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Orienting Cylindrical Microdomains in an SEBS Triblock Copolymer / Diluent Sheet by Application of Temperature Gradient

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1 Introduction

Control of orientation of nanostructures in polymeric materials has been attracting interests from academic and technological viewpoints because of demands of producing functional materials having anisotropic properties. Applying temperature gradient is one of the most promising tactics for controlling orientation in polymer systems. Perpendicular orientation was achieved for cylindrical microdomains in block copolymer thin films by the application of temperature gradient. It was also reported that the crystalline lamellae were formed parallel to the applied temperature gradient for a crystalline polymer. These examples of the experimental studies clearly indicate the significance and the superiority of the application of the temperature gradient.

2 Experiment

The sample used in this study is an polystyrene-*block*-poly(ethylene-*co*-butylene)-*block*-polystyrene (SEBS) triblock copolymer with $M_n = 6.60 \times 10^4$ and $M_w/M_n = 1.03$ (M_n: number-average molecular weight, M_w: weight-average molecular weight). The total volume fraction of PS (polystyrene) end-blocks is 0.16. Dioctylphthalate (DOP) was used as the diluent. Note that DOP has selectivity in solubility for the SEBS; good solubility for PS while poor solubility for PEB. The composition of SEBS/DOP was 6/4.

To impose temperature gradient to a specimen, we fabricated a set up such that the specimen was filled in the 3-mm gap space (36 mm × 3 mm) in an aluminum plate with thickness of 1 mm. After the specimen was filled, the top and bottom of the specimen were covered with the polyimide film (25 μm thickness; Du Pont-TORAY Co, Ltd., Japan) and cover slip (0.12 - 0.17 mm thickness; Matsunami Glass Ind., Ltd., Japan), respectively. The reason of using the polyimide film is to minimize the absorption of X-ray due to such window materials when conducting measurements of the two-dimensional small-angle X-ray scattering (2d-SAXS) for the nanostructures analyses, noting that the polyimide film is thinner than the cover slip so that the absorption is lesser. The sample cell filled with the specimen was then fabricated so as to impose the temperature gradient, where the right and left sides of the sample cell were sandwiched by the metal blocks of which temperatures were relatively lower and higher, respectively. The high temperature block was maintained by the electric heater, while the cold temperature by the water circulation supplied from a reservoir. Thermosensors (the adhesive-type thermocouple (Chromel-Alumel), ST-50, RKC Instrument, Inc., Tokyo, Japan) were attached on the surface of the sample cell at positions very close to the specimen space to check their temperatures of both hot and cold sides.

The 2d-SAXS measurements were carried out at room for the specimen after the application of the temperature gradient to analyze nanostructures and their orientation. The sample cell (the alminum plate) was picked up from the set-up and was subjected to the 2d-SAXS measurements without removing the cover slip and the polyimide film. The 2d-SAXS measurements were conducted at the BL–10C beamline of the Photon Factory, High Energy Accelerator Research Organization, Tsukuba, Japan, using X-ray with a wavelength of 0.1488 nm. The sample-to-detector distance was 2.0 m. A PILATUS-2M (DECTRIS Ltd., Baden, Switzerland) was used as a two-dimensional detector.

3 Results and Discussion

Fig. 1 shows a schematic illustration of the revealed orientation of cylinders in the specimen thermally annealed under the temperature gradient with 86 °C / 143 °C for 3 h. Closer to the cold temperature side, the overall orientation is random, while the cylinders are perpendicularly oriented near the high temperature side. Furthermore, the result of the almost perfect hexagonal spots in the 2d-SAXS pattern indicates an orientation a single grain state.

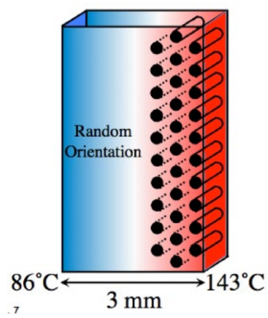

Fig. 1 Schematic illustration of the revealed orientation of cylinders in the specimen thermally annealed under the temperature gradient with 86 °C / 143 °C for 3 h.

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