Stable domain size and conformational segregation of short and long blocks during microphase separation in random block copolymers

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ABSTRACT

In this Letter we use computer simulations and test microphase separation for AB-diblock copolymers with different block's statistics. We show that the domain size during microphase separation is stable only for the system with large enough polydispersity, namely with exponential (Flory-type) block length distribution. The reason for stable domain size is a conformational segregation of short and long blocks during the increase of the incompatibility in the system. While short blocks became elongated and occupy the surface of the interphase region, long blocks pushed out to the center of the domain and formed their compact conformations.

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1. Introduction

Self-assembling in block copolymer systems attracts great interest in recent decades [1–3], especially with developing of novel synthetic routes by living polymerization [4] and advanced techniques for studying the microstructure by grazing-incidence small-angle scattering or environmental transmission electron microscopy. In a set of recent publications there is clear evidence that even highly polydisperse block copolymers could also self-assemble into ordered structures [5–7] and polydispersity in block weight distribution could be a useful factor for tuning ordered structures and corresponding properties [8]. Therefore, understanding the fundamental physics related to the block-mass distribution statistics on block copolymer phase behavior is important.

It should be noted that despite of some promising properties, there are not so many works on experimental investigation and comparison of random copolymers, mainly due to the difficulties associated with the experimental characterization of such systems. The common and general conclusion is that the structure period increases with increasing polydispersity. The question of polydispersity influence on the order–disorder transition (ODT) is the matter of intensive discussions in the literature, and sometimes antagonistic opinions were presented in the literature, see review [9] and links therein. In general our results lies in agreement with the recent studies on computer simulation of similar system (e.g.

[10]). But in this letter we will focus only within the regions where both Flory and Poisson systems have already microphase separation to lamellar (LAM) or hexagonally packed cylinders (CYL) phases and will not discuss the ODT. Here we address the question of domain size dependence on the incompatibility of the random copolymer species, which was not studied in the literature yet.

The self-consistent field theory (SCFT) [11] gives the tool for theoretical studies of block copolymer phase behavior, while particle-based approaches utilizing various versions of coarse-grained Monte Carlo and molecular dynamics simulation techniques were believed as less-suitable methods, because of the restrictions in system size and equilibration time. But recent progress in accessibility and power of modern supercomputers, in addition to some improvements in simulation technique and parallel programming gives some benefits to particle-based simulations. A considerable advancement was made in simulation methodology about 20 years ago by introducing the mesoscopic dissipative particle dynamics (DPD) method [12,13] utilizing the bead–spring model of a polymer fluid with reasonable fast relaxation to the equilibrium. It was already used for studying the general features of microstructure formation in diblock copolymers [14,15], as well as for visualizing expectable morphologies for several specific diblock [10,16–18] and multiblock [19] copolymer systems.

In our recent paper [20] we presented DPD construction of polydisperse copolymer phase diagram when both blocks are polydisperse and compared to that of the same monodisperse melt, as well as to the diagrams obtained for the polydisperse AB diblock copolymer melts using SCFT [21] and Monte Carlo simulations [22]. It was found that the domain spacing for polydisperse diblocks with mean chain length N is nearly independent of the species incompatibility

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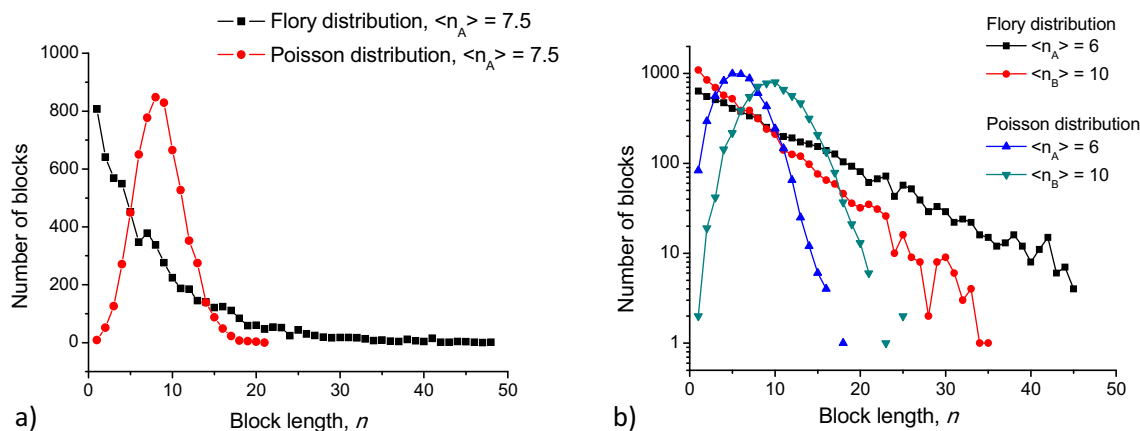
Figure 1. The block-mass distributions used in our study. Mean chain length $N = 16$. (a) Nearly symmetric system with $\langle n_A \rangle = 7.5$ and $\langle n_B \rangle = 8.5$ will result in lamellar structure, while (b) is the asymmetric system with $\langle n_A \rangle = 6$ and $\langle n_B \rangle = 10$ will give cylinder morphology. The Y-axis gives the real number of given length blocks in the simulation box, plot (b) presented in $\log(Y)$ scale for visibility.

parameter χN, where χ is the so-called Flory–Huggins parameter. That contrary to the known results of strong segregation theory (SST) behavior for domain spacing D in monodisperse diblocks: $D/N^{1/2} \sim (\chi N)^{1/6}$ [23], which was successfully reproduced in several experiments and simulations. At this letter we compare two common random distributions, namely Flory-type and Poisson-type randomness in the block length. We show that the independence of the domain size at different segregation values is valid only for the system with broad enough distribution, i.e. Flory-type. We study the block's conformations inside the separated domains and give the reasonable interpretation of this phenomenon.

2. Methodology

Consider an ensemble of particles (beads) obeying Newton's equations of motion

$$\frac{dr_i}{dt} = v_i; \quad m_i \frac{dv_i}{dt} = f_i, \quad f_i = \sum_{i \neq j} (F_{ij}^b + F_{ij}^c + F_{ij}^d + F_{ij}^r), \quad (1)$$

where r_i, m_i, v_i are the coordinate, mass, and velocity of an ith bead, respectively, f_i is the force acting on it. The summation is performed over all other beads within the cut-off radius r_c. Below we assume that all quantities entering Eq. (1) are dimensionless and for simplicity set r_c and m_i for any i to unity. First two terms in the sum are conservative forces. Macromolecules are represented in terms of the bead and spring model. F_{ij}^b is a spring force describing chain connectivity of beads, F_{ij}^c is a soft core repulsion between i and jth beads:

$$F_{ij}^c = \begin{cases} a_{ij}(1 - r_{ij})r_{ij}/r_{ij}, & r_{ij} \leq 1 \\ 0, & r_{ij} > 1 \end{cases}, \quad (2)$$

where a_{ij} is a maximum repulsion between beads i and j attained at $r_i = r_j$. The standard Flory–Huggins parameter of polymer–polymer interaction could be calculated using common expression $\chi_{ij} = 0.306\Delta a_{ij}$ from the work [13]. Since F_{ij}^c has no singularity at zero distance, a much larger time step than in the standard molecular dynamics could be used. Other constituents of f_i are a random force F_{ij}^r and a dissipative force F_{ij}^d acting as a heat source and medium friction, respectively, they are taken as dictated by the Groot–Warren thermostat in [13]. More detailed description of the simulation methodology could be found somewhere else [20].

The time step for integrating Eq. (1), $dt = 0.04$, was chosen according to [13]. A simulation box of sizes $32 \times 32 \times 32$ containing $98\,304\,(\sim 10^5)$ particles was used. An average polymer chain length was set to 16, thus more than 6000 polymer chains was simulated simultaneously within the same box. The periodic boundary conditions were imposed in all three directions. All other details about simulation technique and phase diagram construction are available in [20]. All simulations were performed at Lomonosov Moscow State University Supercomputer facilities [24].

We consider two types of block-mass distributions:

1. Random diblock copolymer characterized by an bell-curve distribution of A and B block lengths, described by Poisson discrete distribution: $p(x) = \lambda^x e^{-\lambda}/x!$ with PDI = 1.2 and hereafter referred as 'Poisson diblock'. Such distribution is a good approximation for typical block-mass distribution obtained in living polymerization such as ATRP and RAFT techniques, which are the mostly used synthetic routes to obtain diblock copolymers nowadays.
2. Random diblock copolymer characterized by an exponential distribution of A and B block lengths, described by Flory-type distribution: $p(x) = \lambda \exp(-\lambda x)$ which gives PDI = 2.0, hereafter referred as 'Flory diblock'. Such distribution is the most probable distribution during common non-living routes of polymer synthesis.

In all cases mean chain length was fixed at $\langle N \rangle = 16$ and parameter λ regulate the average block length. The block-mass distributions for random copolymers under study presented at Figure 1. The initial state all copolymer melts was a random distribution of Gaussian chains in the simulation box. Then, the non-zero value of χ was instantaneously introduced and the system was relaxed for 1×10^7 time steps to achieve the equilibrium state. We use 64 different χ-values for each composition that enables us to study all segregation regimes. While we can observe the whole diagram space, all our results lies in general agreement with the recent studies on computer simulation (e.g. [10,20]), but most other papers focused on copolymers where only one block has a nonzero polydispersity, while our system has equal polydispersity for both blocks. Later we will focus only within the regions where both Flory and Poisson systems have microphase separation to lamellar (LAM) or hexagonally packed cylinders (CYL) phases. We note here that LAM and CYL phases are the most common and intelligible phases both in theory and experiments, besides these two phase occupy the majority of the phase diagram space, thus we decided to study these two phases.