



# Computer simulation study of polydispersity effect on the phase behavior of short diblock copolymers



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## ABSTRACT

Recent progress in producing short chain length diblock copolymers facilitates the fabrication of block copolymer nanostructures with extremely small feature sizes. In this work, phase diagrams for mono-disperse, one-sided and two-sided polydisperse short diblock copolymer melts are constructed using dissipative particle dynamics (DPD) simulations. Detailed comparisons are carried out between these systems to elucidate the influence of chain length polydispersity on the phase behavior of short diblock copolymers. In particular, we find an unexpected stability of a bicontinuous structure over a wide composition range between  $0.7 < f \leq 0.8$  in one-sided polydisperse system, where  $f$  is the volume fraction of the polydisperse component. In the case of the two-sided polydisperse system, due to the presence of highly asymmetrical block copolymers and the pulling-away of short blocks of these molecules into opposite domain, an up-shift is found in the order–disorder transition boundary to larger  $\chi N$  values over the composition range we investigated.

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## 1. Introduction

Due to the intrinsic mutual incompatibility between distinct blocks, block copolymers (BCPs) have an intrinsic capability of forming novel ordered structures [1,2]. Many investigations have shown that these ordered structures and their formation processes can be influenced by many factors, for instance, a competing length scale effect imposed by different internal molecular architectures [3,4], or spatial confinement effects caused in spherical [5] or cylindrical [6] spaces. It can be also directed by topographical templates [7]. Despite these complex influence factors, recent developments in the field also show that the chain length of the BCPs is also very important, especially in the case of short chain length systems. From a practical point of view, an important practical application of these BCP ordered structures is in the field of modern nanotechnology where these structures are being demanded. For instance, lamella is a common structure utilized for nanolithography, while gyroid structure favoring exciton or ion transportations are often used for fabrication of photovoltaic films in solar cells or separator membranes in batteries [8]. Conventionally, synthetic diblock copolymers, which can form ordered

structures, usually have very long chain lengths ( $N$ ) and therefore have large enough  $\chi N$  values exceeding the microphase separation threshold,  $(\chi N)_{ODT} = 10.495$ . However, with the development of nanotechnology, ordered structures with smaller dimensions are demandingly required [9]. Recent progress in synthesizing short diblock copolymers [10,11] with strong segregation strength (small  $N$ , large  $\chi$ ) enables the fabrication of sub-10 nm sized patterns, making block copolymer nanolithography a potential priori to traditional photolithography. Most importantly, it offers a possibility of breaking down the bottle-neck of shrinking the domain size of integrated circuits, which is extremely important to fabricate more faster, cheaper and energy-efficient microchips. Therefore, it's practically very important to understand the phase behavior of short diblock copolymers.

On the other hand, understanding the phase behavior of short block copolymers [12] are also very important from a fundamental point of view since Leibler's mean-field theory is only applicable to infinite- $N$  systems with a weak segregation assumption at ODT boundary. Even with correction developed by Fredrickson and Helfand (FH) [13], it is still only strictly valid with a very long chain length ( $N \sim 10^9$ ). A recent work by Morse and coworkers [14] showed that competing phases near the ODT boundary become strongly segregated in short (low- $N$ ) diblock copolymer system and violate the weak segregation assumption, therefore resulting a stronger correction term in  $(\chi N)_{ODT}$ . In practice, a good comparison

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of the experiment and simulation results to the theory needs an effective estimation of  $\chi$  parameter. However, conventional way of fitting  $\chi(T)$  relation according to experimentally observed  $T_{\text{ODT}}$  data based on mean-field theory prediction of  $(\chi N)_{\text{ODT}} = 10.495$  neglects the consequences may caused by finite chain length  $N$ . A more sophisticated way is to determine the  $\chi$  parameter by fitting results for structure factor  $S(q)$  in the disordered phase to predictions of the renormalized one-loop (ROL) theory developed by Morse and coworkers [14]. Using this new fitting, very recent experiments done by Bates and coworkers [15] shown that chain length induced fluctuations are more overwhelming for short polymers with  $N < 100$ , such strong fluctuations can cause large deviations of order–disorder transition points from the prediction of FH theory. In particular, experimental ODTs are found to be closer to the predictions of particle-based computer simulation models since both experiment and simulations have similar finite chain length  $N$ . These comparisons also confirm the fidelity of the coarse-grained simulations which has more similarity with experimental system.

Variations in the chain length also can cause interesting consequences in polydisperse block copolymer systems where the chain length of the either block has a wide distribution. In the past decades, the effect of polydispersity on the melt phase behavior of long diblock copolymers has been widely investigated both experimentally [16] and theoretically [17]. Some consistent conclusions have been drawn on the polydispersity effect: it can (i) enlarge the domain spacing of the ordered structures [18–20] and (ii) consequently shift the OOT boundaries [16,17,21,22] to a larger volume fraction ( $f$ ) of minority component; (iii) it can also cause a reduction effect in  $(\chi N)_{\text{ODT}}$  before  $f$  approaching 0.6 [16,23]. The underlying mechanism for the reduction of  $(\chi N)_{\text{ODT}}$  can be attributed to the accumulation of short blocks at interface region and therefore a reduction of interfacial free energy [20]. Similarly, a recent Monte Carlo simulation shows that polydispersity of copolymer length or gradient width in synthesized copolymers can be utilized to effectively tune the interfacial properties [24]. For the two-sided polydisperse system, Matsen [19] found that the equal polydispersity in both A and B blocks will enlarge the domain spacing by a factor of 1.4 when PDI ( $\text{PDI} \equiv \text{PDI}_A = \text{PDI}_B$ ) approaching to 2.0. In the same year, Shi and coworkers [21] showed that the two-sided polydisperse diblock system still has a symmetric phase diagram, while the stable region for lamella structure was shrank to a smaller size. At the same time,  $(\chi N)_{\text{ODT}}$  was found to be decreased more obviously than in the one-sided polydisperse system. Similarly, experimental results [25] and our simulations [26] have also shown a strong polydispersity effect in the phase behavior of ABA triblock copolymers, which enhances the stability of a bicontinuous phase in a wide composition range. Real-space self-consistent-field theory study also shown that the polydispersity can influence the vesicle formations from amphiphilic diblock copolymers in solution [27]. Other than the phase behavior of block copolymers, recent dynamic Monte Carlo simulations also show that chain length polydispersity can also influence the crystal nucleation in rubbers [28] and the interfacial properties of gradient copolymers [29].

Although the polydispersity effect has been well studied for conventional long-chain block copolymer systems, there is still a lack of a systematic investigation on the polydispersity effect in short-chain block copolymer systems. As have been discussed in the above, particle-based simulations have a better similarity to experiment due to the short chain length in the system. For instance, for the one-sided polydisperse diblock copolymer system, Lynd and Hillymer's experiment [16] predicted an obvious up-shift of the ODT boundary when the volume fraction of the polydisperse component exceeds  $f = 0.6$ , however the SCFT work by Matsen [17] predicted a reduction in  $(\chi N)_{\text{ODT}}$  over the whole composition range. Instead, particle-based Monte Carlo simulations [23] showed a very

good agreement with experiment. However, Gavrilo et al. [30] studied the phase behavior for two-sided polydisperse AB diblock copolymers by using DPD simulations. They constructed the phase diagram for the system where both A and B blocks are polydisperse with  $\text{PDI}_A = \text{PDI}_B \approx 2.0$ . Up-shift of the ODT boundaries over the whole composition range [30] was reported, but the reason was simply attributed to calculation errors. One may wonder if there are more sophisticated explanations? In addition, are there any distinguishable differences between one-sided and two-sided systems?

With the above considerations, we use particle-based dissipative particle dynamics simulation method to investigate the effect of polydispersity on the phase behavior of short diblock copolymer melts. The phase diagrams have been constructed for the mono-disperse, one-sided and two-sided polydisperse diblock copolymer systems. The influences of block chain length polydispersity on the changes in ODT boundaries are investigated and the detailed molecular mechanisms are provided. In addition, an unexpected stability of a bicontinuous structure is reported in the case of one-sided polydisperse system.

## 2. Simulation method and details

Dissipative particle dynamics simulation is a mesoscale simulation technique, which has been well established and tested in the past two decades for the studies of block copolymer phase behaviors [31–33]. In the DPD model, a single particle usually represents a group of atoms or molecules and interparticle interactions are composed of a conservative force  $\mathbf{F}^C$ , a dissipative force  $\mathbf{F}^D$  and a random force  $\mathbf{F}^R$ , all of these forces are pair-wise. The conservative force is a soft repulsive interaction acting along the connecting line of particle centers:

$$\mathbf{F}_{ij}^C = \begin{cases} \alpha_{ij}(1 - r_{ij}/r_c)\mathbf{e}_{ij} & (r_{ij} < r_c) \\ \mathbf{0} & (r_{ij} \geq r_c) \end{cases}, \quad (1)$$

where  $\alpha_{ij}$  is the maximum repulsion between particle  $i$  and  $j$ ;  $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ ,  $r_{ij} = |\mathbf{r}_{ij}|$  and  $\mathbf{e}_{ij} = \mathbf{r}_{ij}/r_{ij}$ . The cutoff radius,  $r_c$ , is the only length-scale in the system. The dissipative force and random force, serving as the thermostat, are given by:

$$\begin{aligned} \mathbf{F}_{ij}^D &= -\gamma\omega^D(r_{ij})(\mathbf{v}_{ij} \cdot \mathbf{e}_{ij})\mathbf{e}_{ij}, \\ \mathbf{F}_{ij}^R &= \sigma\omega^R(r_{ij})\xi_{ij}\Delta t^{-1/2}\mathbf{e}_{ij}, \end{aligned} \quad (2)$$

where  $\xi_{ij}$  is a random number with zero mean and unit variance,  $\mathbf{v}_{ij}$  is the relative velocity between particles. According to the fluctuation–dissipation theorem [34], the amplitudes of the dissipative force,  $\gamma$ , and the random force,  $\sigma$ , as well as  $r$ -dependent weight functions,  $\omega^D$  and  $\omega^R$ , have the relations of  $\sigma^2 = 2\gamma k_B T$  and  $\omega^D(r_{ij}) = [\omega^R(r_{ij})]^2$ . Following Groot and Warren [31], a simple form was chosen as:

$$\omega^R(r_{ij}) = \begin{cases} (1 - r_{ij}/r_c) & (r < r_c) \\ \mathbf{0} & (r \geq r_c) \end{cases}. \quad (3)$$

For an easy numerical handling, the cutoff radius  $r_c$ , the particle mass  $m$ , and the temperature  $k_B T$  are chosen as the basic units  $r_c = m = k_B T = 1$ , therefore the unit of time is  $\tau = r_c m / k_B T = 1$ .

Polymers are described by the bead-spring model and the adjacent beads in a single polymer chain are tied up by harmonic springs,  $\mathbf{F}^S = -k_s \mathbf{r}_{ij}$ , with  $k_s$  set to 4.0 according to Ref. 32. The time evolution of the interaction particles is governed by Newton's equation of motion. The so-called DPD-VV algorithm is used to propagate the equations of motion with a time step of  $\Delta t = 0.02$ . Each simulation is performed in a simulation box with a size of

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