Coarse-grained molecular dynamics simulation on the placement of nanoparticles within symmetric diblock copolymers under shear flow

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(Received 4 December 2007; accepted 26 March 2008; published online 29 April 2008)

We present molecular dynamics simulations coupled with a dissipative particle dynamics thermostat to model and simulate the behavior of symmetric diblock copolymer/nanoparticle systems under simple shear flow. We consider two categories of nanoparticles, one with selective interactions toward one of the blocks of a model diblock copolymer and the other with nonselective interactions with both blocks. For the selective nanoparticles, we consider additional variants by changing the particle diameter and the particle-polymer interaction potential. The aim of our present study is to understand how the nanoparticles disperse in a block copolymer system under shear flow and how the presence of nanoparticles affects the rheology, structure, and flow behavior of block copolymer systems. We keep the volume fraction of nanoparticles low (0.1) to preserve lamellar morphology in the nanocomposite. Our results show that shear can have a pronounced effect on the location of nanoparticles in block copolymers and can therefore be used as another parameter to control nanocomposite self-assembly. In addition, we investigate the effect of nanoparticles on shear-induced lamellar transition from parallel to perpendicular orientation to further elucidate nanocomposite behavior under shear, which is an important tool to induce long-range order in self-assembling materials such as block copolymers. © 2008 American Institute of Physics. [DOI: 10.1063/1.2911690]

I. INTRODUCTION

With modern synthetic techniques, the magnetic, electrical, or optical properties of inorganic nanoparticles (NPs) can be tailored for a wide range of applications. While significant effort must be made to avoid NP aggregation and thereby ensure a homogeneous distribution of NPs in a polymeric matrix, the effectiveness of these NPs can often be enhanced if they are periodically arranged in three dimensions. One can combine the functionality of NPs with the phenomena of block copolymer self-assembly to achieve hierarchical spatial distributions of NPs. Having the NPs periodically spaced can lead to synergistic effects of optical1 and mechanical properties,2,3 for example, and can potentially be used in novel applications such as magnetic storage media and catalysis.4-6

Recently, there has been a flurry of reports that explore how various system parameters affect the equilibrium location of NPs within block copolymers (BCPs). Such systems have been studied with experiments, theory, and computer simulations. In these studies, researchers varied parameters such as the interaction between the NP and the A or B monomer of an AB diblock copolymer or the size of the NPs (relative to the BCP end to end distance, $R_0$). In computer simulations or theory, the interaction between NP and monomers is relatively straightforward to define (e.g., pairwise Lennard–Jones interactions). Experimentally, a panoply of procedures is available to chemically modify the surface of the NPs. In one possible scenario, short ligands, which are composed of the same monomer as one of the blocks of a copolymer, can be chemically tethered to the NP surface. In this case, the surface modified NP (at low volume fraction) would be completely miscible within one of the phases. In describing a polymer solution, a solvent with these properties would be deemed as “selective.” Another possible case would be to coat the NP surface with ligands that are made up of monomers that have the same composition as both blocks of the copolymer. This type of surface treatment would render the NPs miscible in either copolymer phase. From polymer solution terminology, the analogous label for this condition would be “nonselective.”

As expected, the equilibrium location of the NPs within a block copolymer melt is dictated by thermodynamics, namely, by the balance between enthalpy and entropy. There are enthalpic interactions between the chemically altered NP and the copolymer blocks. The entropic contribution has two prominent components: the translational entropy of the NPs and the configurational entropy of the polymer chains. Chiu et al. demonstrated that the NP surface chemistry could be used to direct the placement of NP within diblock copolymers.7 The selective NPs gathered at the center of one domain, while the population of the nonselective NPs are centered around the AB interface. These two cases were also studied with computer simulations by Schultz et al., and their results agree qualitatively with experiments.8

To study the effect of NP size on their equilibrium location, a mean field theory was used by Thompson et al.9 They chose model systems where there is a selective interaction

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between the NP and one of the blocks. They found that for the case where the A-coated NP is small, the NPs are exclusively located throughout the A domain. For the other extreme of large NP, they tend to be located at the center of the A domain, where most chain ends lie in spite of the loss of translational entropy. This loss is offset because if the large NPs were throughout the A domain, then the A polymer segments would have to stretch around the NP, thereby resulting in loss in polymer configurational entropy. These theoretical predictions were affirmed by experimental observations as well as the computer simulations of Schultz et al. To summarize, the equilibrium location of NPs within BCPs can be controlled by the type of interaction between the NP and the copolymer blocks or by the size of the NP relative to the $R_g$ of the BCP.

Besides investigating the spatial arrangement of NPs, there is an interest in determining how the addition of NPs affects the formation of self-assembled structures or the phase diagram of block copolymers. The thermodynamics of BCP/NP mixtures was first studied with theory and simulation by Huh et al. Using a theory based on the strong segregation limit as well as lattice Monte Carlo simulations, they generated plots of the volume fraction of the minority component of the BCP versus volume fraction of NPs at a fixed high value of $\chi N$ and for various NP sizes. Here, the NPs were selective toward monomers of one of the blocks. For these mixtures, it was found that the addition of NPs induced phase transitions between the thermodynamically stable self-assembled structures such as spheres, cylinders, and lamellae. Schultz et al. performed molecular dynamics (MD) simulations of symmetric block copolymers over a series of $\chi N$ and volume fractions ($\phi_p$) of NPs to map out a phase diagram. They modeled NPs of various sizes with selective and nonselective interactions. The nonselective NPs had no dramatic effect on the self-assembled lamellae except that their presence shifted the $\chi N$ ODT to higher values; moreover, for a given $\chi N$, above a certain $\phi_p$, the structure transitioned from ordered to disordered. Addition of selective NPs to a symmetric BCP melt resulted in an interesting phase diagram: for a given $\chi N$ at low $\phi_p$, there were lamellae, then with increasing $\phi_p$ perforated lamellae, cylinders, and then an order-disorder transition in agreement with the earlier simulation results of Huh et al. Hence, we expect that keeping the volume fraction of NP low within the symmetric BCP matrix leads to the formation of lamellae when the $\chi N$ value is sufficiently high.

BCPs can be subjected to external fields, such as electric fields or shear flow, to induce structural changes. Both of these fields have been demonstrated to produce favorable effects which include the inducement of long-range order and order-disorder or order-order structural transitions, as well as the orientation of self-assembled structures. As documented in a review by Hanley, the effects of shear flow on self-assembled spheres, cylinders, and lamellae have been well-studied. In a more focused review, Wiesner surveyed the current progress in understanding how shear flow affects the lamellae formed by symmetric diblock copolymers. When symmetric BCPs are annealed at high temperature, lamellae form but usually there is only local ordering and grain boundaries pervade throughout the bulk sample. Shear can help to remove these grain boundaries, thus resulting in the formation of large lamellae. For BCPs that are at temperatures (or $\chi N$ values) slightly above the order-disorder transition, shear can induce the formation of lamellae. The shear is thought to suppress concentration fluctuations and therefore stabilize the lamellae. Three lamella orientations have been observed: at low shear rates, the lamellae are parallel to the flow direction, and at higher shear rates, the lamellae are perpendicular to the flow direction (with the lamellae normal pointing in the neutral direction); the more elusive orientation is called transverse where the lamellae normal is parallel to the flow direction. These transitions have been shown to depend on the shear rate (or frequency with oscillatory shear). Fraser et al. and Schultz et al. used MD simulations to model the shear-induced transition of lamellae in the parallel and perpendicular orientations. Based on our literature survey, only a handful of publications have directly addressed the dynamic behavior of BCP/NP mixtures. A relevant work was reported by Pozzo et al., where they dispersed silica nanoparticles into Pluronic triblock copolymer systems that exhibited a micellar cubic morphology. The thrust of their work was to test how the temperature profile during sample preparation or particle size and concentration affected their equilibrium placement within the cubic matrix. Rheological measurements were performed to probe the structure that resulted from varying the aforementioned parameters. They did not utilize shear flow to induce the formation of a self-assembled structure or to guide the placement of NPs within the matrix. Similar work was reported independently by Castelletto et al. and by Lee et al. for BCPs mixed with silicate or clay particles. In the current work, we present results on the computational simulations we performed to model BCP/NP mixtures that are subjected to a simple shear flow. From what has already been reported in the literature, we can anticipate the equilibrium location of the NPs that are mixed with symmetric BCPs. The NP placement, as was noted earlier, can depend on the interaction between the NP and either of the two immiscible monomers of the diblock copolymer, or on the NP size. We narrow our investigation to probe the effect that shear flow has on the NP placement. To this end, we define potentials such that the NP is either selective to one block or nonselective to either of the two blocks, and we increment the shear rate over a range of a few orders of magnitude. To further limit the scope of the analysis, we model the NPs as spheres that have the Lennard–Jones diameter=1–1.5 times the monomers size, and we keep the volume fraction of NPs fixed to 0.1. From these simulations we aim to address four questions: (1) How does shear flow affect the spatial distribution of NPs? (2) How does the presence of NPs affect the shear-induced transition in lamellae orientation? (3) How is the rheology of the BCPs affected by the inclusion of NPs? (4) How does the effect of shear vary for NPs with different diameter and interaction potential? Our ultimate goal is to elucidate the conditions that are necessary to gain even greater control of the highly ordered placement of NPs.

In the following section, we describe the manner in which we modeled the block copolymer and the nanopar-
particles. We show the pairwise potentials for all species, and we provide details on the computational method employed. In Sec. III, we present simulation results on the different nanocomposite systems that we studied under shear flow. Finally, in Sec. IV, we suggest mechanisms that could explain our findings.

II. MODEL AND METHODS

A. Potentials

The copolymer chains in the current study are modeled as fully flexible bead-spring chains where the monomers are never allowed to overlap. Since we deal with a diblock copolymer, the chains consist of A and B blocks of monomers. The excluded volume interactions between the A and B monomers are accounted for by the purely repulsive, cut and shifted, Lennard-Jones (LJ) potential which is often referred to as the Weeks–Chandler–Anderson potential,

\[ u_{\text{REP}}(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] + \varepsilon = u_{\text{LJ}}(r) + \varepsilon, \]

\[ r \leq 2^{1/6}, \]

\[ u_{\text{REP}}(r) = 0, \quad r > 2^{1/6}, \]  

where \( r \) is the separation distance between beads, and \( \sigma \) and \( \varepsilon \) are the Lennard Jones parameters, taken to be unity for the sake of simplicity. Within a polymer, the neighboring monomers are connected by a finitely extensible nonlinear elastic (FENE) potential,

\[ u_{\text{FENE}}(r) = -\frac{1}{2}kR_{\text{max}}^2 \ln \left[ 1 - \left( \frac{r}{R_{\text{max}}} \right)^2 \right], \]

where we set the spring constant \( k \) to 30, and the maximum extensibility \( R_{\text{max}} \) to 1.5, as described by Kremer and Grest.

To incorporate the physics of microscopic phase separation between the A and B species, we utilize an attractive potential between like monomers (i.e., A-A or B-B). This interaction taken together with the repulsive A-B potential ensures that phase separation will occur if the temperature is below the order-disorder transition temperature. We use the same attractive potential that was used by Horsch and coworkers to model the equilibrium properties of diblock copolymer melts. This is again a LJ potential but now it is cut and shifted at values that differ from those presented in Eq. (1),

\[ u_{\text{ATT}}(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] - u_{\text{LJ}}(2.5), \quad r \leq 2.5, \]

\[ u_{\text{ATT}}(r) = 0, \quad r > 2.5. \]  

The higher cutoff means that this is not purely repulsive and that monomers of the same type are attracted to each other. With this potential, Horsch et al. generated various points in the phase diagram, and found good agreement with the phase diagram from mean field theory. These authors derived the Flory–Huggins \( \chi \) parameter between the A and B sites as a function of the simulation temperature. In the present work, we performed all simulations at a temperature that results in \( \chi N \) value (~50) well above the order-disorder transition.

For the nanoparticles, we model two different types of particles, namely, selective and nonselective. For selective particles, we use a purely repulsive potential between monomer B and particle \( P \) and for the interaction between monomer A and \( P \), we consider two different cases of potential that are both attractive with \( k = 1.0 \) and \( k = 0.9 \) in the equation below. \( P-P \) potential is kept same in all systems = \( u_{\text{ATT}} \).

\[ u_{\text{ATT}}^{A-P}(k)[k] = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] + \text{ecut}, \quad r \leq 2^{1/6} \]

\[ = k^2 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] + u_{\text{LJ}}(2.5), \]

\[ 2^{1/6} \leq r \leq 2.5 \]

\[ = 0, \quad r > 2.5, \]  

where \( \text{ecut} \) is the value by which \( u_{\text{ATT}}^{A-P}(k) \) needs to be shifted to make the potential continuous at \( r = 2^{1/6} \). \( u_{\text{ATT}}^{A-P}[1.0] \) is essentially the same as \( u_{\text{ATT}} \) and \( u_{\text{ATT}}^{A-P}[0.9] \) represents an A-P potential that is slightly less attractive than \( u_{\text{ATT}}^{A-P}[1.0] \). Any value of \( k \) below 0.9 causes the nanoparticles to get aggregated due to strong P-P attraction compared to the A-P attraction. For nonselective particles, we use \( u_{\text{ATT}} \) for both A-P and B-P contacts. Table I summarizes the interactions between different elements in various systems. Our simulation model neglects the effect of nanoparticle rotational dynamics on the rheological behavior of our systems. Note that although such rotational effects are irrelevant for thermodynamic behavior, they may be important for flow behavior. It is expected, however, that such effects will become more significant, the higher the concentration of nanoparticles in the system, the higher the shear rate. We assume that the nanoparticle surface functionalization is such that rotation modes tend to be suppressed and that for the relatively low nanoparticle concentration used in this work (10 vol %), such rotational effects are small compared to those of the translational modes. This is clearly an approximation but is expected not to greatly affect the qualitative response of our systems under shear flow.

B. Thermostat

We use a thermostat that preserves hydrodynamic interactions, i.e., the dissipative particle dynamics (DPD) thermostat. DPD is a simulation technique that was originally conceived to model the interaction of mesoscopic units. The interactions between sites are treated as “soft” potentials meaning that the mesoscopic units can overlap. It was dem-

| TABLE I. Summary of interactions between the nanoparticles (P) and the A and B monomers of the diblock copolymer. |
|---------------------------------|---------------------------------|---------------------------------|
| Selective[1] | \( u_{\text{ATT}}^{A-P} \) or \( u_{\text{ATT}}^{A-P}[1.0] \) | A-A, B-B, P-P, A-P |
| \( u_{\text{REP}} \) | A-B, B-P |
| Selective[0.9] | \( u_{\text{ATT}}^{A-P}[0.9] \) | A-P |
| \( u_{\text{ATT}} \) | A-A, B-B, P-P |
| \( u_{\text{REP}} \) | A-B, B-P |
| Nonselective | \( u_{\text{ATT}} \) | A-A, B-B, P-P, A-P, B-P |
| \( u_{\text{REP}} \) | A-B |

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shown by Soddemann et al. that this thermostat is effective when using “hard” LJ potentials as is being used in this work. In DPD, we solve the equations of motion,

\[
\frac{d\vec{r}_i}{dt} = \frac{\vec{p}_i}{m_i},
\]

\[
\frac{d\vec{p}_i}{dt} = \sum_{i \neq j} F^c_{ij} + \sum_{i \neq j} F^D_{ij} + \sum_{i \neq j} F^R_{ij},
\]

(5)

where, \( F^D \) is a dissipative (or damping) force and \( F^R \) is a random force. These two terms act as a heat source and drain, thus regulating the simulation cell temperature. \( F^c \) is the conservative force that acts between two particles. The dissipative force can be expressed as

\[
F^D_{ij} = -\zeta \omega^0(r_i)(\vec{v}_i \cdot \hat{n}_i)\vec{r}_{ij},
\]

(6)

where \( \zeta \) is a friction parameter and \( \omega^0(r) \) is a weight function. The random force is

\[
F^R_{ij} = \sigma_N \omega^0(r_i) \xi \vec{r}_{ij},
\]

(7)

where \( \sigma_N \) is a noise parameter and \( \xi \) is a white noise variable. From the fluctuation-dissipation theorem, we have

\[
\sigma_N = (2k_B T \xi)^{1/2},
\]

\[
\omega^0(r) = [\omega^0(r)]^2.
\]

(8)

As reported by Fraser et al., we used weight functions that have the form,

\[
\omega^0(r) = \omega^0(r) = \omega(r),
\]

\[
\omega(r) = \begin{cases} 1 & \text{if } r < r_c \\ 0 & \text{if } r \geq r_c. \end{cases}
\]

(9)

C. Simple Shear Flow

Shear flow can be used to control the structure made from self-assembled molecules. This external field can induce order-disorder transitions or long-range ordering in relatively short amounts of time. In our MD code, we implemented shear flow with the SLODD algorithm using the following equations of motion:

\[
\frac{d\vec{r}_i}{dt} = \frac{\vec{p}_i}{m_i} + \gamma \vec{y},
\]

(10)

\[
\frac{d\vec{p}_i}{dt} = \vec{F}_i - \gamma \vec{p}_y,
\]

(11)

where \( \vec{p}_i \) is the peculiar momentum of particle/bead \( i \), \( \gamma \) is the shear rate, and \( \vec{y} \) is the unit vector in the \( \gamma \) direction. By this method, we can impose a linear velocity profile in the \( x \) direction with a constant gradient in the \( y \) direction (with \( z \) as the neutral direction). These equations of motion are implemented with compatible Lees–Edwards periodic boundary conditions, wherein two opposing periodic images are incrementally moved in opposite directions consistent with the applied shear rate. Plots of shear viscosity versus shear rate for polymeric fluids have been widely published in literature, and they clearly demonstrate that these fluids exhibit a Newtonian regime at low shear rates and shear thinning at higher shear rates. The pressure tensor can be calculated from simulations using

\[
P = \frac{1}{V} \left( \sum_{i} \frac{n}{m_i} P_{ii} + \sum_{j \neq i} r_{ij} F_{ij} \right).
\]

(12)

From this, we can determine the shear viscosity by the following relationship:

\[
\eta = \frac{P_{xy}}{\gamma}.
\]

(13)

D. Computational Details

Throughout these simulations, we fixed the polymer chain length to ten monomers or beads. The particle volume fraction was fixed at 0.1 for both selective and nonselective NPs to preserve lamellar morphology in the nanocomposite. The site density \( \rho \) was kept fixed at 0.85 and the temperature \( k_B T \) was kept at 1.0. Although the copolymer chain length adopted here is relatively short, it is considered appropriate to capture the essential behavior of symmetric copolymers since five beads (approximately five Kuhn lengths) is about the minimum chain length that a block can have to possess oligomeric character (the shortest block in a nonsymmetric copolymer should also be approximately five beads long). To prevent undue periodic boundary artifacts, we varied the system size from \( L=36 \) down to \( L=26 \) until the system attained its natural lamellar spacing. Figure 1 shows a typical box size study performed for selective NP/BCP system at \( \gamma=0.005 \). Due to the limited number of repeat units, the system is very sensitive to slight changes in the lamellar spacing caused by addition of NPs or by application of shear, therefore, similar box size studies were conducted for various systems and shear rates. From our box size study, we do not find any effect of shear on the domain spacing in a particular system in the range of shear rates studied. The velocity Verlet algorithm was used to integrate the equations.
of motion with a time step=0.01. To make the code efficient, we used a cell list algorithm. The simulations were run for a sufficiently long time until variables such as pressure, potential energy, radius of gyration, and mean squared end-to-end distance remained constant. In addition, we monitored the equilibration of order parameter $O$ (see Fig. 2 for some test cases), which is the largest eigenvalue of the Saupe tensor, with time until it stabilized to an equilibrium value.

$$Q_{\alpha\beta} = \frac{3}{2N_F} \sum_{i=1}^{N_F} e_i a_i e_{\beta} \cdot \frac{1}{2} \delta_{\alpha\beta},$$

where $e_i$ is the unit vector along the end-to-end direction of a diblock copolymer and $\delta_{\alpha\beta}$ is the Kronecker delta. $O$ is zero in a completely disordered state and it is unity if the system is perfectly aligned.

We note that the NP size used for most part of the current work is same as the size of the Kuhn monomer, and one could then consider such NPs to actually represent a solvent or small oligomer. However, the “NP size/polymer end to end distance” ratio corresponding to such small NPs has been found, in practice, in several instances. From our preliminary results, we find that the end-to-end distance of a copolymer chain in the pure block copolymer system used in this work is $R_0=4.62$, corresponding to $\sigma_p/R_0=0.216$, where $\sigma_p$ (NP size) = 1. Moreover, using the entanglement length as reference, a bead-spring polymer chain with 10 beads would typically represent a molecular weight of $\sim 9$ K (Ref. 19) for a material such as polystyrene, which corresponds to a domain spacing of $\sim 9$ nm for a symmetric diblock copolymer or an end-to-end distance of $\sim 4.5$ nm. This comparison leads a nanoparticle size of $\sim 1$ nm in our simulations, which although on the borderline, does fall in the nanometer regime. To further ensure that our results are not peculiar to the particle size of one Kuhn monomer, we additionally studied selective-particle systems using NP diameter=1.2 and 1.5. The volume fraction of the NPs is kept fixed at 0.1 for all systems. Table II summarizes some of the parameters used in this work.

Table III summarizes the different NP/BCP systems used in this work, specifying the potential and particle diameter.

<table>
<thead>
<tr>
<th>Type</th>
<th>Name</th>
<th>Potential</th>
<th>$\sigma_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selective</td>
<td>Sel[1.0]-1.0</td>
<td>Selective[1]</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>Sel[0.9]-1.0</td>
<td>Selective[0.9]</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>Sel[1.0]-1.2</td>
<td>Selective[1]</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>Sel[1.0]-1.5</td>
<td>Selective[1]</td>
<td>1.5</td>
</tr>
<tr>
<td>Nonselective</td>
<td>NonSel-1.0</td>
<td>Nonselective</td>
<td>1.0</td>
</tr>
</tbody>
</table>
In Fig. 3, we present the particle concentration profiles that were obtained over a range of shear rates that covers three orders of magnitude. We find that the peaks become sharper with increasing shear rate, and despite the significant level of shear being imposed on the system, the particles do not mix into the domain where the interactions are not favorable. This could be attributed to the shear-induced suppression of fluctuations in the system morphology stabilizing the chain end density at the domain center, and hence, causing an increase in the NP concentration at the center of the preferred domain. These simulation results suggest that the entropic contributions play a significant role and indicate that shear flow can be used to further control the location of selective particles. To further elucidate our findings and understand the effect of A-P interaction and particle diameter, we studied concentration profiles as a function of shear rate for “Sel[0.9]-1.0” and “Sel[1.0]-1.5” and we found a similar sharpening of peak with increasing shear rate (Fig. 4). As expected, the volume fraction peak sharpens with increasing particle diameter (at a given shear rate) due to an increase in entropic penalty of chain stretching (around particles) for larger particles [Fig. 4(c)].

B. Spatial distribution of nonselective particles within diblock copolymers

In Fig. 5(a), we present a snapshot of the structure we obtained from our simulations of nonselective NP/BCP sys-
In this case, the particles are equally attracted to both monomers. Our results qualitatively agree with the findings of Schultz et al., who studied similar systems under no flow conditions. In Fig. 5, we present a log-log plot of the shear viscosity that was calculated with Eqs. (12) and (13) as a function of shear rate for four systems from Table III and a pure block copolymer system. For pure block copolymer systems taken over a range of shear rates. For the various flow rates, we observe that the nonselective particles remain predominantly segregated at the domain interface. Unlike the case of selective particles, the nonselective NPs at the interface experience two competing forces: the first one trying to locate the NPs at the A-B interface to reduce the tension between strongly segregated ($\chi N=53.3$) blocks, the second force trying to push the particles toward the chain ends away from the interface to avoid the penalty of chain stretching. Therefore, shear effect is much more constrained, causing only small fluctuations in the NP concentration profile and no significant effect with increasing shear rate. This effect of shear, we believe, would be dependent on both the NP size and the block copolymer segregation strength. These results indicate that the particle positions can be preserved, while shear is applied to induce long-range order in block copolymer nanocomposites.

### C. Shear-induced transitions in lamellae orientation

As noted in the Introduction, shear flow can be used to control the lamellar orientation of symmetric diblock copolymers. Moreover, the transitions between the various lamellar orientations can depend on the imposed shear rate. At low shear rates, the lamellae tend to align in a parallel configuration, while at higher shear rates, there can be a transition to the perpendicular alignment. Using a computational method very similar to the one used in this work, Fraser et al. studied how simple shear flow affected the orientation of lamellar structures. Starting with lamellae in both orientations, they plotted the potential energy as a function of shear rate. They found that shearing the lamellae that were initially perpendicular always resulted in a lower potential energy and that the lamellae that were initially parallel converted to the perpendicular arrangement at higher shear rates. In this work, we sheared disordered systems which eventually evolved to either parallel or perpendicular lamellae. In Figs. 6(a) and 6(b), we show snapshots of the parallel configurations obtained for pure BCP systems at $\dot{\gamma}=0$ and 0.001, respectively. In Fig. 6(c), we show the perpendicular lamellae obtained at the critical shear rate ($\dot{\gamma}=0.005$), where the transition from parallel to perpendicular lamellae takes place. Previous studies on the flip of lamellar orientation have reported a decrease in lamellar spacing in perpendicular orientation at shear rates much higher than the critical shear rate. Both literature and our box size study confirm that there is no effect of shear on domain spacing around the critical shear rate value. Therefore, we do not expect the flip of orientation seen in this work to be a manifestation of stresses that could arise due to a box size that is incommensurate with the lamellar spacing.

Rheological measurements can be performed to resolve the structure of a self-assembled copolymer system. A sharp decrease in shear viscosity is seen at the critical shear rate, where a transition from parallel to perpendicular takes place. In Fig. 7, we present a log-log plot of the shear viscosity that was calculated with Eqs. (12) and (13) as a function of shear rate for four systems from Table III and a pure block copolymer system. For pure block copolymer sys-
tem, the shear viscosity sharply drops at a shear rate of 0.005, indicating an orientation flip to perpendicular morphology, also seen from the snapshots in Fig. 6. Similar plots for nanocomposite systems show a shift of critical shear rate to a higher value for selective NP/BCP and a lower value for non-selective NP/BCP as compared to a neat block copolymer. To further understand the effect of particle-polymer potential and particle diameter on the critical shear rate, we plotted the viscosity curves for selective NP systems. For both cases, we find that the critical shear rate is higher compared to a pure block copolymer system, which is consistent with our earlier finding. However, the critical shear rate is lower for both a larger particle size and less attractive particle-polymer potential within selective particle systems. For the “Sel[1.0]-1.2 particles (not shown in the figure), we find a similar viscosity curve as Sel[1.0]-1.0 with critical shear rate=0.02. Figure 8(a) shows the root mean squared end-to-end distance in the x direction for one selective, nonselective, and pure BCP system, and we find a sharp increase in $\langle R_x^2 \rangle^{1/2}$ at the critical shear rates. $\langle R_x^2 \rangle^{1/2}$ grows steadily with increasing shear rate, showing an orientation of chains along the flow direction. Finally, Fig. 9 shows the snapshots of two nanocomposite systems (Sel[1.0]-1.0, “NonSel-1.0) for $\dot{\gamma}=0.001$ and at respective critical shear rates for the two systems (0.02 for Sel[1.0]-1.0 and 0.002 for NonSel-1.0), confirming the results obtained from Figs. 7 and 8. Guo studied the effect of segregation strength between the two blocks in a diblock copolymer on the critical shear rate for symmetric diblock copolymers. He found that the critical shear rate decreases as the segregation between two blocks decreases. A similar analogy can be drawn for our system as the addition of nanoparticles is seen to affect the segregation between repelling blocks. We discuss this aspect in the following sec-
tion in more detail. We note that shear viscosity plots for all systems collapse on the same curve for high shear rates similar to the findings of Kroger et al. for polymers of different chain length.

IV. DISCUSSION

In the first part of our results section, we considered the effect of shear on two qualitatively different kinds of particles in a symmetric diblock copolymer melt system, namely, selective and nonselective NPs. For the case of selective particles, we studied four systems to examine the effect of different particle-polymer potentials and NP sizes. For all selective particles, we find that the NP concentration profile exhibits a maxima at the center of the preferred domain \(A\) where most chain ends lie. This finding is in agreement with literature results (for quiescent systems, i.e., \(\dot{\gamma}=0\)) for the NP size to polymer ratios considered in this work.\(^{25,30,31}\) Here, the entropic contribution plays a dominant role and pushes the NPs close to the chain ends since the energetics remain the same for NPs throughout the \(A\) domain. A sharpening of these peaks is seen with the application of shear. We suggested that this finding can be attributed to the shear-induced suppression of fluctuations, causing the particle layer to get more defined at the domain center. To further support this argument, we plotted the concentration profiles of the “\(A\) chain end” both for a pure block copolymer system and Se\([1.0]-1.0\) nanocomposite and we found a similar trend as the NP profile (Fig. 10). From these curves, it is clear that shear tends to reduce conformational fluctuations and localizes the \(A\)-block chain ends at the \(A-A\) interface (i.e., the middle of the \(A\) domain). This effect of shear is justified for it facilitates the \(A\) domains to slide past one another during shear flow. For the nonselective particles, however, there is a competition between energetic and entropic contributions. The former tries to place the particles at the interface between strongly segregated blocks to reduce \(A-B\) contacts and interfacial tension, while the latter tries to push the particles away from the interface towards the chain ends to avoid the penalty of chain stretching. The localization of particles at the \(A-B\) interface [as seen in the Fig. 5(b)] is a consequence of greater energetic effect than entropic contribution. However, unlike the case for selective NPs, the dominant force (energetic for nonselective particles) faces a competition, and hence, its effect is much more restricted. Hence, even though we expect similar fluctuation suppression for the case of nonselective particles, the effect of shear is much more constrained and, therefore, no clear shear dependence is seen. Please note that in the arguments considered above for both kinds of particles, we neglect the effect of translational entropy of the nanoparticles, as we believe that in both cases, it tries to disperse the particles away from the peak and hence does not provide a basis for comparison.
In the second part of Sec. III, we study how the presence of particles affects the shear rheology of such block copolymer systems; in particular, the shear-induced transition from parallel to perpendicular lamellar. For selective particles, we consistently find that the critical shear rate (at which the parallel lamellar switches to a perpendicular orientation) increases compared to a pure block copolymer system. We suggest that the NPs help in bridging different A chains and strengthening the cohesive forces within block A, thereby increasing the \((\chi N)_{\text{eff}}\) between block A and B causing a rise in the critical shear rate, similar to the one found by Guo.\(^{34,36}\) An increase in A-B incompatibility can be viewed as an increase in the order-disorder transition temperature \(T_{\text{ODT}}\), thereby resulting in a “colder” system (with a larger effective gap from the \(T_{\text{ODT}}\)) which makes the transition to perpendicular orientation more difficult. This effect of temperature on the critical shear rate has been often seen in experimental lamellar systems by Wiesner and coworkers\(^{37,38}\) and Kornfield and coworkers.\(^{39–41}\) Previous studies on the rheology of polymer nanocomposites have suggested that due to the comparable sizes of polymers and interparticle distances, NPs act as nodes of association for the polymer resulting in the formation of transient networks and slower dynamics of polymer chains in the presence of particles.\(^{42,43}\) Such kinetic constraints join together with the effect on \((\chi N)_{\text{eff}}\) between A and B blocks mentioned above to delay the orientation switch to a higher shear rate for selective nanoparticles. Contribution of selective NPs on \((\chi N)_{\text{eff}}\) is also evident from the shear viscosity plots for two different particle-polymer potentials for selective particles (Sel1[1.0]-1.0, Sel[0.9]-1.0). As the attractive potential between particle and polymer reduces, the bridging effect is weakened, causing a slight decrease in critical shear rate. We note that the transition shear rate is still much larger than that for a pure block copolymer system. A similar decrease in critical shear rate is also seen for the case of larger sized particles. With a 1.5 times increase in particle diameter, the interfacial area between NPs and polymer chains is reduced by 33\%. This leads to a smaller polymer-particle interface and a weakening of the and polymer chains is reduced by 33\%. This leads to a an increase in particle diameter, the interfacial area between NPs for the case of larger sized particles. With a 1.5 times increase in critical shear rate. We note that the transition shear rate compared to smaller polymer chains in the presence of particles.\(^{42,43}\) Such kinetic constraints join together with the effect on \((\chi N)_{\text{eff}}\) between A and B blocks mentioned above to delay the orientation switch to a higher shear rate for selective nanoparticles. Contribution of selective NPs on \((\chi N)_{\text{eff}}\) is also evident from the shear viscosity plots for two different particle-polymer potentials for selective particles (Sel1[1.0]-1.0, Sel[0.9]-1.0). As the attractive potential between particle and polymer reduces, the bridging effect is weakened, causing a slight decrease in critical shear rate. We note that the transition shear rate is still much larger than that for a pure block copolymer system. A similar decrease in critical shear rate is also seen for the case of larger sized particles. With a 1.5 times increase in particle diameter, the interfacial area between NPs and polymer chains is reduced by 33\%. This leads to a smaller polymer-particle interface and a weakening of the effect of both transient network formation and rise in \((\chi N)_{\text{eff}}\) thereby decreasing the critical shear rate compared to smaller particle diameter.

For the case of nonselective particles, NPs prefer to place themselves close to the interface between opposing blocks to reduce the number of A-B contacts. They work to decrease the interfacial tension between A and B and effectively reduce the segregation strength between the two blocks. By a similar analysis as for selective particles, a decrease in \((\chi N)_{\text{eff}}\) leads to a decrease in the critical shear rate. However, unlike selective particles, the effect on \((\chi N)_{\text{eff}}\) and the kinetic constraints posed due to the presence of non selective NPs work in opposite directions. The former would reduce the critical shear rate, while the latter would work to increase it by slowing the dynamics of the system. This could possibly explain the little effect seen on critical shear rate on addition of nonselective particles compared to a neat BCP. Moreover, for the selective particles, since the particles only go into one domain and prefer to stay close to chain ends, their role as network nodes would be stronger and more concentrated.

To conclude our discussion, we would like to draw a comparison of our system with the vast literature available for block copolymer in solvent systems. This comparison is valid as our system consists of nanoparticles that are comparable in size to the Kuhn segment of our polymer chains. Hanley et al., found a significant increase in \(T_{\text{ODT}}\) on the addition of a strong styrene-selective solvent in poly(styrene-b-isoprene) \((\chi_{\text{AS}}<\chi_{\text{BS}})\) due to an increase in the degree of segregation of an A-B diblock copolymer.\(^{34,36}\) This is also analogous to an increase in segregation between A and B blocks found on addition of A homopolymer by Matsen.\(^{45}\) Similarly, it was found that a neutral solvent dilutes the monomer-monomer contacts and reduce the effective segregation. This analogy further validates our findings and widens the scope of this work.

\section*{V. SUMMARY AND CONCLUSIONS}

In this work, we have performed MD simulations to model the behavior of diblock copolymer/nanoparticle systems subjected to simple shear flow. Specifically, we investigated symmetric diblock copolymers with nanoparticles that had either selective or nonselective interactions with the copolymer. For selective NPs, we studied additional cases with different particle diameter and particle-polymer interaction to clarify the mechanisms behind our findings. We kept the volume fraction of particles relatively low so that we could maintain lamellar structures for all systems. Our aim was to determine how the particles were dispersed within the self-assembled copolymer matrix while under flow. We also wanted to know how the presence of the particles affected the shear-induced transition of the lamellar orientation.

For all of the systems at equilibrium, we found qualitative agreement between our simulation results and the results reported in literature. The selective nanoparticles were exclusively gathered within the domain where there were attractive interactions between the NPs and monomers. The concentration profiles exhibited a maximum at the center of the domain and the concentration was zero in the other domain. We varied the shear rate and our simulation results show that the concentration peaks become sharper as the shear rate increases for all selective particle systems. We also studied nonselective NPs and we found that they segregated to the interface between the AB domains. For the range of shear rates and the NP size studied, the shape of the NP concentration profiles remained similar. For the pure copolymer, we found that at low shear rates, the stable structures were lamellae oriented parallel to the flow direction. At higher shear rates, the lamellae changed to the perpendicular orientation. These transitions were observed in the snapshots and they were also monitored with plots of the shear viscosity versus shear rate and mean squared end to end distance in the y direction versus shear rate. The transition found for pure copolymers were likewise observed when NPs were introduced into the BCP. Specifically, selective NPs shifted the transition to higher shear rate while the nonselective NPs
shifted it to lower values. Further, we found that among the selective NP composites, larger NP size and lower particle-polymer interaction shifted the critical shear rate to a lower value.

It is widely known that shear flow can have beneficial effects on the self-assembled structures, and that self-assembling copolymers can be used as a nanoscale template to control the three-dimensional arrangement of nanoparticles. In this paper, we married these two concepts and, based on our modeling and simulation, we speculate that shear rate can be used as another parameter to further control nanoparticle location.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Manuel Marquez at Philip Morris, USA for providing funds via Nanotek Consortium and Interdisciplinary Network of Emerging Technology Program to support this work.