

Nano-scale structure of amphiphilic block copolymer / homopolymer blends

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Introduction

For di-block copolymers with fine controlled block sequences, lamellar, hexagonal-packed cylinder, bicontinuous cubic gyroid and body-centered cubic structures are confirmed as equilibrium structures. These nano-scale ordered structures are formed mainly by the results of repulsive interaction between copolymer components. We have reported the nano-scale ordered structure and phase transitions of amphiphilic di-block copolymer consisted with hydrophilic and hydrophobic sequences having azobenzene moieties ($p(\text{EO})_m p\text{MA}(\text{Az})_n$) [1-4]. The di-block copolymers composed of block sequences including azobenzene moieties, which acts as a mesogen of side chain type liquid crystalline polymer, form the hexagonal-packed cylinder phase as a nano-scale ordered structure, and demonstrate several phase transitions including liquid crystalline and isotropic transitions [1, 2].

From the polymerization difficulty of $p(\text{EO})_n p\text{MA}(\text{Az})_m$ with high degree of polymerization of $p(\text{EO})$, the nano-scale ordered structure of $p(\text{EO})_n p\text{MA}(\text{Az})_m$ having higher $p(\text{EO})$ content had not investigated yet. In this study, the nano-scale ordered structure and the mixing state of blends of $p(\text{EO})_{114} p\text{MA}(\text{Az})_m$ and homo $p(\text{EO})_{114}$ polymer having same degree of polymerization of $p(\text{EO})$ were discussed.

Experimental

The amphiphilic di-block copolymer, $p(\text{EO})_{114} p\text{MA}(\text{Az})_{40}$ (Scheme 1) and poly(ethylene oxide) homopolymer, $p(\text{EO})_n$ ($n = 40, 114$ and 454) were used through this study. The blends were prepared by solution casting method from toluene solution, and were dried under reduced pressure. The $p(\text{EO})$ content of blends, $\phi_{p(\text{EO})}$, were shown as B40-n in wt %. Before SAXS measurement, all samples containing $p(\text{EO})_{114} p\text{MA}(\text{Az})_{24}$ were annealed at 140°C for 24 hrs in order to form the equilibrium nano-scale ordered structure.

The SAXS measurements were carried out at the beam line 10C at Photon Factory, High Energy Acceleration Organization, Tsukuba, Japan. The wavelength of monochromatic X-ray was 0.1488 nm . The distance between sample and detector (PSPC, Rigaku Co. Ltd, 512 channels) was 860 mm , which covered $1.02\text{ nm} < s^{-1} = q/2\pi = \lambda/2\sin\theta < 60.8\text{ nm}$.

Results

The nano-scale ordered structure for blend samples through micro-phase separation was determined by small-angle X-ray scattering (SAXS). The SAXS profiles of

copolymer $p(\text{EO})_{114} p\text{MA}(\text{Az})_{40}$ and these blend systems showed the SAXS peaks observed at scattering vector in the relation of $1 : \sqrt{3} : \sqrt{4} : \sqrt{7}$, which indicated that the nano-scale order structure was a hexagonal packed cylinder for $p(\text{EO})_{114} p\text{MA}(\text{Az})_{40}$ and blends with $p(\text{EO})_{40}$ in the $\phi_{p(\text{EO})}$ range below 35%. With increasing $\phi_{p(\text{EO})}$, the high-order SAXS peaks ($\sqrt{4}$ and $\sqrt{7}$) became smaller, the SAXS profiles of the blends with $\phi_{p(\text{EO})}$ above 40% has no high-order peaks corresponding to $\sqrt{4}$ and $\sqrt{7}$. The lattice distance of (100) plan for $p(\text{EO})_{114} p\text{MA}(\text{Az})_{40}$ and blends $p(\text{EO})_{114} p\text{MA}(\text{Az})_{40} / p(\text{EO})_{40}$, $p(\text{EO})_{114} p\text{MA}(\text{Az})_{40} / p(\text{EO})_{114}$, and $p(\text{EO})_{114} p\text{MA}(\text{Az})_{40} / p(\text{EO})_{454}$ were shown in Fig.1 as a function of $\phi_{p(\text{EO})}$.

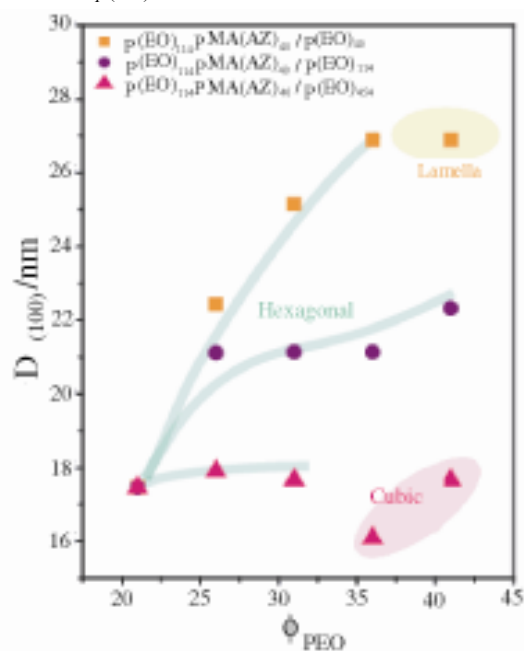


Fig.1 Effect of blend content on the lattice length of (001) plan for $p(\text{EO})_{114} p\text{MA}(\text{Az})_{40}$ and these blends

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