

Effect of mesogenic group on micro-phase phase separated structures of block copolymers studied by DSC-SAXS method

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Introduction

Block copolymers consisted with immiscible components form the nano-scale ordered phase separated structures. The phase transitions and the nano-scale order structure of amphiphilic di-block copolymers, $\text{PEO}_{114}\text{-}b\text{-PMA}(\text{R})_n$, consisted of hydrophilic poly(ethylene oxide) (PEO) and hydrophobic poly(methacrylate) derivatives PMA(R) containing liquid crystalline mesogen unit (R) were reported [1-3]. Two types of R unit, azobenzene (Az) and stybene (Stb) were used to compare the phase diagram of $\text{PEO}_{114}\text{-}b\text{-PMA}(\text{Az})_n$ and $\text{PEO}_{114}\text{-}b\text{-PMA}(\text{Stb})_n$.

Experiments

The simultaneous DSC-XRD measurements [4] were performed by SAXS optics at BL-10C, PF, KEK. The wavelength of X-ray and the measurement range of scattering vector were 0.1488 nm and $0.06 \text{ nm}^{-1} < q (=4\pi\sin\theta/\lambda) < 3 \text{ nm}^{-1}$, respectively. DSC scanning rate and XRD time resolution were 2 K min^{-1} and 30 sec, respectively.

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$\text{PEO}_{114}\text{-}b\text{-PMA}(\text{Az})_n$ showed four transitions on heating, melting of PEO, glass transition of PMA(Az), SmC-SmA transition and isotropic transition. $\text{PEO}_{114}\text{-}b\text{-PMA}(\text{Stb})_n$ showed three transitions on heating, melting of PEO, glass transition of PMA(Az), and isotropic transition. The nano-scale order structures of both block copolymers were determined as functions of temperature and the degree of polymerization of PMA(R) by DSC-SAXS. The phase diagrams of $\text{PEO}_{114}\text{-}b\text{-PMA}(\text{Az})_n$ and $\text{PEO}_{114}\text{-}b\text{-PMA}(\text{Stb})_n$ obtained by DSC-SAXS are shown in Fig.1 SAXS profiles for both block copolymer indicated that the nano-scale ordered structure at the temperature range below the isotropic transition. The order-order transition from hexagonal packed cylinder to body centered cubic was observed at the isotropic transition for $\text{PEO}_{114}\text{-}b\text{-PMA}(\text{Az})_n$ and $\text{PEO}_{114}\text{-}b\text{-PMA}(\text{Stb})_n$ containing higher n as shown in Fig. 1. Gibbs energy gain due to liquid crystal formation overcame the excess surface energy of interface between micro-phase separated domains.

The isotropic transition of $\text{PEO}_{114}\text{-}b\text{-PMA}(\text{Stb})_n$ was 40 K higher than that of $\text{PEO}_{114}\text{-}b\text{-PMA}(\text{Az})_n$, due to the higher enthalpy effect of Stb units, which induced higher glass transition temperature comparing with $\text{PEO}_{114}\text{-}b\text{-PMA}(\text{Az})_n$.

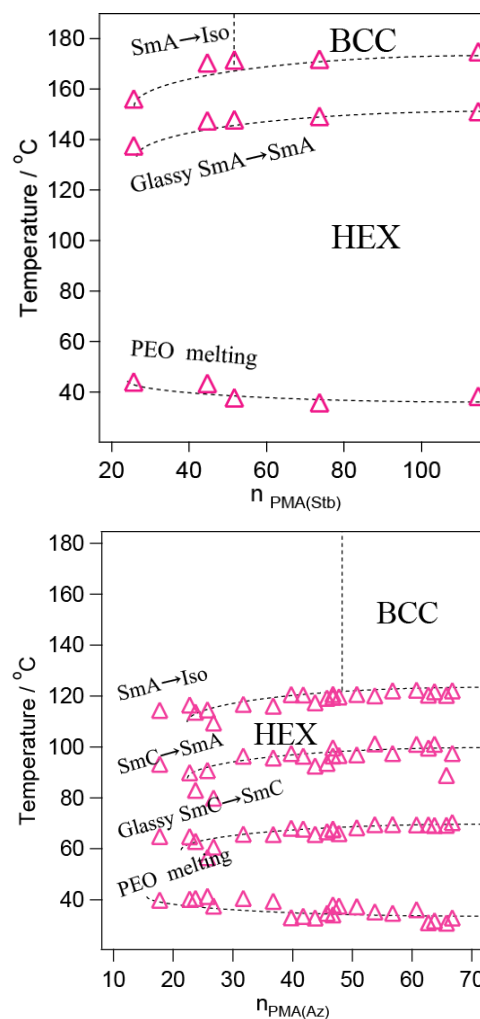


Fig. 1 Phase diagrams for $\text{PEO}_{114}\text{-}b\text{-PMA}(\text{Stb})_n$ (upper) and ob $\text{PEO}_{114}\text{-}b\text{-PMA}(\text{Az})_n$ (lower)

References

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