



Monte Carlo simulations of self-assembling star-block copolymers in dilute solutions

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ABSTRACT

Computer simulations have been performed to analyze the aggregation behavior in dilute solutions of star-block copolymers of the type $(AB)_n$ in a selective solvent for the B block. We found spontaneous aggregation of single stars and formation of roughly spherical aggregates. By changing the solvophobic/solvophilic length ratio of the two blocks, and keeping the total arm length constant, we observed significant changes in the resulting micellar properties, such as the critical micellar concentration (CMC) and aggregation number. More specifically, by increasing the length of the solvophobic A block, we observe micellization at higher temperatures; whereas by increasing the length of the solvophilic B block, we observe micellization at very low temperatures. We also found a dependence of the CMC on the temperature which is in very good agreement with a recent theoretical description based on a simple thermodynamic framework. We compare our results with this theory and predict the enthalpy and entropy of micellization as a function of the temperature.

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1. Introduction

The phase and aggregation behavior of amphiphilic block copolymers has been of remarkable scientific interest for over fifty years because of their distinctive physical properties, which are essential in a significant number of industrial applications [1]. However, most of the scientific output has focused mainly on linear diblock or triblock copolymers [2,3], leaving other more complex structures on a secondary level. In the last two decades, the development of several experimental techniques to synthesize star-like copolymers [4–8] and, in particular, advances in controlled radical polymerizations, such as atom transfer radical polymerization [9–12], has triggered an increasing interest toward intriguing non-linear architectures, such as heteroarm, miktoarm, and star-block copolymers, which consist of several arms radiating from a common central core. More specifically, heteroarm and miktoarm copolymers, concisely denoted as A_nB_n and A_nB_m , respectively, consist of n arms containing only units of type A , and the remaining (n or m) arms containing only units of type B . Star-block copolymers, usually referred to as $(AB)_n$, may be described as star polymers where each of the arms is a linear block copolymer [13]. They consist of n arms with a bridging block of A units attached to the central core, and a terminal block of B units. The structural properties of star-like copolymers and in particular their ability to self-assemble, make them of significant interest as drug delivery vehicles [14–19],

polymer films [20], and in catalysis [21–23]. For instance, star-block copolymers made of biocompatible poly(ethylene oxide) arms find important applications in biomedical and pharmaceutical areas [24], and they are especially promising for functionalization [25]. There are three general ways of synthesis which are usually referred to as *core first*, *arm first*, and *coupling onto* methods [26]. In the *core first* approach, a multifunctional initiator starts the simultaneous polymerization of the arms; the *arm first* approach involves the reaction between a linear copolymer and a multifunctional cross-linker; the last technique can be considered as a combination of the other two, and involves a reaction between a functionalized polymer and a multifunctional linking agent [27].

Star-like copolymers show an interesting micellization behavior which may deviate from that of the analogous linear block copolymers with either the same molecular weight or the same arm block length [28–30]. By means of static and dynamic light scattering and viscometry, Voulgaris et al. found that the micellization properties of polystyrene/poly(2-vinylpyridine) star copolymer in a selective solvent for polystyrene (PS), are significantly different from those of the corresponding diblock copolymer having the same block lengths as those of the star arms [29]. In particular, the star-block copolymer exhibits a much higher critical micellar concentration (CMC) and a lower aggregation number with respect to the linear copolymer. By applying the same experimental techniques, Mountrichas et al. studied the aggregation behavior of star-block copolymers made of PS and polyisoprene blocks in PS-selective solvents [30]. These authors concluded that such stars self-assemble in micelles of smaller size, lower aggregation number and shorter coronas than those generated from the aggregation of a copolymer

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with approximately the same molecular weight and composition. On the other hand, they did not observe significant differences with the structure of the micelles obtained from the aggregation of the corresponding single arms.

Thanks to computer simulations, in the last two decades it has been possible to increase the level of understanding of the physics behind the formation of micelles in various types of amphiphilic solutions [31,32]. Molecular Dynamics [33–35], Brownian Dynamics [33], Dissipative Particle Dynamics [36,37], and Monte Carlo simulations [38–41], have been applied to study the phase and aggregation behavior of block copolymers. Most of these simulation techniques were performed on simplified models to handle the usual time and length scales involved in soft matter as detailed atomistic models are often too computationally demanding [42]. Coarse-grain models significantly reduce the number of atoms or molecules in the systems and the relative interactions established by grouping them together in a simplified manner [43]. Recently, Sheng et al. performed Dissipative Particle Dynamics (DPD) to compare the equilibrium structures of $(AB)_n$ and $(BA)_n$ star-block copolymers in a selective solvent for the A block [44]. Interestingly, they detected unimolecular micelles made of $(BA)_n$ stars, which are very similar to those observed in systems containing linear diblock AB copolymers. They showed that star-block copolymers can form uni- or supramolecular micelles according to (i) the distribution of the solvophobic and solvophilic units in the arms, (ii) their relative length, and (iii) the number of arms. In particular, for an $(AB)_n$ star in a good solvent for B , the uni- or supramolecular micellization strictly depends on the ability of B units to properly shield the solvophobic A -core from the contact with the solvent. This ability is a consequence of the delicate balance between the strength of AA , AB , and BB interactions, and the conformational entropy of the polymer. Unimolecular micelles can represent a significant improvement as drug delivery vehicles over multimolecular copolymer micelles. The covalent bond between the amphiphilic arms in unimolecular aggregates ensures a higher thermodynamic stability with respect to a micelle formed by distinct linear blocks, and reduces the probability to release the drug molecules to the surrounding solution. Because of their dynamic equilibrium with the free chains in solutions, multimolecular micelles made up of linear block copolymers might not accomplish this important task entirely [45–47]. Unimolecular and multimolecular micelles have been also observed more recently by Chou et al., who applied the DPD method to analyze the effect of arm number and length, solvent quality, and block length ratio, on the mean aggregation number in solutions of $(AB)_n$ star-block copolymers [48]. Jo and coworkers applied Brownian Dynamics simulations and a mean field theory to study the effect of the number of arms on the aggregation behavior of an $(AB)_n$ star-shaped copolymer, modeled as a bead-spring chain, in a selective solvent for the B block [49]. They found that the CMC shows a minimum when plotted as a function of the arm number, representing the optimal compromise between the entropic loss due to steric constraints in the micellar state, and large interfacial areas exposed to the solvent in the singly dispersed state.

In this work, we perform Monte Carlo simulations to study the aggregation behavior of a model star-block copolymer of general formula $(AB)_n$, with $n = 5$, in a selective solvent for the terminal B -group. We aim to understand how the main features of the self-assembly of this copolymer in micellar structures can be affected by the temperature, concentration, and by the solvophobic/solvophilic ratio of the block lengths. To this end, we model three different star-block copolymers whose block lengths ratio ranges from 0.5 to 2 and analyze their micellization properties. Moreover, we compare our simulation results with the recent theoretical model proposed by Kim and Lim, which provides the dependence of the CMC on the temperature [50]. By means of such a correlation, we could

estimate the standard free energy of micellization and analyze the thermodynamics behind the formation of micelles. In this context, we discuss the dual enthalpic–entropic nature of the driving force leading to the self-assembly of star-block copolymers.

The paper is organized as follows. In the next two sections, we describe the coarse-grained model and the simulation methodology applied, with a particular focus on the techniques used to study the aggregation properties of the micelles in equilibrium. In Section 4, we present and discuss the aggregation behavior and the thermodynamics of micellization by comparing the three architectures analyzed on the basis of their block length ratios. Finally some conclusions wrap up the paper.

2. Model

The coarse-grained model used in this paper was originally proposed by Larson who studied the aggregation behavior of linear surfactants in systems with oil and water [51]. In this model, the simulation box is organized into a three-dimensional cubic network of sites, and the amphiphilic chains are represented as sequence of connected beads. Each bead occupies a single site, and interacts with its nearest or diagonally-nearest neighbors along $z = 26$ directions, where z is the lattice coordination number. In our study, the amphiphilic star-like monomers occupy 31 sites, whereas the solvent occupies a single site. The monomers are composed of one central bead connected to five arms, as illustrated in Fig. 1. Each arm contains a solvophobic bridging group directly connected to the central bead, which is also solvophobic, and a solvophilic terminal group. The solvophobic and solvophilic beads are denoted by A and B , respectively. The solvent is denoted by S . Here, we use the abbreviation $A(A_xB_y)_5$ to indicate a star-block copolymer with five arms containing x solvophobic and y solvophilic beads, with $(x, y) = (3, 3), (4, 2),$ or $(2, 4)$.

The interaction between two beads i and j is given by the global interchange energy, ω_{ij} , which is the only relevant energetic parameter, and reads:

$$\omega_{ij} = \epsilon_{ij} - \frac{1}{2}(\epsilon_{ii} + \epsilon_{jj}) \quad (1)$$

with ϵ_{ij} being the individual interaction energies of a given pair of sites. We fixed the global interchange energies according to the main factors affecting the micellization process, which are (i) the repulsion of the solvophobic beads with the solvophilic beads and the solvent, and (ii) the solubility of the B beads in the solvent. In particular, $\omega_{AB} = 1$, $\omega_{AS} = 1$, and $\omega_{BS} = 0$. Note that from Eq. (1), $\omega_{ii} = 0$.

The dimensionless temperature reads

$$T^* = \frac{k_B T}{\omega_{AB}} \quad (2)$$

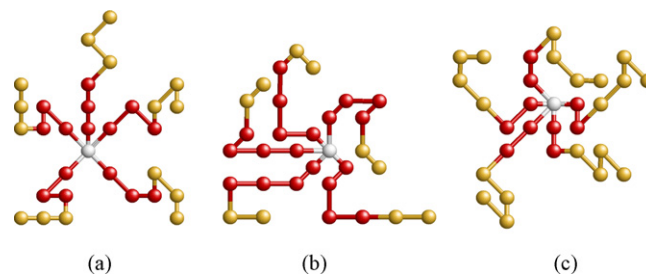


Fig. 1. Model star-block copolymers. $A(A_3B_3)_5$ (a); $A(A_4B_2)_5$ (b); $A(A_2B_4)_5$ (c). Solvophobic and solvophilic beads are in red and yellow, respectively. The central bead, in gray, is as solvophobic as any red bead. (For interpretation of the references to color in the figure caption, the reader is referred to the web version of the article.)

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