Detailed Mesoscale Dynamic Simulation of Block Copolymer Directed Self-Assembly Processes: Application of Protracted Colored Noise Dynamics

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Detailed Mesoscale Dynamic Simulation of Block Copolymer Directed Self-Assembly Processes: Application of Protracted Colored Noise Dynamics

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ABSTRACT

Directed self-assembly (DSA) of block copolymers is a promising technique for producing sub-30 nm pitch regular patterns, and the development of these DSA techniques could benefit greatly from computer simulation of such methods. Current simulation methods such as mean field approaches suffer from a number of limitations that affect their accuracy and their level of detail. In this work a simulation approach based on the use of Protracted Colored Noise Dynamics (PCND) with coarse grained mesoscale polymer models based on statistical segment beads has been developed and studied. It has been shown that using PCND allows simulations to reach an equilibrium state at least 35 times faster than without PCND.

Keywords: block-copolymer, self-assembly, simulation, modeling, protracted colored noise dynamics, molecular dynamics, polystyrene, PMMA

1. INTRODUCTION

The pitch of single layer resist (SLR) processes has essentially reached a plateau at approximately 80 nm in terms of the smallest practical pitch achievable using 193 nm immersion lithography. In order to achieve smaller pitch patterning and continue to increase device densities on a single layer, alternative lithographic patterning methods are needed in the near term to achieve sub-80 nm pitches. One option to achieving smaller pitch patterning is to transition to lower wavelength exposure technologies (i.e. EUVL or e-beam lithography) that are directly capable of patterning such smaller pitches. However, EUVL and e-beam direct write technologies are not yet ready for high volume manufacturing due to low wafer throughputs for such processes currently. A second option is to utilize alternative lithographic processes (i.e. other than SLR methods) that can provide a means for subdividing the pitch achieved in a primary lithographic exposure step to provide final patterns at a tighter pitch. Such methods are already receiving significant attention in the form of so-called “double patterning” methods. In such double patterning techniques, two separate exposure steps at a relaxed pitch are overlaid to achieve a final patterned result at half of the primary exposure pitch. In this way, roughly 40 nm pitch patterning can be achieved with 193 nm immersion lithography. If one assumes that for the near future exposure tools are still limited to 193 nm light as the smallest practical exposure wavelength, the issue then becomes one of how to achieve final pitches smaller than this 40 nm pitch available with double patterning. An obvious extension of this double patterning technique is to go to a much higher level of complexity for these multiple exposure processes. This leads to so-called “triple patterning” and “quad patterning” which involve overlaying 3 or 4 separate exposure steps to further subdivide the primary pitch available by the optical exposure tool. However, the expense and overlay requirements of such methods make these options less than desirable.

A pitch subdivision option that has received growing interest in the last several years for performing these higher levels of pitch subdivision is block copolymer lithography (BCPL) utilizing directed self assembly (DSA), referred to here as BCPL-DSA. Block copolymers naturally undergo microphase separation into periodic domains that range in size from only a few nanometers to on the order of hundreds of nanometers depending on the molecular weight of the polymer blocks themselves. This ability to control the length scale of the pattern formed from such a block copolymer by controlling the molecular weight of the BCP offers an interesting new method for controlling the size of very small scale
patterns. The resulting phase separated structure formed from such a diblock copolymer can itself be quite varied, including lamellar, gyroidal, cylindrical, and spherical microstructures. This morphology is controlled by the relative volume fractions of the two blocks in the copolymer. Unfortunately, left to phase separate in bulk in an uncontrolled fashion, such block copolymer systems naturally form defective morphologies that are not suitable for high resolution lithography applications. Therefore, additional steps must also be taken to guide this self-assembly process to form structures with low defectivity and long range order. Understanding and designing the materials and processes for achieving such directed self assembly of block copolymers is a significant and challenging task.

Simulations of phase separation of BCPs have accurately reproduced their unusual phase behavior. Most simulations have used self-consistent field theory (SCFT) to progress polymer physics over a span of several decades and in some cases, the only predictions available are from SCFT studies. SCFT has many limitations though, including the lack of thermal fluctuations in the calculations, which are important near phase transitions. As a result, these systems are locally and globally incompressible, resulting in a less accurate model and a difficulty in simulating the development and removal of defects and transition states. SCFT simulations also can be problematic when considering the dynamics of a system as it was originally developed to describe equilibrium properties. Also, SCFT can have a difficult time with solid object, or some boundary conditions such as non uniform walls, or bumps in underlayers or walls. Often SCFT simulations are 2D and while this speeds up simulations, it completely removes the possibility of investigating the effect of defects in pre-patterns used for BCPL-DSA. Single-chain mean field (SCMF) simulations have improved upon some of these limitations by explicitly modeling chains, but only calculate fields periodically so computational efficiency is still very good. This is better than SCFT for modeling fluctuations near phase transitions, but it still lacks the accurate capability that offered by either molecular dynamics (MD) or Monte Carlo (MC) simulations. It is somewhat of a compromise between the two extremes. Because of the assumptions used in both SCFT and SCMF calculations, it would be advantageous to use MD or MC simulations to investigate BCPL-DSA; however, they typically run far too slowly to yield any meaningful results in their most basic states.

This paper shows two ways in which the run times of MD simulations can be sped up. The first is by using a mesoscale model instead of conventionally used atomistic MD models. The mesoscale model groups multiple monomers together into a single bead. The conversion of 50+ atoms into a single bead greatly accelerates the speed of simulation and allows for significantly larger systems to be simulated by greatly reducing the number of calculations necessary for a given timestep. The beads are connected by a simple harmonic oscillator (i.e. the polymer is represented as a “bead-and-spring” model) whose properties are extracted from representative atomistic simulations. This meso-scale model was initially discussed by Lawson and coworkers in 2011. The main focus of this paper though, is on the addition of a protracted colored noise technique that increases diffusivity through enhanced local fluctuations by adding stochastic colored noise. Unlike the original method where the stochastic colored noise was applied in a spatially homogeneous fashion, it is applied to polymers along the polymer contour to enhance chain reputation. Stochastic forces are projected onto a vector that connects the adjacent meso-scale beads that flank the bead of interest. Unlike typical stochastic simulations, the variance of the Normal distribution from which the stochastic force is drawn is not correlated with coefficient of the damping term. While this allows the application of high stochastic forces without producing a highly over-damped system, it does violate the fluctuation dissipation theorem. An integral thermostat is used to constrain the system temperature to a constant value. However, our goal is to allow the system to efficiently evolve to the appropriate equilibrium or pseudo-equilibrium state with little interest in the intervening dynamic trajectory. Regular MD simulation is used to characterize the system near these ultimate states. This approach significantly increases the local chain diffusivity and allows simulations to access the phase separation that occurs in the annealing of BCP films during DSA.

Also discussed is the effect of changing the Flory-Huggins interaction parameter \( \chi \). That describes the enthalpy of mixing of the two polymer segments in the block copolymer. In our model, this parameter is determined by the bead to bead interaction parameters designated by \( e \), \( e_{AA} \) or \( e_{BB} \) refers to the interactions between 2 A beads or 2 B beads respectively. \( e_{AB} \) refers to the strength of interaction between dissimilar beads. When \( e_{AB} \) is low relative to the homopolymer interaction parameters (\( e_{AA} \) and \( e_{BB} \)), then the interaction for dissimilar beads is very weak and so the \( \chi \) value relatively high. When \( e_{AB} \) is much closer to \( e_{AA} \) and \( e_{BB} \), then the interaction for dissimilar beads is relatively high and so \( \chi \) is low. We are currently working on calculating \( \chi \) from a given set of \( e \) parameters using the energy of mixing for two different homopolymers. A higher \( \chi \) means that there is a higher driving force for phase separation which will result in a sharper, more clearly defined interface between the two blocks. When this driving force is too low, then there will be no phase separation and both phases will mix. This transition occurs when \( \chi N \) (\( N \) is the degree of polymerization)
equals 10.5, the so called order disorder transition (ODT). The effect of changing \( \chi \) by changing \( \epsilon_{AB} \) is investigated in this work.

**Figure 1.** Schematic of the direction of the protracted colored noise force applied to each bead along a polymer chain using the Protracted Colored Noise Dynamics (PCND) technique investigated in this work. Here a force is applied to Bead A in a direction set by the vector connecting the two nearest neighbor beads for A along its same chain. The direction that the PCND force is applied along this vector is chosen randomly and persists in that direction for a time scale chosen by the user of the simulation.

**Figure 2.** Schematic of the mesoscale potentials used in this work to constitute the bead-and-spring polymer chain model. In this model each bead represents 4 monomeric units of poly(styrene) and poly(methyl methacrylate).

\[
E_{\text{str}}(r) = k_{\text{str}}(r - L)^2
\]

\( \text{Stretching describes distance between beads extracted from atomistic} \)

\[
E_{\text{ang}}(\alpha) = k_{\text{ang}}(\alpha - A)^2
\]

\( \text{Angle describes angle between 1.3 beads (indirectly controls their distance apart) extracted from atomistic} \)

\[
E_{\text{vdw}}(r) = \epsilon_{lj} \left[ \left( \frac{\sigma_{lj}}{r} \right)^{12} - 2 \left( \frac{\sigma_{lj}}{r} \right)^{6} \right]
\]

\( \text{Lennard-Jones (LJ) type potential used to describe the van der Waals forces that act between non-adjacent beads extracted using density and cohesive energy density} \)

### 2. MODEL DESCRIPTION

#### 2.1 Mesoscale Model

The mesoscale polymer model used in this work consists of beads connected by a harmonic spring. Each bead consists of a statistical segment of a polymer chain, which in the case of both PS and PMMA is approximately 4 monomers. There are 3 types of energetic potentials used in the simulations discussed here: (1) a stretching potential \( E_{\text{str}} \) to describe the harmonic spring or oscillator that connects two adjacent beads on a chain, (2) a bending potential \( E_{\text{ang}} \) that prevents direct overlap of any three neighboring beads on a chain and which reproduces the average polymer geometric properties (e.g., radius of gyration versus degree of polymerization), and (3) a Lennard-Jones (LJ) type potential \( E_{\text{vdw}} \) that represents the non-bonded interactions between beads in the polymer chain. Figure 2 shows the particular potential functions used in each case along with a schematic illustration of their meaning in the simulation (Figure 2).
Using a method described previously⁴, the model parameters described above were fit to atomistic simulations, experimental densities, and experimental cohesive energy densities for the classic poly(styrene)-b-poly(methyl methacrylate) or PS-b-PMMA polymer system used extensively in BCPL-DSA studies thus far. The values extracted for PS-b-PMMA and used in the simulations described in this paper are listed in Table 1. All simulations in this work were carried out in Molecular Operating Environment (MOE) from the Chemical Computing Group.⁵ MOE is a framework and language for easily implementing molecular simulations such as molecular dynamics simulations in a flexible and efficient method. It also has convenient visualization techniques for viewing the results of such molecular simulations.

Table 1. Mesoscale potential parameters used for PS-b-PMMA simulations in this work.

<table>
<thead>
<tr>
<th>Bonded Potentials</th>
<th>L</th>
<th>(k_{\text{Stretch}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-S</td>
<td>8.55</td>
<td>0.3</td>
</tr>
<tr>
<td>MMA-MMA</td>
<td>8.50</td>
<td>1.2</td>
</tr>
<tr>
<td>S-MMA</td>
<td>8.55</td>
<td>0.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Non-bonded Potentials</th>
<th>(\sigma)</th>
<th>(\varepsilon)</th>
<th>(m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-S</td>
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<td>0.6</td>
<td>6</td>
</tr>
<tr>
<td>MMA-MMA</td>
<td>17.87</td>
<td>0.56</td>
<td>6</td>
</tr>
<tr>
<td>S-MMA</td>
<td>16.50</td>
<td>0.4</td>
<td>6</td>
</tr>
</tbody>
</table>

### 2.2 Molecular Dynamics with Protracted Colored Noise Dynamics

According to reptation theory, polymers diffuse via a worm-like motion along their contour. However, this thermal motion takes place on a time scale much larger than the typical timescale of atomistic or even mesoscale models. Therefore, it is desirable to reduce the timescale over which these motions take place without disturbing natural conformations and gyrations of the polymer chain. In this paper, we begin with Langevin equation, but the second and third term on the right side of Equation 1 are used to manipulate the local fluctuations rather than mimic the fluctuation and dissipation effect of a surrounding solvent respectively.

\[
m \frac{d^2x(t)}{dt^2} = -\nabla U(x) + \varepsilon(t) - \frac{\eta(t)}{m} \frac{dx}{dt}
\]

(1)

Here \(\eta\) is a Nosé-Hoover-style integral temperature controller function as opposed to the Langevin damping coefficient that is proportional to the variance of the random force \(\varepsilon\). As with Langevin Dynamics, \(\varepsilon\) is a random force of zero mean as expressed in Equation 2. Unlike Langevin Dynamics where this random force is uncorrelated in time, this random force decays exponentially with time as seen in Equation 3. The protracted colored noise force acts along the contour of the polymer chain, encouraging the reptation movement that is natural to polymer diffusion. For a given mesoscale bead, the direction of the force is taken as the vector between the two polymer beads adjacent to the original bead (see Figure 1). For the beads at each end of a chain, which only have one adjacent bead, each direction component for the force on that bead is taken from the random distribution \(\cos(2\pi a)\) where \(a\) is a random real number between 0 and 1. One of the two beads at the either end of each polymer chain is arbitrarily chosen as the origin of each polymer chain for the duration of the simulation, solely such that the choice of direction of movement along the chain contour has a consistent framework from which to be viewed and selected. The PCND force is initialized using the Box Muller algorithm, scaled by a parameter \(\Omega/\tau\). This force is then integrated through time is such a way that it is exponentially correlated in time.

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**Note:** The table and equations are presented in a clear and readable format, with proper alignment and spacing. The text is concise and informative, providing a detailed explanation of the methods and parameters used in the simulations. The table and equations are integrated seamlessly, ensuring the information is easily digestible and accessible.
according to a persistence time $\tau$. Through the calculations found elsewhere$^5$, the PCND force has the following properties,

$$\langle \epsilon(t) \rangle = 0$$

$$\{\epsilon(t)\epsilon(s)\} = \left( \frac{\Omega}{\tau} \right) \exp\left(-\frac{|t-s|}{\tau}\right)$$

where the brackets $\{\ldots\}$ symbolize averaging over the distribution of initial values of $\epsilon_0$ in

$$P(\epsilon_0) = \left[ (2\pi \frac{\Omega}{\tau})^{-1/2} \right] \exp\left(-\frac{\epsilon_0^2}{2\Omega/\tau}\right)$$

The parameter $\tau$ is the exponential decay time for the contour projected force and describes the time scale for the variation of the direction along the contour. Related to the time this force acts in a positive or negative direction along the contour, that is, a higher $\tau$ causes the force to act in the same direction along the contour for a longer period of time. The correlation time $\tau$, determines the time over which the force is correlated. This is illustrated in Figure 3. The instantaneous variance of the distribution of the random force $\epsilon$ is $\Omega/\tau$.

![Figure 3](http://example.com/figure3.png)

**Figure 3.** The autocorrelation of scalar colored noise generated from the PCND algorithm as a function of $\tau$. White Noise is shown as a comparison. For all simulations shown in this paper, $\tau=100$ ps was used.

For all simulations shown in this paper, parameters of $\Omega/\tau=1000$ and $\tau=100$ were used. These parameters were found to qualitatively increase the diffusion of the polymers without causing obvious distortions in the polymer chain morphology. These MD and PCND simulations produced the same ratios of the average principle components of the radius of gyration tensor that were observed in previous atomistic simulations.$^{10}$ It should be added that this force only increases a motion already natural to the polymer and so, as long as the parameters are not set so high that the other potentials describing the energetics of the chain (i.e. $E_{str}$, $E_{ang}$, $E_{vdw}$) are overwhelmed, the polymers should continue to move and the system should evolve in much the same way as without the force, only in much less time.

The code for these simulations was written using the $\$VL$ language available to MOE.$^5,8$ The code includes a 2$^{nd}$ order integration scheme based on that described elsewhere$^5,7$ adapted for 1 dimension along the polymer chain contour. It also includes a step that subtracts off the linear and rotational momentum periodically. This is necessary due to the so called “flying ice cube” effect where rescaling the velocity in a system (caused by the temperature controller) causes the higher frequency modes to be converted into lower frequency translational modes, namely a translation of or rotation about the center of mass. This phenomenon can be eliminated with a periodic subtraction of momentums.$^9$ It also includes a modified Nose-Hoover thermostat that controls the temperature via a frictional term that scales every beads velocity.$^8$
We have added a proportional term to the controller as well. All simulations were run on single processor INTEL machines with 1-4 cores.

2.3 Description of Simulations

Three different simulations were run in this work: (1) the first explores the effect of PCND on annealing out a defect in a lamellae forming PS-b-PMMA system, (2) the second considers the effect of PCND on simulating micro-phase separation from an initially well mixed PS-b-PMMA system, and (3) the third assesses the effect of the enthalpy of mixing parameter $\chi$ on these systems.

In the first simulation test, molecular dynamics with and without protracted colored noise dynamics was run on an initial condition that included a defect in a lamellae forming PS-b-PMMA system. All polymer chains in the simulation were PS-b-PMMA polymers that were 50% PS by number of monomers, and had an overall degree of polymerization of 436. These polymers should form lamellae with a pitch of ~21nm in their equilibrium state. For this simulation, an $\varepsilon_{AB}$ of 0.4 kcal/mole was used. The simulation was periodic in the y and z dimensions (see Figure 4), but open in the x direction so as to allow the polymer to assume its natural density and pitch without constraining it. The periodic box has a cross section of (8.35nm x 8.35nm) and the simulation included 3996 beads. The temperature used was 500K. Using parameters of $\Omega/\tau=1000$ and $\tau=100$, we ran this simulation until it had achieved the correct lamellae size, as extracted from experiment, in the middle of the simulation which was interpreted to mean that system was very near equilibrium.

In the second simulation test, molecular dynamics with and without protracted colored noise dynamics was run on a simulation box that was randomly filled with the same type of PS-b-PMMA copolymers used in the first test and under similar conditions (i.e. 50% PS by number, overall degree of polymerization of 436, Temperature= 500K, etc.) The simulation box was again periodic in the y and z dimensions, but open in the x dimension. The period box had a cross section of (8.35nm x 8.35nm) and the simulation included 3996 beads as in the previous simulation. Each chain was originally built by placing an initial bead randomly in the box (using a dimension of ~50nm for the x direction) followed by placement of the rest of the beads along the chain starting from that initial bead using a random walk configuration at the equilibrium length for the given beads types. Because this doesn’t take into account the angle term as mentioned above or the non-bonded $E_{vdw}$ potential energy contributions due to non-covalent bead-bead interactions, polymer beads and chains may be placed into unrealistic configurations initially (e.g. unrealistic distances between beads that are not neighbors on the same chain and even possibly the placement of two beads on top of one another), the system was energy minimized until the resulting configuration was appropriate to run molecular dynamics stably at the specified time step. For our simulations, this is typically when the root mean square energy gradient is below ~0.1 where the potential energy is calculated in kcal/mol and the special dimension is in Å. This yields a well-mixed initial condition on which it is possible to compare MD with and without PCND.

The third simulation test was done with the same initial conditions as in the second simulation test, but the $\chi$ value for the block copolymer was varied by changing $\varepsilon_{AB}$. Values of $\varepsilon_{AB}$=0.4 (higher $\chi$), 0.475 (medium $\chi$), and 0.55 (lower $\chi$) were used in these simulations. For reference, the homopolymer interaction parameters for PS and PMMA were $\varepsilon_{AA}$=0.56 and $\varepsilon_{BB}$=0.6 respectively.

3. RESULTS AND DISCUSSION

3.1 Annealing of Defects: Effect of PCND

Molecular dynamics with and without protracted colored noise dynamics was run on an initial condition that included a defect in its lamellae. This simulation was run until it had achieved the correct lamellae size in the middle of the simulation which was interpreted to mean that the simulation had reached a state very near equilibrium. The potential energy is significantly lower at this state than in the defect state. The configuration of the system was only examined at least 5 nm away from the free interfaces. This allows one to better understand what the bulk type micro-phase separated system behavior should be without interference from the lower density polymer near the free surfaces.
Figure 4. Comparison of time evolution of defect annealing using MD with and without PCND. The portions colored red correspond to PS monomers while the portions colored blue correspond to PMMA monomers. Both eventually reach approximately the equilibrium state expected with a ~21nm pitch lamellae in the center. If PCND is included, then the simulation equilibrates over 10 times faster than if it is not included.

As shown in Figure 4, using PCND adapted for polymers allows the system to equilibrate in less than one tenth of the time it takes to equilibrate without it. With PCND, it seems that the polymer chains move far more easily and diffuse much more rapidly towards their ultimate configuration. Both methods of simulation evolve to essentially the same configuration, but on very different time scales. Both have a ~21nm wide lamellae in the center, with essentially the same pattern at the free interfaces. The addition of PCND has not significantly altered the final state, but has managed to reach that same final state over ten times faster. There are some small differences, but these can easily be the result of the stochastic nature of the simulations. In the partial lamellae on the right side of the simulation it seems as though PMMA beads that were trapped in the PS phase simulation without PCND were able to move into the PMMA phase. This is likely due to the increased diffusion in the simulation including PCND.
3.2 Annealing from Random Well-Mixed Configurations: Effect of PCND

Molecular dynamics with and without protracted colored noise dynamics was run on a simulation box that was randomly filled as described in section 2.3. MD with and without PCND was run until the center lamellae had formed a pitch ~21nm, which we have taken as equilibrium for the reasons stated above. For this initial condition, the simulation without PCND ran for 240ns and had not yet equilibrated. If equilibrated, then the lamella in the center of the simulation would be approximately correct at ~21nm but it is far below that as is evident from Figure 5. Because there was no sign of convergence in any reasonable time frame, the simulation without PCND was terminated since it had already run for an extended period of time.

<table>
<thead>
<tr>
<th>MD without PCND</th>
<th>MD with PCND</th>
</tr>
</thead>
<tbody>
<tr>
<td>240,000 ps</td>
<td>6,800 ps</td>
</tr>
</tbody>
</table>

![Initial Condition](image1)

![t=2,500 ps](image2)

![t=20,000 ps](image3)

![t=240,000 ps](image4)

![t=2,400 ps](image5)

![t=4,100 ps](image6)

![t=6,800 ps](image7)

Figure 5. Comparison of time evolution of random configuration annealing using MD with and without PCND. The portions colored red correspond to PS monomers while the portions colored blue correspond to PMMA monomers. MD with PCND reaches equilibrium where the inner lamellae domain is ~21nm in ~6800 ps. MD without PCND does not reach the correct equilibrium even after 240,000 ps (8.3 days wall clock time on our machine).

As can be seen in Figure 5, MD with PCND reaches equilibrium fairly quickly in ~6.8 ns compared to MD without PCND which fails to reach equilibrium even after 240ns. Presumably MD without PCND will eventually reach the correct equilibrium, but not on time scales that can be effectively simulated. In real systems, anneal times at temperatures near 500K are on the order of minutes or hours while the feasible time scales accessible via traditional MD are no more than hundreds of nanoseconds. Notice also that even the initial phase separation takes place faster in the simulation using PCND as can be seen in the comparison at 2.5 ns (for MD without PCND) vs 2.4ns (for MD with PCND) shows. Once the simulation without PCND goes to the smaller incorrect domain size, it seems to be stuck there and completely unable to move, showing almost no movement over the final 220ns of the simulation. There is some
cleaning up of interfaces, but no larger scale movement. On the other hand, PCND allows the simulation to rapidly rearrange, even when possibly trapped in an incorrect local minimum energy state as can be seen from 2.4 ns to 4.1 ns and in the previous section. In this simulation, interfaces in both simulations seem to be approximately equivalently sharp. Interestingly, the phases exposed to vacuum are different in each simulation. We would expect that the PS phase would prefer to be exposed to vacuum since it has a lower cohesive energy density and therefore pays less of a penalty to have an interface with vacuum. However, it is possible that the χ value used here causes PS and PMMA to prefer to associate their beads with beads of their own type so much that the preference of ejecting PS to the surface is far less important than simply getting the two blocks apart. It is also possible that the non-PCND simulation shows an initial enrichment of PMMA at the left interface and this domain simply gets trapped at the interface. This simulation shows that, at least under these conditions, MD with PCND reaches equilibrium at least 35 times faster than without it. MD without PCND shows no noticeable evolution or change in potential energy over >100 ns. Experimentally, it may take minutes at this temperature to see phase separation so it is possible that there is a 1 order of magnitude improvement over a system without this force, but this is as yet uncharacterized.

When comparing these numbers to wall clock time, the MD with PCND completed in ~6.85 hours on a single processor laptop, while the MD without PCND took over 8.3 days to reach its current state with an unknown amount of time still required (i.e. a real-time speed up by a factor of ~30). The MD with PCND time can be improved with further parallelization as compared to the simple dual core processor execution used and shown in this work. Implementation of such simulations on clusters, multi-processor machines, or on GPU-based computers should be able to realize dramatically improved simulation time scaling.

3.3 Effect of Different χ Values

Molecular Dynamics with PCND was performed on the same simulation box as described in the previous section. The potential parameter ε_{AB} was varied from 0.4 to 0.55, corresponding to a higher, medium, and lower χ polymer system. We expect that as ε_{AB} increases, the interface between the phases should get more and more blurry, and as χ increases the interface between the phases should get more and more mixed and upon crossing that value, become completely disordered. Figure 6 shows the time evolution of each ε_{AB} simulation. Both the higher and medium χ simulations eventually reach approximately the same equilibrium state, though as expected there is a slightly larger blur at the edge of the domains in the case of a more moderate χ. There also seems to be an inverse correlation between ε_{AB} and the speed at which the system becomes completely disordered. This is expected because a higher driving force, which corresponds to lower ε_{AB} and higher χ, should drive it to phase separate more quickly. In the case of lowest χ, the system is clearly very near or below the order-disorder transition (ODT). There may be some phase separation, though it is difficult to tell without a more thorough and robust metric for testing. As expected, the system becomes more mixed as χ is lowered.

4. CONCLUSIONS

Molecular dynamics (MD) simulations of block copolymer micro-phase separation were performed and compared for both traditional MD and a new polymer MD technique referred to here as Protracted Colored Noise Dynamics (PCND) in which a random force is applied in a particular direction along the polymer chain contour with a controlled persistence time. This PCND force has a directional correlation with time that can be manipulated via a user selected correlation time τ. Using this force in a simulation modeling PS-b-PMMA caused the simulation to anneal defects over 1 order of magnitude faster than without it. For an initially randomly mixed system of PS-b-PMMA, the simulation annealed to its roughly equilibrium micro-phase separated state at least 35 times faster when using this PCND force. This speed up is a conservative estimate since and could be far greater since equilibrium was never reached from the well-mixed block copolymer melt without PCND. The expected behavior was also observed when the interaction parameter between PS and PMMA (χ) was changed. Lower χ resulted in more mixed systems and longer anneal times.
Figure 6. Comparison of effect of varying $\varepsilon_{AB}$. As $\varepsilon_{AB}$ increases, the boundaries become less and less well defined, ultimately resulting in a state that may not be phase separated at all. The highest $\varepsilon_{AB}$ shown here is near the ODT, but it is unclear which side of the transition is ultimately is for now. An increase in $\varepsilon_{AB}$ also corresponds to a slower evolution time, as can be seen between $\varepsilon_{AB}=0.4$ and $\varepsilon_{AB}=0.475$.

REFERENCES


