

새로운 상거동을 가지는 블록공중합체와 단일중합체 블렌드

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**The new type of Phase Behavior
in Block copolymer & Homopolymer Blend**

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Introduction

Block copolymers have widely used in industry and science as their self-assembled materials.¹⁻⁵ Thermodynamically-incompatible segregation of block segments can produce various nano-scale (10~100nm) structures, such as lamella, cylinder, sphere, gyroid and complex form etc. This microphase separation of a block copolymer can be driven by the enthalpy of repulsive interactions or the entropy of negative volume change on mixing between block units. Here we introduce the novel diblock copolymer with closed-loop phase behavior which is composed of lower critical ordering transition (LCOT) and then upper critical ordering transition (UCOT) on heating process. The control of these two transition zones in a block copolymer let it be able to utilize as a smart material

Also, the phase behavior of a weakly interacting polymer blend consisting of polystyrene and poly(*n*-pentyl methacrylate) (PS/PnPMA) was studied by turbidity, differential scanning calorimetry (DSC), and small angle neutron scattering method (SANS). Blends of PS and

PnPMA exhibited both the upper critical solution transition (UCST) and the lower critical solution transition (LCST) behavior, and for higher molecular weights of PS, an hour-glass type of phase behavior was observed. The influence of temperature on the miscibility of PS and PnPMA in the homogenous state was investigated by using SANS. The phase behavior for the PS/PnPMA blends is discussed using a compressible mean field theory. This phase behavior is compared with PS-PnPMA diblock copolymer where a closed loop phase diagram was observed.

Experimental

All kind of samples were anionically polymerized on symmetric composition with narrow polydispersity.

Samples for SANS were prepared by compression molding plaques at 100°C, followed by annealing at 100 °C for 24 hrs under vacuum. SANS experiments were performed at the Hanaro Reactor (Korea) with a wavelength (λ) of 0.431 nm and $\Delta\lambda/\lambda = 0.12$ at a sample to detector distance of 3 m. Scattering intensities were collected on a 2-D area detector and then circularly averaged. The sample thickness was 1.0 mm and the exposure time was 30 min.

Table 1 Characteraction of block copolymers

sample code	Mn	Mw / Mn	f _{PS} (weight %)
dPS	9150	1.02	
PnPMA-M	7900	1.02	
DPS-PnPMA-L	46000	1.03	50.1

Result & Discussion

SANS was performed for 50/50 (wt/wt) dPS/PnPMA-M blend as a function of increasing temperature from 75 °C to 130 °C. Figure 1(a) shows the SANS profiles at several temperatures. It is seen that with increasing temperature, the SANS intensity ($I(q)$) at all wavelengths ($0.08 \sim 0.7 \text{ nm}^{-1}$) first decreased, went through a minimum, then increased again. The temperature ($\sim 97 \text{ }^\circ\text{C}$) corresponding to a minimum SANS intensity was slightly lower than the midpoint ($102 \text{ }^\circ\text{C}$) between the UCST and LCST of d-PS/PnPMA. From Figure

$I(q=0)$ was determined using the Ornstein-Zernike equation. Using the incompressible random phase approximation (RPA) theory due to de Gennes,⁶ the values of χ shown in Figure 1(b) were obtained. It is seen that with increasing T (or decreasing $1/T$), χ first decreases, and goes through a minimum, then increases again. Since a standard expression of χ ($\chi = a + b/T$) cannot match with experimental data, we fitted the data to $\chi = a + b/T + c/T^2$, yielding $a = 0.104$, $b = -55.0$, and $c = 10355.6$. Since $c > 0$, this blend with higher M_w exhibits an hour-glass type of phase behavior.

The SANS profiles for dPS-PnPMA-L at four different temperatures are shown in Figure 1(c). Using the incompressible RPA theory for block copolymer,⁷ the values of χ shown in Figure 1(d) were obtained. As can be seen, the fits of the incompressible RPA theory are not exact, but they do provide insight into the temperature dependence of χ . When incorporating the contribution of fluctuations to χ may improve the fits, the trends in χ with T would not change. The dPS-PnPMA-L block copolymer was disordered at temperatures studied. By slightly increasing the M_w ($\sim 10\%$), dPS-PnPMA-BH exhibited both LDOT at 160 and UODT at 240 °C.⁸ As shown in Figures 1(c) and 1(d), $I(q_{max})$ and χ increased initially with increasing T , achieved maximum values, and then decreased. Such behavior is in keeping with mixtures or block copolymers that would exhibit a closed-loop phase behavior.

Consequently, the differences in phase behavior between the blend and diblock copolymer of dPS and PnPMA originates in the differences in the temperature dependence of χ . However, the origin of this difference is not known. In addition, the absolute values of χ are not much different in the two cases. Subtle changes in the entropic contribution to χ could be an origin of this behavior.

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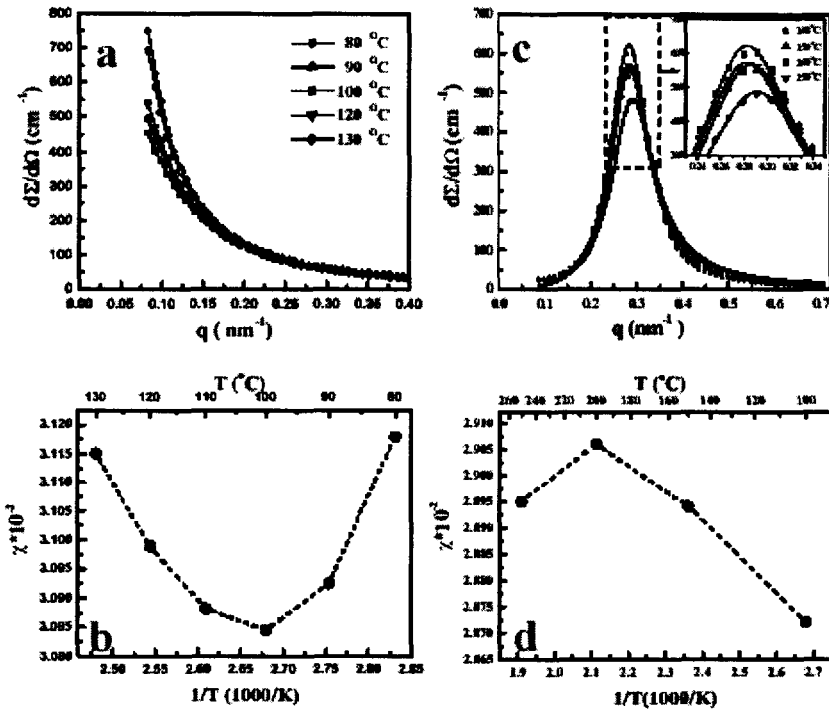


Figure 1. (a) and (b). SANS profiles [$I(q)$ versus q] and χ at various temperatures for 50/50 (wt/wt) DPS/PnPMA-M blend. (c) and (d). SANS profiles and χ at four different temperatures for dPS-PnPMA-L block copolymer.