Colloids and Surfaces A: Physicochem. Eng. Aspects 384 (2011) 212–218

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Mesoscale simulation on patterned core–shell nanosphere model for amphiphilic block copolymer

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ARTICLE INFO

Article history:
Received 20 December 2010
Received in revised form 9 March 2011
Accepted 29 March 2011
Available online 9 April 2011

Keywords:
Patterned model
Mesoscale simulation
Block copolymer

ABSTRACT

Self-assembly of ABA triblock copolymer confined in concentric-spherical nanopores was studied using MesoDyn simulation. Our calculation shows that in this confined geometry a zoo of exotic structures can be formed. These structures include perforated vesicle like carbon fullerene, strip pattern and hybrid structure. Moreover, the dependence of the chain conformation on the volume fraction, the interactions between blocks and the diameter of the spherical pore are also investigated. The results of these simulations can be used to predict the amphiphilic triblock copolymer morphologies confined in concentric-spherical nanopores and should be helpful in designing polymeric nanomaterials in future.

1. Introduction

In recent years, a surge of research interests has been directed to the synthesis and properties of nanosphere on assembling inorganic compounds or inorganic–organic composites and macromolecules for their various applications [1–6]. Recent synthesis were concentrated on the supermolecular porous nanospheres of organic aggregates and shell-core assembly of block polymers [7,8]. In fact, block polymer self-assembly provides novel and exciting means to generate templates in creating structures at nano-scale. Specifically, the confinement effects of boundaries influence self-assembly processes and lead to many novel mesostructures. The self-assembly morphologies of block copolymers have been used in many areas such as soft nanotechnology, drug delivery and even served as templates for fabricating advanced materials [9]. For self-assembled aggregates, the patterned nanostructures play a critical role in these applications. In order to facilitate a better understanding of the pattern formation besides experimental efforts, computer simulation is a promising tool in offering efficient evaluation of aggregate formation and properties of nanostructures [10–12].

In principle, quantum or molecular mechanical methodologies would furnish detailed electronic and atomic information for the investigation of nanosphere, however, they are highly infeasible to be adopted in studying the properties of nanosphere at the nanoscale level of a reasonably representative-sized model needed to be used. Therefore, coarse-graining or mesoscopic simulations must be resorted for the study of nanosphere or nanosphere template at the mesoscale level.

In last decade, Monte Carlo studies [13,14] based on coarse-graining model and mesoscopic simulations based on MesoDyn [15–17] have been carried out to identify microphase transitions of block copolymer under the effect of one-dimensional (1D) to three-dimensional (3D) confinement. Geisinger et al. [13] and Wang et al. [14] applied Monte Carlo simulation to study symmetric diblock copolymer thin films confined between two identical parallel and homogenous surfaces. In this 1D confined model, they found that the observed morphologies have relationship with the match between bulk lamellar period and the simulation box. And a variety of novel morphologies different from bulk structures of triblock polymer (ABA or ABC) in thin films were observed through the experiments and mesoscopic simulation [16,18]. Under two-dimensional (2D) cylindrical pore confinement, Monte Carlo or MesoDyn methods were also carried out to study the morphology of symmetric block copolymer [9–11]. The confined pore sizes have an influence on the structure and symmetry of the self-assembled morphologies, which is in agreement with the experiment about the self-assembly of styrene/butadiene block copolymers (PS-b-PBD) confined in nanoporous anodized aluminum membranes [12]. In addition, Yu et al. [19] recently studied block copolymers under 3-dimensional (3D) confinement spherical nanopores using simulated annealing Monte Carlo simulation. Many interesting morphologies were observed in their 3D-confined simulation. These simulations have provided useful insights about the self-assembly aggregates in the confined models on the mesoscale level.

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doi:10.1016/j.colsurfa.2011.03.055

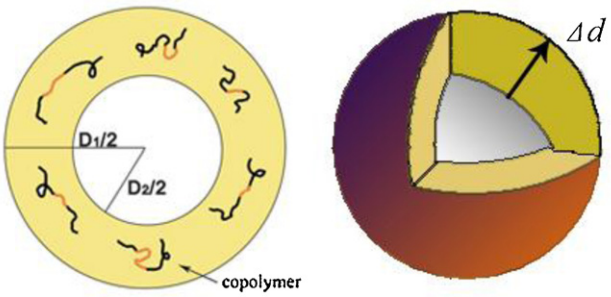

Fig. 1. Schematic diagram of polymer in the nanosphere, a cross-section view (left) and steoropicture (right).

In this paper, we investigated 3D core–shell nanosphere template formation from amphiphilic ABA block copolymer using mesoscale simulation based on MesoDyn method [20–26]. This method can reduce degrees of freedom for a large system size and obtain the properties of nanospheres in less time than the simulations on other length. The effects of the block volume fraction, the interaction of block and solvent, and the sphere diameter on the morphology transitions of symmetric and asymmetric cases are examined in details.

2. Theoretical models

The basic idea of MesoDyn simulation is that the Helmholtz free energy F of an inhomogeneous liquid is a function of the local density function ρ, from which all thermodynamic functions can be derived. The MesoDyn model consists of various types of beads with intramolecular interactions approximated by harmonic oscillator potentials. Compared with the conventional particle simulation methods, field-based methods like MesoDyn have relatively high computational efficiency enabling significant advances in the investigation of microphase separation of block amphiphilic copolymers [26–28]. In these simulations, different patterned nanospheres are modeled in several tens of nanometer.

Firstly each core–shell nanosphere model of various radii was placed in the center of a simulation box. To avoid artifacts resulting from applying periodic boundary conditions, ample space has been made between the nanosphere surface and the boundaries of the computational box. In the simulation, the polymer and solvent are only allowed to exist in the shell domain, as shown in Fig. 1. Here, D_1 and D_2 are respectively the diameters of outer shell and inner core, and Δd ($\Delta d = D_1/2 - D_2/2$) is the shell thickness. In this model, the two surfaces of nanosphere are identical that have the same interaction with the polymer segment in the following simulation. Different patterned structures were generated by quenching a homogeneous solution of polymer surfactant. Certain amounts of solvent molecules were released locally or globally following the quench, depending on the particular morphology being formed. Finally the patterned nanosphere was analyzed as an isosurface of solvent or block copolymer in a self-consistent-field condition. Simulation was terminated whenever the order parameters converged to a set tolerance. The order parameter is indicative of the dynamics of phase separation. It represents the mean-squared deviation from homogeneity in the system and captures the effects of both phase separation and compressibility [29–31].

In the MesoDyn simulations, two sets of parameters are defined to specify the chemical nature of the system: one is the chain topology in terms of the repeating segments (or beads), and the other is the interaction between the various components. For the first set, the MesoDyn method uses a Gaussian chain "spring-and-beads" description [32–35], where all segments are of the same size, and the chain topology depends on the coarsened degrees of freedom of the original system. In our simulation, we focused on the Pluronics solution. Pluronics are block copolymers of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO). In the chain topology of Pluronics, each bead or statistical unit corresponds to 4.3 ethylene oxide (EO) monomers (as one solvophilic solvent bead A) and 3.3 propylene oxide (PO) monomers (as one solvophobic solvent bead B) [36–39]. In the simulation, 11 water molecules are taken as one water bead. Secondly, the interaction energies between different types of segments represent the pairwise interactions of beads, which is based on the regular solution theory and similar to the Flory–Huggins model. The interaction parameters can be considered in the context of non-ideal interaction. It is characterized by $\varepsilon_{AB} > 0$ as the repulsion between two components. As an example, the block polymeric surfactant $A_nB_{N-2n}A_n$ is parameterized by $\chi_{AB} \cdot N = 60$, $\chi_{AS}/\chi_{AB} = 0.47$ and $\chi_{AS}/\chi_{BS} = 0.82$ (*i.e.* when $N = 20$, $\chi_{AB} = 3.0$). These parameters are similar to the ones in the Fraaije's work [24,25,27,29,35]. They represent the binary interaction strengths among components A (slightly solvophilic), B (slightly solvophobic) and S (solvent, like water). In the mean-field model any polymer surfactant solution with the same properties and the scaled interaction parameters will behave in exactly the same way. The parameters defined here were compared with the experimental microphase diagrams of concentrated Pluronic aqueous solution [40]. With the selected parameters, χ_{ij}, N and n, the polymers are insoluble in the nanosphere. Hence, the deformations of the nanosphere are at certain mass of polymer.

In order to study the aggregate of hydrophobic block A on the surface of the nanosphere model, one side of A bead in the polymer $A_nB_{N-2n}A_n$ was defined to interact with the model surface. Thus the polymer can also be defined as $A_nB_{N-2n}A'_n$, where A′ represents one terminal A bead attracted with the core–shell nanosphere surface, and others (*i.e.*, S, A or B bead) repel the surface. The attract interaction was chosen as $\varepsilon_{A\text{-wall}} = 0$ kJ/mol, and other repelled interaction were chosen as $\varepsilon_{i\text{-wall}} = 10$ kJ/mol. For all simulations, the dimensionless parameters in MesoDyn program have been chosen as (see details in Refs. [12,24]): the time step $\Delta\tau = 50$ ns (dimensionless time step $\Delta\tau = 0.5$), the noise scaling parameter $\Omega = 100$, the compressibility parameter $\kappa'_H = 25$, the grid parameter $d = ah^{-1} = 1.1543$ and the total simulation time is 50,000 steps (*i.e.*, 2.5 ms). The simulations were performed at 298 K. All the simulations were carried out using the MesoDyn module in the commercial software package Material Studio (version 4.1).

3. Results and discussion

3.1. Effect of f_A and χN on the morphologies of ABA triblock copolymer

The microphase behaviors of block copolymer $A_nB_{N-2n}A_n$ depend on the Flory–Huggins parameter χ_{AB} the total length of copolymer N, and the volume fraction of the constituents blocks $f_A = 2n/N$ Fig. 2 shows the typical phase diagram of copolymer under core–shell geometrical confinement with varying χN and f_A while the volume fraction of polymer is kept at a constant concentration 85%. In Fig. 2, four types of morphologies were found: (i) the hollow-spherical structures (Fig. 3a) were just like that of single lamellar vesicle, located in region (a). The lamellar vesicle phase was formed at the lower of χN and f_A. (ii) With the increase of χN, the self-assembly transformed from vesicle to perforated vesicle (Fig. 3b), located in region (b) in Fig. 2, which represents the bicontinuous phases confined in two constrain walls. These