polymer communication

Morphologies of diblock copolymer / homopolymer blends near the order–disorder transition

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The morphologies of three low-molecular-weight poly(styrene-*b*-isoprene) diblock copolymers and their blends with homopolystyrene (hPS) at 66 vol% styrene have been investigated. Addition of hPS to one copolymer produces lamellar-catenoid or double-diamond morphologies, depending on hPS chain length. In another blend, microstructural disorder arises.

(Keywords: block copolymer; microphase separation; order–disorder transition; copolymer/homopolymer blends; lamellar catenoid; ordered bicontinuous double diamond)

A diblock copolymer consists of a contiguous sequence of one monomer species covalently bonded to a contiguous sequence of another. Materials of this type microphase-separate under conditions of sufficient chemical incompatibility (χN) and molecular composition (ϕ_i), where χ is the Flory–Huggins interaction parameter (which scales as the reciprocal of absolute temperature, T), N is the number of statistical segments (monomers) per molecule, and ϕ_i is the volume fraction of block i. Leibler[1] employed a mean-field formalism to predict that, in the limit of infinite N, the order–disorder transition (ODT) for symmetric diblock copolymers is a second-order phase transition occurring at $\chi N \approx 10.5$. Fredrickson and Helfand[2] considered the effect of critical fluctuations on the ODT for symmetric copolymers of finite N and found that such fluctuations induce a weak first-order phase transition at

$$\chi N \approx 10.5 + \Lambda N^{-1/3} \qquad (1)$$

where Λ is the coefficient of the fluctuation correction and is equal to approximately $41.0(\bar{b}^6 \rho_m^2)^{-1/3}$, where $\bar{b}$ is the average monomer statistical length and ρ_m is the monomer number density. For a 50/50 (w/w) poly(styrene-*b*-isoprene) copolymer, $\bar{b} \approx 0.61$ nm and, assuming incompressibility, $\Lambda \approx 30.4$. Density fluctuations are responsible for anomalous rheological behaviour just above the ODT at finite N (ref. 3), but become vanishingly small as $N \rightarrow \infty$, where predictions from both formalisms converge.

Within the strong-segregation regime ($\chi N \gg 10$), repulsive forces between the chemically dissimilar blocks dominate, and a diblock copolymer undergoes self-organization into any one of several ordered morphologies. Highly asymmetric molecules exhibit spheres (arranged on a body-centred cubic lattice) or cylinders (arranged on a hexagonal lattice) of one block dispersed in a continuous matrix of the other. Alternating lamellar morphologies are representative of symmetric copolymers, and an ordered bicontinuous double-diamond (DD) morphology has been observed[4] to exist between the cylindrical and lamellar morphologies. Theoretical formalisms[1,2] addressing the weak-segregation regime (in close proximity to the ODT) predict that one or more ordered morphologies may coexist at constant ϕ_i between the ODT and the strongly segregated morphology. This predicted behaviour suggests that multiple morphologies and order–order transitions should be observed near the ODT as T is increased (and χ is decreased). Transitions of this nature, along with a modified lamellar morphology (inferred from scattering data), have recently been reported by Almdal *et al.*[5] for a poly(ethylenepropylene-*b*-ethylethylene) (PEP–PEE) diblock copolymer. Non-classical morphologies, such as the lamellar catenoid (LC), are predicted[6,7] to be stable near the ODT.

The previous discussion has been devoted to pure diblock copolymers. Winey *et al.*[8–10] have shown that, within the strong-segregation limit, analogous morphologies are produced in binary blends of a diblock copolymer and one of the parent homopolymers. These blend morphologies can be accurately tailored on a molecular level by controlling the spatial distribution of homopolymer within its preferred microdomain. An added homopolymer of relatively high molecular weight, if solubilized within a given microstructure, will localize at the centre of the microdomain in which it resides, pushing the interphase regions further apart but having little effect on their curvature. A homopolymer of lower molecular weight will be more uniformly distributed within its microdomain and will increase the interphase volume occupied per copolymer junction and, consequently, the curvature of the interphase.

The copolymer/homopolymer blends studied by Winey *et al.*[8–10], as well as some investigated by us[11], have relied upon strongly segregated copolymers. As far as we are aware, few efforts[12,13] have addressed the microstructural characteristics of binary blends within close proximity to the ODT. The objective of the present work is to identify, with transmission electron microscopy (TEM), the morphologies which develop in a series of blends, each composed of a diblock copolymer of relatively low χN and a low-molecular-weight parent homopolymer, along the isopleth corresponding to 66 vol% styrene.

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The three copolymers employed in this study were symmetric poly(styrene-*b*-isoprene) (SI) diblock copolymers synthesized via anionic polymerization and possessing blocks of equal mass: 15000, 10000 and 5000 daltons. Two polystyrene homopolymers (hPS) of 6500 and 3000 daltons were also synthesized. All of these materials were effectively monomolecular ($M_w/M_n < 1.05$) and, for brevity, they are designated as either SI*M* or hPS*M*, where *M* denotes the total molecular weight rounded to one significant figure and multiplied by 10^{-3}. In the blends studied here, hPS was presumed to be completely solubilized within the styrenic microdomains, since $0.20 \leqslant N_{\mathrm{hPS}}/N_{\mathrm{S}} \leqslant 0.43$, where the subscripts hPS and S refer to the homopolystyrene and the styrene block of the copolymer, respectively.

Thin films ($\sim$3 mm thick) of the SI copolymers and SI/hPS blends were obtained from 5% (w/v) solutions in reagent-grade toluene. The concentration of styrene in each blend was held constant at 66 vol%, which is known[8–11] to produce the DD morphology in strongly segregated SI/hPS blends. Films were dried slowly over 3 weeks and heated to 90°C under low vacuum to remove residual solvent. They were subsequently encapsulated in glass tubes, exposed to high vacuum ($\sim$1.33 mPa), cycled between vacuum and Ar, and sealed in an Ar atmosphere before being annealed at 165°C for 1 week. No signs of gross oxidative degradation were observed. Electron-transparent sections were obtained by ultramicrotoming normal to the film surface at -100°C. To avoid complications arising from surface effects (e.g. preferential hPS segregation[14,15]), sections 50–70 nm thick were obtained only from the centre of each bulk film. These sections were stained with OsO_4 vapour from a 2% aqueous solution and examined on a Zeiss EM902 transmission electron microscope, operated at 80 keV and $\Delta E = 50 \pm 30$ eV.

Figure 1 consists of a pair of electron micrographs revealing the morphologies of two of the SI copolymers: SI20 (*Figure 1a*) and SI10 (*Figure 1b*). Both SI20 and SI30 (not shown) are microphase-separated and exhibit alternating lamellae, which is expected for these symmetric block copolymers. *Figure 1b* reveals that SI10 does not possess an ordered microstructure, due presumably to its low χN. A qualitatively similar trend of microdomain organization has been reported previously[16] for a series of nearly symmetric SI diblock and SIS triblock copolymers with varying molecular weight. Morphologies resembling *Figure 1b* in particular have been observed in a low-*N* SIS copolymer[16] and in an SIS copolymer rapidly quenched from its high-*T* disordered state[17]. Since $\chi = A + B/T$, where $A \approx -0.0857$ and $B \approx 71.4$ for S–I monomer interactions[18], χN can be estimated for each of these copolymers at any given *T*.

The temperature above ambient at which molecular motion within an SI copolymer melt decreases dramatically and microstructure becomes frozen-in is the glass transition temperature (T_g) of the styrene block. The relationship between T_g and N_S is provided by the Fox–Flory[19] equation when $N_S > 100$. For shorter chain lengths ($N_S \geqslant 20$), Lu and Jiang[20] have derived the following expression:

$$T_g = \frac{2N_S T_g^{\infty}}{2N_S + C_{\infty} f(y)} \qquad (2)$$

where $T_g^{\infty} = 373.15$ K and $C_{\infty} = 10.68$ for hPS. The function $f(y)$, obtained from the worm-like chain model, is given by

$$f(y) = 1 - 3y + 6y^2 - 6y^3(1 - e^{-1/y}) \qquad (3)$$

For a vinyl polymer chain, $y = C_{\infty}/[4N_S \sin^2(\theta/2)]$, where θ is the angle formed by the single C–C bonds along the backbone (109.5°). Neglecting interphase mixing, values of $\chi(T_g)N$ calculated from equations (2) and (3) for the three SI copolymers investigated here are 41, 28 and 15 for SI30, SI20 and SI10, respectively. Equation (1) is rigorously correct only when $N > 10^6$, but is nonetheless employed to estimate[21] χN at the ODT, inclusive of critical fluctuations[2], for each copolymer: 15 (SI30), 15 (SI20) and 17 (SI10). Comparison of these χN with the $\chi(T_g)N$ from above indicates that both SI20 and SI30 are safely removed from the ODT, whereas SI10 possesses a χN below that of the predicted ODT, which explains why this copolymer appears to lack long-range structure (*Figure 1b*). Critical fluctuations near the ODT must therefore be considered to explain the phase-mixed morphology seen in the SI10 copolymer (for related phenomena see ref. 22). Since addition of hPS to SI10 will only serve to decrease χN further into the disordered regime, no SI10/hPS blends are presented.

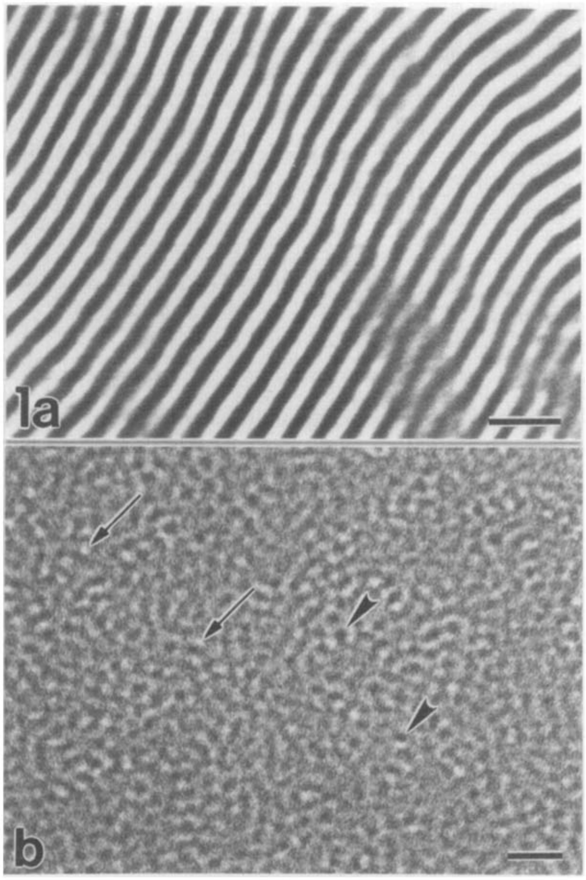

Figure 1 Energy-filtered TEM micrographs of the symmetric SI diblock copolymers SI20 (a) and SI10 (b). SI20 and SI30 (not shown here) are microphase-separated at the T_g of the styrene block and exhibit alternating lamellar morphologies. SI10 possesses a $\chi N \approx 15$ at $T_g \approx 70$°C and remains phase-mixed. Discrete isoprene microphases, such as those in (a), appear dark due to selective OsO_4 staining, whereas phase-mixed morphologies (b) consist of both styrene and isoprene and appear grey. [Photographic contrast is identical for (a) and (b).] Styrene- and isoprene-rich micelles (arrows and arrowheads, respectively), measuring about 8 nm in diameter, are observed to coexist in (b). Bars = 50 nm

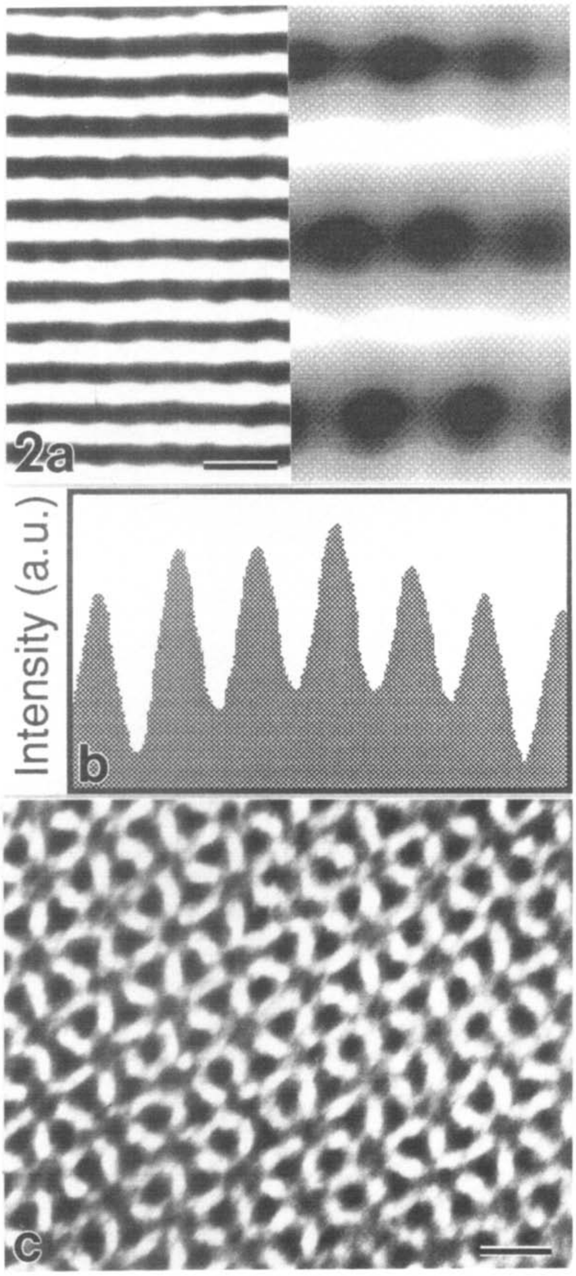

Figure 2 Series of micrographs obtained from SI/hPS blends composed of SI30 and hPS at 66 vol% styrene. The blend in (a) consists of hPS7 and exhibits a modified lamellar, or lamellar-catenoid, morphology. An enlargement processed with two-dimensional Fourier filtering is also shown to clarify the connective catenoids. A trace through an isoprene-rich 'lamella' is provided in (b) to demonstrate the catenoid periodicity. If N_{hPS} is reduced by employing hPS3 in the blend, an ordered bicontinuous double-diamond morphology is produced, as seen along the [1 1 1] axis in (c). Bars = 50 nm

The morphologies observed in blends containing SI30 depend on N_{hPS} and are provided in *Figure 2.* This copolymer is similar in composition and molecular weight to the copolymer (denoted HY8) employed in the blends studied by Tanaka *et al.*[12,13]. At a concentration of 66 vol% sytrene, the SI30/hPS7 blend shown in *Figure 2a* exhibits an interconnected lamellar morphology reminiscent of the LC morphology observed by Thomas *et al.*[23] in a partially annealed copolymer and predicted by Fredrickson[6] and Olvera de la Cruz *et al.*[7]. The generalized LC morphology, not considering the precise mathematical definition, consists of lamellar channels connected by periodic orthogonal struts. Application of a two-dimensional Fourier filter to images of this microstructure, using first-order reflections only, results in the enlargement also presented in *Figure 2a.* The catenoids are more clearly visible in this processed image. An optical density trace along approximately 0.22 μm of an isoprene-rich 'lamella' is illustrated in *Figure 2b* to demonstrate the periodicity of the styrenic catenoids. If SI30 is blended with hPS of lower molecular weight, a DD morphology is produced, as depicted in *Figure 2c* for the SI30/hPS3 blend.

Winey *et al.*[8–10] have demonstrated that addition of high-molecular-weight hPS to an SI diblock copolymer ($N_{\mathrm{hPS}}/N_{\mathrm{S}} \approx 1.0$) tends to promote a morphology with low constant mean curvature, due to localization of the homopolymer near the microdomain centre. As $N_{\mathrm{hPS}}/N_{\mathrm{S}}$ is decreased, the hPS becomes more evenly distributed within its preferred microdomain[24,25] and acts as a preferential plasticizer, causing the blend morphology to either swell[12,13,26] or transform into another morphology[8–10]. This morphological trend is also qualitatively observed here in the SI30/hPS blends, in which $N_{\mathrm{hPS}}/N_{\mathrm{S}}$ is equal to 0.43 (SI30/hPS7) or 0.20 (SI30/hPS3). Comparison of *Figures 2a* (unprocessed image) and *2c*, both shown at the same magnification, reveals that the LC morphology (*Figure 2a*) in the SI30/hPS7 blend possesses lower mean curvature than the DD morphology seen in the SI30/hPS3 blend (*Figure 2c*). The lamellar morphology characteristic of the pure SI30 copolymer exhibits zero curvature.

Addition of hPS3 to SI20 produces a morphology without long-range order, as seen in *Figure 3.* Fourier analysis of micrographs such as this, along with those from SI10 (*Figure 1b*), fails to reveal any characteristic periodicities. However, some organized isoprene-rich microdomains are seen in this blend, resembling those observed in an SIS copolymer quenched from its disordered state[17]. This difference between SI10 and SI20/hPS3 suggests that the latter is not completely phase-mixed and possesses a χN within close proximity to, but not far below, the effective ODT of the blend.

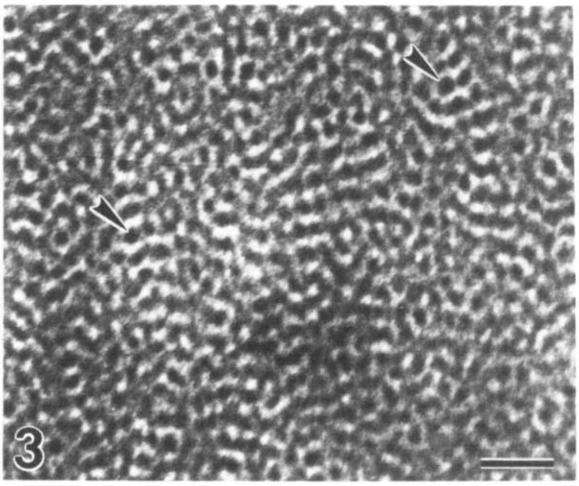

Figure 3 Micrograph of the SI20/hPS3 blend at 66 vol% styrene. No ordered (periodic) microstructure is observed, but the electron contrast between isoprene and styrene is greater than that seen in *Figure 1b*, suggesting that this blend is less phase-mixed than the SI10 copolymer and possesses a χN in close proximity to the effective ODT. Some regions exhibit local order as micelle-like structures (arrowheads), measuring up to 11 nm in diameter, or irregular struts. Bar = 50 nm

Since specific details of the predicted diblock copolymer phase diagram are ambiguous at low N (<400 in the present study), due to limitations associated with the Hartree approximation[2], no direct comparison is made between the morphologies seen in *Figures 2* and *3* and predicted phase behaviour. Banazak and Whitmore[25] have recently proposed a semiquantitative mean-field formalism for copolymer/homopolymer blends in the weak-segregation regime, but limit the predictive capability of their model to lamellar swelling without addressing morphological transformations.

This preliminary study, in conjunction with those performed by Tanaka *et al.*[12,13], has demonstrated that diblock copolymer/homopolymer blends can be employed to study the morphologies found within close proximity to the ODT and to probe the effect of critical fluctuations on morphological development. The influence of bulk composition and homopolymer localization on constant mean curvature, elucidated in the strong-segregation limit by Winey *et al.*[8–10], can be exploited to produce novel morphologies and determine their regime of stability. The results presented here are the first to reveal that LC and DD morphologies exist in weakly segregated diblock copolymer/homopolymer blends. Additional studies of such non-classical morphologies will be forthcoming.

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