Kinetics of the Morphological Transition of Diblock Copolymer Micelles by the Dynamic Density Functional Simulation

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両親媒性のジブロックコポリマーは選択溶媒中で球状ミセル、円柱状ミセル、ベシクルといった様々なミセル構造を形成する。形成されるミセル構造は溶媒や温度等を調整することで熱力学的にコントロールするできることが知られている。本研究では動的密度汎関数理論に基づき、溶媒と疎水性モノマーの相互作用の大きさを変化することでミセルの形態転移ダイナミクスのシミュレーションを行い、ミセル形態転移の動力学を調べた。

1 Introduction

Amphiphilic diblock copolymers in selective solvents form micellar structures such as spherical micelles, cylindrical micelles or vesicles. It is reported that micellar structures can be thermodynamically controlled by changing the temperature or the solvent condition [1].

The dynamical simulations for amphiphilic diblock copolymer solutions have been carried out by using the dissipative particle dynamics (DPD) method [2] or by the dynamic density functional method [3]. In this work, we apply the dynamic density functional method [3] to the morphological transition dynamics of diblock copolymer micelles.

2 Simulation

In this work we employ the dynamic density functional method used in Ref 3. In the dynamic density functional simulation, we use the three density field $\phi_A(\boldsymbol{r},t), \phi_B(\boldsymbol{r},t)$, and $\phi_S(\boldsymbol{r},t)$ (A, B and S represents the hydrophilic subchain, the hydrophobic subchain and the solvent, respectively). The dimensionless dynamic equation for the density field is described as follows.

$$\frac{\partial \phi_i(\boldsymbol{r},t)}{\partial t} = \psi_i(\boldsymbol{r})\nabla^2\mu_i(\boldsymbol{r}) - \mu_i(\boldsymbol{r})\nabla^2\psi_i(\boldsymbol{r}) + \xi_i(\boldsymbol{r},t) \tag{1}$$

where $\psi_i(\boldsymbol{r}) \equiv \sqrt{\phi_i}$ and $\mu_i(\boldsymbol{r})$ is the chemical potential field defined as $\mu_i(\boldsymbol{r}) \equiv \delta(F[\{\psi_i\}]/k_BT)/\delta\psi_i(\boldsymbol{r})$. $F[\{\psi_i\}]$ is the free energy functional of the system and is expressed by using parameters such as the polymerization degree, block ratio, or the Flory-Huggins χ parameter (the explicit form of $F[\{\psi_i\}]$ is found in Ref 3). $\xi_i(\boldsymbol{r},t)$ is the thermal noise which satisfies the following

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fluctuation-dissipation type relation.

$$\langle \xi_i(\boldsymbol{r},t)\rangle = 0, \qquad \langle \xi_i(\boldsymbol{r},t)\xi_j(\boldsymbol{r}',t')\rangle = -4\tilde{\beta}^{-1}\delta_{ij}\nabla\cdot\left[\psi_i^2(\boldsymbol{r})\nabla\delta(\boldsymbol{r}-\boldsymbol{r}')\right]\delta(t-t') \tag{2}$$

where $\tilde{\beta}^{-1}$ is the parameter which represents the magnitude of the thermal noise.

The dynamic simulations are carried out for the system with following parameters. The block ratio $f_A = 1/3, f_B = 2/3$, the polymerization index $N = 10$, the volume fraction of the diblock copolymer $\phi_p = 0.2$, and the Flory-Huggins interaction parameters $\chi_{AB} = 2.5, \chi_{AS} = -0.5, \chi_{BS} = 2.5, 3, 5$. It has been shown that the spherical micelles, the cylindrical micelles, and the vesicles are formed for the case of $\chi_{BS} = 2, 5.3$, and 5, respectively. χ_{BS} is changed during the simulation to induce the morphological transition.

3 Discussion

From the simulation results, it is shown that morphological transition processes can be roughly categorized into two types of kinetic processes.

One is the collision and coalescence type growth kinetic process. In this case, smaller micellar structures collide each other and grow to larger structures (the schematic draw is shown in Figure 3(a)). This type of transition is observed when χ_{BS} is increased. This process is relatively slow, because the collision is governed by the diffusion driven by the thermal noise. This kinetic pathway is similar to one observed in the vesicle formation dynamics simulations [2–4].

Another is the fracture type kinetic process or some sort of instability. In this case, larger miceller structures become unstable and fracture into smaller pieces (the schematic draw is shown in Figure 3(b)). This type of transition is observed when χ_{BS} is decreased. This process is somehow similar to the spinodal decomposition in usual phase separation dynamics and thus relatively fast.

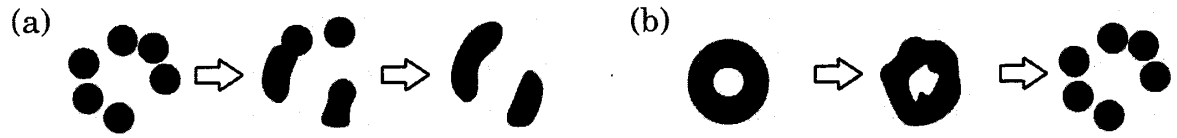

Figure 1: Schematic draws of morphological transition processes. Gray and black colors represent the hydrophobic subchain (A) and the hydrophilic subchain (B). (a) The transition from a spherical micelles to cylindrical micelles and (b) the transition from a vesicle to spherical micelles.

References

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