Polymer 49 (2008) 2797–2800

Contents lists available at ScienceDirect

Polymer

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

Polymer Communication

Block copolymer nanoshells

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ARTICLE INFO

Article history:
Received 11 January 2008
Received in revised form 18 April 2008
Accepted 21 April 2008
Available online 26 April 2008

Keywords:
Block copolymer
Nanostructure
Simulation

ABSTRACT

With the help of cell dynamics simulation we investigate morphology of thin block copolymer film around a nanoparticle. The obtained structures include: parallel, perpendicular, mixed and perforated lamellae, parallel and perpendicular cylinders and spheres. Analogy and difference with planar films are discussed. Our simulation suggests that novel porous nanocontainers can be formed by the coating of a sacrificial nano-bead by a block copolymer layer with a well controlled nanostructure.

Nanoparticles, nanocontainers, nanowires and nanopores with block copolymers have recently attracted intensive research interest because of the easy tailorability of their properties [1–7]. The combination of nanosize and nanostructure can lead to a plethora of unique and complex materials [3,7]. In the present communication we report on computer simulation of the structure of a block copolymer thin film covering a nanosize particle, *e.g.* a colloid (see Fig. 1a). There are experimental techniques available for polymer encapsulation of spherical particles. Fig. 1b shows experimental image of such encapsulation in the case of homopolymer [6]. If the particle is removed after block copolymer film is formed, we obtain a nanostructured shell. There is a very recent experimental work where the particle template is removed to form polymer capsules [8]. However, to our knowledge, microphase-separated block copolymer spherical capsules have not been yet studied. There are many experimental and theoretical works investigating morphologies of block copolymers in planar thin films (for reviews see Refs. [9–11]). For instance, in a thin film, block copolymer, which forms cylinders in the bulk, can assemble into perpendicular or parallel cylinders, flat or perforated lamellae depending on the film thickness and block interactions with surfaces [12]. The fundamental question is can the same structures fold around a curved surface and how would they do so? There has been very recent work on block copolymer self-assembly in cylindrical nanopores, both experimental [4,13] and computational [13–20]. Confinement in a sphere differs from that in a cylinder because the structure has to adapt to a non-zero principal curvature everywhere (while one of the principal curvatures of a cylinder is zero). There were computer simulations on block copolymer confined inside a sphere modelling formation of block copolymer vesicles [14,21] and block copolymer

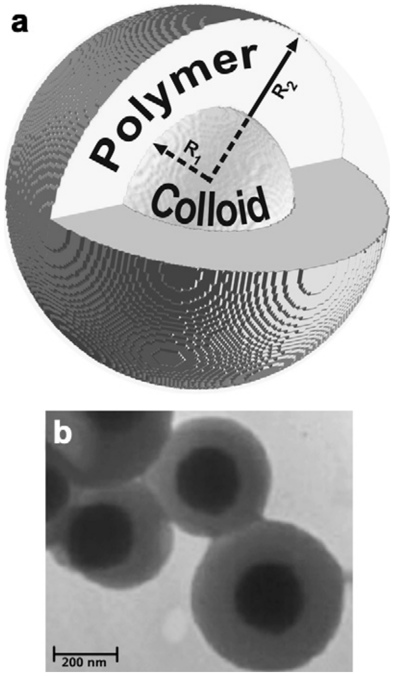

Fig. 1. (a) Schematic representation of the investigated system. (b) TEM micrograph of polymer-encapsulated spherical particles. Reproduced with permission from Ref. [6].

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doi:10.1016/j.polymer.2008.04.038

droplets [20,22]. There were also theoretical works on two-dimensional (2D) microphase separation of block copolymer on a sphere [15,18,23]. Our system is essentially different as the block copolymer film has a non-zero thickness. As we show below, the film morphologies cannot be reduced to patterns on the infinitely thin 2D spherical surface. Moreover, our system is closer to the possible experimental situation. In the present work, we use cell dynamics simulation (CDS) to study various block copolymer morphologies confined in a film around a sphere (see Fig. 1a). CDS is a very fast computational technique [24–30] and can serve as a precursor in computer-aided design of block copolymer systems. For AB diblock copolymer, the structure can be described by an order parameter $\psi(\mathbf{r},t)$ [26]:

$$\psi = \phi_A - \phi_B + (1-2f) \tag{1}$$

where ϕ_A and ϕ_B are the local volume fractions of A and B monomers, respectively, and f is the volume fraction of A monomers in the diblock, $f = N_A/(N_A + N_B)$. The time evolution of the order parameter is given by a Cahn–Hilliard–Cook equation [24,25,27–30]:

$$\frac{\partial\psi}{\partial t} = M\nabla^2\left(\frac{\delta F[\psi]}{\partial\psi}\right) + \eta\xi(\mathbf{r},t) \tag{2}$$

where M is a phenomenological mobility constant. The dimensionless time is tM/a_0^2, where the lattice cell size a_0 and M are set to 1. The last term in Eq. (2) is a noise with amplitude η and $\xi(\mathbf{r},t)$ being a Gaussian random noise. The free energy functional is [25,26,28]:

$$F(\psi(\mathbf{r})) = \int \mathrm{d}\mathbf{r}\left[H(\psi) + \frac{D}{2}|\nabla\psi|^2\right] + \frac{B}{2}\int \mathrm{d}\mathbf{r}\int \mathrm{d}\mathbf{r}' G(\mathbf{r}-\mathbf{r}')\psi(\mathbf{r})\psi(\mathbf{r}') \tag{3}$$

where

$$H(\psi) = \left[-\frac{\tau}{2} + \frac{A}{2}(1-2f)^2\right]\psi^2 + \frac{v}{3}(1-2f)\psi^3 + \frac{u}{4}\psi^4 \tag{4}$$

with τ, A, v, u, D, B being phenomenological parameters, and $G(\mathbf{r}-\mathbf{r}')$ is the Laplace equation Green function [27]. All these parameters can be related to molecular characteristics. According to Ohta and Kawasaki [31] $\tau' = -\tau + A(1-2f)$, D, and B can be expressed in terms of degree of polymerisation N, the segment length b and the Flory–Huggins parameter χ as:

$$\tau' = -\frac{1}{2N}\left(N\chi - \frac{s(f)}{4f^2(1-f)^2}\right),\; D = \frac{b^2}{48f(1-f)},$$
$$B = \frac{9}{4N^2b^2f^2(1-f)^2}$$

where $s(f)$ is an empirical fitting function of the order of 1 (*e.g.* $s(0.5) = 0.9$, $s(0.3) = 1.0$) [31]. In simulation we use dimensionless parameters $\tilde{D} = D/a_0^2$ and $\tilde{B} = Ba_0^2$ (for simplicity we use notations D and B instead of $\tilde{D}$ and $\tilde{B}$). Different morphologies (lamellae, spherical, cylindrical) can be obtained by varying two main controlling parameters, molecular composition f and the temperature-like parameter τ' [30]. The parameters u and v do not allow for a compact representation, they can be computed by evaluating the appropriate vertex functions given by Leibler [32]. These are very complex functions which can be only approximately replaced by constants. A practical approach, we employ, is to use their values for different morphologies given in the literature [27]. We believe that the phenomenology we are studying is quite general and, hence, we allow the freedom of choosing the parameters in Eq. (5) as phenomenological constants not specifically limited to diblock copolymers. The schematic picture in Fig. 1a shows the 3D structure of our model. Block copolymer is confined in-between two concentric spheres with radii R_1 and R_2, where the inner sphere models the surface of nanoparticle and the outer sphere models the free surface of block copolymer film. We choose the most simple model in which the preference of copolymer blocks to both surfaces is the same and is described by Dirichlet boundary condition $\psi(r = R_1 \text{ or } R_2) = \psi_0$. For instance, for a symmetric lamellae $f = 0.5$, and the order parameter in Eq. (1) becomes $\psi = \phi_A - \phi_B$. Therefore, varying ψ_0 we effectively model the affinity of the surfaces towards one or another block copolymer component. A high performance parallel CDS code was used in our simulations [31]. Fig. 2 shows the results for different block copolymer morphologies and various surfaces. First, we consider lamellae system, Fig. 2a–c. Preferable affinity of one of the blocks to the surface induces lamellae being wrapped around a nanoparticle, Fig. 2a. By changing the surface preference we can flip the lamellae sequence (say, AB to BA), Fig. 2b. The morphology is similar to parallel lamellae $L_{||}$ in the planar thin films [10,11]. In the case of neutral surfaces the lamellae stand up as shown in Fig. 2c. The situation is similar but not identical to perpendicular lamellae $L_\perp$ in planar thin films [10,11]. In a spherical geometry the curvature changes with the radius. Therefore, purely perpendicular lamellae cannot exist as they cannot be always parallel to each other. We observe two types of defects which are necessary in order $L_\perp$ morphology can accommodate itself to the spherical geometry. Either lamellae become thicker when the radius increases or they develop characteristic Y-shape defects, Fig. 2c. Both situations do not occur in planar thin films. For intermediate strengths of surface interaction a mixed morphology develops combining both $L_{||}$ and $L_\perp$, Fig. 2d. This mixed lamellar morphology has necessary many defects in the form of perforations and channels, Fig. 2d. In a thinner film, a single perforated lamellae (PL) sheet develops instead of a mixed lamella morphology, Fig. 2e. This is similar to the situation in the planar thin films [12]. However, the PL morphology wrapped around a sphere has not always hexagonal arrangement of perforation, but a mixture of five and six neighbouring perforations, Fig. 2e.

In the case of cylinders the situation is similar: non-neutral surfaces induce formation of parallel cylinders ($C_{||}$), Fig. 2f, while neutral surface induces formation of standing or perpendicular cylinders, Fig. 2g. Standing cylinders have defects in order to accommodate to the curvature around the spherical nanoparticle. They are Y-shape defects and dislocations when a shorter cylinder squeezes in-between of longer ones, Fig. 2g. In the case of spherical morphology the block copolymer spheres arrange themselves in layers around the colloid particle, Fig. 2h. Fig. 3b provides more details on $C_{||}$ and spherical morphologies. Fig. 3b demonstrates that, similar to the perforations in the PL phase in Fig. 2e, block copolymer spheres have a packing which is a mixture of five and six neighbours. Fig. 3b shows that in order to wrap around a sphere, the cylinders have to follow a pattern which is similar to Earth parallels.

In conclusion, with the help of cell dynamics simulation we investigated morphology of thin block copolymer films around a spherical nanoparticle. If after the preparation the film would be chemically cross-linked and the particle chemically removed, one would obtain nanoshells with the structure being controlled by the interplay between film thickness, block copolymer characteristics, surface parameters as well as curvature. Such nanoshells can potentially serve as drug delivery vehicles and nanoreactors. CDS can be employed in the computer-aided design of such nanoshells.

Acknowledgements

This work is supported by Accelrys Ltd via EPSRC CASE research studentship. All simulations were performed on SGI Altix 3700 supercomputer at UCLan High Performance Computing Facilities.

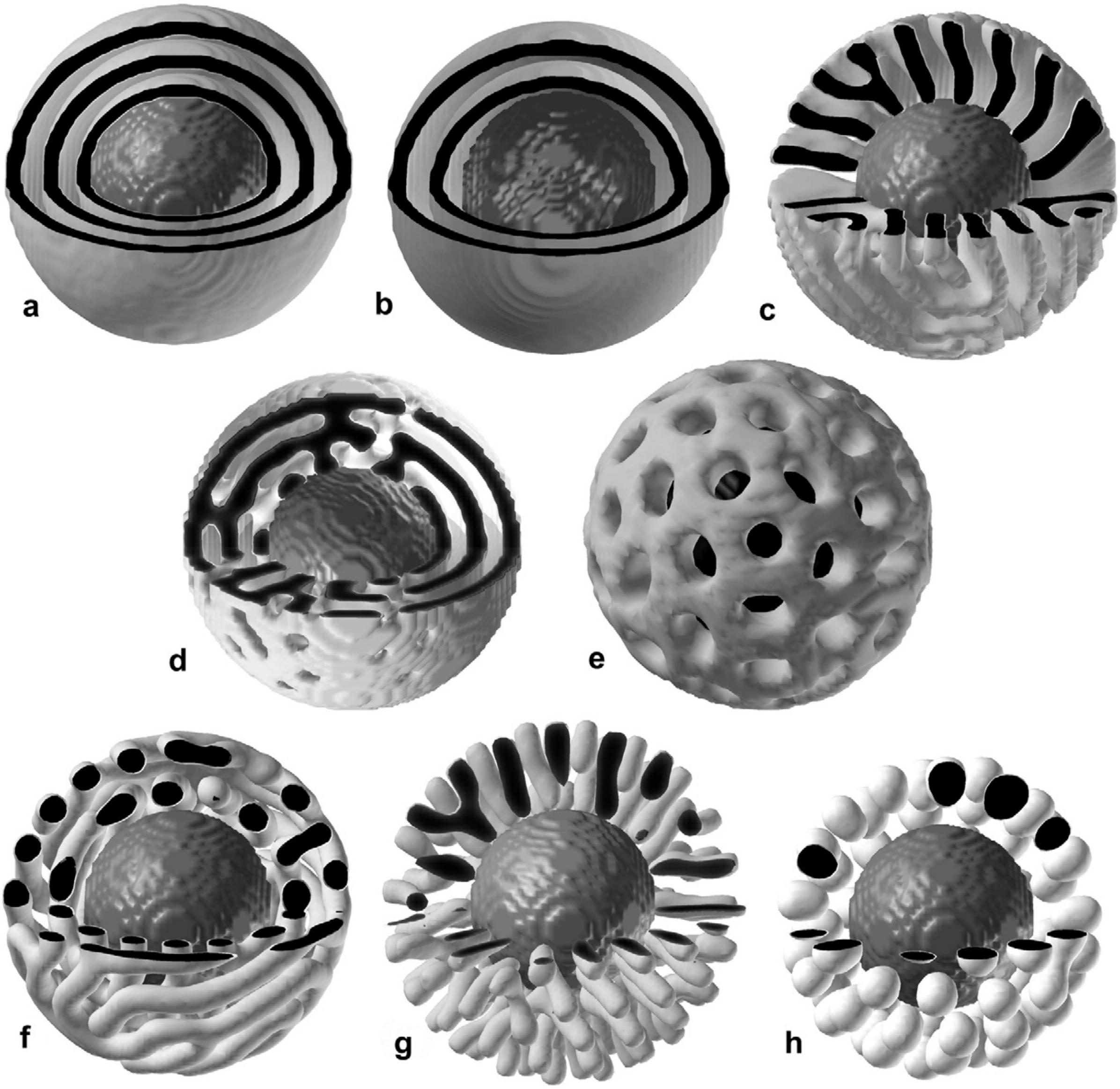

Fig. 2. Various nanoshells. Shells in (a–d) and (f–h) are cut in 1/4 with the particle shown in dark gray. In the cuts, A-rich regions are seen in black. The film thickness is: $R_1 = 16$, $R_2 = 32$ lattice cells (a–d, f–h) and $R_1 = 16$, $R_2 = 6$ (e). The boundary conditions are: $\psi_0 = 0.4$ (a,f,h), 0.2 (d,e), 0 (c), −0.1 (g) and −0.2 (b). The block copolymer composition f and the temperature-like parameter τ are: $f = 0.5$ and $\tau = 0.36$ (a–e), $f = 0.4$ and $\tau = 0.30$ (f–g), $f = 0.4$ and $\tau = 0.20$ (h). The remaining parameters are $u = 0.5$, $v = 1.5$ (a–g) and $u = 0.38$, $v = 2.3$ (h); $A = 1.5$, $D = 0.5$.

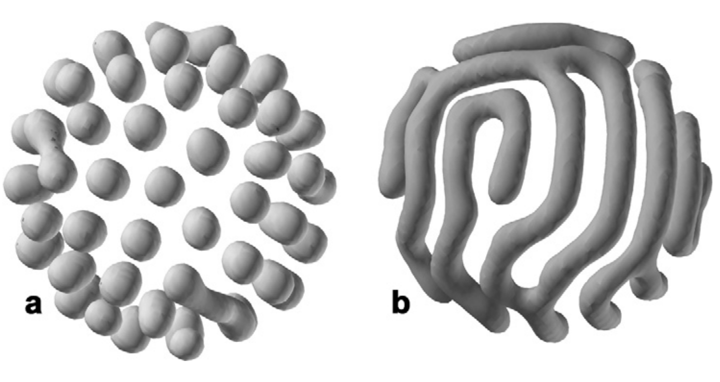

Fig. 3. Outside view on sphere- and cylinder-structured nanoshells. The opposite side and nanoparticle inside are not shown.

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