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Magnetic orientation of microdomains in amorphous block copolymers

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Introduction

This study concerns improvement of the effect of the magnetic field on the orientation of microdomains, for which our previous study revealed trivial but authentic effects. For this purpose, we intended to increase the difference of the magnetic susceptibility between the microdomain and the matrix phase by doping metal chelate selectively in the microdomain space. We used a polystyrene-*block*-poly(ethylene-*co*-but-1-ene)-*block*-polystyrene triblock copolymer (SEBS), which forms PS (polystyrene) cylinders in PEB (poly (ethylene-co-but-1-ene) matrix, and a dichloromethane as a solvent which is selectively good for PS. Therefore, the solvent swells the PS component and after the solvent evaporates completely, the sample forms the non-equilibrium lamellar microdomain, and metal-chelate dissolved in the solvent is selectively doped in the PS lamellar phase. This is the protocol of the selective doping. The SEBS sample was cast in the presence of a high magnetic field of 12T. The sample was further annealed at 190ºC for 3 h in the magnetic field and then the orientation of PS cylinders was examined with small angle X-ray scattering (SAXS) experiments.

We also examined the reverse case, namely the morphology transition from cylinder to lamella. For this purpose, a polystyrene-*block*-polybutadiene-*block*-polystyrene triblock copolymer (SBS) was used, which forms lamella microdomains at the thermodynamically equilibrium state. For this sample, a methyl ethyl ketone (MEK) was used as a selective solvent which is selectively good for polystyrene but poor for polybutadiene (PB). Therefore, the solvent swells exclusively the PS component in the solution. As a result, the sample forms the non-equilibrium cylindrical microdomain in the as-cast film, and metal-chelate dissolved in the solvent is selectively doped in the PS cylinder phase. The SBS sample was cast in the presence of a high magnetic field of 12T. The sample was further annealed at 190ºC for 12 h in the magnetic field and then the orientation of the alternating lamellae was examined with SAXS experiments.

Experimental

The characteristics of the SEBS sample is as follows. The number-average molecular weight, M_n, is 6.6×10^4. The heterogeneity index of the molecular weight distribution (M_w/M_n) is 1.03, where M_w denotes the weight-average molecular weight. The volume fraction of PS is 0.16. The characteristics of the SBS sample is as follows. M_n, is 6.31×10^4, M_w/M_n is 1.15, and the volume fraction of PS is 0.53. We conducted SAXS experiments at BL-9C and 15A beamline in the Photon Factory, and we used 12Tesla cryogen-free magnet in the Tsukuba Magnet Laboratory.

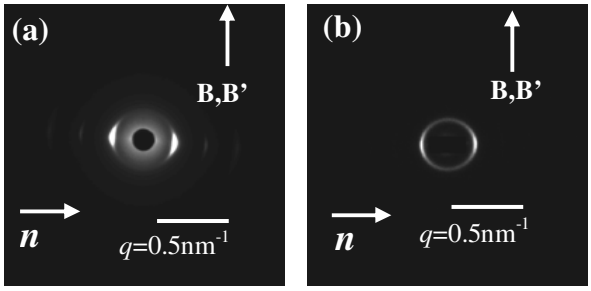

Fig. 1 Results of the 2d-SAXS measurements for the annealed SBS films, which were annealed in the presence of the magnetic field (**B'**: 12Tesla). The original as-cast film before annealing was obtained by casting from the MEK solution (a) with and (b) without the chelate in the presence of the magnetic field (**B**: 12Tesla).

Results and Discussion

It was found that in the as-cast film of the SEBS sample lamellar microdomains were oriented parallel to the magnetic field. After annealing the oriented lamellae in the presence of the magnetic field, 6-folded pattern appeared being ascribed to a well-ordered hexagonal lattice for closely-packed cylinders. This result confirms effectiveness of the selective chelate-doping for the magnetic orientation of the lamellar microdomains via the morphological transformation from cylinders.

As for the SBS sample, results of 2d-SAXS measurements for the annealed films are shown in Figure 1, where n indicates film normal. As a result, it was found that lamellar microdomains were oriented parallel to the magnetic field, and chelate-doping enhanced the effect of the magnetic field. It can be considered that after annealing the non-equilibrium cylinders in the presence of the magnetic field, cylinders were transformed into lamellae and they aligned parallel to the applied magnetic field. This result also confirms effectiveness of the selective chelate-doping for the magnetic orientation of the lamellar microdomains via the morphological transformation from cylinders.

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