The Ordered Bicontinuous Double-Diamond Morphology in Triblock Copolymer/Homopolymer Blends

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The ordered bicontinuous double-diamond (OBDD) morphology is an intricate and elegant morphology recently shown to exist in both linear and star diblock copolymers[1–3] and their blends with homopolymers.[4] It is demonstrated that the observed OBDD morphology in copolymer systems minimizes the free energy with respect to the preferred interfacial curvature, the interfacial area, and chain conformations for these systems. According to Thomas et al.,[3] the preferred interfacial curvature for OBDD structure is a classical Schwarz-D minimal surface. Both the minority and the majority components of the OBDD structure are periodic and continuous in all three dimensions. This structure leads to potential industrial uses as an ordered microcomposite. Applications may arise in the form of separation devices, membranes, and self-assembled composites. Furthermore, block copolymer systems with OBDD structures possess mechanical properties different from those exhibiting spherical, cylindrical, and lamellar structures.[5]

Researchers have observed the OBDD morphology over relatively narrow composition regimes. For example, the OBDD microstructure in linear styrene–isoprene (SI) diblock copolymers exists within the ranges of 62–66 vol % PS.[2] Such narrow composition ranges require precise control of the copolymer synthesis to obtain the proper composition which results in the OBDD morphology. This feature greatly limits the potential industrial use since the synthesis of such well-defined diblock copolymers in industry is rather difficult. To our knowledge, up to now, there are still no commercial products of pure diblock copolymers. Even the mechanical properties of blends composed of an A–B diblock copolymer and an A or B homopolymer (e.g., SI/PS blends) cannot be tailored to the extent that might be desired. On account of these limitations, model systems based on triblock copolymers and triblock copolymer/homopolymer blends, especially with chemically dissimilar homopolymers, were selected in the work to study their self-assembling processes and patterns. In this Communication, we present the first results from transmission electron microscopy studies of the OBDD structures in linear triblock copolymer/homopolymer blends composed of a styrene–butadiene–styrene (SBS) triblock copolymer and poly(vinyl methyl ether) (PVME).

The polystyrene and poly(vinyl methyl ether) blends are of great importance and have been well studied.[6,7] As for the polystyrene–polybutadiene–polystyrene and poly(vinyl methyl ether) blends, due to the introduction of the polybutadiene block, the phase behavior of the blends would be greatly different from that of the PS/PVME blends. However, only a few studies on the miscibility and phase diagram as well as on the effects of PVME on concentration fluctuation in the single-phase state, on the microphase transition, and on the size, morphology, and long-range order of the ordered microdomains as well as on micelle formation have been carried out.[8,9] The first results on the self-assembly and patterns in binary mixtures of styrene–isoprene diblock copolymer and poly(2,6-dimethylphenylene oxide) have recently been reported.[10]

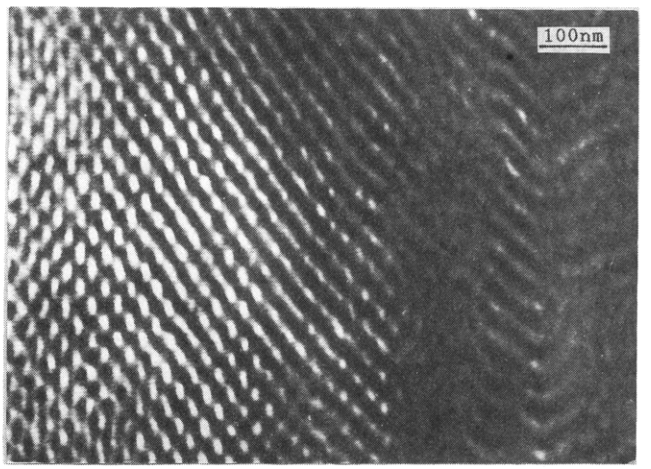

Figure 1. Transmission electron micrograph of an ultrathin section of neat SBS film cast from toluene solution. The section was stained with osmium tetraoxide.

The triblock copolymer SBS used here is a commercial product of Aldrich Chemical Co., consisting of 28 wt % PS with number- and weight-average molecular weights of 52 000 and 70 000, respectively, evaluated by GPC. Poly(vinyl methyl ether) (PVME) is a commercial product of Polysciences Inc.; GPC results show that it has number- and weight-average molecular weights of 37 000 and 63 000, respectively. Blends of SBS/PVME at a desired composition were first dissolved in toluene to form a 3 wt % solution. Films were prepared by casting the solutions in PTFE dishes and slowly evaporating off the solvent over the course of 1 week at room temperature. The film specimens thus prepared were further dried in a vacuum oven at room temperature until a constant weight was attained. The samples were then ultramicrotomed into ultrathin sections ca. 50 nm thick at ca. −60 °C. The sections were then subjected to staining by osmium tetraoxide vapor on a microscope grid before the transmission electron microscope (TEM) investigation (Hitachi H-500 electron microscope operated at 100 kV).

Figure 1 shows an electron micrograph of an ultrathin section of a neat SBS film cast from toluene solution. The dark regions correspond to polybutadiene (PB) microdomains selectively stained with osmium tetraoxide, while the bright regions correspond to the unstained polystyrene (PS) microdomains. The pattern resembles hexagonally packed PS cylinders in a PB matrix. A detailed description of the morphology of this block copolymer will be presented elsewhere.[11]

Figure 2 shows the coexistence of a kind of almost disordered morphology (left bottom corner) and the modified lamellae of a SBS/PVME blend at 5 wt % PVME, with an overall total volume fraction of the hard phase (PVME and PS mixed together) of ca. 30%. The butadiene-rich "lamellae" exhibit a relatively invariant optical density under the conditions presented here, while the polystyrene microdomains appear to be with regularly spaced catenoidal connectors. The modified lamellae in this micrograph were first observed in styrene–isoprene diblock copolymers by Thomas.[3] Recently, this morphology was observed in styrene–isoprene diblock copolymer/polystyrene homopolymer blends at near-equilibrium conditions with an overall total volume fraction of polystyrene of ca. 66%.[12]

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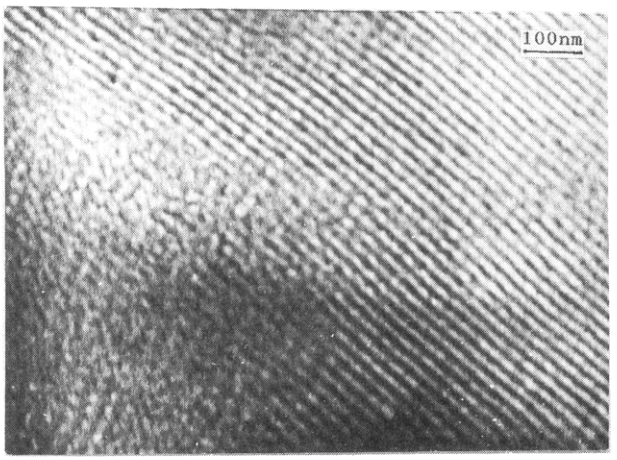

Figure 2. Transmission electron micrograph of the binary blend 5 wt % PVME and SBS which exhibits the coexistence of a kind of disordered morphology (left) and the modified lamellae (right).

Figure 3 shows electron micrographs of SBS/PVME blend films at 10, 12, and 15 wt % PVME. Figure 3a shows a blend of 10 wt % PVME, exhibiting the ordered bicontinuous double-diamond morphology projected along the [100] direction and resembling a square lattice pattern characteristic of a cubic cell.[2] PVME is fully solubilized in the triblock copolymer, as evidenced by the absence of separate domains of pure PVME appearing in the micrographs. The blend self-assembles from the initial homogeneous solution into the OBDD morphology rather than the cylindrical morphology of the neat triblock copolymer. Figure 3b, the micrograph for the SBS/PVME blend with 12 wt % PVME, shows a "wagon-wheel" image with a hexagonal symmetry. Each hexagonal cell in Figure 3b contains a single tetrapod unit, with three arms of the tetrapod reaching every other corner of the hexagon. The other three corners of the hexagon and the center of the tetrapod appear as white spots, which indicate that the rodlike arms pointing normal to the section surface are attached to them. The homopolymer PVME and the PS blocks of the copolymer mix together in the channels of the OBDD microstructure, while the PB blocks of the copolymer occupy the matrix region. The "wagon-wheel" projection in Figure 3b, also known as the [111] projection, is the unique signature of the OBDD morphology since no other known morphology in block copolymer systems exhibits such a TEM projection. Figure 3c, the micrograph for a SBS/PVME blend with 15 wt % PVME, also shows the OBDD "wagon-wheel" image with hexagonal symmetry. Apart from the size of the tetrapod unit, which is much larger than that in Figure 3b, the essence of the structure is the same as that in the blend containing 12 wt % PVME.

It is of interest to note that the polydispersities of the triblock copolymer and the homopolymer used here are both high (1.33 and 1.70, respectively). Yet, the OBDD morphology is produced in these blends. It seems that monodisperse materials are not a precondition in making the OBDD morphology. Furthermore, as demonstrated by Winey et al.,[4] the molecular weight of added polystyrene homopolymer (M_{hPS}) is another prime consideration in producing the OBDD morphology, as M_{hPS} must be less than M_S, the styrene block length of the copolymer. They report finding this microstructure in blends in which the ratios of M_{hPS} to M_S are ca. 0.2 and 0.5 only when the overall composition lies within the range 65–67 vol % styrene. However, the ratio of M_{hPVME} to M_S is as high as 6.0, while the OBDD morphology is generated in such blends. The difference may arise from the interaction between the PS segments and the PVME homopolymers.[9] Last, the composition regime which favors formation of the OBDD morphology in triblock copolymer/homopolymer blends with the OBDD morphology is much larger than those for the diblock copolymer/homopolymer blends.[4] The SBS/PVME blends investigated here exhibit the OBDD microstructure over the composition range of 33–37 vol % total hard phase (PS + PVME). Thus, it is much easier to generate the OBDD morphology in this kind of system since the restrictions are relatively flexible compared with the other systems. On account of these, the block copolymer system used here does appear to possess desirable advantages.

To the best of our knowledge, this is the first time that the OBDD microstructure has been generated in block copolymer/homopolymer blends when the total hard phase volume fraction has been ca. 30%.[4] Multiple attempts to prepare a polydiene-rich OBDD morphology in blends

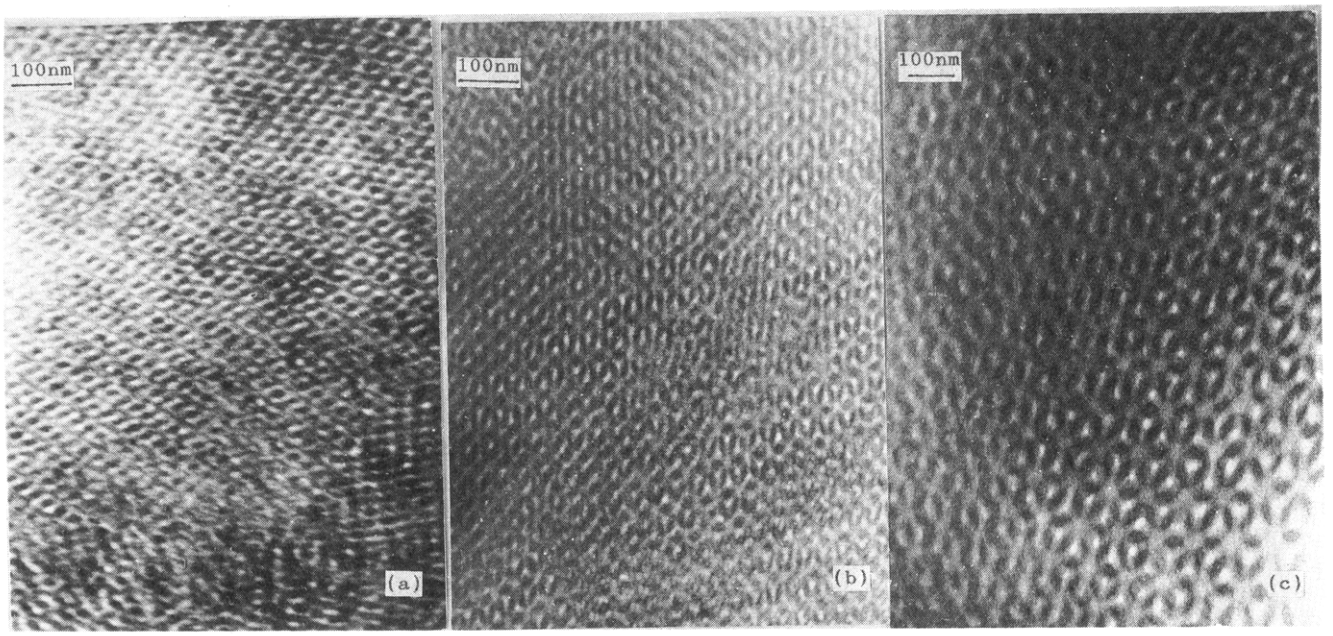

Figure 3. Transmission electron micrographs showing the homopolymer concentration dependence of the morphology in blends of PVME and SBS: (a) 10 wt %, OBDD ([100] projection); (b) 12 wt %, OBDD ([111] projection); (c) 15 wt %, OBDD ([111] projection).

composed of a styrene–isoprene (SI) diblock copolymer and PS have failed as reported by Thomas et al.[4] This is also the first time that the OBDD morphology based on a triblock copolymer has been successfully produced. Detailed results on this aspect will be reported soon.

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