Tricontinuous Double-Diamond Structure Formed by a Styrene–Isoprene–2-Vinylpyridine Triblock Copolymer

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Received October 4, 1993
Revised Manuscript Received April 5, 1994

A remarkable feature of block copolymers is that they form microphase-separated structures in the bulk. Recently, the ordered bicontinuous double-diamond structure (OBDD) was found in both linear diblocks[1] and star-shaped block copolymers.[2–4] Furthermore, the ordered tricontinuous double-diamond structure (OTDD) was found in isoprene–styrene–2-vinylpyridine (ISP) triblock copolymers of the ABC type over a wide composition range of the center block, polystyrene.[5,6] Here, we report that the OTDD structure arises in styrene–isoprene–2-vinylpyridine (SIP) triblock copolymers, which consist of the same components as the ISP triblock copolymers but in different sequence.

Two samples were prepared by anionic block copolymerization with cumylpotassium as the initiator and tetrahydrofuran (THF) as the solvent in almost the same manner as reported previously for ISP triblock copolymers.[6] The only difference between SIP and ISP copolymers is the sequence of monomer addition. The polymers were purified by precipitation in water, dried, and then characterized by the same procedures as in the previous work.[6,7] The total number-average molecular weight, M_n, of one sample, denoted SIP-2, is 201 000, and its S/I/P volume ratio is 0.31/0.43/0.26. The M_n of another sample, SIP-4, is 196 000, and its volume ratio is 0.18/0.66/0.16. Films for morphological observations were prepared by solvent-casting from 3 to 5% solutions of THF, which is a common good solvent. The solubility parameter values, δ, of polystyrene, polyisoprene (cis-1,4), and poly(2-vinylpyridine) are 18.6, 16.6, and 21.7 M Pa$^{1/2}$, respectively, and that of THF is 18.6 MPa$^{1/2}$. Polyisoprene of the present samples consists of 40% of 1,2-vinyl and 60% of 3,4-vinyl configurations because of the polymerization condition adopted. The δ value for isoprene having a high vinyl content is not known in the literature, but it is expected to be larger than that for *cis*-1,4-polyisoprene. The films were annealed under vacuum at 120 °C for a week and then were cut into small and thin pieces and embedded in an epoxy resin. The ultrathin sections for transmission electron microscopy (TEM) were obtained by cutting the embedded specimens by a LKB ULTROTOME Model 8800. The thickness of the sections was 50–70 nm, that was controlled by setting the feed step of the specimens. Then thin sections were stained by placing them under the vapor of the fixing agent, osmium tetroxide, for 24 h.

Figure 1 is a typical electron micrograph obtained from SIP-2. Since ultrathin sections were stained with osmium tetroxide, it is apparent in the case of the lamellar structure shown in Figure 1 that the dark, gray, and white regions correspond to I, P, and S microdomains, respectively.[8] The domain spacing, D, of this structure, i.e., the total length of a series of white, black, gray, and black stripes, is about 100 nm. This value is consistent with that calculated using the D–M_n relationship, $D = 0.0086M_n^{0.77}$ (nm), which was experimentally determined for ISP triblock copolymers possessing the lamellar structure.[8]

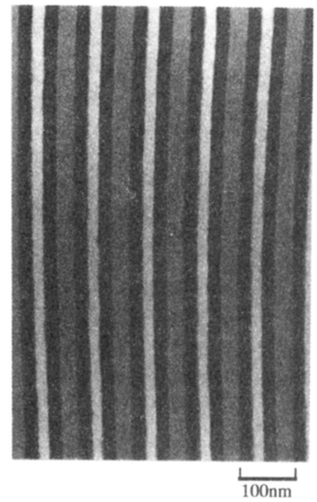

Figure 1. Electron micrograph of SIP-2 showing the three-phase four-layer lamellar structure.

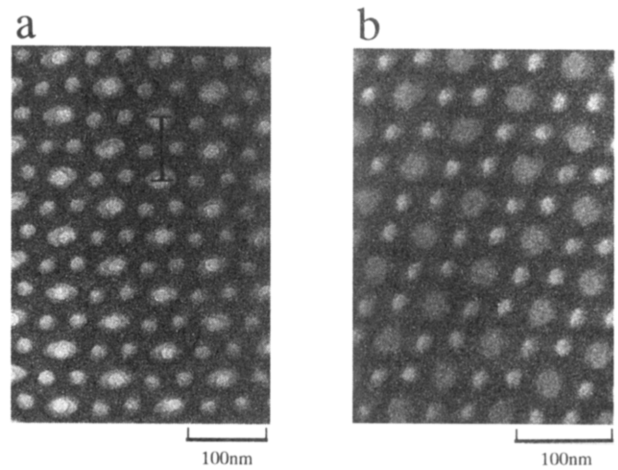

Figure 2. Typical electron micrographs of SIP-4 exhibiting the ordered tricontinuous double-diamond structure.

Gido et al.[9] observed a different structure, which has a projection appearing similar to the one in Figure 1, in a micrograph of an SIP triblock copolymer in which the S/I/P volume ratio was 0.33/0.33/0.33. They concluded, on the basis of other projections which showed hexagonal symmetry, that the morphology consists of hexagonally-arrayed coaxial microdomains of P and I in an S matrix with a nonconstant mean curvature I–S interface. We observed no projection other than the one seen in Figure 1 for SIP-2, for which the volume ratio is 0.31/0.43/0.26. Thus, we conclude that the structure of SIP-2 is the same three-phase four-layer lamellar morphology as that of ISP triblock copolymers with similar composition.

On the other hand, parts a and b of Figure 2, which are two typical electron micrographs of SIP-4, reveal that the morphology is very regular but complicated, so that straightforward assignment of each region to a certain polymer domain is not facile. Light and gray dispersions appearing circular in cross section are observed in both parts a and b of Figure 2. Here, attention should be paid to the fact that the matrix consists of the I block so that the matrix was more heavily stained than the P domains. The lighter circles in Figure 2a have lightly stained coronas, and they are surrounded by six smaller gray circles. Large circles possessing coronas were also observed in TEM images of the OTDD structure in ISP triblock copolymers.[5] Since the composition ratio of the middle block to the end

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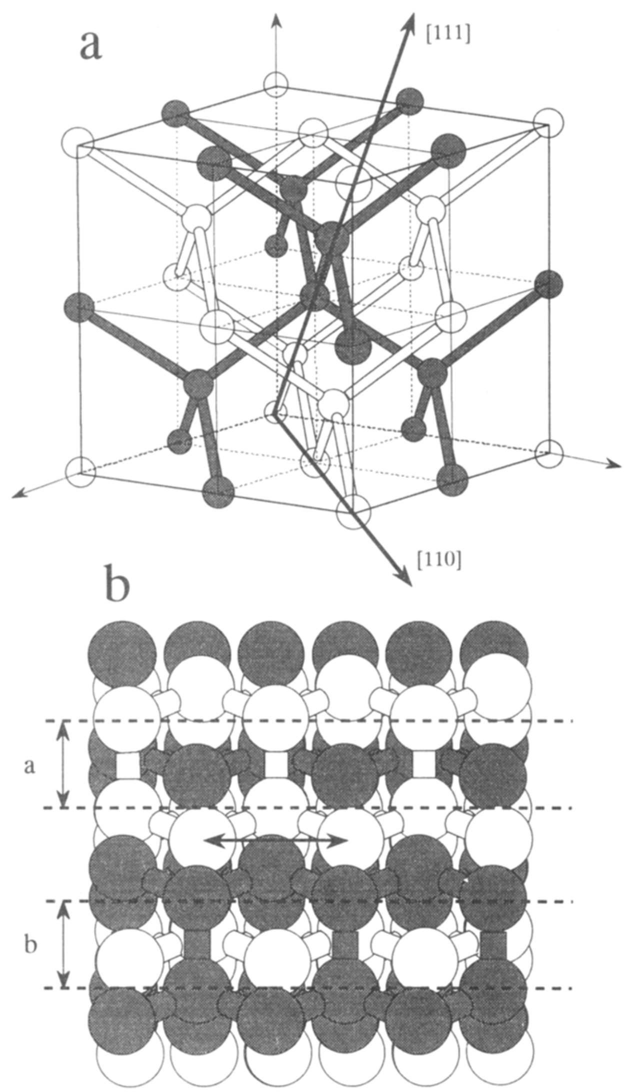

Figure 3. Framework of the ordered tricontinuous double-diamond morphology. (a) Cartesian coordinates and the definition of the [111] direction; (b) [112] view of the model defined in the text.

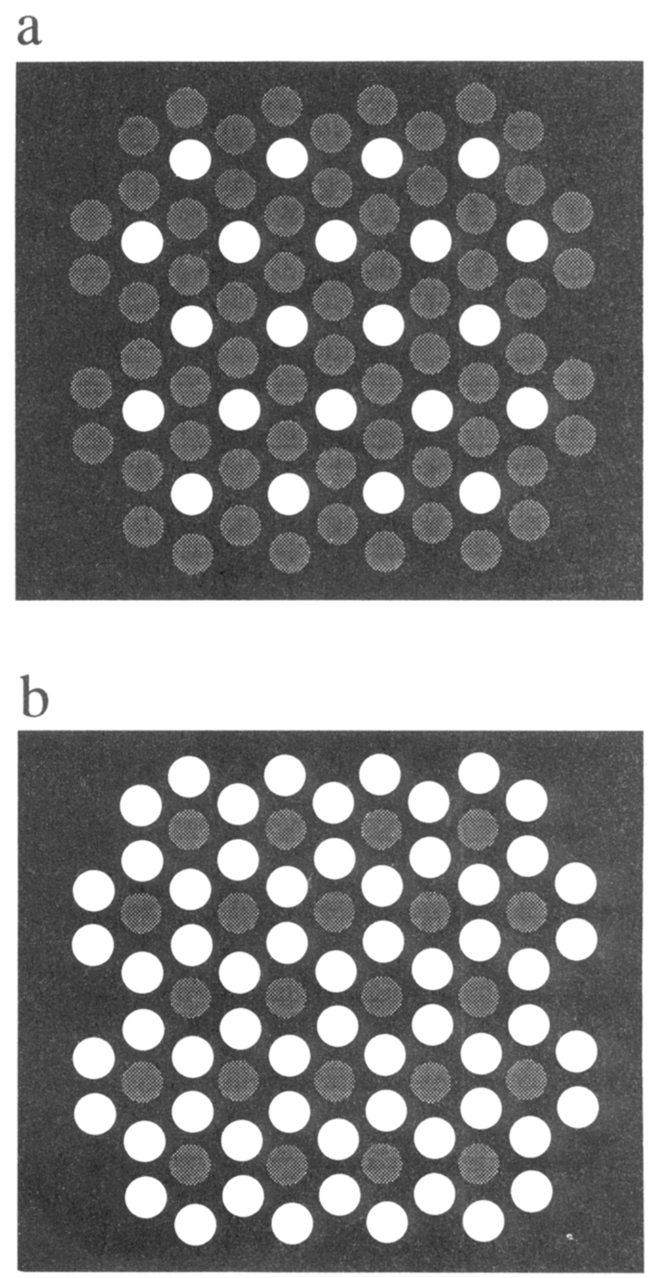

Figure 4. Predicted images in the [111] direction. Images a and b were obtained by slicing the model to the thicknesses designated as *a* and *b*, respectively, in Figure 3b.

block of SIP-4 lies within the composition range of the OTDD structure for ISP triblock copolymers, we attempt here to interpret the present micrographs in terms of the same structure.[5] A schematic illustration of mutually interpenetrated double-diamond frameworks is shown in Figure 3a and assumes a combination of four cylindrical struts with one sphere at the center as a basic tetrahedral unit. Figure 3b represents the [112] view of the OTDD model and shows one of the side views of the [111] projection. In this figure, the volume fractions of S and P are both $^1/_6$, and the ratio of the radius of a cylinder to that of a sphere is assumed to be $^1/_3$. If the solid could be sliced to the thickness designated as *a*, it would include parts of the S layers and a whole P layer (see Figure 3b) along the [111] direction. The resulting projected image is presented in Figure 4a and is in good agreement with the micrograph shown in Figure 2a. Here, we assume that the struts composing the S and P microdomains cannot be seen because their dimensions are small relative to that of the heavily stained (i.e., dark) I matrix.

Comparison of parts a and b of Figure 2 reveals that the arrangement between the gray and light circles in the latter is the reverse to that in the former, though no coronas are seen in the gray circles in the latter (presumably since the P domains are heavily stained). If we slice the postulated morphology to the thickness designated as *b* in Figure 3b and project the structure along the [111] direction, we obtain the image shown in Figure 4b, which agrees well with the micrograph in Figure 2b. The gray circles are apparently larger than the light ones in Figure 2b, and, conversely, the light circles are larger than the gray ones in Figure 2a. This fact may be understood by introducing the idea of "lamination" of the hyperbolic microdomain interfaces.[10]

Further, if the morphological model is correct, the distance between the repeating units of the tetrahedral structure (shown by a thick arrow in Figure 3b) corresponds to the length of a bar in Figure 2a, which is approximately 85 nm. On the other hand, the length of *a* or *b* in Figure 3b is about two-thirds the distance shown by the thick arrow, that is, approximately 57 nm. Since this distance is in good agreement with the nominal thickness of each specimen cut by a microtome, the above discussion is expected to be valid.

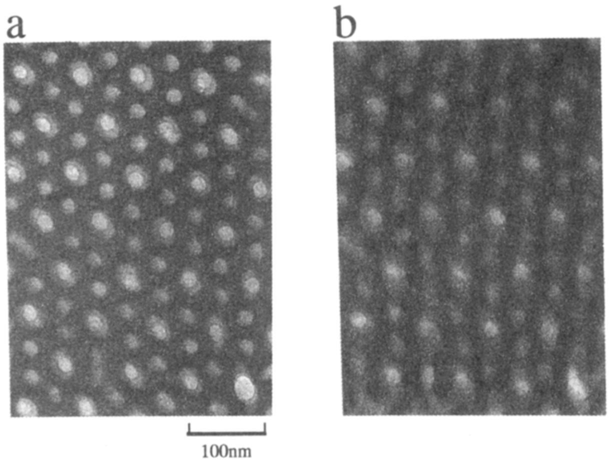

Figure 5. Change of image by tilting an ultrathin section of SIP-4 on the TEM stage. b was obtained by tilting the section which gives the image shown in a by 30° about a horizontal axis.

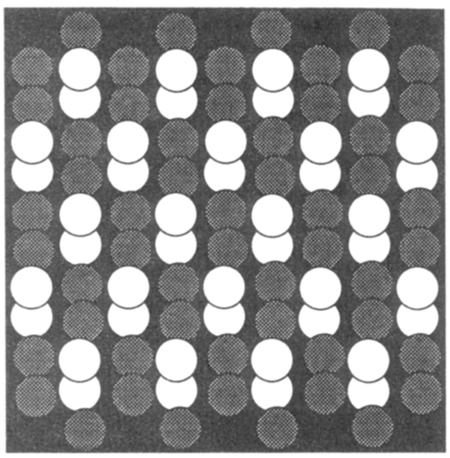

Figure 6. Predicted image obtained by tilting an ultrathin section designated as *a* in Figure 3b by 30° and by projecting the through image on the horizontal plane.

Another piece of evidence of the three-dimensional feature of this structure was presented in Figure 5. These figures show the change of the image by tilting an ultrathin section on the TEM stage. Figure 5a is a typical [111] view, and Figure 5b is the image obtained by tilting the section by 30° about a horizontal axis. The latter is still keeping the periodicity, but the lighter region looks like a continuous microdomain. Figure 6 shows an image obtained by tilting the model within *a* in Figure 3b by 30° and projecting it on the horizontal plane. Therefore, it should be pretty close to the [110] view, which was assigned in Figure 3a. It is clear that the structure in Figure 5b agrees reasonably well with the model in Figure 6, considering two adjacent white circles in Figure 6 are actually a continuous polystyrene microdomain. Thus, we conclude that the morphology of SIP-2 is the OTDD structure, though the definite shape of the tetrahedral unit is not known, but most likely of hyperbolic constant mean curvature.

Using the theory of Ohta and Kawasaki[11] in the strong segregation limit, Anderson and Thomas[3] reported that the total free energy of a bicontinuous double-diamond structure with a constant mean curvature surface is slightly higher than that of other structures at any composition for two-component star-shaped block copolymers. Assuming that the tetrahedral unit consists of a sphere with four cylindrical struts, on the other hand, Nakazawa and Ohta[12] derived the free energy for the OTDD structure of the ABC triblock copolymer using the ratio of the radius of a cylinder (R) to that of a sphere (P) as an adjustable parameter. According to their theory, the OTDD structure can appear in almost the same range as observed by experiments[6] if $R/P = 0.9$. However, the free energy strongly depends on the structure of the basic unit, which means that more detailed studies of the tetrahedral structure are needed to understand the tricontinuous structures more precisely.

Acknowledgment. This work was partially supported by a grant from The Daiko Foundation, and Y. Matsushita is grateful for their support. The authors wish to thank Mr. H. Choshi for his help in preparing polymer samples and also in printing the electron micrographs. We also express our thanks to Dr. H. Hasagawa of Kyoto University for his helpful discussion and suggestions.

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