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Effects of pressure on spontaneous orientation of hexagonally packed cylindrical microdomains in polystyrene-*b*-polybutadiene-*b*-polystyrene triblock copolymers

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Block copolymers consisting of two or more chemically different monomer units connected at their chain ends form various types of microphase-separated structures, and their morphologies depend on composition and molecular weight of block copolymers. Numerous studies on the control of the microphase-separated structure have been reported, but so far the effect of pressure on microphase-separated structure has not been studied. So in this study we have investigated the effect of the pressure on cylindrical microdomains in polystyrene(PS)-*b*-polybutadiene(PB) -*b*-polystyrene(PS) triblock copolymers using the small-angle X-ray scattering (SAXS). The characterization of the sample is as follows: $M_n = 6.07\times10^4$, w_{PS} (weight fraction of PS) = 0.183, the PB midblocks were partially hydrogenated, by which polyethylene-butylene type chemical structure is resulted, and the fraction of 0.51 of the PB blocks was hydrogenated.

The sample was subjected to one-dimensional flow with a load of 1065g at 150°C for 20 seconds to align cylinders packed in a hexagonal lattice. After the load was completely removed, SAXS measurements were conducted under 0.1, 50, 100, 150, and 200MPa with increasing temperature from 40 to 180°C. The two-dimensional (2d-) SAXS measurements were performed at BL45XU SAXS beamline of SPring-8.

Fig.1 shows the 2d-SAXS pattern obtained under 0.1MPa at 40°C and that obtained under 0.1MPa at 180°C, indicating that orientation of the cylinders was spontaneously improved without application of the flow. We evaluated sharpness of the hexagonal spots to discuss the degree of orientation. In fact, an average peak width (hwhm; half width at half maximum) of the six spots was evaluated when the scattering intensity was plotted as a function of the azimuthal angle. Fig. 2 shows changes in thus obtained value of hwhm when increasing temperature from 40 to 180°C at a given pressure. For clear comparison of the changes at various pressures, the value of hwhm was normalized by its initial value at 40°C ($hwhm_0$). Therefore, $hwhm/hwhm_0$ can be a measure of cylinder orientation, although it is inversely proportional.

Then, the following facts can be concluded from the results shown in Fig. 2. At 0.1MPa, or relatively low pressure, the cylinder orientation was remained constant below a certain temperature (around 100°C for the case of 0.1MPa), and then it was improved exponentially above this temperature. Suddenly around 160°C, this trend was turned over such that the cylinder orientation started to become worse abruptly for the subsequent increase of temperature. On the contrary, for 200MPa or relatively high pressure, the cylinder orientation was linearly improved with temperature. Interestingly, it was found that the trend was also turned over around 160°C. Close examination reveals that the temperature of the turning point has little dependence of pressure. However, there seems to be discernible pressure dependence on the minimum value of $hwhm/hwhm_0$ at the turning point, such that the most improved cylinder orientation can be obtained at high pressure, 200MPa (around 160°C).

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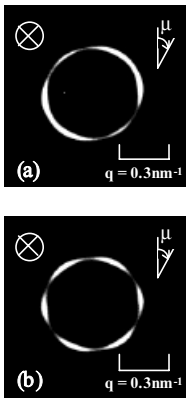

Fig.1 2d-SAXS patterns obtained under 0.1MPa at 40°C(a) and at 180°C (b).

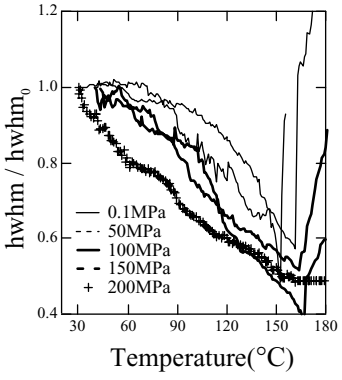

Fig.2 Change in the normalized peak width of the first-order hexagonal diffraction spots as a function of temperature for various values of pressure, 0.1 – 200 MPa.