Phase Behavior of Diblock Copolymer and Its Blends with Homopolymer Exhibiting Lower Critical Ordering Transition

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Abstract

Most block copolymer systems display the upper critical ordering transition (UCOT) behaviour, where the order-disorder transition (ODT) occurs on heating. A very limited number of systems exhibit the lower critical ordering transition (LCOT), with the ODT taking place on cooling. Using temperature-dependent synchrotron small angle X-ray scattering (SAXS) conducted at BL23A1 of NSRRC, we investigate the solubilization behavior of poly(4-vinyl pyridine) homopolymer (h-P4VP) in its blends with a lamellae-forming poly(ethylene oxide)-*block*-poly(4-vinyl pyridine) (PEO-*b*-P4VP) to resolve the wet brush criterion in terms of the molecular weight ratio of P4VP homopolymer and P4VP block for diblock system exhibiting LCOT behavior. The temperature-dependent SAXS profiles revealed that the segregation strength of PEO-*b*-P4VP decreased with decreasing temperature, and the LCOT behavior persisted in the PEO-*b*-P4VP/h-P4VP blends. In the microphase-separated state, the interdomain distance D of the lamellar structure increased with increasing molecular weight of h-P4VP ($M_{h\text{-}4VP}$), as h-P4VP formed wet- or dry-brush mixture with P4VP blocks in the P4VP microdomain. In contrast to the classical UCOT system such as PS-b-PI / homopolymer blends, the critical value of the molecular weight ratio r (= $M_{h\text{-}4VP}/M_{b\text{-}4VP}$) below which the system showed completely wet brush behavior was found to lie well below 1.0. This phenomenon was attributed to the enhanced roles of both the repulsive interaction energy and conformational entropy at high temperature. In the wet-brush blend, an order-order transition (OOT) from lamellar morphology to hexagonally-packed cylinder (HEX) structure was found to take place on cooling through an epitaxial mechanism. The tendency of the OOT was in opposite direction from that of the UCOT system with respect to the temperature change, which was consistent with the reduction of effective interaction parameter on increasing temperature.

Keywords - Lower Critical Ordering Transition (LCOT), order-order transition, SAXS, blends, wet brush, dry brush