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Synchrotron SAXS Studies on Lattice Structure of Spherical Micelles in Binary Mixtures of Block Copolymers and Homopolymers

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Abstract: The lattice structures of spherical micelles in binary mixtures of polybutadiene-poly(ϵ -caprolactone) diblock copolymers and polybutadiene homopolymers were investigated using synchrotron small angle X-ray scattering technique. In the blend sample with a weight fraction of added homopolymer (ϕ_{homo}) of 40 wt%, hexagonally packed cylinders were formed, while spherical morphologies were arrayed into the Frank-Kasper σ phase at $\phi_{\text{homo}} = 50$ wt%. Closely packed spheres in hexagonal closely packed (HCP) and face-centered cubic (FCC) lattices were observed for the sample with $\phi_{\text{homo}} = 56$ and 67 wt%, respectively. It was found that the lattices of spherical micelles assembled into the following phases with increasing ϕ_{homo} : Frank-Kasper σ , HCP, and FCC phases.

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1. Introduction

When the compositional asymmetry in a block copolymer increases significantly, block copolymer self-assembly results in the formation of spherical morphologies [1]. In general, spheres composed of block copolymers are arranged in body-centered cubic (BCC) lattice in many block copolymer systems. In a simple diblock copolymer system, it is predicted that the closely packed spheres in hexagonal closely packed (HCP) and face-centered cubic (FCC) lattices exist outside as an ordered phase in the phase diagram [2], and the subsequent experiments confirmed that the FCC phase was found in a diblock copolymer [3].

Recently, it was reported that spherical micelles could be arrayed in a variety of lattices [4]. For example, in a polystyrene-polyisoprene-polystyrene-poly(ethylene oxide) linear tetrablock copolymer (PS-PI-PS-PEO), the Frank-Kasper σ phase and the associated dodecagonal quasicrystal were observed

[5,6]. The σ phase is often found in close proximity to quasicrystals, and contains 30 particles in the unit cell with $P4_2/mnm$ space group symmetry. Recent experiments revealed the formation of the Frank-Kasper A 15 phase (space group $Pm3n$) in PS-PI-PS-PEO [7]. Various types of lattices were also seen in simple diblock copolymer systems. The Frank-Kasper σ phase and the dodecagonal quasicrystal were observed in a polyisoprene-poly(lactide) diblock copolymer (PI-PLA) [5,8,9]. Most recently, Frank-Kasper C 14 and C 15 Laves phases were also discovered in PI-PLA [10]. Note that it was reported that the dodecagonal quasicrystals observed in diblock copolymers were in a non-equilibrium state and transformed into the stable phase after annealing over a long period of time [9].

Such well-defined nanostructures have been studied for application as optical materials [11]. In particular, photonic crystals attract increasing interest in the field of nanotechnology [4,12–15]. Some research groups reported photonic crystals composed

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of soft materials, such as colloids [13], high-molecular-weight block copolymers [14], and block copolymer solutions [15]. Quasiperiodic structures can induce and widen the photonic band gap easily due to their high symmetry, prohibiting light within a range of wavelengths from propagating in any direction.

The region within which the Frank-Kasper σ phase exists in a phase diagram has also been studied. The self-consistent field theory (SCFT) calculations demonstrated that the σ phase becomes stable in the region between hexagonally packed cylinders (HEX) and BCC on a phase diagram, and the thermodynamical stable range of the σ phase extends with increasing conformational asymmetry $\varepsilon^2 = v_{AA}^2 / (v_{BA}^2)$, where v and a are the molecular volume and the statistical segmental length, respectively [16]. With the increase in ε , spherical micelles are transformed into polyhedral shapes, and thus, polyhedral particles can form complex lattices. A recent experimental study elucidated that the σ phase was not observed in poly (ethylene - *alt* - propylene) - polylactide diblock copolymer with $\varepsilon = 1.06$, while the σ phase appeared as a stable phase in modestly asymmetric polyisoprene-polylactide diblock copolymer ($\varepsilon = 1.32$); increasing the conformational asymmetry to $\varepsilon = 1.68$ (polyethylethylene-polylactide diblock copolymer) broadened the σ phase region, which was consistent with SCFT calculation results [17].

Our research group has investigated the phase behavior of a binary mixture of a block copolymer and a homopolymer. Recently, the Frank-Kasper σ phase was observed in polybutadiene-poly(ε -caprolactone) (PB-PCL) diblock copolymer/polybutadiene (PB) blends [18]. In this study, we investigated the type of lattice structure formed depending on the amount of the added homopolymers in spherical-morphology-forming block copolymer/homopolymer blends. It was found that the lattice changed in the following order with increasing amount of homopolymers: the Frank-Kasper σ , HCP, and FCC phases.

2. Experimental section

2.1 Materials

PB-PCL and PB were synthesized by living anionic polymerization [18]. The number-average molecular weight (M_n) and its heterogeneous index (M_w/M_n) were determined by size-exclusion chromatography (SEC) using PB standards. The volume fraction of PCL (f_{PCL}) was calculated using

Table 1 Molecular characteristics of PB-PCL and PB.

	M_n^a	M_w/M_n^a	f_{PCL} (vol.%) ^b
PB-PCL	7600 ^c	1.08	41
PB	900	1.1	-

^a Determined by SEC using PB standards.

^b Determined by ¹H-NMR.

^c Determined by SEC and ¹H-NMR.

proton nuclear magnetic resonance (¹H-NMR) spectroscopy. The parent PB-PCL shows a crystalline-amorphous alternating lamellar structure in the crystalline state and a lamellar structure in molten state ($T > 60$ °C). The molecular characteristics of PB-PCL and PB are presented in Table 1. The blend samples were prepared according to the standard method [18].

2.2 Small angle X-ray scattering

Synchrotron small angle X-ray scattering (SAXS) measurements were conducted at the beamline BL-6 A [19] and BL-15A2 [20] in Photon Factory (PF) of High Energy Accelerator Research Organization in Tsukuba, Japan (KEK). The detector was PILATUS3 1M (Dectris) in BL-6A. In BL-15A2, PILATUS3 2M and a silicon-on-insulator photon imaging array sensor (SOPHIAS) detectors were used. The pixel size of SOPHIAS detector is 30 μ m, which is smaller than that of PILATUS3 (172 μ m) [21]. The X-ray energy was 8.3 keV, and the sample-detector distance was 2.5 m in BL-6A experiments. In BL-15A2 experiments, the X-ray energy was 10.2 keV, and the sample-detector distance was 3.5 m. Silver behenate and collagen (chicken tendon) were used as the standard specimens to calibrate SAXS detector. The scattering intensities were corrected for background scattering and sample absorption. The magnitude of the scattering vector (q) is given by

$$q = \frac{4\pi}{\lambda} \sin \theta \quad (1)$$

where λ is the wavelength of the X-ray and 2θ is the scattering angle. The sample temperature was controlled using Linkam LK-600 M equipment (Japan Hightech). In the SAXS experiments, the sample was heated to a target temperature at a rate of 100 °C/min. After the sample was held for 600 s at the target temperature, the scattering data were recorded. Just before recording the data, X-ray irradiation was not performed to avoid X-ray damage to the sample. The temperature was raised from 60 °C to 220 °C in increments of 20 °C. It has been previously discussed that the thermal degradation of copolymer chains

occurred at high temperatures [7,22]. In this study, the total time above 220 °C is only ca. 20 min, meaning that the amount of thermally degraded copolymer chains should be relatively small. In addition, thermo-reversibility of SAXS patterns was also confirmed. Thus, it was considered that there was no effect of thermal degradation on the phase behavior. Data processing was conducted using *SAnGLer* software [23].

3. Results and discussion

SEC charts of synthesized PB-PCL (solid line) and PB (dashed line) are shown in Fig. 1. SEC charts for both PB-PCL and PB show a monomodal and symmetric peak ($M_w/M_n \leq 1.1$).

Fig. 1 SEC elution curves for synthesized polymers. The solid line represents PB-PCL, and the dashed line corresponds to PB.

Fig. 2 displays SAXS profile for the PB-PCL/PB blend obtained at 200 °C. The weight fraction of added homopolymer (ϕ_{homo}) was 40 wt%. Data are plotted as the logarithm of the relative scattered intensity $\log I(q)$ versus the magnitude of the scattering vector q . The sharp scattering peaks are clearly seen at the relative q -peak position of $1:3^{1/2}:7^{1/2}:9^{1/2}$ as marked by arrows. This result indicates that HEX were formed. Generally, the diffraction peaks of HEX can be observed at the relative q -peak position of $1:3^{1/2}:4^{1/2}:7^{1/2}:9^{1/2}$. The lack of the $4^{1/2}$ peak should be attributed to the superposition of the peak position of a hexagonal structural factor and the valley position of a cylindrical form factor. Theoretically, the $4^{1/2}$ peak almost disappears when the volume fraction is around 27.4 vol% [24]. In the blend sample with $\phi_{\text{homo}} = 40$ wt%, the overall volume fraction of PCL is 26.6 vol%, which is almost consistent with the theoretical extinction condition. Thus, the $4^{1/2}$ peak was not observed in this sample.

The SAXS profile for the blend sample with ϕ_{homo}

Fig. 2 SAXS profile of the PB-PCL/PB blend ($\phi_{\text{PB}} = 40$ wt%) obtained at 200 °C. Arrows indicate scattering peaks of HEX.

= 50 wt% obtained at 220 °C is shown in Fig. 3 (a). Fig. 3 (b) displays the enlarged SAXS profile around $0.25 \leq q \leq 0.38 \text{ nm}^{-1}$ using SOPHIAS detector, which has the advantage of smaller pixel sizes (30 μm) than PILATUS 3 detector (172 μm). Arrows in Figs. 3 (a) and (b) represent the peak positions, while the numbers in brackets represent the reflection indexes of the Frank-Kasper σ phase ($P4_3/mnm$ space group) [18]. The calculated and observed scattering peak positions in $0.23 \leq q \leq 0.4 \text{ nm}^{-1}$ are listed in Table 2. It is easily seen in Figs. 3 (a) and (b) and Table 2 that all of the observed scattering peaks are in good agreement with calculated ones. In addition, the value of the lattice parameter ratio of a -axis/ c -axis is 1.90 (a -axis = 85.9 nm and c -axis = 45.3 nm). This value is almost coincident with values obtained in previous studies [4,18]. Therefore, it was found that the Frank-Kasper σ phase was observed at 220 °C.

Fig. 4 displays the SAXS profile for the sample with $\phi_{\text{homo}} = 56$ wt% obtained at 200 °C. The scattering peaks are observed at the relative peak position of $1:1.06:1.13:1.43:1.72:1.86:2.06:2.69$. The calculated relative q -peak positions and the reflection indexes for HCP and FCC phases are listed in Table 3. The series of observed scattering peaks are correspond very well with the HCP lattice structure. Here, to compare the experimental SAXS profiles with the theoretical ones, the theoretical scattering curves were calculated [25]. The scattering intensity can be expressed as

$$I(q) = (b_1 - b_2)^2 \rho_N P(q) S(q) \quad (2)$$

Fig. 3 (a) SAXS profile of the PB-PCL/PB blend ($\phi_{PB} = 50$ wt%) obtained at 220 °C and (b) the SAXS profile obtained using SOPHIAS detector (see text). Arrows indicate scattering peaks and the numbers in brackets mean the reflection indexes of the Frank-Kasper σ phase.

Table 2 Calculated and observed peak positions of the σ phase.

<i>hkl</i>	<i>q</i> calc.	<i>q</i> obs.
310	0.231	0.231
221	0.249	0.247
301	0.259	-
320	0.264	0.263
311	0.27	0.269
200	0.278	0.278
400	0.293	-
112	0.296	0.296
321	0.298	-
410	0.302	0.302
330	0.311	0.309
202	0.313	0.314
212	0.322	0.322
420	0.327	0.328
411	0.332	0.332
331	0.34	0.339
222	0.346	0.345
421	0.355	-
312	0.361	0.360
430	0.365	-
510	0.373	-
322	0.383	-
501	0.392	-
520	0.394	-
511	0.398	0.398

Fig. 4 SAXS profile of the PB-PCL/PB blend ($\phi_{PB} = 56$ wt%) obtained at 200 °C. The solid line shows the calculated SAXS curve obtained using eq. (2). Arrows represent HCP diffraction peaks.

b_1 and b_2 are scattering length densities of the particles and the surrounding matrix, respectively, and ρ_N is the number density of the particles. $P(q)$ is the form factor and $S(q)$ is the structural factor. $S(q)$ is given by

$$S(q) = 1 + \beta(q) [Z(q) - 1] G(q) \quad (3)$$

$\beta(q) = \langle F(q) \rangle / \langle F^2(q) \rangle$ is the ratio of the squared scattering amplitude, $G(q)$ is the Debye-Waller factor, and $Z(q)$ is the lattice factor. The spherical micelles with radius R was used as $P(q)$

$$P(q) = \left[\frac{3(\sin(qR) - qR \cos(qR))}{(qR)^3} \right]^2 \quad (4)$$

The size distribution of $P(q)$ was modeled using a Shultz-Zimm distribution. The solid line in Fig. 4 indicates the calculated SAXS profile. The calculated profile is also in excellent agreement with the experimental one. Consequently, spherical micelles are arranged in the HCP lattice.

Fig. 5 presents the SAXS profile for the blend with $\phi_{\text{homo}} = 67$ wt% obtained at 160 °C. The relative q -peak position of 1:1.15:1.61:1.91:2.53 is observed. As shown in Table 3, these scattering peak positions agree with those of the FCC lattice structure. Moreover, the calculated scattering curve for the FCC lattice structure using eq. (2) is also shown in Fig. 5 (solid line). The dash line represents the form factor obtained using eq. (4). Both experimental and theoretical profiles seem to resemble each other,

Table 3 Reflection indexes and relative peak positions of the lattice of FCC and HCP.

FCC		HCP	
Reflection Index (<i>hkl</i>)	Relative position	Reflection Index (<i>hkl</i>)	Relative position
(111)	1	(100)	1
(200)	1.15	(002)	1.06
(220)	1.63	(101)	1.13
(311)	1.91	(102)	1.46
(222)	2	(110)	1.73
(400)	2.31	(103)	1.86
(331)	2.52	(112)	2.04
		(201)	2.07
		(004)	2.12
		(202)	2.26
		(104)	2.34
		(203)	2.56
		(210)	2.65
		(211)	2.7

indicating that the lattice structure is FCC.

Here, we calculated the sphere radius (*R*) in each blend sample using the scattering peak position and the volume fraction of PCL. The radii in the FCC, HCP, and the σ phases are given respectively by

$$R_{FCC} = \sqrt{3} \left(\frac{3f_c}{16\pi} \right)^{1/3} d_{111} \quad (5)$$

$$R_{HCP} = \frac{2}{\sqrt{3}} \left(\frac{3\sqrt{2}f_c}{8\pi} \right)^{1/3} d_{100} \quad (6)$$

$$R_{\sigma} = \left(\frac{2\sqrt{17}f_c d_{002}^2 d_{410}}{40\pi} \right)^{1/3} \quad (7)$$

where f_c is a volume fraction of PCL and d_{hkl} is a domain spacing of (*hkl*) plane. We obtained $R_{FCC} = 7.8$ nm, $R_{HCP} = 8.0$ nm, and $R_{\sigma} = 8.4$ nm. In addition, the first maximum peak position of the spherical form factor is seen in Fig. 5 marked by the thick arrow. *R* can be also calculated from the maximum peak position of the form factor. The spherical morphology is given by $q^*R = 5.765$, where q^* is the scattering maximum value of the spherical form factor. *R* calculated from the form factor is 8.1 nm. Thus, the radius of spherical micelles does not change regardless of the amount of homopolymers.

Next, the change in the lattice structure of spherical micelles depending on the amount of added homopolymers is studied. Theoretical studies demonstrate that the Frank-Kasper σ phase, which is the most complicated lattice observed in this study, can become stable only when the conformational asymmetry is relatively large [16]. The spherical

Fig. 5 SAXS profiles of the PB-PCL/PB blend ($\phi_{PB} = 67$ wt%) obtained at 160 °C and the calculated SAXS profile obtained using eq. (2) (solid line). The dash line shows the form factor calculated using eq. (4). Thin arrows show FCC diffraction scattering peaks, and the thick arrow shows the maximum value of the form factor.

surface of micelles is deformed to polyhedral shapes with the increase in ϵ , leading to the formation of the complicated lattices. Since ϵ_{PB-PCL} is determined to be 1.55, which is relatively larger than the critical value ($\epsilon = 1.5$) [18], the σ phase emerges as a stable phase in the blend sample.

On the other hand, because the region corresponding to FCC and HCP phases in the theoretical phase diagram hardly changes with the increase in ϵ [16], there are other reasons of the observed HCP and FCC phases. It is well known that the differences in the free energy between FCC and HCP phases in a hard sphere model is very small, and the FCC phase is only slightly more stable than the HCP phase [26]. It was also found that the HCP phase cannot be stable in case of weakly charged hard spheres [27] and charged hard spheres [28]. Moreover, theoretical study results predict that elastic spheres are never arrayed into only the HCP lattice [29]. The FCC lattice structure was found mainly in soft matter systems, but the HCP lattice structure was only rarely observed in block copolymers thin films [30], block copolymer solutions [31,32], and surfactants [33–35]. It was reported that both FCC and HCP lattice structures appeared as equilibrium structures in a tetrablock copolymer, and the region corresponding to the FCC phase existed outside that corresponding to the HCP phase in the experimental phase diagram

[7], which is consistent with our result. Since the radius of spherical micelles used in blend samples did not change irrespective of ϕ_{homo} as described above, the distance between spheres in the case of $\phi_{\text{homo}} = 67$ wt% was the longest among the blend samples due to the largest amount of homopolymers. Overlap of neighboring corona chains was smallest in the sample with $\phi_{\text{homo}} = 67$ wt%. Thus, spherical micelles behaved almost like hard spheres, indicating that the FCC lattice became stable. On the other hand, when the amount of blended homopolymers was low, the corona chains overlapped strongly, and spherical micelles softened. Consequently, it is speculated that the transition from FCC to HCP phase occurred.

4. Conclusion

The lattice structures of spherical micelles in PB-PCL/PB blends were investigated using SAXS. The blend sample with $\phi_{\text{homo}} = 40$ wt% showed a cylindrical morphology. In the sample with $\phi_{\text{homo}} = 50$ wt%, spherical microdomains arrayed into the Frank-Kasper σ phase. The HCP lattice structure appeared in the blend with $\phi_{\text{homo}} = 56$ wt%, whereas the FCC lattice structure was observed for $\phi_{\text{homo}} = 67$ wt%. Thus, spherical micelles assembled in the following order with increasing ϕ_{homo} : Frank-Kasper σ , HCP, and FCC phases. In addition, the radius of spheres was almost constant in any type of lattice. The σ phase could be observed as a stable phase, because $\varepsilon_{\text{PB-PCL}} (= 1.55)$ was slightly larger than the critical value. On the other hand, it is speculated the spherical micelles in the FCC phase behaved like hard spheres such as colloids, leading to stabilization of the FCC lattice. When the distance between spheres was reduced, the corona chains overlapped and softened. Therefore, the FCC lattice should be transformed into the HCP lattice.

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