Molecular Disorder and Mesoscopic Order in Polydisperse Acrylic Block Copolymers Prepared by Controlled Radical Polymerization

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ABSTRACT: Self-assembly of high molecular weight polydisperse acrylic block copolymers and their blends is presented under conditions as close as possible to thermodynamic equilibrium. Di- and triblock copolymers comprising a poly(butyl acrylate) (PBA) first or middle block, and poly(methyl methacrylate) (PMMA) second or outer blocks, denoted MBA and MBAM, respectively, are prepared by nitroxide-mediated polymerization (NMP). Their particularity is that the acrylic block is controlled while the methacrylate block is polymerized via an uncontrolled radical process under the synthesis conditions used. Overall composition and molecular weight polydispersities are large. Molecular disorder does not yield macrophase separation, and TEM on solvent cast films reveals lamellar and poorly ordered bicontinuous, cylindrical, or spherical morphologies. Except for the lamellar phase, clear multiple orders of diffraction are not visible in SAXS, and scattering profiles instead indicate a liquidlike order of microdomains. More importantly, morphology boundaries are strongly shifted compared to those commonly accepted for model monodisperse block copolymers. Hence, symmetric copolymers adopt morphologies with highly curved interfaces while lamellae are displaced to PMMA-rich compositions. These results suggest that unbalanced polydispersity between the two blocks can induce interfacial curvature toward to broadest molecular weight distribution, thereby releasing stretching energy of the whole chain. This effect is expected to be encountered in radical or hybrid block copolymer syntheses whenever control cannot be optimized for all blocks.