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Stabilizing co-continuous polymer blend morphologies with ABC block copolymers

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Abstract. We suggest that ABC triblock copolymers provide a convenient and effective route to emulsifying blends of A and C homopolymers into co-continuous morphologies over a wide range of compositions. Direct transitions between disordered tricontinuous phases ("ABC microemulsions") and spatially-periodic tricontinuous phases (*e.g.* gyroid or double-diamond cubic phases) should be possible in appropriately formulated alloys. We envision a broad range of potential applications to thermoplastic and thermoset polymeric materials.

PACS. 61.12.Ex Neutron scattering techniques (including small-angle scattering) – 64.60.Fr Equilibrium properties near critical points, critical exponents – 64.60.Kw Multicritical points

1 Introduction

Polymer blends with co-continuous phase morphologies have proven to be quite useful in a variety of plastic technologies. For example, bicontinuous structures composed of a percolating conjugated (conducting) polymer phase and a second (percolating and) insulating polymer phase have been used in fabricating all-plastic LED's [1]. More familiar are interpenetrating networks (IPN's) of crosslinked polymers for structural applications [2]. In such materials, phase bicontinuity is known to impart superior mechanical properties, such as high strain at break and toughness index [3].

Co-continuous structures in polymer alloys are invariably produced by quenching *nonequilibrium* states resulting from a phase transformation process (*e.g.* spinodal decomposition) or by mechanical agitation (*e.g.* shear). Quenching is effected either by cooling to a temperature at which one or more components crystallizes or vitrifies, or by carrying out a crosslinking reaction to fix the structure. Unfortunately, such materials often lose their co-continuity on subsequent processing, or in the case of crosslinked systems, are incapable of further processing.

A means of producing co-continuous polymer morphologies from *equilibrium* self-assembly processes is clearly very desirable. Such structures could be repeatedly processed as normal thermoplastics, yet local thermodynamic forces would conspire to reform the co-continuous network at rest. One reliable route to *long-range ordered* bicontinuous structures are melts of AB diblock copolymers with block compositions carefully tuned to stabilize the Ia$\bar{3}$d "gyroid" mesophase [4]. Ordered tricontinuous mesophases (most likely the ordered-tricontinuous-double-diamond, OTDD, structure) are apparently stable over even larger regions of block compositions in molten ABC triblock copolymers [5]. While such pure block copolymer systems offer an elegant solution to the problem of co-continuity, their relatively high cost of synthesis precludes a number of important applications.

A route to *equilibrium*, bicontinuous morphologies with no long-range order has recently been identified in blends of A and B homopolymers with an AB diblock copolymer [6]. Such "polymeric microemulsions" resemble microemulsion or "sponge" phases in oil/water/surfactant mixtures [7], but are composed entirely of macromolecular components. They are also attractive from the standpoint of plastic technology, because they require only small amounts of block copolymer, and thus constitute a more economical route to equilibrium bicontinuous structures. The strategy for constructing such an alloy is to target blend compositions near an isotropic Lifshitz point [8] located by mean-field theory [9]. At such a multicritical point, competing tendencies for macrophase separation and mesophase separation are precisely balanced. Thermal fluctuations, however, apparently destroy the Lifshitz point and replace it with a narrow channel of highly structured, fluctuating disordered phase (the "polymeric microemulsion") that persists down to low temperatures [6]. In a symmetric blend, *i.e.* an equimolar mixture of homopolymers of the same molecular weight blended with a compositionally symmetric diblock, the microemulsion channel is bounded on the diblock-rich side by a lamellar mesophase, and on the homopolymer-rich side by two coexisting disordered liquid phases.

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Another way of understanding the presence of a polymeric microemulsion in a symmetric blend near the Lifshitz composition is by adopting a low temperature perspective, as is typical in the analysis of oil/water/surfactant systems [7]. In such an approach, one focuses on the statistical mechanics of monolayer surfactant films that separate oil and water-rich regions. For symmetric films with no spontaneous curvature (*i.e.* tendency to bend in a particular direction) and for systems with roughly equal amounts of oil and water, the boundary between the two phase region of coexisting oil and water (droplet emulsion) phases and the bicontinuous microemulsion phase is identified with the vanishing of the interfacial tension, *i.e.* the point at which the oil/water interfaces become saturated with surfactant. Indeed, one can show that the tension of the symmetric A/B/A-B polymer blend vanishes very near the Lifshitz composition, consistent with the onset of the bicontinuous microemulsion phase. In contrast, the boundary between the microemulsion phase and the lamellar phase is usually explained as a fluctuation-induced melting of the lamellar phase [7]. As the surfactant (or block copolymer) concentration is reduced, the interfacial films composing the lamellae are separated by larger distances, allowing for more significant thermally-populated fluctuations. Eventually, the mean spacing between films is comparable to the in-plane persistence length (a type of Lindemann criterion) and the lamellar phase melts into a microemulsion. Because films composed of polymeric surfactants (*i.e.* diblock copolymers) are known to be very stiff to bending [10], it is sensible that the lamellae-to-microemulsion transition was observed at a homopolymer content just slightly less than the Lifshitz composition in the experiments of Bates *et al.* [6].

An unfortunate feature of these diblock copolymer blends is that the width of the microemulsion channel is quite narrow, spanning only a few percent in volume fraction of copolymer. Thus, reproducibly achieving bicontinuous structures in such systems is difficult. In the present paper, we put forward theoretical arguments to suggest that equilibrium co-continuous morphologies are much easier to produce in ternary blends of an ABC triblock copolymer with A and C homopolymers. The basis for our assertion, which is described in more detail below, is that the saddle-splay (Gaussian) bending modulus $\bar{K}$ of a swollen ABC triblock film can be driven positive in the vicinity of the mean-field Lifshitz point by appropriate choice of the center B-block length. A positive $\bar{K}$ in the language of a Helfrich curvature expansion of the film free energy (per chain) [11]

$$F_{\text{film}} = (1/2)K(c_1 + c_2 - 2c_0)^2 + \bar{K}c_1c_2 \tag{1}$$

implies an instability of a flat copolymer film towards saddle-shaped deformations, *i.e.* those with principal curvatures c_1 and c_2 of opposite signs. If in addition the system is symmetrically composed (see below), the spontaneous curvature c_0 can be made to vanish. Under such conditions, a *tricontinuous* microemulsion produced by fluctuations near the mean-field Lifshitz point would be expected to transform into an *ordered tricontinuous* mesophase (*i.e.* OTDD or gyroid) on increasing the copolymer content [12], rather than a lamellar phase as in the symmetric A/B/AB system. Thus, tricontinuous structures might be obtained over a broad range of ABC triblock concentrations.

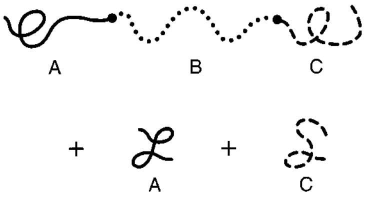

Fig. 1. The symmetric polymer alloy under consideration consists of an ABC triblock copolymer with equal-sized A (solid) and C (dashed) end blocks, blended with equal amounts of comparable molecular weight A and C homopolymers. The central (dotted) B-block constitutes a volume fraction f_B of the copolymer and the ratio of homopolymer to copolymer molecular weights is denoted α.

2 Theory

The specific polymer blend under consideration in this paper consists of two equal molecular weight type A and C homopolymers and a "symmetric" ABC triblock copolymer (see Fig. 1). The block copolymer is symmetric in the sense that the A and C blocks have equivalent molecular volumes. Moreover, we assume that the (unfavorable) A-B and B-C segmental interactions are *matched* and are weaker than the A-C interactions. Thus, we require that the binary Flory segmental interaction parameters satisfy [13] $\chi_{\text{AB}} = \chi_{\text{BC}} < \chi_{\text{AC}}$. One simple way of meeting these criteria is to choose the central B block to be a random copolymer composed of A and C monomers. We denote the overall degree of polymerization of the triblock copolymer by N and the mid-block (B) volume fraction by f_{B}. Because the A and C end blocks have the same molecular volumes, it follows that $f_{\text{A}} = f_{\text{C}} = (1 - f_{\text{B}})/2$. For simplicity, the segment volumes (denoted v) and statistical segment lengths (denoted b) of all three monomeric species (A, B and C) are taken to be the same and all polymers are assumed to be monodisperse. Furthermore, the ratio of the homopolymer to block copolymer molecular weights is denoted α, so that αN is the degree of polymerization of the two homopolymers. Finally, the two homopolymer components are to be mixed in equal proportions with the triblock; hence, there is only one independent composition variable other than f_{B}. We choose the total (A + C) homopolymer volume fraction, denoted ϕ, as this free variable.

We have used mean-field theory to locate the isotropic Lifshitz point for the symmetric A/C/ABC blend described above. The appropriate order parameter is the field $\eta(\mathbf{r}) = \delta\phi_{\text{A}}(\mathbf{r}) - \delta\phi_{\text{C}}(\mathbf{r})$, where $\delta\phi_i(\mathbf{r})$ is the local deviation of the volume fraction of type i segments (contributed by both the homopolymers and copolymer) from

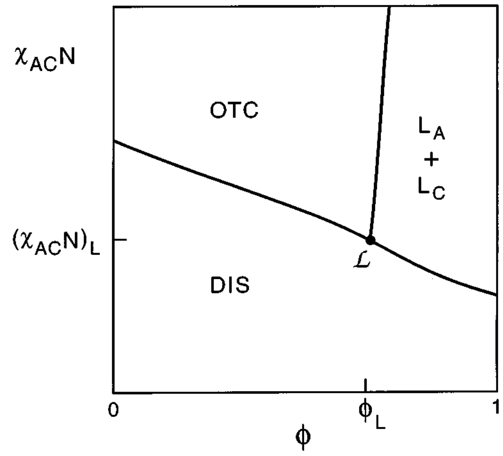

Fig. 2. Schematic *mean-field* phase diagram of incompatibility degree, $\chi_{AC}N$, verses total homopolymer volume fraction, ϕ, for an alloy with $f_B \approx 0.65$ and $\alpha \approx 0.1$. Phases denoted by DIS, OTC, and $L_A + L_C$, correspond respectively to the disordered liquid, an ordered-tricontinuous mesophase (either the OTDD or gyroid structure), and coexisting A-rich and C-rich liquid phases. The isotropic Lifshitz point, denoted by $\mathcal{L}$, is located with the use of equations (3, 4).

the uniform average value of this volume fraction. The order parameter $\eta(\mathbf{r})$ vanishes in a disordered molten alloy, attains a nonvanishing uniform value in situations of coexisting disordered liquid phases, and is a spatially-periodic function of finite amplitude under conditions where an ordered mesophase is present. A Landau expansion of the blend free energy density (appropriate for weakly ordered phases) is helpful in locating the Lifshitz point:

$$F = A_2\eta^2 + A_4\eta^4 + C_2|\nabla\eta|^2 + C_4(\nabla^2\eta)^2 + \cdots \qquad (2)$$

The Landau coefficients A_2, A_4, C_2, and C_4 are functions of f_B, ϕ, $\chi_{AC}N$, $\chi_{AB}N$, and α; the absence of terms with odd powers of η is a consequence of the symmetry of the system under interchange of the A and C labels.

We have obtained mean-field expressions for the Landau coefficients by applying the random phase approximation (RPA) [9,14]. The critical line between the disordered phase and coexisting A-rich and C-rich disordered liquid phases, traced out by varying ϕ away from 1, is identified by the condition $A_2 = 0$. This leads to

$$\chi_{AC}N = 2/(\alpha\phi). \qquad (3)$$

For ϕ very close to unity, we find that A_4, C_2, and C_4 are all positive, confirming that the critical line describes a liquid-liquid phase separation. In Figure 2, this curve is shown schematically in the $\chi_{AC}-\phi$ plane [15].

As the homopolymer content ϕ is lowered further, the coefficient C_2 eventually vanishes; the conditions $A_2 = C_2 = 0$, $A_4 > 0$, $C_4 > 0$ locate the mean-field isotropic Lifshitz point. This occurs for $\phi = \phi_L$, where

$$\phi_L = \frac{1 - 3f_B^2 + 2f_B^3}{1 - 3f_B^2 + 2f_B^3 + 2\alpha^2}\,\cdot \qquad (4)$$

The condition $A_4 > 0$ ensures that the Lifshitz point is stable (in mean-field theory) and is not preempted by a tricritical point. Tricritical behavior is generally undesirable because it leads to three-phase coexistence of two (A-rich and C-rich) liquid phases with a (ABC-rich) mesophase. If we adopt the regular solution theory estimate [13] of $\chi_{AB} = \chi_{AC}/4$, the Lifshitz point proves to be stable for

$$\alpha < 1 - 3f_B^2 + 2f_B^3. \qquad (5)$$

Because the expression on the right hand side of this inequality varies between 1 and 0, respectively, as f_B is varied between 0 and 1, we see that homopolymers of lower molecular weight than the ABC triblock are required for stable Lifshitz points. For larger values of α, we anticipate that the ABC triblock would be sufficiently incompatible with the homopolymers that it would macroscopically separate out to form its own mesophase [9,16,17].

When the homopolymer fraction of the blend, ϕ, is decreased below ϕ_L, the Landau coefficient C_2 becomes negative and swollen mesophases are energetically favored over homogeneous phases. As shown in Figure 2, the critical line for $\phi < \phi_L$ is a line of order-disorder transitions (ODT's) that connects the Lifshitz point to the ODT of a pure ABC triblock copolymer melt. We will subsequently argue that, for certain values of f_B, the mesophase above this line can be an ordered tricontinuous (OTC) structure, either OTDD or gyroid.

The discussion concerning the phase behavior of our model A/C/ABC blend has, up to this point, ignored the role of thermal fluctuations. As discussed previously, Lifshitz points in such systems are suppressed by fluctuations and a "channel" of polymeric microemulsion invades the (mean-field) ordered phase (see Fig. 3). For the present model alloy, this microemulsion is expected to be tricontinuous — *i.e.* A, B and C all form continuous networks that percolate through the fluid (see Fig. 4). While a detailed calculation of the shape and width of this channel is quite difficult, we can make a few qualitative statements. The *right* boundary of the channel in Figure 3 should be located at a composition quite close to ϕ_L, since homogeneous phases are much less susceptible to thermal fluctuations than swollen mesophases [6,7]. From a low temperature perspective (*i.e.* large $\chi_{AC}N$), this transition from two coexisting liquid phases to the microemulsion can be identified with a point where the A-C interfaces are *saturated*, *i.e.* the effective A-C interfacial tension vanishes. In contrast, a low temperature view of the *left* boundary of the channel is of an unbinding transition, whereby the ordered mesophase melts into a disordered microemulsion on increasing the homopolymer fraction ϕ.

In order to say anything more specific about the phase diagram, we now need to address the type of mesophase to be expected in the composition range, $0 < \phi < \phi_L$. In the extreme limit of pure (symmetric) ABC triblock, *i.e.* $\phi = 0$, there is both experiment [5] and theory [18] to guide us. The experimental situation [5] is that for $0 < f_B \lesssim 0.42$, lamellar mesophases are observed. In the composition range of $0.48 \lesssim f_B \lesssim 0.66$, a tricontinuous cubic mesophase is evident — most likely an OTDD

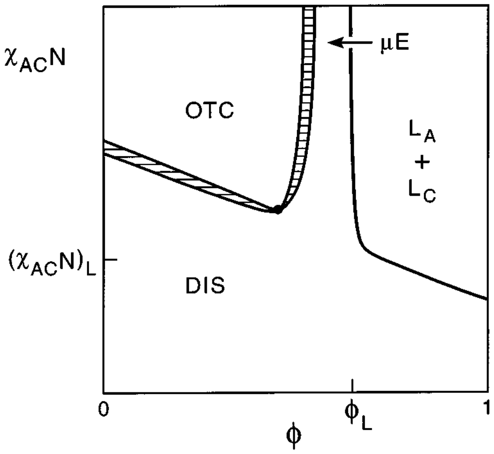

Fig. 3. Schematic phase diagram for the alloy treated in Figure 2, but taking account of the effect of *thermal fluctuations*. Fluctuations destroy the isotropic Lifshitz point and open up a channel of tricontinuous microemulsion, denoted by μE. The microemulsion is a continuous extension of the disordered phase, but more strongly fluctuating and with larger amplitude inhomogeneities. Narrow two-phase regions of coexistence between ordered and disordered phases are schematically indicated.

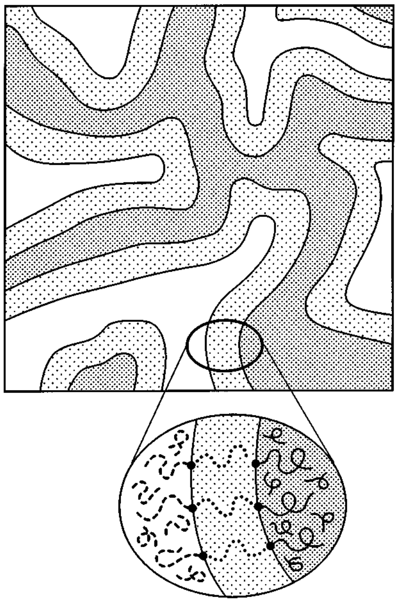

Fig. 4. Schematic illustration of the tricontinuous microemulsion phase. The B-blocks form a molten film (dotted) that separates A-rich and C-rich regions. The A-rich regions are composed of the A end blocks of the copolymer, swollen by the low molecular weight A homopolymer (solid curves). Similarly, the C-rich regions are composed of the C end blocks, swollen by the C homopolymer (dashed curves). This case of swollen A and C layers is referred to as "wet brush" conditions.

structure, although this assignment is not yet definitive. In the range $0.68 \lesssim f_{\mathrm{B}} \lesssim 0.76$, square arrays of A and C cylinders are observed in a continuous B matrix (tetragonal structure). Finally, for $0.78 \lesssim f_{\mathrm{B}} < 1$, a body-centered-cubic (CsCl) array of A and C spheres in a continuous B matrix is found [19]. These observations are consistent with recent theories [18], although most do not address the complex tricontinuous phase.

Since our objective is to stabilize co-continuous phases over the broadest range of ϕ possible, we now restrict consideration to ABC triblocks with block fractions in the tricontinuous range, $0.48 \lesssim f_{\mathrm{B}} \lesssim 0.66$, and ask whether an *ordered* tricontinuous mesophase can be swollen by the symmetrical addition of A and C homopolymer to continuously connect with the *disordered* tricontinuous microemulsion in the vicinity of ϕ_{L}. To answer this question, we have performed low temperature (strong segregation) calculations of the bending moduli for a film of ABC triblock copolymer that separates bulk phases of A and C homopolymers.

We begin with a calculation of K and $\bar{K}$ for a triblock film under conditions of saturation, *i.e.* homopolymer concentrations near ϕ_{L} in the microemulsion channel. Restricting consideration to low molecular weight homopolymers, *cf.* equation (5), the A and C polymer brushes of the film are swollen by the corresponding homopolymers. This is the so-called "wet brush" regime [10]. We further assume that the central B-block is molten and strongly segregated from the A and C layers, and that mean-field exponents can be used to describe the conformational statistics of tethered chains in the swollen layers. By following established procedures [10,20] to compute the free energy per chain of films bent into cylinders and spheres and combining these results with equation (1), the two elastic constants can be evaluated. We find

$$\begin{aligned} K\alpha^2/(b^2N) = {} & (1/4)f_{\mathrm{B}}^3S^{-4} + 0.33782\, f_{\mathrm{B}}^2(1-f_{\mathrm{B}})S^{-8/3} \\ & +0.18750\, f_{\mathrm{B}}(1-f_{\mathrm{B}})^2S^{-2} \\ & +0.02602\,(1-f_{\mathrm{B}})^3S^{-4/3} \end{aligned} \tag{6}$$

$$\begin{aligned} \bar{K}\alpha^2/(b^2N) = {} & (1/2)f_{\mathrm{B}}^3S^{-4} - 0.09376\, f_{\mathrm{B}}(1-f_{\mathrm{B}})^2S^{-2} \\ & -0.01586\,(1-f_{\mathrm{B}})^3S^{-4/3} \end{aligned} \tag{7}$$

where S is the interfacial area per triblock chain, Σ, normalized by a characteristic area per chain, $(v/b)(\alpha N)^{1/2}$. The condition of saturation leads to an algebraic equation for S

$$3\, f_{\mathrm{B}}S^{-3} + 0.81077\,(1-f_{\mathrm{B}})S^{-5/3} - 2G = 0 \tag{8}$$

where G is related to the A-B (or, equivalently, B-C) interfacial tension γ_{AB}: $G \equiv \gamma_{\mathrm{AB}}(v/b)N^{1/2}\alpha^{3/2}$. Use of Helfand-Tagami theory [21] to relate γ_{AB} to χ_{AB}, *i.e.* $\gamma_{\mathrm{AB}} = b(\chi_{\mathrm{AB}}/6)^{1/2}/v$, together with the regular solution theory [13] estimate of $\chi_{\mathrm{AB}} = \chi_{\mathrm{AC}}/4$, leads to an alternative expression for G:

$$G = \frac{\alpha}{2(3\phi_{\mathrm{L}})^{1/2}}\left[\frac{\chi_{\mathrm{AC}}N}{(\chi_{\mathrm{AC}}N)_{\mathrm{L}}}\right]^{1/2}. \tag{9}$$

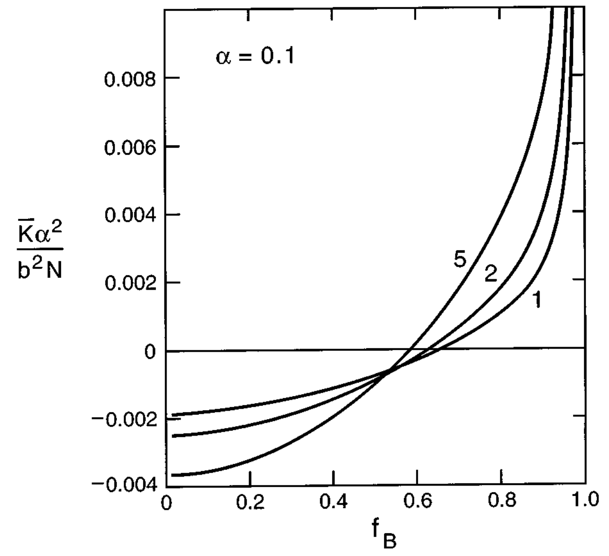

Fig. 5. Normalized saddle-splay modulus $\bar{K}$ verses mid-block fraction f_{B} for a monolayer film of ABC triblock copolymer swollen with A and C homopolymer at saturation ($\phi \approx \phi_{\mathrm{L}}$). The molecular weight ratio is fixed at $\alpha = 0.1$ and the labels 1, 2, and 5 correspond to the respective values of $\chi_{\mathrm{AC}}/(\chi_{\mathrm{AC}})_{\mathrm{L}}$.

Here, $(\chi_{\mathrm{AC}}N)_{\mathrm{L}}$ denotes the degree of incompatibility at the mean-field Lifshitz point, which is obtained from equation (3) with $\phi \to \phi_{\mathrm{L}}$.

From equation (6), it is clear that the bending modulus K is positive regardless of the state of swelling (value of S). This implies that a flat film is stable with respect to long-wavelength cylindrical deformations. Furthermore, it is straightforward to show that a flat film is also stable to bending into spheres of large radius ($2K + \bar{K} > 0$), regardless of the value of S. The expression for the saddle-splay modulus $\bar{K}$, however, contains terms of both signs, so numerical studies are needed to establish the stability of a flat film to long-wavelength saddle-shaped deformations.

Figure 5 shows a plot of the normalized saddle-splay modulus, $\bar{K}\alpha^2/(b^2N)$, verses the mid-block fraction f_{B} for $\alpha = 0.1$ and several values of $\chi_{\mathrm{AC}}/(\chi_{\mathrm{AC}})_{\mathrm{L}}$. Evidently, $\bar{K}$ changes sign in the vicinity of $f_{\mathrm{B}} = 0.6$, signaling an instability of the film to saddle-splay for larger f_{B} values. This instability arises from the frustration of both A-B and B-C interfaces desiring to curve away from B to minimize the elastic free energy; the frustration is partially alleviated by saddle-splay of the overall film. A closely related phenomenon was noted in studies of dry A-B diblock copolymer bilayers immersed in B homopolymer [22]. As the temperature is lowered, *i.e.* $\chi_{\mathrm{AC}}/(\chi_{\mathrm{AC}})_{\mathrm{L}}$ increased, there is a gradual shift of the saddle-splay instability to lower f_{B}. This shift is limited, however, because our wet brush calculation is predicated on the volume fraction of tethered chains in the A and C layers being small compared with unity. This translates into the criterion $S \gg 2.2$. For $\alpha = 0.1$, this threshold is reached for $\chi_{\mathrm{AC}}/(\chi_{\mathrm{AC}})_{\mathrm{L}} \approx 10$, at which point the A and C layers of the film are nearly "dry".

We have also performed a dry brush calculation in which all three layers are assumed to be strongly segregated and the homopolymers are completely excluded from the film. The result for the saddle-splay modulus is

$$\bar{K} = \bar{K}_0 \left[\frac{1}{2} f_{\mathrm{B}}^3 - \frac{3\pi^2}{64} f_{\mathrm{B}}(1 - f_{\mathrm{B}})^2 - \frac{\pi^2}{80}(1 - f_{\mathrm{B}})^3 \right] \qquad (10)$$

where $\bar{K}_0 = v^4 N^3/(b^2 \Sigma_0^4)$ is related to the equilibrium area per triblock in a flat film, Σ_0. The expression in square brackets changes sign from negative to positive at $f_{\mathrm{B}} \approx 0.51799$, again indicating a saddle-splay instability. Evidently, the instability threshold is higher in a wet brush because the swollen A and C layers tend to reduce the elastic frustration of the individual A-B and B-C interfaces. We also note that this predicted *long-wavelength* saddle-splay instability of a molten film lies quite close to the experimental phase boundary between lamellae and OTC in neat ABC triblock copolymers [5].

3 Discussion

The above results suggest that a window of opportunity exists in A/C/ABC alloys for connecting ordered tricontinuous mesophases with the disordered tricontinuous microemulsion present near ϕ_{L}. The mid-block fraction must be maintained in the range of $0.48 \lesssim f_{\mathrm{B}} \lesssim 0.66$ to ensure that tricontinuous ordered phases are present for $\phi \to 0$. The constraint of stable Lifshitz points, equation (5), then demands that we choose $\alpha \lesssim 0.27$. However, if α is too small, the saddle-splay instability is moved to larger f_{B} (at least for temperatures near the Lifshitz point), outside of the acceptable range. In such a case, the microemulsion would likely transform to a lamellar phase on the addition of further copolymer, rather than to the desired tricontinuous cubic mesophase. In practice, blends with $f_{\mathrm{B}} = 0.65$ and $\alpha = 0.1$, or $f_{\mathrm{B}} = 0.60$ and $\alpha = 0.2$ appear ideally suited for experimental studies. Such alloys should exhibit co-continuity over an exceptional range of triblock copolymer compositions; *i.e.* $0 \leq \phi \leq \phi_{\mathrm{L}}$, where $\phi_{\mathrm{L}} = 0.93$ and 0.81, respectively.

To date, there have been very few experimental studies of A/C/ABC systems. Auschra and Stadler [23] considered a related A'/C'/ABC blend in which specific (attractive) interactions between A and A' and C and C' were used to generate strong interfacial adhesion of the copolymer film to the bulk homopolymer phases. However, in their experimental system, $\chi_{\mathrm{AB}} \sim \chi_{\mathrm{BC}} \gg \chi_{\mathrm{AC}}$, which violates the assumptions of the present paper. Moreover, f_{B} was not chosen large enough to stabilize tricontinuous structures. Nevertheless, Auschra and Stadler did observe a fascinating "raspberry-type" morphology, in which the "hated" B center block was collapsed into bead-like droplets that decorated the A-C interfaces.

A study more closely related to the model system of the present paper was that of Harrats *et al.* [24]. These authors examined morphologies obtained by melt blending low-density polyethylene (LDPE) and polystyrene (PS) homopolymers with a tapered block copolymer of PS and hydrogenated polybutadiene (HPB). The tapered region of the copolymer could be crudely modeled as a central "B" block with $f_{\mathrm{B}} \approx 0.3$. At relative proportions 75/15/10 of PS, LDPE, and tapered block copolymer, Harrats *et al.* [24] observed very stable co-continuous structures that were robust under annealing. Moreover, closely related blends with PS-HPB diblock copolymers substituted for the tapered "triblocks" yielded co-continuous structures that were considerably less stable to heat treatment. While rheological contrast (*e.g.* differences in viscosity) was likely responsible for the formation of co-continuous structures in these blends (under melt processing conditions), it is interesting to note the stabilizing influence of inserting a tapered B block. Based on the present findings, we speculate that tapered copolymers with $f_{\mathrm{B}} \approx 0.6$ might actually render co-continuous structures thermodynamically stable in blends with PS and LDPE, and therefore resistant to indefinite thermal treatment.

We close with a few comments about applications. Alloys of the type proposed in the present paper could be used as conventional thermoplastics and processed in the high-temperature disordered state. Vitrification or crystallization of A, B and/or C on cooling would arrest the structure for solid state applications, *e.g.* for membranes, electrodes, etc. An interesting alternative would be to use A and/or C materials that could be thermally or radiatively crosslinked (cured) after processing. The low homopolymer molecular weight requirement could then be used to advantage, as self-assembly into co-continuous structures would be facile and processing easy. Curing would permanently fix the structures. Themoset materials prepared in this way might include novel epoxy resins and hybrid organic/inorganic structures.

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