Unique Phase Behavior of Inverse Tapered Block Copolymers: Self-Consistent Field Theory and Molecular Dynamics Simulations

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Abstract

Using theory and simulation, we study the microphase separated structures of inverse tapered block copolymers. These are AB block copolymers with a gradient region inserted between the pure A and B blocks that smoothly changes in composition from B to A, with the B-side of the taper bonded to the pure A block. Tapering is a means to increase miscibility between polymer blocks, and by controlling the length of the taper, the phase behavior and domain spacing can be adjusted. In contrast to better known ABAB tetrablock copolymers that also have four alternating A-rich and B-rich regions, here the intermediate region has a partially mixed composition, promoting relatively diblock-like behavior for shorter inverse tapers or low segregation strength but unique behavior as a function of increasing segregation strength for some systems. In particular, for systems in which 50% of the backbone is the taper, the larger of the two pure end blocks - composed of the overall majority component - can phase separate analogously to the minority component of a diblock copolymer, creating cylinder and
network phases in which the majority component’s pure block is the minority phase in a matrix of a relatively disordered mixture of the tapered region and the minority component’s pure block.

Introduction

Along with the development of block copolymers that form microphase separated structures whose nanoscale domains of different monomer types can have significantly different local properties, there has been a longstanding interest in controlling these microphase structures and their domain spacing. In addition to choosing the monomer types and polymer length, one can adjust the copolymer sequence to gain such control. For instance, many groups have studied gradient copolymers whose statistical composition smoothly transitions between polymer components, including with a variable sharpness of the transition and local sequence blockiness. Tapered block copolymers, in which a gradient region (or taper) is placed between pure blocks, have garnered significant recent attention as one can fine tune the miscibility of the polymer components by adjusting taper length. The taper can be placed in the normal direction such that it allows a single smooth transition from A to B, or in the inverse direction such that the B-rich side of the taper is connected to the pure A block in an AB copolymer and the A-rich side is connected to the B block. Inverse tapering modifies the microphase interface more significantly than normal tapering, and inverse tapered systems require a higher segregation strength (meaning a larger $\chi N$ where $\chi$ is the Flory-$\chi$ parameter and $N$ is the chain length) to microphase separate.

In the limit of 100% tapering, our systems are gradient copolymers, whose composition varies along the entire chain length; such systems and their mixtures with homopolymers or block copolymers have been studied by multiple groups. For instance, theoretical work of Lipson and coworkers on linear gradient copolymer melts and micelles of block and gradient copolymers in a homopolymer melt found an increase in compatibility between the monomers leading to a broader interface. Similar broadening was observed for gradient and tapered polymers by Shull and coworkers using self-consistent mean field techniques.
recent studies, Epps and coworkers have synthesized and analyzed linear tapered copolymers (in which the composition changes linearly from A to B along the taper) and demonstrated their potential in a variety of applications. The introduction of the taper shifts the order-to-disorder transition while still allowing access to bicontinuous network structures, in both diblock tapered copolymers and triblock copolymers. This work showed that tapered copolymers are attractive because the increased miscibility of the blocks can alleviate processing challenges of high molecular weight block copolymers, and adjusting taper length allows some control over the materials’ glass transition temperature, phase behavior, and conductivity.

In our prior work, we first studied the phase behavior of linearly tapered block copolymers using self-consistent field theory (SCFT), for a variety of normal taper lengths, and for short inverse tapers. It was found that the normal tapered systems had a much wider region of the phase diagram showing the double gyroid network phase, of interest because this phase can be difficult to access experimentally for some diblock systems. We also found that the non-lamellar phases existed in a more narrow region of the phase diagram for small (30%) inverse tapers. We have also modelled this system using fluids (or classical) density functional theory (fDFT). The fDFT results in general agree with SCFT results, but the fDFT model is more directly comparable to bead-spring models used in molecular dynamics (MD) simulations (the same parameters, including constant pressure calculations, can be used in both systems), and we introduced a method to reduce the time needed for equilibration in MD by using fDFT density profiles to guide the initial placement of chains in MD. In a recent paper, we also showed that fDFT results closely matched the experimentally determined density profiles of diblock, tapered, and inverse tapered copolymers, after adjusting only one parameter (the segregation strength) for a good fit across all three of these systems.

The dynamics of tapered copolymers have been studied using MD simulations, both by our group and by others. In our study of diblocks and short normal tapered systems in which the simulations were simply started from a random initial state, these systems spon-
taneously formed lamellar, hexagonally packed cylinder, and network phases in the same regions as were predicted by SCFT.\textsuperscript{21,23} We also showed that that having a taper (versus a diblock) changes the dynamics of the polymers differently than one would expect based on comparing the diblock and tapered systems’ structural properties (domain spacing).\textsuperscript{23} Additionally, Sethuraman and Ganesan compared the relaxation behavior of tapered and diblock copolymers for systems in which the two different monomers had different mobilities, to relate to experimental systems in which one phase can have a very different glass transition temperature than the other. Their tapered systems had faster dynamics than diblock copolymers with analogous parameters, in agreement with experimental observations.\textsuperscript{17,25}

While several of these prior studies included inverse tapers as a comparison, significantly more attention was focused on normal tapers, as normal tapering is a more straightforward way to tune interfacial mixing while still using systems analogous to standard diblock copolymers. However, several interesting features of inverse tapered systems were observed that motivated us to examine them further. For example, we found that the domain spacing of long inverse tapered systems was relatively constant as a function of segregation strength, in contrast to that of diblocks or normal tapers, due to cancellation of the competing effects of local chain stretching versus chain conformational changes (folding) that may be a unique advantage of the peculiar inverse tapered type of sequence.\textsuperscript{21} (Note we have not directly compared inverse tapered systems to others that may fold in a similar manner, such as tetrablock copolymers.)

In this work, we focus on inverse tapered copolymers, using SCFT calculations to understand their microphase separated structures and map out their phase diagrams. We also perform molecular dynamics (MD) simulations to further investigate certain phases and the individual chain conformations within them. We consider linearly inverse tapered copolymers (including the limiting case in which the pure block length is 0) with a special emphasis on 50\% inverse tapered copolymers in which one of the pure blocks (A) is shorter than the other (for non-symmetric polymers, B refers to the overall majority component). Certain
results for symmetric normal and inverse tapered systems are provided in the Supporting Information for comparison.

Figure 1: a) Schematic of the multiblock model used to represent the inverse tapered copolymers in SCFT. The taper is broken into small equal sized BA diblock sections (of length 2% of the polymer chain) with composition matching the composition of the taper in that region. b) Schematic showing the relevant variables in chain composition (the fraction of taper $f_T$ and the fraction of A $f_A$) for the inverse tapered polymers.

Methods

*Self-consistent field theory*

The SCFT methods employed were identical to previous work, and details can be found in Ref. 21. In particular, the commercial software package PSim$^{26}$ was used to solve the standard incompressible Gaussian chain SCFT equations. The inverse tapered polymers are modeled using a multiblock region to represent the taper as shown in Figure 1. The multiblock region is composed of short diblocks that have the same average composition as the corresponding region of a linear gradient,$^2$ and enough blocks are used such that the model’s order-disorder transition is very similar to that found from the random phase
approximation using a true linear gradient in the tapered region.\textsuperscript{21} We note that the amount of blockiness is chosen to be relatively small and each chain is identical, thus the blockiness characteristics are not meant to mimic those of any particular synthetic process, though gradient blockiness is known to have an effect on phase behavior.\textsuperscript{5} In previous work, we have compared the density profiles of tapered lamellae from theory and MD implemented with a single sequence for all chains (with no sequential polydispersity) to those from MD implemented from a sequentially polydisperse system with approximately the same ensemble average sequence. There were measurable but relatively small differences due to sequential polydispersity for these tapered copolymers, which have gradient regions only on part of the polymer backbone.\textsuperscript{23,27} Phase diagrams are created by comparing the free energies of the following phases: lamellae (L), doubly layered lamellae (L*, alternating layers of primarily A and primarily B, but with two alternating types of B layers—one composed mostly of the pure B block and the other of the B part of the taper), double gyroid of A in a matrix of B (G), double gyroid of B in a matrix of relatively disordered A and B (G'), hexagonally packed cylinders of A in a matrix of B (C), hexagonally packed cylinders of B in a matrix of disordered A and B (C'), BCC packed spheres of A in a matrix of B (S), and BCC packed spheres of B in a matrix of disordered A and B (S'). A schematic representation of the L* phase and a comparison of the C and C' phases are shown in Figure 2. We do not consider other 3D phases, such as perforated lamellae (PL), double diamond, or the orthorhombic \textit{Fdd}d \textit{d} phases in the SCFT calculations, and these did not form spontaneously during our calculations (in contrast, L* and C' were initially found because they formed spontaneously from 1D or 2D calculations seeded in L or C).

\textit{Molecular dynamics simulations}

We use a simple bead spring Kremer-Grest model where each polymer has 40 equal-sized beads of either type A or B. Each segment in the tapered region is chosen to be type A or B, with a linearly varying probability from 0 to 1 such that the A-rich part of the taper is attached to the B pure block and vice versa. The detailed scheme of generating tapered
Figure 2: a) Schematic diagram of the doubly layered lamellar phase L* in which one repeat unit of the lamellae as shown has two distinct B phases, one made up mostly of the pure B block (labelled B) and the other made up of the B side of the taper (labelled B*), overlaid with cartoons of possible polymer conformations. b) Density profiles of cylinder phases C (left) and C’ (right) from SCFT calculations at $\chi N = 40$, overlaid with cartoons of possible polymer conformations.

bead sequences can be found in our previous work.23

We use the following finitely extensible nonlinear elastic (FENE) potential for bonds, where the parameters are set to $k = 30\epsilon/\sigma^2$ and $R_0 = 1.5\sigma$ to prevent chains crossing through each other:25

$$U_{FENE}(r) = -0.5kR_0^2\ln \left(1 - \frac{r^2}{R_0^2}\right) \tag{1}$$

For all pairwise interactions, we use the cut-and-shifted Lennard-Jones (LJ) potential:

$$U_{ij}(r) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6} - \left(\frac{\sigma_{ij}}{r_c}\right)^{12} + \left(\frac{\sigma_{ij}}{r_c}\right)^{6}\right], \quad r \leq r_c$$ \tag{2}

where $\epsilon_{ij}$ and $\sigma_{ij}$ are the interaction strength and length scale of interaction between bead i and j. In our model, all beads have the same size ($\sigma_{ij} = 1\sigma$), $\epsilon_{AA} = \epsilon_{BB} = 1\epsilon$, and $\epsilon_{AB}$ is set to be $< 1\epsilon$ to drive the systems to microphase separate. The cutoff distance $r_c = 2.5\sigma$ for non-bonded pairs and $2^{1/6}\sigma$ for bonded pairs. The parameters, $\sigma$, $m$, and $\epsilon$ (in standard
LJ units) represent the bead diameter, mass, and interaction strength, respectively, and the time unit $\tau = \sigma \sqrt{m/\epsilon}$. Polymers are initially placed as random walks (from a randomly placed first monomer). For all systems, before the LJ potential is turned on between non-bonded pairs, the initially overlapping beads are pushed off using a soft potential, $U(r) = A(1 + \cos(\pi r/r_c)); \ r < r_c$, where $r_c = 2^{1/6} \sigma$ and $A$ is linearly changed from 0 to 30 (or 150) over $11.5\tau$ (or $57.5\tau$). All simulations are performed in the open-source MD package LAMMPS with a timestep of $0.0115\tau$ and using a Nosé-Hoover thermostat to keep the temperature at $T = 1.0\epsilon/k_B$ with a damping parameter of $1.0\tau$.29,30

To make the phase table (Table 1), we ran systems of $f_A = 0.25, 0.3, 0.35,$ and $0.4$ starting from disordered states of 800 polymers in a cubic box with the initial density of $0.88\sigma^{-3}$ at a range of $\epsilon_{AB} = 0.1-0.7$. For all the systems, we performed a first run for $460000 – 690000\tau$ using a Nosé-Hoover barostat with a damping parameter of $10\tau$ to keep the pressure 0 without coupling the x, y, and z box dimensions. Except for the L and PL phases and the G phase of $f_A = 0.35$ at $\epsilon_{AB} = 0.1$, all other systems did not show particular nanostructures during the first run. Thus, we further simulated these systems, starting from the end of the first run, with a Monte Carlo double-bridging algorithm to allow bond swapping (and faster equilibration); if the same bonds on two different chains are close enough, they attempt to swap using a Boltzmann acceptance criterion.31 The bond swapping criterion is attempted if their distance is less than $1.3\sigma$, and this test occurs for 50% of bond pairs every $0.115\tau$. The second simulations were run for $115000 – 920000\tau$ using the same barostat as the first run. The observed nanostructures are given in Table 1.

The observed G phases, which are composed of 800 polymers, indeed have two interweaving structures apart from each other that appear to be similar to a gyroid structure, but in a non-cubic box. This is likely because the number of polymers in the box does not allow for an integer number of unit cells of the gyroid phase at its preferred spacing. (Unlike the case for lamellar systems which require a commensurate spacing of the microphase domain with the periodic box in only one dimension, a system which forms a 3D structure cannot inde-
pendently adjust its domain spacing and its density.) Thus, for \( f_A = 0.35 \) at \( \epsilon_{AB} = 0.1 \), we ran additional simulations for \( 575000 – 805000\tau \) with different box sizes (changing the number of polymers) following the same procedure as for the second run (with bond-swapping) but starting from random initial states. Specifically, we tested 600, 700, 900, 1000, and 1600 polymers; 600 polymers microphase separated into the G phase in a nearly perfect cubic unit cell and 700 polymers formed a structure similar to the \( Fddd \) (see details in the supporting information) while the other three systems did not show a particular nanostructure during our simulation times. Note that between the observed G and \( Fddd \)-like network phases, we did not perform further analysis, such as such as free energy calculations, that would be needed to allow us to compare the stability of the two phases. For the G phase of 600 polymers, we further tested the effect of independently fluctuating box dimensions by repeating the same run but with either coupling all three directions or fixing the box volume, i.e. no use of barostat, using the final density from the previous run. Both of these simulations did show network phases but not the G phase during the simulation over \( 575000\tau \).

To further investigate the chain conformations in the L* phase, we ran simulations from an initial state close to the L* phase where two groups of polymers (400 each) of \( f_A = 0.33 \) fully stretch with the pure B blocks facing each other with the bond length \( 0.97\sigma \) between the end beads and for all bonds. We tested two chain lengths of \( N = 40 \) and 100 at \( \epsilon_{AB} = 0.3 \) and followed the same procedure as for the first run above (without bond-swapping) for these systems. For \( N = 100 \), during the total simulation time of \( 310500\tau \), the layer initially composed of short pure A blocks became merged into the layer initially composed of the tapered block A monomers. The final morphology of this system is shown in Figure 7 with several examples of typical chain conformations. The \( N = 40 \) system also showed an analogous structure during the simulation time of \( 230000\tau \) but the structure was unstable.

**Results and Discussion**

The phase diagrams found from the SCFT calculations for \( f_T = 30\% \), 50\%, and 70\% are given in Figure 3. The phase diagram for the 30\% inverse tapered system (Figure 3a)
appears to be homomorphic to the SCFT phase diagram of a standard diblock copolymer, but with the nonlamellar structures occupying a much narrower region of the phase diagram. This phase diagram was discussed in our previous work, and it was hypothesized that the folding behavior of the inverse tapered systems, particularly at high $\chi N$, made the curved nonlamellar structures more difficult to form. However, for 50% inverse tapered systems (Figure 3b), several curved structures are found. As discussed below, in this case the taper is large enough so that the A and B sides of the taper can effectively act as their own blocks that help to determine the overall structure (rather than the main structural features being determined primarily by the A and B pure blocks).

The $f_T = 50\%$ system has a number of unique features that will be discussed in more detail in the next section. Primarily, it forms the interesting structures that we have labelled $S'$, $C'$, and $G'$, in which the pure B block (where B is the overall majority component) is forming the minority part of the sphere, cylinder, and gyroid phases, respectively, and the majority part is a mixture of the taper and the pure A block. Broadly, there are three regimes in the phase diagram as a function of $f_A$: 1) for $f_A \approx 0.5$ the polymer is symmetric and forms lamellae, 2) for $f_A \approx 0.25$, the pure A block is so small the system is acting more like an asymmetric BAB triblock copolymer, forming cylinders and lamellae in the usual way, and 3) for $f_A \approx 0.3$ to 0.45, the pure B block acts like the minority component of a diblock copolymer, transitioning from lamellae to gyroid to cylinders as composition is varied. Additionally, for large $\chi N$, region (3) also has another unique structure, a doubly layered lamellae (see Figures 6 and 7 below), which we have labeled $L^\ast$. As with the low $\chi N$ case, this phase segregates the pure B block into its own rather pure B phase that does not include the B part of the taper. The difference is that in $L^\ast$ (higher $\chi N$) the B part of the taper is segregated into its own region apart from the A; as in the majority of the $f_T = 0.3$ and 0.7 phase diagrams, the interfacial curvature goes to zero.

Note that the behavior of $f_T = 0.5$ inverse tapers is distinct from the behavior of both symmetric and asymmetric AB-type block copolymers, as well as normal tapered and
Figure 3: Phase diagram of inverse tapered copolymers with fraction of taper $f_T = a) 30\%$, b) 50\%, and c) 70\% of the polymer backbones. Phases are labeled as follows: lamellae (L), doubly layered lamellae with alternating layers of B mostly from the pure B block and B from the taper (L*), double gyroid (G) of A in a matrix of B, double gyroid of B in a matrix of disordered A and B (G'), hexagonally packed cylinders of A in a matrix of B (C), hexagonally packed cylinders of B in a matrix of disordered A and B (C'), BCC packed spheres of A in a matrix of B (S), and BCC packed spheres of B in a matrix of disordered A and B (S'). The vertical black bars in (b) and (c) represent the composition at which the taper is at the end of the polymer chain (see Figure 1b). The line between L* and L was not determined to same level of detail as the other curves, and is given as a straight dashed line between available data points.
gradient copolymers. In those systems, the phase diagrams are isomorphic to the standard diblock phase diagram (with shifted phase boundaries). However, ABC triblock copolymers were previously predicted (via SCFT) to show a similar behavior in which, depending on the relative $\chi N$ values, two of the blocks can be poorly segregated but one block more cleanly segregates from the mixture of the other two; specifically, C’ and G’ and a related lamellar phase were observed. Another example in which a majority component was observed to form the usual minority phase was in recent work by Olvera de la Cruz and coworkers on block ionomers, which were seen to form the C’ phase when strong ion correlations were included in SCFT calculations.

The $f_T = 70\%$ phase diagram is also different from that of a diblock copolymer; only the lamellar and cylinder phases were found to be stable in this case. This is unsurprising because most of the chain is a linear gradient, and gradient copolymers tend to form lamellae. Similarly, the phase diagram for 70% normal tapered systems was shown to be dominated by the lamellar phase. However, in these inverse tapered systems, the asymmetric polymers more easily order than the symmetric ones because the asymmetric polymers have a larger pure block on one end and a less consequential minority pure block attached to the majority region of the taper.

To further analyze the 50% inverse tapered systems, a series of MD simulations were run starting from random initial configurations; the resulting observed phases are shown in Table 1 (cases which did not form a stable structure during the simulation time are also noted). While the phase formed in a given simulation should not be construed to be a prediction of the minimum free energy phase, the MD simulations can show in greater detail what the SCFT-predicted phases may look like and assess qualitatively whether they may be stable in MD simulations (which, unlike the SCFT, use finite length polymers and include fluctuation effects). The observed phases were usually similar to those shown in the SCFT phase diagram, with lamellae at low and high values of $f_A$ and the G’ phase in between. We also find perforated lamellae for one system; it has been shown in prior work that SCFT without
fluctuations predicts standard lamellae in regions where simulations/experiments including fluctuations can show perforated lamellae. Interestingly, instead of the doubly layered lamellae $L^*$ phase forming, in the MD, an imperfect lamellar phase $L^\dagger$ forms, in which only the pure A and B blocks are well segregated (see Figure S5 in the supporting information). No C’ phase was observed; it is not clear whether 1) the systems were not simulated long enough for it to form, or 2) the differences in the MD and SCFT models mean that they lead to different phase behavior in this region.

It’s important to note that total density and the three box dimensions cannot all be independently adjusted at a given pressure in NPT simulations (including in this work). Therefore, systems with periodicity in all three dimensions, such as the network phases and hexagonally perforated lamellae, are not ensured to reach their preferred equilibrium domain spacing and density (though in the case of perforated lamellae, we expect that the effect of perforations being forced into a cubic or imperfect hexagonal arrangement would be relatively small and this would not significantly impact the overall trends in phase behavior). This means that any 3D structure that would tend to be formed in an infinitely large simulation will experience an artificial increase in its free energy in our finite sized simulations, by an amount that depends on box size and is sometimes close to zero. This effect is especially likely to be important in regions of the phase diagram where multiple network structures with relatively similar free energies have the potential to form. By simulating across a range of system sizes that includes systems with close to the appropriate number of polymers in a unit cell, we can potentially show that it is possible to form certain network phases and we can assess the details of the structures that do form. The Methods section explains the different box sizes used in our simulations at $f_A = 0.35$ and $\epsilon_{AB} = 0.1$, and further snapshots/analysis of the G’ and orthorhombic $Fddd$ like structures is given in the supporting information.

Two simulations formed the G’ structure, and this can be seen visually in Figure 4 and in the static structure factor (Figure S3 in the supporting information). Figure 4 shows selected chain conformations; for some chains, the B part of the taper folds back onto the
Table 1: Summary of observed phase behavior of 50% inverse tapered systems from MD simulations. The labels are the same as in Figure 3 with the following additional observed phases: lamellae in which the pure blocks are well segregated but the taper is not (L†), orthorhombic Fddd-like network (F‡), perforated lamellae in which the pure B block forms lamellae that are perforated (PL'). Blank spaces indicate that no simulation was run for those parameters, and dashes indicate that no clear structure was formed during the simulation.

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same gyroid network as the chain’s pure B block, while other chains cross from one network to the other. Using a clustering algorithm to classify B monomers into the two separate interpenetrating networks of the G’ systems, we determined that approximately 40% of polymers bridged across networks (their pure B block was in one network but their tapered B region was in the other network; details are given in the supporting information). Further study of the dynamics of these systems is of interest because it is plausible that such links between the different networks could have important impacts on these systems’ transport and mechanical properties.

The reversed gradient region of inverse tapered copolymers means that chains can better segregate their A-rich and B-rich regions by folding back and forth across the interface. As known from prior work, this leads to relatively shorter domain spacing and more interfacial area per chain, and the amount of folding depends strongly on $\chi N$. To clarify visually how the parts of the taper segregate, multiple color plots of C’ data are given in Figure 5, showing where the pure B, A-rich half of the taper, and B-rich half of the taper are located at low and high values of $\chi N$. In Figure 5c and d, the system is at a low value of $\chi N$, and the two halves of the taper are nearly indistinguishable. Whereas, in Figure 5g and h, the B side of the taper is more likely to be found near the pure-B rich cylinders, corresponding to the
Figure 4: Snapshots of a G’ structure found for 600 polymers at $f_A = 0.35$, $\epsilon_{AB} = 0.1$. a) Pure block A, B and tapered block A, B are colored in red, blue, pink, and cyan, respectively, and a typical chains is show to the lower right for reference. b) Only the pure B block monomers are shown. These beads form the two interweaving gyroid structures. c,d) Each interweaving structure (colored blue and cyan) is shown with its 7 adjacent image boxes. e) Same as (b), but recolored as in (c,d). f) Three typical individual polymers are shown in the cyan-colored gyroid: all B monomers of chain #1 belong to the cyan gyroid while only some B monomers do for chains #2 and #3. The individual polymers are shown smoothed by averaging over 21 snapshots each 115τ apart.
folding behavior seen in Figure 4f. In contrast, in symmetric \( f_T = 0.5 \) inverse tapers, the taper’s most likely location remains in the middle of its respective lamella (see Figure S1 in the supporting information), even at high \( \chi N \).

Figure 5: SCFT density profiles of the C’ phase at \( f_A = 0.35, f_T = 0.5 \) and a-d) \( \chi N = 40 \) and e-h) \( \chi N = 77.5 \). (a,e) shows the total density of B, (b,f) shows density of pure B block, (c,g) shows the density of the A-rich half of the taper, and (d,h) shows the density of the B-rich half of the taper.

The doubly layered lamellar structure \( L^* \) is shown in Figure 6. In this structure, between relatively pure B lamellae composed primarily of monomers of the pure B block are alternating A-rich, B-rich, and A-rich layers. As can be seen in Figure 6b, the A-rich layers are a mixture of the pure A black and the taper, but the intermediate B-rich layer consists primarily of the B from the taper.

Although the \( L^* \) phase did not spontaneously form from our MD simulation started in
Figure 6: SCFT density profiles for the doubly layered lamellae (L*) structure at $f_A = 0.35$ and $\chi N = 90$, where (a) shows the total density of A and B and (b) shows the A and B contributions from the pure blocks (solid) and taper (dashed).

a random initial state, when our MD system was started close to the L* phase, it was at least meta-stable in that it held the structure throughout our simulation time. Snapshots in Figure 7 show three typical chain conformations in this phase, which qualitatively agrees with the density profiles from SCFT (Figure 6).

**Conclusion**

We used SCFT calculations accompanied by MD simulations to study the phase behavior of inverse tapered block copolymers. As mentioned in our previous work, at sufficiently high segregation strength, the inverse tapered copolymers have chain conformations fundamentally dissimilar from those of a standard diblock copolymer; inverse tapered copolymer chains can fold back and forth across the microphase interface or bridge between different domains, depending on the size of the taper.

In this work we expand beyond symmetric or short inverse tapered systems and explore the phase behavior of a wide range of inverse tapered polymers. We find that inverse tapering
Double lamellae: snapshots (using a Kremer-Grest-like initial approach) - Artificially stretching linear polymers as initial Run in NPT coupled in \( x \) \( y \) \( N = 100, M = 800 \) (\( N = 40 \) systems seriously wavy and collapsing)

- \( A = 0.33, \epsilon_{AB} = 0.3 \)

*Individual chains smoothed by averaging for 20 snapshots \( 115\tau \) apart.

3 typical chain conformations found:

Original Box

z

Figure 7: MD snapshot of \( L^\star \) structure for chain length of \( N = 100 \) at \( f_A = 0.33 \) and \( \epsilon_{AB} = 0.3 \). The side view of of the original box is shown along with an image box to clearly show the double layering. Polymers in each of three different typical chain conformations are shown with A monomers in red and B in blue (the background structure is transparent). Each conformation’s prevalence is similar for this system; 28% of chains are classified as folding as shown in the top left, while the rest of the system is approximately equally split into the other two types of conformations.

The individual chains are smoothed by averaging over 21 snapshots each 115\( \tau \) apart.

...can act to suppress the formation of non-lamellar microphases, which would need to form curved interfaces, and the resulting phase diagrams for 30% and 70% inverse tapered systems are dominated by lamellae, with only very asymmetric systems near the ODT forming curved phases. However, at the intermediate (50%) inverse taper length, the phase diagram is quite different. In this system the pure B-block, where B is the overall majority phase, separates from the rest of the polymer; in this case, it is not the tapered region of the polymer that primarily makes up the interfacial region. Interestingly, low \( f_A \) systems at \( f_T = 0.5 \) form very narrow A lamellae despite the asymmetry of the total composition of the polymer, and the folding chain conformations are once again common.

The MD simulations of 50% inverse tapered systems often show similar phases as predicted from SCFT calculations, but we also found hints of phases not considered in our SCFT study, namely the orthorhombic \( Fddd \) phase and perforated lamellae. Note that our SCFT work considered only the gyroid network phases, so our phase diagram does not distinguish...
between gyroid and Fddd or between lamellae and perforated lamellae, which would require further study. In combination, the SCFT and MD support the conclusion that an interesting network phase is possible in inverse tapered copolymers in which the pure B-block forms the minority region of the microphase and some chains bridge between networks. The network phases can be formed over a significant region of the phase diagram, including in relatively close-to-symmetric copolymers; such bicontinuous phases are of interest to provide good mechanical properties of one phase at the same time as connected pathways of the other phase for ion or small molecule transport. Furthermore, the local segregation of the taper and the overall chain conformations change qualitatively with $\chi N$, suggesting interesting changes in dynamical and mechanical properties may be possible as a function of temperature.

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Supporting Information. Chain conformations in lamellae, gyroid phase structure, snapshots of $f_T = 0.5$ inverse tapered systems, domain spacing of lamellae, additional data on equilibration of lamellae.

References


Unique Phase Behavior of Inverse Tapered Block Copolymers: Self-Consistent Field Theory and Molecular Dynamics Simulations

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