Field-theoretic simulations of random copolymers with structural rigidity†

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Copolymers play an important role in a range of soft-materials applications and biological phenomena. Prevalent works on block copolymer phase behavior use flexible chain models and incorporate interactions using a mean-field approximation. However, when phase separation takes place on length scales comparable to a few monomers, the structural rigidity of the monomers becomes important. In addition, concentration fluctuations become significant at short length scales, rendering the mean-field approximation invalid. In this work, we use simulation to address the role of finite monomer rigidity and concentration fluctuations in microphase segregation of random copolymers. Using a field-theoretic Monte-Carlo simulation of semiflexible polymers with random chemical sequences, we generate phase diagrams for random copolymers. We find that the melt morphology of random copolymers strongly depends on chain flexibility and chemical sequence correlation. Chemically anti-correlated copolymers undergo first-order phase transitions to local lamellar structures. With increasing degree of chemical correlation, this first-order phase transition is softened, and melts form microphases with irregular shaped domains. Our simulations in the homogeneous phase exhibit agreement with the density–density correlation from mean-field theory. However, conditions near a phase transition result in deviations between simulation and mean-field theory for the density–density correlation and the critical wavemode. Chain rigidity and sequence randomness lead to frustration in the segregated phase, introducing heterogeneity in the resulting morphologies.

Introduction

Statistical random copolymers are multiblock copolymers consisting of monomers with fixed but random chemical identities. The microphase segregation of random copolymers is important in a variety of applications such as polymer electrolyte membranes,1–3 styrene-butadiene rubbers,4 surface modification,5,6 and polymer mixing.7 Recent studies show that incorporating sequence stochasticity can enhance stability of assembled microstructures.8–12 The self-assembly of random copolymers is also relevant in a range of biological phenomena, including protein folding and chromatin organization.13–17 Most previous and current studies of block copolymers are based on mean-field formulations of flexible polymers.18–23 When the polymer chains are flexible such that phase-segregation domains correspond to many Kuhn steps, a mean-field treatment based on random-walk statistics is a reasonable approximation. However, this approach suffers from several shortcomings for understanding the phase behavior of random copolymers.

Phase segregation of random copolymers often occurs on length scales comparable to a monomer unit. Therefore, structural rigidity of the monomer segments significantly influences the local microstructure. With small length scales of microphase segregation, concentration fluctuations become significant near the order–disorder transition (ODT),24,25 rendering the mean-field approximation inaccurate. Due to chemical-sequence randomness, the local chemical environment surrounding a random copolymer chain has more variation than a polymer chain in a regular block copolymer melt. As a result, the free-energy landscape for microphase segregation from the melt phase is very rugged, resulting in frustration that can dramatically influence the phase behavior. In studying the thermodynamics of random copolymers, incorporating both chain rigidity and density fluctuations is critical.

Previous studies considering chain rigidity effects are limited to systems of homopolymers and diblock copolymers using mean-field approximations. For example, wormlike chains with Maier–Saupe type interactions are used to study transitions to a nematic liquid-crystalline phase.26–28 Semiflexible diblock copolymers are studied based on the wormlike chain model,
predicting an influence of semiflexibility on the long-range microphases at high chemical incompatibility.29–34

On the other hand, most studies on chemical-sequence disorder are limited to flexible random copolymers. Fredrickson et al.35,36 used random phase approximation (RPA) to examine microphase segregation of random copolymers, predicting the Flory–Huggins parameter at the ODT and phase diagrams at different degrees of chemical correlation. Simulations using flexible chain models identify emulsion-like mesostructures in uncorrelated random copolymer melts.24,25,37–39 When random copolymers have only a few monomers, phase fractionation of polymers with different chemical compositions is found.40–42 To specifically address the role of concentration fluctuations in random copolymer melts, Houdayer and Müller used Monte-Carlo simulations to show that random copolymer phase behavior deviates from mean-field predictions.24,25 The phase-segregation frustration due to chemical sequence randomness has been considered using the replica trick on a free-energy expansion with respect to concentration fluctuations.15,43–45 It has been shown that frustration along with density fluctuations can have significant effects on phase behavior of correlated random copolymers.45–48

All aforementioned theories on random copolymers using either analytical or computational methods assume random-walk chain statistics. Recently, our work has addressed phase segregation in a semiflexible random copolymer system (based on the wormlike chain model and RPA), demonstrating that structural and chemical correlations significantly impact the ODT and the critical wavemode of instability.39 The present paper focuses on using simulation to show the effect of structural and chemical correlations on random copolymer phase behavior in the presence of density fluctuations. Using field-theoretic Monte-Carlo simulations of semiflexible polymers, we show that both the phase diagram and the resulting morphologies are strongly influenced by chain rigidity and chemical correlation.

Model and simulation method

In this section, we introduce our field-theoretic simulation approach to modeling random copolymer phase segregation incorporating finite monomer rigidity, illustrated in Fig. 1. We start by defining the chemical sequences of polymers followed by a description of the system energy and simulation method.

We consider a polymer melt containing \( n_p \) polymers. Each polymer chain in the melt consists of \( M = 8 \) monomers, each of which can be either A-type or B-type. The chemical identity of the \( l \)th monomer (\( l \) runs from 1 to \( M \)) on the \( i \)th chain is denoted as \( \sigma_{il}^A \) (\( x = A \) or B), where \( \sigma_{il}^A \) takes the value of 1 if the \( l \)th monomer on \( i \)th chain is \( x \)-type, and \( \sigma_{il}^A = 0 \) otherwise. We assume the chemical sequence \( \sigma_{il}^A \) follows Markov statistics, and the chemical sequence \( \sigma_{il}^B \) remains fixed during the course of the simulation. The chemical-sequence statistics are defined by the fraction of A-type monomers \( f_A \) and the chemical correlation parameter \( \lambda \).45,36,49 In this paper, we focus on symmetric random copolymers with chemical composition \( f_A = 0.5 \). At this chemical composition, the conditional probability that a monomer is A-type given that another monomer on the same chain is also A-type is written as

\[
P\left(\sigma_{il}^A = 1 | \sigma_{ij}^A = 1\right) = \frac{1}{2} + \frac{1}{2} \lambda |i-j|.
\]

We note that \( P\left(\sigma_{il}^B = 1 | \sigma_{ij}^B = 1\right) = P\left(\sigma_{il}^B = 1 | \sigma_{ij}^A = 1\right) = 1 - P\left(\sigma_{il}^A = 1 | \sigma_{ij}^A = 1\right) \) and \( P\left(\sigma_{il}^B = 1 | \sigma_{ij}^B = 1\right) = 1 - P\left(\sigma_{il}^B = 1 | \sigma_{ij}^B = 1\right) \). When \( \lambda \) is negative, monomers are chemically anti-correlated along the chain, i.e. a B-type monomer is more likely to follow an A-type monomer and vice versa. At \( \lambda = -1 \), polymers exhibit perfectly alternating chemical sequences. On the other hand, if \( \lambda \) is positive, an A-type monomer is more likely to follow another A-type monomer. If \( \lambda \) is identically 1, the polymers do not switch their chemical identity along the entire chain and are thus homopolymers. Ideal random copolymers with \( \lambda = 0 \) are composed of chemically uncorrelated monomers.

The energy function sampled by our Monte-Carlo routine is the sum of the polymer conformation energy and the interaction energy between monomers. Prior to discretization the total energy of the melt is given by

\[
\beta E = \beta E_{\text{poly}} + \beta E_{\text{int}},
\]

where \( \beta = 1/(k_B T) \) and \( k_B \) is the Boltzmann constant. We model the polymers as wormlike chains,50,51 with the conformational energy proportional to the square of the chain curvature

\[
\beta E_{\text{poly}} = \frac{l_p}{2} \sum_{i=1}^{n_p} \int_0^L ds \left( \frac{\partial \vec{n}_i}{\partial s} \right)^2,
\]

where \( l_p \) is the persistence length and \( \vec{n}_i(s) = \frac{\partial \vec{r}_i(s)}{\partial s} \) is the chain tangent vector for the \( i \)th chain at arclength position \( s \).

We model the interactions of monomers in the melt using a Flory–Huggins interaction along with a quadratic potential to enforce incompressibility of the melt. This leads to the interaction energy

\[
\beta E_{\text{int}} = \chi \int d\vec{r} \phi_A(\vec{r}) \phi_B(\vec{r}) + \kappa \int d\vec{r} \left[ \phi_A(\vec{r}) + \phi_B(\vec{r}) - 1 \right]^2,
\]
where \( \phi_x(\vec{r}) \) is the local density of \( x \)-type monomers (explicitly defined below). The first term in eqn (4) captures the Flory–Huggins repulsive interactions between \( A \) and \( B \)-type monomers. When \( \kappa \) is chosen to be large, the second term maintains the local density \( \phi_x(\vec{r}) + \phi_y(\vec{r}) \) close to 1. To implement a Monte-Carlo simulation of a melt with energy given by eqn (2), we discretize both the polymer path \( s \) into beads as well as space \( \vec{r} \) into bins. The two discretization steps are summarized in Fig. 1.

The chain conformation energy \( E_{\text{poly}} \) in eqn (3) is calculated using the discrete shearable–stretchable wormlike chain model\(^{52,53} \) with each monomer represented by \( G = 5 \) beads spaced an arclength \( l_0 \) apart. Each bead within a monomer (i.e. each of the \( G \) sub monomer beads) has the same chemical identity, and beads in different monomers have identities that are chosen based on the aforementioned statistics. This model is shown to reproduce the statistical behavior of the continuous wormlike model over the entire range of structural rigidity and bead discretization length. Since larger discretization length leads to fewer beads, this approach is capable of substantially reducing the number of degrees of freedom while maintaining the same chain statistical properties.

The polymer conformation energy is composed of quadratic energy penalties associated with stretch, shear, bend, and coupling between the bend and shear degrees of freedom. We write

\[
\beta E_{\text{poly}} = \sum_{i=1}^{n_p} \sum_{j=1}^{MG} \frac{f_k}{2l_0} \left( \vec{u}_y - \vec{u}_{ij-1} - \eta \vec{R}_{ij} \right)^2 + \frac{f_0}{2l_0} \left( \vec{R}_y \cdot \vec{u}_{ij-1} - l_0 \gamma \right)^2 + \frac{f_1}{2l_0} \left( \vec{R}_{ij} \right)^2 ,
\]

where the chain conformations are defined by the position \( \vec{r}_{ij} \) and unit orientation \( \vec{u}_{ij} \) of the \( j \)th submonomer bead on the \( i \)th chain. The unit vectors \( \vec{u}_{ij} \) on each bead are additional degrees of freedom from the bead positions \( \vec{R}_{ij} \) that represent the tangent orientations along a continuous wormlike chain that is modeled by the discrete shearable–stretchable wormlike chain. The inter-bead vector \( \vec{R}_{ij} = \vec{r}_{ij} - \vec{r}_{ij-1} \) connects adjacent submonomer beads, and \( \vec{R}_{ij}^2 = \vec{R}_y - (\vec{R}_y \cdot \vec{u}_{ij-1}) \vec{u}_{ij-1} \) is the component of \( \vec{R}_{ij} \) vector perpendicular to \( \vec{u}_{ij-1} \). The energetic coefficients of bending \( \kappa \), compression \( \kappa \), and shearing \( \kappa \), as well as parameters \( \eta \) and \( \gamma \) are obtained from work by Koslover and Spakowitz\(^{22} \) at different degrees of chain flexibility \( l_0/l_p \). We define monomer flexibility using the number of Kuhn lengths per monomer \( N_M = L_M/(2l_0) \), where \( L_M = G l_0 \) is the monomer length. When characterizing the impact of monomer flexibility on microphase domain size, we vary \( N_M \) while fixing the unperturbed average end-to-end separation of a monomer \( R_M \) given by

\[
r_{R_M} = \left( \frac{P(L_M) - P(0)}{P(0)} \right)^{1/2} = 2l_p \left[ N_M - \frac{1}{2} (1 - e^{-2N_M}) \right]^{1/2} .
\]

We discretize the spatial coordinates \( \vec{r} \) into \( n_{\text{bin}} \) lattice bins and include the contributions to the interaction energy as\(^{54-56} \)

\[
\beta E_{\text{int}} = \chi \Delta \sum_{k=1}^{n_{\text{bin}}} \sum_{k} (\phi_A^{(k)} \phi_B^{(k)} + \kappa \Delta \sum_{k=1}^{n_{\text{bin}}} (\phi_A^{(k)} + \phi_B^{(k)} - 1)^2 ,
\]

where \( \Delta \) is the discretization length of each bin and \( \phi_x^{(k)} \) is the monomer density field of chemical species \( x \) in the \( k \)th bin. This simple interaction potential includes a pairwise interaction between \( A \) and \( B \) segments (Flory–Huggins interaction, first term) and a local compressibility energy (second term) that approximately enforces incompressibility of the melt. This approach neglects interactions that lead to local chain alignment (e.g. using a Maier–Saupe interaction potential\(^{26,28} \) or local packing contributions. Given that phase segregation occurs on the monomer length scale, more granular interactions may lead to more local packing heterogeneity and frustration than is captured in our model. In this work, we introduce a simple interaction model that has the basic physical effects, and future work will address a more detailed representation of the interactions. The monomer density \( \phi_x^{(k)} \) is numerically obtained from a first-order particle-to-mesh interpolations,\(^{55,56} \) such that

\[
\phi_x^{(k)} = \frac{V}{A \sum_{j=1}^{n_{MG}} \sigma_j^2 \phi_x \left( \vec{R}_k - \vec{r}_j \right) .
\]

where \( \vec{R}_k \) defines the location of \( k \)th bin grid vertex, \( \nu \) is the monomer volume, and \( \omega \) is a weighting factor combining linear interpolations of density in 3 dimensions.\(^{55} \) The monomer index \( i \) is given by \( i = \text{ceil} (j/G) \), resulting in the same monomer index for all submonomer beads within the same monomers. In our simulations, we choose \( \kappa/\nu \) to be 10.0, resulting in an average variability of local density \( (\phi_x^{(k)} - \phi_x^{\Lambda(k)})^2)^{1/2} \approx 0.066 \). At this choice of incompressibility factor, the unperturbed single-chain statistics are accurately reproduced at different monomer rigidities in the well-mixed phase when \( \chi = 0 \) (see ESF). This formalism of interaction energy accounts for the interactions from instantaneous concentration fluctuations that are absent in a mean-field approximation. It allows us to investigate the effects of concentration fluctuations on the ODT and have a direct assessment of the detailed microstructures above the ODT. However, the discretization lengths \( l_0 \) and \( \Delta \) introduce cutoffs in the length scale of the density fluctuations that are captured in the model. The ratio of the bead volume \( \nu \) to bin discretization volume controls the number of beads that interact with each other within a bin. We choose \( \Delta = 10 \nu \) such that each bead interacts with about 9 other beads within the same bin. To capture microphase segregation on length scales of a few monomer lengths, we choose \( \Delta = R_M/2 \) and perform simulations in a cube with edge length \( L_{\text{box}} = 20.1 \) with periodic boundary conditions. We choose number of beads per monomer \( G = 5 \), such that we can resolve phase segregation and permit density fluctuations at single monomer length scales. Our choice for number of monomers \( M = 8 \) is sufficiently large such that the phase behavior is no longer sensitive to \( M \) (based on our previous work)\(^{49} \) and that concentration fluctuation effects no longer dramatically depend on \( M \).\(^{25} \) The cube is filled by \( n_p = L_{\text{bin}}^3/(\nu MG) = 2000 \) polymers each consisting of \( MG = 40 \) beads.

We employ a custom Monte-Carlo routine to sample the energy defined by eqn (5) and (7). The source code and documentation are available on our group website.§ The Monte-Carlo move types

\[\text{http://www.stanford.edu/~ajspakow/}.\]
include chain-segment translation, chain-segment crankshaft, end-segment pivot, full-chain translation, full-chain rotation, single \( \hat{u} \) rotation, reptation, and chain swap moves. To maintain a target acceptance ratio in the Metropolis algorithm of 50%, the move amplitudes and move segment lengths are dynamically adjusted. To overcome the considerable frustration in the system, we employ parallel tempering in the \( \chi \) parameter. The differences in the \( \chi \) values between the parallel tempering replicas are dynamically adjusted during an initialization period with a target acceptance of 12–22% to achieve optimal replica mixing.\(^{37,58}\)

**Results and discussion**

To analyze microphase segregation of random copolymer melts, we perform simulations described above for a range of monomer flexibility \( N_M \), chemical correlation \( \lambda \), and Flory–Huggins interaction strength \( \chi_M \), where \( \chi_M = G \nu \) is the volume of a monomer used to nondimensionalize \( \chi \). The results are organized as follows. First, the simulation morphologies and phase diagrams for different \( N_M \) and \( \lambda \) are presented. Second, the degree of mixing at different \( \chi_M \) are examined. Third, the calculated structure factors are provided to facilitate the discussion of the nature of ordering. Finally, the scattering peak locations and intensities are discussed.

**Phase diagrams and morphologies**

We first focus on phase behavior of rigid, ideal random copolymers. The images along the top of Fig. 2 show morphologies for rigid ideal random copolymers with increasing Flory–Huggins parameter \( \chi_M \). With increasing segregation strength (i.e. increasing \( \chi_M \)), the simulation exhibits a progression from a well-mixed homogeneous phase at low \( \chi_M \) to an increasingly segregated microphase morphology at high \( \chi_M \). To quantify the degree of segregation, we look at the degree of mixing \( \langle \phi_A(\vec{r})\phi_B(\vec{r}) \rangle \), where the brackets \( \langle \ldots \rangle \) are defined as both spatial average over density discretization bins and ensemble average over Monte-Carlo samples. The degree of mixing is proportional to the interaction energy \( \chi V(\phi_A\phi_B) \) due to chemical incompatibility between unlike segments (see eqn (4)). In principle, the degree of mixing \( \langle \phi_A\phi_B \rangle \) ranges from 0 in the limit of a strongly segregated phase to \( f_A^0 = 0.25 \) for a perfectly mixed melt.

Fig. 2 shows the degree of mixing as a function of \( \chi_M \) for rigid, ideal random copolymers (\( N_M = 0.05 \)). When \( \chi \) is identically equal to zero, the melt is well-mixed with \( \langle \phi_A\phi_B \rangle \approx 0.23 \). This is below the mean-field value of 0.25 for \( f_A = 0.5 \) primarily due to spontaneous concentration fluctuations. With increasing \( \chi_M \), \( \langle \phi_A\phi_B \rangle \) decreases. In the strong-segregation limit, regions of pure A and pure B form with interfacial boundaries, giving nonzero \( \langle \phi_A\phi_B \rangle \) values.

To identify the phase transitions with increasing \( \chi_M \), we look at the \( \chi \) component of the heat capacity

\[
c_{\chi} = -\frac{1}{V_M} \frac{\partial^2 F}{\partial \chi^2} = \frac{\partial (\phi_A\phi_B)}{\partial (\chi_M)}.
\]

where \( V = L_{box}^3 \) is the size of the simulation, and \( F \) is the free energy of the system. The last equality is derived from eqn (4), resulting in a straightforward approach to calculating the heat capacity from our simulations.

Fig. 2 shows that \( c_{\chi} \) exhibits two prominent features: a broad peak at \( \chi_M \approx 3.10 \) and sharp peaks when \( \chi_M \geq 8.71 \). We associate the broad peak at \( \chi_M \approx 3.10 \) with the transition from the well-mixed homogeneous phase (H) to a random microphase (RM). The first sharp peak at \( \chi_M = 8.71 \) indicates an abrupt drop in degree of mixing. We associate this peak with a phase transition from the RM phase to an aligned microphase (AM). The name AM is derived from the orientational alignment of the chains in the AM phase (see ESI†).

We find that the two-stage phase transition (from H to RM to AM) is a common feature in our simulations over a range of chain flexibilities and chemical correlations. Fig. 3 shows the phase diagram for rigid random copolymers. In Fig. 3, we use solid blue curves to identify the phase boundary between the H phase and the RM phase. We compare this phase transition with the mean-field spinodal obtained from ref. 49, shown as the dotted blue curve. The apparent elevation of the transition \( \chi \) above the mean-field spinodal is due to density-fluctuation effects and frustration during microphase segregation. The red curve denotes a first-order phase transition to the AM phase either from the H phase or the RM phase. The large free energy barrier between the AM phase and the other two phases breaks the replica-exchange coupling in the Monte-Carlo sampling (see ESI†). Hence, a different transition point is found depending on
Fig. 3 Phase diagram of rigid random copolymers ($N_M = 0.05$). The blue line marks the phase transition from the H phase to the RM phase, and dotted blue curve shows the mean-field prediction of the H-phase spinodal.\textsuperscript{49} The dashed blue line is inferred phase boundary from the H phase to the RM phase near $\lambda \approx -0.45$. The phase boundary to the AM phase, indicated as solid red curve, is determined from cooling (increasing $\lambda$) simulations, and the dashed red boundary is obtained from melting (decreasing $\lambda$) simulations. The simulated morphologies shown on the left correspond to the snapshots obtained from conditions labeled on the phase diagram as h, rm, D, and am. Scale bars indicate the unperturbed monomer size $R_m$ (eqn (6)).

whether the initial state of the system is the AM or the H/RM phase. We denote the cooling phase transition (i.e. increasing $\lambda$) from the H/RM phase to the AM phase with the solid red curve, and the melting phase transition from the AM phase to the H/RM phase with the dashed red curve. The two different transition boundaries can be seen as hystereses in Fig. 5. All snapshots shown in this paper are obtained from cooling simulations. The filled small circles in Fig. 3 indicate the individual simulations based on which phase boundaries are determined from cooling.

Approaching $\lambda = -0.5$ from $\lambda > -0.5$, we observe a narrowing domain of $\varphi_{VM}$ between which the RM phase exists. We use a dashed blue line to indicate the inferred extension of phase boundary between the H phase and the RM phase near $\lambda \approx -0.45$. In addition, we note that near the chemical correlation $\lambda = -0.3$, the width of the hysteresis in $\varphi_{VM}$ direction is smaller than the width at other $\lambda$ values. We hypothesize that the diminishing hysteresis is due to the coupling between the H $\rightarrow$ AM transition and the potential H $\rightarrow$ RM transition. Near the potential H $\rightarrow$ RM transition, large density fluctuations facilitate the sampling of a variety of melt conformations and decrease the width of the hysteresis between the H phase and the AM phase.

Next, we examine the effect of chain flexibility and chemical correlation on the random copolymer melt morphology. Fig. 4A shows morphologies of random copolymer melts at different monomer flexibility $N_M$ and chemical correlation $\lambda$ at a Flory–Huggins parameter four times the mean-field spinodal ($\chi = 4\chi_{MF}^S$). The top row shows the melt snapshots of rigid polymers corresponding to points A1–E1 in Fig. 3. To understand the effect of chemical correlation $\lambda$, we first define a chemical block as a sequence of same-type monomers. Perfectly alternating copolymers with $\lambda = -1$ only have single-monomer blocks. When $\lambda$ increases from $-1$, random copolymers are composed of a widening distribution of block lengths of one, two, three, or more monomers. As $\lambda$ approaches 1, the chemical blocks approach the chain size.

Snapshot A1 in Fig. 4A ($\lambda = -0.75$) shows an AM structure with two lamellar domains with different orientations. The multiple orientations of the lamellar structures are a result of the large free energy barrier to a global fully aligned lamellar structure. When the polymers are more chemically correlated with increasing $\lambda$, the domains grow in size and become more irregular, as evident from the progression from left to right in the top row of Fig. 4A. At $\lambda = -0.75$, $-0.50$, and $-0.25$, we notice that snapshots A1, B1, and C1 show segregated domains with bulges of A-type monomers into the B-type lamellae and vice versa. We attribute this qualitative morphological feature to double or triple-monomer blocks being incorporated into lamellar spacings set by single-monomer blocks. As $\lambda$ is increased further, rigid polymers play a complex tetris-like game to align blocks of varying lengths into A and B regions. This represents added frustration and drives the phase boundary of the AM phase to higher $\varphi_{VM}$ values, as shown by the solid red line in the phase diagram in Fig. 3.

The lower two rows of Fig. 4A show morphologies of semiflexible ($N_M = 0.50$) and flexible ($N_M = 5.00$) random copolymer melts at $\lambda = 4\chi_{MF}^S$, where $\chi_{MF}^S$ is the mean-field spinodal from ref. 49. They correspond to points A2–E2 and A3–E3 in Fig. 4B and C. At these chain flexibilities, the same qualitative progression from lamellae to disordered structures is observed. However, semiflexible and flexible random copolymers form regular lamellar structures over larger windows of $\lambda$ (A2–B2 for semiflexible polymers, and A3–C3 for flexible polymers). Regular structuring is accommodated by the alleviation of phase-segregation frustration by chain flexibility, allowing polymers to bend to accommodate blocks of two or more monomers into the lamellar structures. Flexible random copolymers also have larger domain sizes at the same $\lambda$. For instance, at $\lambda = -0.75$, a flexible random copolymer melt has four lamellae, while the snapshot of a semiflexible random copolymer melt displays five. This is due to the ability of flexible random copolymers to stretch at high chemical incompatibility $\varphi_{VM}$ (see ESI†).

Fig. 4B and C show the phase diagrams of semiflexible and flexible random copolymer melts. The phase boundaries are determined the same way as Fig. 3 (see ESI\textsuperscript{2} for complete data of $\langle \phi_A \phi_B \rangle$). As the chains become more flexible, the phase transition from the H phase to the AM or RM phases occurs at higher $\varphi_{VM}$, which can be explained by the increased entropic penalty of stretching flexible polymers. In comparison with the phase diagram of rigid random copolymers in Fig. 3, we note that rigid polymers phase segregate into the AM phase without first traversing the RM phase. Since chain flexibility alleviates phase segregation frustration, the phase transition $\gamma$ to the AM phase also becomes flatter compared to that of rigid polymers.

The phase diagrams shown above can be used as a guide to engineer microphase segregation of random copolymer materials. We demonstrate that the phase behavior of random copolymer materials is strongly dependent on both the physical flexibility.
and the chemical sequence of the polymers. Specific melt morphologies can be achieved through appropriate choice of polymer chemistry and temperature.

**Degrees of mixing and heat capacities**

We investigate the nature of the phase transitions in random copolymers by examining the quantitative progressions of the degree of mixing and the structure factors. Fig. 5 shows $c_w$ versus $w_{vM}$ for rigid random copolymers ($N_M = 0.05$) at chemical correlations $\lambda = -1.00, -0.75, -0.50, -0.25, 0.00, \text{ and } 0.25$ (see ESI† for the results of semiflexible and flexible random copolymers). Note, each subplot in Fig. 5 is generated with a particular set of random chemical sequences $s_{il}$. In a first-order phase transition, the heat capacity has a $\delta$ function singularity due to latent heat. 59 In Fig. 5 for $\lambda = -1.00$ we observe a sharp peak of $c_w$ at $\nuM = 5.96$ (red vertical line), bounded by the finite simulation size 60 and $\nuM$ spacing. This sharp peak corresponds to the transition to the AM phase with step discontinuity in degree of mixing $h_f$. As $\lambda$ increases, the size of this discontinuity in degree of mixing decreases and moves to higher $\nuM$ values. This phase behavior can be understood in terms of polymer sequence and chain configuration. Perfectly alternating copolymers ($\lambda = -1$) exhibit a sharp transition into an aligned lamella phase with the lamellar spacing set by the monomer length. At $\lambda \approx -1$, copolymers are essentially alternating with an impurity of two-monomer blocks. As $\lambda$ increases, the impurity concentration reduces the energy barrier to the AM phase with reduced latent heat during the phase transition from the H to the AM phase. This rounding of the first-order phase transition due to impurity effects is characteristic of systems with quenched disorder. 59,61

In a similar but dual way, chains with $\lambda \approx 1$ are close to homopolymers with occasional A–B bonds acting as impurities that must be segregated to interfaces. At $\lambda = 0.25$, a maximum of $c_w$ appears at $\nuM = 2.01$ (blue vertical line), indicating the transition from the H to the RM phase. With further decrease of $\lambda$, the height of the maximum of $c_w$ decreases, and the value of $\nuM$ at the transition increases. This is because the impurities in block lengths becomes more prevalent, which softens the transition from H to RM phases. As $\lambda$ reaches a value of $0.50$, the peak in $c_w$ vanishes. Whether such a transition is a higher-order phase transition or simply a peak in the heat capacity is beyond the resolution of our simulations.

**Structure factors**

The spatial correlation of local volume fraction deviation $\psi(r) = \phi_A(r) - f_A$ can be used to quantify the concentration correlation of the polymer melt both in the well-mixed phase and the ordered phase. Due to melt incompressibility (approximately enforced in our simulations by $\kappa v$), the fluctuation of the A-type...
monomer composition is equal to the negative of the fluctuation of the B-type monomer composition (i.e. \( \phi_B(r) - f_B = -\phi_B(r) + f_B \)).

The Fourier transform of the concentration correlation function corresponds to the structure factor \( S(q) \) at different wavevector magnitudes \( q = |\vec{q}| \), which is proportional to the scattering intensity in neutron and X-ray scattering experiments. We define the structure factor \( S(q) = \langle \hat{\psi}(\vec{q})\hat{\psi}(-\vec{q}) \rangle \), where \( \hat{\psi}(\vec{q}) \) is the Fourier transform of \( \psi(r) \). The structure factor is calculated from simulation as

\[
S(q) = \langle \hat{\psi}(\vec{q})\hat{\psi}(-\vec{q}) \rangle = \frac{1}{n_pMG} \left( \sum_{i=1}^{n_p} \sum_{j=1}^{MG} (\sigma_i^A - f_A \exp(i\vec{q} \cdot \vec{r}_i)) \right)^2, \tag{10}
\]

where wavevector \( \vec{q} \) is selected from

\[
\vec{q} = \frac{2\pi}{L_{\text{box}}} (n_x\hat{x} + n_y\hat{y} + n_z\hat{z}), \tag{11}
\]

and \( n_x, n_y, \) and \( n_z \) are restricted to integer values due to the periodic boundary conditions. The bracket in eqn (10) represents an average over ensembles and all possible \( \vec{q} \) orientations given in eqn (11) with the same magnitude \( q = |\vec{q}| \). For comparison, we calculate the mean-field prediction of the concentration correlation, using our previous work on semiflexible random copolymers,\(^{49}\) given by

\[
S_{\text{MF}}(q) = \langle \hat{\psi}(\vec{q})\hat{\psi}(-\vec{q}) \rangle_{\text{MF}} = \frac{1}{n_f(q^2(q) - q^2)} \tag{12}
\]

where \( \hat{F}^{(2)}(q) \) is a correlation function consisting of both structural and chemical correlations. The analytical form of \( \hat{F}^{(2)}(q) \) is given in ref. 49.

Mean-field theory predicts a peak in \( S_{\text{MF}}(q) \) at a finite wavevector \( q_{\text{MF}}^* \) when the random copolymers are sufficiently anti-correlated, while increasing the chemical correlation \( \lambda \) leads to \( q_{\text{MF}}^* = 0 \), corresponding to macrophase separation. This critical chemical correlation, below which \( q_{\text{MF}}^* \) is finite, is called the Lifshitz point \( \lambda_{\text{L}} \), whose value depends on chain stiffness.\(^{35,36}\) For 8-monomer random copolymers, the Lifshitz points are found for our choice of monomer rigidities: \( \lambda_{\text{L}} = -0.115 \) (\( N_M = 0.05 \)), \(-0.124 \) (\( N_M = 0.50 \)), and \(-0.144 \) (\( N_M = 5.00 \)). To distinguish the feature of finite versus zero wavevectors in the structure factors, we refer to the \( q \)-value near the size of the simulation box as “zero \( q \)” in subsequent discussions. This is a valid approximation since this is the largest wavelength the simulation permits, and the largest average block size \( 2L_m/(1 - \lambda) \) is much smaller than the box size.

Fig. 6A shows structure factors for anti-correlated rigid copolymers (\( N_M = 0.05, \lambda = -0.75 \)). We focus on \( S(q) \) within the range from the simulation box size \( qR_M = (2\pi/L_{\text{box}})R_M \approx 0.6 \) to the cutoff of interaction length \( qR_M = (2\pi/L)R_M \approx 12.6 \) in the field-theoretic formulation. The structure factors from simulations are shown from blue to red as solid lines in the range \( \chi/\chi_{\text{L}}^{\text{MF}} = 0.0, 0.25, 0.50, 0.75, 1.0, 2.0, 3.0, \) and \( 4.0 \). The inset simulation snapshot corresponds to the strong-segregation limit \( \chi/\chi_{\text{L}}^{\text{MF}} = 4.0 \), which is the same as snapshot A in Fig. 4. The dashed curves correspond to the mean-field structure factor \( S_{\text{MF}}(q) \) from eqn (12) at \( \chi/\chi_{\text{L}}^{\text{MF}} = 0.0, 0.25, 0.50, 0.75 \), with colors matching the same Flory–Huggins parameters \( \chi \).
simulation. We only show the mean-field structure factors at these values since above $\chi_2^{MF}$ the quadratic-order mean-field approximation becomes invalid, resulting in a diverging $S_{MF}(q)$ at $q_{MF}^*$. In the well-mixed phase at zero Flory–Huggins parameter $\chi$, the anti-correlated rigid copolymer melt exists in the H phase. At this $\chi_{PH}$, the concentration correlation sampled from simulation agrees with the prediction of the mean-field theory. Specifically, a peak in the structure factor is found at the critical wavemode $q_{MF}^*$ predicted from mean-field theory with a matching peak width. This agreement demonstrates the validity of the mean-field approximation in the homogeneous phase when concentration fluctuations are modest.

When $\chi$ increases, both structure factors from simulation and mean-field theory increase at all wavemodes, most predominantly near peak $q_{MF}^*$. However, mean-field theory overestimates concentration correlation, as shown in Fig. 6A. When $\chi$ increases to twice the mean-field spinodal ($\chi/\chi_2^{MF} = 2.0$), the random copolymer melt remains in the H phase, and the peak in the structure factor becomes more prominent with a noticeable shift to a lower wavemode $q^*$. At $\chi/\chi_2^{MF} = 3.0$, the random copolymer melt forms an AM structure with spikes at $q^*_{RME}$ and at $q^*_{3}$ in the structure factor. At this point, the polymers align to form repeating domains composed of A and B-type monomers. When $\chi$ further increases to four times the mean-field spinodal ($\chi/\chi_2^{MF} = 4.0$), the intensity of the structure factor at low $q$ increases. This low-$q$ intensity growth corresponds to the formation of frustration-induced local bulge structures that are shown and discussed in the surrounding texts of Fig. 4. Qualitative features of structure factors of anti-correlated random copolymers include suppressed concentration correlations compared with mean-field theory and $q^*$ shifting to lower wavemodes. These effects are also observed for diblock copolymers.62–67

Fig. 6 (A) Structure factor $S(q)$ of rigid, statistically anti-correlated random copolymers ($N_M = 0.05$, $\lambda = -0.75$). Solid curves indicate Monte Carlo simulation results, and dashed curves show the mean-field theory. Data from blue to red correspond to the range $\chi/\chi_2^{MF} = 0.0, 0.25, 0.50, 0.75, 1.0, 2.0, 3.0, \text{ and } 4.0$, noting that the mean-field theory only provides curves $\chi/\chi_2^{MF} = 0.0, 0.25, 0.50, \text{ and } 0.75$. (B) Structure factor $S(q)$ for a rigid, ideal random copolymer ($N_M = 0.05$, $\lambda = 0.00$) with the same labeling as in (A). (C) Structure factor $S(q)$ for a range of monomer lengths $N_M$ and chemical correlation $\lambda$ corresponding to those provided in Fig. 4. Snapshot inset in each plot is obtained from four times the mean-field spinodal ($\chi = 4\chi_2^{MF}$), i.e. same as in Fig. 4.
Since anti-correlated random copolymers have statistically alternating chemical sequence, such resemblances to diblock copolymers are not unexpected. Furthermore, finite-sized interactions are shown to suppress ordering in diblock copolymers.\textsuperscript{68} Although the weighting function used introduces a finite-range of interaction, we do not directly make this comparison in the current work. However, such effects would likely act to suppress phase segregation in random copolymers.

In Fig. 6B, we consider copolymers with uncorrelated chemical sequence (\textit{i.e.} ideal random copolymers with \( \lambda = 0.00 \)) at the same chain rigidity (\( N_M = 0.05 \)) and the same range of \( \chi/\lambda_{MF}^* \) as in Fig. 6A. Since degree of chemical correlation is greater than the Lifshitz point, the mean-field theory predicts a critical wave-mode \( q_{MF}^* = 0 \) in the H phase at \( \chi = 0 \), corresponding to macrophase segregation at infinite wavelength. When \( \chi \) increases from 0 up to \( \chi/\lambda_{MF}^* = 4.0 \), the uncorrelated random copolymer melt forms an RM phase with increased structure factor intensity near \( q^* = 0 \). Although \( q^* \) remains zero over a wide range of simulated \( \chi \), the snapshot inset shows finite size domains instead of macrophase segregation of chemically incompatible monomers. Therefore, the peak intensity in structure factor at \( q^* = 0 \) should be understood as resulting from phase separations occurring over a wide range of length scales. In contrast to the prediction of the mean-field by Fredrickson, Milner and Leibler (FML) for flexible, ideal random copolymers\textsuperscript{35,36} the characteristic peak at high \( R_{PM} \) values are absent in our simulation for rigid polymers.

To further illustrate the effects of polymer rigidity, Fig. 6C provides concentration correlations for a range of monomer flexibilities \( N_M \) and chemical correlation \( \lambda \). This grid of simulation results coincides with the parameters shown in Fig. 4A, and the inset image for each plot is identical to the strong-segregation snapshots shown in Fig. 4A (\textit{i.e.} \( \chi/\lambda_{MF}^* = 4.0 \)). For flexible (\( N_M = 5.00 \)) and semiflexible (\( N_M = 0.50 \)) chains when \( \lambda > \lambda_{MF}^* \), a peak in the structure factor at finite wave-mode \( q^* \) appears at sufficiently large \( \chi \) values, indicating phase segregation at finite correlation length. The emergence of this peak suggests that, when \( \chi \) becomes sufficiently large, the large-scale phase domains begin to remix resulting in the formation of smaller domains. This behavior was predicted by the FML theory. It shows that, as the value of \( \chi \) increases, a homogeneous mixture of random copolymers with \( \lambda > \lambda_{MF}^* \) first loses its stability to a macroscale liquid–liquid coexistence region, and then the coexistence region loses its stability to the formation of randomly oriented microscopic domains, giving rise to the emergence of a non-zero \( q^* \).\textsuperscript{35,36} No liquid–liquid coexistence has been identified in our simulations, possibly because the width of the coexistence window, which is of order \( 1/M \), is too narrow\textsuperscript{35,36} or due to the finite simulation size (see ESI†). In the next subsection, we provide a detailed analysis for the variation of peak position and intensities with \( \chi \) and chain stiffness.

**Peak positions and intensities**

The wavevectors used for the calculation of structure factors have to be commensurate with the box dimension. For systems in the AM phase, the scattering peaks are narrow and sharply defined; the peak properties are obtained directly. For systems in the RM phase, the peaks tend to be smeared. To determine the peak position and intensities, we fit the structure factors \( S(q) \) near peak locations with a Lorentzian function

\[
S(q) = \frac{1}{S(q^*)^{-1} + 2G^{-1}(R_{RM} - R_{MF}q^*)^2} \quad \text{eqn (13)}
\]

for each value of \( \chi, \lambda \) and \( N_M \) displayed in Fig. 6C. In eqn (13), the number of monomers \( G \) is included to account for the scaling of \( S(q) \). To perform the fitting, we first identify an initial guess of peak location \( q^* \) that maximizes \( S(q) \). When initial guess of \( q^* \) is nonzero, we fit the Lorentzian function at \( 7 \) consecutive \( q \) values centered around the guessed peak location. We then obtain fitted estimates of inverse peak intensity \( S(q^*)^{-1} \) and new peak location \( q^* \). When the initial guess of \( q^* \) is indistinguishable from zero, we instead set \( q^* \) to zero in eqn (13) and fit the familiar Orstein–Zernike function to estimate the inverse of peak intensity \( S(q^*)^{-1} \) near \( q = \frac{2\pi}{L_{box}} \).

Note smaller critical wave-mode \( R_{MF}q^* \) indicates larger average domain size \( \left( \frac{D}{R_{RM}} = \frac{2\pi}{R_{MF}q^*} \right) \), since we kept \( R_{RM} \) constant throughout simulations.

Fig. 7 shows the fitted peak positions of anti-correlated random copolymers (A) and ideal random copolymers (B), at monomer flexibility \( N_M = 5.00 \) (red), 0.50 (purple), and 0.05 (blue). For anti-correlated random copolymers, the domain size grows with increasing Flory–Huggins parameter at all monomer flexibilities. This is analogous to the behavior of diblock copolymers in presence of density fluctuations.\textsuperscript{65–67} The small-sized aggregation domains grow in the H phase to form locally ordered lamellae, and the lamellar domains continue to grow in size at higher \( R_{PM} \). A simple physical argument for domain swelling is that domains stretch to reduce the interfacial free energy with increasing \( R_{PM} \) at the entropic expense associated with chain stretching. Our simulations exhibit a modest degree of chain stretching for flexible random copolymers at large \( R_{PM} \) (see ESI†), consistent with this physical argument.

Fig. 7B shows results for ideal random copolymers. For flexible copolymers (red circles), \( q^* \) grows continuously from zero above the phase transition to the RM phase, consistent with the prediction of the FML theory,\textsuperscript{35,36} its fluctuation corrections,\textsuperscript{45,69} and previous simulation.\textsuperscript{37} To make comparisons with the FML theory, one needs to identify the onset of finite \( q^* \). Due to the limitation of a finite-sized simulation, \( q^*/2 \) near zero is hard to resolve. Therefore, such a quantitative comparison becomes difficult.

The behavior of semiflexible ideal random copolymers, also shown in Fig. 7B, is more complicated. A large fitting error is involved since the peaks are rather weak, and a weak dependence on \( \chi \) is found. Furthermore, as already mentioned, for rigid, ideal random copolymers, the peak locations are always zero (\( q^* = q_{MF}^* = 0 \)) within the range of \( \chi \) values explored. This behavior may be attributed to the frustration experienced by monomers in the ordering process. Flexible polymers, on the
other hand, can rearrange and accommodate such microphase segregation with a characteristic wavelength. The possibility that chain flexibility alleviates frustration and facilitates microphase segregation has been proposed by Sfatos et al.\textsuperscript{44,70} In their work, replica field theory is used to demonstrate that replica symmetry breaking prevents microphase segregation in random copolymers, and flexible random copolymers with a wider range of energy fluctuation spectra recover the microphase segregation.

Here we emphasize that the nonzero $q^*$ observed at $\lambda > \lambda_L^{MF}$ in flexible polymers differs essentially from that observed at $\lambda < \lambda_L^{MF}$. Fig. 7A show that the microstructures with domain spacing near $q^*$ is seeded by the characteristic wavemode in the homogeneous phase $q_{MF}^*$. Such microstructures increase in size with increasing Flory–Huggins parameter $\chi_{VM}$. In contrast, when $\lambda > \lambda_L^{MF}$, the peak in structure factor grows continuously from $q_{MF}^* = 0$ in the H phase. This is because when $\chi_{VM}$ increases, a microstructure with $q^* > 0$ becomes more stable than the H phase. The domain sizes of such microstructures decrease in size with increasing Flory–Huggins parameter $\chi_{VM}$.

Next, we evaluate the role of concentration fluctuations by examining the inverse peak intensities $S(q^*)^{-1}$. Fig. 8A and B display $S(q^*)^{-1}$ of anticorrelated polymers ($\lambda = -0.75$) and ideal random copolymers ($\lambda = 0.0$) with monomer lengths $N_M = 0.05$, 0.50 and 5.00. The intercepts of $S(q^*)^{-1}$ in mean-field theory with the $x$-axis ($S(q^*)^{-1} = 0.0$) correspond to diverging density–density correlations and give values of the mean-field spinodal $\lambda_S^{MF}$.

When the chemical sequence is anticorrelated, Fig. 8A shows considerable deviations of $S(q^*)^{-1}$ at all monomer rigidities from mean-field theory, again showing suppressed peak intensities due to concentration fluctuations. The phase transition from the H phase to the AM phases are indicated by discontinuity of inverse peak intensities at elevated phase transition $\gamma_{VM} > \chi_S^{MF}$ $\nu_{VM}$. We note that the qualitative trend in deviation of $S(q^*)^{-1}$ is similar to that of diblock copolymers.\textsuperscript{65–67} In particular, rigid polymers show more pronounced deviations from mean-field theory than flexible polymers.

When the monomer chemical identities are uncorrelated at $\lambda < \lambda_L$, statistical size of a block with continuous chemically identical monomers is large enough that the phase behavior of
the random copolymer melt is independent of monomer rigidity. Our previous work predicts identical critical wave mode \( q^* = 0 \) with universal mean-field spinodal \( \lambda_{l/M}^{MF} \) above the Lifshitz point \( (\lambda > \lambda_{l/M}^{MF}) \)

\[
\lambda_{l/M}^{MF} > r_m = \frac{1}{2f_{A/B}} \left[ 1 + \frac{2}{M(1 - \lambda^{-1})} \left( \frac{\lambda - \lambda_{l/M}^{MF}}{1 - \lambda} - M + 1 \right) \right]^{-1},
\]

(14)

independent of monomer flexibility \( N_m \). This universal phase transition behavior of ideal random copolymers at all monomer rigidities is represented by the single dashed line in Fig. 8B. Despite the emergence of peaks in the structure factor at high \( \lambda \),Noticeably, the deviations of \( S(q^*)^{-1} \) for polymers at all monomer rigidities, indicating concentration fluctuation effects are not sensitive to chain rigidity when monomer chemical identities are uncorrelated.

**Conclusion**

The nature of microphase segregation of random copolymer melts can be understood in terms of the length and energy scales. Four critical length scales are polymer length \( L_{B/M} \), persistence length \( L_p = L_{B/M}(2N_m) \), block length \( 2L_{B/M}(1 - \lambda) \), and monomer radius \( \sqrt{\lambda} \). In this paper, we investigate the phase behavior of random copolymers over a broad range of persistence and block lengths by varying the monomer rigidity \( N_m \) and chemical correlation \( \lambda \).

We observe two types of phase transitions for random copolymers that arise for varying \( N_m \) and \( \lambda \). One type of transition is first-order, when polymers align to form more regular domain structures (identified as the AM phase). Another type of phase transition is a continuous phase transition, when polymers segregate into irregularly shaped domains rich in A and B-type monomers (identified as the RM phase).

Anti-correlated random copolymers \( (\lambda < \lambda_{l/M}^{MF}) \) undergo first-order phase transition to an AM phase. The first-order nature of phase transition to the AM phase is not predicted by mean-field theories. As previous studies on correlated random copolymers \( (\lambda \neq 0) \) point out, fluctuations induce first-order phase transitions to classical microstructures (lamellar, cylindrical, and body-centered cubic). Similarly in our simulation, the phase transition to the AM phase with multiple lamellar domains is due to both fluctuation effects and phase transition frustration. When chains are rigid, the AM phase is more accessible at lower Flory-Huggins parameter \( \lambda_{l/M} \) and wider window of chemical correlation \( \lambda \).

For ideal random copolymers, we find flexible copolymers undergo a direct phase transition from the H phase to the RM phase. This is consistent with mean-field theory predictions. However, we do not find a phase transition to liquid-liquid coexistent phase (or too narrow to resolve). The absence of a liquid-liquid coexistence phase is possibly due to the formation of multiphases by partitioning chains with different monomer compositions (see ESF). Rigid, ideal random copolymers, on the other hand, phase transitions to an RM phase without characteristic structure factor peak, followed by an AM phase at higher \( \lambda \).

Our formalism using field theoretic simulation with wormlike chains provides an alternative to existing simulation frameworks based on flexible polymers. This simulation method is especially useful in studying microphase segregation of polymers when backbone rigidity becomes significant. In this work, we apply the simulation method for microphase segregation of random copolymers when phase segregation occurs on monomer length scales. In the future, a larger-scale simulation with more monomers can help reveal the phase diagram dependence on molecular weight. Additionally, this simulation technique can be implemented to study block copolymers when polymer backbone rigidity results from finite molecular weight, \( \pi \)-conjugations or peptide bonds to investigate how concentration fluctuation and chain semiflexibility influence phase behaviors in the melt phase.

The authors gratefully acknowledge helpful discussions with Jie Lu, Michael Essien, Michael Toney, and Curtis Frank. This work was supported by NSF Interfacial Processes and Thermodynamics, Award 1511373.

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