The non-centrosymmetric lamellar phase in blends of ABC triblock and ac diblock copolymers

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The phase behaviour of blends of ABC triblock and ac diblock copolymers is examined using self-consistent field theory. Several equilibrium lamellar structures are observed, depending on the volume fraction of the diblocks, \( \phi_2 \), the monomer interactions, and the degrees of polymerization of the copolymers. For segregations just above the order-disorder transition the triblocks and diblocks mix together to form non-centrosymmetric lamellae. As the segregation is increased the triblocks and diblocks spatially separate either by macrophase-separating, or by forming a non-centrosymmetric (NCS) phase of alternating layers of triblock and diblock (...ABCcaABCca...). The NCS phase is stable over a narrow region near \( \phi_2 = 0.4 \). This region is widest near the critical point on the phase coexistence curve and narrows to terminate at a triple point at higher segregation. Above the triple point there is two-phase coexistence between almost pure triblock and diblock phases. The theoretical phase diagram is consistent with experiments.

I. INTRODUCTION

Materials which lack a centre of symmetry in the absence of a polarizing field are rare in nature, and have attracted much recent interest \[1\]. These non-centrosymmetric (NCS) materials can exhibit dipolar second-order nonlinear optical activity (second-harmonic generation) \[2\], in addition to piezoelectricity and pyroelectricity \[3\], without the need to apply a polarizing field. As such, NCS materials are of great technological interest. Recently, the capability to make NCS structures in block copolymer blends has been demonstrated experimentally \[1\]. Block copolymers consist of two (or more) chains, or blocks, of chemically distinct monomers covalently bonded end-to-end to form a single polymer. Competition between the repulsion of unlike blocks and the constraint that the blocks are attached together leads to the formation of ordered periodic structures. Block copolymers are promising materials to use in the design of NCS structures created using polymers have longer periods than those created previously using small molecules \[4\]. The periodicity of the structure can be changed by adjusting the block size, creating the potential to tune the wavelengths for second-harmonic generation. The dielectric properties of the blocks can be tailored to the desired application. Finally, block copolymers self-assemble into periodic NCS structures, so no microscale fabrication techniques are necessary to produce the NCS structure.

The key breakthrough in Ref. \[4\] that made possible the formation of NCS structures in block copolymers was the recognition that blends of ABC triblock copolymers and ac diblock copolymers, instead of pure melts of ABC triblock copolymers are required \[4\]. Here A, B and C refer to the chemical species of each block — the a and c blocks on the diblock are the same chemical species as the A and C blocks on the triblock. Pure ac diblock melts produce stable lamellar, hexagonally-packed cylindrical, body-centred cubic, and gyroid phases — all of which have centres of symmetry. Pure ABC triblock melts have an even richer phase diagram (see Refs. \[5\] and \[6\] for a discussion), but almost all of the phases so far discovered are centrosymmetric (CS) \[7\]. Compared to the pure phases, the behaviour of blends of triblocks and diblocks is relatively unexplored and is a topic of current fundamental interest.

In Ref. \[4\] only lamellar structures were reported, and we will restrict ourselves to discussing lamellar structures in this paper. As discussed in Refs. \[4\] and \[8\] and shown here in Fig. 1, possible lamellar structures in blends of ABC triblock and ac diblock copolymers include: triblock-rich and diblock-rich phases where the triblock and diblock mix together to form a “mixed” centrosymmetric structure (MCS phase), a NCS phase where the triblocks and diblocks spatially separate into alternating triblock and diblock layers (...ABCcaABCca...), a centrosymmetric double-layer phase (CS phase) of alternating double-layers of triblock and diblock (...ABCcaACB...), and regions of two-phase coexistence between these phases. When it is favourable for the triblocks and diblocks to spatially separate, it is unclear whether the system will achieve this by forming a structure with alternating triblock and diblock layers, or by macrophase separation. However, by carefully tuning the system parameters the authors of Ref. \[4\] were able to find the NCS structure.

Given the complexity of the pure ABC triblock phase diagram, and the even greater complexity of the phase diagram for the blend, a theoretical guide to experimental searches for the NCS structure would be helpful. The two main questions one would like to answer are: “What is the driving mechanism behind the formation of the NCS phase?” and “Where in phase space should one expect the NCS structure to be stable?” To date, the only theoretical studies of these blends are those of Leibler et al. \[9\].
Theoretical understanding of the driving mechanism, we do not focus on this here. Rather, our aim is to answer the second question by examining the effect of blend composition on the phase behaviour, the possibility for phase-separation, and the phase behaviour in the weak to intermediate segregation regime.

Consider an incompressible blend of ac diblock copolymers and ABC triblock copolymers in a volume $V$. The total degree of polymerization of the diblock is $N$; for the triblock it is $\Omega N$ (thus $\Omega$ is the ratio of the triblock degree of polymerization to that of the diblock). The diblock consists of an $a$-block, with a degree of polymerization $f_{2A}N$, and a $c$-block, with a degree of polymerization $f_{2C}N$. The diblock composition variables satisfy $f_{2A} + f_{2C} = 1$. Similarly, the triblock consists of three blocks with degrees of polymerization $f_{3\alpha}\Omega N$, where $\alpha = A$, $B$, or $C$. The triblock composition variables satisfy $f_{3A} + f_{3B} + f_{3C} = 1$. We scale distances by the Gaussian radius of gyration of the diblock, $R_g = b(N/6)^{1/2}$. The monomer statistical Kuhn length $b$ and the bulk monomer density $\rho_0$ are assumed to be the same for all three chemical species. In what follows, we will scale the chain arc-length by the diblock degree of polymerization $N$.

Beginning with the many-chain Edwards Hamiltonian, we can derive the free-energy $F$ of the blend in the mean-field approximation. The suitably-scaled free-energy density $f$ at temperature $T$ has the form

\[
f = \frac{NF}{\rho_0 V k_B T} = \frac{1}{V} \int d\mathbf{r} \left\{ \chi_{AB} N \phi_A(\mathbf{r})\phi_B(\mathbf{r}) + \chi_{AC} N \phi_A(\mathbf{r})\phi_C(\mathbf{r}) + \chi_{BC} N \phi_B(\mathbf{r})\phi_C(\mathbf{r}) - \sum_{\alpha=A,B,C} \omega_\alpha(\mathbf{r})\phi_\alpha(\mathbf{r}) \right\} - e^{\mu_2} Q_2[\omega] - Q_3[\omega]. \tag{2.1}
\]

We derived Eqn. (2.1) using the grand canonical ensemble. Multiple phase-coexistence, which we will encounter below, is most conveniently studied using this ensemble. The three Flory-Huggins interaction parameters $\chi_{AB}$, $\chi_{AC}$, and $\chi_{BC}$ are responsible for repulsion between unlike blocks. We denote the volume fraction of $\alpha$ monomers from the $n$-blocks at position $\mathbf{r}$ as $\phi_{na}(\mathbf{r})$ and write the volume fraction of $\alpha$ monomers, $\phi_\alpha(\mathbf{r})$, and of diblocks, $\phi_2(\mathbf{r})$, as

\[
\phi_\alpha(\mathbf{r}) = \phi_{2\alpha}(\mathbf{r}) + \phi_{3\alpha}(\mathbf{r}) \tag{2.2}
\]

\[
\phi_2(\mathbf{r}) = \phi_{2A}(\mathbf{r}) + \phi_{2C}(\mathbf{r}). \tag{2.3}
\]

The chemical potential for the diblocks is $\mu_2$, in units of $k_B T$. Since the blend is incompressible, the chemical potential for the triblocks can be set to zero without loss of generality.

In Eqn. (2.1), $Q_2[\omega]$ is the partition function of a single diblock copolymer interacting with the mean-fields $\omega_\alpha(\mathbf{r})$. Similarly, $Q_3[\omega]$ is the partition function of a single triblock copolymer interacting with these mean-fields. These partition functions may be written in terms of the propagators $Q_\alpha(\mathbf{r}, s|\mathbf{r}')$, which give the probability that the $\alpha$ monomer at arc-length $s$ is at position $\mathbf{r}$, given that the $\alpha$ monomer at arc-length $0$ is at $\mathbf{r}'$.

FIG. 1. Some possible lamellar structures in a blend of ABC triblock and ac diblock copolymers: (a) triblock-rich mixed centrosymmetric, (b) diblock-rich mixed centrosymmetric, (c) non-centrosymmetric, (d) centrosymmetric double-layer phase, (e) two-phase coexistence.
\[ Q_2[\omega] = \frac{1}{V} \int \! dr_1 \! dr_2 \! dr_3 \ Q_A(r_1, f_2A|r_2) \ Q_C(r_2, f_3C|r_3) \]
\[ Q_3[\omega] = \frac{1}{V} \int \! dr_1 \! dr_2 \! dr_3 \! dr_4 \ Q_A(r_1, f_3A|r_2) \]
\[ \times Q_B(r_2, f_3B|r_3) \ Q_C(r_3, f_3C|r_4) \]

The factors of \( 1/V \) are inserted above for convenience. The propagators satisfy the modified diffusion equation
\[ \frac{\partial}{\partial s} Q_\alpha(r, s|r') = \nabla_c^2 Q_\alpha(r, s|r') - \omega_\alpha(r) Q_\alpha(r, s|r') \]  
with the initial condition
\[ Q_\alpha(r, 0|r') = \delta(r - r'). \]

In the mean-field approximation the fields \( \omega_\alpha \) are related to the monomer volume fractions through the relations
\[ \omega_A(r) = \chi_{AB} N \phi_B(r) + \chi_{AC} N \phi_C(r) + \eta(r) \]
\[ \omega_B(r) = \chi_{AB} N \phi_A(r) + \chi_{BC} N \phi_C(r) + \eta(r) \]
\[ \omega_C(r) = \chi_{AC} N \phi_A(r) + \chi_{BC} N \phi_B(r) + \eta(r), \]
where the field \( \eta \) is to be adjusted to enforce the incompressibility condition
\[ \phi_A(r) + \phi_B(r) + \phi_C(r) = 1. \]

The monomer volume fractions are, in turn, related to functional derivatives of \( Q_2[\omega] \) and \( Q_3[\omega] \):
\[ \phi_{2\alpha}(r) = -V \ e^{\mu_2} \ \frac{\delta Q_2[\omega]}{\delta \omega_\alpha(r)} \] 
\[ \phi_{3\alpha}(r) = -V \ \frac{\delta Q_3[\omega]}{\delta \omega_\alpha(r)}. \]

These functional derivatives are evaluated using Eqs. (2.2)–2.7).

To obtain the exact mean-field solution for a given point in parameter space, Eqs. (2.8)–2.13) need to be solved self-consistently using numerical methods. The method of solution involves selecting a set of basis functions appropriate to the space group of the periodic structure to be examined, and reformulating the theory in the reciprocal space of these basis functions [14]. With initial guesses for the periodicity, \( D \), and monomer profiles, \( \phi_\alpha \), of the structure, the reciprocal space versions of Eqs. (2.8)–2.13) are solved iteratively to obtain the mean-field profiles and free-energy density \( f \) corresponding to the chosen \( D \). This procedure is repeated for different choices of \( D \) until the free-energy density is minimized at the system's preferred periodicity. The numerical procedure and the reciprocal space formulation are discussed in more detail in Refs. [14][18] [19]. The preferred periodicity and minimal free-energy density are determined for all possible structures. These free-energy densities are compared and the structure with the lowest \( f \) at a given point in phase space is the equilibrium structure at that point. In the \( f-\mu_2 \) plane, two-phase coexistence occurs when the free-energy density curves for two structures cross at a given value of \( \mu_2 \). Three-phase coexistence occurs when three such curves intersect at a point. Even though we compare free-energy density curves as a function of \( \mu_2 \), when we plot phase diagrams we use the average diblock volume fraction, \( \hat{\phi}_2 \), as a variable, instead of its thermodynamic conjugate, \( \mu_2 \).

A pure triblock copolymer melt can form many different periodic structures [1]–13. The number of structures formed by blending triblock copolymers with diblock copolymers is even more diverse. In this paper, we restrict ourselves to discussing lamellar structures, since they have been the subject of experimental investigations of non-centrosymmetry [14]. The problem is then one-dimensional with cosines and sines as basis functions. The non-centrosymmetric phase was obtained using both sines and cosines and an initial monomer profile that was NCS (...ABCca...), to begin the iteration procedure. Centrosymmetric phases have only cosines as basis functions. The MCS structure was found at about the period of the NCS structure. A centrosymmetric double-layer structure was found at about twice the NCS period, using the sequence (...ABCcaacCBa...), as an initial profile for the iteration step. The number of basis functions in our computation of the free-energy density is selected to achieve an accuracy of \( 10^{-6} \), which is more than sufficient to resolve the small differences in free-energy between these phases. As the blend segregation increases the interfaces become sharper and more basis functions are needed to achieve this accuracy.

III. RESULTS AND DISCUSSION

Since the parameter space for this system is large – \( \chi_{AB}N, \chi_{AC}N, \chi_{BC}N, \Omega, f_2A, f_3A, f_3B \) and \( \hat{\phi}_2 \) can all be varied independently – we have to be careful to select parameters which favour a stable lamellar phase. A stable lamellar phase is most likely when the block compositions are symmetric, \( f_2A = 1/2, f_3A = f_3B = 1/3 \), and the Flory-Huggins interaction parameters are equal, \( \chi_{AB} = \chi_{AC} = \chi_{BC} \equiv \chi \). Accordingly, we fix the block compositions to be symmetric, and examine only situations where the Flory-Huggins interaction parameters are equal or nearly equal. Even within these bounds, the phase behaviour of the blend is rich.

The phase diagram in the \( \chi N-\hat{\phi}_2 \) plane, for the case where all the Flory-Huggins interaction parameters are equal, is shown in Fig. 2. The ratio of triblock to diblock lengths is \( \Omega = 1.5 \). At the lowest values of \( \chi N \) the blend is disordered. As \( \chi N \) increases there is a transition to a mixed centrosymmetric (MCS) phase where the triblocks and diblocks mix together uniformly, but form a lamellar phase [15]. If \( \hat{\phi}_2 \) is small, and the blend is triblock-rich, the lamellar structure will be alternating triblock layers (...ABCcaacCBa...), as in Fig. 1a. As \( \hat{\phi}_2 \) increases the blend...
becomes diblock-rich and the structure becomes alternating diblock layers (...acca...), as in Fig. 1b. A typical density profile for the MCS phase is shown in Fig. 3.

Below the phase coexistence line, the MCS phase goes from being triblock-rich to diblock-rich, as the average diblock volume fraction $\phi_2$ increases. The critical point for the MCS to NCS transition is indicated by a solid circle. The narrow region of NCS phase stability terminates at a triple point, indicated by a solid square. Regions of two-phase coexistence are indicated. Above the horizontal line at $\chi N \approx 28$ there is two-phase coexistence between an almost pure triblock phase and an almost pure diblock phase.

For larger values of $\chi N$ (in the intermediate segregation regime around $\chi N \approx 14$) the B block tends to expel the diblock $a$ and $c$ blocks from its domain, and it becomes favourable for the triblocks and diblocks to spatially separate. The transition from mixed to spatially-separated states is indicated by the phase coexistence line in Fig. 2. Above the transition, the existence of a stable NCS phase of alternating triblock and diblock layers (...ABCca... as in Fig. 1c) in a narrow region around $\phi_2 \approx 0.4$ prevents the system from phase separating into coexisting triblock-rich and diblock-rich phases. Instead, for values of $\phi_2$ lower than the stability region for the NCS phase, the triblock-rich phase coexists with the NCS phase, while for values of $\phi_2$ higher than this stability region the NCS phase coexists with the diblock-rich phase. The volume fraction of each coexisting phase is given by the lever rule. As $\phi_2$ increases and the longer triblocks are removed, the periodicity $D$ of the structure decreases. Thus, for a given $\chi N$, the triblock-rich MCS phase has a longer period than the NCS phase, and the NCS phase has a longer period than the diblock-rich MCS phase. A typical density profile for the NCS phase is shown in Fig. 4.

The widest region of NCS stability occurs near the bottom of the phase-coexistence curve. Figure 5 shows this region in more detail. The phase boundaries appear to converge at a point where $\phi_2 \approx 0.365$ and $\chi N \approx 13.72$. Since the free-energy differences between the structures become very small near this point and the NCS phase is only slightly stable with respect to the MCS phase, it becomes difficult to numerically compute the phase boundaries in this region. The dashed lines in Fig. 5 are thus extrapolations of the phase boundaries. Given the fact that the free-energies of the structures appear to merge at this point, and the fact that the difference between the period of the stable NCS and the metastable MCS structure approaches zero as this point is approached, we believe that the point of convergence is a second-order critical point. The order-parameter for this transition is the amplitude of the odd-parity basis functions (sines) for the monomer profiles.
When $\chi N > 17$ the region of NCS stability narrows to a sliver, as shown in Fig. 2. The NCS stability region terminates at a triple point at $\phi_2 \approx 0.381$ and $\chi N \approx 28.0$ where the triblock-rich, diblock-rich and NCS phases coexist. For larger values of $\chi N$ the NCS phase is unstable, and there is only two-phase coexistence between almost pure triblock and diblock phases. This part of the phase diagram is similar to the phase diagram of a eutectic material, where a liquid phase (here the NCS phase) intervenes between two solid phases (here the MCS phases) and terminates at a eutectic point (here the triple point) $\phi_2$.

We have slightly varied the relative values of the Flory-Huggins interaction parameters and examined the effects on the phase diagram. To try to avoid non-lamellar phases, we have kept the interactions in the triblock symmetric ($\chi_{AB} = \chi_{BC}$) and examined the effect of having only slightly weaker repulsion between the middle and outer blocks ($\chi_{AB} = \chi_{BC} = 0.8 \chi_{AC}$) and only slightly stronger repulsion between these blocks ($\chi_{AB} = \chi_{BC} = 1.1 \chi_{AC}$). The value $\Omega = 1.5$ is used. It is known, however, that for large variations in the Flory-Huggins interaction parameters non-lamellar phases may arise (such as B cylinders or spheres on AC interfaces when $\chi_{AB} = \chi_{BC} > \chi_{AC}$).

In Fig. 6 the phase diagram in the $\chi_{AC}N - \phi_2$ plane is shown for the case where $\chi_{AB} = \chi_{BC} = 0.8 \chi_{AC}$. The overall structure of the phase diagram is the same as in Fig. 2 where the Flory-Huggins interaction parameters were equal (to emphasize the region around the critical point, we only show the lower part of the phase diagram in Fig. 6). The region of NCS stability is shifted to slightly higher values of $\phi_2$. More noticeably, the phase coexistence line is shifted to higher values of $\chi_{AC}N$. The critical point now occurs at $\phi_2 \approx 0.414$ and $\chi_{AC}N \approx 16.79$ and the triple point occurs at $\phi_2 \approx 0.391$ and $\chi_{AC}N \approx 48$. Since the repulsion between the B block and the diblock a and c blocks drives the triblocks and diblocks to spatially separate, decreasing this repulsion raises the phase coexistence line. In Fig. 7 the phase diagram in the $\chi_{AC}N - \phi_2$ plane is shown for the case where $\chi_{AB} = \chi_{BC} = 1.1 \chi_{AC}$. Again, the basic structure of the phase diagram is unchanged from Fig. 2, while the phase coexistence line is shifted to lower values of $\chi_{AC}N$. The region of NCS stability is shifted to slightly lower values of $\phi_2$. The critical point occurs at $\phi_2 \approx 0.350$ and $\chi_{AC}N \approx 12.69$ and the triple point occurs at $\phi_2 \approx 0.376$ and $\chi_{AC}N \approx 23$. The increased repulsion between the B block and the diblock a and c blocks drives the triblocks and diblocks to spatially separate at lower values of $\chi_{AC}N$, lowering the phase coexistence line. Interestingly, the phase coexistence line in Fig. 7 is more asymmetric than the phase coexistence lines in either Fig. 2 or Fig. 6. This is due to the increased repulsion of the B block in Fig. 7, which accentuates the difference between the triblock and the diblock.
FIG. 6. The phase diagram in the $\chi_{AC}N - \bar{\phi}_2$ plane, for the case where $\chi_{AB} = \chi_{BC} = 0.8 \chi_{AC}$. The triblock to diblock length ratio is $\Omega = 1.5$. The notation used is the same as in Fig. 2. We have chosen to focus on the region of the phase diagram near the critical point. The disordered phase exists below $\chi_{AC}N \approx 10.5$, and the triple point exists for $\chi_{AC}N \approx 23$.

It was hoped that by looking at variations in the relative values of the Flory-Huggins interaction parameters the region of NCS stability could be expanded beyond that of Fig. 2. In the parameter range we have examined, we have found little, if any, dependence of the width of the NCS stability region on such variations. It appears that, other than an upward (or downward) shift of the phase coexistence curve and triple point, the structure of the phase diagram is insensitive to slight variations in the relative values of the Flory-Huggins interaction parameters.

To examine the effect of varying the relative degrees of polymerization of the triblocks and diblocks we show the phase diagram in the $\Omega - \bar{\phi}_2$ plane in Fig. 8. In this case, the Flory-Huggins parameters are constant and equal: $\chi N = 15$. Since an increase in the triblock polymerization index results in an increased effective segregation in the triblock, the B block will expel the diblock $a$ and $c$ blocks for large enough $\Omega$. Thus Figs. 2 and 8 are similar. There is a critical point at $\bar{\phi}_2 \approx 0.391$ and $\Omega \approx 1.34$ and a triple point at $\bar{\phi}_2 \approx 0.370$ and $\Omega \approx 1.72$. It is significant that the region of NCS stability slopes to lower $\bar{\phi}_2$ as $\Omega$ is increased, and that this region roughly corresponds to the condition that the number of diblock copolymers in the blend equals the number of triblock copolymers,

$$\bar{\phi}_2^* = \frac{1}{1 + \Omega}. \quad (3.1)$$

Equation (3.1) is plotted in Fig. 8 for comparison. For the phase diagram in Fig. 2, where the region of NCS stability is almost vertical, Eqn. (3.1) with $\Omega = 1.5$ gives $\bar{\phi}_2^* = 0.4$, which is close to what is seen.

FIG. 7. The phase diagram in the $\chi_{AC}N - \bar{\phi}_2$ plane, for the case where $\chi_{AB} = \chi_{BC} = 1.1 \chi_{AC}$. The triblock to diblock length ratio is $\Omega = 1.5$. The notation used is the same as in Fig. 2. We have chosen to focus on the region of the phase diagram near the critical point. The disordered phase exists below $\chi_{AC}N \approx 10.5$, and the triple point exists for $\chi_{AC}N \approx 23$.

FIG. 8. The phase diagram in the $\Omega - \bar{\phi}_2$ plane, for the case where all the Flory-Huggins interaction parameters are equal ($\chi N = 15$). The notation used is the same as in Fig. 2. The dashed straight line corresponds to Eqn. (3.1).
We now comment on the stability of the centrosymmetric (CS) phase consisting of alternating triblock and diblock double-layers (…ABCcaacCBA…). Naively, one might expect that a flip of every other period of the NCS phase would lead to a periodic structure which is degenerate in free-energy with the original NCS phase, and has exactly twice the period of the original phase. However, in the phase diagrams shown in Figs. 2, 6, 7 and 8 the CS structure is metastable [24]. Below the triple point the CS structure has a slightly higher free-energy density than the NCS structure. Above the triple point the CS structure has a slightly lower free-energy density than the NCS structure, but is still metastable with respect to two-phase coexistence. This makes sense since, above the triple point, a metastable NCS structure may phase-separate by going through a series of CS phases of longer period and lower free-energy. We also observe that the period of the metastable CS structure is only approximately twice that of the NCS structure. Subtle differences between the chain conformations in Aδ interfaces (where one chain comes from the diblock and the other from the triblock) and those in Aδ interfaces are probably responsible for breaking the degeneracy of the NCS structure, but is still metastable with respect to two-phase coexistence. This makes sense since, above the triple point, a metastable NCS structure may phase-separate by going through a series of CS phases of longer period and lower free-energy.

As we have shown in Fig. 7, when \( \chi_{AB} = \chi_{BC} > \chi_{AC} \) the region of MCS stability narrows as the MCS-to-NCS critical point moves to lower values of \( \chi_{AC} N \), closer to the order-disorder transition. However, our preliminary investigation into the possibility of a direct transition from the disordered to NCS phase suggests that for a large relative repulsion between the triblock middle and outer blocks (\( \chi_{AB} = \chi_{BC} = 1.5 \chi_{AC} \)) the NCS phase can become unstable to phase separation into triblock- and diblock-rich phases, while a narrow region of MCS stability remains. Thus a compromise must be found between decreasing the width of the MCS region and maintaining the stability of the NCS phase.

**IV. CONCLUSIONS**

We have examined the phase behaviour of blends of ABC triblock and ac diblock copolymers using self-consistent field theory. A representative phase diagram is shown in Fig. 2. For segregations just above the order-disorder transition the blend forms a centrosymmetric lamellar phase where the triblocks and diblocks mix together (the MCS phase). For stronger segregation (increased \( \chi N \) or increased \( \Omega \)) the B block tends to expel the diblock a and c blocks from its domain. As a result, the triblocks and diblocks spatially separate by forming either alternating layers of triblock and diblock or a phase-separated state. In the former case, we observe a narrow region around \( \phi_2 \approx 0.4 \) where a pure NCS lamellar phase (Fig. 1c) is stable. In the latter case, we observe large regions of two-phase coexistence between the NCS phase and either a triblock-rich or a diblock-rich MCS phase, depending on the value of \( \phi_2 \). The structure of this phase diagram is insensitive to slight variations in the relative values of the Flory-Huggins interaction parameters. The only effect is an upward (or downward) shift of the phase coexistence curve and the triple point. Such variations do not measurably affect the width of the NCS region.

For intermediate segregation, our results suggest that there is a second-order critical point where a continuous transition from the MCS phase directly to the NCS phase occurs. The order-parameter for this transition is the amplitude of the odd-parity basis functions (sines) for the monomer profiles. As the segregation is increased, the region of stability for the NCS phase narrows to a sliver, and terminates at a triple point. Above the triple point there is two-phase coexistence between almost pure triblock and diblock phases. This is the first work to suggest the existence of the critical point and the triple point in the phase diagram for this blend.

The phase diagram in Fig. 2 is consistent with the experiments of Goldacker et al. [4], who observed coexisting triblock-rich and NCS lamellae for \( \phi_2 \approx 0.18 \), and a predominance of NCS lamellae for \( \phi_2 \approx 0.4 \). The narrowness of the region of NCS stability suggests that careful adjustment of the blend parameters is necessary to observe...
the pure NCS phase. Our theory predicts that the width of the NCS stability region can be maximized by studying blends near the phase coexistence curve which have a triblock to diblock length-ratio less than 1.5.

Earlier theoretical work by Leibler et al. \cite{1} and Birshtein et al. \cite{8} on these blends focused on the mechanism responsible for the stability of the NCS phase in the strong-segregation limit. In Ref. \cite{1}, subtle entropic interactions arising from the asymmetric interpenetration of a and A blocks from the diblock and triblock, respectively, cause the system to favour mixed AA interfaces over AA (or aa) interfaces, and lead to a stable NCS phase. In Ref. \cite{8} the different grafting densities of the brush coming from the triblock and the brush coming from the diblock favoured mixed AA interfaces. Our work complements this earlier work since we can examine the blend phase diagram without the need to assume the strong-segregation limit. However, in contrast to Refs. \cite{1} and \cite{8}, our calculations show that the NCS phase is only stable for intermediate segregation, and that for strongly-segregated blends there is two-phase coexistence between triblock-rich and diblock-rich phases. A reconciliation between our results and those of Refs. \cite{1} and \cite{8} in the strong-segregation regime is necessary. A clue to the nature of the entropic interaction driving the stability of the NCS phase is our observation that the region of NCS stability roughly corresponds to Eqn. (3.1), the condition for there to be equal numbers of triblock and diblock copolymers in the two polymer brushes composing the AA interface. It would be interesting to examine the interpenetration of the triblock and diblock chain profiles at the AA interface using self-consistent field theory. This would allow a more direct comparison to be made with the theories of Refs. \cite{1} and \cite{8}. It may be that with increasing segregation the chain interpenetration at the AA interfaces becomes more symmetric and the brush grafting densities more similar, reducing the stability of the NCS phase in the strong segregation regime and leading to the triple point seen in Fig. 2. An analytical calculation of the stability of the MCS phase towards the NCS phase, near the critical point, may also be illuminating.

Only lamellar structures are considered in this study. Even though we have been careful to select parameters that favour the lamellar phase, it is possible that stable non-lamellar structures exist in our phase diagram (some observations of non-lamellar structures in these blends are discussed in Ref. \cite{8}). We can however say that, for the parameters examined, the size of the region of NCS stability is the maximum possible. Also, we have ignored composition fluctuations in the present mean-field treatment. Fluctuations may modify some of the detailed structure of the phase diagram, especially near the critical point, but we believe a region (perhaps a smaller one) of NCS stability will survive the effects of composition fluctuations.

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[20] We have performed a preliminary survey of the phase diagram for the case where all the Flory-Huggins parameters are different ($\chi_{AB} = 1.1 \chi_{AC}$, $\chi_{BC} = 0.9 \chi_{AC}$). Our results suggest that, in this case, the CS phase can become stable (and the NCS phase metastable) with increasing segregation, but before the triple point is reached. However, in this phase diagram the possibility for non-lamellar phases complicates the interpretation.

[21] T. P. Russell, private communication.