Tricontinuous Morphology of Triblock Copolymers of the ABC Type

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ABSTRACT: A complicated three-dimensional equilibrium morphology, named an ordered tricontinuous double-diamond (OTDD) structure, similar to the ordered bicontinuous double-diamond structure for diblock copolymers was found for the microphase-separated structure of poly(isoprene-*b*-styrene-*b*-2-vinylpyridine). When the contents of both end-block polymers are equal, this structure occurs from 0.48 to 0.66 for the volume fractions of middle-block polymer, i.e., polystyrene. The transmission electron micrographs at the two different directions, i.e., the [111] and [001] directions, are in good agreement with the corresponding images formed by assuming the OTDD structure proposed here.

Introduction

The variation of morphology with the composition of diblock copolymers has been extensively studied, so that the Molau's rule[2] was confirmed experimentally[3–5] and the transition between the morphologies was understood by the thermodynamic equilibrium theories of microphase separation.[6,7] Recently, however, the existence of a new equilibrium morphology in addition to the three basic morphologies, i.e., spherical, cylindrical, and lamellar structures, was reported on styrene–isoprene (SI) diblock copolymers[8] and SI star-shaped block copolymers.[9,15] The new morphology is considered to consist of continuous domains formed by double-diamond frameworks, which are mutually interpenetrated, and a matrix, which is also a continuous domain.

Several works have been carried out on the variation of morphology with composition of the triblock copolymers of the ABC type. In these works[10–13] the appearance of peculiar and complicated structures was reported, but the data were fragmentary, and even the composition ranges were not well established. This is not only because the preparation of the well-characterized samples is difficult but because the equilibrium morphologies have not been systematically studied.

Studying the morphology of triblock copolymers having the two end-block polymers (A and C) with the same chain lengths and the middle-block polymer (B) with various chain lengths as reported previously,[14] we found that the complicated but three-dimensionally ordered morphology appears in the composition range from A:B:C = 1:2:1 to 1:4:1 approximately. In this work, therefore, we discuss this morphology in detail. The study on this morphology is very important not only for understanding thermodynamics of microphase separation in general but also for using the material for a practical purpose.

Experimental Section

Isoprene–styrene–2-vinylpyridine (ISP) triblock copolymer samples were prepared by an anionic polymerization technique, and they were characterized as reported previously.[14] Film specimens for transmission electron microscopy (TEM) were prepared by solvent-casting from dilute solutions of tetrahydrofuran, which is a good solvent for all the block components. The details of the preparation were described previously.[14] TEM observations were performed with a JEOL 2000FX. In this study, moreover, we observed the change of TEM image with changing the observation direction.

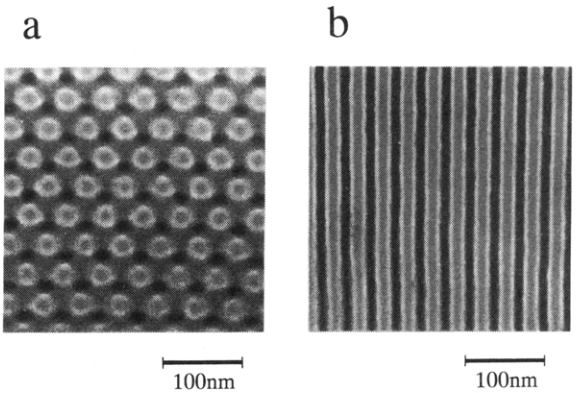

Figure 1. Typical electron micrographs of the ordered tricontinuous double-diamond structure (a) and the three-phase four-layer lamellar structure (b). Samples (a) ISP-3 and (b) ISP-5.

Results and Discussion

Figure 1 shows transmission electron micrographs of microphase-separated structures of ISP triblock copolymers. Since the film specimens were stained with OsO_4, black, white, and gray images denote primarily polyisoprene, polystyrene, and poly(2-vinylpyridine) domains, respectively. Figure 1b shows a micrograph of three-phase four-layer lamellar structure for the triblock copolymers with the composition I:S:P = 1:1:1 for comparison. In the case of the simple morphology like the lamellar structure, the domain can be easily identified by the shade of the image on micrograph.

Figure 1a shows a typical example of the image for the three-dimensionally ordered structure. The image is complicated, and various types of images similar to this one were observed on the micrographs of the same specimen. In this case, therefore, it is not easy to correlate the two-dimensional TEM image to the three-dimensionally connected structure from the shade of the image in contrast to the lamellar structure. Table I summarizes the molecular characteristics of ISP triblock copolymers forming the three-dimensionally ordered structure. All the samples have narrow molecular weight distributions, and the chain length of the middle-block polymers in the samples was varied in keeping those of the end-block polymers equal as mentioned above. The composition ranges approximately from I:S:P = 1:2:1 to 1:4:1. Since the image of the ordered structure did not change by annealing, and this structure appears in a considerably

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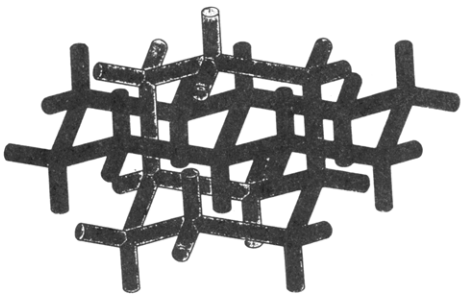

Figure 2. Schematic view of double-diamond frameworks represented by cylindrical struts.

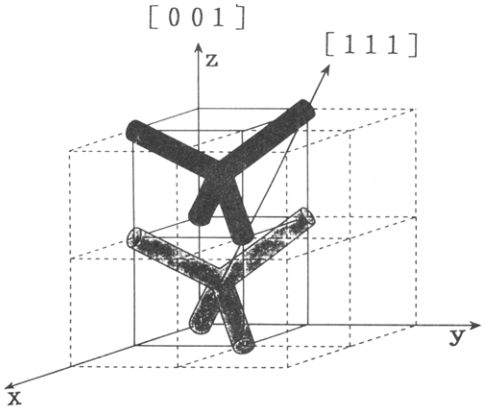

Figure 3. Unit cell of the double-diamond framework and coordinates.

Table I
Molecular Characteristics of Samples

sample	$M_n \times 10^{-3}$	M_w/M_n	volume fraction I	S	P
ISP-5	58	1.04	0.32	0.35	0.33
ISP-3	100	1.05	0.26	0.48	0.26
ISP-1	88	1.05	0.25	0.50	0.25
ISP-14	64	1.04	0.22	0.59	0.19
ISP-23	91	1.02	0.20	0.66	0.14

wide range of composition as mentioned above, this ordered structure can be assumed to be an equilibrium one.

Figure 2 shows our model for this structure, which consists of two kinds of diamond frameworks mutually interpenetrated. The end-block polymers in triblock copolymers constitute two kinds of diamond framework domain, while the middle-block polymers constitute a matrix domain. Figure 3 shows the arrangement of two diamond frameworks. They can be superposed upon each other by parallel translation. Here, we assume tetrapod structures formed by the identical four cylindrical struts as the basic units of the diamond framework for simplicity, though the actual surfaces may have a constant mean curvature and could be close to "minimal surfaces".[15]

In transmission electron micrographs the end-block or I and P domains make primarily dark and gray images, respectively, while the middle-block, or S domain, forms a white background. However, the shade of the image in micrographs also depends on the strength of transmitted electron beams through the structure within the sample specimen, so that it depends on the thickness of the structure. Therefore, the I domain (primary dark domain) makes a dark image if it is thick enough, while it makes a gray image if it is thin. On the other hand, the P domain (primary gray domain) makes a gray image if it is thick enough, while it makes almost no image if it is thin. The overall image from the three-dimensional domains can be

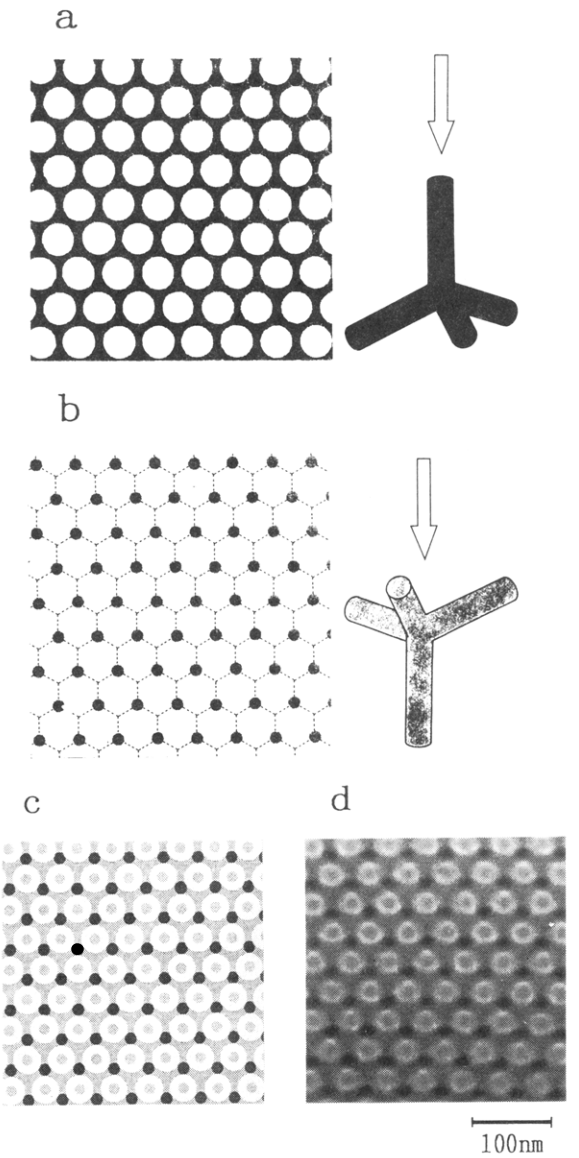

Figure 4. Comparison between observed and assumed images at the [111] direction. (a) Assumed image for the I framework; (b) assumed image for the P framework; (c) superposition of the images in (a) and (b); (d) an electron micrograph for ISP-3.

obtained by overlapping two kinds of image from the I and P domains.

Figure 4 shows comparison between the assumed and observed electron micrographs at the [111] direction. Figure 4a shows only the image for a single layer of diamond framework of I domain with 3-fold symmetry. The I strut, which is thick enough along the direction of observation, gives a dark image, whereas the remaining three struts give gray images because the actual thicknesses of these struts along the [111] direction are relatively small. On the other hand, Figure 4b shows only the image for single layer of the diamond framework of the P domain. One of the P struts gives a gray image, whereas the other struts give almost no image, for the same reason as the case of the I domain. Superposing the two images in parts a and b of Figure 4, considering the relationship between their positions shown in Figure 3, we have the overall image as shown in Figure 4c, which is in good agreement with the electron micrograph shown in Figure 4d.

Figure 5 shows comparison between assumed and observed images at the [001] direction in the same way as in Figure 4. Figure 5a shows the image for a single layer of the diamond framework of the I domain with apparent

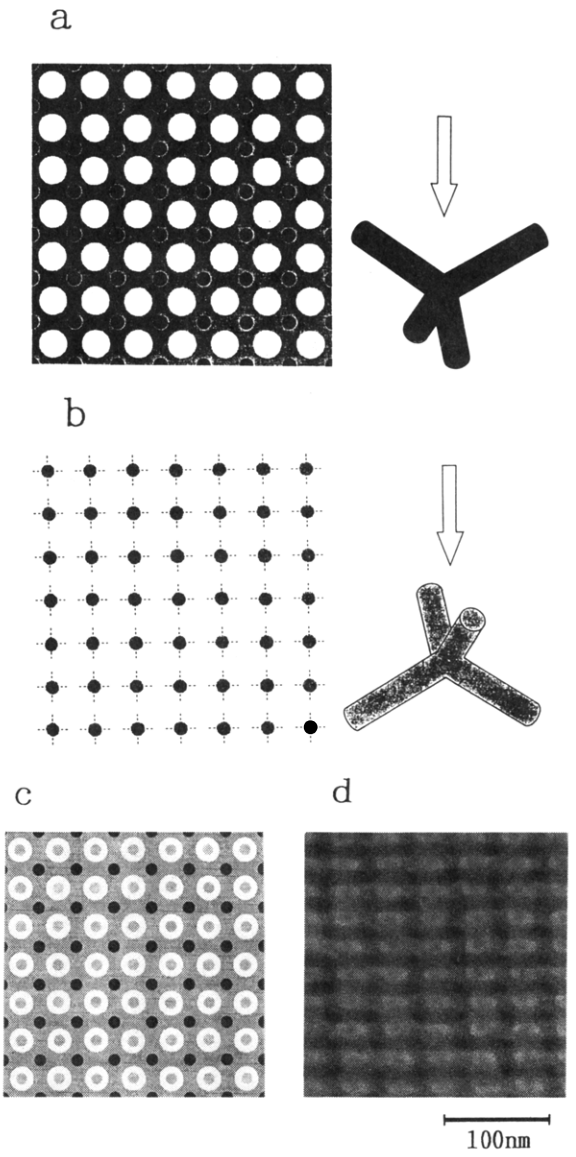

Figure 5. Comparison between observed and assumed images at the [001] direction. (a) Assumed image for the I framework; (b) assumed image for the P framework; (c) superposition of the images (a) and (b); (d) an electron micrograph for ISP-3.

4-fold symmetry. In this view, the center part of a tetrapod unit gives a dark image because this part is thick enough to absorb the electron beam, whereas all four struts give gray images for the same reason as in Figure 4a. On the other hand, Figure 5b shows the image from a single layer of the diamond framework of the P domain. For the same reason as mentioned for Figure 4b, only the center of a tetrapod unit gives a gray image, whereas the struts give almost no image. The images in parts a and b of Figure 5 should have actually 2-fold symmetry because the horizontal and vertical direction are not equivalent as shown by the basic tetrapod units at the right-hand side in both figures. Thus, we have the overall image at this direction as shown in Figure 5c, which is in good agreement with the observed electron micrograph in Figure 5d.

As mentioned above the two typical images on electron micrographs of ISP triblock copolymers are well explained by the OTDD model observed at the two different directions, [001] and [111]. As shown in Figure 6, the rotational angle between the [001] and [111] directions is 54.7°. If the model is correct, the spatial relationship between the two images should be naturally satisfied. To confirm that this model is reasonable for this structure,

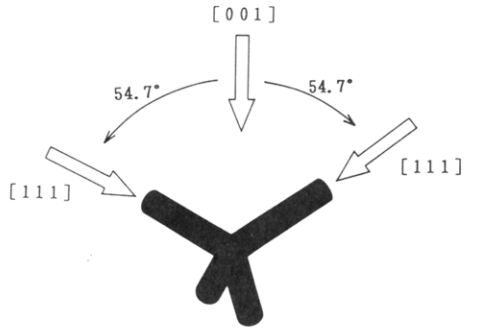

Figure 6. Angular relationship between the [001] and [111] directions for a tetrapod unit.

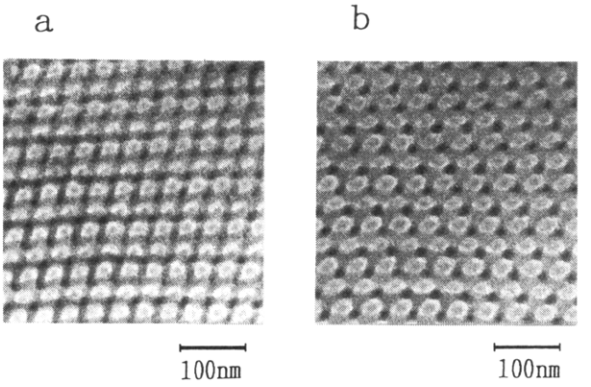

Figure 7. Change of electron micrograph by rotating the ultrathin film specimen on the TEM stage. Sample ISP-3. (a) The original image; (b) the image after rotating to an angle of 55° from the original position.

therefore, we examined if the image in Figure 5 corresponding to the OTDD model at the [001] direction changes to the image in Figure 4 corresponding to that model at the [111] direction by tilting the specimen on the TEM stage to the angle of 55°, as shown in Figure 6. Here, it is to be noted that the image at the [001] direction can be always obtained from that at the [111] direction after the 55° rotation, but the reverse is not always attained. Figure 7 shows the images before and after tilting. It is apparent that parts a and b of Figure 7 are almost the same as the images at the [001] and [111] direction in Figures 5 and 4, respectively, though the image is somewhat skew.

In summary, we can conclude that the complicated but three-dimensionally ordered structure considered as an equilibrium morphology for the microphase-separated structure of the present ISP triblock copolymers is well explained by the tricontinuous double-diamond structure model proposed here. Thus, we name this structure "ordered tricontinuous double-diamond" (OTDD) structure after "ordered bicontinuous double-diamond" (OBDD) structure named for the similar structure of styrene–isoprene star-shaped block copolymers by Thomas et al.[9,15]

References and Notes

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