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Note: Effects of polydispersity on the phase behavior of AB diblock and BAB triblock copolymer melts: A dissipative particle dynamics simulation study

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Block copolymers have attracted considerable attention in the past decades due to their inherent ability to self-assemble into intriguing ordered structures.^{1,2} Among the various block architectures, diblock and triblock copolymers are the simplest cases whose phase behaviors have been extensively studied and well documented.³ For monodisperse systems, it has been shown that the BAB triblock copolymer has a similar phase diagram as the corresponding homologue AB diblock copolymer, which is obtained by simply snapping triblock molecules at the middle A-block.^{4,5} For polydisperse systems, recent experiments^{6–8} showed that in general the polydispersity can increase the domain spacing, shift the order-order transitions (OOTs) towards larger volume fractions of polydisperse component A, f_A , and reduce order-disorder transition point $(\chi N)_{\text{ODT}}$ to a smaller value, where χ is the Flory-Huggins parameter and N the chain length. More interestingly, it has been observed that these effects caused by polydispersity are much more pronounced for BAB triblock⁸ than for AB diblock copolymer.^{6,7} In particular, both reduction in $(\chi N)_{\text{ODT}}$ and increase in domain spacing can reach a factor of 2 in BAB triblock copolymer, which are unexpectedly larger when comparing with the case of diblock homologue systems, as A block polydispersity index (PDI) approaches $\text{PDI}_A = 2.00$. In order to elucidate and understand the difference of phase behavior between monodisperse and polydisperse systems, we use dissipative particle dynamics (DPD) method to study the effects of A block polydispersity on the phase behavior of AB diblock and BAB triblock copolymer melts.

In the DPD simulations, polymers are described by a bead-spring model, where adjacent coarse-grained particles are tied up with harmonic springs. Particles interact with each other through a conservative force, $\mathbf{F}_{ij}^C = \alpha_{ij}(1 - r_{ij}/r_c)\mathbf{e}_{ij}$, a dissipative force, $\mathbf{F}_{ij}^D = -\gamma(1 - r_{ij}/r_c)^2(\mathbf{v}_{ij} \cdot \mathbf{e}_{ij})\mathbf{e}_{ij}$, and a random force, $\mathbf{F}_{ij}^R = \sigma(1 - r_{ij}/r_c)\xi_{ij}\Delta t^{-1/2}\mathbf{e}_{ij}$. All the forces are pairwise additive. The cutoff radius r_c , the particle mass m , and the temperature $k_B T$ are set as the units, i.e., $r_c = m = k_B T = 1$, so the unit of time is $r_c\sqrt{m/k_B T} = 1$. The strength of the conservative force α_{ij} can be mapped to the Flory-Huggins χ parameter by $\alpha_{ij} = 25.0 + 3.27\chi$ at particle number density

$\rho = 3$. It is further calibrated to an effective $(\chi N)_{\text{eff}}$ value corresponding to long chain limit by $(\chi N)_{\text{eff}} = \chi N/(1 + \zeta N^{2/3-2\nu})$, where $\zeta = 3.90$ and 5.36 for diblock and triblock copolymers, respectively. All the details of the DPD model are referred to Ref. 9. Both the $A_x B_{N-x}$ diblock and symmetric $B_y A_{N-2y} B_y$ triblock copolymer melts with average chain lengths of $N_n = 8$ – 18 are simulated in a simulation box with size of $40 \times 40 \times 40$. In order to facilitate the comparison with available self-consistent field theory (SCFT) calculations,¹⁰ polydispersity is only introduced into A block with $\text{PDI}_A = 1.50$, while keeping the B block monodisperse. The Schulz-Zimm distribution is used, $p(\theta) = k^k \theta^{k-1} \exp(-k\theta)/\Gamma(k)$, where $\theta \equiv N/N_n$. The polydispersity index $\text{PDI}_A = (k + 1)/k$. Note that the resulted values of PDI_A and N_n will have a negligible deviation for the short chains we have adopted. For each point in phase diagram, 5 parallel simulations are performed with a time step of $\Delta t = 0.02$ for 3×10^6 steps.

The simulated phase diagrams ($\chi N \sim f_A$) for AB diblock and BAB triblock copolymers are shown in Fig. 1. First of all, the ordered sphere (S), cylinder (C), irregular bicontinuous (BIC)/perforated lamellar (PL), and lamellar (L) structures are observed to occur sequentially with an increase in f_A for both diblock and triblock copolymer systems. It has been confirmed in previous studies that the center of the lamellar region is located at $f_A \approx 0.5$ for both monodisperse AB diblock¹² and BAB triblock copolymers.⁴ By introducing a polydispersity into A block with $\text{PDI}_A = 1.50$, the lamellar region is shifted to larger f_A values for both diblock (Fig. 1(a)) and triblock copolymers (Fig. 1(b)), which is in good agreement with SCFT,¹³ Monte Carlo,¹⁴ and experimental⁸ results. The shift of lamellar region is larger for triblock copolymers if compared with diblock copolymers, i.e., at the symmetric composition of $f_A = 0.5$, polydisperse diblock copolymers form lamellar structure, while complex L+BIC coexistence phase is observed for polydisperse triblock copolymers. In addition, the center of the lamellar region can be located at $f_A \sim 0.6$ for the diblock copolymers, while at a value of $f_A > 0.6$ for the triblock copolymers. All the above results lead to the same conclusion as Matsen¹⁰ in that the polydispersity induced shift in OOTs is larger for triblock copolymer than for diblock copolymer. As suggested by Matsen,¹⁰ such enhanced shift in the OOTs for triblock copolymer can be attributed to

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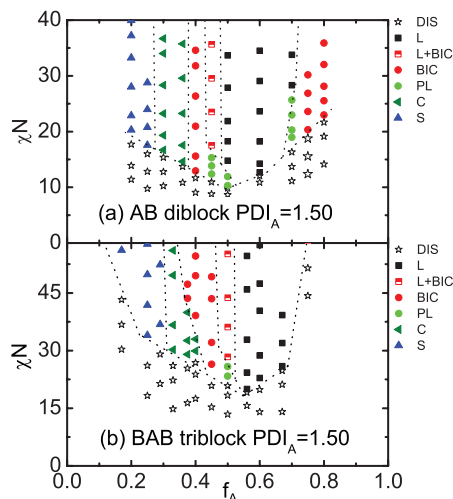


FIG. 1. Simulated phase diagrams for (a) AB diblock and (b) BAB triblock copolymers with monodisperse B and polydisperse A blocks ($\text{PDI}_B = 1.00$, $\text{PDI}_A = 1.50$). The morphologies are labeled as DIS: disordered melting phase; S: spheres; C: cylinders; PL: percolated lamellae; L: lamellae; BIC: bicontinuous; L+BIC: coexistence of L and BIC. The dotted lines are drawn to guide the eye.

a reduction in entropy of A-rich domain due to the absence of chain ends.

In order to compare the polydispersity effects on domain spacing of diblock and triblock copolymers, we focus on lamella-forming A_6B_4 diblock and $B_2A_6B_2$ triblock copolymers with PDI_A values of 1.00, 1.25, 1.50, and 1.75 at segregation strengths of $\chi N = 36$ and 100. Following the experimental strategy, the domain spacing (D) is measured by the position of primary peak q^* in scattering function, i.e., $D = 2\pi/q^*$. The D values are all normalized by the corresponding domain spacing value for monodisperse system, D_0 . Results are plotted in Fig. 2 in comparison to the prediction of strong-segregation theory (SST) (dotted line). As expected, the lamellar domain spacing increases monotonically with the increase of PDI_A . At the strong segregation of $\chi N = 100$, the trend is comparable to that of SST prediction. Most importantly, our simulation results show that the expansion of domain spacing induced by polydispersity is slightly larger for triblock than that for diblock copolymers at both segregation strengths. However, the ratios of D/D_0 are all less than 1.25

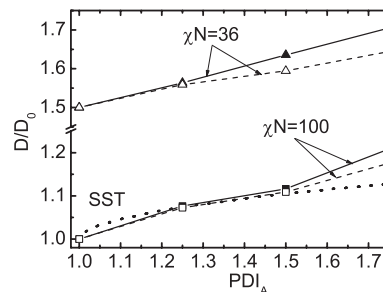


FIG. 2. Calculated lamellar domain spacing (D), with the increase of PDI_A for A_6B_4 diblock (empty symbols) and $B_2A_6B_2$ triblock (solid symbols) copolymers at $\chi N = 36$ (triangle) and 100 (square). To clarify, the data points for $\chi N = 36$ have been shifted by +0.5. The dotted line shows the prediction of strong-segregation theory.¹¹

for both systems, which are in good agreement with SCFT prediction.¹⁰ It is much smaller than the factor of 2 found in BAB triblock copolymer experiments.⁸ The difference may be attributed to the Schulz-Zimm distribution model used in SCFT and DPD simulations can not represent the shape of the molecular weight distribution in experimental triblock system.¹⁰

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