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Persistence of the Gyroid Morphology at Strong Segregation in Diblock Copolymers

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Introduction. Block copolymers are fascinating hybrid materials that self-assemble into ordered nanoscopically structured morphologies. Several comprehensive reviews of both theoretical and experimental work on diblock copolymer phase behavior are available.[1−4] Of the morphologies commonly observed in diblock copolymers, the bicontinuous double gyroid phase (G) is the most intriguing. Generally this phase is found at low to intermediate segregation values (i.e., $\chi N \leq 40$, where χ is the interaction parameter and N is the degree of polymerization).[5−7] This result is consistent with the most recent self-consistent-field calculations, in which G is found to be stable relative to other complex phases and to the "classical" lamellar, hexagonal, and spherical phases, in a range of composition and segregation strength.[8−10] The calculations of Matsen and Bates suggest that G ceases to be stable at strong segregations ($\chi N \geq 60$) due to packing frustration effects.[9] However, these calculations are extremely intensive as χN increases due to the number of basis functions required.[9] Similarly, several others have also predicted that the nonclassical phases will cease to be stable at strong segregations.[11,12]

The experimental picture is far from clear. A thermoreversible order−order transition between cylinders (C) and lamellae (L) at high χN could be strong evidence for the elimination of G, but as far as we are aware this has not been reported. On the other hand, G has been observed in polystyrene-*b*-polyisoprene (PS-*b*-PI) systems in strong segregation. For example, Hasegawa et al. examined melts of PS-*b*-PI with high molecular weights (100−207 kg/mol)[13] and described the tetrapod morphology now known to be G.[14] More recently, Urbas and co-workers found G in a very high molecular weight PS-*b*-PI copolymer (750 kg/mol).[15] In both these instances, the strong segregation regime was accessed by materials with relatively low χ values ($\chi_{PS-PI} \sim 0.09$ at 25 °C)[16] but relatively large degrees of polymerization ($N \geq 1000$). Equilibration is therefore a key issue since the inherently slow dynamics of the high molecular weight chains coupled with the high T_g of the PS blocks may produce long-lived metastable states. Indeed, a metastable perforated layer phase has been observed in several systems as an intermediate when accessing G from either L or C, and G itself can be supercooled to a significant extent.[7,17−23]

In this study, we reexamine the stability of G at large segregation values. We employ relatively low molecular weight materials (10−13 kg/mol) with low T_g's to alleviate barriers to equilibration. The large segregation values are achieved by the controlled and selective chemical modification of a precursor block copolymer, allowing χ to be varied over a large range at constant N.

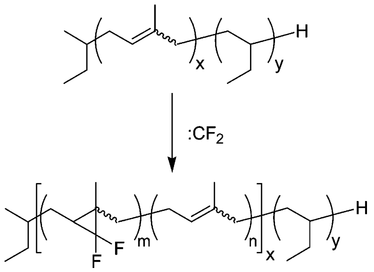

Figure 1. Reaction scheme showing the insertion of difluorocarbene (CF$_2$) into the backbone of the PI-*b*-PEE block copolymers.

Experimental Section. The parent 1,4-polyisoprene-*b*-1,2-polybutadiene (1,4-PI-*b*-1,2-PB) block copolymers were synthesized by sequential living anionic polymerization. Solvents, monomers, and reagents were purified using established procedures.[24] Molecular weights were determined by reaction stoichiometry and confirmed by size exclusion chromatography combined with light scattering. Compositions were determined by ^{1}H NMR spectroscopy. The parent block copolymers were subjected to selective hydrogenation using a homogeneous ruthenium catalyst to achieve essentially complete saturation of the PB block into poly(ethylethylene) (PEE), with little or no saturation of the PI block.[25,26] The recovered samples were modified to various extents by the addition of difluorocarbene (CF$_2$), generated by the thermal decomposition of hexafluoropropylene oxide (HFPO), to the PI backbone to yield a fluorinated material (FPI) as shown in Figure 1.[27,28]

Three parent diblock copolymers and one diblock copolymer blend were employed. Samples are designated PIPEE(x, y)Fz, where x and y are the molecular weights in kg/mol of the PI and PEE blocks, respectively, and z is the molar percentage of CF$_2$-modified PI repeat units. The pure diblock copolymers after hydrogenation are PIPEE(7.1, 4.4)F0, PIPEE(6.9, 3.7)F0, and PIPEE(8.5, 3.4)F0. The blend is designated PIPEE(7.8, 3.9)F0 and was prepared by solution blending equal weights of PIPEE(7.1, 4.4)F0 and PIPEE(8.5, 3.4)F0 before subjecting it to the difluorocarbene modification. Narrow molecular weight distributions were maintained throughout, with $M_w/M_n \leq 1.10$.

Bulk samples were annealed under vacuum (<30 mTorr) at approximately 75 °C for at least 24 h and slowly cooled to facilitate structural equilibration. Thin films were cast by preparing polymer solutions (10 wt %) gravimetrically. The solutions were placed on glass watch plates under a nitrogen atmosphere, and the solvent was allowed to evaporate slowly for 24 h. The films were subsequently dried under vacuum at room temperature for at least 24 h to ensure complete removal of the solvent.

SAXS measurements were made at the University of Minnesota on a home-built beamline using Cu Kα X-rays (λ = 1.542 Å) generated from a Rigaku RU-200BVH rotating anode. Franks mirror optics were used

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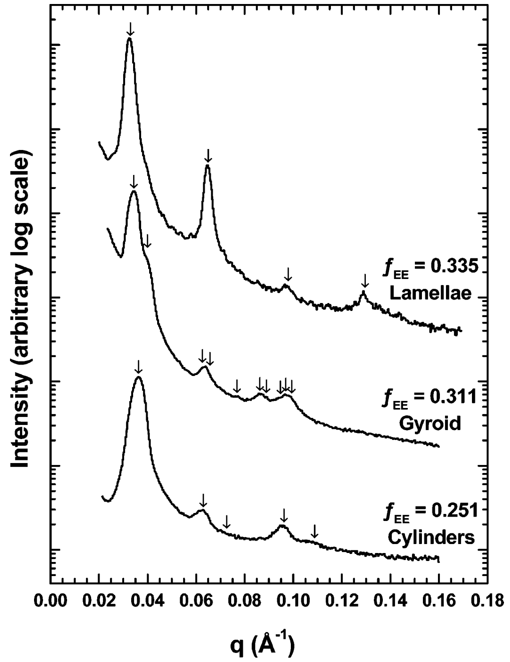

Figure 2. 1-D SAXS scattering profiles obtained for three completely modified samples in the bulk state at 100 °C: (a) PIPEE(7.1, 4.4)F100, (b) PIPEE(6.9, 3.7)F100, and (c) PIPEE(8.5, 3.4)F100. The arrows indicate the expected reflections for the morphologies noted based on the principal peak.

to focus the beam onto a two-dimensional area detector (Siemens HI-STAR), located at the end of either a 1.0 or 1.5 m evacuated flight tube. The two-dimensional images were corrected for detector response, azimuthally integrated, and placed on a one-dimensional intensity vs wave vector (q) scale. The sample temperature was controlled using a water-cooled, electrically heated brass block inside an evacuated sample chamber. Exposure times ranged from 10 to 30 min at a given temperature, and samples were annealed for at least 10 min at a given temperature prior to measurement.

Results and Discussion. Sample morphologies were determined by SAXS on the basis of the ratios of the peak spacings, at temperatures greater than that of the largest T_g component in the system ($T_{g,FPI} \approx 43$ °C,[27] whereas $T_{g,PEE} \approx -20$ °C and $T_{g,PI} \approx -60$ °C[24]). The SAXS patterns in Figure 2 show the scattering profiles obtained for the three completely modified (F100) diblock copolymers at 100 °C. PIPEE(7.1, 4.4)F100 exhibits a pattern consistent with L, with reflections located at integral spacings; PIPEE(6.9, 3.7)F100 has reflections at ratio spacings of $\sqrt{3}$, $\sqrt{4}$, $\sqrt{10}$, $\sqrt{11}$, $\sqrt{15}$, $\sqrt{19}$, $\sqrt{20}$, $\sqrt{23}$, $\sqrt{24}$, and $\sqrt{25}$, corresponding to G; PIPEE(8.5, 3.4)F100 has reflections consistent with C, i.e., ratio spacings of 1, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, and $\sqrt{9}$.

The experimental domain spacings, D, were found using the relation $D = 2\pi/q^*$, where q^* is the wavevector of the principal scattering peak. Estimates of the effective interaction parameters (χ_{eff}) were obtained from D using the strong-segregation relation[29]

$$D = 1.10\bar{a}N^{2/3}\chi^{1/6} \tag{1}$$

where $\bar{a}$ and N are the weighted average statistical segment length and the total degree of polymerization, respectively. Equation 1 is strictly applicable for lamellar materials in the strong-segregation limit ($\chi N \geq 100$), but its use provides a reasonable and internally consistent estimate of χ since only the prefactor changes for the other morphologies.[29] This approach was used previously on PS-*b*-PI/FPI diblock copolymers and was found to give comparable χ values to those obtained from the N dependence of the order−disorder transition temperatures.[28] At 100 °C, χ_{eff} increases smoothly with the extent of CF$_2$ modification (z) from ca. 0.002 at F0 to ca. 0.74 at F100. For a given sample decreasing temperature leads to increases in D, and hence χ, as expected;[30] in this manner a full expression for $\chi_{eff}(z,T)$ was obtained, as demonstrated previously for PS-*b*-PI/FPI diblocks.[28]

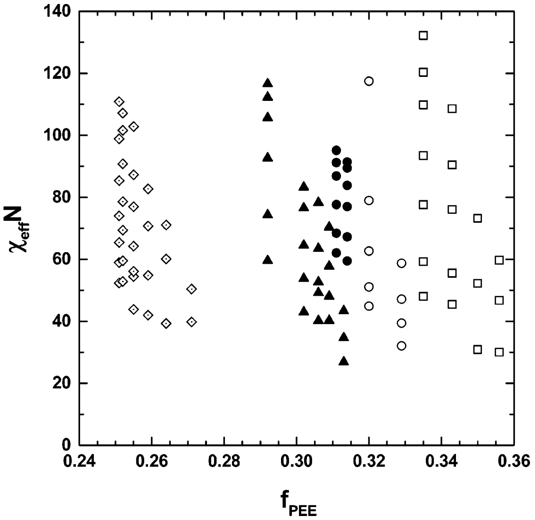

Figure 3. Experimental morphology map: center dotted symbols, cylinders; solid symbols, gyroid; open symbols, lamellae structures. Sample representations are: diamonds, PIPEE(8.5, 3.4)Fz; triangles, PIPEE(7.8, 3.9)Fz (blend); circles, PIPEE(6.9, 3.7)Fz; squares, PIPEE(7.1, 4.4)Fz.

Figure 3 shows the experimental morphology map obtained for the three diblocks and the blend. This phase diagram was constructed by varying the extent of CF$_2$ modification and/or the temperature of each sample. Samples with low extents of fluorination ($z \leq 35\%$) are not shown because they lack sufficient electron contrast between the two blocks for a useful scattering profile to be acquired, and thus no estimate of χ_{eff} was obtained. Using the $\chi_{eff}(z,T)$ relationship described above, sufficient contrast would not be expected until segregation levels of $\chi_{eff}N \approx 30$ were achieved, consistent with the experimental results. Consistently, PIPEE(7.1, 4.4)Fz is lamellar and PIPEE(8.5, 3.4)Fz is hexagonal. PIPEE(6.9, 3.7)Fz has a lamellar morphology at low and moderate levels of CF$_2$ modification, but above $z \approx 85$, the morphology changes to G. The blend, PIPEE(7.8, 3.9)Fz, was also found to exhibit G consistently. As can be seen from the plot, G is found in several cases at $\chi_{eff}N$ values up to 120, significantly beyond the anticipated theoretical limit around 60.[31] Furthermore, there is no obvious indication from the trends in the plot that the G phase is about to pinch off in favor of L or C.

The most important issue, clearly, is to assess the state of equilibrium for these G samples at large χN. As a first step, the bulk samples were annealed at ca. 120 °C for 4 weeks and reevaluated by SAXS. Negligible differences in the scattering profiles were obtained. Second, thin films of the G samples of PIPEE(6.9, 3.7)F100, PIPEE(6.9, 3.7)F92, and the blend PIPEE(7.8, 3.9)F100 were cast from a number of solvents of various selectivities. If the solvent was selective for PEE, it

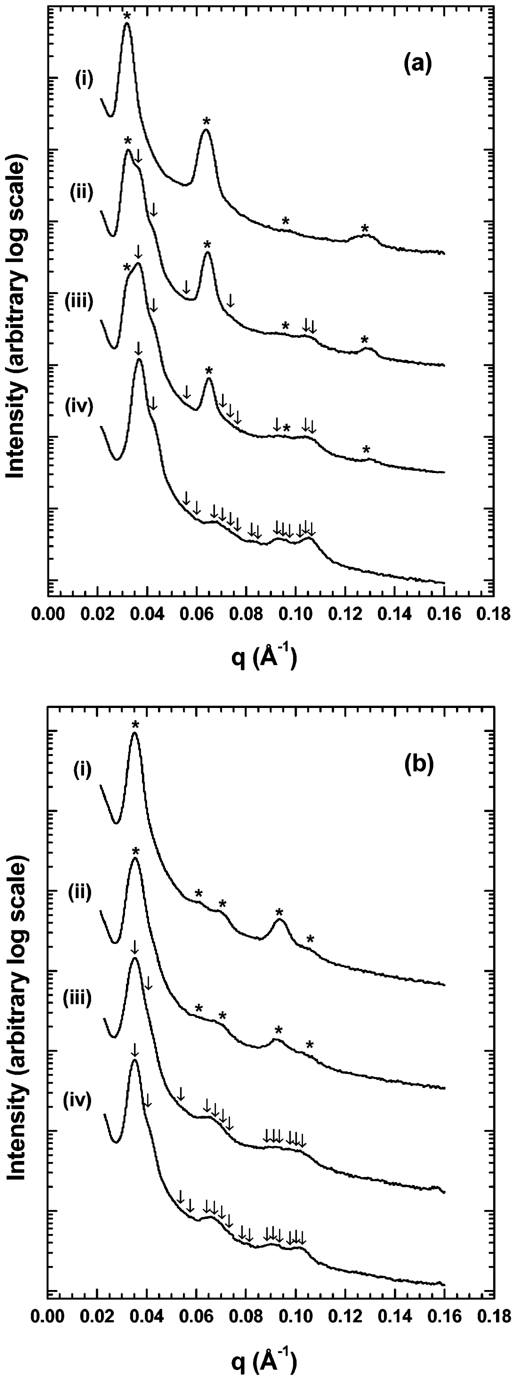

Figure 4. (a) Scattering profiles at 50 °C obtained for PIPEE(6.9, 3.7)F100 cast from chloroform: (i) cast morphology corresponding to lamellae (*); (ii) after annealing for 1 h at 150 °C, gyroid peaks (↓) begin to develop; (iii) after annealing for 2 h at 150 °C, gyroid phase begins to dominate; (iv) after annealing for 3 h at 150 °C, gyroid morphology is fully recovered. (b) Scattering profiles at 50 °C obtained for PIPEE(7.8, 3.9)F100 cast from methylene chloride: (i) cast morphology corresponding to cylinders (*); (ii) after annealing for 1 week at 130 °C, higher order cylinder peaks decrease in intensity; (iii) after annealing for 2 weeks at 130 °C, gyroid phase (↓) begins to appear; (iv) after annealing for 3 weeks at 130 °C, gyroid morphology is almost fully recovered.

should shift the material to the right in the phase diagram (Figure 3), and the expected as-cast morphology would be L or G. If the solvent was selective for FPI, the opposite should be true, and the expected as-cast morphology would be C or G.

A more complete discussion of the solvent casting results will be presented elsewhere,[30] but the central result is that when bulk G samples were cast into L or C, they always annealed back into G. The rate at which G was recovered varied substantially with sample and with solvent. Examples are given in Figure 4a,b. In the former, PIPEE(6.9, 3.7)F100 cast from chloroform showed L, but recovered to G within 3 h of annealing at 150 °C. In the latter, the blend PIPEE(7.8, 3.9)F100 was cast into C from methylene chloride. After annealing for 3 weeks at ~130 °C, the structure is clearly much closer to G, although perhaps still not fully recovered. Collectively, these results are strong evidence that G is the equilibrium phase for these samples.

The reason why these results appear to conflict with the self-consistent-field calculations remains to be elucidated. One factor to consider is the role of polydispersity. Even narrowly distributed samples such as those employed here have some heterogeneity, with respect to both length and composition. Chang et al.[32] have recently demonstrated that a narrow distribution, anionically polymerized PS-*b*-PI copolymer can be fractionated into separate materials that exhibit L, G, or C. However, it is not obvious that polydispersity should stabilize G, as opposed to favoring segregation into coexisting lamellae and cylinders. Indeed, the latter course has been consistently observed in G phases produced in selective solvents, when the degree of segregation is increased.[33] Another possibility to consider is that the estimates of χ_{eff} are systematically high by a factor of at least 2. However, if this were the case, then samples that we observed to be ordered at relatively low $\chi_{\mathrm{eff}}N$ should be well within the disordered state, so this possibility may be discounted. We also made independent estimates of χ_{eff} using order−disorder transition (ODT) measurements (SAXS) and fluctuation theory[34] using two polymers with lower degrees of fluorination. These independent estimates were in reasonable agreement with the value of χ_{eff} determined using eq 1. This provides further support for the use of eq 1 in the determination of $\chi_{\mathrm{eff}}N$.

Conclusion. The complex bicontinuous gyroid structure has been found to exist in a narrow window between the classical lamellar and cylindrical morphologies in difluorocarbene-modified PI-*b*-PEE block copolymers. Remarkably, the gyroid window is found to persist to segregation values (χN) much higher than those predicted by theory and commonly found experimentally. Annealing experiments in the bulk G phase showed no change in either morphology or domain spacing. Selective solvents were used to cast the G samples into lamellar and cylindrical morphologies. Subsequent annealing at elevated temperatures consistently showed the recovery of G from the cast phase (L, G, or C), indicating that G can be stable in the strong segregation regime.

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