Orthorhombic *Fddd* Network in Triblock and Diblock Copolymer Melts

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The phase behavior of *ABC* triblock and *AB* diblock copolymer melts is investigated by self-consistent field theory, while allowing for (among other candidates) the orthorhombic *Fddd* (O^{70}) network phase identified in recent experiments with poly(isoprene-*b*-styrene-*b*-ethylene oxide) (ISO) triblocks. Predicted phase diagrams for triblocks similar to ISO contain an O^{70} phase bordered by gyroid, lamellar, and alternating gyroid phases, in agreement with experiment. The O^{70} network is also found to be stable in diblock melts within a narrow region that overlaps the weak segregation end of the gyroid region found in previous calculations.

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The formation of periodic microstructures in diblock copolymer melts is among the best understood phenomena in soft condensed matter physics. Several decades of research culminated in the mid 1990s in broad agreement between experimental observations and the phase diagram calculated by self-consistent field theory (SCFT) by Matsen and Schick [1]. The resulting phase diagram contains four types of observed structure: body-centered-cubic spheres (*S*), hexagonally ordered cylinders (*C*), lamellar (*L*) (or smectic-*A*), and a double-gyroid network (*G*). Several groups have since begun to explore the much larger parameter space of so-called *ABC* triblock copolymers. The types of *ABC* triblocks that are easiest to understand are those in which the thermodynamic repulsion between the *A* and *C* end blocks is significantly larger than those between the *B* block and either end block [2]. These characteristically form structures with no *AC* interfaces, and have been found to form several structures that are either core-shell analogs of those found in diblock copolymers, such as the core-shell gyroid in which a *B* domain forms a shell around an *A* or *C* network, or alternating versions of the diblock phases, in which the *A* and *C* blocks organize on alternating sublattices, as in an NaCl structure of alternating *A* and *C* spheres. In addition, Bates and coworkers [3–5] have identified one equilibrium structure, an orthorhombic network that they call the O^{70} phase (denoting orthorhombic, space group 70, or *Fddd*), that is not a variant of any equilibrium phase observed in diblock copolymers or small molecule surfactants. The O^{70} phase, like the gyroid, is a network of threefold connected struts of a minority component. In this Letter, we first report SCFT calculations for this class of *ABC* triblocks, focusing on the region of parameter space in which O^{70} phase has been experimentally observed, and then revisit the diblock copolymer phase diagram.

The phase behavior for *ABC* triblocks composed of monomers with specified statistical segment lengths is governed by 5 additional parameters: two independent volume fractions, e.g., f_A and f_B, and the products $\chi_{AB}N$, $\chi_{AC}N$, and $\chi_{BC}N$ of three Flory-Huggins binary interaction parameters with the total degree of polymerization N. We focus here on *ABC* triblocks in which $\chi_{AC} \gg \chi_{BC}$ and $\chi_{BC} \sim \chi_{AB}$. Investigations of such systems have included studies of poly(butadiene-*b*-polystyrene-*b*-poly-vinyl-pyridine) (PB-PS-PVP) and poly(methylmethacrylate-*b*-styrene-butadiene) (PMMA-PS-PB) by Abetz and co-workers [6,7], of poly(isoprene-*b*-styrene-*b*-vinylpyridine) (PI-PS-PVP) by Matsushita and co-workers [8–10], and of poly(isoprene-*b*-styrene-*b*-ethylene-oxide) (PI-PS-PEO) by Bates and co-workers [3–5]. Matsushita and co-workers [8–10] studied PI-PS-PVP triblocks with $f_A = f_C$, and observed the phase sequence lamellae (*L*), alternating gyroid (G^A), alternating cylinders (C^A), and alternating/NaCl spheres (S^A) with increasing f_B. Matsen subsequently calculated phase diagrams for *ABC* triblocks with $f_A = f_C$ and $\chi \equiv \chi_{AB} = \chi_{BC}$, and found the observed sequence L-G^A-C^A-S^A with decreasing f_B. Matsen [11] also proposed the proper identification of the alternating gyroid phase, which Matsushita *et al.* had initially reported to be a double-diamond structure. Bates and coworkers [3–5] have explored the region of the phase triangle for PI-PS-PEO (ISO) that is shown in Fig. 1. At temperatures near the order-disorder transition (ODT), they found regions of two-domain and three-domain lamellae (*L*) separated by a sequence of three different network phases with increasing f_B: core-shell gyroid network (*G*), the O^{70} network, and an alternating gyroid network (G^A). In addition, Cochran and Bates [12] have observed a distinct orthorhombic network with space group *Pnna*, denoted O^{52}, as a shear-induced metastable phase of a poly(cyclohexane-*b*-ethyl ethylene-*b*-ethylene) melt that forms an O^{70} network in equilibrium.

We have studied the phase behavior of triblock copolymer melts as functions of composition for two sets of values of the parameters χ_{ij}, b_i, and N, both of which correspond roughly to the ISO systems of Refs. [4,5]: we considered both a somewhat "idealized" model in which (following Matsen) we take $\chi_{AB} = \chi_{BC}$ and equal statistical segment lengths $b_A = b_B = b_C$, in which we take

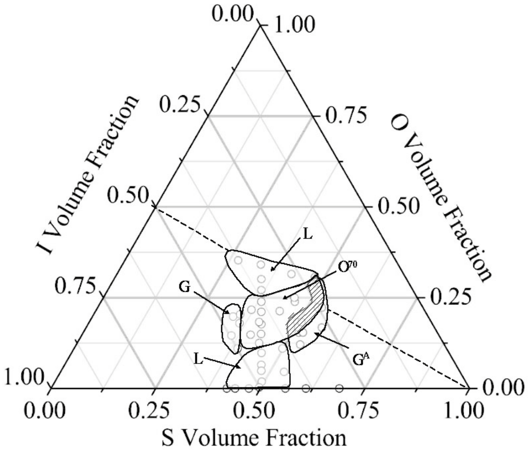

FIG. 1. Phase behavior of ISO at temperatures near the ODT, in the range 100 °C $< T <$ 225 °C near the ODT. Open dots represent compositions of polymers that were studied; solid lines are guides to the eye that enclose different phases. Within the cross-hatched region, there is a transition from O^{70} to G^A with increasing temperature. Adapted from Epps *et al.* [4].

$\chi_{AB}N = \chi_{BC}N = 13$ and $\chi_{AC}N = 35$, and a more realistic model in which we use published values for the χ's and b's. In the more realistic model, we used published values of $\chi_{ij}(T)$ at 100 °C [13] to obtain $\chi_{IS}N = 11.0$, $\chi_{SO}N = 14.2$, and $\chi_{IO} = 45.8$ for $N = 250$ (Epps *et al.* studied $N = 200$–300) and $b_I = 6.0$ Å, $b_S = 5.8$ Å, and $b_O = 7.8$ Å [14], with all parameters defined using a monomer reference volume of 118 Å^3.

The phase behavior of both models has been investigated by comparing free energies of 13 candidate phases that have been either observed or postulated previously in AB diblock or this class of ABC triblock copolymers. These candidates, listed with symbols and space groups, are: the four observed equilibrium diblock copolymer phases [disordered (D), lamellar (L), hexagonal cylinders ($C/P6mmm(2d)$), and double gyroid ($G/Ia\overline{3}d$)], double diamond ($Q^{228}/Fd\overline{3}c$), perforated lamellar phases with both ab stacking ($PL_{ab}/P6_3mmc$) and abc stacking ($PL_{abc}/R\overline{3}m$), alternating spheres/NaCl ($S^A/Pm\overline{3}m$), alternating cylinders ($C^A/p2mm$), alternating gyroid ($G^A/I4_132$), and alternating diamond ($Q^{228}/Fd\overline{3}m$), the orthorhombic $Fddd$ network ($O^{70}/Fddd$), and a $Pnna$ network ($O^{52}/Pnna$). For each of these phases, we solve the SCFT equations using a spectral method similar to that of Matsen and Schick [1], using the variable unit-cell algorithm described in Ref. [15].

Figure 2 shows the calculated phase diagram for our idealized model, with $\chi_{AB}N = \chi_{BC}N = 13$. In addition to the phases present in the diblock phase diagram, we find regions where G^A, S^A, and the O^{70} network are stable. None of the other candidate phases are stable anywhere in the phase triangle. The O^{70} phase is bordered by L, G, and G^A, as found in Refs. [4,5]. For these parameters, the O^{70} phase occupies a region between a G phase that contains a network of A domains within a matrix of B and dissolved C, and a G^A phase of alternating A and C networks. Here, the O^{70} phase is a network of A in a matrix of B that contains rather weakly segregated domains of C. Despite some similarities, the phase diagram for the idealized model is qualitatively different from that found for ISO by Epps *et al.* [4], who found a much wider O^{70} region that straddles the $f_A = f_B$ isopleth.

Figure 3 is a partial phase triangle for our more realistic model of ISO, in the region $f_I \geq 0.25$ and $f_S \geq 0.25$. For this choice of parameters, the phase diagram is strikingly similar to that found by Epps *et al.*: the O^{70} phase window straddles the $f_A = f_B$ isopleth, it is bounded above and below by distinct two- and three-domain L regions, and it borders a core-shell G phase with an A-rich matrix and an alternating G phase. In this case, the O^{70} phase near $f_A = f_B$ is best described as a network of C domains surrounded by a matrix of B and A, with A only partially segregated from B within the matrix. The predicted sizes and locations of the L, O^{70}, G, and G^A phases are similar to those found experimentally, with some notable discrepancies: the predicted transition from two-domain lamellae to O^{70} occurs at significantly higher values of f_C than those found experimentally, and the model does not predict the observed phase progression $G \rightarrow O^{70} \rightarrow G^A$ with increasing f_B along any line of fixed f_C. The sensitivity of the phase boundaries to changes in our choice of parameters will be discussed further elsewhere.

For both of these sets of parameters, we were surprised to find regions in which the O^{70} phase is stable that extend to the line $f_C = 0$, implying that O^{70} must be a stable phase of AB diblock copolymer melts. In light of this, we have recalculated the phase diagram for a diblock melt as a

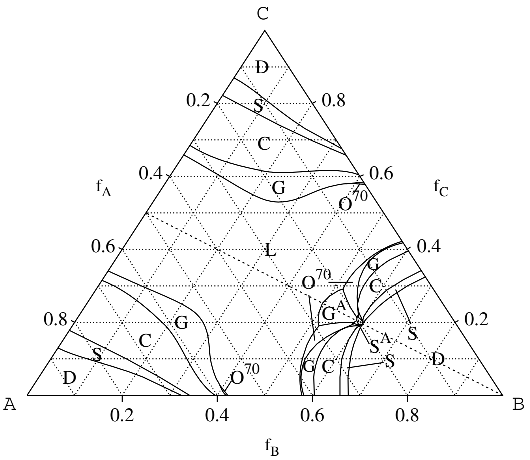

FIG. 2. SCFT phase behavior of an idealized triblock copolymer with $\chi_{AC}N = 35$, $\chi_{AB}N = \chi_{BC}N = 13$, and $b_A = b_B = b_C$. This phase diagram is symmetric about the $f_A = f_C$ isopleth, shown as a dashed line.

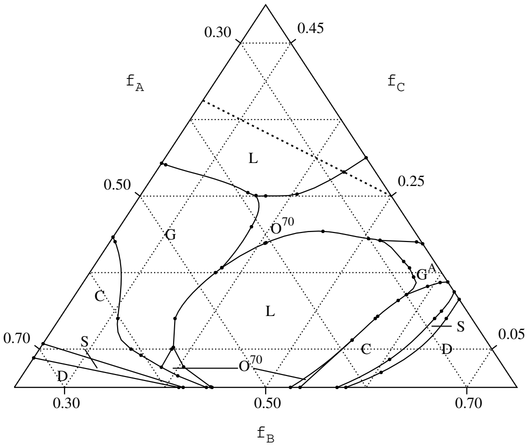

FIG. 3. A partial phase triangle for a model ISO triblock copolymer, with interaction parameters $\chi_{IS} = 11.0$, $\chi_{SO} = 14.2$, and $\chi_{IO} = 45.8$. The dashed line shows where $f_A = f_C$. Points represent compositions at which the position of a phase boundary has been accurately determined, which have been connected by smooth lines to generate the phase boundary lines.

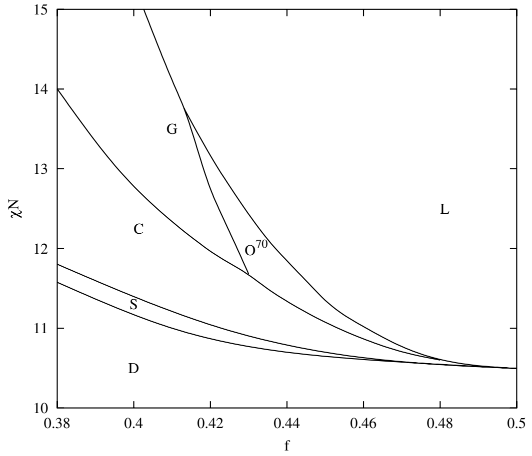

FIG. 4. SCFT phase diagram of a diblock copolymer with segment lengths $b_A = b_B$, as a function of $f = f_A$ and χN.

function of $f = f_A$ and χN, for systems with $b_A = b_B$, while including the O^{70} phase as a candidate structure. The relevant part of the resulting phase diagram is shown in Fig. 4. The O^{70} network is found to be stable within a narrow window that overlaps the low χN end of the region in which Matsen and Schick [1] predicted a stable G phase. The formation of an O^{70} phase thus supercedes the $L/G/C$ triple point found by these authors at $\chi N = 11.14$ and $f = 0.452$. The boundaries of this phase instead meet at an $L/G/O^{70}$ triple point at $\chi N = 13.76$ and $f = 0.413$ and at a $C/G/O^{70}$ triple point at $\chi N = 11.64$ and $f = 0.431$. It appears that the O^{70} phase may extend as a narrow sliver all the way to the critical point at $\chi N = 10.495$ and $f = 0.5$, though we remain uncertain about this point due to limited numerical accuracy. Figure 5 shows an O^{70} phase with $f_A = 0.43$ and $\chi N = 12.0$. As in the gyroid phase, the minority A domain forms a network of threefold connected junctions within a matrix of B. At these low values of χN, the interfaces are diffuse, and neither monomer exceeds 85% purity at any point within the unit cell. The shape of the calculated phase diagram, and the underlying similarity of the O^{70} and gyroid phases as threefold networks, suggests a view of the O^{70} network as a competitor to the G network, which is apparently preferred over the G phase in the limit of weak segregation.

Laradji *et al.* [16] have calculated the local stability within SCFT of the previously known diblock phases with respect to arbitrary, infinitesimal perturbations of the monomer density fields. They concluded that the G phase is locally unstable for all $\chi N \leq 12$ along a path for which the C and L phases have equal free energies. This path passes through the center of the region in which the O^{70} phase is stable, and includes a segment with $\chi N \geq 11.14$ along which G has a lower free energy than C or L. It is thus tempting for us to associate the reported instability of the G phase, at least for $\chi N > 11.14$, as an instability towards the O^{70} phase. Regarding the nature of the instability, however, Laradji *et al.* [16] reported only that, at $\chi N = 10.75$, it appears to represent an epitaxial transformation from G to C. Matsen later studied the epitaxial pathway between G and C [17] in greater detail, and has argued that the reported instability of G above the G-C-L triple point may have been a result of numerical inaccuracy [18]. The stability of the G phase, and the nature of any instabilities, deserves a reexamination.

A striking feature of small-angle x-ray scattering (SAXS) from the O^{70} phase of ISO triblocks [5] is the near-coincidence of the wave numbers for the first three scattering peaks, which are the {004}, {111}, and {022} reflections. These three peaks would coincide exactly for

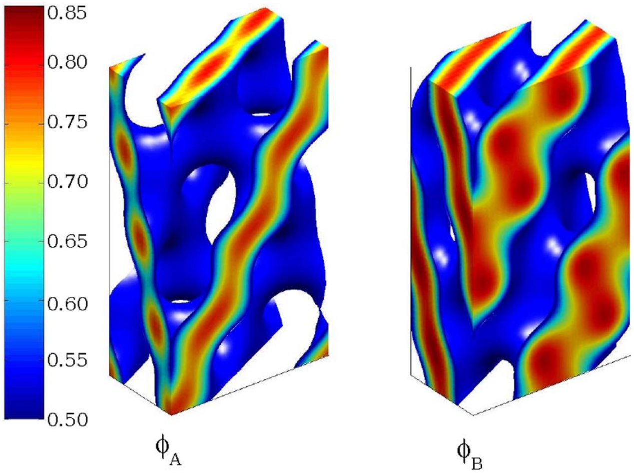

FIG. 5 (color online). The $\phi_A = \phi_B = 0.5$ isosurfaces, as well as composition profiles along cross sections of the A- and B-rich domains where they cross the unit-cell boundaries, for a diblock copolymer with $b_A = b_B$, $f_A = 0.43$, and $\chi N = 12$.

a unit cell with cell parameters (a, b, c) with ratios

$$(a{:}b{:}c) = (1{:}2{:}2\sqrt{3}). \quad (1)$$

Bailey *et al.* [3] originally proposed a ball-and-stick model of the O^{70} phase as a network of equal length struts connected at 120 ° angles at threefold junctions. This model yields ratios $(a{:}b{:}c) = (1{:}\cot\theta{:}\sqrt{3}\csc\theta)$, in which θ is an adjustable angle, that do not agree with those given in Eq. (1) for any choice of θ.

Our SCFT predictions for the unit-cell parameters coincide closely with Eq. (1), and thus agree with the SAXS data of Epps *et al.* [5]. The agreement with Eq. (1) is particularly striking for very weakly segregated structures near the critical point at $\chi N = 10.495$: for example, at $\chi N = 10.61$ and $f = 0.48$, we find fractional deviations of b/a from 2 and of c/a from $2/\sqrt{3}$ of less than 10^{-3}. SCFT predictions for the ratios c/a and b/a generally differ slightly from these values in both diblocks and ABC triblock, but remain within 3% of these values throughout the stable O^{70} regions in both the diblock melt and in our realistic model of ISO.

The near-coincidence of the first three families of Bragg peaks of the O^{70} phases may be understood in terms of Leibler's weak segregation theory [19]. Leibler constructed a Landau expansion of the SCFT free energy, in which the quadratic term becomes unstable at the spinodal to ordering of composition modes with wave numbers equal to a critical value $q^{\star}$. The composition fields for an $Fddd$ phase with unit-cell parameters that obey Eq. (1) can be well approximated near the spinodal as superpositions of 14 plane waves with wave numbers all equal to q^*, corresponding to the {004}, {111}, and {022} families of reciprocal lattice vectors. An analysis of the stability of this structure relative to other ways of superposing sets of wave vectors of magnitude q^* would require a comparison of cubic and quartic contributions to the Landau expansion. We will pursue this elsewhere. We note here only that the $Fddd$ phase, like the S, C, and G phases, is stabilized by cubic contributions that are nonzero only for crystals in which there exist triplets of wave vectors of magnitude q^* that sum to zero. In the O^{70} phase, these triplets are $(022), (0\bar{2}2), (00\bar{4})$ and $(111), (\bar{1}11), (0\bar{2}\,\bar{2})$, and relatives thereof.

The O^{70} phase is found to be a stable phase of ABC triblocks that, in both our calculations and experiment, appears bordered by lamellar, core-shell gyroid and alternating gyroid phases. The predicted phase behavior of ISO is strikingly similar to that found experimentally when literature values are used for the interaction parameters, but is quite sensitive to the choice of parameters. We were surprised to find the O^{70} phase is also predicted to be a stable phase of diblock copolymer melts, for which it competes closely with the G phase, and is preferred over the G phase at weak segregations. The O^{70} phase has never been experimentally identified in a diblock melt. Since it is predicted to be stable only within a narrow very weakly segregated region, it is quite possible that this phase is suppressed by fluctuation effects in systems of moderate molecular weight [20]. Analysis of future experiments (or old data) on both diblock and ABC triblock copolymers should, however, be carried out with the possibility of an O^{70} network in mind.

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