percentages, as in ‘SB50/SBR50 (90/10)’.

2.2. Methods

Synchrotron small-angle X-ray scattering (SAXS) measurement was performed at the 4C1 and 4C2 X-ray Beamline (1.608 Å in wavelength) at the Pohang Accelerator Laboratory (PLS) in Korea. The beam path was maintained under a vacuum to reduce air scattering, and the measured intensity was corrected for ring current decrease, background scattering, detector noise, and sample absorption. Since the optics of the SAXS equipment are point focused, the intensity was not corrected for the smearing effect by the primary beam. The heating and cooling rate was fixed at 2 °C/min, and the data were collected every 5 °C between room temperature and the experimental limit. Since reproducibility was shown between the heating and cooling results, we mainly used the cooling data in the present study.

The cloud temperature was determined from light scattering (LS) experiments by monitoring the intensity of scattered light at a fixed angle ($\sim 30^\circ$) through a mixture film located on a heating stage. A He–Ne laser (4 mW) was used as a light source. Heating and cooling experiments were performed several times to increase the validity of the experimental results. The same heating system was used as in the SAXS experiments, which made it possible to compare the two independent data sets directly without any further corrections between them.

Thermal analysis was performed with a Perkin–Elmer DSC7. T_{ODT} was determined from the change of exothermic enthalpy during the cooling scan. Each sample was heated far above the melt state and then cooled to room temperature at the rate of -10 °C/min. Glass transition temperatures were measured during reheating at a rate of 20 °C/min after the samples had been held at 150 °C and then cooled to -150 °C at -20 °C/min.

The transmission electron microscopy (TEM) samples were prepared by placing a drop of solution on a carbon/Formvar-coated copper grid and letting the solvent evaporate at room temperature on a sealed glass vessel. To remove the solvent evaporation effect that could have affected the observed morphology of solution-cast block copolymers, the solvent was very slowly evaporated and the samples were annealed at 35 °C for a day. To attain equilibrium morphology, the samples were further annealed above the glass transition temperatures of both blocks in a vacuum oven for 5 h. The samples were then exposed to the

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