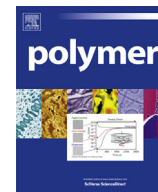




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Vesicles from the self-assembly of coil–rod–coil triblock copolymers in selective solvents

Zenglei Chen^a, Xianghong Wang^b, Linxi Zhang^a, Linli He^{a,*}

^a Department of Physics, Wenzhou University, Wenzhou 325035, PR China

^b Wenzhou Vocational & Technical College, Wenzhou 325035, PR China

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ABSTRACT

Self-assembled vesicles formed by symmetrical coil–rod–coil triblock copolymer in selective solvents are investigated by dissipative particle dynamics method. With varying the coil length L_c and the rod length L_r , five kinds of typically ordered micelles are observed, including the special vesicles formed in the range of the rod block ratio $f_r \approx 30\% \sim 50\%$ and the rod length $L_r \leq 9$. The kinetic process of vesicle formation is also observed. The aggregates firstly experience the fusion, elongation, and deformation, and then encompass the solvents, and finally close up to a vesicle membrane, where the bilayer disc is observed as an intermediate phase transitioned from solid micelles to hollow vesicles. A scaling behavior of the average aggregate size with time is also obtained during the process of the self-assembly. Furthermore, the effects of polymer concentration f_p and solvent property are discussed. Vesicle structure only appears in the range of $f_p = 6\% \sim 25\%$, where vesicle size exhibits a well linear increase with polymer concentration. Meanwhile, vesicle size decreases with an increase in the interactions a_{CS} between coil blocks and solvents. Due to the interfacial energy increased with a_{CS} , the system minimizes interfacial energy by compressing the vesicle size.

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1. Introduction

Induced by the solvent selectivity, amphiphilic block copolymer solutions can self-assemble into a variety of microphase structure, such as micelle, cylinder, vesicle, and lamellae [1]. Due to the unique hollow structure, recently, vesicle phase has attracted more and more attention. A vesicle is a closed bilayer membrane with hollow inner space, which can be divided into three layers: two hydrophilic layers (the inside and outside hydrophilic surface) and one hydrophobic layer between the two hydrophilic layers. Vesicle is an important model for biological cells and has great potential applications in the biomedical sciences and industries, such as microreactors, microcapsules, drug delivery and so on [2–6]. Therefore, the kinetics and mechanisms of vesicle formation has received increasing attention, both theoretically [7–9] and experimentally [10–12].

In 1995, Zhang et al. prepared the vesicles formed by PS-PAA amphiphilic diblock copolymers in aqueous solutions [1]. Then, researchers began to pay attentions to the structural characteristics,

preparation methods, formation mechanisms of polymeric vesicle, and so forth. Shen et al. studied the morphological transitions of PS-b-P4VP block copolymers as a function of pH for the DMF/H₂O solvent systems. They found that as the pH increased from 7.0 to 12.3, the aggregate morphology transitioned from large compound micelles to a mixture of spheres, rods, and vesicles, and then back to spheres [13]. Bhargava et al. reported temperature-induced reversible morphological transitions of PS₉₆₂-b-PEO₂₂₇ micelles in DMF/H₂O solvent. In increasing the temperature case, the morphology changed from vesicles to worm-like cylinders and then to spheres. During cooling of the system, the micelle morphology returned from spheres to worm-like cylinders and finally reached vesicles [14]. Chen et al. studied the dynamic phase transformation of PS-PAA block copolymers in dilute solution from rod-like micelles to vesicles. They further proposed the formation mechanism of copolymer vesicle [15].

In theory and simulation, Han et al. used Monte Carlo simulation combined with experimental method to investigate the dynamic process of vesicles formed by ABA block copolymer solutions. They found that the kinetics pathway of vesicle formation depended greatly on the solvent addition rate [16]. Cui et al. also utilized Monte Carlo to study the microphase behavior of ABC copolymers in selective solvent for A and C blocks. Their results show that the

* Corresponding author.

E-mail address: linlihe@wzu.edu.cn (L. He).

chain length and hydrophilicity difference between blocks A and C are key factors that determine the formation of three-layer vesicle [17]. Meanwhile, Yamamoto et al. used dissipative particle dynamics (DPD) to study the budding and fission dynamic of two-component vesicle [18]. Then they also investigated the vesicle formation of amphiphilic molecules in aqueous solution. The coarse-grained model of amphiphilic molecule contains a hydrophilic head group and a hydrophobic tail. Their results show that the vesicle is formed through the intermediate state of an oblate micelle or a bilayer membrane [19]. All of the above work is based on the vesicles self assembled from the classic coil–coil block copolymer systems.

Recently, more attention has been given to the self assembly of rod–coil (RC) block copolymer consisted of rigid rods and flexible coils. Phase behavior of rod–coil block copolymer is fundamentally different from that of the classic coil–coil block copolymer. Due to both the conformation entropy of the chain stretch and the orientational interaction between anisotropic rods, rod–coil block copolymers are expected to exhibit more complex self-assembly behavior, leading to new physics, new morphologies, and new applications. A few experimental studies also found the vesicle structure formed in rod–coil block copolymer solutions [20–27]. Jenehke et al. observed the spherical vesicles formed by (PPQ-b-PS-b-PPQ) rod–coil–rod triblock copolymers [20]. Nolte and co-workers investigated the morphological transitions of PS-b-polyisocyanopeptide block copolymers in a rod-selective solvent. They observed a variety of different morphologies, including cylindrical micelles for longer rod blocks and vesicle structures for shorter rod blocks, and found the effect of solvent selectivity on the vesicle structure [21]. Checot et al. investigated PB-b-PLGA block copolymer in rod-selective solvents, which formed vesicles at low pH. With the pH increased, the PLGA went through a rod–coil transition, and the vesicles radius became larger [23,24]. Lee et al. observed the self-assembly behavior of (PHIC₅₀-b-P2VP₁₇₀) rod–coil diblock copolymers in THF/water mixed solvent. They presented a solvent-induced morphological transition from spherical micelles to vesicles and found the size of the aggregates increased with increase of water content in the mixed solvent [26].

Although there are some experimental advances in the study of the vesicles formed by whether coil–coil or rod–coil block copolymer systems, some questions are still unclear, due to the limitations of experimental conditions. Overall, computer simulation has been seen as an indispensable supplement to the experimental study. However, the simulation on vesicle phase of rod–coil block copolymers has rarely been reported up to now. In this paper, we perform a dissipative particle dynamics simulation (DPD) to investigate the vesicle micelles self-assembled from coil–rod–coil (CRC) triblock copolymers in selective solvent. We first present the morphological phase diagram with rod and coil length varied. We further analyze the vesicle structure and dynamic mechanism of vesicle formation. Finally, we explore the controlling factors for vesicle size deeply.

2. Model and method

The DPD method is typically considered as a coarse-grained simulation technique introduced by Hoogerbrugge and Koelman in 1992 [28]. The DPD ‘beads’ or particles represents a group of atoms clustered together [29]. The position and momentum of the particle are updated by Newton’s equation of motion. The total force acting on a particle i by the particle j contains three parts: conservative force \vec{F}_{ij}^C , dissipative force \vec{F}_{ij}^D , and random force \vec{F}_{ij}^R .

The interaction between two particles can be written as the sum of these forces.

$$\vec{f}_i = \sum_{i \neq j} \left(\vec{F}_{ij}^C + \vec{F}_{ij}^D + \vec{F}_{ij}^R \right) \quad (1)$$

$$\vec{F}_{ij}^C = a_{ij} \omega(r_{ij}) \hat{r}_{ij} \quad (2)$$

$$\vec{F}_{ij}^D = -\gamma \omega^2(r_{ij}) (\hat{r}_{ij} \cdot \vec{v}_{ij}) \hat{r}_{ij} \quad (3)$$

$$\vec{F}_{ij}^R = \sigma \omega(r_{ij}) \theta_{ij} \hat{r}_{ij} \quad (4)$$

The conservative force \vec{F}_{ij}^C is the soft repulsion acting along the intermolecular vector, where r_c is the cutoff radius. The a_{ij} is repulsion parameter between beads i and j , $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$, and $r_{ij} = |\vec{r}_{ij}|$, $\hat{r}_{ij} = \vec{r}_{ij}/r_{ij}$, $\vec{v}_{ij} = \vec{v}_i - \vec{v}_j$. The weight function $\omega(r_{ij})$ is given by $\omega(r_{ij}) = 1 - r_{ij}/r_c$ for $r_{ij} < r_c$ and $\omega(r_{ij}) = 0$ for $r_{ij} > r_c$. The other two forces (\vec{F}_{ij}^D and \vec{F}_{ij}^R) each act as a heat sink and a heat source, respectively, which effectively combines to thermostat the system, and θ_{ij} is a randomly fluctuating variable with Gaussian statistics: $\langle \theta_{ij}(t) \rangle = 0$ and $\langle \theta_{ij}(t) \theta_{kl}(t') \rangle = (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \delta(t - t')$. Also, there is a relation between the friction coefficient γ and the noise amplitude σ as $\sigma^2 = 2\gamma k_B T$, where k_B is the Boltzmann’s constant and T is the temperature, respectively. In our simulations, the radius of interaction, the particle mass, and the temperature are all set to be unity, i.e. $r_c = m = k_B T = 1$. The repulsion parameters a_{ij} in Eq. (2) can be translated easily to the more familiar Flory–Huggins χ -parameters by Ref. [29]

$$a_{ii} \rho = 75 k_B T, \quad (5)$$

$$a_{ij} \approx a_{ii} + 3.27 \chi_{ij} \quad (\rho = 3) \quad (6)$$

$$a_{ij} \approx a_{ii} + 1.45 \chi_{ij} \quad (\rho = 5) \quad (7)$$

where a_{ii} is the repulsion parameter between particles of the same type to correctly describe the compressibility of the water. In our study, the particle density ρ is kept to 5 [29,30].

Our model system consists of the symmetric coil–rod–coil triblock copolymers and solvent molecules. Coil blocks (C) are constructed by connecting the adjacent particles via an extra harmonic

spring force $\vec{f}_i^S = \sum_j C \vec{r}_{ij}$, where parameter C is the spring constant, which is chosen to be equal to 4. Referring to previous DPD

studies on rod–coil systems [31], rod blocks (R) are constructed by DPD beads arranged in a straight line with a fixed distance D_{b-b} . D_{b-b} is set to be 0.3 in our study. Solvent molecules (S) are represented by single DPD beads. The simulations are performed in a cubic box of constant volume $V = L \times L \times L$. Periodic boundary conditions are applied in all three directions. Initially, we simulated two systems with different sizes of $20 \times 20 \times 20$ and $25 \times 25 \times 25$ DPD units, in which the same results are obtained. In addition, we also checked the thermodynamic consistency of simulated structures by monitoring the local temperature and pressure [32], to remove thoroughly the finite simulated size effect. Finally, we focus on the simulated systems with size of $25 \times 25 \times 25$ DPD unit, containing 78125 DPD beads. Time evolution of motion equations is calculated by a modified velocity–verlet algorithm with timesteps of $\Delta t = 0.04$ and $\lambda = 0.5$ [29,30]. The values of a_{ij} among the three types of DPD beads (C, R and S), are given by $a_{CC} = a_{RR} = a_{SS} = 15$ and $a_{RC} = 45$, $a_{RS} = 15$. We keep $a_{CS} = 45$ except section E, where

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