Coarsening dynamics of ternary polymer solutions with mobility and viscosity contrasts

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Using phase-field simulations, we investigate the bulk coarsening dynamics of ternary polymer solutions undergoing a glass transition for two models of phase separation: diffusion-only and with hydrodynamics. The glass transition is incorporated in both models by imposing mobility and viscosity contrasts between the polymer-rich and polymer-poor phases of the evolving microstructure. For microstructures composed of polymer-poor clusters in a polymer-rich matrix, the mobility and viscosity contrasts significantly hinder coarsening, effectively leading to structural arrest. For microstructures composed of polymer-rich clusters in a polymer-poor matrix, the mobility and viscosity contrasts do not impede domain growth; rather, they change the transient concentration of the polymer-rich phase, altering the shape of the discrete domains. This effect introduces several complexities to the coarsening process, including percolation inversion of the polymer-rich and polymer-poor phases—a phenomenon normally attributed to viscoelastic phase separation.

Keywords: coarsening, mobility contrast, viscosity contrast, diffusion, hydrodynamics

I. INTRODUCTION

Coarsening is a phenomenon that occurs during the late stages of phase separation, characterized by an increase in the size of domains that proceeds until complete phase separation is reached at bulk scales. An everyday example of coarsening is the separation of oil and water in a homemade vinaigrette. Coarsening plays a central role in the development of microstructure or pattern formation for numerous complex fluids and soft materials. For example, coarsening drives the formation of the microstructure of porous polymer materials¹⁻³ yielding membranes and fibers with network structures that are useful for separation processes.⁴ Similarly, coarsening can be used to create microstructured particles and capsules that find use for pharmaceutical and other chemical delivery applications. 5-10 Coarsening is likewise critical for the structure of consumer products, food, and other emulsions.^{11–15} Finally, coarsening is important in biological systems where the resulting microstructure creates structural color and useful mechanical properties.^{9,16–21}

While coarsening can proceed until bulk phase equilibrium is reached, in many complex fluids the microstructure *kinetically arrests* in a solid state, locking in a nonequilibrium microstructure or pattern. We define kinetic arrest as a spontaneous cessation or radical retardation of coarsening that arises endogenously from interactions between the components of the system. There are different mechanisms by which a structure can arrest depending on the particulars of the complex fluid, including vitrification, crystallization, gelation, or jamming.^{1,11,13,22} However, we exclude externally imposed solidification processes (*e.g.*, UV-polymerization of a phase-separating fluid) for our present discussion.

While the kinetics of coarsening are largely known, $^{19,23-27}$ the coupling between coarsening and kinetic arrest remains an active and fruitful area of research. From a pure science perspective, our knowledge of phase transition dynamics is currently incomplete without an understanding the final stage of the process. Indeed, while coarsening and arrest are clearly different, the two cannot be neatly separated, since both arise from interactions between the same components within the complex fluid. More practically, understanding the process of structural arrest is key to rationally designing the microstructure of many complex fluids and soft materials. Therefore, a better understanding of how coarsening leads to kinetic arrest will provide opportunities to create new manufacturing techniques and to optimize existing ones for creating microstructured materials. For example, recent work^{3,28} studying the formation of polymer membranes by nonsolvent-induced phase separation $(NIPS)^{2,29-31}$ showed the need for an arrest mechanism to correctly predict the formation of an asymmetric pore-size distribution.

In the present manuscript, we study bulk coarsening

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and kinetic arrest for a ternary polymer solution consisting of a polymer, good solvent, and poor solvent using simulations of a phase-field model³² that includes an explicit glass transition. We model the glass transition by imposing mobility and viscosity contrasts between the polymer-rich and polymer-poor phases. While similar models have been used in previous studies, $^{3,28,33-38}_{,328,33-38}$ we focus here on systematically characterizing the bulk coarsening and arrest dynamics, which remains unaddressed in the literature. One straightforward benefit of such a study is a better understanding of the dynamics that lead to microstructure formation in NIPS processes. In NIPS, a homogeneous polymer solution (polymer plus solvent) film is put in contact with a nonsolvent bath. Diffusion of nonsolvent into the film induces phase separation of the film into a polymer-rich phase that becomes the membrane matrix and a polymer-poor phase that becomes the membrane pores. The subsequent coarsening of the phase-separated domains and solidification¹ of the polymer-rich phase determine the final membrane microstructure. NIPS has been used for several decades to create porous polymer materials, yet we have only begun to fully understand the physics that creates this microstructure.^{2,3,28,39-42}

However, there are broader benefits to studying coarsening and arrest with this model as well. A ternary polymer solution with a glass transition provides a valuable minimal model to demonstrate the physics of coarsening and arrest for systems with *dynamic asymmetry*. As has been pointed out by Tanaka,⁴³ many complex fluids and soft materials have one component that drives kinetic arrest, while the others remain relatively mobile. This is the certainly the situation in NIPS, and the present model provides a good "case study" of the effects of this dynamic asymmetry on coarsening and kinetic arrest.

With this in mind, the rest of the paper is organized as follows. In the next section, we very briefly review foundational principles of coarsening dynamics and relevant prior work on kinetic arrest. We then introduce the phase-field model and other methodological necessities. We organize the Results and Discussion around two key physical effects that can be turned on and off in our simulation model: hydrodynamics and kinetic arrest. In the first section, we perform a comprehensive analysis of the bulk coarsening dynamics for systems without hydrodynamics (diffusion-only or "Model B")²³ and no mechanism for kinetic arrest. In the second section, we perform a similar analysis, but hydrodynamics are included ("Model H").²³ In the remaining two sections, we build on the previous work to study the process of coarsening with kinetic arrest for systems without and with hydrodynamics. Interestingly, we find in the final section that the imposition of mobility and viscosity contrasts alone can also give rise to phase inversion—a phenomenon often associated with viscoelastic phase separation-even though our model does not include elastic effects. We then conclude with a summary of our results and offer a perspective on future research.

TABLE I. Power-law exponents for coarsening modes in two dimensions (2D).

Coarsening Mechanism	n	Ref.
Ostwald Ripening	1/3	55,56
Interfacial Diffusion	1/4	48, 49
Coalescence	1/2	$52,\!53$
Hydrodynamics (San Miguel)	1/2	53
Hydrodynamics (Siggia)	1	24

A. Overview of Coarsening and Arrest Kinetics

We give a very brief overview of the dynamics of coarsening and kinetic arrest, noting that additional details are given when discussing the results below. The theory of the late stages of phase separation are grounded on the so-called dynamic scaling hypothesis which postulates that large length-scale modes of phase separation dynamics are *universal*, meaning they do not depend on the molecular details of the system.^{19,23,25,27,44,45} Hohenberg and Halperin identified two *universality classes* of phase transition dynamics that are relevant for the present discussion: the dynamics of a conserved order parameter that relaxes via diffusion, *i.e.*, Model B, and the dynamics of a conserved order parameter that is coupled to hydrodynamics, *i.e.*, Model H.²³

For Model B, coarsening can occur via diffusive transport or by droplet coalescence. Diffusive coarsening is typically recognized to proceed via two mechanisms: Ostwald ripening (diffusive exchange between droplets) 46,47 and interfacial diffusion (diffusion along the interface of a droplet).^{48,49} Droplet coalescence can occur as neighboring droplets grow and impinge 50,51 or as droplets move via Brownian motion and collide.⁵² The inclusion of hydrodynamics in Model H adds another possible coarsening mode for surface-tension-driven flows to influence coarsening.²⁴ However, the existence of this mode is disputed for 2D flows.^{53,54} All of these modes can occur simultaneously and the relative importance of one mode or the other is influenced by the volume fraction of the dispersed phase. For example, one expects Ostwald ripening between isolated droplets to dominate if the dispersed phase is dilute, but one expects interfacial diffusion to become important once the dispersed phase crosses the percolation threshold.

In accordance with dynamic scaling, theories of the modes of coarsening for Model B and Model H predict scaling laws of the form $L \sim t^n$, where L is the characteristic domain size and n is a power-law exponent. Table I summarizes the scaling-law predictions of these theories for the different coarsening mechanisms for Model B and Model H. As mentioned above, the scaling laws are expected to be universal with respect to molecular details, but they are predicted to be sensitive to dimensionality. In the present paper, our simulations are limited to 2D to allow them to reach the large length and time scales that are required to probe late-stage coarsening behavior.

Beyond the fundamentals of coarsening, we are interested in how phase transition dynamics become arrested. Kinetically arrested materials, such as glasses or gels, are themselves a large topic within the field of soft matter and complex fluids.^{13,57} Here, we focus only on the aspects of kinetic arrest related to coarsening.

From a macroscopic perspective, coarsening can kinetically arrest when a fluid becomes solid because (i) diffusion ceases, (ii) hydrodynamic modes become inactive, or (iii) elastic forces resist structural evolution. These different mechanisms of arrest can vary with the type of experimental system and the dominant mode can even change during coarsening,⁴³ making arrest a subtle and complicated process. For example, Girelli et al.⁵⁸ recently characterized the different mechanisms of arrest in a protein solution undergoing liquid-liquid phase separation using x-ray photon correlation spectroscopy. As previously mentioned, the fact that one of the phases usually arrests while the other remains mobile (i.e., the system is dynamically asymmetric) further complicates the dynamics.

The most commonly used computational tool for studying coarsening and kinetic arrest has been numerical solutions of various phase-field models (though there are other approaches). We also adopt a phase-field model in the present study, so our discussion of prior results is limited to these types of models. Several researchers have examined kinetic arrest of coarsening via diffusion only (Model B). For example, Sappelt and Jäckle studied this problem in two dimensions (2D) using a binary Cahn-Hilliard model.^{33–35} More recent work has extended these results to include a Flory-Huggins free energy functional, 3,28,37 three dimensions (3D), 38,59 and a more realistic diffusivity.⁶⁰ There has also been work simulating arrest via diffusion with a "Model C" that includes a coupled non-conserved order parameter for embedding a gel transition.⁶¹

There is also significant work on so-called viscoelastic phase separation with models that include both hydrodynamics and elasticity.^{43,62–66} These studies supplement Model H with an explicit constitutive equation (e.g., the upper-convected Maxwell model) for the elastic stress.⁶² Recently, Yoshimoto and Taniguchi⁶⁴ introduced a viscoelastic model to study a ternary polymer solution with Flory–Huggins thermodynamics, similar to the system in this present study.

Phase-field simulations examining arrest of coarsening that focus on hydrodynamics (Model H), but do not include viscoelasticity, are more rare. There are multiple papers that look at the coarsening behavior of Model H,^{67–69} but most of these have a constant mobility and viscosity. Henry and Tegze⁷⁰ recently studied the coarsening behavior of a model with a composition-dependent viscosity, but the model was linear, which is not characteristic of typical forms of kinetic arrest.

The present contribution takes the latter approach, modeling a ternary system with a Flory–Huggins free energy in 2D with both diffusive and hydrodynamic modes of arrest. However, we impose arrest with a mobility and viscosity that are highly nonlinear functions of composition, mimicking a glass transition. As shown below, the model shows significantly more complex behavior than Model B alone, but is significantly less expensive to simulate than models that include elasticity. Of course, employing a full viscoelastic model would include a richer set of phenomena that are needed to model some systems. However, we believe that our present approach complements existing studies that include elastic effects. Benefits of the computationally efficient model include the ability to simulate very long times and the capacity to carefully examine the effect of average system composition on coarsening and arrest behavior. The latter is understudied in the literature, but has important effects in a dynamically asymmetric system. The present model thus provides an excellent case-study (i) for teasing out the different effects of diffusion and hydrodynamic modes on coarsening and arrest (and separating them from elastic modes) and (ii) for examining the role of composition in dynamic asymmetry. Finally, the model provides a rigorous foundation for the coarsening and arrest behavior of models relevant to NIPS processes.^{2,3,28,31,37,42,71,72}

II. MODEL AND METHODS

A. Phase-field model

We use the nondimensional ternary phase-field model derived in our earlier work² for the study of ternary polymer solutions commonly found in NIPS processes:

$$\frac{\partial \phi_i(\boldsymbol{r}, t)}{\partial t} + \boldsymbol{v} \cdot \boldsymbol{\nabla} \phi_i = \boldsymbol{\nabla} \cdot \left[\sum_{j}^{p, n} M_{ij}(\{\phi_i\}) \boldsymbol{\nabla} \mu_j(\{\phi_i\}) \right]$$
(1)
$$-\boldsymbol{\nabla} p + \boldsymbol{\nabla} \cdot \left[\eta(\{\phi_i\}) (\boldsymbol{\nabla} \boldsymbol{v} + \boldsymbol{\nabla} \boldsymbol{v}^T) \right] = N_r \boldsymbol{\nabla} \cdot \boldsymbol{\Pi}$$
(2)

$$\cdot \boldsymbol{v} = 0 \tag{3}$$

where $\phi_p(\mathbf{r}, t)$ and $\phi_n(\mathbf{r}, t)$ are the polymer and nonsolvent volume fractions, M_{ij} is the mobility matrix, p is the pressure, η is the concentration-dependent viscosity, N_r is a reference polymer degree of polymerization, \mathbf{v} is the total mixture velocity,

 ∇

$$\boldsymbol{v} = \sum_{i}^{p,n,s} \phi_i \boldsymbol{v}_i,\tag{4}$$

 $\nabla \cdot \Pi$ is the divergence of the osmotic stress tensor,

$$\boldsymbol{\nabla} \cdot \boldsymbol{\Pi} = \sum_{i}^{p,n} \phi_i \boldsymbol{\nabla} \mu_i, \qquad (5)$$

and the chemical potential, μ_j , is calculated as the functional derivative of the free energy of the system, $\mu_i =$ $\delta F/\delta \phi_i$, where the nondimensional free energy functional is given by,

$$F\left[\left\{\phi_{i}\right\}\right] = \int d\mathbf{r} \left[\sum_{i}^{p,n,s} \frac{\phi_{i}}{N_{i}} \ln \phi_{i} + \frac{1}{2} \sum_{i\neq j}^{p,n,s} \chi_{ij} \phi_{i} \phi_{j} + \frac{1}{2} \sum_{i}^{p,n,s} \kappa_{i} \|\nabla \phi_{i}\|^{2}\right].$$
(6)

In this study, the degree of polymerization for each component is set to $N_p = 20, N_n = N_s = 1$, the Flory-Huggins interaction parameters are fixed at $\chi_{pn} = 1.1$, $\chi_{ps} = \chi_{ns} = 0$, and the square-gradient coefficients are set to $\kappa_p = \kappa_n = \kappa_s = 2.5$. Finally, we note that due to the assumption of incompressibility, the solvent volume fraction is implicitly determined from

$$\phi_s(\boldsymbol{r},t) = 1 - \phi_p(\boldsymbol{r},t) - \phi_n(\boldsymbol{r},t).$$
(7)

As presented in the Supporting Information of our recent study,³ we modified the mobility and viscosity models given in our original methods paper² to incorporate the effects of a glass transition. The mobility matrix is given by

$$M_{pp} = \phi_p (1 - \phi_p) / \eta \tag{8a}$$

$$M_{pn} = M_{np} = -\phi_p \phi_n / \eta \tag{8b}$$

$$M_{nn} = \phi_n (1 - \phi_n) / \eta, \qquad (8c)$$

where the concentration-dependent mixture viscosity, η , is calculated as a sigmoidal function of the polymer volume fraction, ϕ_p ,

$$\eta = 1 + \frac{\eta_p / \eta_s - 1}{1 + \exp\left(-\frac{1}{w} \left(\phi_p(\mathbf{r}) - \phi_p^*\right)\right)}.$$
 (9)

In this definition, η_p/η_s is the pure-component viscosity ratio of the polymer and the solvent (implicitly assuming $\eta_n = \eta_s$, w is the sigmoid width, and ϕ_p^* is the glass-transition concentration. A sigmoidal function for η mimics the exponential growth in viscosity described by the Vogel-Fulcher-Tamman-Hesse (VFTH) and Williams-Landel-Ferry (WLF) relations⁷³ for mixtures that approach a glass transition. The sigmoidal form also serves to improve computational stabilityinstead of diverging to infinity, the local viscosity for a glassy domain is bounded by the viscosity contrast, η_p/η_s . Since the local mobilities of all components are scaled by the inverse of the mixture viscosity, the mobility contrast between the glassy polymer-rich and the liquid polymer-poor phases is set by the value of η_p/η_s . Crucially, for $\eta_p/\eta_s \gg 1$, the viscosity becomes large and the mobilities of *all* species become small wherever ϕ_p locally exceeds ϕ_p^* . This is consistent with a jamming or glass transition. The sigmoid width is set to $w = 1 \times 10^{-3}$ to approximate η as a step function, narrow enough such that $\eta = 1$ at $\phi_p = 0$, but wide enough to avoid numerical issues from a mathematical discontinuity. For most simulations in this study, the glass-transition concentration was set to $\phi_p^* = 0.40$ (the only exceptions are the ϕ_p^* values used in the dynamic phase inversion simulations shown in Figures 11 and 15). The value for ϕ_p^* was conveniently chosen to allow study of coarsening dynamics for a variety of average compositions within the spinodal, as dictated by the thermodynamic parameters chosen for this study.

The nondimensional model above was scaled using the following characteristic quantities:² R_0 , the root-meansquare (RMS) end-to-end distance of a reference polymer with degree of polymerization N_r , as the characteristic length scale ($R_0 = bN_r^{1/2}$); τ , the Rouse time of the reference polymer in a solvent of viscosity η_s , as the characteristic time scale ($\tau = N_r^2 \eta_s b^3/k_B T$); b^2/η_s as the characteristic mobility scale; η_s as the characteristic viscosity scale; $N_r k_B T/b^3$ as the characteristic chemical potential scale; and η_s/τ as the characteristic pressure scale. For this study, the reference degree of polymerization was set to $N_r = N_p$.

The phase-field model presented so far is consistent with the 'Model H' universality class outlined by Hohenberg and Halperin,²³ describing the dynamics of a conserved incompressible system that evolves by diffusion and with hydrodynamics. To identify the contribution of hydrodynamics to the coarsening process, we also study 'Model B' simulations where the conserved incompressible system evolves by diffusion only. In our formulation, Model B can be achieved by setting all velocities in Model H to zero:

$$\frac{\partial \phi_i(\boldsymbol{r}, t)}{\partial t} = \boldsymbol{\nabla} \cdot \left[\sum_{j}^{p, n} M_{ij}(\{\phi_i\}) \boldsymbol{\nabla} \mu_j(\{\phi_i\}) \right], \quad (10)$$

where the mobility matrix, M_{ij} , and the chemical potentials, μ_j are determined in the same manner as they were in Model H. Although the momentum equation (Eq 2) loses significance in Model B, the local viscosity, η , remains as a sigmoidal function that scales the component mobilities, *i.e.*, the mobility contrast in Model B is still set by η_p/η_s in Eq 9.

To focus on the effects of mobility and viscosity contrasts to domain coarsening in both Model B and Model H for different average compositions, we limit the scope of this paper to deterministic bulk simulations of spinodal decomposition. Simulations in this study are set in a $512R_0$ \times $512R_0$ box, discretized by a 1024 \times 1024 grid. Periodic boundary conditions are imposed on all sides of the box to simulate bulk conditions. Compositions are initialized homogeneously within the spinodal region and seeded with random noise of zero mean to kick off phase separation. In the case of Model H, velocity fields are homogeneously initialized to zero. The phasefield models were numerically solved using the pseudospectral method⁷⁴ combined with a semi-implicit timestepping scheme.^{48,67,75} Requisite details of our computational techniques can be found in our original methods paper.²

B. Domain characterization: size and shape

The characteristic domain size of a 2D microstructure is calculated using

$$L = \frac{2\pi}{\langle q \rangle} \tag{11}$$

where the first moment of the time-dependent structure factor is given by

$$\langle q \rangle = \frac{\sum_{q} q \, s_p(q, t)}{\sum_{q} s_p(q, t)}.$$
(12)

The normalized structure factor of the polymer is calculated using

$$s_p(q,t) = \frac{S_p(q,t)}{\sum\limits_{q} S_p(q,t)}$$
(13)

where $S_p(q,t)$ is isotropically averaged from the Fourier transform of the pair-correlation function,

$$S_p(\boldsymbol{q},t) = \frac{1}{V} \sum_{\boldsymbol{r}} \sum_{\boldsymbol{r'}} e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} \Big[\phi_p(\boldsymbol{r}+\boldsymbol{r'},t)\phi_p(\boldsymbol{r'},t) - \langle \phi_p \rangle^2 \Big]$$
(14)

and V is the system volume, which is proportional to the number of lattice points.

The characteristic domain shape of a 2D microstructure is quantified using the average 'circularity' of its discrete domains. The circularity of a single discrete domain is calculated as,

$$c = \frac{P^2}{4\pi A} \tag{15}$$

where P is the perimeter of the domain and A is its area. A large c-value corresponds to a thin and elongated— "stringy"—domain, while a small c-value describes a domain that is qualitatively more circular, with c = 1 characteristic of a perfect circle. The perimeter of a domain is measured using the Freeman chain code⁷⁶ and the area is estimated by the number of pixels within the domain. The shape factor for the entire 2D microstructure is then calculated as the weighted average of c for all discrete domains:

$$C = \frac{\sum_{i} c_i A_i}{\sum_{i} A_i}.$$
(16)

The threshold for circularity was determined heuristically as $C_{circle} = 1.20$, *i.e.*, a 2D microstructure with $C \leq 1.20$ exhibits qualitatively circular domains.

C. Phase characterization: compositions, fraction, and continuity

The compositions of the polymer-rich (α) and the polymer-poor (β) phases are measured by building a histogram of the independent volume fraction fields (ϕ_p and

 ϕ_n) where each bin has a width of 0.04. The polymer concentrations in the α and β phases, ϕ_p^{α} and ϕ_p^{β} , are calculated as the averages of the highest-occupied bin and the lowest-occupied bin, respectively. Calculation of the nonsolvent phase compositions, ϕ_n^{β} and ϕ_n^{α} are done in a similar way. In our experience, using a histogram is a more robust approach to measure phase compositions than simply taking the extrema of ϕ_i as measures of ϕ_i^{α} and ϕ_i^{β} .

The fraction of the polymer-rich phase, f^{α} , is computed by thresholding the ϕ_p field into a binary image, where the threshold value is set as the average of ϕ_p^{α} and ϕ_p^{β} . Phase continuity is then determined using the burning algorithm⁷⁷ on the binary image. A phase is considered continuous across a 2D microstructure if it percolates two opposing sides of a periodic simulation box. Otherwise, the phase is considered discrete.

D. The fastest-growing mode, q_m , and the rate of spinodal decomposition, λ_m

Our earlier work² showed that the differences in coarsening dynamics of two systems with qualitatively similar microstructures (*e.g.*, discrete polymer-poor clusters in a polymer-rich matrix), but with different quench depths, are due to the differences in their fastest-growing modes, q_m , and in their (linearized) rates of spinodal decomposition, λ_m . In that same paper, we derived expressions for q_m and λ_m using a linear stability analysis of Model B.

In Figures 3 and 5 of this study, we examine the coarsening dynamics of qualitatively different microstructures. To facilitate our analysis, we normalize the domain size vs simulation time curves to eliminate the effects introduced by differences in quench depth. The domain size is scaled by the fastest growing mode, $q_m/2\pi$, and the simulation time is scaled by the linearized rate of spinodal decomposition, λ_m .

III. RESULTS AND DISCUSSION

Figure 1 includes two schematic phase diagrams to demonstrate the important regions of composition in the present study. The union of Regions A and B is the binodal region; these two regions are distinguished by the morphologies produced by phase separation kinetics starting from a homogeneous state of the same composition: Region A microstructures are discrete polymerpoor clusters in a polymer-rich matrix, and vice-versa for Region B. The boundary between Regions A and B is the static symmetry line (SSL). Compositions on this line have equal parts of polymer-rich and polymer-poor phases. The shape of the binodal is asymmetric as a consequence of Flory-Huggins thermodynamics for polymer solutions ($N_p > N_n$), thus leading to the slanted SSL. Region G is the glassy region where $\phi_p > \phi_p^*$. During



FIG. 1. Representative ternary (polymer-solvent-nonsolvent) phase diagrams (a) without and (b) with mobility and viscosity contrasts. The phase diagram in (a) corresponds to Sections III A and III B in this paper, while (b) corresponds to Sections III C and III D. Region H is the homogeneous region. Regions A and B are within the binodal. Morphologies in Region A produced by a quench from a homogeneous state have a polymer-rich matrix surrounding polymer-poor clusters and vice-versa for Region B. The red line between A and B is the static symmetry line (SSL) between dominance of polymer-rich and polymer-poor morphologies. Region G is the glassy region, where $\phi_p > \phi_p^*$. Note that the spinodal boundaries between the unstable and metastable areas of the binodal region are not shown.

phase separation, when the polymer-rich phase concentration enters Region G, mobility and viscosity contrasts become active to simulate a glass transition.

The bulk coarsening dynamics of ternary polymer solutions is explored in four sections. Figure 1a shows the setup for Sections III A (Model B) and III B (Model H) where no mobility or viscosity contrasts are applied, *i.e.*, $\eta_p/\eta_s = 1$ in Eq 9. Figure 1b shows the setup for Sections III C (Model B) and III D (Model H) where mobility and viscosity contrasts of different magnitudes are applied by setting η_p/η_s accordingly. For each model of phase separation outlined above, we examine the effects of the average mixture composition on the coarsening dynamics. Note that due to mass conservation and incompressibility, the average composition of a simulation box is constant, and thus equivalent to its initial composition, $(\phi_p^0, \phi_n^0, \phi_s^0)$. In this study, we consider average mixture compositions within the spinodal region; although morphologies formed from nucleation are not considered, we expect that coarsening kinetics of such microstructures are similar (although not identical) to those produced by spinodal decomposition for dilute concentrations, *i.e.*, compositions near the spinodal boundaries.

A. Coarsening by diffusion (Model B), without mobility contrasts ($\eta_p/\eta_s=1$)

Figure 2 illustrates coarsening by diffusion for a nearsymmetric mixture without mobility contrasts. Before spinodal decomposition $(t/\tau < 1.1 \times 10^1)$, the measured domain size in Figure 2a exhibits an anomalous downward trend. This anomaly can be attributed to two factors: (1) the variance of the white noise introduced in the homogeneous initial composition fields to start spinodal



FIG. 2. (a) Domain size growth by diffusion without mobility contrast $(\eta_p/\eta_s = 1)$, for an average composition of $(\phi_p^0=0.24, \phi_n^0=0.56, \phi_s^0=0.20)$. The dashed black line is a least-squares fit of the model, $L = kt^n$, where the estimated parameters are, k = 3.12, and n = 0.310. The unfilled symbols in (a) correspond to the morphologies shown in (b), where the colorbar represents ϕ_p . From left to right, the shape factor is C=5.3, 4.9, 1.6, and 1.2.

decomposition, and (2) finite-size effects in calculating the average structure factor mode according to Eq 12. As spinodal decomposition begins, the measured domain size reaches a minimum as the fastest-growing mode sets the characteristic domain size of the percolated morphology; *i.e.*, before the measured domain size reaches its minimum, the morphology observed is qualitatively white noise.

By the first frame $(t/\tau = 1.0 \times 10^2)$ of Figure 2b, coarsening has broken phase percolation from spinodal decomposition, leading to discrete stringy domains of the polymer-lean phase. The transition time to a discrete morphology depends on the average composition: phase percolation persists longer for compositions closer to symmetry. Active coarsening mechanisms from spinodal decomposition to the first frame include bulk and interfacial diffusion. In bulk diffusion—also known as Ostwald ripening 46,47 or the evaporation-condensation mechanism—mass from smaller domains travel across the continuous phase towards the larger domains, increasing the size of larger domains that contribute less to the total interfacial energy. In interfacial diffusion,^{48,49} material moves along the interfaces. The significance of interfacial diffusion is intuitive for percolated morphologies; however, even in discrete microstructures, interfacial diffusion remains active as it reshapes domains from stringy to circular, decreasing the interfacial energy of a single domain, and by extension the whole system.

By the second frame $(t/\tau = 1.6 \times 10^3)$ of Figure 2b, domains have grown large enough that coalescence has also become active as a coarsening mechanism. Since our simulations are deterministic, thermal fluctuations are not responsible for domain coalescence, *i.e.*, in this study, domain coalescence is not driven by the Binder-Stauffer mechanism.⁵² Instead, as two neighboring domains grow in size by bulk and interfacial diffusion, their interfaces grow closer to each other and the two domains eventually coalesce by diffusional interactions.^{50,51} Thus, domain coalescence in this study cannot be active without other mechanisms driving domain growth.

Bulk diffusion, interfacial diffusion, and domain coalescence have continued to drive domain growth from the second frame $(t/\tau = 1.6 \times 10^3)$ to the third frame $(t/\tau = 2.5 \times 10^4)$ of Figure 2b. By the fourth frame $(t/\tau = 4.0 \times 10^5)$, however, interfacial diffusion has become less active; at this point the reshaping of domains from stringy to circular has been mostly completed, as quantified by the transition of the shape factor to $C \leq C_{circle}$. Domain coalescence has also become less frequent due to the reduced number of discrete domains and the increased distance among these domains. Bulk diffusion, on the other hand, has continued to drive domain coarsening, and will continue to do so, until there are only two domains left in the microstructure: a circular discrete polymer-poor domain surrounded by a continuous polymer-rich matrix.

As described for Figure 2b, several coarsening mechanisms are simultaneously active at any given point in Taking advantage of the dynamic scaling hytime. pothesis,^{27,45} the dominant coarsening mechanism is often identified by the exponent in the power law, $L \sim$ t^n . Domain growth by bulk diffusion scales with $t^{1/3}$ (widely known as the Lifshitz-Slyozov-Wagner (LSW) result), 55,56 interfacial diffusion follows $t^{1/4}$ growth, 48,49and coalescence in 2D is theorized to follow a $t^{1/2}$ power law.⁵³ A least-squares fit of the model, $L = kt^n$, to the data in Figure 2a, from spinodal decomposition $(t/\tau \approx$ 12) to the end of the simulation $(t/\tau = 10^6)$, reveals the power-law exponent to be n = 0.310, suggesting that bulk diffusion is the dominant coarsening mechanism throughout the simulation. This result is quite intuitive. Even when bulk and interfacial diffusion are both active, $t^{1/3}$ growth due to the former dominates $t^{1/4}$ growth due to the latter. Meanwhile, domain coalescence cannot be dominant in these deterministic simulations as the mechanism itself depends on bulk and interfacial diffusion to drive discrete domains closer to each other before they can interact and fuse. Thus, bulk diffusion is the dominant mechanism throughout the coarsening process.

Diffusion-only coarsening dynamics change with the average composition, $(\phi_p^0, \phi_n^0, \phi_s^0)$. Figure 3a shows domain size growth for different average compositions along a constant ϕ_s^0 -axis within the spinodal, *i.e.*, average compositions that lie on the same horizontal line within Regions A and B, as shown in Figure 1. To remove the effects of quench depth from the dynamics, domain size and



FIG. 3. (a) Domain size growth by diffusion for different average compositions with the same solvent content $(\phi_s^0 = 0.20)$: $\phi_p^0 = 0.12$ (blue circles), 0.16 (blue triangles), 0.20 (blue diamonds), 0.24 (orange pluses), 0.28 (orange pentagons), and 0.32 (orange squares). Orange and blue curves correspond to compositions in Regions A and B, respectively, as shown in Figure 1. To remove the effects of quench depth from the dynamics, domain size was scaled with the fastest growing mode $(q_m/2\pi)$, while simulation time was scaled with the rate of spinodal decomposition (λ_m) . Unfilled symbols indicate when the discrete phase turns circular, *i.e.*, transition to $C < C_{circle}$. The same data is shown in (b) but simulation time is shifted by a factor of N_p/N_n earlier for the blue curves than for the orange curves. Black line is a guide for $t^{1/3}$ growth.

Scaled simulation time for orange curves, $\lambda_m t$

simulation time were scaled accordingly as discussed in Section II D. Curves in Figure 3a are colored consistently with Figure 1, where the orange and blue curves correspond to average compositions in Regions A and B, respectively. The long-time coarsening trend for each curve corresponds to their equilibrium microstructure: orange curves collapse onto one trend while the blue curves eventually follow the trend set by the blue circles, the average composition with the least polymer content. The difference between these two long-time coarsening trends (the orange trend and the blue-circles trend) can be understood by examining the diffusivities in our phase-field

$$\lim_{\phi_p \to 0} D_{pp} = \frac{k_B T}{\zeta_0 N_p \eta} \tag{17}$$

$$\lim_{\phi_p \to 0} D_{pn} = 0, \tag{18}$$

and the nonsolvent diffusivities in the dilute–nonsolvent limit are given by,

$$\lim_{\phi_n \to 0} D_{nn} = \frac{k_B T}{\zeta_0 N_n \eta} \tag{19}$$

$$\lim_{\phi_n \to 0} D_{np} = 0, \tag{20}$$

where ζ_0 is the monomer friction coefficient.

As discussed in Figure 2, long-time microstructures constitute circular clusters that coarsen by bulk diffusion only. For the orange curves in Region A, the long-time microstructures are discrete polymer-poor clusters in a polymer-rich matrix, and vice-versa for the blue curves in Region B. In the former, the long-time coarsening mechanism is the diffusion of nonsolvent between clusters across a polymer-rich matrix, and vice-versa for the latter. Comparing Eqs. 17 and 19 reveals that bulk diffusion of nonsolvent across a polymer-rich matrix is faster than the diffusion of polymer material across a polymerpoor matrix by a factor of N_p/N_n . Note that this inference is only valid because the polymer-rich matrix has not become glassy, *i.e.*, the mobility contrast is still set at $\eta_p/\eta_s = 1$ in the current discussion. Figure 3b demonstrates this inference with the long-time collapse of all curves by shifting the time axis for the blue curves by a factor of N_p/N_n earlier than that for the orange curves. Also, note that the long-time coarsening rate follows $t^{1/3}$ growth, consistent with the LSW scaling law for bulk diffusion. 55,56

In addition to long-time coarsening behavior, Figure 3a also illustrates transient coarsening kinetics for different average compositions. No significant differences are observed among the transient behavior of the orange curves after accounting for quench-depth effects, *i.e.*, the coarsening rate of an average composition closer to symmetry (where phase percolation persists longer) is equivalent to that of an average composition closer to the spinodal boundary. This observation can be explained with coarsening mechanisms. In a percolated morphology, both bulk and interfacial diffusion are active, whereas only the former is active in a microstructure that consists of discrete circular domains; however, since bulk diffusion scales with $t^{1/3}$, it dominates over interfacial diffusion that scales with $t^{1/4}$, resulting in equivalent coarsening rates for both types of microstructures.

While the orange curves follow the same power law at all times, the blue curves follow different coarsening rates at different times for different average concentrations. To understand these trends shown by the blue curves in Figure 3a, let us first consider the limiting case of the blue circles. The average composition of the blue circles is dilute enough in polymer such that its characteristic domain shape is circular immediately after spinodal decomposition, *i.e.*, its average composition is so dilute in polymer that its phase-separated morphology resembles microstructures engendered from nucleation. Thus, even immediately after spinodal decomposition, blue-circle microstructures can only coarsen by bulk diffusion of polymer across a polymer-poor matrix.

Moving away from the limiting case of the blue circles, blue curves with greater average polymer content (ϕ_n^0) keep up with the growth of the orange curves for longer times, suggesting that more persistent phase percolation aids in the initial coarsening of the blue curves. In a percolated morphology, growth of the characteristic domain size relies on two mechanisms: the bulk diffusion of nonsolvent and interfacial diffusion. As percolation is broken for the blue curves, bulk diffusion of nonsolvent becomes inactive as a coarsening mechanism since the discrete domains are polymer-rich (in contrast, bulk diffusion of nonsolvent would remain active as a coarsening mechanism for the orange curves since the discrete domains would be polymer-poor). Thus, after percolation is broken, blue-curve morphologies can only coarsen by interfacial diffusion—that is, until the delayed effects of bulk polymer diffusion (delayed by N_p/N_n) eventually catch up and drive further coarsening. In fact, the transition of the blue curves from the orange trend to the blue-circle trend correlates with the transition of the morphology from discrete stringy domains to discrete circular domains. The unfilled symbols in Figure 3 mark the shape metric transition, $C \leq C_{circle}$. Before the shape transition of the blue curves, domains are stringy and interfacial diffusion is active; however, after the shape transition, the discrete domains become circular and can only coarsen by bulk diffusion of the polymer, slowing down their growth towards the limiting case set by the blue circles.

B. Coarsening with hydrodynamics (Model H), without mobility and viscosity contrasts ($\eta_p/\eta_s = 1$)

Figure 4 shows coarsening with hydrodynamics for a near-symmetric mixture without mobility and viscosity contrasts. Immediately after spinodal decomposition, domains start percolated but quickly break up into discrete stringy domains, as shown in the first frame $(t/\tau = 2.5 \times 10^1)$ of Figure 4b. Unlike diffusion-only coarsening, surface-tension-driven $flows^{24,78}$ due to the non-circular interfaces of the stringy domains accelerate domain growth, as demonstrated by the dramatic increase in domain size from the first frame to the second frame $(t/\tau = 4.0 \times 10^1)$. The velocity magnitude fields of the first and second frames, and the left panel of Figure 4c, illustrate these capillary flows. Hydrodynamics continue to accelerate domain growth until the third frame $(t/\tau = 7.9 \times 10^1)$, corresponding to the shape transition, $C \leq C_{circle}$. Since circular interfaces do not gener-



FIG. 4. (a) Domain size growth with hydrodynamics, without mobility and viscosity contrasts $(\eta_p/\eta_s = 1)$, for an average composition of $(\phi_p^0=0.24, \phi_n^0=0.56, \phi_s^0=0.20)$. The solid blue line is a least-squares fit of the model, $L = kt^n$, where the estimated parameters are, k = 0.330, and n = 1.08. The dashed black line $(L \sim t^{0.31})$ is the same least-squares fit line for the diffusion-only coarsening data shown in Figure 2. The unfilled symbols in (a) correspond to the morphologies shown in the top row of (b), where the colorbar represents ϕ_p . From left to right, the shape factor is C=2.9, 2.4, 1.2, 1.1. The bottom row of (b) shows velocity magnitude fields, $\|\boldsymbol{v}\|$. (c) Partial (upper-left corner) velocity fields for $t = 2.5 \times 10^1 \tau$ and $t = 7.9 \times 10^1 \tau$, overlayed on top of their respective microstructures.

ate surface-tension-driven flows, coarsening at this point proceeds only by bulk diffusion and domain coalescence.

A least-squares fit (solid blue line) of the model, $L = kt^n$, to the data in Figure 4a, from spinodal decomposition $(t/\tau \approx 1.1 \times 10^1)$ to the shape transition $(t/\tau = 7.9 \times 10^1)$, reveals a power-law exponent of n = 1.08, close to the linear growth law $(L \sim t^1)$ for coarsening by surface-tension-driven flows proposed by Siggia,²⁴ but far from the theoretical prediction $(L \sim t^{1/2})$ of San Miguel et al.⁵³ for coarsening in 2D. The linear growth law by Siggia can be derived in two ways: first, by dimensional analysis of the force balance between capillary and viscous forces in creeping flow, and second, by linear stability analysis^{53,79} of a cylinder of fluid against longwavelength fluctuations. The prediction by San Miguel et al. was based on adapting the latter procedure to 2D, conducting a linear-stability analysis of a strip, with the prediction that the stability of the strip precludes surfacetension-driven flows in 2D. However, in addition to this present study, other hydrodynamics simulations^{64,80} have

Due to the loss of capillary flows as a coarsening mechanism, domain growth from the third frame (t/τ) 7.9×10^{1}) of Figure 4b onward is driven by bulk diffusion and domain coalescence. In fact, non-zero velocities observed in the third frame are mostly due to domain coalescence, as demonstrated by the right panel of Figure 4c. Coalescence with hydrodynamics—akin to coalescence by diffusion—does not require thermal fluctuations to be active; domains grow larger due to bulk diffusion, driving the interfaces of neighboring domains closer, until they fuse by hydrodynamic interactions.⁸¹ However, as coarsening continues, the number of discrete domains decrease and the spacing among them increase, making coalescence less significant as a coarsening mechanism. By the fourth frame $(t/\tau = 2.5 \times 10^4)$, flows due to domain coalescence are no longer visible; from this point, coarsening proceeds mostly by bulk diffusion.

reported the existence of surface-tension-driven flows in 2D, seemingly invalidating the $(L \sim t^{1/2})$ prediction by

San Miguel et al.

Although bulk diffusion and domain coalescence remain active after the third frame of Figure 4b, Figure 4a shows that domain size growth after this point is remarkably slower than diffusion-only coarsening, *i.e.*, the apparent growth rate after the transition is significantly weaker than $t^{1/3}$. Crist⁸² attributes this observation to the cross-over kinetics between two regimes dominated by different growth laws. Before the shape transition $(C \leq C_{circle})$ in Figure 4, domain size grows linearly due to surface-tension-driven flows. Domain size growth in this regime can be described by,

$$L = k_h t, \tag{21}$$

where k_h is a measured constant corresponding to the effects of surface-tension-driven flows. The domain size at the moment of the shape transition, t_h , can then be calculated as

$$L_h = k_h t_h. \tag{22}$$

After the shape transition, however, hydrodynamic effects disappear and bulk diffusion becomes dominant, leading to the following growth law⁸² for $t > t_h$,

$$L^{3} = L_{h}^{3} + k_{d}^{3}(t - t_{h}), \qquad (23)$$

where k_d is a measured constant corresponding to the effects of bulk diffusion. To facilitate analysis, we can

rewrite Eq 23 as,

$$\left(\frac{L}{L_h}\right)^3 = 1 + K^3(t - t_h) \tag{24a}$$

$$K = \frac{k_d}{k_h t_h}.$$
 (24b)

In the right-hand-side of Eq 24a, two factors determine the domain size for $t > t_h$: the final domain size due to hydrodynamic effects, L_h (represented by unity), and the contributions of bulk diffusion, $K^3(t-t_h)$. For $K^{3}(t-t_{h}) \ll 1$, the contributions from bulk diffusion are muted due to the significantly larger L_h , *i.e.*, bulk diffusion effects appear weaker than usual because the current domain size is so large. In contrast, for $K^3(t-t_h) \gg 1$, bulk diffusion dominates and the scaling law, $L \sim t^{1/3}$ becomes manifest. To demonstrate this transition, the same least-squares fit (dashed black line) of the diffusiononly coarsening data in Figure 2a is also shown in Figure 4a. Using the data in Figure 4a ($t_h = 79, k_d = 3.12$, $k_h = 0.33$), we calculate that $K = 1.20 \times 10^{-1}$. Arbitrarily setting $K^3(t-t_h) = 10^2$ for the $K^3(t-t_h) \gg 1$ regime, we get a regime cross-over time of $(t - t_h) =$ 5.83×10^4 , *i.e.*, this is how long it would take after the shape transition point before $L \sim t^{1/3}$ becomes manifest. This prediction is consistent with the trends shown in Figure 4a.

Although the present study deals with a ternary polymer solution, a similar slow-down in coarsening has been reported for binary polymer blends, referred to as domain pinning.⁸³ Since a symmetric binary polymer blend $(N_A = N_B)$ has no dynamic asymmetry between its components, it is not surprising that aspects of its coarsening behavior are similar to a ternary polymer solution without a viscosity contrast. Two explanations were proposed to explain domain pinning in polymer blends. The first was that transport of long chains across sharp interfaces is not thermodynamically favored, thus hindering bulk diffusion and leading to an apparent arrest in coarsening.⁸⁴ The second was that domain pinning is simply the manifestation of crossover kinetics from coarsening accelerated by hydrodynamics to coarsening due to bulk diffusion.^{85,86} The results from this study supports the crossover kinetics mechanism.

Returning our discussion to the present study, we examine how coarsening dynamics with flow change with the average composition of the ternary polymer solution. Figure 5a shows domain size growth, with hydrodynamics, for different average compositions along a constant ϕ_s^0 -axis within the spinodal. As in Figure 3, differences in the dynamics due to quench depth were removed by scaling the domain-size and simulation-time axes as described in Section II D. Curves are colored consistently with Figure 1, where the orange and blue curves mark average compositions in Regions A and B, respectively. Two long-time trends are manifest, one set by the orange squares, and another by the blue circles. The orange squares represent the limiting case in Region A, where



FIG. 5. (a) Domain size growth with hydrodynamics for different average compositions with the same solvent content $(\phi_s^0 = 0.20)$: $\phi_p^0 = 0.12$ (blue circles), 0.16 (blue triangles), 0.20 (blue diamonds), 0.24 (orange pluses), 0.28 (orange pentagons), and 0.32 (orange squares). Orange and blue curves correspond to compositions in Regions A and B, respectively, as shown in Figure 1. To remove the effects of quench depth from the dynamics, domain size was scaled with the fastest growing mode $(q_m/2\pi)$, while simulation time was scaled with the linearized rate of spinodal decomposition (λ_m) . Unfilled symbols indicate when the discrete phase turns circular, *i.e.*, transition to $C \leq C_{circle}$. The same data is shown in (b), but simulation time is shifted by a factor of N_p/N_n earlier for the blue curves than for the orange curves. Dashed and solid black lines are guides for t^1 and $t^{1/3}$ growth, respectively.

the average composition has enough polymer such that the morphology immediately after spinodal decomposition is composed of circular polymer-poor clusters in a polymer-rich matrix. The blue circles represent the limiting case in Region B, where the morphology immediately after spinodal decomposition consists of circular polymerrich clusters in a polymer-poor matrix. By analogy to Figure 3a, the difference between the orange-square and blue-circle trends can be explained by comparing Eqs 17 and 19: diffusion of nonsolvent across a polymer-rich matrix is faster than the opposite case by a factor of N_p/N_n . Again, this statement is only true in the absence of mo-

bility and viscosity contrasts. Figure 5b demonstrates this inference by presenting the same set of data with the simulation time axis for the blue curves shifted earlier by a factor of N_p/N_n , leading to the collapse of both long-time trends that follow $t^{1/3}$ growth, consistent with the LSW growth law for bulk diffusion.^{55,56}

Figure 5 also reveals transient differences in coarsening behavior due to different average compositions. Average compositions closer to symmetry (orange pluses and blue diamonds) preserve stringy domains for longer times, leading to more sustained surface-tension-driven flows. Thus, average compositions closer to symmetry maintain growth rates that scale with t^1 for longer times; in the context of Eq 24, we can say that t_h values for nearsymmetric mixtures are larger. However, the accelerated growth for near-symmetric mixtures is not a permanent advantage. As explained for Figure 4, apparent domain growth significantly weakens after the shape transition point (marked by unfilled symbols in Figure 4) due to the cross-over between two kinetic regimes. As described in Eq 24, the regime, $K^3(t-t_h) \ll 1$, lasts longer for near-symmetric mixtures, since $K \propto t_h^{-1}$, *i.e.*, near-symmetric mixtures that benefited the most from surface-tensiondriven flows experience the greatest reduction in apparent domain growth after their respective shape transition, allowing average compositions farthest from symmetry to catch up in domain coarsening. In the end, all compositions transition to the $K^3(t-t_h) \gg 1$ regime where bulk diffusion is dominant, resulting in the eventual collapse of all curves, as shown in Figure 5b.

C. Coarsening by diffusion (Model B), with mobility contrasts ($\eta_p/\eta_s > 1$)

In this section, we study the effects of mobility contrast (η_p/η_s) on microstructure evolution by diffusion. We examine three different average compositions along a constant ϕ_s^0 -axis: an average composition in Region A (Figure 6, polymer-poor clusters in a polymer-rich matrix), an average composition in Region B (Figure 7, polymer-rich clusters in a polymer-poor matrix), and a near-symmetric average composition that lies in what we will refer to as Region C (Figure 9, transient morphologies in Region A but ultimate morphologies in Region B). Region C compositions can give rise to an inversion of percolation between the polymer-rich and polymer-poor phases. Simulation times in this section are limited to $t/\tau = 10^4$ due to practical restrictions of our computational tools.

Figure 6 shows domain size growth for an average composition in Region A with different levels of mobility contrast. The circles $(\eta_p/\eta_s = 1)$ in Figure 6 represent the same data shown by the orange pentagons in Figure 3, providing a reference coarsening behavior for this composition without mobility contrast. From this base case, we observe that increasing the mobility contrast, η_p/η_s , slows down the coarsening of domains.

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(a)

FIG. 6. (a) Domain size growth by diffusion in Region A $(\phi_p^0=0.28, \phi_n^0=0.52, \phi_s^0=0.20)$ for different mobility contrasts: $\eta_p/\eta_s = 10^0$ (circles), 10^2 (triangles), 10^4 (squares), 10^6 (diamonds), and 10^8 (crosses). Darker symbols correspond to higher η_p/η_s . (b) Corresponding microstructures for $\eta_p/\eta_s =$ 10^{0} (top row), 10^{4} (middle row), and 10^{8} (bottom row), where the colorbar represents ϕ_p .

This observation is intuitive for Region A morphologies: discrete polymer-poor domains rely on bulk diffusion to coarsen, but diffusion of nonsolvent across the polymerrich matrix is reduced by a factor of η_p/η_s , thus serving as an effective structural arrest mechanism. We also observe that within the limits of $t/\tau = 10^4$, there is not much difference in the coarsening dynamics among $\eta_p/\eta_s = 10^4$ (squares), 10^6 (diamonds), and 10^8 (crosses). We do expect that differences in their growth rates would be magnified for longer simulation times; coarsening dynamics for lower values of η_p/η_s begin to relax to the base case of $\eta_p/\eta_s = 1$ sooner than for higher values of η_p/η_s .

Figure 7 shows coarsening dynamics for an average composition in Region B with different levels of mobility contrast. The circles $(\eta_p/\eta_s = 1)$ in Figure 7a repre-



FIG. 7. (a) Domain size growth by diffusion in Region B $(\phi_p^0=0.16, \phi_n^0=0.64, \phi_s^0=0.20)$ for different mobility contrasts: $\eta_p/\eta_s = 10^0$ (circles), 10^2 (triangles), 10^4 (squares), 10^6 (diamonds), and 10^8 (crosses). Darker symbols correspond to higher η_p/η_s . (b) Corresponding microstructures for $\eta_p/\eta_s = 10^0$ (top row), 10^4 (middle row), and 10^8 (bottom row), where the colorbar represents ϕ_p .

sent the same data shown by the blue triangles in Figure 3, representing coarsening behavior for this composition without mobility contrast. Compared to this base case, we observe that increasing the mobility contrast, even to $\eta_p/\eta_s = 10^8$, does not slow down the coarsening of phase-separated domains. For Region B morphologies, discrete polymer-rich domains rely on bulk diffusion of the polymer across the polymer-poor matrix. Unlike Region A, mobilities in Region B are reduced by a factor of η_p/η_s in the discrete phase, not the continuous phase. As polymer diffusion across the polymer-poor matrix is unhindered, any level of mobility contrast applied would not slow down the coarsening of Region B morphologies.

Closer inspection of domain size and morphologies at $t/\tau = 10^4$ in Figure 7 reveals that higher levels of mobil-



FIG. 8. Evolution of the polymer volume fractions in (a) the polymer-rich α -phase, ϕ_p^{α} , and (b) the polymer-poor β -phase, ϕ_p^{β} , and (c) the evolution of the fraction of the polymer-rich α -phase, f^{α} , for (ϕ_p^0 =0.16, ϕ_n^0 =0.64, ϕ_s^0 =0.20) with mobility contrasts: $\eta_p/\eta_s = 10^0$ (circles), 10^2 (triangles), 10^4 (squares), 10^6 (diamonds), and 10^8 (crosses). Darker symbols correspond to higher η_p/η_s . The dashed line in (a) marks the glass-transition concentration, ϕ_p^* .

ity contrast lead to slightly larger domains. This counterintuitive observation is a consequence of composition change in the polymer-rich phase. Figures 8a and 8b illustrate how mobility contrast changes the local polymer concentrations in the polymer-rich and polymerpoor phases, respectively. We designate the polymerrich phase as the α -phase and its polymer concentration as ϕ_n^{α} . Similarly, we denote the polymer-poor phase

as the β -phase, and its polymer concentration as ϕ_p^{β} . For $\eta_p/\eta_s = 1$, ϕ_p^{α} reaches its equilibrium value almost immediately after phase separation, as demonstrated by the circles in Figure 8a. The enrichment of the α -phase slows down with increasing levels of mobility contrast. As ϕ_p^{α} crosses the glass-transition concentration, ϕ_p^* , mobilities in the α -phase are reduced by a factor of $\hat{\eta}_p/\eta_s$. In fact, raising the mobility contrast to $\eta_p/\eta_s \ge 10^6$ practically freezes enrichment of the α -phase to just above ϕ_n^* , within the accessible simulation time, $t/\tau = 10^4$. Similar to the enrichment dynamics of the squares $(\eta_p/\eta_s = 10^4)$, we expect the diamonds $(\eta_p/\eta_s = 10^6)$ and crosses $(\eta_p/\eta_s = 10^8)$ to reach equilibrium concentrations for longer simulation times. On the other hand, Figure 8b shows that ϕ_p^{β} reaches its equilibrium value with the same dynamics regardless of the mobility contrast applied. Due to the conservation of mass, the decrease in ϕ_p^α combined with the unchanged ϕ_p^β increases the fraction of the polymer-rich phase, $f^\alpha,$ as shown in Figure 8c. This increase in f^{α} due to the redistribution of polymer content is demonstrated by a mass-balance equation often referred to as the "lever rule":

$$f^{\alpha} = \frac{\phi_p^0 - \phi_p^\beta}{\phi_p^\alpha - \phi_p^\beta}.$$
 (25)

Holding all other variables the same, a decrease in ϕ_n^{α} leads to an increase in f^{α} . We refer to this resultfirst explained by Sappelt and Jäckle³⁵—as the *lever* effect. The increase in f^{α} results in stringier discrete domains that have an advantage in coarsening, as previously demonstrated in Figure 3. Yoshimito and Taniguchi⁶⁴ also demonstrated the lever effect. In their study, coarsening of discrete polymer-rich domains with constant mobilities by diffusion and with hydrodynamics were shown to have qualitatively equivalent morphologies, while those that coarsen with elastic effects exhibited larger but less enriched domains. As demonstrated here, a full viscoelastic model is not required for the lever effect to manifest; a large mobility contrast between the polymer-rich and polymer-poor phases is sufficient. At $t/\tau = 10^3$, the shape metric for the morphologies in Figure 7 are C = 1.05, 1.31, and 1.34 for $\eta_p/\eta_s = 10^0$, 10^4 , 10^8 , respectively; the stringier domains for higher mobility contrasts at $t/\tau = 10^3$ lead to slightly larger domains at $t/\tau = 10^4$. The average composition of these morphologies is dilute enough that the lever effect only leads to limited microstructural differences at different levels of mobility contrast. The lever effect becomes more consequential to both the microstructure and the coarsening behavior of average compositions closer to the static symmetry line (SSL).

Figure 9 shows coarsening dynamics by diffusion for a near-symmetric average composition in Region B. When $\eta_p/\eta_s = 1$, bulk diffusion dominates, as evidenced by the power-law exponent of n = 0.300 (dashed black line). Although this average composition still lies within Region B (polymer-rich clusters at equilibrium), applying a mobility contrast of $\eta_p/\eta_s = 10^4$ significantly hinders the

coarsening rate. This effect can be attributed to the inversion of the polymer-rich and polymer-poor domains as the continuous and discrete phases. This phase inversion is most evident by comparing microstructures for different mobility contrasts at $t/\tau = 10^4$ (rightmost column) in Figure 9c. Since the polymer-rich phase becomes continuous at higher mobility contrasts, bulk diffusion becomes reduced by a factor of η_p/η_s , similar to the structural arrest mechanism in Region A. However, since this average composition is near-symmetric, interfacial diffusion remains active in reshaping the stringy domains, evidenced by the power-law exponent of n = 0.225 (solid red line). Interfacial diffusion—unhindered by the low mobilities in the continuous phase—explains why domain coarsening at $\eta_p/\eta_s = 10^4$ still proceeds at the same rate as coarsening at $\eta_p/\eta_s = 10^8$. We expect that at some point beyond $t/\tau = 10^4$, effects of higher mobility contrasts will eventually manifest as soon as the shape transition is reached and interfacial diffusion becomes inactive; from this point onwards, bulk diffusion weakened by η_p/η_s , would remain as the only active coarsening mechanism.

The phase inversion shown in Figure 9 is simply another consequence of the lever effect, and has been reported before for Model B simulations of binary mixtures described with Cahn-Hilliard thermodynamics.^{35,36,38} Figures 9b and 9d show the dynamics of ϕ_p^{α} and f^{α} , respectively. By analogy to the dynamics in Figure 8, a larger mobility contrast decreases ϕ_p^{α} which in turn increases f^{α} . In this case, however, the average composition is near-symmetric, allowing the lever effect to increase f^{α} from $f^{\alpha} < 0.5$ to $f^{\alpha} > 0.5$, leading to the inversion of the continuous majority phase from polymerpoor to polymer-rich.

As demonstrated by morphologies in Figures 6, 7 and 9, the significance of the lever effect is compositiondependent. In Region A (polymer-poor clusters in polymer-rich matrix), the lever effect pushes f^{α} farther away from symmetry, leading to smaller and more circular domains. In Region B (polymer-rich clusters in polymer-poor matrix), the lever effect pushes f^{α} closer to symmetry. For polymer-dilute average compositions, the lever effect makes discrete domains stringier, thus slightly increasing coarsening rates. On the other hand, nearsymmetric average compositions in Region B experience a phase inversion that hinders coarsening. Average compositions that experience phase inversion is introduced as Region C in the schematic shown in Figure 10a. In this region, equilibrium (ultimate long-time) morphologies belong to Region B, but transient morphologies belong to Region A.

The boundaries of Region C are determined by both thermodynamics and the glass-transition model. Theoretical predictions of the static symmetry line (SSL) and the dynamic symmetry line (DSL) are shown in Figure 10b. Given the corresponding polymer-rich $(\phi_p^{\alpha}, \phi_n^{\alpha})$ and polymer-poor concentrations $(\phi_p^{\beta}, \phi_n^{\beta})$ on the binodal, theoretical prediction of the SSL can be done by setting



FIG. 9. (a) Domain size growth by diffusion and (b) the evolution of the polymer volume fraction in the polymer-rich phase, ϕ_p^{α} , for a mixture in Region C ($\phi_p^0=0.22$, $\phi_n^0=0.58$, $\phi_s^0=0.20$) with different mobility contrasts: $\eta_p/\eta_s = 10^0$ (circles), 10^2 (triangles), 10^4 (squares), 10^6 (diamonds), and 10^8 (crosses). The lines in (a) are least-squares fit of the model, $L = kt^n$, where the pre-factors are k = 3.19 (dashed black) and k = 3.65 (solid red), while the exponents are n = 0.300 (dashed black) and n = 0.225 (solid red). (c) Microstructures for $\eta_p/\eta_s = 10^0$ (top row), 10^4 (middle row), and 10^8 (bottom row), where the colorbar represents ϕ_p . (d) Evolution of the fraction of the polymer-rich phase, f^{α} .

 $f^{\alpha} = 1/2$ in Eq 25:

$$\phi_p^{SSL} = \phi_p^\beta + \frac{1}{2}(\phi_p^\alpha - \phi_p^\beta) \tag{26a}$$

$$\phi_n^{SSL} = \phi_n^{\alpha} + \frac{1}{2}(\phi_n^{\beta} - \phi_n^{\alpha}).$$
 (26b)

Theoretical prediction of the DSL can be carried out in a similar manner. In this case, however, since the imposed mobility contrast freezes polymer-rich phase enrichment at the glass-transition concentration $(\phi_p^{\alpha}, \phi_n^{\alpha})$, the polymer-rich phase concentrations $(\phi_p^{\alpha}, \phi_n^{\alpha})$ in Eq 26 need to be replaced accordingly:

$$\phi_p^{DSL} = \phi_p^{\beta} + \frac{1}{2}(\phi_p^* - \phi_p^{\beta})$$
 (27a)

$$\phi_n^{DSL} = \phi_n^* + \frac{1}{2}(\phi_n^\beta - \phi_n^*).$$
 (27b)

In this study, the polymer concentration was set at a constant value, $\phi_p^* = 0.40$ and ϕ_n^* values were determined from the intersections of the respective tie-lines with the glass-transition line. In this case, predicting the DSL is straightforward due to the use of the sigmoidal viscosity model in Eq 9. Experimentally, locating the SSL and DSL requires mapping the cloud point binodal envelope as well as characterizing the ternary solution viscosity to locate the boundaries of the glassy region.

As shown in Figure 10a, the theoretical SSL and DSL intersect below the critical point of the binodal. The location of this intersection is determined by the relative positions of the glass-transition line and the tie-lines. The



FIG. 10. (a) Schematic ternary (polymer-solvent-nonsolvent) phase diagram with mobility contrast and the dynamic Region C, where morphologies immediately after phase separation belong in Region A (polymer-poor clusters in a polymerrich matrix) while equilibrium morphologies belong in Region B (polymer-rich clusters in a polymer-poor matrix). The solid red line represents the static symmetry line (SSL) while the dashed red line marks the dynamic symmetry line (DSL). Regions G and H are the glassy and homogeneous areas, respectively. (b) Theoretical SSL (solid red line) and DSL (dashed green line) for the model employed here with static symmetry points (open red circles) and dynamic symmetry points (open green circles) determined from simulations. The dot-dash purple, solid blue, and dashed blue lines represent the glass-transition concentration ($\phi_p^* = 0.40$), the binodal, and one of the tie-lines, respectively.

intersection corresponds with the tie-line whose polymerrich phase equilibrium concentration is equal to the glasstransition concentration, $\phi_p^{\alpha} = \phi_p^*$. Above this tie-line $(\phi_p^{\alpha} < \phi_p^*)$, the mobility contrast has no effect on phase separation *i.e.*, there is a minimum quench depth requirement to demonstrate the existence of Region C. The quench depth required for Region C becomes shallower as the glass-transition line approaches the critical point of the binodal. In other words, we expect that systems whose polymer-rich phase is more glassy can manifest phase inversion at shallower quenches. In his review of phase separation mechanisms, Tanaka⁴³ describes a similar quench depth requirement for viscoelastic phase separation to manifest.

Figure 10b shows static symmetry points (SSPs) and dynamic symmetry points (DSPs) determined from simulations for the specific model parameters employed. The symmetry point (where both phases percolate) was determined using iterative simulations of different average concentrations (ϕ_p^0, ϕ_n^0) along a constant- ϕ_s^0 line. The symmetry points would have ideally been determined from iterative simulations across a tie-line, but using a constant- ϕ_s^0 line was more convenient and either method would have led to the same results. The SSPs were determined from morphologies at $t/\tau = 10^3$ for simulations without any mobility contrast, while the DSPs were determined from transient morphologies that manifested shortly after phase separation for simulations with a viscosity contrast of $\eta_p/\eta_s = 10^8$.

Figure 10b shows two SSPs and three DSPs. The SSP at the shallower quench agrees well with the SSL, while a significant difference is observed for the SSP at the deeper quench. Determining the precise location of the SSP becomes more difficult with increasing quench depth. These simulations require higher accuracy to resolve the faster rate of spinodal decomposition and the increasingly dilute concentration of the polymer-poor phase. In other words, we attribute the mismatch between the SSP and the SSL as a consequence of inaccuracies in our methods for deeper quenches. Meanwhile, the three DSPs roughly correspond with the theoretical DSL. Note that the SSP and DSP locations are all slightly closer to the non-solvent rich side of the phase diagram than expected. This offset can be attributed to the N_p/N_n mobility contrast discussed in Figure 3.

So far, we have only demonstrated how the lever effect leads to phase inversion when comparing different levels of mobility contrast. In simulations of viscoelastic phase separation,⁴³ phase inversion can be demonstrated in one long dynamic simulation. Figure 11a shows that it is indeed possible for dynamic phase inversion to manifest due to mobility contrasts alone within a single simulation by careful selection of parameters. As we can only access a maximum simulation time of $t/\tau = 10^4$, a modest mobility contrast of $\eta_p/\eta_s = 10^2$ was required to enable the microstructure to relax back to its equilibrium morphology by the end of the simulation. The average polymer composition, ϕ_p^0 , and the glass transition concentration, ϕ_p^* , were also set close to each other to allow phase inversion to manifest as clearly as possible.

Figure 11b reveals an interesting consequence of setting the glass-transition concentration, ϕ_p^* , closer to the average polymer composition, ϕ_p^0 . Changing the glasstransition concentration affects when the dynamic asymmetry from the mobility contrast becomes "active" in composition space. Comparing Figure 11b with the data for $\eta_p/\eta_s = 10^2$ in Figures 8 and 9 shows that the polymer-rich phase in the former takes significantly longer $(t/\tau \approx 8 \times 10^2)$ to relax to equilibrium than it does in the latter $(t/\tau \approx 10^2)$. Thus, the phase separation and coarsening dynamics can be significantly influenced depending on when the mobility contrast becomes active. This behavior is different than many models of viscoelastic phase separation where the constitutive model provides the dynamic asymmetry. In these viscoelastic



FIG. 11. (a) Dynamic phase inversion by diffusion in Region C due to the lever effect, where $(\phi_p^0 = 0.16, \phi_n^0 = 0.64, \phi_s^0 = 0.20)$ and $\phi_p^* = 0.20$. The mobility contrast was set to $\eta_p/\eta_s = 10^2$ and the point of inversion happens between the second and third frames. Until the second frame, the polymer-rich phase is percolated, but from the third frame, the polymer-poor phase is percolated. Color bar represents ϕ_p . (b) Evolution of the polymer volume fraction in the polymer-rich phase, ϕ_p^{α} , and in the polymer-poor phase, ϕ_p^{β} . (c) Domain size growth dynamics where the dashed black line serves as guide for $t^{1/3}$ growth. Note that the simulation box in (a) is only a quarter of a full periodic box to aid the reader in discerning phase percolation by eye. Data for (b) and (c) were calculated for the full periodic box.

models, dynamic asymmetry is present from the beginning of the phase separation.

Figure 11c shows the corresponding domain size growth for the dynamic phase inversion simulation in Model B. Before the inversion of percolation (between the second and third points), the applied mobility contrast significantly hinders domain growth. Fitting the data from the first point to the third point reveals an apparent power-law close to $t^{1/6}$. This slow rate of growth is expected before inversion, because the microstructure exists in Region A. After the inversion of percolation, the coarsening rate increases and eventually follows a late-stage $t^{1/3}$ growth law, consistent with a Region B microstructure.

Although we have demonstrated that phase inversion is achievable by the simple application of a mobility contrast in diffusion-only dynamics, we do not claim that other idiosyncrasies of viscoelastic phase separation can be reproduced by our considerably simpler model. In particular, we are not able to reproduce the *moving droplet phase*⁴³—a phase stabilized by elastic collisions between discrete polymer-rich droplets driven by thermal fluctuations. We are also unable to reproduce dynamical arrest as reported by Yuan et al. from their fluid-particle simulations.⁸⁷

D. Coarsening with hydrodynamics (Model H), with mobility and viscosity contrasts ($\eta_p/\eta_s>1$)

In this section, we study the effects of mobility and viscosity contrasts (η_p/η_s) on microstructure evolution with hydrodynamics. For the rest of this section, we will refer to the combined effects of mobility and viscosity contrasts simply as a viscosity contrast for convenience. As in Section IIIC, we examine three different average compositions along a constant ϕ_s^0 -axis: an average composition in Region A (Figure 12, polymer-poor clusters in a polymer-rich matrix), an average composition in Region B (Figure 13, polymer-rich clusters in a polymerpoor matrix), and an average composition in Region C, (Figure 14, transient morphologies in Region A but equilibrium morphologies in Region B). Simulation times in this section are again limited to $t/\tau = 10^4$ and the viscosity contrast is limited to $\eta_p/\eta_s = 10^4$, as solving the Stokes equation at higher values with current numerical $methods^2$ is computationally limiting.

Figure 12 shows domain size growth in Region A for different levels of viscosity contrast. The circles $(\eta_p/\eta_s = 1)$ in Figure 12a represent the same data shown by the orange pentagons in Figure 5, providing a reference coarsening behavior for this composition without viscosity contrast. From this base case, we observe that increas-



FIG. 12. (a) Domain size growth with hydrodynamics in Region A (ϕ_p^0 =0.28, ϕ_n^0 =0.52, ϕ_s^0 =0.20) for different viscosity contrasts: $\eta_p/\eta_s = 10^0$ (circles), 10^2 (triangles), and 10^4 (squares). (b) Corresponding microstructures for $\eta_p/\eta_s = 10^0$ (top row), 10^2 (middle row), and 10^4 (bottom row), where the colorbar represents ϕ_p .

ing the viscosity contrast slows down coarsening; not only does η_p/η_s reduce the mobilities in the polymer-rich matrix as they were in Figure 6, but it also shuts down capillary flows normally generated from stringy interfaces after phase separation. In fact, comparing the corresponding growth curves and microstructures between Figure 6 (diffusion only) and Figure 12 (with hydrodynamics) reveals virtually equivalent coarsening dynamics, even for a viscosity contrast as low as $\eta_p/\eta_s = 10^2$. This observation is not surprising; considering that the average composition examined in this case is far from symmetry, capillary flows can only be short-lived, even for the base case without viscosity contrast. Thus, similar to our conclusions from Figure 6, we expect that imposing $\eta_p/\eta_s = 10^4$ would be equivalent to setting an extremely high contrast of $\eta_p/\eta_s = 10^8$, *i.e.*, we expect

that $\eta_p/\eta_s = 10^4$ is sufficient to impose structural arrest in Region A within the simulation time of $t/\tau = 10^4$.

Figure 13 shows coarsening dynamics in Region B for different levels of viscosity contrast. The circles $(\eta_p/\eta_s = 1)$ in Figure 13c represent the same data shown by the blue triangles in Figure 5, setting a baseline coarsening behavior without viscosity contrast. Compared to this base case, we observe that increasing the viscosity contrast accelerates coarsening. As before, the lever effect is responsible for this counterintuitive result. Similar to the diffusion-only case demonstrated by Figures 7 and 8, the transient f^{α} increases with greater viscosity contrast, making discrete domains stringier; the shape factors for the microstructures shown in the first column $(t/\tau = 1.0 \times 10^2)$ of Figure 13a are, C = 1.03 $(\eta_p/\eta_s =$ 10⁰), 1.36 $(\eta_p/\eta_s = 10^2)$, and 2.70 $(\eta_p/\eta_s = 10^4)$. The increased shape factor leads to two advantages in domain growth. First, interfacial diffusion remains active for longer times. A least-squares fit (orange line) of the model, $L = kt^n$, to the squares $(\eta_p/\eta_s = 10^4)$ in Figure 13c exhibits a power-law exponent of n = 0.251, consistent with interfacial diffusion as the dominant coarsening mechanism.⁴⁸ Second, as shown in the first column $(t/\tau = 1.0 \times 10^2)$ of Figure 13b, capillary flows become more active with higher η_p/η_s . The high-velocity areas observed for the top frame of the first column $(\eta_p/\eta_s = 10^0)$ correspond to sites of domain coalescence; in contrast, the high-velocity areas for the middle $(\eta_p/\eta_s = 10^2)$ and bottom $(\eta_p/\eta_s = 10^4)$ frames correspond to capillary flows. Due to the applied viscosity contrasts, however, the capillary flows in Figure 13b (middle and bottom rows) are considerably weaker than those in Figure 4b (note the change in the colorbar scale between the two figures). Nevertheless, these weak flows remain significant to domain growth, as evidenced by comparing the microstructures for $\eta_p/\eta_s = 10^4$ between Figure 7b (diffusion only) and Figure 13a (with hydrodynamics).

Viscosity contrast also changes the mechanism of domain coalescence for Region B compositions. As previously described in Figure 4, domain coalescence for $\eta_p/\eta_s = 1$ is highly dependent on other coarsening mechanisms; as domains grow larger due to bulk and interfacial diffusion, their interfaces approach each other, eventually fusing due to hydrodynamic interactions.⁸¹ This dependence on other coarsening mechanisms is due to the absence of thermal fluctuations in our simulations. In contrast, weak capillary flows drive domain coalescence for $\eta_p/\eta_s = 10^4$. As shown in the second frame $(t/\tau = 1 \times 10^3)$ of the bottom rows $(\eta_p/\eta_s = 10^4)$ of Figures 13a and 13b, the high viscosity contrast combined with the stringy domains that remain (C = 8.03)produce weak capillary flows. These flows are illustrated more clearly in the left panel of Figure 13d. Even though they are too weak to drive domain growth to scale linearly with time, these weak capillary flows are strong enough to drive the glassy domains to move, collide, and eventually coalesce. Thus, weak capillary flows serve a similar purpose for domain coalescence in deterministic



FIG. 13. Evolution of the (a) polymer volume fraction field, ϕ_p , and (b) the velocity magnitude field, $||\boldsymbol{v}||$, in Region B $(\phi_p^0=0.16, \phi_n^0=0.64, \phi_s^0=0.20)$, for different viscosity contrasts: $\eta_p/\eta_s = 10^0$ (top row), $\eta_p/\eta_s = 10^2$ (middle row), and $\eta_p/\eta_s = 10^4$ (bottom row). (c) Corresponding domain size growth for $\eta_p/\eta_s = 10^0$ (circles), 10^2 (triangles), and 10^4 (squares). The solid orange line is a least-squares fit of the model, $L = kt^n$, where the estimated parameters are, k = 4.85, and n = 0.251. (d) Partial (upper-right corner) velocity fields for $\eta_p/\eta_s = 10^4$, overlaid on top of their respective microstructures. Velocity magnitude scales were changed in (d) to exhibit flow structures that would be difficult to observe using the scale in (b).

simulations as thermal fluctuations in stochastic simulations. Of course, the effect of the former in our data is much weaker than the effect of the latter for stochastic simulations;⁵² weak capillary flows are not strong enough to make domain coalescence the dominant coarsening mechanism over interfacial diffusion. By the end of the simulation $(t/\tau = 1 \times 10^4)$, the number of domains has decreased and the distance among them has grown that domain coalescence has become inactive; in fact, as shown in the right panel of Figure 13d, capillary flows have also grown too weak to drive domain coalescence.

Figure 14 shows coarsening dynamics in Region C for different levels of viscosity contrast. For the green circles $(\eta_p/\eta_s = 1)$ in Figure 14a, capillary flows accelerate coarsening from spinodal decomposition to the shape transition, as evidenced by the estimated power-law exponent of n = 1.01 for the dashed black line. After the shape transition, coarsening proceeds by bulk diffusion only, and we observe an apparent slow-down in growth due to the cross-over between two kinetic regimes, as previously explained in Figures 4 and 5. Meanwhile, setting $\eta_p/\eta_s \geq 10^2$ induces phase inversion of the continuous phase to polymer-rich, thus slowing down bulk diffusion and attenuating capillary flows, similar to the effects described earlier in Figure 9.

Although viscosity contrasts made capillary flows weaker, they remain strong enough to aid in the coarsening process. The effects of hydrodynamics are most obvious when comparing the coarsening data of $\eta_p/\eta_s = 10^4$ in Figure 9 (diffusion only) and Figure 14 (with hydrodynamics). Least-squares fit (solid red lines) of both data sets reveal power-law exponents of n = 0.225 and



FIG. 14. (a) Domain size growth with hydrodynamics in Region C ($\phi_p^0=0.22$, $\phi_n^0=0.58$, $\phi_s^0=0.20$) for different viscosity contrasts: $\eta_p/\eta_s = 10^0$ (circles), 10^2 (triangles), and 10^4 (squares). The lines in (a) are least-squares fit of the model, $L = kt^n$, where the pre-factors are k = 0.514 (dashed black) and k = 4.90 (solid red), while the exponents are n = 1.01 (dashed black) and n = 0.233 (solid red). (b) Corresponding microstructures for $\eta_p/\eta_s = 10^0$ (top row), 10^2 (middle row), and 10^4 (bottom row), where the colorbar represents ϕ_p .

n = 0.233, for the former and the latter, respectively, suggesting that interfacial diffusion is the dominant coarsening mechanism in both cases. Nevertheless, their final microstructures are significantly different. The discrete domains in the former are remarkably stringier (C = 8.34) than those of the latter (C = 1.30); since interfacial diffusion is dominant in both cases, we can only attribute this difference in domain shape to residual effects of capillary flows.

Hydrodynamic effects are also evident when comparing the coarsening data of $\eta_p/\eta_s = 10^2$ in Figure 9 (diffusion only) and Figure 14 (with hydrodynamics). Setting $\eta_p/\eta_s = 10^2$ in the former was enough to make its coarsening dynamics equivalent to simulations with greater viscosity contrasts, but the same does not hold true for the latter; although $\eta_p/\eta_s = 10^2$ hinders domain coarsening from following a linear growth law, this level of contrast is not strong enough to eliminate hydrodynamic effects for average compositions in Region C. Note that capillary flows are more sustained in Region C as these compositions are always near symmetry. However, we expect that even for Region C compositions, we only need to raise the viscosity contrast high enough to make Model H dynamics equivalent to that of Model B, similar to the conclusions made for dilute compositions in Region A.

For diffusion-only dynamics, we demonstrated dynamic phase inversion in Region C by imposing a modest mobility contrast $(\eta_p/\eta_s = 10^2)$ relative to the maximum simulation time $(t/\tau = 10^4)$. We applied a similar strategy in Figure 15 to illustrate dynamic phase inversion in Model H. The polymer-rich phase remains percolated until the end of the simulation $(t/\tau = 10^4)$, where $f^{\alpha} = 0.19$, a value far from symmetry. This tendency of minority polymer-rich domains to remain elongated and form persistent networks has been reported for phasefield simulations of viscoelastic phase separation,^{43,63,64} molecular dynamics^{88,89}, and fluid-particle simulations⁸⁷.

Figure 15 also reveals the role of hydrodynamics in dynamic phase inversion in Region C. Despite the stringy domains, capillary flows remain relatively weak until the third frame $(t/\tau = 6.3 \times 10^2)$, as expected of setting $\eta_p/\eta_s = 10^2$. A magnified view of the velocity fields in Figure 15b shows that velocity fields tend to follow the direction of stretched-out polymer domains, pushing them to contract and grow thicker. By the end of the simulation $(t/\tau = 1 \times 10^4)$, capillary flows have become inactive as most discrete domains have become qualitatively circular, and only one large continuous polymerrich domain remains. Of course, we expect the polymerrich phase to lose its continuity eventually at some point beyond $t/\tau = 10^4$, as domains continue to coarsen by diffusion.

Figure 15c shows that the enrichment of the polymerrich phase in dynamic phase inversion for Model H is similar to that of Model B as shown in Figure 11c. Although the expected relaxation time is $t/\tau = 10^2$, the equilibrium value is not reached until approximately $t/\tau = 8 \times 10^2$. Meanwhile, equilibration dynamics of the polymer-poor phase appears to be slower than it was in Model B. This anomaly could be attributed to the differences in the accuracy of methods for solving Model B and Model H.

Finally, Figure 15d reveals the coarsening dynamics for the dynamic phase inversion simulation in Model H. From the first point $(t/\tau = 10^2)$ to the second point $(t/\tau = 3.2 \times 10^2)$, coarsening follows $t^{1/4}$ growth due to interfacial diffusion. From the third point $(t/\tau = 6.3 \times 10^2)$ to the fifth point $(t/\tau = 3.5 \times 10^3)$, domain growth is consistent with the t^1 power law, as expected from the



FIG. 15. (a) Evolution of the polymer volume fraction field, ϕ_p (top row), and the velocity magnitude field, $\|v\|$, (bottom row) in Region C ($\phi_p^0 = 10$, $\phi_n^0 = 0.70$, $\phi_s^0 = 0.20$), where the viscosity model parameters were set to $\phi_p^* = 0.14$ and $\eta_p/\eta_s = 10^2$ to demonstrate dynamic phase inversion. (b) Partial (upper-right corner) velocity fields for $t = 3.2 \times 10^2 \tau$, $t = 6.3 \times 10^2 \tau$, and $t = 1.0 \times 10^3 \tau$, overlaid on top of their respective microstructures. (c) Evolution of the polymer volume fraction in the polymer-rich phase, ϕ_p^{α} , and the polymer-poor phase, ϕ_p^{β} with $\phi_p^* = 0.14$, as shown by the dashed purple line. (d) Domain size growth dynamics where the dashed and solid black lines serve as guides for $t^{1/4}$ and t^1 growth, respectively.

strong velocity fields shown in Figure 15a. From the fifth point to the last point $(t/\tau = 10^4)$, domain coarsening appears to significantly slow down, an anomaly we can attribute to finite-size effects. If we were able to extend this simulation in a larger box and for longer times, we expect that domain growth will eventually cross-over to the long-term $t^{1/3}$ growth law, similar to the case without viscosity contrasts as described in Figure 5.

IV. CONCLUSIONS AND FUTURE OUTLOOK

In this study, we explored the coarsening behavior of a ternary polymer solution whose dynamics evolve by diffusion only (Model B) and with hydrodynamics (Model H). In the absence of applied mobility or viscosity contrasts, the coarsening behavior for both models were shown to be concentration-dependent. Polymer-rich clusters grow slower than polymer-poor clusters due to the difference in the diffusivity of a long polymer chain and that of the smaller molecules in the system. The domain shape was also shown to play a crucial role in determining coarsening rates. In Model B, interfacial diffusion is only active before the characteristic domain shape transitions to a circle. In Model H, surface-tension-driven flows accelerate coarsening up to the same shape transition, after which domain growth slows down due to a cross-over between two regimes with different dominant coarsening mechanisms.

In the case of applied mobility and viscosity contrasts, the average composition becomes even more critical to the coarsening behavior of the system. In concentrated polymer solutions (Region A, polymer-poor clusters in a polymer-rich matrix), setting mobility and viscosity contrasts to be at least the same order of magnitude as the simulation time was shown to be effective in mimicking structural arrest. In dilute polymer solutions (Region B, polymer-rich clusters in a polymer-poor matrix), imposing any mobility or viscosity contrasts was shown to have the counter-intuitive effect of promoting coarsening. This observation is a consequence of the lever effect. Enrichment of the polymer-rich phase towards its equilibrium composition is slowed down due to the lower local mobility in this phase; however, the polymer-poor phase reaches its equilibrium value almost immediately after phase separation. This asymmetry in enrichment dynamics leads to an increase in the volume fraction of the polymer-rich phase, thus producing larger and stringier domains. This effect is more pronounced in Model H as stringier phases drive surface-tension-driven flows that accelerate coarsening even more.

The lever effect not only changes coarsening rates, but also leads to dramatic changes in morphology. The lever effect pushes Region A morphologies away from symmetry, while it pushes Region B morphologies toward symmetry. Thus, for Region B morphologies whose average concentrations are close enough to symmetry (Region C), the lever effect can lead to a transient morphology within Region A, but an equilibrium morphology within Region B. Our study demonstrated the existence of this Region C, for both Model B and Model H coarsening. Such *phase inversion* between the polymer-rich and polymer-poor phases characteristic of Region C has been previously attributed to viscoleastic phase separation.⁴³ This study confirms that asymmetry in the mobilities of the polymer-rich and polymer-poor phases is sufficient for phase inversion to manifest in either Model B or Model H, *i.e.*, a full viscoelastic model is not essential for phase inversion.

This study focused on the concentration-dependence of the bulk coarsening dynamics of a ternary polymer solution. To maintain this focus, the effects of many other important parameters were left unexplored. For instance, the roles of polymer/solvent, polymer/nonsolvent, and solvent/nonsolvent miscibilities (χ parameters) were left unexplored. No essential differences between the coarsening dynamics of binary systems reported in literature and that of the ternary system in this present study were found; however, we believe that any differences would be easier to identify if we extended our analysis to different formulations of ternary polymer solutions. A recent study by Alhasan et al.¹⁰ showed that polymersolvent and solvent-nonsolvent miscibility compete with each other as driving forces in the mass-transfer processes within a ternary polymer solution system. Thermal fluctuations were also neglected in the present work. As demonstrated by Shimizu and Tanaka,⁸¹ stochastic thermal fluctuations can lead to non-random droplet motion. Such fluctuations might have unexpected implications for the conclusions drawn here. Finally, all simulations here were conducted in 2D to maximize system size and simulation time, as they are essential to the physics of coarsening. With the continued advancements in high performance computing software and hardware, we hope that it will soon become practical to study systems of similar size and duration fully in three dimensions.

V. DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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