CSIAM Trans. Appl. Math.
doi: 10.4208/csiam-am.SO-2022-0036

Vol. **4**, No. 3, pp. 592-618
September 2023

Modeling and Simulation of Linear Triblock Copolymers under Three-Dimensional Confinement

Yuqi Yang[1], Zhen Xu[2] and Guanghua Ji[1,*]

[1] *Laboratory of Mathematics and Complex Systems (Ministry of Education), School of Mathematical Sciences, Beijing Normal University, Beijing 100875, P.R. China.*
[2] *Faculty of Science, Beijing University of Technology, Beijing 100124, P.R. China.*

Received 27 September 2021; Accepted 17 February 2023

Abstract. We studied linear triblock copolymer and homopolymer mixtures and constructed a new Nakazawa-Ohta-type model to describe the phase separation of the system. For this high-order, nonlocal and multicomponent phase field system, we construct two second-order, linear and energy-stable schemes. We also proved the energy dissipation and mass conservation of the schemes. Finally, numerical simulations were presented in the 3D case, which verified the theoretical analysis. In addition to those reported phase structures, we found some new ones, which can give some guidance to experimenters.

AMS subject classifications: 65M12, 82B21, 70K75

Key words: Triblock copolymer, soft confinement, phase separation, Nakazawa-Ohta model, high efficient energy stable.

1 Introduction

Block copolymers are a special type of polymer that are formed by two or more kinds of polymer segments with different physical and chemical properties and are linked together by chemical bonds. Compared with blend polymers, due to the chemical bonds, block copolymers are more likely to undergo microscopic phase separation and form diverse ordered nanoscale structures. Thus, block copolymers are widely applied in many fields, such as drug delivery [7, 56], photonic materials [1, 55, 57, 58], electronic ink [2, 62] and so on [28, 29].

Block copolymers are usually placed into a confined environment to assemble into some unique nanostructured particles. The simplest confinement is one-dimensional

*Corresponding author. *Email addresses:* yangyuqi0950@163.com (Y. Yang), ghji@bnu.edu.cn (G. Ji), xuzhenmath@bjut.edu.cn (Z. Xu)

confinement, where block copolymers are placed between two parallel solid plates or on a substrate with the other surface being in direct contact with the atmosphere. If the block copolymers are placed into cylindrical pores, the system is under two-dimensional confinement. Many structures, such as layered, helical, and stacked rings, can be obtained, most of which cannot be obtained under one-dimensional confinement [54]. Three-dimensional confinement is implemented by placing block copolymers into spherical pores or using the self-organized precipitation (SORP) method, which is proposed in [61].

In physical experiments, diblock copolymers can form layered, onion-type, Janus-type, tennis, mushroom, wheel, screw and other structures under three-dimensional confinement [3,11,17,25,26,41,42,47,48,61]. In numerical simulation, the above structures are also obtained based on the simulated annealing method [13], which is applied to lattice model of polymers, scalar auxiliary variable method [30, 34] for phase field model and Monte Carlo method [64]. In addition, multipods, spirals, stacked layers, cylinders and other structures are also predicted [4, 5, 10, 21, 24, 35, 67] under different confinements.

The Ohta-Kawasaki (O-K) model is often used to describe the phase separation of diblock copolymer systems. This theory was first proposed by Leibler [33] based on the mean field theory developed from the statistical mechanics of polymers. Then, Ohta and Kawasaki [40] derived this model again based on an extrapolation formulation of the second-order correlation function. In [6, 14, 39], the Cahn-Hilliard type equations were given to describe the dynamics of the system. Nishura *et al.* [39] expressed the free energy functional of the diblock copolymer system as follows:

$$F[v]=\int_\Omega \left\{ \frac{\epsilon^2}{2}|\nabla v|^2+\frac{1}{4}(v^2-1)^2+\frac{\sigma}{2}|(-\Delta)^{-\frac{1}{2}}(v-\bar{v})|^2 \right\} d\mathbf{x},$$

where the value ± 1 of the order parameter v represents the rich domain of the two polymers. The first two terms of functional $F[v]$ describe the short-term interactions between the diblock copolymers, and the last term (nonlocal term) describes the long-range interactions. ϵ is a relatively small parameter to describe the thickness of the propagating front, and σ is inversely proportional to the square of the degree of polymerization. It is a measure of the connectivity between the two polymers that constitute the copolymer chain. To describe the phase-separated structure of the diblock copolymers under three-dimensional confinement, Avalos *et al.* [4, 5] added a new order parameter u to the O-K model to describe the macroscopic phase separation of the system. The free energy is expressed as follows:

$$\begin{aligned} F[u,v]&=\int_\Omega \left\{ \frac{\epsilon_u^2}{2}|\nabla u|^2+\frac{\epsilon_v^2}{2}|\nabla v|^2+W(u,v)+\frac{\sigma}{2}|(-\Delta)^{-\frac{1}{2}}(v-\bar{v})|^2 \right\} d\mathbf{x},\\ W(u,v)&=\frac{1}{4}(u^2-1)^2+\frac{1}{4}(v^2-1)^2+\alpha uv+\beta uv^2+\gamma u^2 v, \end{aligned}$$

where α,β,γ are coupling parameters.

For the phase-separated structures of diblock copolymers under three-dimensional confinement, there have been many related studies on both physical experiments and