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Chain Folding in Crystallizable Block Copolymers

Anthony J. Ryan,*[†,‡] J. Patrick A. Fairclough,[†] Ian W. Hamley,[§] Shao-Min Mai,[‖] and Colin Booth[‖]

Manchester Materials Science Centre, UMIST, Grosvenor Street, Manchester M1 7HS, U.K., CLRC Daresbury Laboratory, Warrington WA4 4AD, U.K., School of Chemistry, University of Leeds, Leeds LS2 9JT, U.K., and Department of Chemistry, University of Manchester, Manchester M13 9PL, U.K.

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ABSTRACT: The crystallization of oxyethylene/oxybutylene (E/B) diblock copolymers has been studied by simultaneous SAXS and WAXS. The copolymers crystallized from their melts (disordered, lamellar, or hexagonal) with folded E blocks. Rapid crystallization (quench) of lamellar melts was accompanied by a change in length scale and led to structures with multiply-folded E blocks and the B blocks slightly stretched from their melt conformation. Quenching the hexagonal melts gave no change in length scale and led to structures with multiply-folded E blocks and the B blocks unstretched from their melt conformation. These metastable folded structures formed during rapid crystallization did not unfold on heating but could be self-seeded to grow equilibrium once-folded (or multi-folded) structures. The folded states are discussed in terms of contributions to the Gibbs energy of crystallization from E-block folding and B-block stretching.

Introduction

Block copolymers are self-assembling materials with remarkably rich structural and dynamic behavior[1] which has been extensively studied experimentally and theoretically for noncrystallizable systems.[2−6] If one or more of the blocks can crystallize, the microphase separation behavior becomes more complicated. For nonglassy block copolymers, it may be taken for granted that crystallization of one block will result in separation into lamellar microphases, as the negative Gibbs energy of crystallization will greatly outweigh the Gibbs energy of dislocation of any microphase-separated structure in the melt. There are, however, important effects due to the crystallizing chain being covalently bonded to a noncrystallizable chain. The ongoing flux of noncrystallizable chains of the second block has to be accommodated, and the ratio of cross-sectional areas of the two types of blocks is an important consideration if space is to be filled at normal densities. Published theories[7−9] recognize this competition between preferred low-Gibbs-energy conformations, i.e. unfolded chains for the crystallized component and randomly-coiled chains for the noncrystallized component, and minimize the Gibbs energy by introducing an equilibrium degree of chain folding in the crystalline layer. Thus there is an important distinction to be drawn between homopolymers, where chain folds are metastable and are introduced by crystallization kinetics, and block copolymers where an equilibrium degree of chain folding exists in the crystalline layer. Many experimental studies of mobile block copolymers have been on fairly high molar mass copolymers, where it did not prove possible to quantify low extents of chain folding.[10−15] We have recently studied[16] a range of E_nB_m copolymers (E = oxyethylene unit, B = oxybutylene unit) which formed either unfolded or once-folded crystals on crystallization from their disordered melts. In that work the influence of the noncrystallizable block was illustrated by the fact that the E block of copolymer $E_{31}B_{30}$ folded on crystallization at room temperature, whereas the E blocks of copolymers in the range $E_{29}B_{20}$ to $E_{32}B_3$ were unfolded.

Table 1. E_mB_n Block Copolymers

copolymer	M_n (E block), g mol^{-1}	ϕ_E (solid)	r_v (liquid)	liquid state structure
$E_{76}B_{38}$	3340	0.49	147	lamellar
$E_{70}B_{69}$	3080	0.33	200	hexagonal
$E_{115}B_{103}$	5060	0.35	310	hexagonal

If coil dimensions increase with an increase in temperature, then the number of folds at equilibrium should increase with temperature. However, the behavior generally observed, e.g. in the work of Gervais and Gallot,[11] is that more folds form as the crystallization temperature is decreased, indicating that kinetic (nonequilibrium) effects may dominate. In this paper we present results obtained for E_mB_n copolymers which illustrate this competition between kinetic and equilibrium factors.

Experimental Section

The synthesis of the copolymers by sequential anionic polymerization and their characterization by GPC and NMR has been described elsewhere.[16,17] All copolymers were of low polydispersity ($M_n/M_w < 1.05$). Formulas are quoted as E_nB_m, where n and m are number-average degrees of polymerization. Their structures in the solid and melt phases, and their degrees of crystallinity, were determined by a combined SAXS/WAXS/DSC instrument, the construction and operation of which is detailed elsewhere.[18] A total of 20 copolymers have been studied by the SAXS/WAXS technique, with block lengths in the ranges E_{30}−E_{209} and B_7−B_{102}. Depending on composition and chain length, their melt-state structures could be disordered, lamellar, or hexagonal.[17] In all cases WAXS showed that the copolymers crystallized with their E blocks in helical conformation in the usual structure.[19] The present account concerns three of these copolymers: see Table 1, where ϕ_E is the volume fraction of E in the solid state and r_v is the segment length of the copolymer in the liquid state, a segment having the volume of an E unit.

Results and Discussion

The SAXS pattern from the melt of copolymer $E_{76}B_{38}$ at 80 °C (see Figure 1) shows two orders of reflection consistent with an ordered melt lamellar structure with

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[†] UMIST.

[‡] CLRC Daresbury Laboratory.

[§] University of Leeds.

[‖] University of Manchester.

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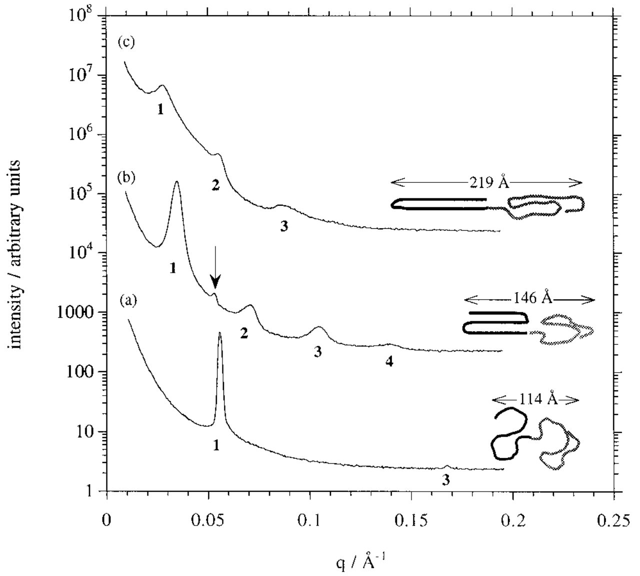

Figure 1. SAXS patterns for copolymer $E_{76}B_{38}$ showing (a) the ordered melt structure (T = 90 °C), (b) the metastable structure (T_c = 42 °C), and (c) the equilibrium, once-folded structure grown at 50 °C by a self-seeding process. Numbers indicate the positions of the reflections from the stacked lamellae, and the arrow indicates the position of the peak arising from the ordered melt. The insets show calculated repeat lengths for possible conformations.

$d_m = 2\pi/q^* \approx 114$ Å. Assuming that the block copolymer is stretched from its Gaussian conformation in the melt,[1,2] the radius of gyration (R_g) of this polymer is estimated to be 64 Å using the relation $R_g = r_v^{2/3}b/6^{1/2}$,[1] with the statistical segment length b = 5.6 Å.[17] The measured spacing is twice the R_g, as expected for a lamellar structure. The SAXS patterns of the solid copolymer (see Figure 1) show three or four orders of reflection and indicate semicrystalline lamellar structures with long range order and little polydispersity in lamellar thickness. A residue of supercooled melt phase, indicated by a small peak at $q \approx 0.05$ Å^{-1} (see Figure 1), was a feature of all initially crystallized (as distinct from self-seeded) copolymers. The "solid-state" patterns could be fitted with Gaussian functions for the peaks and a smooth Porod background.

Estimates of the lamellar spacing to be expected for a structure with unfolded E blocks having their helices normal to the lamellar end plane, l_0, were obtained from

$$l_0/\text{Å} \approx 0.95 z_E/\phi_E$$

where z_E is the number of chain atoms (C and O) in the E block and 0.95 Å is the length per chain atom along the poly(oxyethylene) helix.[20] It is simple, therefore, to estimate the repeat length in a system in which the E blocks have n folds

$$l_n = l_0/(n + 1)$$

As indicated in Figure 1 for copolymer $E_{76}B_{38}$, the structure grown at 50 °C by a self-seeding process (see below for details) had d_c = 220 ± 4 Å compared with the spacing calculated for a once-folded structure, l_1 = 219 ± 5 Å. By contrast, the structures grown in the range 38 °C < T_c < 45 °C had 160 ± 4 Å ≤ d_c ≤ 170 ± 4 Å, and as l_2 = 146 ± 3 Å there was no direct match to integer folding. The experimental result could be rationalized for a structure with twice-folded E blocks if either some of the E blocks did not crystallize and contributed to the noncrystalline layer, or if the longer E blocks were preferentially crystallized (the polydispersity of the E blocks was also 1.05) and the molecules with shorter E blocks were excluded from the lamellar stacks. An alternative explanation is that the E blocks were once-folded but were tilted in the lamellar stack. There is published evidence for tilted chains in low-molar-mass copolymers and co-oligomers containing E blocks, e.g. for $P_nE_mP_n$[21] (P = oxypropylene), $C_nE_mC_n$,[22] and E_mC_n[23] (C = methylene) copolymers. Displacing adjacent poly(oxyethylene) helices by one E unit (chain spacing 4.6 Å and E unit length 2.85 Å) gives an angle (relative to the lamellar end plane) of 58° and $l_{\text{tilted}}/l_{\text{untilted}}$ = 0.85, leading to $l_{1,\text{tilt}}$ = 186 Å. Similarly displacing adjacent helices by two E units leads to $l_{1,\text{tilt}}$ = 133 Å. Neither of these calculations fits the experimental results, and since the experimental results are broadly consistent with an untilted structure, we adopt this simple model in subsequent discussion.

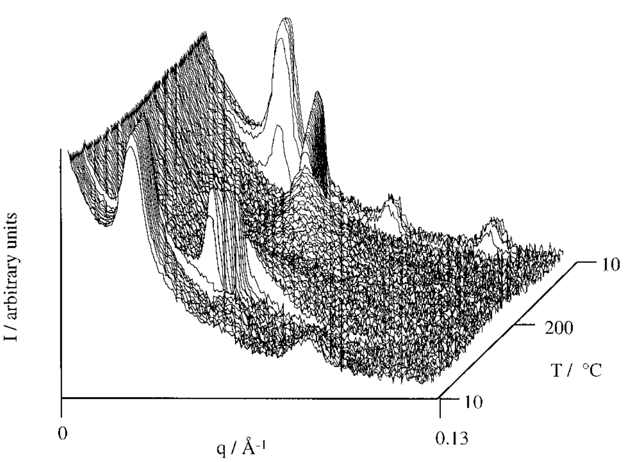

Figure 2. Temperature-resolved SAXS of $E_{76}B_{38}$ during heating and cooling at 10 °C min^{-1} between 10 and 200 °C. There are thermally reversible transitions from the metastable, twice-folded crystal to the ordered melt (≈54 °C) and from the ordered melt to the disordered melt (≈114 °C). The length scale changes continuously at the ODT, but the discontinuous change in length scale on melting and recrystallization is obvious. There is a hysteresis of ≈4 deg on the disorder−order transition and ≈23 deg on recrystallization.

Figure 2 shows time-resolved SAXS from copolymer $E_{76}B_{38}$ during heating and cooling at 10 °C min^{-1} between 10 and 200 °C. There are thermally reversible transitions between metastable twice-folded crystals (d_c = 160−170 Å) and the ordered melt ($T \approx 54$ °C) and between the ordered melt and disordered melt ($T \approx 114$ °C). On cooling, there is a high-temperature ODT which is fluctuation driven; the lower temperature transformation from a wholly amorphous lamellar melt to semicrystalline lamellae is driven by crystallization of the E-block. On heating, the initially-formed melt was a stretched structure compared to the equilibrium melt, the discrepancy in length scale being ≈15%. Relaxation to the equilibrium value occurred within 100 s. Post-melt stretch has also been observed in a poly(oxyethylene)−poly(methylene) block copolymer[4] and is due to the difference in length scales between the crystalline and molten states which imposes a packing constraint on melting because of the need to conserve density. There was a difference of 4 deg between the ODT (heating) and the DOT (cooling), but a difference of 23 deg between melting and crystallization temperatures. This last value was significantly larger than that observed (7 °C) for a poly(oxyethylene) of molar mass similar to that of the E block (M_n = 3000 g mol^{-1}, E_{68})

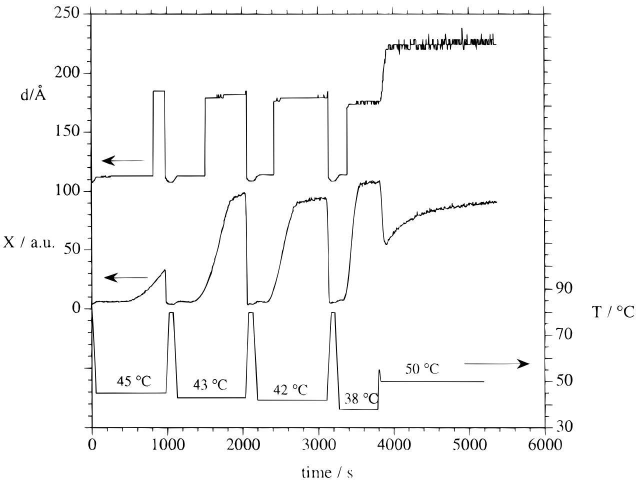

Figure 3. Time series showing the degree of crystallinity (X) and dominant length scale (d) as a function of temperature during the melting and recrystallization of copolymer $E_{76}B_{38}$. The repeated selection, due to crystallization kinetics, of the metastable structure with $d_c = 160-170$ Å at $T_c < 45$ °C is obvious, as is the formation of the equilibrium, once-folded structure at $T_c = 50$ °C by the self-seeding process.

which was melted and crystallized under similar conditions. A significant contribution to the barrier to crystallization is the change in length scale that needs to be accommodated. If the copolymer were to recrystallize in its once-folded condition ($l_1 = 219$ Å) both E and B blocks would need to stretch by a factor of 2 from their equilibrium values in the melt ($d_m = 114$ Å). In order to overcome the consequent Gibbs energy barrier to nucleation, the polymer must be undercooled to such an extent that the formation of a more-folded metastable state is kinetically preferred. The undercooling needed for the first-order process of crystallization, which is accompanied by discontinuous changes in length scale, enthalpy, and density, is clearly much larger than that required for the weak first-order process at the DOT, where the length scale changes continuously.

The effect of the Gibbs energy barrier to nucleation of the equilibrium phase is illustrated in Figure 3, which is a time series showing the degree of crystallinity and dominant spacing at a series of temperatures during the melting and recrystallization of copolymer $E_{76}B_{38}$. The repeated selection of the kinetically determined, metastable, twice-folded conformation when $38 < T_c < 45$ °C is obvious, and this occurred despite the fact that the rate of crystallization changed by 1 order of magnitude between 38 and 45 °C. To obtain the once-folded structure of copolymer $E_{76}B_{38}$ a self-seeding technique was required, similar to that used by Buckley and Kovacs.[24] In the present case, this involved crystallizing the copolymer at 38 °C, holding it for a short time at 55 °C so that most of the twice-folded crystals melted, and then quickly dropping the temperature to 50 °C when once-folded crystals were observed (by time-resolved SAXS) to grow on the nucleating surface provided. This melting and recrystallizing process was required for the transformation: holding the sample at a temperature just below the melting point was not sufficient. Crystallization at 38 °C followed by partial melting at 55 °C and then quenching to 47 °C resulted in a mixture of once-folded and twice-folded crystals. Furthermore, direct crystallization from the melt did not occur over a period of 1 h at 50 °C, whereas twice-folded crystals grew from the melt at a reasonable rate at 48 °C. Primary crystallization to form metastable, multiply-folded structures occurred in many of our lengthy E_mB_n copolymers, and the stable less-folded structures could only be formed when there was already a crystal surface present to reduce the nucleation barrier. This effect in a lengthy copolymer is understandable in terms of a nucleation barrier dominated by the difference in length scale between the ordered melt and the stable solid. Since $d_m \sim r_v^{2/3}$[1] and (to a fair approximation) $l_n \sim r_v$, the activation energy for nucleation of a given n-folded structure should scale as $\Delta E \sim r_v^{1/3}\phi_E/n$.

The quantization in length scale found for the initially crystallized copolymers is similar to that observed in low-molar-mass poly(oxyethylene)s (i.e. polyethylene glycol, PEG, $3000 \le M_n \le 10\,000$ g mol^{-1}, chain length E_{68} to E_{230}[24−28]), where crystallization occurs with integer numbers of folds depending on the chain length and crystallization temperature. The effect occurs in the homopolymers because the Gibbs energy finds a metastable minimum in a system where the chain ends and folds are located at the lamellar surface. Slow crystallization of the lower PEGs (E_{136} and lower) resulted in crystals with unfolded chains.[28] Annealing the lower PEGs (E_{90} and lower) at temperatures below their melting points resulted in rapid unfolding of any folded crystals.[24] Initially-formed once-folded (and possibly twice-folded) crystals of the higher PEGs (E_{136} and higher) were stable to annealing: unfolded structures were formed by self-seeding.[25] In the present work on copolymer $E_{74}B_{37}$ the twice-folded structure could not be unfolded by heating below T_m, and only the once-folded structure could be obtained by self-seeding. In view of the relatively short length of the E blocks of copolymer $E_{76}B_{38}$ compared to most of the PEGs, we use our inability to unfold an E block (either by annealing or self-seeding) as an indication of an equilibrium state, or at least a state as close to equilibrium as is experimentally attainable. All our present observations for copolymer $E_{76}B_{38}$ are consistent with formation (by self-seeding) of a once-folded equilibrium state. The unfolded structure could not fill space with regular lamellae at normal density because the contour length of B_{38} (134 Å) is much less than the unfolded length of E_{76} (217 Å). The equilibrium state is determined by the balance of contributions to the Gibbs energy from E-block folding (positive contribution) and B-block relaxation (negative contribution). In that the entropy increase dominates the contribution from B-block relaxation, the process

$$\text{unfolded structure} \rightarrow \text{equilibrium folded structure}$$

is entropy driven.

The polymorphism imposed by the attachment of an amorphous chain to a crystallizable one is well illustrated by results obtained for copolymer $E_{115}B_{103}$, which fortuitously has coincidence between d_m and l_4. SAXS patterns for $E_{115}B_{103}$ (see Figure 4a) show this epitaxial relationship between q^* for the ordered melt and q^* for the metastable four-times-folded crystalline solid. The metastable structure was formed by a deep quench ($T \approx 10$ °C), when the rapid phase transformation resulted in smearing of the rods into layers with no further stretching of the B block, as illustrated in Figure 4b. Copolymer $E_{115}B_{103}$ could be crystallized slowly (by self-seeding) to a structure with three-times-folded E blocks. Crystallization of copolymer $E_{70}B_{69}$, which has a similar composition but a shorter chain length (see Table 1), showed similar effects (see Figure 5). Because of the epitaxy of its lamellar crystalline and hexagonal melt forms, the crystalline phase that was

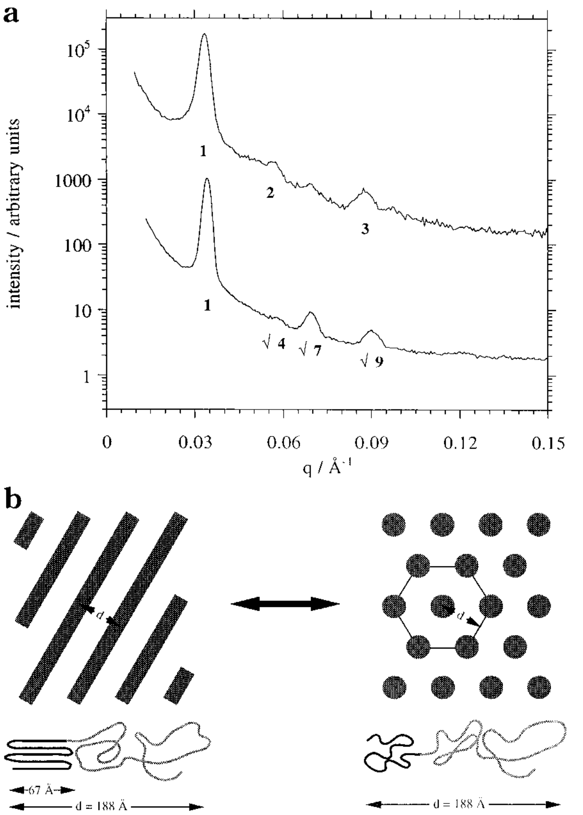

Figure 4. (a) SAXS patterns for copolymer $E_{115}B_{103}$ showing the epitaxial relationship between q^* for the ordered melt and q^* for the metastable crystalline structure. (b) The metastable structure was formed during a deep quench, where rapid phase transformation caused the smearing of the rods into the layers without extra stretching of the B block, as shown in the schematic diagram. Possible chain conformations in the melt and crystal are also shown.

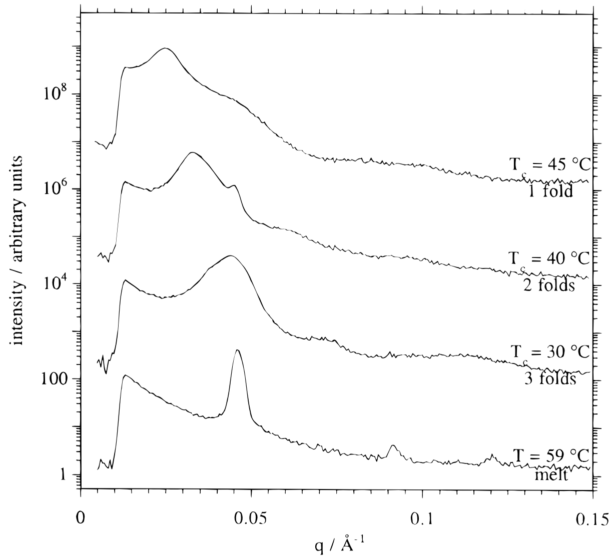

Figure 5. SAXS patterns of $E_{70}B_{69}$ showing the epitaxy between the three-times-folded structure that forms on a deep quench and the melt. The polymer could be recrystallized (using the self-seeding technique) to the metastable twice-folded structure and subsequently to the stable once-folded structure. The coexistence of the metastable twice-folded structure and the melt may be readily observed. The higher order reflections from the lamellar solids are not so well resolved as those illustrated in Figure 4a ($E_{115}B_{102}$), which could be due to the formation of mixtures of crystals.

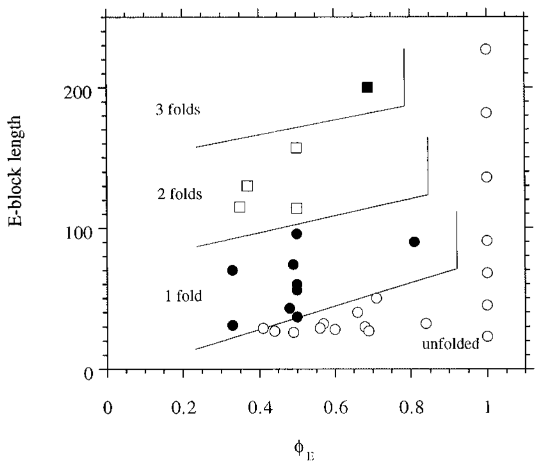

Figure 6. Extent of E-block folding at equilibrium (or near equilibrium) as a function of E block length and overall composition ϕ_E. This is a summary of results obtained for all E_mB_n copolymers investigated to date, including results reported previously,[16] and also includes established results for homopoly(oxyethylene)s.[24] The lines drawn are speculative and are intended as a guide to the eye.

directly grown from its melt at 30 °C was the three-times-folded structure, as illustrated in Figure 5. Subsequent self-seeding of this copolymer allowed the twice-folded and once-folded structures to grow at 40 and 45 °C, respectively. As described previously (see Figure 1 and associated discussion), the solid and supercooled melt phases coexisted in the rapidly-crystallized materials. The epitaxy between the length scales in the hexagonal melt and the multi-folded metastable crystals was unique in our experiments, since all the copolymers with lamellar or disordered melts showed a change in length scale on crystallization. Epitaxy between the hexagonal melt and the lamellar crystalline phase has been previously observed in polyolefin diblocks, which form polydisperse structures with many (nonintegral) folds.[29] In contrast to the copolymers described here, which have crystal stems perpendicular to the lamellar interface, the copolyolefins have crystal stems parallel to the lamellar interface.[29]

A summary of results obtained for all E_mB_n copolymers investigated to date, including results reported previously,[16] is given in Figure 6. The plot shows the extent of E-block folding at equilibrium (or near equilibrium) as a function of E block length and overall composition ϕ_E. At this stage in the investigation it is not possible to define folding regimes on the diagram with confidence, but the impression gained is that E-block length and composition together determine the extent of folding, rather than composition alone.

Summary and Conclusions

E_mB_n copolymers that have disordered or lamellar melt phases show an increase in the characteristic length scale on crystallization of the E block, which implies stretching of the amorphous B block above that experienced in the melt. When crystallized rapidly, the higher-molar-mass coplymers form kinetically-determined, highly-folded structures. These metastable structures are stable to annealing but can be melted and self-seeded to grow equilibrium less-folded structures in which the extent of folding is determined by the balance between the Gibbs energies of E-block folding and B-block stretching. Epitaxy between hexagonal melt and lamellar solid phases allows the formation of metastable many-folded structures with no change in length scale. The published results for kineticallyinduced folded structures of homopoly(oxyethylene) show them to have much larger stem lengths than those of the equilibrium folded structures of the E_mB_n copolymers, which provides an additional illustration of the importance of the competition between the two low-Gibbs-energy conformations: i.e. unfolded E blocks and unstretched B blocks.

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