Monte Carlo structure factors and selected physical properties of symmetric copolymer melts at low temperatures

S. Wołoszczuk, M. Banaszak *

Faculty of Physics, A. Mickiewicz University, ul. Umultowska 85, 61-614 Poznan, Poland

ABSTRACT

Static and dynamic properties of diblock and triblock copolymer melts are simulated over a wide range of temperatures in vicinity of the order-disorder transition and also in the strong segregation regime. Dynamic Monte Carlo method, known as the Cooperative Motion Algorithm, is used with a parallel tempering scheme in order to determine a variety of physical properties. Structure factors are of particular interest since they can be directly related to Small Angle X-ray Scattering data. We also report energy, specific heat, mean-squared end-to-end distance, and the translational diffusion coefficient. Moreover, we determine order-disorder temperatures and investigate the behavior of the melts at low temperatures. We show that the finite size effects can be associated with the spatial reorientations of lamellae. Furthermore, we confirm the existence of a sharp low-temperature peak in specific heat, which we relate to the transition from a state with the diffused domain interface to a state with the sharp domain interface. The chain length dependence of the order-disorder temperatures and the interfacial smoothing temperatures are also presented. Below order-disorder transition temperature a significant loss of the chain mobility is observed, as indicated by an abrupt decrease of the diffusion coefficient.

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1. Introduction

Incompatibility of the covalently bonded blocks of the copolymers and their inability to segregate on a macroscopic scale lead to a process of order-disorder transition (ODT). As a result, block copolymers can form a variety of ordered nanophases [1–25] that show a significant promise in technological applications [26]. This process is mostly governed by a competition between enthalpic interfacial and entropic stretching energies. A-B-C triblock copolymers are known for their ability to form tens of different phases [26]. On the other hand, A-B diblock and A-B-A triblock copolymers organize into only a few stable nanophases such as layers, hexagonally packed cylinders, gyroid with the $Ia\bar{3}d$ symmetry, cubic or face-centered micelles, and the O^{70}-phase [27,28]. While the phase behavior of diblocks and triblocks is similar, their mechanical properties differ significantly. Triblocks in ordered phase can form looped and bridged configurations. Bridges, capable of connecting neighboring domains, can promote the formation of molecular network. Recently we found [29,30] that strongly asymmetric (with

respect to A_1/A_2 composition) A_1-B-A_2 triblocks with very short one A-block can form a novel kind of molecular network. In this case short terminal blocks organize, at low temperatures, into a subnetwork of A-micelles within the B-domain.

In previous papers [31,32] we reported the simulation of structural and static properties of the 7-16-7 triblock and 8-8 diblock copolymer melts over a wide range of temperatures. Both systems self-assembled into a lamellar nanophase, exhibiting two characteristic peaks in the specific heat. The first peak, recorded at a high-temperature, was interpreted as corresponding to the order-disorder transition, whereas the second one, recorded at low-temperature, was associated with an abrupt transition from a state with slightly diffused domain interfaces to a state with almost perfectly smooth interdomain surface. We described that effect quantitatively by introducing a new parameter, Λ, which was a measure of the spatial distribution of the junction points within a given interface in a direction normal to layers. The junction point was defined as a connection between two different blocks within a single chain. The effect of smoothing was also accompanied by a significant energy drop and chain stretching described by the rise of mean-squared end-to-end distance.

More recently, Yang et al. [33] studied the interfacial ordering in a symmetric diblock copolymers below the ODT temperature. In order to prevent periodicity trappings they also used quenching

method rather than slow cooling. Their results confirmed our findings [31,32] that the interface thickness becomes narrower as the temperature is decreased. However, they did not report the second C_V peak because they did not probe at sufficiently low temperatures.

While the quenching method works quite well for higher temperatures, it generates long relaxation times in the strong segregation limit. This can lead to unreliable estimates of the sampled properties. To overcome this problem the parallel tempering (PT) method was proposed [34–37]. This method allows exchange of configurations between neighboring temperatures and thus the energy barriers between the local free energy minima can be overcome. As a result we have a more efficient equilibration, sharp peaks in specific heat, and much better accuracy in the localization of both the order-disorder and order-order transitions [36–39].

The goal of this paper is to simulate the dynamic and static properties of the lamellar phase, as shown in Fig. 1, for a series of symmetric diblock and triblock copolymer melts of varying chain length.

2. Model and method

The simulations are performed using the Cooperative Motion Algorithm (CMA) for a face-centered cubic lattice with a coordination number $z = 12$ and lattice constant $a = 2$. Chain bonds of length $\sqrt{2}a/2$ cannot be broken or stretched. Standard periodic boundary conditions are applied. Lattice is completely filled with the monomers and the chains satisfy excluded volume condition. The segments of type i and j interact by ϵ_{ij}, where $\epsilon_{AB} = \epsilon$, and $\epsilon_{AA} = \epsilon_{BB} = 0$. This interaction is limited to the nearest neighbors. The parameter ϵ is used as an energy unit. We define the reduced energy per lattice site as $E^* = E/\epsilon$, and the reduced temperature as $T^* = k_B T/\epsilon$, where k_B is the Boltzmann constant.

The Metropolis method is not used because the dynamics of the system is of interest in this paper. At a given temperature, T^*, the Boltzmann factor $p = \exp(-E^*_{final}/k_B T^*)$ is compared with a random

number $r \in \langle 0, 1 \rangle$, and if $p > r$ the move is accepted. The CMA algorithm was developed by Tadeusz Pakula and successfully applied to study the dynamics of homopolymer melts [40,41] and diblock copolymer melts [12], yielding results that were in agreement with a dielectric spectroscopy measurements for polystyrene-polyisoprene systems.

We use a parallel tempering method, where M replicas of the system are simulated in parallel, each at different temperature, T^*_i, where $i = 1, \ldots, M$. An attempt to move a segment defines $1/n_a$ Monte Carlo step (MCS), where n_a is the number of lattice sites. After 20000 MCS we attempt to exchange replicas with neighboring T^*_i's in random order with a probability

$$p(T^*_i \leftrightarrow T^*_{i+1}) = \min[1, \exp[-(\beta_i - \beta_{i+1})(U_{i+1} - U_i)]], \qquad (1)$$

where $\beta_i = 1/k_B T_i$, and U_i is the potential energy of the replica at T^*_i. This method allows efficient equilibration, especially at low temperatures. The initial $8 \cdot 10^6$ MCS are used to equilibrate the system using PT method and the following $2 \cdot 10^6$ MCS are used, without replica exchange, to collect the data. We repeat this experiment three times, starting from different initial configurations. In each starting configuration the polymer chains are uniformly distributed within the simulation box, assuming statistical conformations and random orientations. We can relate T^* to the Flory χ parameter by the following approximate relation:

$$\chi = \frac{7.5}{T^*}, \qquad (2)$$

as demonstrated earlier[42]. This equation can be used to relate the experimental χ's with the theoretical T^*'s.
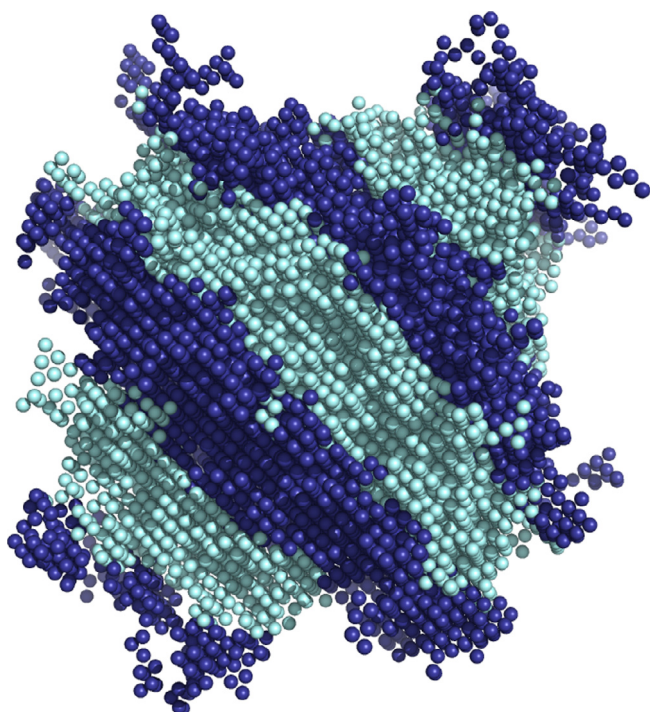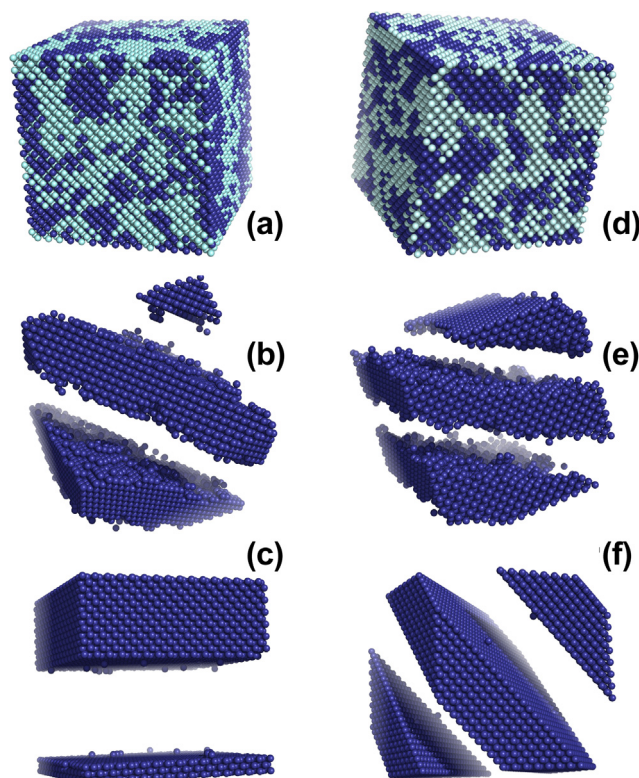
Fig. 2. Snapshots of the simulated the 16-16 diblock melt (a, b, c), and the 8-16-8 triblock melt (d, e, f); (a) and (d) present the state above order-disorder transition temperature; (b) and (e) are taken at $T^* = 3.0$; (c) and (f) show lamellae at $T^* = 1.0$. Only the B segments are shown.

Fig. 1. Lamellar nanophase from the simulation of 16-16 diblock copolymer melt in a weak segregation regime.