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Catenoid–Lamellar Phase in Blends of Styrene–Butadiene Diblock Copolymer and Homopolymer

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Diblock copolymers show a menagerie of morphologies[1] as a function of the relative lengths of the blocks and the temperature (or the magnitude of χN, where χ is the Flory interaction parameter and N the degree of polymerization). These structures range from spheres to hexagonally ordered cylinders and lamellae, corresponding to decreasing mean curvature of the interphase boundary. More recently[2] a three-dimensionally ordered structure called the ordered bicontinuous double diamond (OBDD) phase is found at styrene compositions ϕ_s between 0.62 and 0.66 for polystyrene-*b*-polyisoprene diblock copolymers. When a homopolymer is mixed with a diblock copolymer, the occurrence of macrophase separation adds a new dimension to the possible morphological variations that can be realized, and the phase diagrams of such blends exhibit fascinating complexities.[3,4] Even when the amount of added homopolymer is below its solubility limits so that a single macroscopic phase is realized, a range of structure, similar to that observed with block copolymer alone, is exhibited as the amount of the added homopolymer is varied.[5] Transitions between the various ordered structures have been described theoretically in terms of energy-minimizing constant mean curvature surfaces.[6] The dependence of these transitions on molecular weight is not fully understood, but observations have led to a generalization that the OBDD morphology occurs when the ratio of the homopolymer molecular weight to the molecular weight of the like component of the copolymer is less than 1.[7] The additional complexity resulting from the variation of the amount and molecular weight of the added homopolymer provides a means to tailor new morphologies that have enhanced strength or diffusion properties.

We report our initial observations of a new morphology in a blend of a symmetrical (lamellar) styrene–butadiene diblock copolymer and a styrene homopolymer, in which the two blocks and the homopolymer all have approximately the same molecular weight of 25 000. We associate this new morphology to the catenoid–lamellar (CL) structure recently discussed in the literature.[6,8,9] The CL phase contains lamellae where the layers of component A are penetrated by channels of component B, and the shape of the interphase dividing-surface resembles a minimal surface based on revolution of a catenary about the central axis of the channel. A related structure has been observed in sodium dodecyl sulfate lipids[10] and assigned a three-dimensional rhombohedral space group. To the best of our knowledge, the morphological measurements presented here give the first detailed picture of the CL structure for a diblock copolymer plus homopolymer system.

Table I. Weight Fraction of Homopolymer Polystyrene, Total Styrene Volume Fraction, "Lamellar" Spacing (d) from SAXS, and the Topological Structure from TEM and SAXS

wt % hPS	ϕ_s	d (nm)	structure
30	0.62	46.7	lamellae
35	0.65	49.4	lamellae + catenoid–lamellae
40	0.67	53.5	catenoid–lamellae
52	0.74		disordered struts

The microstructure of these blends of poly(styrene-*b*-butadiene) (SB) with varying amounts of polystyrene homopolymer (hPS) has been examined by means of small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). The styrene–butadiene diblock copolymer is the same material used in our previous study.[11] It was kindly synthesized by Dr. H. Tung of the Dow Chemical Co. with a weight-average molecular weight of 49 800 (with the ratio M_w/M_n equal to 1.04) and 51.1% styrene, making the styrene block molecular weight 25 500 and the butadiene block molecular weight 24 400. The polystyrene of weight-average molecular weight 26 000 was synthesized by anionic polymerization at the University of Cincinnati. The blends were prepared from a toluene solution from which the solvent was evaporated at ambient conditions for 3 days. The toluene was then evaporated thoroughly at room temperature in a vacuum oven for 2 days. Finally the samples were annealed for 2 days at 130 °C under vacuum. This annealing temperature is well below the microphase-separation temperature for these polymers, as estimated from the known values of χ for polystyrene–butadiene systems. Work is in progress to check for variations in the CL structure that might accompany longer annealing times. Small-angle X-ray scattering experiments were performed on Beam line X10A at the National Synchrotron Light Source, Brookhaven National Laboratory. Using a Bonse-Hart type setup,[12] we were able to obtain SAXS intensities from these samples down to a momentum transfer q of about 0.002 Å^{-1}. For transmission electron microscopy, thin sections of the blends were prepared by shaping the as-cast films, staining the planar region of the shaped surface with OsO_4 vapors from a 4 wt % aqueous solution for 2 h, and then making final cuts of the stained sample at −90 °C. Images were obtained with a 100-kV accelerating voltage in a Philips EM420ST transmission electron microscope under bright-field imaging conditions with an objective aperture cutoff of ~2.0 nm^{-1}.

Although we prepared and studied blends that contain polystyrene from 0 to 100% by weight, only results obtained with the blends listed in Table I, having compositions close to the CL phase composition, are reported here. We note that this brackets the region of styrene volume fraction (ϕ_s range 0.65–0.67) where Winey et al.[13] observed the OBDD structure in blends of diblock

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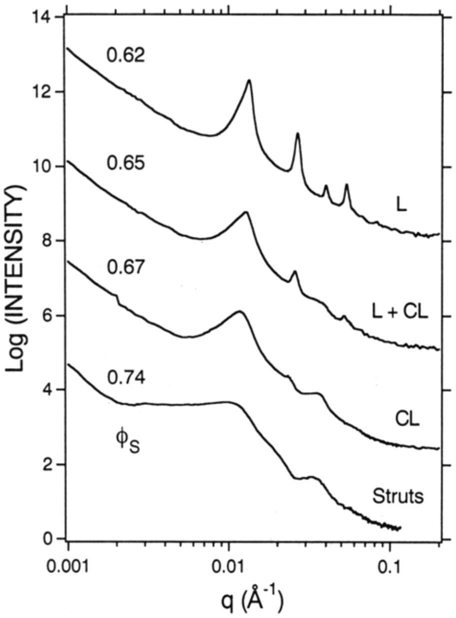

Figure 1. SAXS scattering intensities obtained with blends containing 30, 35, 40, and 52% hPS corresponding to total styrene volume fractions ϕ_s of 0.62, 0.65, 0.67, and 0.74, respectively.

copolymer and homopolymer. Figure 1 shows the background-corrected SAXS intensities obtained from the four samples studied. The SAXS patterns reveal diffraction peaks on top of a diffuse scattering that monotonically decreases in intensity with increasing q. The diffuse intensity follows an approximate power law relation with the exponent in the vicinity of -2.2 in a q range of 0.05 Å^{-1} and smaller. Such a diffuse scattering component is usually observed even with block copolymer samples containing no homopolymers. The cause for the diffuse scattering is not well understood but is believed to be associated with the presence of inhomogeneity due to mosaic assembly of coherent microdomains. At 30 wt % hPS ($\phi_s = 0.62$) the four peaks are clearly the first to fourth order harmonics due to a lamellar structure with periodicity equal to 46.7 nm. This corresponds to 23% swelling of the lamellae compared with pure diblock copolymer for which the periodicity is equal to 37.9 nm. At 40 wt % hPS the SAXS pattern has undergone a qualitative change, indicating that the lamellar structure no longer persists, and a new diffuse peak at $q \approx 0.0373$ Å^{-1} has become prominent. At 52 wt % hPS ($\phi_s = 0.74$) the lamellar peaks are essentially gone. Since these patterns are quite diffuse and the associated structures cannot be determined uniquely from these patterns, further examination was carried out with TEM.

Transmission electron micrographs confirm the presence of lamellae up to 30 wt % hPS ($\phi_s = 0.62$). At 52 wt % hPS ($\phi_s = 0.74$) a three-dimensional structure of interconnected butadiene "struts" forms a network morphology similar to that reported recently by Hashimoto et al.[14] The most significant finding with TEM is the presence of the CL structure at 40 wt % hPS ($\phi_s = 0.67$). Observations that we describe below show two projections of the CL morphology, confirming our model that the two views are different orientations of the same three-dimensionally ordered phase. The CL phase is also present for 35 wt % hPS ($\phi_s = 0.65$) mixed with regions of uniform lamellae. Morphologies at compositions other than the CL value ($\phi_s = 0.67$) will be discussed in more detail in a later paper. We will focus here on the 40 wt % hPS ($\phi_s = 0.67$) structure.

Figure 2 shows TEM images of thin sections where the incident electron beam is nearly parallel to the CL phase lamellae (Figure 2a) or normal to the CL layers (Figure 2b). In the edge-on view in Figure 2a, the catenoidal PS-rich channels are nearly aligned with the viewing direction, and thus the modulation in the stain contrast of the PB layers is pronounced. The light regions within the PB layers represent regions where, upon projecting through the sample, there is significant unstained PS present. In regions where the dark PB ovals are most distinct, an hourglass-like shape is clearly visible. While this shape resembles what is expected for the CL phase viewed in projection, it has not yet been confirmed quantitatively whether the shape truly agrees with a catenoidal model. In regions where the layers are normal to the incident electron beam, a clear view of polystyrene-rich channels in the butadiene layers is evident (Figure 2b). Observation of this structure was made possible by the attainment of extremely thin cryosections. Since numerous regions with only one layer in the beam direction were present and a single layer is ~40 nm thick, we estimate the thickness of the cuts is less than 60 nm.

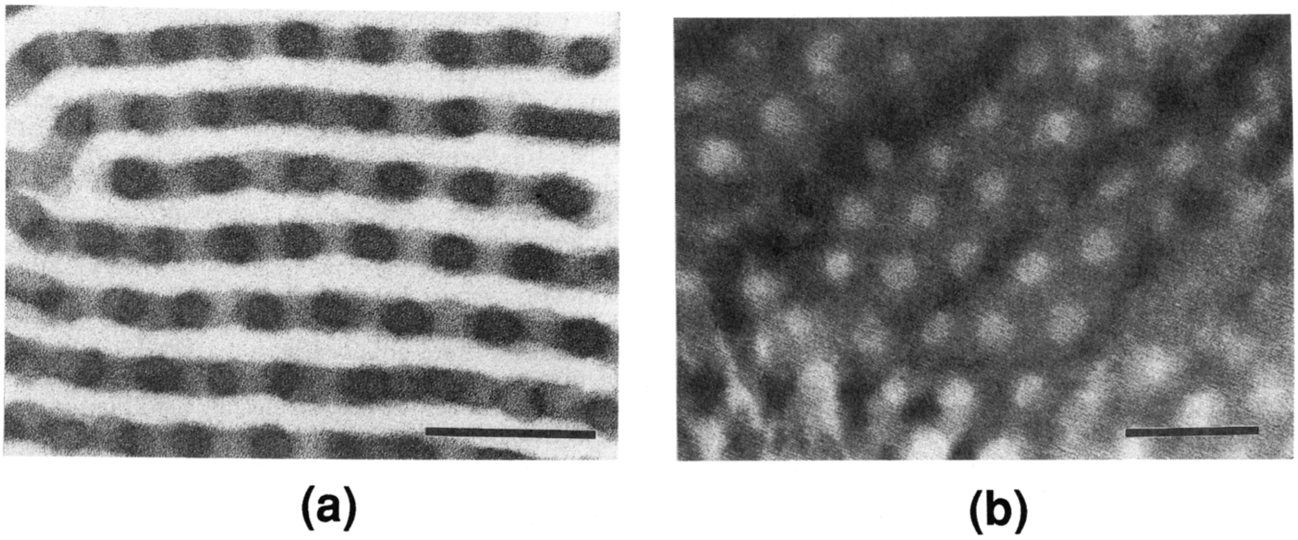

Figure 2. Transmission electron micrographs of an OsO$_4$-stained sample prepared from a blend ($\phi_s = 0.67$) of hPS and a nearly symmetric SB diblock for an edge-on view that is parallel to the lamellae (a) and a view normal to the lamellae of a thin section parallel to the layers (b). The shapes of punctured butadiene layers suggest a catenoidal shape for the PS (unstained) regions that penetrate the butadiene layers. Scale markers are 100 nm.

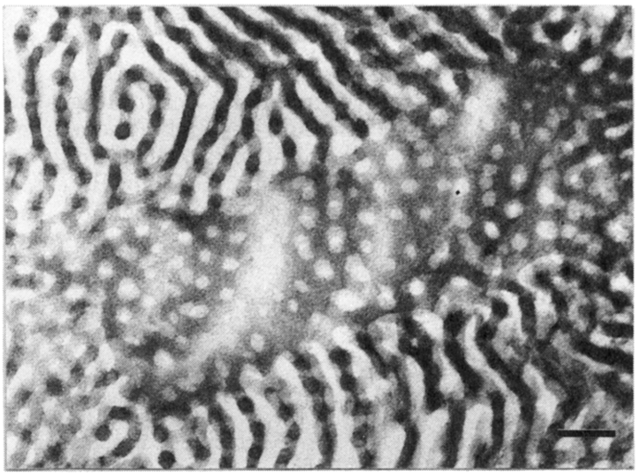

Figure 3. Layers of butadiene punctured by polystyrene channels visible in both edge-on and normal to lamellar sheet orientations in a region where the lamellae undergo a change in orientation. The marker is 100 nm.

A structure made up of lamellae punctured by catenoidal channels can have zero mean curvature defined by $H = (c_1 + c_2)/2$, where c_1 and c_2 are the principal curvatures evaluated at any point on the CL minimal surface. The interphase surface for the CL structure appears to have $H \approx 0$ and thus has nearly the same mean curvature as uniform lamellae. The OBDD structure ($H > 0$) was observed for an SB diblock plus hPS blend for ϕ_s between 0.65 and 0.67.[13] It is surprising that we observe the CL phase with nearly the same ϕ_s. It is possible that the difference arose because in this study the blocks and homopolymer are all of the same molecular weight.

Lower magnification views of this phase show a complex morphology due to the presence of multiple orientations of the punctured lamellae, with edge-on, normal to lamellae, and intermediate orientations all visible (Figure 3). The lamellar spacing apparently widens near boundaries where lamellae normal to the incident beam make an orientation change approaching 90°, or where the CL layers are only a few times as long as the lamellar spacing.

Figure 4 shows schematics of oblique perspective (a) and nearly edge-on plan views (b) of the proposed structure. Layer to layer ordering of the projection of catenoidal channels in the edge-on views indicates a staggered arrangement of channels in alternate layers. An ABAB... type packing is suggested in Figure 4, analogous to hexagonal close-packing. An ABCABC... stacking sequence analogous to face-centered-cubic packing is also consistent with the edge-on observations. Several sheet-normal views from thicker regions have shown two sets of PS channels pass over each other as the sample tilt was varied over ±30°. The curved surfaces of the sheets, and limit of two layers viewed in projection, have made it difficult to conclusively determine the stacking sequence. Tilting experiments with regions that were initially near the edge-on orientation show transformations to nearly sheet-normal views, consistent with the structure depicted in Figure 4.

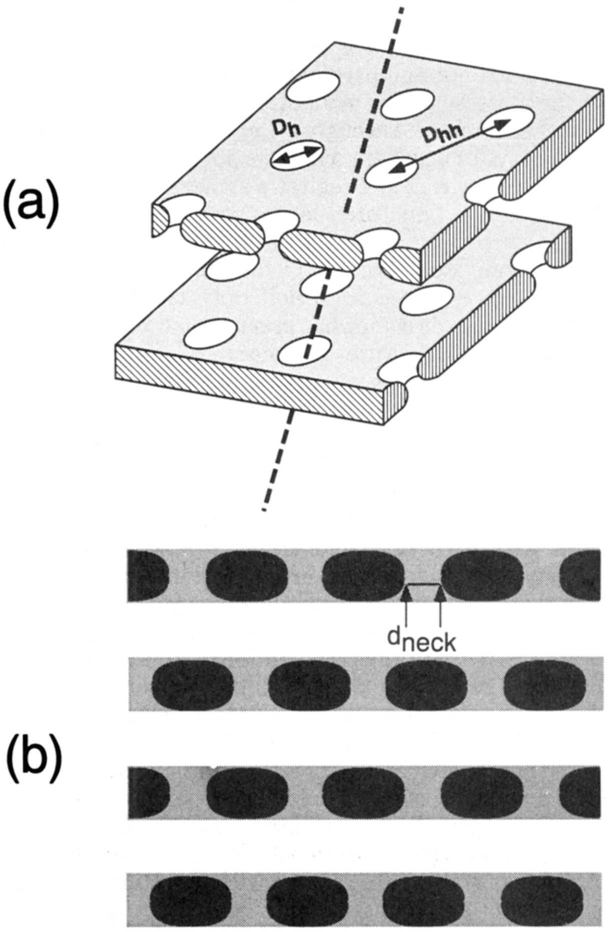

Figure 4. Model for catenoid–lamellar structure showing a possible packing of channels in successive layers in an oblique perspective view (a) and a rendering of the structure observed in an edge-on view (b). TEM images similar to Figure 4b allow stacking sequences where the channels in successive layers are staggered, though the detailed stacking sequence cannot be specified.

Measurements from the edge-on and sheet-normal TEM views illustrated in Figure 4 help explain the features in the SAXS patterns. The interchannel spacing from the sheet-normal view $D_{hh} \sim 50$ nm agrees fairly well with the *d* spacing 53.5 nm obtained from the lowest order peak in the SAXS pattern of the CL phase in Figure 1. Both the apparent channel diameter, D_h, in the normal view and the narrowest width of the PS channels in the edge-on view, d_{neck}, are approximately 20 nm. From the uniformly spaced lamellar regions in the micrographs we estimate the lamellar periodicity L to be 36 nm, which suggests that the styrene layer thickness l_s should be equal to $L\phi_s = 24$ nm if all the styrene components are actually confined to the styrene layer. From the micrographs we obtain an approximate l_s of 17 nm, with the deviation from the above-estimated value 24 nm due to diversion of some of the styrene volume to fill the catenoidal channels. The first-order SAXS peak is relatively broad for the CL structure because of contributions from the one-dimensional lamellar spacing, as well as three-dimensional in-plane and interplane channel correlations that are not resolved. We note in passing that inclined views in TEM imaging of thin sections can give artificially high values for the lamellar spacing L but not smaller values.

Our TEM and SAXS observations show a three-dimensional structure that is lamellar to first order but is modified by channels in the butadiene layers that are apparently catenoidal in shape. Styrene-rich channels in this CL structure are approximately hexagonally ordered *within* the butadiene layers and staggered *between* successive butadiene layers. We note that a related structure in which catenoidal channels perforate both the A and B layers was described previously[6] for neat diblock copolymers. More recently, the result of neutron scattering performed on a neat deuterated diblock of poly(ethylenepropylene-*b*-ethylethylene) prepared under shear was interpreted by assuming the existence of perforations in only one of the layers.[9] A theoretical study by Fredrickson[8] examines the stability of such a CL phase in the strong segregation limit and predicts that the CL morphology is not the most favorable structure. Olvera de la Cruz and co-workers[15] show, through a Landau expansion of the free energy for a system with components A and B, that in the weak segregation regime a structure similar to the CL phase with punctured layers occurs for ϕ_A near 0.5. This is surprising since lamellae are expected at this composition. Furthermore, Olvera de la Cruz et al. find stability for a phase in which only the B layers are perforated if ϕ_A is somewhat greater than 0.5. However, this predicted structure has channels of component A aligned between successive layers, not staggered between layers as we observe here. No experimental observation or theoretical prediction has been offered so far for the existence or stability of a CL structure in a blend of diblock copolymer and homopolymer.

The results we present here offer initial evidence that such a CL phase with A channels in B layers (no B channels in A) exists in a blend. Several questions still remain to be answered about this new morphology. The structure needs to be determined more quantitatively and precisely. We speculate that the concentration of hPS is likely to be high near the opening of the CL perforations where the distance from the nearest SB junction is highest. Neutron scattering experiments with samples that contain deuterated homopolymer may provide additional information about any segregation of the homopolymer. The conditions which favor the formation of this phase are at present not well understood. Specifically, is the catenoid-lamellar morphology stable for mixtures with the same molecular weight ratios and higher or lower molecular weights? We plan to continue along these lines of analysis.

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