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Order-Order Transition Mechanism of Block Copolymers Having Highly Oriented Microdomains

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Introduction

It was confirmed experimentally that block copolymers could exhibit order-order transition (OOT) in the weak segregation regime about ten years ago[1]. Many studies about OOT have been reported since then. In most of them, the static states before and after OOT were mainly observed by changing temperature.

Recently, it has been increasingly attractive to elucidate the process and mechanism of OOT from a viewpoint of controlling morphology of block copolymers. So we have investigated a thermally-induced OOT process from hexagonally packed cylinders (hex-cylinder) to spheres in a body-centered cubic lattice (bcc-sphere) *in situ* by using time-resolved small angle X-ray scattering (SAXS) method. In this study, hex-cylinders were aligned to one direction like Figure 1 by imposing an oscillatory shear deformation. Therefore we could easily pursue the change of microdomain structure itself during the OOT and get 2D scattering patterns which reflected the structure symmetry.

Experimental

We employed a polystyrene-*block*-polyisoprene-*block*-polystyrene triblock copolymer with the weight-averaged molecular weight of 1.4×10^5, 0.183 weight fraction of polystyrene blocks, and the polydispersity index of 1.11. It forms hex-cylinder below OOT temperature (T_{OOT}) of 185˚C and bcc-sphere above it. Bcc-sphere is transformed to disordered sphere at 215˚C[2]. The hex-cylinders were oriented with the Cartesian coordinate *OXYZ* described in Figure 1 by imposing the oscillatory shear deformation with strain amplitude of 1.0 at angular frequency of 0.3409rad/s at temperature of 180˚C under nitrogen atmosphere[3]. The OOT for the oriented hex-cylinder was induced by *T*-jump from 170˚C to 190˚C, and then the OOT process was investigated by time-resolved SAXS

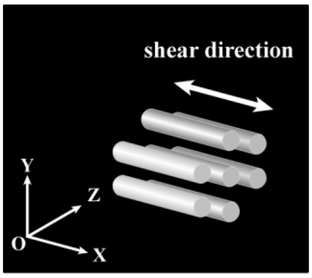

Figure 1. Schematic representation of hex-cylinders oriented by imposing the oscillatory shear deformation.

Results and Discussion

The 2D scattering patterns were obtained from the three directions, OX, OY and OZ. Those obtained from OX and OY directions did not change during the OOT. However those from OZ direction changed as described in Figure 2. The 2D scattering pattern right after *T*-jump did not differ from that before it (Figure 2(a)). As time passed, four spots of first-order peak along diagonal direction, which are scatterings arising from (110) plane of bcc, appeared and then became intense. On the other hand, two meridional spots, which are scatterings arising from (110) plane of hex-cylinder, disappeared. Therefore, it was confirmed that hex-cylinders were broken into a series of spheres with the cylindrical axes corresponding to [111] direction of bcc[4] and then formed two bcc-spheres which are mirror images of each other, and we could succeed in the *in situ* and real-time investigation of time change in the microdomain structure during the OOT.

References

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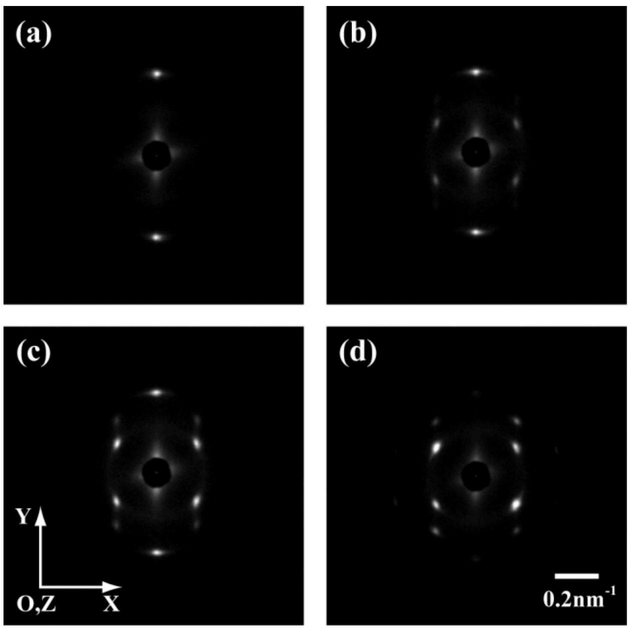

Figure 2. The 2D SAXS patterns obtained *in situ* at (a)20s, (b)115s, (c)165s and (d)915s after *T*-jump to 190˚C, obtained with an exposure time of 288ms/frame.