Evaluation of the Micro-Phase Separated Interface Formed by the Amiphiphilic Di-Block Copolymer by Transition Entropy

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Recently we have reported phase transitions and micro-phase separated structures of the amphiphilic di-block copolymer (PEO_m-b-$PMA(Az)_n$) consisted of hydrophilic poly(ethylene oxide) (PEO) and hydrophobic poly(methacrylate) derivatives having azobenzene moieties as a liquid crystalline mesogen PMA(Az). PEO_m-b-$PMA(Az)_n$ formed hexagonal packed PEO cylinder structure as an equilibrium state in wide PEO fraction and temperature, which was results of a strong segregated system having a sharp interface profile. In this study, the micro-phase separated interface was evaluated by the isotropic transition entropy of PMA(Az) domain. About 60 PEO_m-b-$PMA(Az)_n$ di-block copolymers (m = 40, 114, 454 and n = 4 ~ 150) and 5 $PMA(Az)_n$ homo polymers (n = 20, 24, 39, 57 and 139) were used throughout the experiment. DSC measurements were performed by DSC-6200 (Seiko Instrument Inc.) between –50 and 150 ^oC at 10K/min under dry nitrogen. Small angle X-ray Scattering investigation was performed at BL-10C (PF, KEK, Japan). The molar entropy of isotropic transition and the degree of polymerization of PMA(Az) domain showed good linear relationship in both case of PEO_m-b-$PMA(Az)_n$ di-block copolymers and $PMA(Az)_n$ homo polymers. The x-intercept of these linear relationships were 2 ~ 4 repeating units of PMA(Az) domain. The micro-phase separated structure of PEO_{114}-b-$PMA(Az)_4$ was a lamellar structure at room temperature. The transition from hexagonal to lamellar occurred at room temperature changing n from 10 to 4. These results indicated that the PEO_m-b-$PMA(Az)_n$ di-block copolymer was strong segregated system and the micro-phase separated interface consisted of 2 ~ 4 repeating units of PMA(Az) domain.