

Monte Carlo Study of Patchy Nanostructures Self-Assembled from a Single Multiblock Chain

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Abstract: We present a lattice Monte Carlo simulation for a multiblock copolymer chain of length $N=240$ and microarchitecture $(10 - 10)_{12}$. The simulation was performed using the Monte Carlo method with the Metropolis algorithm. We measured average energy, heat capacity, the mean squared radius of gyration, and the histogram of cluster count distribution. Those quantities were investigated as a function of temperature and incompatibility between segments, quantified by parameter ω . We determined the temperature of the coil-globule transition and constructed the phase diagram exhibiting a variety of patchy nanostructures. The presented results yield a qualitative agreement with those of the off-lattice Monte Carlo method reported earlier, with a significant exception for small incompatibilities, ω , and low temperatures, where 3-cluster patchy nanostructures are observed in contrast to the 2-cluster structures observed for the off-lattice $(10 - 10)_{12}$ chain. We attribute this difference to a considerable stiffness of lattice chains in comparison to that of the off-lattice chains.

Key words: multiblock chain, Monte Carlo, patchy nanostructure

I. INTRODUCTION

Block copolymers are studied mainly due to a fundamental interest in the soft matter research and also in the industrial applications [1]. The physical properties, such as elasticity, toughness or electrical conductivity, depend mainly on chemical composition and microarchitecture of the polymer chain. Numerous studies show that diblock polymer melts can spontaneously form a variety of nanostructures such as: ordered layers, hexagonally packed cylinders, cubically ordered spheres and the celebrated gyroid structures [2, 3]. It has been shown that one can also obtain different phases by varying the chain microarchitecture [1, 4-6]. We expect that increasing the complexity of microarchitecture leads to more nanostructures. Indeed, triblock copolymers show new phases like lamella-cylinder or lamella-sphere combinations, which have been confirmed experimentally. Synthesizing more complex microarchitectures, including the cyclic and the branched ones, results in a plethora of new phases [7]. Moreover, not only polymer melts are prone to self-assembly into various

phases but also a single copolymer polymer chain can self-assemble into various structures, referred to as “patchy nanostructures” or patchy particles [8]. Recent studies in both computer simulation and supramolecular chemistry show that such systems are thermodynamically stable and, more importantly, can be obtained by chemical synthesis [8, 9]. Such patchy nanostructures can be used as building blocks for self-assembling nanodevices. It has been shown that due to well defined symmetry of such particles they can form aggregates with an ordered spatial structure. This behavior can be used for the bottom-up approach, overcoming the size limits of producing particles of sizes from 7 to 17 nm with a defined symmetry, in one step [9, 10].

In previous studies, using an off-lattice Monte Carlo method with a discontinuous (square-well) potential [11] and using the Lennard-Jones (LJ) potential [12], the stability of patchy nanostructures was investigated. In order to probe the free energy landscape more efficiently, the parallel tempering (PT) method [13-17] was employed in ref. [11] and Wang-Landau method [18] in ref. [12].

In this study we intend to focus on one of the chain microarchitectures, specifically $(10 - 10)_{12}$, but using a lattice Monte Carlo method. While the off-lattice models are more realistic, they also require more computational effort. Therefore it is significant to assess the relative merits of the lattice model. If the lattice model gives similar results, then it may be reasonable to use the lattice model rather than the off-lattice models.

The aim of this paper is to answer the following questions:

- are the nanostructures obtained in the lattice simulation the same as those obtained in the off-lattice simulation?
- is the phase diagram obtained in the lattice simulation the same as that obtained in the off-lattice simulation?

II. MODEL AND METHOD

In this study, a coarse-grained model is used. The polymer chain is placed on the face centered cubic (FCC) lattice with coordination number $z=12$ and the bond length equal to $\sqrt{2}a$. Chain bonds are not allowed to be broken or stretched. The periodic boundary conditions are applied. The size of the simulation box is chosen to fit a fully extended chain. The polymer-solvent interactions are included in an implicit manner in the polymer-polymer interaction potential. Polymer chain consists of two types of monomers: A and B. Interaction energy between monomers is defined as follows: $\epsilon_{AA} = \epsilon_{BB} = -\epsilon$ and $\epsilon_{AB} \in \langle -\epsilon, -0.1\epsilon \rangle$. The ϵ parameter is positive and serves here as an energy unit. We define reduced energy as

$$E^*/N = E/(\epsilon N), \quad (1)$$

and reduced temperature as

$$T^* = k_B T / \epsilon \quad (2)$$

where N is the number of chain monomers and k_B is the Boltzmann constant. Negative value of interaction energy means that there is a net attraction between monomers. Reduced temperature parameter is used to control the quality of solvent, from good to bad which causes a transition from a swollen state to a globular state. Dimensionless parameter $\omega = -\epsilon_{AB}/\epsilon$ is a measure of compatibility between two monomers of different type. Lower values of ω mean that an attraction between monomers A and B is lower than between monomers of the same type. For $\omega = 1$ the copolymer chain becomes a homopolymer chain. The chain consists of 120 monomers of type A and 120 monomers of type B which form the multiblock microarchitecture $(10 - 10)_{12}$. During the simulation various T^* 's and ω 's are probed; T^* from 2.27 to 20.0 (because below 2.27 nothing seems to change in the polymer structure), and ω from 0.1 to 1.0.

The simulation was performed by a standard Monte Carlo simulation method with Metropolis acceptance criteria [19]. In order to perform a Monte Carlo move we use the pull-move

algorithm, which employs chain movements, reminiscent of the reptation moves, by pulling the chain in a random direction as described in detail in reference [20]. We define one Monte Carlo Step (MCS) as the attempt to perform one move according to the algorithm. Each simulation consists of 4×10^7 MCS. First the system is equilibrated athermally, and next 2×10^7 steps are run in the thermal condition. We calculate the thermal averages from last 2×10^7 steps.

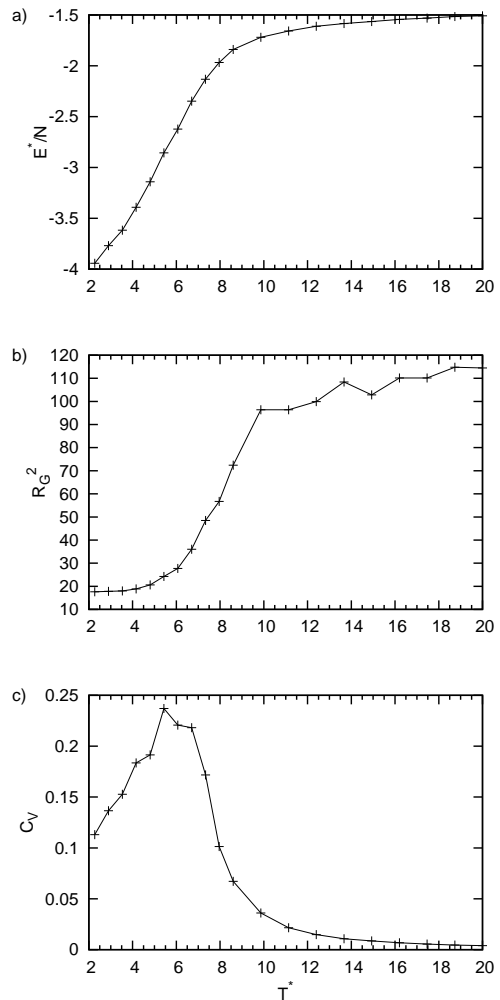


Fig. 1. Reduced energy per monomer E^*/N (a), squared radius of gyration R_g^2 (b) and specific heat C_v (c) as a function of T^* for $\omega = 0.1$.

III. RESULTS AND DISCUSSION

We start the simulation by equilibrating the system in the athermal limit, where $\epsilon/(k_B T) = 0$. After the system reaches its thermal equilibrium we start to cool it down to a variety of T^* 's. First, we present results for the lowest compatibility parameter $\omega = 0.1$. As T^* is decreased, it is expected that the chain undergoes a transition from a swollen state to an

intermediate state “pearl-necklace”, and after that to the globular state [21]. In Figure 1 we show the Monte Carlo results for the energy per monomer, E^*/N , mean squared radius of gyration, R_g^2 , and heat capacity C_v of the polymer chain, as a function of T^* . The heat capacity, C_v , is obtained from the energy fluctuations as follows

$$C_v = \frac{\langle (E^* - \langle E^* \rangle)^2 \rangle}{NT^{*2}} \quad (3)$$

where N is the number of monomers, and $\langle \dots \rangle$ denotes the thermal average. The reduced energy does not change much from high temperatures to about $T^* = 10$ where it starts to decrease. A similar behavior is observed for a mean squared radius of gyration which also decreases below $T^* = 10$. In Figure 1c) we show the temperature dependence for the heat capacity, C_v . The maximum in C_v corresponds approximately to the inflection point in the reduced energy presented in Figure 1a). From those two observations we can estimate the coil-to-globule transition temperature, $T^*_{CG} = 5.43$.

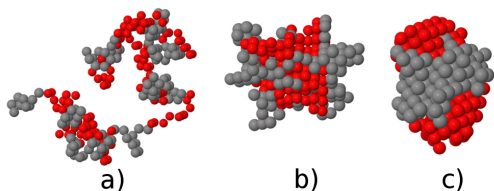


Fig. 2. Sample snapshots of the chain for $\omega = 0.1$ at different temperatures: swollen state at $T^*=13.67$ (a), coil-to-globule transition at $T^* = 5.43$ (b) and 3-cluster structure at $T^*=3.53$ (c).

In Figure 2 we present the equilibrated structures in a coiled state (a), in a state which is a close coil-to-globule transition (b) and in a globular state (c) for $\omega = 0.1$. As expected, upon cooling the chain collapses.

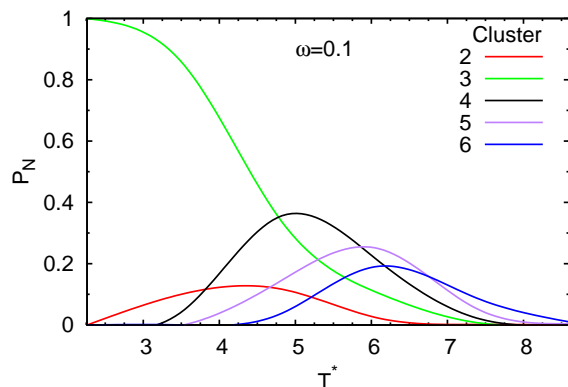


Fig. 3. Probability of finding structures with n -clusters for $\omega=0.1$.

In order to better distinguish different patchy nanostructure, we use cluster count distribution as in ref. [11]. In Figure 3, we present a histogram of probability of clusters with number of segments set to 2, 3, 4, 5, and 6, for $\omega = 0.1$.

We show that the 6-cluster structure (and also n -cluster structures, with $n > 6$) is most stable at T^* 's that higher than $T^* = 6.75$, but from $T^* = 5.90$ to $T^* = 6.75$ the 5-clusters occur with the highest probability. Next from $T^* = 4.75$ to $T^* = 5.90$ the 4-clusters prevail. It is also worthwhile noting that within this range falls the coil-to-globule transition, $T^*_{CG} = 5.43$. For $T^* < 4.75$ the 3-clusters are the most probable patchy nanostructures. The representative 2-clusters are shown in Figure 4 and they seem to be similar to the lamellar nanophase which is observed in diblock copolymer melts.

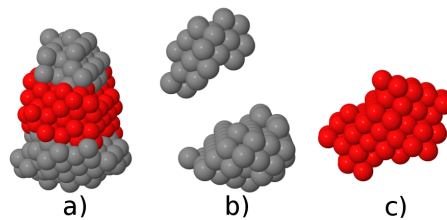


Fig. 4. Example of 3-cluster structure for $\omega=0.1$ and $T^*=2.27$: (a) - whole molecule, (b) - structure with hidden segments of type A, (c) - molecule with hidden segments of type B.

Probability of observing the 3-clusters gradually increases, reaching unity at low temperatures. Variations in the number of clusters and, as a result, in the patchy nanostructure can also be discerned by measuring the heat capacity with higher temperature resolution (more T^* 's), but additional Monte Carlo simulations would be required.

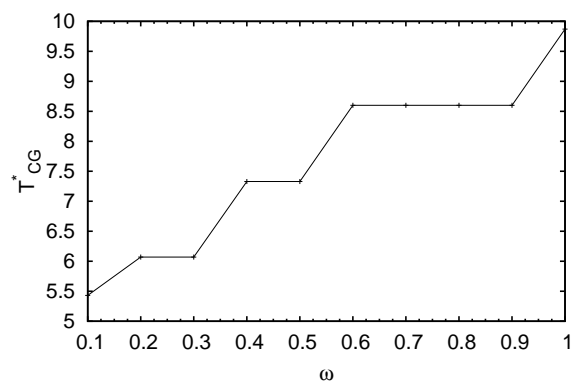


Fig. 5. The reduced temperature T^*_{CG} as the function of ω .

Next, we describe the simulation results for ω 's from 0.2 to 1.0, in more detail. In Figure 5 we show the ω dependence of the coil-to-globule transition temperature, T^*_{CG} , which is similar to that observed in ref. [11], indicating that T^*_{CG} increases upon increasing ω .

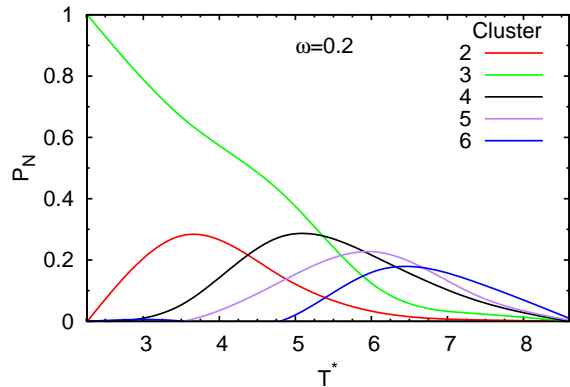


Fig. 6. Probability of finding n -cluster structure for $\omega=0.2$.

Similarly as for $\omega = 0.1$, we determine the temperature dependencies for the heat capacity, the mean squared radius of gyration and the energy per monomer. In Figure 6 we present cluster count distribution for $\omega = 0.2$. In this case we also observe that the 3-cluster structure has the highest probability at low T^* , but the probability of obtaining the 2-cluster structures increases to 0.3 at $T^* = 3.51$. Transition between 4- and 5-cluster is shifted towards higher temperatures, as expected. The T^* range for 4-clusters shrinks significantly from (4.75, 5.90) for $\omega = 0.1$ to (5.5, 5.92) for $\omega = 0.2$. The transition temperature from 4-cluster to 5-cluster patchy structure ($T^* = 5.92$) is close to the coil-to-globule transition temperature, $T_{CG}^* = 6.06$. Above that temperature there is no obvious prevalence of any structure as it becomes increasingly disordered upon heating.

In Figure 7 we show cluster count distribution for the representative ω 's: 0.4, 0.5, 0.8 and 1.0. We observe that the probability maxima for different cluster counts (for $n > 3$) are shifted towards higher temperatures as ω is increased. It is interesting to identify the most probable patchy nanostructures at low temperatures, as they may correspond to the native states in biopolymers [22]. The most probable structures for $\omega = 0.1, 0.2$ and 0.3 are the 3-clusters. On the other hand, for ω 's which are equal or greater than 0.4 the 2-cluster are most probable. However, it is interesting to record that the probability of the dominant nanostructures, either 2-cluster or 3-cluster, approaches unity at low temperatures. Sample snapshots of molecules for various ω 's at $T^* = 2.27$ are shown in Figure 8a). For lower ω 's segments are strongly segregated which leads to formation of a nanostructure consisting of two hemispheres (double-drop structure). Other structures which can be observed are the hand-shake-like structures which are shown in Figure 8b and 8c. Above $\omega = 0.7$ the structures become more disordered.

In this paper as well as in the previous study [11] we do not observe a single native state for the polymer chain. Structures with a different number of clusters can coexist. Only for the lowest temperature T^* , the probability for a given number of clusters is approximately 1.0. therefore we can conjecture

that instead of one native state for given (ω, T^*) we obtain numerous stable states with a different spatial order but with the same energy.

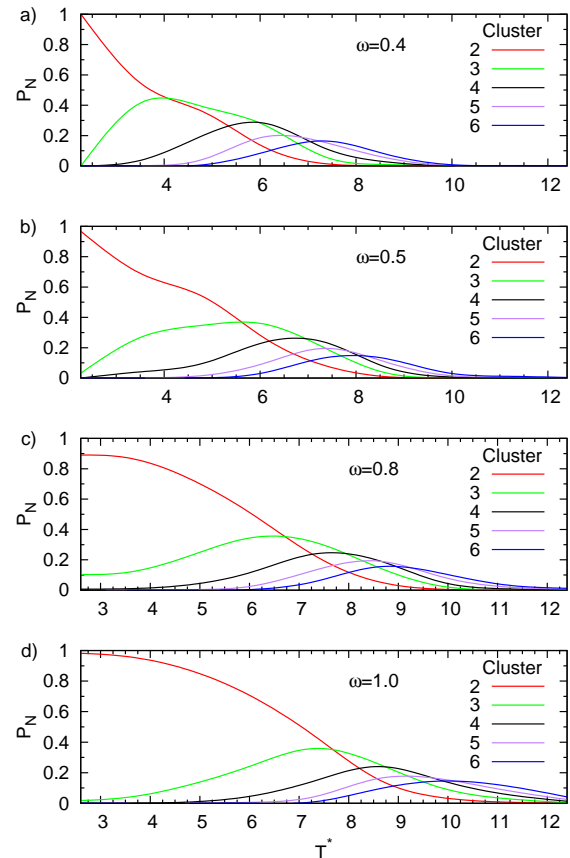


Fig. 7. Probability of finding different cluster structures as a function of reduced temperature T^* with compatibility: (a) $\omega=0.4$, (b) $\omega=0.5$, (c) $\omega=0.8$, (d) $\omega=1.0$.

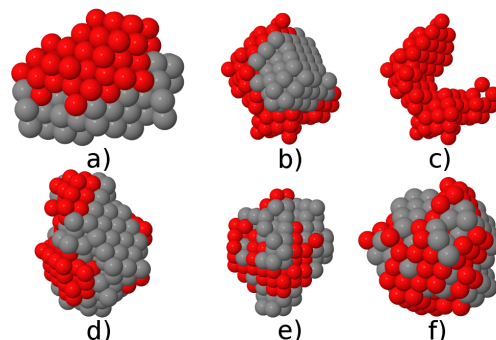


Fig. 8. Variety of 2-cluster structures for the $(10-10)_{12}$ chain at $T^* = 2.27$ for compatibility parameter: (a) $\omega = 0.4$ double droplet, (b) $\omega = 0.5$ hand-shake (c) $\omega = 0.5$ (without the B segments) (d) $\omega = 0.7$, (e) $\omega = 0.9$, (f) $\omega = 1.0$.

In order to compare the present lattice model with the off-lattice model we construct a phase diagram in the

(ω, T^*) space. According to previous multiblock studies we expect that those two models should give similar results [21]. In particular, from ref. [21] we learn that in order to match the coil-to-globule transition temperature for the lattice model, T_{CG}^{*latt} , with that for the off-lattice model, T_{CG}^{*off} , we need to use a multiplicative factor, R , defined below:

$$T_{CG}^{*latt} = R \times T_{CG}^{*off} \quad (4)$$

The value of R depends on both the chain length and microarchitecture, but to a good approximation it is equal to about 6.5 [21]. In Figure 9 we present both the results for the off-lattice model (a) and the results for the lattice model (b), using the $(10 - 10)_{12}$ microarchitecture. In both cases most probable structure remains the same: 2, 3, 4, 5, 6-clusters.

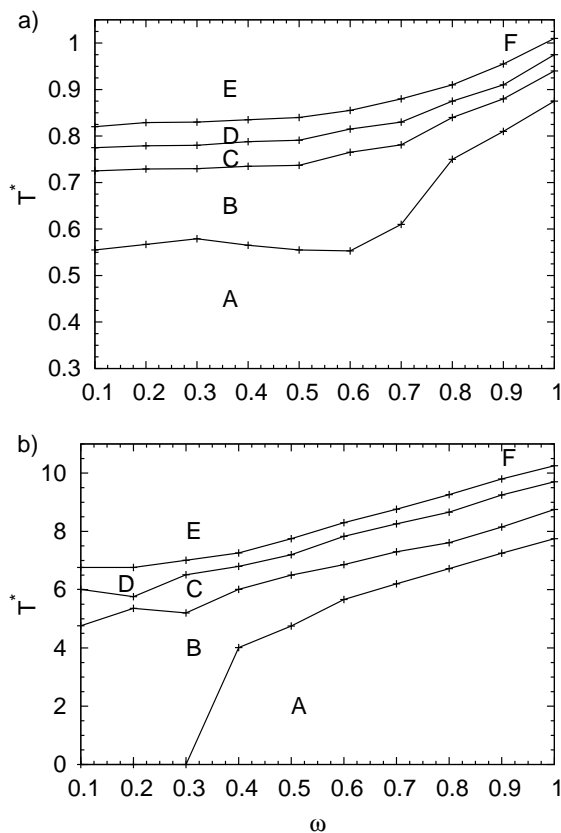


Fig. 9. Phase diagram in the (ω, T^*) parameter space that shows highest probability of finding different counts of clusters for off-lattice (from ref. [11]) model (a) and lattice model (b). A - 2-cluster, B - 3-cluster, C - 4-clusters, D - 5-clusters, E - 6-clusters, F - disordered

Comparing maxima of probability of obtaining certain clusters we can observe that in both cases those maxima shift to higher temperatures as the compatibility increases. The most significant difference is for $\omega < 0.4$. In the previous work (ref. [11]) for lower temperatures and for all values of ω the most probable structure was the 2-cluster. In this paper for

lower T^* 's and $\omega < 0.4$ the most probable structure is the 3-cluster. However, if we compare the transition temperature from the B (2-cluster) region to the C (3-cluster) region at $\omega = 0.1$ then their ratio is about 7 which is close to $R \approx 6.5$ from ref. [21]. It is reassuring to notice if we were to rescale the off-lattice phase diagram by this factor, then both phase diagrams would be very similar to each other, with the exception of a region which is roughly determined by the following inequalities: $\omega < 0.4$ and $T^* < 5$.

The reason for this discrepancy may be related to the fact that the lattice chain is stiffer than the off-lattice chain with the same number of segments. Indeed, when we compare the off-lattice phase diagrams for the $(10 - 10)_{12}$ microarchitecture with that for the $(6 - 6)_{20}$ microarchitecture (see ref. [11]), we notice that for the $(6 - 6)_{20}$ microarchitecture the 3-cluster is the most stable structure at low temperatures. Obviously, the 6-block of the $(6 - 6)_{20}$ microarchitecture is stiffer than the 10-block of the $(10 - 10)_{12}$ microarchitecture, and therefore we can conclude that the block stiffness promotes the 3-cluster structure, as also observed for the lattice $(10 - 10)_{12}$ microstructure.

IV. CONCLUSIONS

Two different approaches, off-lattice and lattice Monte Carlo simulations confirm that multiblock copolymer chain in the globular state forms variety number of different patchy nanostructures. We observed the expected behavior of phase coil-to-globule transition upon cooling. We report thermodynamic and structural properties such as energy, specific heat, and mean square radius of gyration. We constructed the phase diagram in the (ω, T^*) space which presents the same results as for the off-lattice simulation in the case of $\omega > 0.4$. For lower compatibility we report that the most probable phase is 3-cluster.

Finally we answer the questions posed in the introduction:

- the nanostructures obtained in the lattice simulation are the same as those obtained in the off-lattice simulation,
- the phase diagram obtained in the lattice simulation is mostly similar to that obtained in the off-lattice simulation, but qualitatively different for ω 's smaller than 0.4 and T^* 's smaller than 5 (3-cluster is more probable than the 2-cluster). This discrepancy, however, can be tentatively attributed to a considerable stiffness of lattice chains in comparison to that of the off-lattice chains.

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