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New Equilibrium Microdomain Morphology in a Triblock Copolymer

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A–B and A–B–A block copolymers consist respectively of two and three long segments chemically bonded together. In forming an equilibrium structure, such a material may separate into distinct phases, resulting in domains of components A and B. Recently, the ordered equilibrium morphology in block copolymers has attracted more and more interest and attention. New kinds of microdomain morphology have been reported in both the weak and the strong segregation limits.[1–4] The newly discovered ordered bicontinuous double-diamond (OBDD) morphology and the lamellar-catenoid (LC) structure have been found to possess intermaterial surfaces satisfying the mathematical condition called constant mean curvature (CMC). The geometry of such surfaces strongly influences the physical properties of the materials, which have been proposed as candidates for microstructural models in a variety of physical and biological systems.[1]

Equilibrium phase behavior of block copolymers is usually expressed in terms of the polymer composition f and the reduced parameter χN where χ is the Flory–Huggins interaction parameter and N refers to the overall degree of polymerization. A representative phase diagram based on polystyrene–polyisoprene (SI) diblock copolymers is presented in Figure 1;[5] a similar phase diagram has been found for other molecular architectures. It is interesting to note that the existence of the OBDD morphology has been demonstrated in star-block copolymers,[2] diblock copolymers,[3] and diblock[4] or triblock[6] copolymer/homopolymer blend over a relatively narrow composition. It was believed that the cylinder–lamellae transition occurred in this narrow region before the OBDD morphology was observed. A critical question may be raised: i.e., what kind of morphology exists in triblock copolymers over such a narrow composition? Is there any new kind of morphology existing in the region where the composition-induced sphere–cylinder or cylinder–OBDD transition takes place? In this paper, we report the observation of a new equilibrium microdomain morphology in the styrene–butadiene–styrene triblock copolymer containing 26.5 vol % of polystyrene by transmission electron microscopy and small-angle X-ray scattering technique.

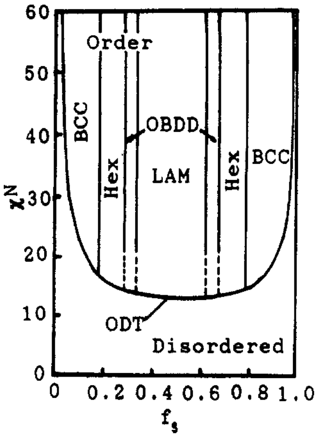

Figure 1. Phase diagram of polystyrene–polyisoprene (SI) diblock copolymers.[5] BCC: body-centered-cubic sphere. Hex: hexagonally packed cylinder. OBDD: ordered bicontinuous double-diamond morphology. LAM: lamellar. ODT: order–disorder transition.

The styrene–butadiene–styrene triblock copolymer used here is a commercial product of Aldrich Chemical Co. (Catalogue No. 20.045–9). It was further purified by multiple precipitation from a toluene solution into methanol. The copolymer contains 26.5 vol % of polystyrene as characterized by nuclear magnetic resonance (NMR). The number- and weight-average molecular weights are 63 000 and 70 000, respectively, as determined by gel permeation chromatography (GPC). The copolymer was first dissolved in toluene to form a 3 wt % solution. The solution was then poured through a glass filter into a PTFE dish, which was placed in a covered, temperature-controlled glass vessel on a horizontal bench, and allowed to evaporate slowly in a dry atmosphere at 30 °C until the solvent smell vanished (about 4 weeks). The film (ca. 1 mm) was further dried at 50 °C for 2 days in air and then in a vacuum oven at 80 °C for a week. A small-angle X-ray scattering (SAXS) experiment was performed with the Kratky compact small-angle system which was equipped with a stationary-anode copper-target X-ray tube (wavelength 1.54 Å). The measured intensity was corrected for background scattering and desmeared with the method proposed by Strobl.[7] A Hitachi H-500 electron microscope was used for the observation of microdomain morphology of ultrathin sections (ca. 50 nm) obtained with a LKB-4800 microtome at ca. −60 °C and stained with osmium tetroxide.

Electron microscopic examinations on sections cut perpendicular to the film surface reveal a complicated, yet highly ordered, two-phase morphology. Micrographs A and B of figure 2 show two symmetric projections of the structure. In the upper part of Figure 2A, the white spots, corresponding to the PS microdomains, are elliptic; the dark region, selectively stained by osmium tetroxide, is the PB matrix. It is clearly seen that the PS ellipses locate in the six corners of the hexagons and have 2*mm* symmetry about the center of the ellipsis white region, as marked in the figure. Obviously, the assembly pattern is not due to hexagonally packed cylinders projected in the direction perpendicular to the cylinder orientation as there are no polystyrene phases in the centers of the hexagons. In the bottom of Figure 2A, the micrograph exhibits a “double-chain” image, which is much clearer in Figure 2B. Each “chain” is composed of units of a double PS ellipsis with parallel axes. The units arrange in a line resembling the form of a double chain. However, the double chain is not continuous everywhere. The spacing between two double chains, l_1, is much larger than that (l_2) between the two ellipses in the double chain, as schematically shown in Figure 2C. The difference between l_1 and l_2 implies that the image is not a result of cutting through tilt cylinders. It is significant that the double-chain image also possesses 2*mm* symmetry about the center of two parallel ellipses. The different images shown in the upper part of parts A and B of Figure 2 could very possibly be due to the difference of the ultramicrotoming direction. Obviously, these patterns cannot be expected from the projections of the well-known body-centered-cubic spheres, alternate lamellae, or the bicontinuous double-diamond morphology in any direction and in any thick sections. Thus, we have no choice but to attribute it to a new equilibrium microdomain morphology.

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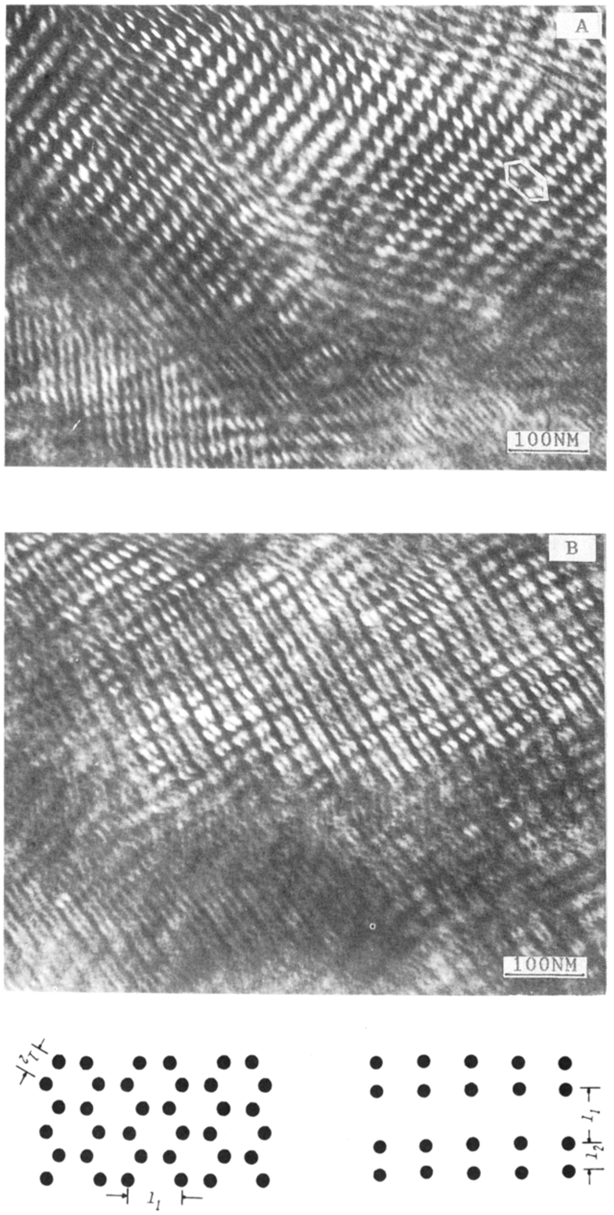

Figure 2. Transmission electron micrographs of an as-cast SBS specimen from a toluene solution. (A) Hexagonally seated ellipsis, 2*mm* symmetry. (B) Double-chain image, 2*mm* symmetry. (C) Schematic representations.

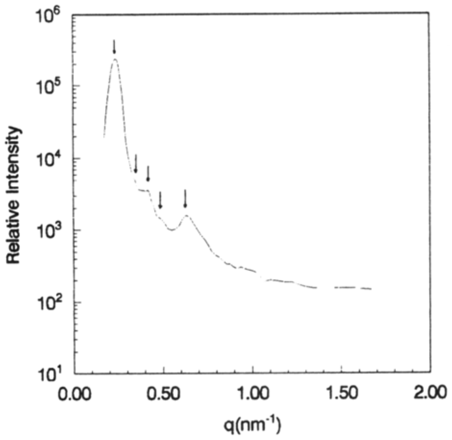

Figure 3. Small-angle X-ray scattering pattern for the observed structure.

Table 1. First Four Allowed Reflections and Their Relative Spacings for Various Structures

SC		BCC		FCC		OBDD		HEX		LAM	
hkl	d_n/d_1	*hkl*	d_n/d_1	*hkl*	d_n/d_1	*hkl*	d_n/d_1	*hk*	d_n/d_1	00*l*	d_n/d_1
100	1.00	110	1.00	111	1.00	110	1.00	10	1.00	001	1.00
110	0.71	200	0.71	200	0.87	111	0.82	11	0.58	002	0.50
111	0.58	211	0.58	220	0.61	200	0.71	20	0.50	003	0.33
200	0.50	220	0.50	311	0.52	211	0.58	21	0.38	004	0.25

The morphology images shown in Figure 2 limit the selection of the lattice structure for the new equilibrium microdomain morphology: (1) the structure unit is likely to be an ellipsoid. (2) The ellipsoids are not connected with each other. (3) The lattice belongs to a crystal system with point space group projection symmetry of 2*mm*, at least in two different types of lattice planes. Thus, the ways to assemble the ellipsoids in a three-dimensional lattice are reduced.

Small-angle X-ray scattering has been proved to be valuable in determining the crystal lattice of self-assembling structures in block copolymers.[2] The SAXS pattern from the SBS triblock copolymer is presented in Figure 3. The curve shows five distinct lattice peaks, being evidence of an extremely high degree of order for a block copolymer. The ratios of the *d* spacings for these peaks relative to the *d* spacing of the main interference peak are 1:0.61:0.56:0.49:0.37. The ratios of the *d* spacings of the first four allowed reflections for structures commonly found in block copolymer are given in Table 1. Obviously, the observed ratios match poorly with the predicted ratios for any documented morphologies in block copolymers, which implies that the observed morphology under TEM belongs to a new lattice structure.

Since the documented morphologies in block copolymers, such as cylinder, sphere, and the ordered bicontinuous double-diamond morphologies, belong to the cubic and hexagonal systems, respectively, it is recommended to assemble the ellipsoids in the point groups belonging to these two systems to produce images in various types of lattice planes and compare the resulting projected symmetry and pattern with those shown in Figure 2. However, a prerequisite is that the possible reflections of the point groups should be in agreement with those observed for the new microdomain morphology. Of the 36 cubic space groups listed in the *International Tables for X-ray Crystallography*,[8] not one contains reflections whose relative *d* spacings and relative peak intensities match with those observed for the new microdomain structure. Thus, the point group for the new microdomain morphology is likely to be one of the hexagonal space groups. Nevertheless, as the possible reflections of a hexagonal space group depend on the a/c ratio (a and c are the hexagonal indexes), there are too many possibilities for the first several reflections, even for a determined space group. It seems that the practical step at this time is to obtain the a/c ratio from the TEM micrographs. Unfortunately, the a/c ratio cannot be determined from the TEM images unless the space group for the structure is well-known.

There is another unsolved problem. It is well-known that an ellipsoid is unstable in energy, and it will evolve into a sphere at equilibrium. On account of this, the ellipsoid is obviously not a favorable unit. If the PS microdomains were spheres, one could not get the ellipsis pattern shown in parts A and B of Figure 2 in any sectioning direction, and the ellipsis PS microdomains are obviously not due to the deformation of spheres induced by a microtome considering the sectioning temperature and the different axis directions of the ellipses shown in the upper and lower parts of Figure 2A. Certainly, a rodlike object can product an ellipsis pattern when sectioned in a specific direction. Unfortunately, we still do not have any clear idea of how to assemble rodlike objects in a hexagonal lattice to produce images shown in Figure 2. A transmission electron microscope tilt series would be of great help to solve the problem and provide correlation of images and simulated projections from possible models, and maybe eventually to provide critical determinations of the observed new morphology. However, due to the present limitation of the experimental technique at our laboratory, systematic studies on this aspect have to be put off. Monte Carlo and molecular simulations of the observed structure are now in progress.

Someone might doubt whether the observed morphology is in equilibrium, because the annealing temperature used here is much lower than that used to obtain the OBDD morphology.[2,4] However, as the OBDD morphology (demonstrated to be an equilibrium morphology) has also been obtained under almost the same preparation conditions in styrene–isoprene (SI) diblock coplymers[3] and SBS/PVME blends[6] and as the glass transition temperature of the PS phase in SBS (T_g = 62 °C) is close to those in SI and in the blend (T_g = 33 °C for a SBS/PVMe blend containing 10 wt % PVME[9]), annealing at 80 °C is sufficient and cannot bring about any differences in achieving the equilibrium morphology between the systems. Furthermore, the annealing temperature has almost no effect on the microdomain morphology in triblock copolymers[10] due to the entanglements between blocks, which is in sharp contrast to the case of diblock copolymers. Thus, a critical step in this procedure is to keep the solution evaporating slowly. Under these considerations, the observed morphology was obtained at or very close to the equilibrium conditions.

It can be concluded that the TEM observations and SAXS analyses reveal a new equilibrium microdomain morphology in a SBS triblock copolymer containing 26.5 vol % polystyrene. They show different images and scattering patterns from those observed for the documented block copolymers, although the details of the morphology remain unknown. In a diblock copolymer of this composition, an OBDD or cyliner morphology is expected. As for the triblock copolymer, there is no report about the observation of OBDD morphology over the composition range $0.28 < f < 0.34$, yet. We suspect that the new morphology is a substitute of the OBDD structure existing only in triblock copolymers, or it is a new member to be added to the family of documented equilibrium ordered phases in both di- and triblock copolymers. As the observed morphology has been obtained near equilibrium conditions, the preferred interfacial curvature for this morphology is a pressing task. Detailed investigations of the new morphology are in progress.

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