Mesoscopic Simulations of Coarsening Kinetics within Block-Copolymer/Homopolymer Thin Films

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Abstract

The simulated evolution of thin-film blends of immiscible AB diblock-copolymers and C homopolymers are presented and analyzed in terms of the time-dependent evolution of the three respective domains. In the current model, all polymer species are mutually incompatible, however the C homopolymers are considered to be less incompatible with the B-block of the diblock copolymer relative to the A-block, hence B-C interfaces develop rather than A-C interfaces. The collective phase-separation within these films leads to microdomains of the AB diblock copolymers along with macrodomains of C homopolymers, in which a growing disparity in domain length scales develops. Technologically, such films may be exploited to fabricate porous membranes with a bimodal distribution of through-thickness pore diameters.

1. Introduction

The process of phase-separation within immiscible polymer blends can be exploited to fabricate functional nanostructured or mesostructured materials. Porous materials, for example, can be created by selectively etching one of the polymer domains, with the remaining polymer domain(s) serving as a scaffold onto which metallic or ceramic material may be deposited [?]. Moreover, block copolymer (BCP) microphase separation can be exploited for nanoscale surface patterning useful for semiconductor manufacturing or filtration membranes [?]. In both of these contexts, polymeric phase-separation is considered a preliminary step towards advanced materials manufacturing.

Immiscible blends consisting of multiple homopolymer species undergo macroscopic phase separation characterized by nucleation/growth/coarsening or spinodal decomposition, depending on the composition [? ?]. This phase separation is conceptually similar to that observed in binary alloys or even immiscible liquids, albeit the mechanisms of molecular transport will vary. In these polymeric blends, multiple phase domains emerge and grow at a particular power-law rate (typically $\sim t^{1/3}$) indefinitely in

time, scaled by both the interfacial energy and polymer chain mobilities. On the other hand, A-B BCP systems with a sufficiently high χ parameter will also separate into A-rich and B-rich domains; however, due to the fact that the A- and B-blocks are physically connected, the domains are periodic and their sizes remain commensurate with the total chain length - typically on the order of 20 - 100 nm [?]. Hence, A- and B-rich domains in phase-separated BCPs are routinely called microdomains. The coarsening behavior of BCP systems relates not to the growth of individual microdomains, but rather to the growth of uniformly-oriented grains consisting of many microdomains [?].

Phase-separation in systems containing both BCPs and homopolymers broadens the spectrum of possible domain patterns. For AB diblock copolymers with A homopolymer (AB/A) blends, the morphologies strongly depend on the relative chain lengths and the relative quantities of the copolymer and homopolymer species [? ? ? ?]. Assuming N_A and N_A^{homo} represent the degree of polymerization for the A-block and the A homopolymer, respectively, experiments revealed that when $N_A^{homo} > N_A$, a dual macrophase/microphase separation occurs, whereas when $N_A^{homo} < N_A$ only micro-phase separation occurs in which the homopolymers disperse within the A-block microdomains. For the

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latter case, in which the A homopolymers solubilize in the A-blocks of BCP, the microdomains may swell significantly and/or change their periodic microdomain structure. The interested reader may refer to the works of Winey et al. [?] or Matsen [?] for more details.

There are significantly fewer investigations regarding mutually immiscible blends of A-B BCPs and C homopolymers (referenced here as AB/C blends). The phase morphology depends on the A-B, B-C, and A-C monomer interactions, as well as the various degrees of polymerization. In general, however, given mutual immiscibility, dual microphase/macrophase separation will occur leading to concurrent nanostructured/mesostructured materials [?]. See Fig. 1 for an illustration. From a materials fabrication perspective, a key distinction between an AB/A blend and an AB/C blend lies in the greater prospective control of chemical phase removal that can be accomplished with an AB/C blend (e.g., one or two out of three phases can be removed via selective etching).

There exists a rich variety of microstructures that may emerge within AB/C or AB/A blends. The studies cited above for the most part have focused on the qualitative nature of the phase morphology (e.g., macro/micro-domain structures with various distributions of both domains). On the other hand, very little is understood regarding the time-dependent kinetics associated with the development and coarsening of these domains. This is partly due to the difficulty associated with experimentally measuring domain growth uninterrupted in real time. In this respect, computer simulations can offer unique insight into such processes. Although the theory associated with domain coarsening, particularly Ostwald ripening, has been developing for many decades [? ? ?], these AB/C block copolymer/homopolymer systems present a new complexity to this problem. Namely, how do the macrodomains coarsen when they are surrounded by a heterogeneous (rather than a homogeneous) matrix of microdomains? In order for the macrodomains to coarsen, the C homopolymers must diffuse through this heterogeneous microdomain matrix. Does this heterogeneity alter the C homopolymer diffusion rate within the block copolymer matrix? If so, does this alter the overall coarsening rate?

This paper presents mesoscopic numerical simulations of the time-dependent phase-separation processes in AB/C systems in thin-film confinement.

Figure 1: (top) Simplified models of the block copolymer and homopolymer chains in which the circles represent individual monomer units. (bottom) Schematic depicting the dual macrophase/microphase domain structure that emerges in the AB/C immiscible polymer blend considered herein. The homopolymer macrodomains are the coarsening phase within a block copolymer microdomain matrix.

The mutually-repulsive A-B, B-C, and A-C interactions lead to dual microphase and macrophase separation. In the simulation model, the B-C interactions are less unfavorable compared to A-C interactions, and therefore the B-block of the copolymers maintain complete contact with the C-domains. The simulations focus on the kinetic growth of the C-domains for varying volume fractions of A, B, and C monomer units, with a specific emphasis on how changing f_A (the number-averaged fraction of A monomers on the diblock copolymer chain) may influence the coarsening of the C-domains. The compositions are chosen such that through-thickness discrete cylindrical domains form, which can be utilized as templates to fabricate thin-film membranes with bimodal pore sizes.

2. Methods

The computational approach utilized here closely resembles the work of Ohta and Ito [? ?]. In essence, continuous order parameters that represent the local composition are evolved in space and time. The local volume fractions of monomers are denoted by ϕ_A , ϕ_B , and ϕ_C . If incompressibility is assumed, only two volume fractions are independent, and here we introduce the parameter $\phi_{AB} = \phi_A - \phi_B$. Hence, the tempo-spatial evolution of ϕ_{AB} and ϕ_C can fully describe the kinetics associated with these three-phase microstructures. Here,

Figure 2: Mixing energy for the three different monomer combinations: A-B, B-C, and A-C. The interfacial energy of A-C interfaces is sufficiently large enough to eliminate those interfaces from the microstructures.

a time-dependent Ginzburg-Landau (TDGL) model is applied, in which the microstructure evolution is informed by an assumed, qualitative free energy functional (the TDGL approach [? ?], implemented with finite-difference discretization, is essentially the same as the so-called Cell Dynamical Method of Ohta and Ito [? ?]).

The model free energy for the copolymer-homopolymer blend in terms of ϕ_{AB} and ϕ_C consists of short-range and long-range terms:

$$F(\phi_{AB}, \phi_C) = F_S(\phi_{AB}, \phi_C) + F_L(\phi_{AB}, \phi_C), \quad (1)$$

where the short-range term is taken as:

$$\begin{aligned} F_S(\phi_{AB}, \phi_C) &= \int [f_{AB}(\phi_{AB}) + f_C(\phi_C) + f_{AB/C}(\phi_{AB}, \phi_C)] d\mathbf{r}. \end{aligned} \quad (2)$$

Here, f_{AB} represents the interaction energy between the A- and B-blocks of the diblock copolymer, using the familiar expression:

$$f_{AB}(\phi_{AB}) = a_{AB} \left[\frac{1}{4} \phi_{AB}^4 - \frac{1}{2} \phi_{AB}^2 \right] + \frac{\kappa_{AB}}{2} |\nabla \phi_{AB}|^2, \quad (3)$$

where a_{AB} is an energy scaling term and κ_{AB} is a gradient coefficient that contributes to the energy of the AB interfaces. The first term in Eq. (3) is a common double-well potential in which a_{AB} (> 0) is proportional to the Flory-Huggins parameter $\chi_{AB}N$. The second term in Eq. (2), f_C , represents

the energy of the C homopolymers and is defined as:

$$f_C(\phi_C) = a_C [\phi_C^2 (1 - \phi_C)^2] + \frac{\kappa_C}{2} |\nabla \phi_C|^2, \quad (4)$$

where a_C and κ_C are energy scaling and gradient coefficients, respectively. The third term in Eq. (2) captures the interaction between the AB diblock copolymers and the C homopolymers:

$$\begin{aligned} f_{AB/C}(\phi_{AB}, \phi_C) &= b \phi_{AB}^2 \phi_C^2 \\ &+ c (\phi_{AB} + 1)^2 (\tilde{\phi}_C^2 (1 - \tilde{\phi}_C)^2). \end{aligned} \quad (5)$$

Here, $b \phi_{AB}^2 \phi_C^2$ enforces the condition that the C homopolymers are immiscible with both blocks of the BCP. The second term in Eq. (5) raises the interaction energy of A and C monomer units relative to that of the B and C monomer units, which effectively promotes B-C interfaces within the microstructure. The character $\tilde{\phi}_C = \phi_C$ when $0 < \phi_C < 1$, $\tilde{\phi}_C = 0$ when $\phi_C \leq 0$, and $\tilde{\phi}_C = 1$ when $\phi_C \geq 1$.

The long-range energy term penalizes domain growth, albeit only for the ϕ_{AB} order parameter, which is necessary for modeling microphase separation in block copolymers [?]. For the current two-order-parameter model, the following is used:

$$\begin{aligned} F_L(\phi_{AB}, \phi_C) &= \frac{\alpha}{2} \int \int d\mathbf{r} d\mathbf{r}' G(\mathbf{r}, \mathbf{r}') [\phi_{AB}(\mathbf{r}) \\ &- \tilde{\phi}_{AB}] [\phi_{AB}(\mathbf{r}') - \tilde{\phi}_{AB}], \end{aligned} \quad (6)$$

where $\tilde{\phi}_{AB} = \bar{\phi}_{AB}(1 - \phi_C)$, $\bar{\phi}_{AB}$ is the spatially-averaged ϕ_{AB} , $G(\mathbf{r} - \mathbf{r}')$ is the Green function for the Laplacian equation that satisfies $\nabla^2 G(\mathbf{r} - \mathbf{r}') = -\delta(\mathbf{r} - \mathbf{r}')$, and α is a parameter that introduces a chain length dependence to the free energy of the A- and B-blocks. In essence, α controls the characteristic wavelength, or the spacing, of the AB microdomains.

The kinetic evolution of the local volume fractions of A and C monomers are calculated with Cahn-Hilliard (CH) equations:

$$\frac{\partial \phi_{AB}}{\partial t} = M_{AB} \nabla^2 \frac{\delta F}{\delta \phi_{AB}} + \omega_{AB}, \quad (7)$$

$$\frac{\partial \phi_C}{\partial t} = M_C \nabla^2 \frac{\delta F}{\delta \phi_C} + \omega_C, \quad (8)$$

where M_{AB} and M_C are phenomenological mobility coefficients that are assumed to be homogeneous,

and ω_{AB} and ω_C are random noise terms with zero average. The order parameters are updated using a simple forward Euler time-stepping algorithm:

$$\phi_{AB}^{t+\Delta t} = \phi_{AB}^t + \Delta t \left[M_{AB} \nabla^2 \frac{\delta F}{\delta \phi_{AB}^t} - \alpha \cdot (\phi_{AB}^t - \bar{\phi}_{AB}^t(1 - \phi_C^t)) + \omega_{AB} \right], \quad (9)$$

$$\phi_C^{t+\Delta t} = \phi_C^t + \Delta t \left[M_C \nabla^2 \frac{\delta F}{\delta \phi_C^t} + \omega_C \right]. \quad (10)$$

All simulation parameters are provided in Table 1, and the simulations executed in this paper are performed in non-dimensional length, time, and energy units (energy is assumed to be normalized by $k_B T$). For the parameters displayed in Table 1, the mixing energies for the A-B, B-C, and A-C monomer pairs, as defined by the energy terms in Eq. 2, are plotted in Fig. 2. Here, the x-axis displays the local volume fractions ϕ_C or ϕ_A (the former is used for the A-C and B-C pairs, while the latter is used for A-B pair). These mixing energies assume binary mixtures (e.g., the A-B mixing energy is calculated assuming $\phi_C = 0$).

Numerical solutions are obtained with a standard explicit finite difference method. In Table 1, Δx and Δt represent the grid spacing and time step size, and $\omega_{AB} = \omega_C = 4.0$ indicates a random number range between ± 4.0 for the thermal noise in

Table 1: Simulation parameters used in this study.	
Parameter	Value
a_{AB}	1.0
a_C	3.0
b	4.0
c	20.0
α	0.1
κ_{AB}	1.0
κ_C	10.0
M_{AB}, M_C	1.0
ω_{AB}, ω_C	4.0
Δt	0.001
Δx	1.0

Eqs. (7-8) (note that this value is multiplied by the time step $\Delta t = 0.001$ in Eqs. (9-10)). To improve performance, the simulations are executed in parallel with a domain decomposition technique whereby the overall simulation domain is divided into sub-domains that are each assigned to one processor.

3. Results and Discussion

All of the following simulations utilized periodic boundary conditions in the lateral x- and y-directions, and no-flux boundaries in the z-direction. The simulation domain size was consistently kept at $800\Delta x \times 800\Delta x \times 4\Delta x$. The simulations start from a uniform disordered state with ϕ_{AB} and ϕ_C having small initial fluctuations in the

Figure 3: Simulated coarsening in the AB/C thin films with $\bar{\phi}_{AB} = 0.2$ and $\bar{\phi}_C = 0.25$, illustrating the diffusion-governed ripening of the homopolymer domains (yellow). The block copolymer microdomains maintain a nearly-constant size distribution. The three images correspond to $t = 200, 1000$, and 10000τ , and the lower images are diagonal views of the regions within the black squares in the upper images.

range of ± 0.2 about the global averages, $\bar{\phi}_{AB}$ and $\bar{\phi}_C$, respectively. The start of the simulation corresponds to an instant quench below the critical temperature, thereby initiating phase separation. The average compositions were varied to determine their effect on the coarsening kinetics. Each simulation was run for 10 million time steps, corresponding to a total simulation time of 10000τ .

Figure 3 provides progressive snapshots of the evolving three-phase microstructure in time. The composition is $\bar{\phi}_{AB} = 0.2$ and $\bar{\phi}_C = 0.25$. The block copolymer is asymmetric in that the A-block (colored light blue) is larger than the B-block (colored dark blue), and the equilibrium BCP structure is hexagonal ‘B’ columns which orient in the vertical direction due to the thin thickness of the film (the film is thinner than the periodicity of the BCP). In addition, domains consisting of the ‘C’ homopolymer (colored yellow) develop and coarsen in time. Due to the chosen value of $\bar{\phi}_C$, the homopolymer domains consist of discontinuous droplets which traverse the z-thickness of the film. The interface of each homopolymer phase is fully surrounded by the B-block of the BCP, as evidenced by the dark blue rings surrounding the yellow domains. This is a result of the relative interfacial energies shown in Fig. 2.

In general, this system undergoes simultaneous microphase separation of the BCP and macrophase separation of the homopolymer. As time progresses, a growing disparity in domain sizes develops as the BCP domains remain constant in size while the homopolymer domains continuously increase in size. The coarsening of the homopolymer domains occurs via an Ostwald ripening process [?], whereby smaller domains dissolve thus allowing larger domains to grow. Note that the A-block (light blue) represents a continuous matrix phase that may serve as a scaffold for a bimodal porous thin-film membrane.

To quantify this evolution, the microstructures were monitored throughout time by calculating the areal density and average diameter of both the BCP domains and the homopolymer domains (here, for simplicity, when referring to the BCP domains, I mean the B-block of the BCP). To improve the statistics of the data, three independent simulations were performed for each composition, from which mean and standard deviation values were determined. In Fig. 4, the areal density of the BCP and homopolymer domains (in units of Δx^{-2}) are plotted throughout time in a log-log format. Data

Figure 4: Areal number density of (upper) BCP microdomains and (lower) homopolymer domains throughout time for $\bar{\phi}_{AB} = 0.2$ and three different $\bar{\phi}_C$ values. The data points are averages of three independent simulations, and the deviations are represented by the shaded bands.

is presented for three different homopolymer volume fractions: $\bar{\phi}_C = 0.20, 0.25$, and 0.30 . The density of the BCP domains depends on the value of $\bar{\phi}_C$: a higher $\bar{\phi}_C$ value translates to less overall BCP material in the films. Throughout time, the density of the BCP domains increases slightly, which is likely associated with the coarsening of the homopolymer domains. The presence of the homopolymer domains disrupts the BCP domain periodicity, and early in the phase separation process, when the homopolymer domain density is high, it seems that slightly fewer BCP domains can form. As time progresses, and the homopolymer domains become larger and further spaced apart, the BCP domain density increases, as it seems there is less disruption with a coarser state. The density of the homopolymer domains is also plotted, and these values decrease steadily in time, with a power-law dependence consistent with Ostwald ripening [?]. The observed exponent of -0.55 is exactly the same as previous 2D studies of Ostwald ripening [? ?].

The associated average domain diameters for both the BCP and the homopolymer are plotted in Fig. 5 (the averages are determined using all of the domains within the simulation cell, which are then averaged using the three independent runs).

Figure 5: The average diameter of (upper) the homopolymer domains and (lower) the BCP domains throughout time for $\bar{\phi}_{AB} = 0.2$ and three different $\bar{\phi}_C$ values. The average diameter of the homopolymer domains increases in a power-law fashion, while the diameter of the BCP microdomains remain basically constant.

As can be seen, the homopolymer domain diameter increases with a power-law dependence throughout time (exponent of 0.28, in agreement with previous studies [? ?]), while the BCP domain diameters remain essentially constant. Figure 6 provides a histogram illustrating the size distributions for both the BCP and homopolymer domains (taken from the domain diameter data) at three different moments in time. The BCP domain sizes remain constant in time, with a very narrow distribution. The homopolymer domain sizes increase in time, accompanied by a widening of the size distribution.

Clearly, there are a variety of parameters that one can adjust in this model. Above, the homopolymer volume fraction, $\bar{\phi}_C$, was varied between 0.2 and 0.3, with a fixed BCP composition ($\bar{\phi}_{AB} = 0.2$, i.e. the A-block is larger than the B-block). Next, the BCP composition will be changed to a value of $\bar{\phi}_{AB} = -0.2$, corresponding to a B-block that is larger than the A-block. This will result in hexagonal columns of the A-block. The energy function of the system however is not changed, and therefore the B-block will still interface with the homopolymer domains.

Figure 7 provides progressive snapshots of the evolving thin-film microstructure with $\bar{\phi}_{AB} = -0.2$ and $\bar{\phi}_C = 0.25$. Similar to before, the homopolymer domains coarsen due to Ostwald ripening, while the

Figure 6: Size distribution plots for the diameters of the BCP and homopolymer domains at three different times for $\bar{\phi}_C = 0.2$ and $\bar{\phi}_{AB} = 0.2$. The error bars correspond to the deviations observed in the three independent simulations.

BCP domains (specifically, the A-domains within the BCP) remain essentially fixed in size. The B-block once again interfaces with the homopolymer domains, however because it is now the majority (or continuous) block on the BCP, this amounts to simply a separation buffer between the discrete homopolymer macrodomains and the discrete A-block microdomains.

An interesting question arises: does the relative fraction of the A- and B-blocks of the BCPs influence the coarsening rate of the homopolymer domains, given the fact that the homopolymers have a relative affinity for the B-block compared to the A-block? To investigate this question, the above simulations were re-run with $\bar{\phi}_{AB} = -0.2$ rather than $\bar{\phi}_{AB} = 0.2$, and the resulting domain areal densities and average diameters were calculated. Figure 8 plots the areal densities for both the BCP and homopolymer domains throughout time for $\bar{\phi}_{AB} = -0.2$ with $\bar{\phi}_C = 0.20, 0.25$, and 0.30 . The data in this plot is quite similar to Fig. 4, namely the BCP domain densities remain essentially constant (albeit with a slight increase), and the homopolymer domain densities decrease in a power-law fashion consistent with Ostwald ripening.

The average diameters for the BCP and homopolymer domains are plotted in Fig. 9 (similar to Fig. 5) for $\bar{\phi}_{AB} = -0.2$. Very similar trends are observed: a steady increase in homopolymer domain size, and an essentially constant BCP domain size. Here, the decrease in BCP domain size with

Figure 7: Simulated coarsening in the AB/C thin films with $\bar{\phi}_{AB} = -0.2$ and $\bar{\phi}_C = 0.25$, illustrating the diffusion-governed ripening of the homopolymer domains (yellow). The block copolymer microdomains maintain a nearly-constant size distribution. The three images correspond to $t = 200, 1000$, and 10000τ , and the lower images are diagonal views of the regions within the red squares in the upper images.

Figure 8: Areal number density of (upper) BCP microdomains and (lower) homopolymer domains throughout time for $\bar{\phi}_{AB} = -0.2$ and three different $\bar{\phi}_C$ values. The data points are averages of three independent simulations, and the deviations are represented by the shaded bands.

time is very small given the scale of the y-axis - no more than a 2% decrease. The author attributes this slight decrease in diameter to the reduction in number density of the homopolymer domains, which appear to slightly stretch the BCP domains, as seen in Figure 7 (the author also checked, but found no evidence for numerical drift that can oc-

cur due to round-off error). Figure 10 provides a size distribution plot for the BCP and homopolymer domains at three different moments in time, and again the general trend is the same as was previously discussed with Fig. 6.

In both sets of the above results, for $\bar{\phi}_{AB} = 0.2$ and for $\bar{\phi}_{AB} = -0.2$, the homopolymer macrodomains coarsen in time due to an Ostwald ripening process. The underlying processes here involve the transport of homopolymers from smaller homopolymer domains (which shrink and dissolve) to larger homopolymer domains (which grow). In classical Ostwald ripening theory, the continuous phase (in which the solute molecules travel to and from the dispersed phases) is considered homogeneous. Here, the continuous phase is the microphase-separated BCPs, which is heterogeneous. This heterogeneity arises due to the fact that the homopolymers have unequal interaction energies with the two end blocks (the A-C mixing energy is significantly higher than the B-C mixing energy). Hence, as the homopolymers diffuse through the BCP microdomains, their distribution should be heterogeneous - i.e. a relatively higher homopolymer concentration should be expected in the B-blocks compared with the A-blocks (because the solubility of the homopolymers is higher in the B-blocks compared with the A-blocks).

Figure 11 shows a color contour plot of the spatially-varying homopolymer concentration. The color bar, as shown, has been restricted to a very

Figure 9: The average diameter of (upper) the homopolymer domains and (lower) the BCP domains throughout time for $\bar{\phi}_{AB} = -0.2$ and three different $\bar{\phi}_C$ values. The average diameter of the homopolymer domains increases in a power-law fashion, while the diameter of the BCP microdomains remain basically constant.

small concentration range between $\phi_C = 0.0$ and $\phi_C = 0.05$ to analyze the homopolymer concentrations within BCP regions where the homopolymer solubility is small. Indeed, it can be seen that the distribution of homopolymer in the BCP regions is heterogeneous, with a higher fraction in the B-rich microdomains. This is true for both BCP compositions: $\bar{\phi}_{AB} = 0.2$ and $\bar{\phi}_{AB} = -0.2$.

Given the heterogeneous distribution of the homopolymer in the BCP regions, does changing the BCP composition, $\bar{\phi}_{AB}$, affect the coarsening rate of the homopolymer macrodomains? Figure 12 plots the homopolymer domain density and domain diameter versus time for both $\bar{\phi}_{AB} = 0.2$ and $\bar{\phi}_{AB} = -0.2$ (here, the value of $\bar{\phi}_C = 0.3$). Interestingly, the coarsening rates for the homopolymer domains appear to be essentially the same regardless of the fact that the systems contain different quantities of the B-block which favorably interacts with the homopolymers.

To examine this result further, the theory of Ostwald ripening needs to be discussed. Assuming volume diffusion as the rate controlling factor (rather than molecular detachment/attachment at interfaces), the following relationship has been established:

Figure 10: Size distribution plots for the diameters of the BCP and homopolymer domains at three different times for $\bar{\phi}_C = 0.2$ and $\bar{\phi}_{AB} = -0.2$. The error bars correspond to the deviations observed in the three independent simulations.

$$\bar{R}^3 - \bar{R}_o^3 = k \cdot t \quad (11)$$

where $\bar{R}$ and $\bar{R}_o$ are the current and initial average droplet sizes, t is time, and k is a rate constant. The characteristics of this rate constant k have been studied significantly with many models proposed, all building on the Lifshitz-Slyozov-Wagner theory (see [?] for a review). Regardless of the model, however, the rate constant always has the following proportionality:

$$k \sim \frac{\gamma D c_o}{k_B T} \quad (12)$$

where γ is the interfacial energy, D is the solute

Figure 11: Color contour plots of the spatially-resolved homopolymer concentration within the films for (left) $\bar{\phi}_{AB} = -0.2$ and (right) $\bar{\phi}_{AB} = 0.2$. This illustrates the heterogeneous homopolymer distribution within the BCP regions, whereby a larger quantity of homopolymer resides in the B-rich microdomains relative to the A-rich microdomains.

Figure 12: Homopolymer domain (left) densities and (right) diameters for the two different BCP compositions, $\bar{\phi}_{AB} = 0.2$ and $\bar{\phi}_{AB} = -0.2$. Here, $\bar{\phi}_C = 0.3$ for both data sets. The coarsening kinetics for the homopolymer domains appears to be essentially the same regardless of the fact that the systems contain different quantities of the B-block which favorably interacts with the C homopolymers.

molecular diffusivity in the continuous phase, T is temperature, and c_o is the soluble concentration of the solute molecules in the continuous phase.

The result from Fig. 12 is that the rate constant k is the same for $\bar{\phi}_{AB} = 0.2$ and $\bar{\phi}_{AB} = -0.2$. For the AB/C system here, the interfacial energy γ in Eq. (12) corresponds to the B-C interfacial energy, which is true for both BCP compositions considered. This is due to the fact that the homopolymer domains are always surrounded by the B-block of the BCP (there are no A-C interfaces in either system). So, γ is fixed. The temperature can also be assumed to be fixed. This leaves the diffusivity D and the concentration c_o of the homopolymers in the BCP domains. In the Ostwald ripening models, a Fick's law diffusion flux is assumed to describe the transport of molecules in the continuous phase:

$$\vec{j} = -D\nabla c \quad (13)$$

however, the Cahn-Hilliard models shown in Eqs. (7-8) assume a diffusive flux:

$$\vec{j} = -M\nabla\mu \quad (14)$$

where μ is the chemical potential equal to $\frac{\delta F}{\delta \phi}$ (here, ϕ is analogous to c). The Cahn-Hilliard equation is a generalization of Fick's second law. Using an ideal solution model, equating Eqs. (13) and (14) leads to a mobility coefficient that is proportional (but not equal) to the diffusivity D in the following manner [?]:

$$M = \frac{Dc}{k_B T}. \quad (15)$$

This result is arrived at due to the fact that, in ideal solutions, the chemical potential is $\mu = \mu_o + k_B T \ln c$, and hence $\nabla\mu = \frac{k_B T}{c} \nabla c$. The free energy function defined in Eqs. (3-5) is not an exact ideal solution model, but rather a polynomial that shares the important features of the ideal solution model, and therefore the relationship between mobility and diffusion coefficient remains valid. Comparing the definition of mobility given in Eq. (15) with the rate constant of Eq. (12), it is easy to see that by keeping mobility constant (as was done here), the coarsening rate should be independent of the concentration of C in the BCP domains. In essence, a constant mobility of the C homopolymer translates to a non-constant diffusion coefficient: i.e. D_C is lower in the B-domain where the homopolymer concentration is higher (likewise, D_C is higher in the A-domains where the homopolymer concentration is lower). The author asserts that an expanded study would be insightful, whereby a heterogeneous mobility is used for the homopolymer. In such a study, one would need to rationally choose a homopolymer mobility for each of the three phases. This would of course further increase the parameter range associated with these ternary microstructures.

To briefly demonstrate how a heterogeneous mobility assigned to the homopolymer within the BCP matrix can strongly alter the homopolymer coarsening kinetics, a few additional simulations were executed. In the above results, $M_C = 1.0$ throughout the domain. Here, M_C will be made to depend on ϕ_{AB} such that the homopolymer will have a high mobility in the B-phase (to which it has more favorable thermodynamic interactions) than in the A-phase. This is accomplished with the following expression:

$$M_C = \left(\frac{M_C^A - M_C^B}{2} \right) (\tanh 5\phi_{AB} + 1) + M_C^B, \quad (16)$$

which essentially provides a smooth transition of M_C from one value in the A-phase, M_C^A , to a separate value in the B-phase, M_C^B . Here, values of $M_C^A = 0.0$ and $M_C^B = 1.0$ are used, thus making the homopolymer mobility in the A-phase very small (due to the nature of a tanh function, the mobility in the A-phase never actually becomes zero). Additional simulations were run (taking care to em-

bed M_C into the divergence operator in the Cahn-Hilliard equation), and the coarsening data for the C-homopolymer is presented in Fig. 13 for $\bar{\phi}_C = 0.3$ and $\bar{\phi}_{AB} = \pm 0.2$. Now, it can be seen that the coarsening rate differs greatly for the two BCP compositions. The coarsening rate is much inhibited for the case of $\bar{\phi}_{AB} = 0.2$ corresponding to a BCP matrix consisting of continuous A-phase and discrete B-phase microdomains. For such a microstructure, the C-homopolymer has no option but to diffuse through the A-phase as it travels from C-phase domain to another. Future studies will further explore the dependence of macrodomain coarsening on heterogeneous mobilities.

Figure 13: Homopolymer domain (left) densities and (right) diameters for the two different BCP compositions, $\bar{\phi}_{AB} = 0.2$ and $\bar{\phi}_{AB} = -0.2$ with a heterogeneous mobility coefficient for the homopolymer. Again, $\bar{\phi}_C = 0.3$ for both data sets. The coarsening kinetics for the homopolymer domains now drastically differs for the two values of $\bar{\phi}_{AB}$, as explained in the text.

4. Conclusions

TDGL simulations of microphase and macrophase separation in immiscible AB/C block copolymer/homopolymer thin films were performed and analyzed in terms of how the coarsening kinetics are dependent on composition. With constant mobility conditions, the coarsening of the homopolymer macrodomains was found to be independent of the block copolymer composition, regardless of the fact that the homopolymer has unequal interaction energies with the two end blocks. In the BCP regions, the homopolymer had higher solubility (but lower diffusivity) in the B-block relative to the A-block. Longer annealing periods result in a growing disparity in length

scales between the BCP microdomains and the homopolymer macrodomains. With heterogeneous mobility conditions, the coarsening rate varied significantly with the BCP composition and microstructure. In thin-film confinement, these three-phase microstructures can be used as templates to fabricate porous membranes with a bimodal distribution in pore diameters.

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References

References