Microdomain orientation in chelate-doped block copolymers with high magnetic field

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Block copolymers undergo microphase separation in several tens of nanometers, because of strong segregation between constituent block chains comprising different chemical species. This stems in molecular origins where dimension of block chains is of tens of nanometers. Depending on composition, the morphology of the microphase-separated structures can be altered from spheres, cylinders, or gyroid to lamellae. It is well known that physical properties of block copolymers strongly depend on the morphology. Not only the morphology, but the orientation of microdomains are key factors to be taken into account in order to control materials properties more efficiently, such as imparting anisotropy of properties. To control orientation of microdomains is therefore one of the fundamental ways to novel specialty materials. Generally, imposing a flow field works well to orient cylindrical microdomains such that the cylinders orient parallel to the flow. Several methods are even available such as imposing an electric field to a film, modification of substrate surface chemically or physically, utilizing of amphiphilic block copolymers comprising hydrophilic and hydrophobic chains, or solvent evaporation-assisted perpendicular orientation of cylinders. We show efficiency of the magnetic field applied to an SEBS (polystyrene-block-polyethylene-butylene-block-polystyrene) triblock copolymer.

In order to enhance the effect of the magnetic field, the difference in magnetic susceptibility between the microdomain (dispersed phase) and the matrix phase was increased by doping a metal chelate selectively in the microdomain. The SEBS sample used forms polystyrene (PS) cylinders in the poly(ethylene-co-but-1-ene) (PEB) matrix. By solution casting using dichloromethane, a good solvent selectively for PS, non-equilibrium lamellar microdomains were formed and frozen in the as-cast film. The SEBS sample, cast on aluminum foil in the presence of high magnetic field of 12T, was then annealed at 190°C for 3 h. The orientation of PS cylinders was examined by small angle X-ray scattering at room temperature. It was found that the lamellar microdomains were oriented parallel to the magnetic field. After annealing, 6-folded pattern appeared as shown in Figure 1, which was ascribed to well-ordered hexagonal cylinders aligned parallel to the applied magnetic field.

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Figure 1 Results of the 2d-SAXS measurements for the toluene cast film. Panels (a) and (b) are 2d-SAXS patterns, panels (c) and (d) are 1d-SAXS profiles, and panels (e) and (f) are the intensity distributions as a function of the azimuthal angle \(\mu\) for the 1st-order peak. Panels (a), (c), and (e) are for the through view, and panels (b), (d), and (f) are for the edge view. The geometries for the through and edge views are schematically shown together.