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Some anomalies in pressure-induced ordering of glassy spheres in a rubbery matrix of a microphase-separated triblock copolymer

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Abstract

We report experimental results of pressure-induced ordering of spheres on body-centered cubic (bcc) superlattice in a microphase-separated polystyrene-*block*-poly(ethylene-*co*-but-1-ene)-*block*-polystyrene (SEBS) triblock copolymer. After well-ordered bcc superlattice was prepared by annealing as-cast samples at 140 °C for 10 h, the samples were further pressurized at 50.7, 101.3, 202.7 and 405.3 MPa at room temperature for 24 h. Small-angle X-ray scattering (SAXS) measurements revealed further ordering of the bcc spheres for the samples pressurized at 202.7 and 405.3 MPa, while the bcc regularity became worse for the samples pressurized at 50.7 and 101.3 MPa. On the other hand, starting with an ill-ordered sample, no change in the SAXS profile was detected upon pressurizing at 405.3 MPa up to 27.5 h. Thus, it turned out that the effect of pressure on the ordering of spherical microdomains is not straightforward.

Keywords: Pressure-induced ordering; Microphase separation; Small-angle X-ray scattering

Block copolymers exhibit a variety of pattern because of the microphase separation [1,2]. Ordered superlattice structures are well known with spherical, cylindrical, double gyroid, and lamellar microdomains, according to which various properties of block copolymers vary. In this regard, control of morphology and regularity of the superlattice has been a central issue for producing high performance of block copolymer materials. Now the research trend is proceeding to a next stage, that is a more large-scale control of the microphase-separated domain structures. For this purpose, application of an external field is promising. Few experimental works on the effect of pressure have been reported for control of morphology and ordering of microphase-separated domains. The present study is intended to experimentally elucidate the effect of pressure.

Recently, numerous experimental studies were reported to elucidate the effects of pressure on miscibility of polymer blends and block copolymers [3–13]. Although there is a tendency that pressure enhances miscibility for compressible polymer pairs while it suppresses miscibility for incompressible polymer pairs, it has been found to be not straightforward. A typical example was shown by Schwahn et al. [6,12] for a poly(ethylene–propylene)-*block*-poly(dimethylsiloxane) diblock copolymer that has the upper critical order–disorder transition type phase diagram. They reported that the order–disorder transition temperature (T_{ODT}) first decreased with an increase of pressure up to ca. 50 MPa and then turned to increase up to their experimentally accessed highest pressure of 170 MPa. Here, it is noteworthy that all of the studies elucidated discernible effects of pressure on the miscibility in a homogeneously mixed state and in the weak segregation regime by applying pressure up to at most 170 MPa. On the contrary, there has been no experimental study reported for a possible effect of pressure on morphological transition or ordering of microphase-separated domains, although the above results would be naturally extended to intermediate and strong segregation regimes [1]. Higher pressure may be required for elucidation of the realistic effect of pressure in the intermediate segregation regime. In fact, we applied much higher pressure up to 400 MPa for elucidation of pressure-induced ordering of spherical microdomains on body-centered cubic (bcc) superlattice, which is reported in the current communication.

The sample used was a polystyrene-*block*-poly(ethylene-*co*-but-1-ene)-*block*-polystyrene (SEBS) triblock copolymer,

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which is a hydrogenated version of a polystyrene-*block*-polybutadiene-*block*-polystyrene triblock copolymer. The number-average molecular weight, M_n, is 6.7×10^4, the heterogeneity index for the molecular weight distribution, M_w/M_n, is 1.04, where M_w denotes the weight-average molecular weight, and the volume fraction of polystyrene (PS), ϕ_{PS}, is 0.084. The sample was dissolved in toluene to obtain about 5 wt% solution and then an as-cast film was obtained by evaporating the toluene at room temperature. Since this sample was found to exhibit the lattice disordering transition (LDT) and form well-ordered bcc superlattice structure when annealed at temperatures below T_{LDT} (the LDT temperature) and practically above T_g of PS thus in a range $100 < T < 150$ °C ($\approx T_{LDT}$) [14], we annealed the as-cast samples at 140 °C for 10 h to prepare the bcc superlattice in prior to application of pressure. Note here that the LDT is a well-known phenomenon where the spherical microdomains lose their ordering regularity on a bcc lattice without dissolution of the microdomains. It has been therefore notified that the LDT is different from the so-called order–disorder transition, which takes place above T_{LDT} and is rigorously referred to as a microphase dissolution transition in our previous report [14].

Hydraulic pressure was imposed at room temperature on a high-pressure bomb (PV400, Teramecs Co., Ltd., Kyoto, Japan) filled with purified water by using a pressuring hand pump (TP-500, Teramecs Co. Ltd., Kyoto, Japan). Typical pressurizing duration was 24 h.

Small-angle X-ray scattering (SAXS) technique was utilized to analyze the microdomain structure. The measurements were performed at the RIKEN structural biology beamline I (BL45XU) at the SPring-8, Hyogo, Japan. It is an undulator beamline, providing high flux of X-rays. The detail of the BL45XU is described elsewhere [15]. Two-dimensional SAXS pattern was measured with the Hamamatsu image intensifier with a cooled CCD [16] and the wavelength of X-rays, λ, was tuned at $\lambda = 0.1015$ nm. The one-dimensional SAXS profile (the scattering intensity $I(q)$ vs. q where q denotes the magnitude of the scattering vector, as defined by $q = (4\pi/\lambda)\sin(\theta/2)$ with θ being the scattering angle) was converted from the 2D-SAXS pattern by circular averaging since the pattern was isotropic. Subtraction of the air scattering was further conducted by taking account of the absorption of X-rays. Moreover, the contribution of the density fluctuation (so-called the thermal diffuse scattering) was corrected for according to the conventional method [17].

To identify appropriate experimental conditions for pressurizing duration and an aging time lag at the atmospheric pressure from the release of high pressure, we first examined effects of those parameters on the bcc regularity. Fig. 1(a) shows SAXS profiles measured at room temperature under the atmospheric pressure for the sample annealed at 140 °C (as-annealed) and the samples pressurized at 202.7 MPa for several pressurizing times. Well-ordered bcc superlattice can be confirmed for all samples with almost the same

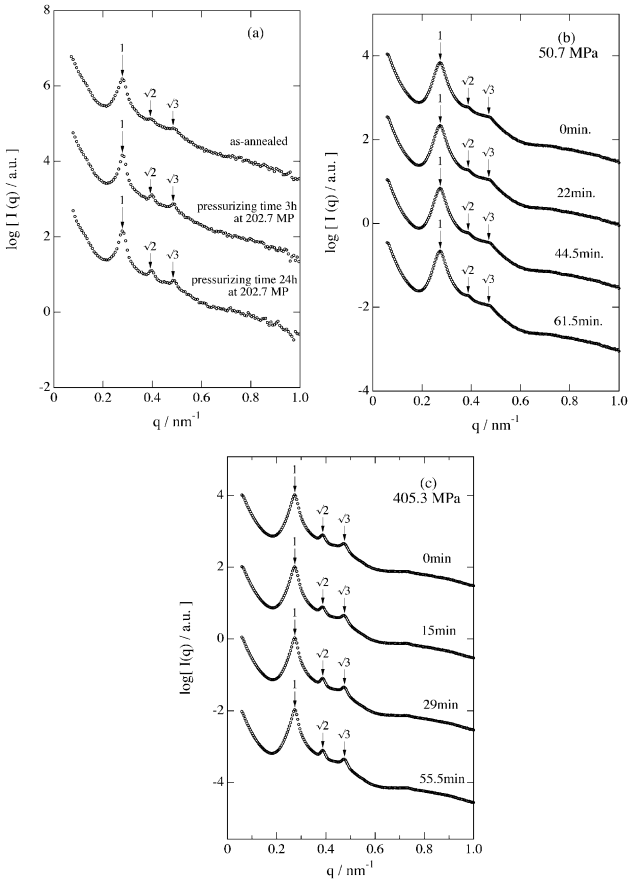

Fig. 1. SAXS profiles measured at room temperature under the atmospheric pressure (ca. 0.1 MPa) for the sample annealed at 140 °C for 10 h and those further pressurized for 3 and 24 h under 202.7 MPa at room temperature (a). Results of SAXS measurements after the release of pressure for samples pressurized at (b) 50.7 and (c) 405.3 MPa for 24 h at room temperature, respectively.

lattice size, because up to third-order diffraction peaks are clearly observed at the q positions relatively assigned to $1 : \sqrt{2} : \sqrt{3}$, with no appreciable change in the respective peak positions. Upon pressuring, the regularity of the bcc lattice improved, as is evidenced by the sharpening of all the diffraction peaks. However, no further improvement was confirmed above 3 h. Fig. 1(b) and (c) show SAXS profiles for samples pressurized at 50.7 and 405.3 MPa, respectively, which were stored under the atmospheric pressure for various times in prior to the SAXS measurement. Since the sharpness of each diffraction peak remains unchanged with the aging time lag from the release of the high pressure for both cases, no appreciable effect of the aging time lag on the bcc regularity is concluded. Based on these results, the samples to examine the effects of applied pressures were to be pressurized for 24 h and the aging time was to be in a range 5–15 min.

Fig. 2 shows SAXS profiles for the sample annealed at 140 °C (as-annealed) and those further pressurized at 50.7, 101.3, 202.7, and 405.3 MPa for 24 h (shown in thin solid

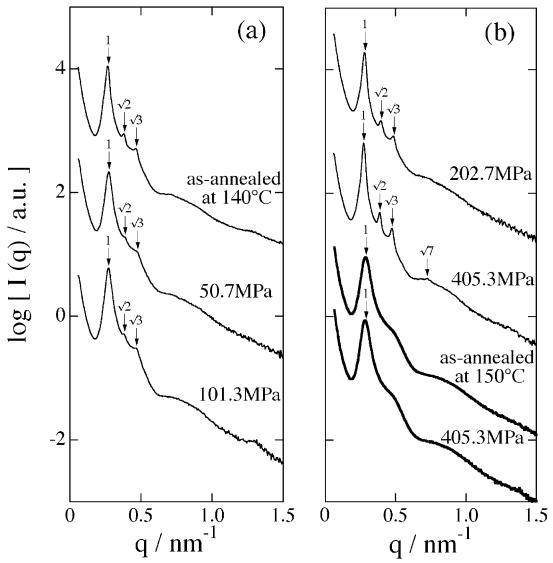

Fig. 2. SAXS profiles for the sample annealed at 140 °C (as-annealed) and those further pressurized at 50.7, 101.3, 202.7, and 405.3 MPa for 24 h at room temperature (shown in thin solid curves). (b) includes SAXS profiles for the sample annealed at 150 °C (as-annealed) and that further pressurized at 405.3 MPa for 27.5 h under the atmospheric pressure at room temperature (shown in thick solid curves). Note that all profiles were vertically shifted to avoid their overlaps.

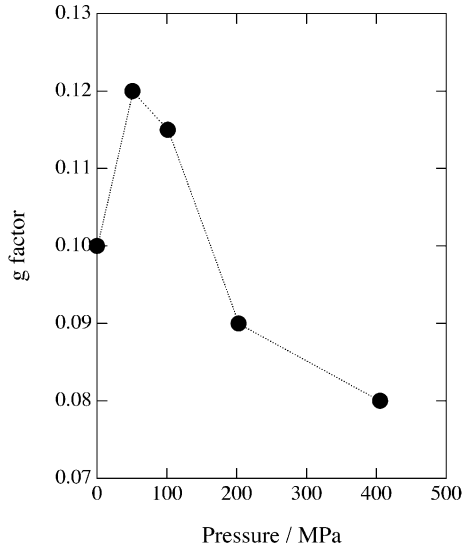

Fig. 3. Pressure dependence of the value of the *g* factor, as evaluated by model calculation of the scattering function for the bcc spheres with the paracrystal theory, for the samples annealed at 140 °C and further pressurized at 50.7, 101.3, 202.7, and 405.3 MPa for 24 h at room temperature.

curves). As previously reported [14], a well-ordered bcc structure was formed upon the thermal annealing at 140 °C. Conducting model calculation of the scattering function for the bcc spheres with the paracrystal theory [18,19], the degree of paracrystal distortion (so-called *g* factor), which is a measure of disorder in the bcc regularity, was evaluated. Regularity of the bcc superlattice was improved by applying pressure higher than 202.7 MPa. However, the effect of the pressure seems to be not straightforward when judged from the values of the *g* factor shown in Fig. 3. Although it was speculated that the glassy polystyrene spheres embedded in the rubbery poly(ethylene-*co*-but-1-ene) matrix can be further ordered on bcc superlattice by applying pressure, the result is against this conjecture for the moderate values of pressure (50.7 and 101.3 MPa). Based on the result shown in Fig. 1(b), it was confirmed that pressure-induced bcc disordering at 50.7 MPa, which is identified by broadening of diffraction peaks, was not an artifact owing to the release of pressure. Thus, there is no concern of gradual disordering during the aging time lag after the release of pressure. This result further assures validity of the conclusion on the pressure effects on the bcc ordering based on the SAXS measurements under the atmospheric pressure (Fig. 3).

A more complex effect was seen in the case when we pressurized the sample without long-range bcc regularity. Fig. 2(b) includes SAXS profiles for the sample annealed at 150 °C and that further pressurized at 405.3 MPa for 27.5 h (shown in thick solid curves). In contrast with the case of thermal annealing at 140 °C, the spherical microdomains in the sample annealed at 150 °C was found ill-ordered, because higher-order diffraction peaks were not resolved in the *q* range where a broad shoulder was presented. Here, no change in the SAXS profile was detected when pressurized at 405.3 MPa up to 27.5 h.

It should be noted that the above results were obtained from the measurements at the atmospheric pressure. Upon release of the applied pressure, it may be considered that simply deformed bcc lattice under the applied hydraulic pressure can recover its original structure. In other words, no dissipation of the input energy takes place during the pressuring and subsequent depressuring processes and no change in the bcc regularity may result after the release of pressure. However, it can be easily anticipated that input energy is dissipated due to consumption as an activation energy for the ordering of the bcc superlattice. A concrete physical picture of mechanism stabilizing the pressure-induced order of the bcc superlattice should be identified in our future study. One candidate is a reorganization of a physical network in the rubbery matrix, which accompanies redistribution of physical entanglements. In this case, due to dissipation of the input energy, if the regularity of the bcc superlattice is improved upon applying pressure, this influence should partly remain even after the release of the pressure, as was observed for pressures above 200 MPa. On the other hand, for the pressures below 200 MPa, the fact that the bcc regularity became worse might suggest excess output larger than the input energy. This is of course unrealistic. At this moment, we presume that a rebound effect of depressuring may degrade the original bcc regularity. Then, it is expected that the bcc regularity may decrease by applying pressure. Although we are not able to conduct the in situ SAXS measurements under

such high pressure at this moment, the re-entrant-type pressure effect on the bcc regularity after the pressuring–depressuring process is worth to be reported.

In summary, pressure-induced ordering of the bcc spheres took place when the sample was pressurized above 202.7 MPa. However, it seemed that the effect of pressure was not straightforward. In contrast with the result for the bcc spheres, no appreciable effect of pressure on the ordering was confirmed for the spheres without long-range order, even though the sample was pressurized at 405.3 MPa up to 27.5 h.

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