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Theoretical modeling and simulations of self-assembly of copolymers in solution

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ABSTRACT

Self-assembly of copolymers in solution is a promising way to prepare novel materials. An accurate control over the self-assembly of copolymers in solution requires a profound understanding about the related thermodynamic rules and kinetic mechanisms. Theoretical modeling and simulation play an increasingly important role in characterizing the structure details and the formation process of polymer assemblies. In this review, we first introduce theoretical modeling and simulation methods that have been applied to investigate the self-assembly of copolymers in solution, including particle-based methods, field-theoretical methods and hybrid modeling methods Then, the application of these methods for the self-assembly of linear block copolymers in solution is highlighted, including the thermodynamic rules and kinetic mechanisms underlying the formation of self-assembled structures. Furthermore, the simulation works of the self-assembly of branched copolymer systems, including graft copolymers, star-like copolymers, dendritic copolymers and bottle-brush copolymers, are addressed. In addition to the one-component polymer systems, simulation investigations of polymer mixture systems are discussed, both the polymer/polymer systems and polymer/nanoparticle systems are considered. Finally, perspectives on the theoretical modeling and simulation in the field of self-assembly of copolymers in solution are presented in the section of concluding remarks and outlook.

Contents

Abbreviations: ADR, Adriamycin; BD, Brownian dynamics; CG, Coarse-grained; CMC, Critical micelle concentration; CUDA, Compute unified device architecture; DDFT, Dynamic density functional theory; DFT, Density functional theory; DLS, Dynamic light scattering; DMFT, Dynamic mean field theory; DPD, Dissipative particle dynamics; EPD, External potential dynamics; GPU, Graphics processing unit; GROMACS, Groningen machine for chemical simulations; HOOMD, Highly optimized object-oriented many-particle dynamics; HPF, Hybrid particle-field; HPH, Solvent-(phobic-philic-phobic) type of triblock copolymer; HS, Hubbard-Stratonovich; LAMMPS, Large-scale atomic/molecular massively parallel simulator; MC, Monte Carlo; MD, Molecular dynamics; MMA, Multimicelle aggregates; MPI, Message passing interface; MV, Multilamellar vesicle; NAMD, Nanoscale molecular dynamics; OpenCL, Open computing language; P2MVP, Poly(2-methylvinylpyridinium iodide); P2VP, Poly(2-vinylpyridine); PAA, Poly(acrylic acid); PAAm, Poly(acryl amide); PB, Polybutadiene; PBLG, Poly(γ-benzyl-L-glutamate); PEE, Polyethylethylene; PEG, Poly(ethylene glycol); PEHA, Poly(2-ethylhexyl acrylate); PEO, Poly(ethylene oxide); PFDA, Poly(1H,1H,2H,2H-perfluorodecyl acrylate); PHH, Solvent-(philic-phobic-phobic) type of triblock copolymer; PHP, Solvent-(philic-phobic-philic) type of triblock copolymer; PLA, Polylactide; PLGA, Poly(L-glutamic acid); POEGA, Poly(oligoethylene glycol acrylate); PPO, Poly(propylene oxide); PS, Polystyrene; PSCF, Polymer self-consistent field; μ-EOF, Poly(ethylethylene-*arm*-ethylene oxide-*arm*-perfluoropropylene oxide); SANS, Small-angle neutron scattering; SAXS, Small-angle X-ray scattering; SCFT, Self-consistent field theory; SMA, Small micelle aggregate; UMA, Unimolecular micelle aggregate.

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1. Introduction

Self-assembly is a spontaneous organization of components driven by enthalpic and entropic effects [1]. Nature fascinates its self-assembled structures with rich functionality, stimulating scientists from polymer areas to make efforts on self-assembly researches. In bulk, a variety of microstructures, such as lamellae, cylinders, spheres and gyroids, can be formed through the microphase separation between different blocks of copolymers. While in solution, the self-assembly of copolymers involves not only the microphase separation between different blocks but also the macrophase separation between solvents and copolymers. And the incompatibility between solvents and copolymer blocks plays a crucial role in determining the morphology and the formation pathway of the self-assembled structures. Various microstructures such as micelles and vesicles can be obtained by the self-assembly of copolymers in solution [2,3], that provides advanced strategies to mimic the self-assembly processes happened in organisms and prepare functional materials. For example, the micelles self-assembled from poly(ethylene glycol)-*b*-poly(aspartate-hydrazone-adriamycin) (PEG-*b*-p(Asp-Hyd-ADR)) are used to deliver the anticancer drug ADR [4], and the vesicles formed from poly(styrene-*b*-acrylic acid) (PS-*b*-PAA) are suggested as organelle-like nanoreactor for bovine pancreas trypsin [5]. Benefiting from the development of the synthetic chemistry of macromolecules, great progress has been made in this field over past decades. However, the rapid development of synthetic chemistry also brings a larger space for polymer design, and the search of the preparation condition for desired self-assembled structures is more empirical than before. To prepare advanced materials through "bottom-up" approaches and explain the self-assembly processes happened in organisms, an in-depth understanding of the principles underlying the self-assembly of copolymers in solution is necessary.

The self-assembly of copolymers in solution is influenced by a large quantity of controlling factors, such as the rigidity of blocks, the selectivity of solvents for different blocks and the molecular architecture of copolymers, etc. From the viewpoint of experimentalists, it is still a challenge to gain insights into the formation principles of the self-assembled structures. Therefore, the precise preparation and rigorous control of the desired self-assembled structures is still beyond our ability. The theoretical modeling and simulation techniques have already proven to be powerful in studying the thermodynamics and kinetics of the self-assembly of copolymers in bulk [6]. Compared with copolymers in bulk, the self-assembly of copolymers in solution is complicated due to the addition of solvents, that makes the modeling of simulations more challenging. As an example, for the simulation of triblock copolymers, three additional interaction parameters need to be considered if the copolymer system is in solution rather than in bulk. Another roadblock to the theoretical simulation of copolymers in solution is the computing resource. For copolymers in bulk, it is efficient to perform the simulations in cells containing microstructures with one or two periodicities. However, for copolymer solutions, the simulation box should be sufficient large to simulate the equilibrium assemblies and ensure the dilute condition. Fortunately, the development of simulation methods, especially the mesoscopic methods, and the upgrade of computer hardware have enabled us to simulate the self-assembly of copolymer solutions. From these aspects, the theoretical modeling and simulation can provide effective approaches to understand the influences of individual factors on the self-assembly of copolymers in solution and distinguish the thermodynamic stable and metastable structures [7]. The aim of this review is to summarize the recent progress in theoretical simulations regarding the self-assembly of copolymers in solution and then provide a guidance for the experiments in this field.

The present review is organized as follows: In Section 2, the theoretical simulation methods used for investigating the self-assembly of copolymer solutions, including particle-based methods, field-theoretic methods and hybrid modeling methods, are introduced. In this section, we do not propose to offer the detailed description of these simulation methods, but to provide the basic principles, advantages and limitations of them. In Sections 3 and 4, the simulation investigations about the self-assembly behaviors of linear block copolymers and graft copolymers in solution are reviewed, respectively. Both the thermodynamics and the formation kinetics of the self-assembled structures are discussed. In Section 5, the simulation studies about the self-assembly of copolymers with complex architectures including the star-