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Preparation and Morphology of Triblock Copolymers of the ABC Type

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ABSTRACT: The variation of morphology of triblock copolymers of the ABC type, poly(isoprene-*b*-styrene-*b*-2-vinylpyridine), with composition was studied by transmission electron microscopy. Four types of morphology were observed for the microphase-separated structures of the samples whose volume fractions of the middle-block polymer, polystyrene, range from 0.3 to 0.8, while keeping the volume fractions of the end-block polymers, i.e., polyisoprene and poly(2-vinylpyridine), equal. They are a three-phase four-layer lamellar structure, an ordered tricontinuous double-diamond structure, a cylindrical structure composed of two kinds of cylindrical domains formed by two end-block polymers in a polystyrene matrix, and a spherical structure composed of two kinds of spherical domains formed by two end-block polymers in a polystyrene matrix. The variation of morphology with composition is discussed in comparison with that of diblock copolymers.

Introduction

It is well-known that block copolymers with mutually incompatible components form microphase-separated structures in bulk. Studies on microphase separation have been conducted extensively for AB diblock copolymers, so that the variation of morphology with composition[2] and the molecular weight dependence of the domain size[3,4] have been elucidated. Moreover, the conformation of block chains in microdomains was studied by using small-angle neutron scattering.[5-8] In clarifying the morphology of block copolymers at the molecular level, studies on the morphology of triblock copolymers of the ABC type in comparison with diblock copolymers of the AB type are of interest because the former have the middle-block chain of which both ends are held at the different domain boundaries. However, the systematic study on the morphology of triblock copolymers of the ABC type has not been carried out, not only because the preparation of well-defined triblock copolymer samples is difficult but also because the morphologies are various and complicated.[9-11]

Since the morphology of diblock copolymers is determined by the volume fraction of a block chain in the strong segregation limit, the equilibrated microdomains formed by the A and B block polymers and by the B and C block polymers in the ABC triblock copolymers are assumed to be geometrically symmetric to each other if the volume fractions of A and C block polymers are equal. In this work, therefore, we prepared triblock copolymers having the middle-block polymers with various chain lengths but having the two end-block polymers with the same chain lengths to study the variation of equilibrium morphology with composition in comparison with that of the diblock copolymers.

Experimental Section

Preparation. Triblock copolymers of the ABC type used here were poly(isoprene-*b*-styrene-*b*-2-vinylpyridine)s, which were prepared by the anionic polymerization of isoprene, styrene, and 2-vinylpyridine in this order in tetrahydrofuran (THF) with cumylpotassium as an initiator at 25 °C under high vacuum ($\sim 10^{-5}$ Torr). The monomers and the solvent used were highly purified before use.[12] The polymer concentrations were planned to be lower than 5 g/dL in order to keep the solutions uniform in the polymerization process. Aliquots were characterized for each step of the polymerization. The polymerization was terminated by adding methyl alcohol to the reaction vessel. To precipitate the triblock copolymers, the reactant solution was put into a poor solvent, methyl alcohol, *n*-hexane, or water, depending on the composition of the samples.

Characterization. The number-average molecular weights, M_n, of triblock copolymers and their precursors were determined in toluene at 25 °C with a Hewlett Packard membrane osmometer Type 502. The index of molecular weight distribution, M_w/M_n, was determined with a Tosoh gel permeation chromatograph (GPC) Type HLC802A, equipped with two columns of GMH_{XL} type, by using the calibration curve determined by the standard polystyrenes. The composition of triblock copolymer was determined with a Perkin-Elmer elemental analyzer Type 240B. The microstructure of a polyisoprene block was determined by ^1H NMR with a Varian Gemini 200-MHz FT.

Morphological Observation. Film specimens for morphological observation were prepared by solvent-casting from 4% solutions of THF,[12] which is a good solvent for all the components of the triblock copolymers. THF was allowed to evaporate slowly from the solution in a Petri dish at room temperature for 3-5 days. Then, the cast films were dried in vacuo for a week at room temperature. Further, some films were annealed at 120 °C in vacuo for 10 days. The thickness of the films thus obtained was about 0.2 mm. As-cast and annealed films were soaked in 4% aqueous OsO_4 solutions for 2 days at room temperature. The stained films were dried and embedded in an epoxy resin. The resin was cut to make film specimens about 500 Å thick with a ultramicrotome. The morphology was observed with a JEOL transmission electron microscope Model 2000FX operated at an accelerating voltage of 75 kV.

Results and Discussion

Molecular Characteristics. Figure 1 shows an example of the GPC diagrams of a triblock copolymer and its precursors in each step of successive polymerization. The diagrams show that the molecular weights increase at each step as expected, and they imply that the molecular weight distributions of the precursors and the triblock copolymer samples are fairly narrow. Table I summarizes the molecular characteristics of triblock copolymer samples used in this work. As shown in the table, the molecular weights of the samples range from 4.9×10^4 to 1.5×10^5, and all the samples have narrow molecular weight distributions, so that the composition distributions can be considered to be fairly narrow too. The compositions of the samples are shown as the volume fraction of three components in the table. The volume

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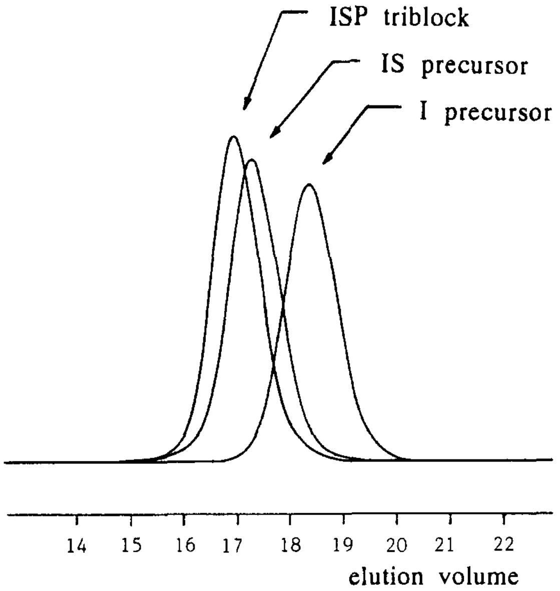

Figure 1. GPC diagrams of a triblock copolymer and its precursors. Sample: ISP-3.

Table I
Molecular Characteristics of Samples

			volume fraction		
sample code	$M_n \times 10^{-3}$	M_w/M_n	I	S	P
ISP-4	61	1.04	0.36	0.31	0.33
ISP-16	152	1.04	0.35	0.34	0.31
ISP-5	58	1.04	0.32	0.35	0.33
ISP-2	94	1.05	0.30	0.42	0.28
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
ISP-18	93	1.02	0.14	0.68	0.18
ISP-19	90	1.02	0.12	0.76	0.12
ISP-15	49	1.03	0.13	0.78	0.09
ISP-12	73	1.03	0.11	0.80	0.09

fractions of both end-block polymers, polyisoprene (I) and poly(2-vinylpyridine) (P) blocks, are almost equal, and the volume fractions of the middle-block polymer, polystyrene (S), to the whole triblock copolymer range from 0.3 to 0.8. A typical microstructure of polyisoprene in the block copolymers was found to consist of 40% of 1,2-vinyl and 60% of 3,4-vinyl configurations.

Morphological Observation. Figure 2 shows examples of transmission electron micrographs of triblock copolymers with various compositions. Four types of morphology were observed for the microphase-separated structures of the triblock copolymers. In the electron micrographs of the film specimen stained by OsO_4, the black, white, and gray images denote polyisoprene, polystyrene, and poly(2-vinylpyridine) domains, respectively. These morphologies in Figure 2 did not change by annealing, so that they are considered to be equilibrium ones.

Figure 2a shows a micrograph of lamellar structure having the repeating unit of four layers consisting of three phases, as polyisoprene, polystyrene, poly(2-vinylpyridine), and another polystyrene layers (I–S–P–S), for the triblock copolymers with a composition of I:S:P = 1:1:1. Thus, we call this structure a "three-phase four-layer lamellar structure".

Figure 2b shows a micrograph of the complicated three-dimensional morphology for the triblock copolymers with a composition of 1:2:1. This morphology is considered to consist of two kinds of mutually interpenetrated diamond frameworks formed by the two end-block polymers, embedded in a matrix composed of the middle-block polymer, as discussed in detail in our following paper.[13] Thus, we name this structure an "*o*rdered *t*ricontinuous *d*ouble-*d*iamond (OTDD) structure" after an "*o*rdered *b*icontinuous *d*ouble-*d*iamond (OBDD) structure" for star-shaped diblock copolymers.[14-16]

Figure 2c shows a micrograph of cylindrical morphology for the triblock copolymers with a composition of 1:4:1. This structure consists of two kinds of cylindrical domains formed by two end-block polymers in the polystyrene matrix. As shown in Figure 3, a tetragonal arrangement may be reasonable for this cylindrical morphology because the two kinds of cylinders arrange more symmetrically in the tetragonal packing than in the hexagonal packing, which is observed for the cylindrical morphology of diblock copolymers. Further studies are needed to confirm this speculation.

Figure 2d shows a micrograph of spherical domains of two end-block polymers in the polystyrene matrix for the triblock copolymers with a composition of 1:8:1. Unfortunately, the micrograph is too vague to discuss this structure in detail because the stained contrast between the spherical domains and the matrix is low, and also the spheres are small due to the low molecular weights of end-block polymers.

Variation of Morphology with the Composition. Figure 4 shows the triangle diagram demonstrating the variation of morphology with the volume fraction of the middle-block polymer in the triblock copolymers having the two end-block polymers with the same chain lengths. As mentioned above, the micrographs in Figure 2 indicate that the shapes of interfaces between I and S domains are essentially the same as those between P and S domains in all four morphologies, as assumed in the Introduction. Therefore, we can conclude that the morphologies are equilibrium ones, and they are determined by the composition in the same manner as for diblock copolymers. In Figure 5 the compositional variation of morphology is given in terms of the volume fraction of the polystyrene block in the triblock copolymer (T), together with the variation of morphology of styrene–isoprene diblock copolymer with the volume fraction of the polystyrene block (D).[18] Comparison between T and D reveals that the composition ranges of double-diamond and lamellar structures are entirely different for both block copolymers, though those of spherical and cylindrical structures are almost the same. In other words, the triblock copolymer with the composition of A:B:C = 1:2*r*:1 has not always the same morphology as the diblock copolymer with the composition of A:B = 1:*r*. In general, therefore, we cannot assume that the triblock copolymer of the ABC type consists of two diblock copolymers of the AB and BC types, obtained by cutting the center of the B block chain in the triblock copolymer, as could be assumed for triblock copolymers of the ABA type.

The essential difference between triblock copolymers of the ABC type and diblock copolymers is in fact that the former has always a "bridge" conformation of the B block chain; the two ends of the B block chain are always held separately at the two different boundaries between the A and B domains and between the B and C domains. As reported in a previous paper,[17] the most probable position of a free-end of the diblock copolymer is in the middle of the domain. This may be the case for the A and C block chains in triblock copolymers of the ABC type. In lamellar structures, particularly, the A or C block chain has a bridgelike conformation similar to that of the B block

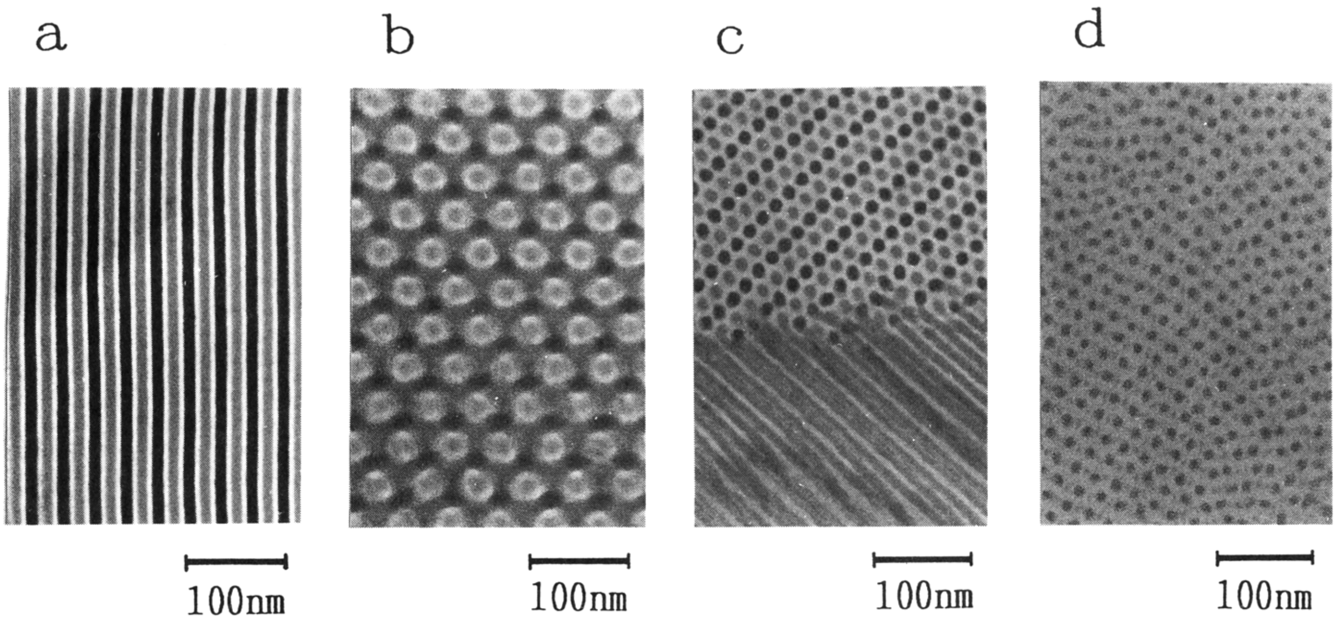

Figure 2. Four types of morphologies of microphase-separated structures of triblock copolymers. Samples: (a) ISP-4, (b) ISP-3, (c) ISP-18, (d) ISP-12.

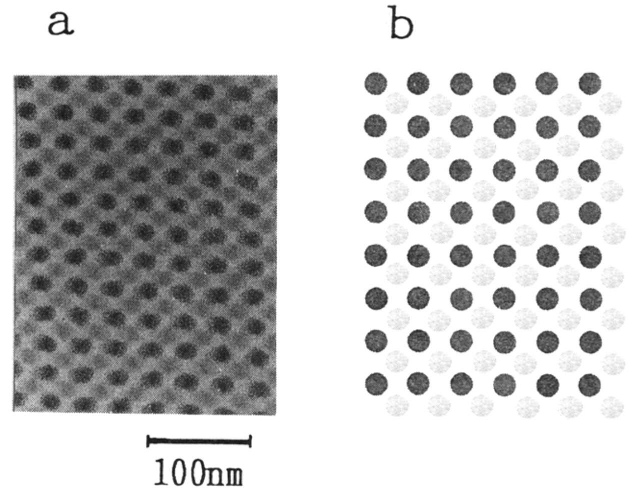

Figure 3. Packing pattern of cylinders in the cylindrical structure. (a) An example of an electron micrograph. Sample: ISP-18. (b) Schematic diagram of mutually tetragonal packing for two kinds of cylinders.

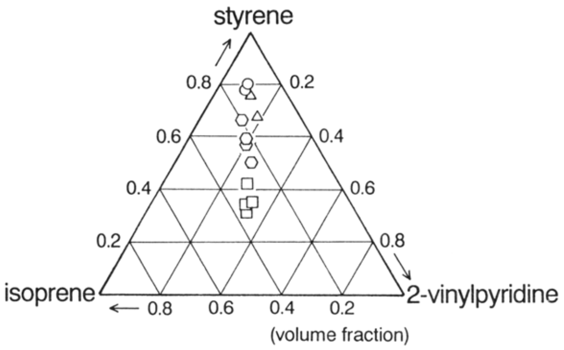

Figure 4. Triangle diagram demonstrating the variation of morphology with the volume fraction of the middle-block polymer in triblock copolymers: three-phase four-layer lamellar structure (□), ordered tricontinuous double-diamond structure (⬡), cylindrical structure (△) and spherical structure (○).

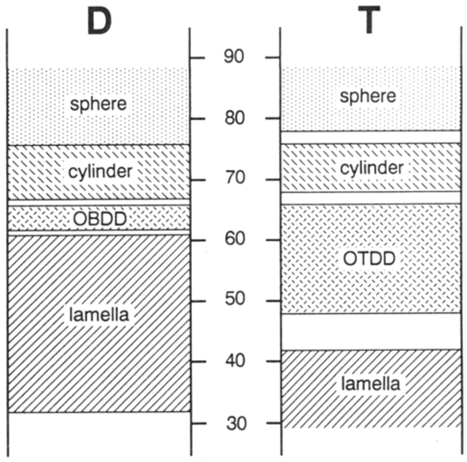

Figure 5. Variation of morphology with the compositions of the ISP triblock copolymers together with that of the SI diblock copolymers. The values along the vertical axis are the volume percentages of the S block in the triblock copolymer (T) and in the diblock copolymer (D).

chain, since we can assume that there is a lamellar boundary in the middle of the A or C domain. In other words, triblock copolymers of the ABC type which form lamellar structures can be assumed to consist of two diblock copolymers of AB and BC types, which hold the same B block chain in common. If the thermodynamic interaction parameter between A and B is similar to that between B and C, the interfacial energies, and hence the conformational entropies to balance the interfacial energies, are almost the same for the lamellar structures of the di- and triblock copolymers in the strong segregation limit. Therefore, the chain lengths of the A, B, and C block polymers must be equal for lamellar structures as shown by the experimental result mentioned above.

Moreover, let us examine if triblock copolymers of the ABC type could form lamellar structures when the volume ratio of the three components is 1:2:1. If the thickness of a B lamella of the triblock copolymers would be determined by the molecular weight dependence of the lamellar thickness of diblock copolymers, it would be 0.79 (=$2^{2/3}/2$) times smaller than the thickness of an A or a C lamella. However, the thicknesses of the A, B, and C lamellae should be the same because the composition of A:B:C is 1:2:1. Therefore, the B block chain must be extended, and the conformational entropy would decrease. Since the interfacial energy of the lamellar structure is independent of composition, the total free energy would increase, and the lamellar structures would be unfavorable.

In other morphologies, i.e., spherical and cylindrical structures, the conformational entropy of the B block of a triblock copolymer with the composition of A:B:C = 1:2*r*:1, which corresponds to A:B = 1:*r* for AB diblock copolymers in Figure 5, would be also lower than that of A:B:C = 1:*r*:1. However, the interfacial energy of a copolymer with a composition of A:B:C = 1:2*r*:1 would be lower than that of a copolymer with A:B:C = 1:*r*:1, when the total chain lengths are the same, because the interfacial energy depends on the interfacial area; for instance, it is proportional to the product of the numbers of the microdomains per unit volume and the radius of the cylinder or the square of radius of the sphere, for cylindrical or spherical structure, respectively. Therefore, the total free energy of triblock copolymer with a composition of A:B:C = 1:*r*:1 would not be lower than that of A:B:C = 1:2*r*:1 for cylindrical and spherical structures in contrast to lamellar structures. In addition, a B block chain also has a bridge conformation, but the conformation cannot be similar to that of A or C block polymers, since the curvature of the boundary between A and B or B and C is entirely different from that of the hypothetical boundary in the middle of the A or C domain. Therefore, we cannot simply assume that a triblock copolymer of the ABC type consists of two diblock copolymers of the AB and BC types, holding the B block chain in common in these morphologies. Thus, it may be reasonable that the composition ranges of both B blocks of di- and triblock copolymers are almost the same for spherical and cylindrical structures.

The composition range of OTDD structures is between those of the cylindrical and lamellar structures. Consequently, it becomes considerably wider than that of the corresponding OBDD structures of diblock copolymers as shown in Figure 5. This implies that the double-diamond structure is more favorable for triblock copolymers of ABC type than for diblock copolymers.

In summary we conclude that the variation of morphology with the composition of triblock copolymers of the ABC type having the same chain lengths for the end-block polymers is similar to that of diblock copolymers, but their composition ranges are different because of the bridge conformation of the middle-block polymers.

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