Journal of the Taiwan Institute of Chemical Engineers 81 (2017) 104–109

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Helical wrapping of diblock copolymers on nanocylinder

Hsing-Lun Wu[a], Heng-Kwong Tsao[b,c,*], Yu-Jane Sheng[a,*]

[a] Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan
[b] Department of Chemical and Materials Engineering, National Central University, Jhongli 32001, Taiwan
[c] Department of Physics, National Central University, Jhongli 32001, Taiwan

ARTICLE INFO

Article history:
Received 10 July 2017
Revised 29 September 2017
Accepted 29 September 2017
Available online 6 November 2017

Keywords:
Helical wrapping
Diblock copolymer
Nanocylinder
Morphological phase diagram
Molecular simulations

ABSTRACT

The development of the helical structure of diblock copolymers in solutions or melts is a challenging task although helices can be readily formed in a confined environment such as nanopore. In this study, dissipative particle dynamic simulations are performed to explore helical supramolecular structures self-assembled from diblock copolymers induced by nanocylinder. At low polymer concentrations, helical ellipsoids are formed on the nanocylinder and they remain stable after the nanocylinder is removed. As the concentration increases, three types of cylindrical morphologies appear: single-single helix, double-double helix, or segmented structures. The influences of block lengths and block-nanocylinder interaction on suprastructures are shown in the morphological phase diagram. When the nanocylinder is bounded by two planes, a helical funnel can emerge. In the presence of a ring-like nanoparticle, a helical toroid can arise. Our simulation results provide a new strategy for the fabrication of various helical assemblies of diblock copolymers in solutions.

1. Introduction

Amphiphilic diblock copolymers can self-assemble in a selective solvent to form various structures such as spherical micelles, worm-like micelles, and bilayered vesicles, depending on the polymer concentration, block lengths, Flory–Huggins interaction parameters, and solvent selection [1,2]. Diverse morphologies of self-assembly can also be observed for diblock copolymers, either in bulk [3,4] or confined environments [5,6], including body-centered cubic arrays of spheres, hexagonally packed cylinders, bicontinuous gyroids, and alternating lamellae. The helical structure has great potential for many applications such as electromagnetic wave absorber [7], and metamaterial [8]. Nonetheless, helical structures formed by diblock copolymers in polymer solutions or melts have seldom been reported. In contrast, it is easier to develop helices by ABC triblock copolymers. For example, double or triple helices can be self-assembled by poly(n–butyl methacrylate-b-2-cinnamoyloxyethyl methacrylate-b–tert–butyl acrylate) in some selective solvents [9]. Moreover, helical structures can be formed by poly(styrene-b-butadiene-b-methyl methacrylate) in their melt phase [10].

It is known that the helix conformation of polymers can be induced by wrapping [11] or confinement [12–15]. In a solution, a long polymer chain can exhibit helical structures by wrapping up a long nano-scale cylinder [16], for example, single stranded DNA on the modified outer surface of single walled carbon nanotubes [17]. The wrapping behavior depends strongly on the polymer stiffness, chirality, and attraction between polymer and cylinder [18,19]. Specific interactions between the polymer and highly curved surface, such as H-bond, π–π, CH-π, and van der Waals attraction [20], must exist for polymer adsorption [21]. For block copolymer melts, helical structures can be developed in a confined environment like nanopores [22]. Confinement can destroy the symmetry of a structure, compelling a transformation from bulk to confined equilibrium morphology [23,24]. For example, helical conformations of diblock copolymers of styrenes and butadienes can be formed in two-dimensional confinement [25].

The formation of helical structures of diblock copolymers in a solution has been a challenge for polymer scientists. However, helical wrapping of a nano-cylinder provides a possibility for developing helices of diblock copolymers. In this study, dissipative particle dynamic simulations are performed to explore the self-assembled morphology of diblock copolymers on a nano-cylinder. It is found that in the presence of a nano-cylinder, besides segmented structures, self-assembled helical wrapping of diblock copolymers is induced. Thus, helical ellipsoids, helical cylinders, helical funnels and helical toroids appear. The influences of polymer concentration, block composition, and the interaction between polymer and nano-cylinder on the morphology are investigated. As a result, a morphological phase diagram is constructed. Our simulation

---

* Corresponding author.
E-mail addresses: hktsao@cc.ncu.edu.tw (H.-K. Tsao), yjsheng@ntu.edu.tw (Y.-J. Sheng).

https://doi.org/10.1016/j.jtice.2017.09.047

results may shed some light on the experimental development for the formation of the helical suprastructure of diblock copolymers in solutions.

Table 1
Interaction parameters (a_{ij}) between all kinds of DPD beads. S, A, B, and W represent solvent, A-block, B-block, and nanocylinder (or nanoring), respectively. $X = 10$–60.

	S	A	B	W
S	25	50	50	60
A		25	50	20
B			25	X
W				25

2. Model and simulation method

The dissipative particle dynamic (DPD) simulation method introduced by Hoogerbrugge and Koelman [26,27] in 1992 is a coarse-grained particle-based, mesoscale simulation technique and DPD obeys the Newton's equation of motion. It has been used to obtain phase diagram of polymers [28]. There are three kinds of forces applied in DPD, conservative, dissipative and random forces, all of these forces are pairwise-additive and short-ranged [29]. The interaction between two beads of different species, including solvent, polymer, and nanocylinder are controlled by the conservative force. It is described as $\boldsymbol{F}_{ij}^{C} = -a_{ij}(r_c - r_{ij})\hat{r}_{ij}$ as $r_{ij} \le r_c$ and $F_{ij}^{C} = 0$ as $r_{ij} > r_c$. Here a_{ij} denotes the maximum repulsion between particles i and j and $r_c = 1$ represents the cut-off distance. For fairly compatible species i and j, the interaction parameter is $a_{ij} \approx 25$. For DPD simulations, the conservative force parameter a_{ij} can be matched to the realistic system by the χ parameter (or Hildebrand type of solubility parameters) determined in experiments or other simulation method, $a_{ij} = 25 + 3.5\chi_{ij}$. The examples include $a_{ij} \approx 20$ for poly(3-hydroxybutyrate) and poly(ethylene oxide) [30], $a_{ij} \approx 40$ for poly(styrene) and poly(vinylpyridine) [31], $a_{ij} \approx 50$ for the fluorine-containing segments and dimethylformamide [32], $a_{ij} \approx 60$ for fluorine and acrylonitrile -containing segments or for poly(3-hydroxybutyrate) and polyethylene [30]. As the incompatibility between i and j grows, a_{ij} is increased. The a_{ij} parameters are list in Table 1, where S stands for solvent, A for A-block, B for B-block, and W for nanocylinder or nanoring. A practical example may be hydrophobic polyhydroxyalkanoate-b-ethylene (diblock copolymer) in water (solvent) for appropriate rods.

In this work, the diblock copolymers are modeled as A_mB_n, where A- and B-block contain m and n beads, respectively. Besides the aforementioned DPD forces, an additional force is required to link the bonded beads for polymers. The spring force is depicted as $F_{ij}^{S} = -C^{s}(r_{ij} - r_{eq})\hat{r}_{ij}$. $C^{S} = 100$ is the spring constant and $r_{eq} = 0.4$ denotes the equilibrium bond length. Both the nanocylinder and nanoring are made by an assembly of DPD beads. They are constructed by removing the beads from a rectangular column built by beads arranged in the face-centered cubic structure. The density of the structure is 4 and those beads are frozen in space once generated. The radius of nanocylinder is 1.5 and that of nanoring is 1.5. The system has the box size 30 × 30 × 60 under periodic boundary conditions. The number density in the box is 3.

The equation of motion is integrated by a modified velocity Verlet algorithm with $\lambda = 0.65$ [33,34]. The total simulation steps are at least 10^6 with the time step 0.04. All the units are scaled by the bead mass m, the cutoff distance r_c, and the thermal energy k_BT. To save the simulation time, all polymer chains are initially placed near the nanocylinder or nanoring in a random fashion. The final results remain essentially the same for different initial configurations.

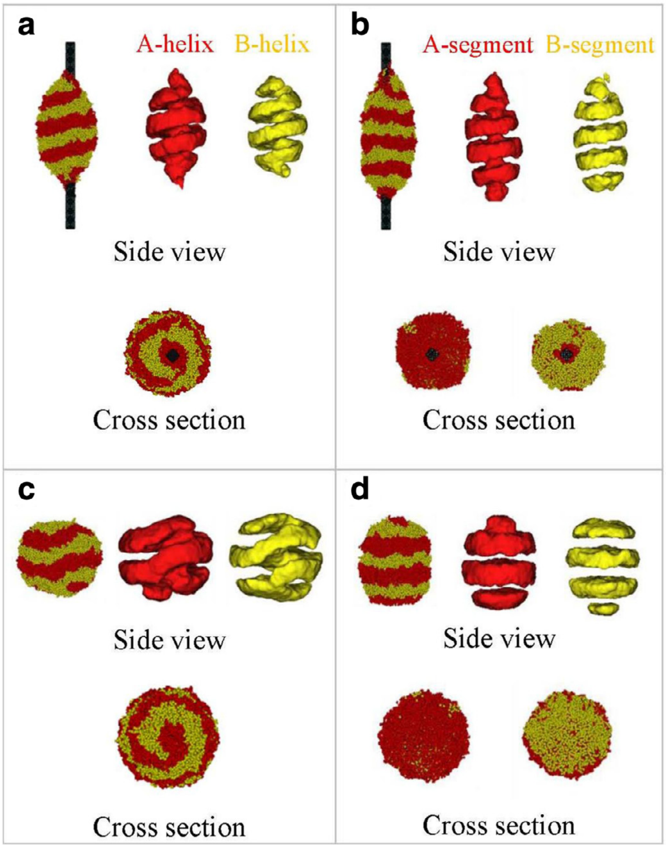

Fig. 1. Self-assembled suprastructures of diblock copolymers: (a) helical ellipsoid on a nanocylinder, (b) segmented ellipsoid on a nanocylider, (c) helical ellipsoid after the removal of the nanocylinder, and (d) segmented ellipsoid without a nanocylinder.

The factors affecting self-assembled morphologies of diblock copolymers on a nanocylinder are investigated, including polymer concentration, block lengths, and block-nanocylinder interaction. In order for diblock copolymers to adsorb onto the nanocylinder (or nanoring), both blocks A and B are solvophobic and at least one of them has strong affinity with the nanocylinder (or nanoring).

3. Results and discussion

3.1. Helical and segmented ellipsoids

In the presence of an infinitely long nanocylinder at the center of the system (30 × 30 × 60), diblock copolymers of $A_{13}B_9$ at low concentration ($N_p = 900$) are aggregated to form an ellipsoid on the nanocylinder of radius 1.5. Note that N_p is the number of polymer chains in the system. It is interesting to find that both blocks self-assemble into a helical supramolecular structure, as shown in Fig. 1a. Clearly, both snapshots of A and B blocks show helical characteristics around the nanocylinder. The horizontal cross-section in the middle of ellipsoid also demonstrates the feature of helix. Since the poor solvent is used, the parameters of block-solvent interactions are chosen as $a_{AS} = a_{BS} = 50$. Moreover, the interaction between A block and cylinder is attractive by setting $a_{AW} = 20$ but the B block-nanocylinder interaction is repulsive, $a_{BW} = 40$. This choice of a_{AW} leads to a total wetting behavior so that the contact angle of the drop of the diblock copolymers approaches zero. Sometimes an ellipsoidal morphology with the lamellar structure appears on the cylinder, referred to as the segmented structure, as illustrated in Fig. 1b. Their layer-by-layer characteristics are evidently observed from the A- or B-segment snapshot and horizontal