Mesoscopic Tiling Patterns of ABC Star-shaped Terpolymers Studied by Microbeam Small-angle X-ray Scattering

It is known that block copolymers with incompatible components exhibit periodic nanophase-separated structures in condensed states due to the strong repulsion forces among different chemical components. Among the block copolymers, ABC star-shaped terpolymers tend to form characteristic cylindrical structures whose cross-sections reveal tiling patterns because the three different polymer components are connected at one junction point which must be aligned one-dimensionally due to geometrical restrictions (Fig. 1). We have found a variety of mesoscopic tiling patterns formed by ISP star-shaped terpolymers composed of polyisoprene (I), polystyrene (S), and poly(2-vinylpyridine) (P) using transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS) [1-5].

By conventional SAXS measurements for which the typical size of the X-ray beam is 0.5 mm × 0.5 mm or larger, typical block copolymer samples give powder patterns because the grains with an average size of a few microns are oriented randomly. This fact has made it difficult to characterize the complex tiling patterns for the ISP star-shaped terpolymers in reciprocal space. In this study, therefore, microbeam SAXS technique is used to probe only one or a few grains oriented along the same crystal axes. The microbeam SAXS measurements were performed for annealed sample films cut into thin sections *ca.* 30 μm thick using beamline **BL40XU**. The wavelength of the X-ray used was 0.12 nm and the size of the collimated beam was approximately 5 μm × 5 μm (FWHM) with a camera length of about 3 m.

The ISP star-shaped terpolymers adopt various tiling patterns depending on their volume fractions. For example, Fig. 2 shows TEM images of the $I_{1.0}S_XP_{2.0}$ series (X = 1.3, 1.6, 2.3, and 2.7) where the volume ratio of I:S:P is 1.0:X:2.0. Because the samples were stained with osmium tetroxide and iodine for TEM observation, the black, white, and gray

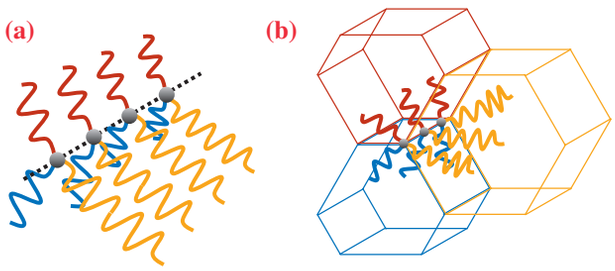

Fig. 1. Schematic drawings of the intramolecular phase separation of ABC star-shaped terpolymer chains **(a)** in bulk and **(b)** their nanodomain assembly.

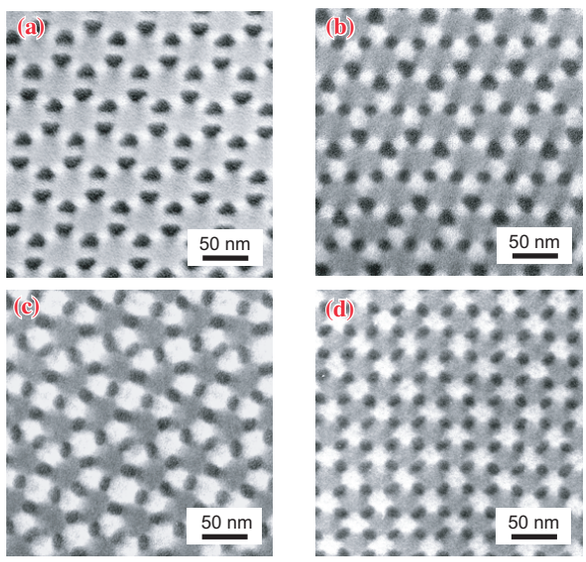

Fig. 2. TEM images of the $I_{1.0}S_X P_{2.0}$ series: **(a)** X = 1.3, **(b)** X = 1.6, **(c)** X = 2.3, **(d)** X = 2.7.

domains represent the components I, S, and P, respectively. For the tiling pattern in Fig. 2(a), the components S, I, and P form the 4-, 6-, and 12-coordinate domains, respectively, and the three kinds of domains contact at every vertex, so it is classified as (4.6.12) Archimedean tiling pattern. In addition to the TEM observation, the (4.6.12) pattern was also characterized by microbeam SAXS. Figure 3(a) shows the microbeam SAXS pattern of $I_{1.0}S_{1.3}P_{2.0}$ and the corresponding d-spacing in real space. This SAXS pattern has 6-fold symmetry, which is consistent with the (4.6.12) tiling pattern having a hexagonal lattice. The $d_{\{10\}}$-spacing, 47 nm, determined by the SAXS pattern agrees well with the value of approximately 50 nm estimated from the TEM image. On the other hand, in the tiling pattern for $I_{1.0}S_{2.3}P_{2.0}$ (Fig. 2(c)), the component I has two types of 4-coordinate domains, the component S consists of 6- and 8-coordinate domains, and the component P has identical 10-coordinate domains. Figure 3(b) shows the microbeam SAXS pattern of $I_{1.0}S_{2.3}P_{2.0}$ and the corresponding d-spacing drawn in a schematic model for the complex pattern. In the SAXS pattern, the {20} and {21} reflections clearly show a 4-fold symmetry, whereas the {10} reflections cannot be confirmed, which suggests the complex tiling pattern has a *P*4*gm* plane group. By applying the imaginary square-triangle tiling manner shown in Fig. 4(a), this complex pattern has been assigned as (3.3.4.3.4), which represents another Archimedean tiling pattern with *P*4*gm* symmetry [2,4].

It should be noted that the (3.3.4.3.4) structure is known as the σ phase in the Frank-Kasper complex crystalline alloy family and is a crystalline analog of a dodecagonal quasicrystal. The quasicrystalline state with non-crystallographic rotational symmetry now represents a new class of ordered state distinct from crystal and amorphous material states. In fact, by exploring a composition range in the vicinity of the (3.3.4.3.4) pattern, we have reached an aperiodic tiling pattern for $I_{1.0}S_{2.7}P_{2.5}$ (Fig. 4(b)) [5]. The square-triangle tiling superimposed on the TEM image has no periodicity, which makes it significantly different from the (3.3.4.3.4) tiling pattern in Fig. 4(a). A microbeam SAXS pattern of $I_{1.0}S_{2.7}P_{2.5}$ is shown in Fig. 4(c). A twelve-fold symmetry pattern up to the higher order can be recognized, suggesting that the square-triangle tiling pattern is a dodecagonal quasicrystal. The length of the sides of the triangles and squares is estimated to be 47.0 nm from the magnitude of the {111100} scattering vector. This result indicates the universality of the dodecagonal symmetry pattern, covering a wide variety of materials including metallic alloys (0.5 nm), chalcogenides (2 nm), organic dendrons (10 nm), and star-shaped polymer (50 nm) herein. We expect that this finding will open a new epoch in self-organization within the field of polymer science and consequently in research on quasicrystals.

In conclusion, the microbeam SAXS technique produces spot-like diffraction patterns, which were never obtained by conventional SAXS measurements, due to scattering from one or a few grains in the polymer samples. These microbeam SAXS patterns enable us to elucidate the complex tiling patterns including the dodecagonal quasiperiodic pattern in reciprocal space. In the future, microbeam SAXS measurements will be widely used to characterize more complex three-dimensional structures such as bicontinuous structures formed by block copolymers.

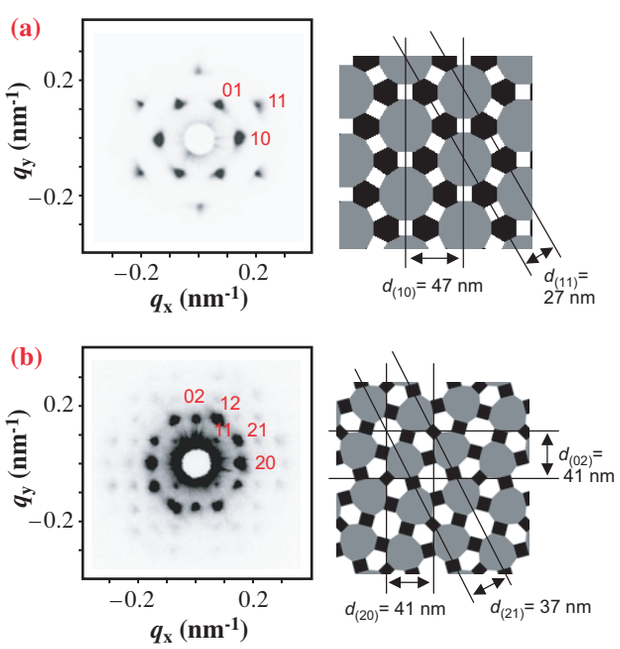

Fig. 3. Microbeam SAXS patterns (left) and the corresponding schematic tiling structures (right): **(a)** $I_{1.0}$ $S_{1.3}$ $P_{2.0}$, **(b)** $I_{1.0}$ $S_{2.3}$ $P_{2.0}$.

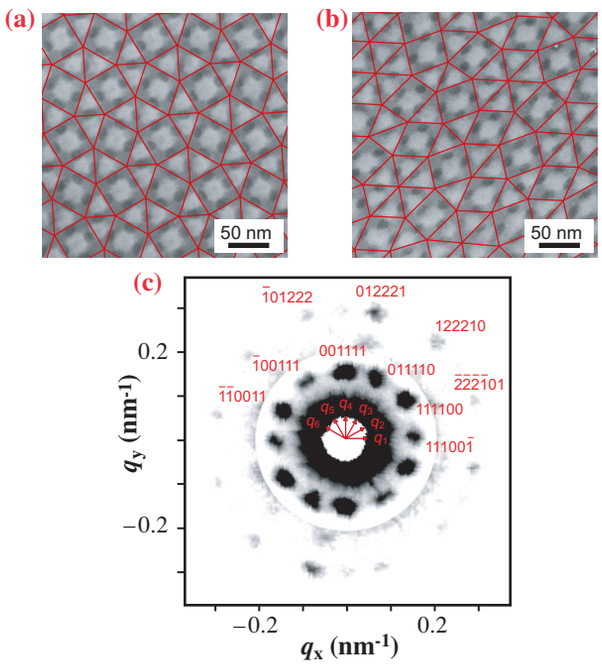

Fig. 4. TEM images of the two ISP samples. The polymer samples are **(a)** $I_{1.0}S_{2.3}P_{2.0}$ and **(b)** $I_{1.0}S_{2.7}P_{2.5}$. An imaginary triangle and square are superimposed on the images. **(c)** Microbeam SAXS pattern obtained for $I_{1.0}S_{2.7}P_{2.5}$. The intensities of the outer twelve diffraction peaks are scaled-up by a factor of 10.

Kenichi Hayashida *, Atsushi Takano, Yushu Matsushita

Department of Applied Chemistry, Nagoya University

*E-mail: hayashid@grace.ocn.ne.jp

References

[1] A. Takano *et al.*: Macromolecules **34** (2004) 9941.
[2] A. Takano *et al.*: J. Polym. Sci. Part B Polym. Phys. **43** (2005) 2427.
[3] K. Hayashida *et al.*: Macromolecules **39** (2006) 4869.
[4] K. Hayashida *et al.*: Macromolecules **39** (2006) 9402.
[5] *K. Hayashida, T. Dotera, A. Takano and Y. Matsushita: Phys. Rev. Lett.* ***98*** *(2007) 195502.*