Journal of Colloid and Interface Science 526 (2018) 75–82

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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

Regular Article

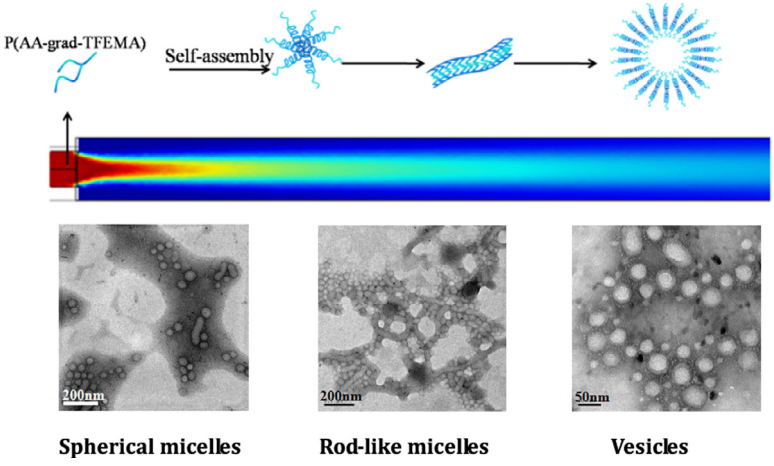
Self-assembly of fluorinated gradient copolymer in three-dimensional co-flow focusing microfluidic

Chengzhi Zhu [1], Rongyi Yao [1], Yanjun Chen *, Mengran Feng, Shuai Ma, Chaocan Zhang

School of Material Science and Engineering, Wuhan University of Technology, Wuhan 430070, China

GRAPHICAL ABSTRACT

The gradient copolymers formed different aggregates with various morphologies by 3D co-flow focusing microfluidic technique.



ARTICLE INFO

Article history:
Received 24 September 2017
Revised 13 April 2018
Accepted 17 April 2018
Available online 18 April 2018

Keywords:
Gradient copolymer
Self-assembly
Co-flow microfluidic
Simulation

ABSTRACT

Hypothesis: The microfluidic technology can drive molecules to organize into aggregates with nano-structures, and gives a possibility to control aggregate morphologies by adjusting hydrodynamic parameters of microfluidics. COMSOL Multiphysics is a useful software to simulate the mixing situation of solutions in microfluidic. Here, experiments and simulation are combined to study the self-assembly of gradient copolymers in the microfluidic device.

Experiments: Fluorinated gradient copolymers self-assembled in a three-dimensional co-flow focusing microfluidic device (3D CFMD). Hydrodynamic parameters of 3D CFMD were adjusted to control morphologies and the sizes of copolymer aggregates. A simulation software, COMSOL Multiphysics, was used to simulate the mixing and diffusion of outer phase stream and inner phase stream to explore the mixing kinetics of two streams in the microchannels.

Findings: 3D CFMD offered a novel platform for the continuous and controllable self-assembly of fluorinated gradient copolymer. Various morphologies of copolymer aggregates were obtained in 3D CFMD,

* Corresponding author.
E-mail address: yanjunchen@whut.edu.cn (Y. Chen).
[1] These two authors have the same contribution to this paper.

https://doi.org/10.1016/j.jcis.2018.04.076

but just spherical micelles were formed by a traditional solvent-inducing method. The flow velocity, initial water content of outer-phase stream, and the copolymer concentration of inner-phase stream had great effects on the morphology and size of copolymer aggregates. The simulation results made us a better understanding on the microfluidic self-assembly.

1. Introduction

Recently, the self-assembly of amphiphilic copolymers has been an attractive research field because a range of self-assembled aggregates with interesting morphologies (e.g., micelles, cylinders, and vesicles). These aggregates always have core-shell structures and condition sensitivities, such as pH-sensitivity, so they have many promising applications in biomedicine, catalysis, drug loading and controlled release [1–7]. Among amphiphilic copolymers, block copolymers (diblock or triblock) and their self-assembly have been extensively studied [8–11], but only a few reports focused on the self-assembly of gradient copolymers [12,13]. Interestingly, aggregates of gradient copolymers have their own characters, such as inherent thermosensitivity and outstanding stimuli-responsiveness [14–16].

The direct dissolving method and the solvent inducing method are conventional ways for amphiphilic copolymers to self-assembly. In these methods, the morphology and size of self-assembled copolymer aggregates mainly rely on chemical parameters, such as copolymer structure, solvent component, water content, and salt acid addition [17–21]. Recently, a microfluidic technology has been utilized for the self-assembly of amphiphilic copolymers, which is based on the manipulation of external forces, such as interfacial forces and shear forces. The emergence of external forces can drive molecules to organize into nano-structures [22,23], and it also gives a possibility to get different self-assembled morphologies by adjusting hydrodynamic parameters of microfluidics, such as the flow velocities of streams, the mixing velocity [24–28].

Two-dimensional (2D) co-flow focusing microfluidics, as a hydrodynamic flow focusing geometry, are always used in microfluidic self-assembly. For example, Wang et al. used a 2D segmented gas-liquid microfluidic to self-assemble block copolymers, and successfully controlled the size and the morphology of self-assembled structures [22,23]. He et al. fabricated aggregates of amphiphilic nanoparticles with various sizes by changing the flow velocity in a 2D focusing microfluidic device [27]. However, for 2D co-flow focusing microfluidics, the polymers in the central stream is only focused in the horizontal dimension, which can encounter several problems [29–31], such as the molecule adhesion on the channel walls, the clogging of the channels due to the precipitation of polymers, and the non-uniform solvent/non-solvent exchange in the vertical direction. It should be noted that the three-dimensional (3D) co-flow focusing offers an opportunity to solve these problems, because 3D co-flow focusing sheaths a solution into a cylindrical core at the center of the channel, and a polymer solution are isolated from the channel walls to preventing aggregation and clogging [32,33]. In addition, the 3D co-flow focusing geometry can be easily realized by a capillary microfluidic device which just needs to assemble two quartz capillaries on a coaxial direction. Therefore, we focus on the 3D co-flow focusing microfluidic, which has not been applied on the self-assembly of amphiphilic gradient copolymers.

In our previous studies, a gradient copolymer of acrylic acid and 2,2,2-Trifluoroethyl methacrylate (coded as P(AA-grad-TFEMA)) has been synthesized by a reversible addition-fragmentation chain transfer (RAFT) polymerization. Interestingly, this fluorinated gradient copolymer can form spherical micelles in selective solvent (e.g. water) [34,35]. Except spherical micelles, micelles with other morphology have different applications. For example, vesicles can be used as nanoscale carriers and the delivery of both hydrophobic and hydrophilic compounds [22]. Therefore, how to obtain other morphologies of the self-assembled aggregates deserves further studies. In this paper, we describe a systematic investigation of a microfluidic self-assembly of P(AA-grad-TFEMA) using a 3D co-flow focusing microfluidic device (3D CFMD), as shown in Fig. 1. Copolymer aggregates with controlled morphologies and sizes are expected to be obtained by adjusting hydrodynamic parameters of 3D CFMD. Off-chip analysis of self-assembled aggregates is performed using transmission electron microscopy (TEM). COMSOL Multiphysics is used to simulate the mixing situation of the inner-phase stream containing gradient copolymer and the outer-phase stream in the microchannels. Experimental results and simulation results are combined to analyze the self-assembly process of gradient copolymers in the microfluidic devices. This work is the first example of efficient use of 3D co-flow focusing microfluidic in the self-assembly of gradient copolymers. It will be a novel strategy to control the size and morphology of aggregates of gradient copolymers. Moreover, this strategy can be suggested to apply for the self-assembly of other gradient copolymers.

2. Materials and methods

2.1. Materials

Acrylic acid (AA, Sinopharm Chemical Reagent Co., Ltd.) were distilled under reduced pressure before use. 2,2,2-Trifluoroethyl methacrylate (TFEMA, Harbin Xeogia Fluorine-silicon Material Co., Ltd., China), 4,4′-Azobis (4-cyanovaleric acid) (V501, Aldrich) and 1,4-dioxane (Sinopharm Chemical Reagent Co.,Ltd., china) were used as received. RAFT agent was synthesized as detailed by Ferguson et al. [36]. Deionized water was used for all reactions. The quartz glass capillaries were purchased from Zhong Cheng Quartz Glass Products Co., Ltd (Beijing, China). The glass capillary dimensions are listed in Table 1.

2.2. Fabrication of co-flow focusing microfluidic devices

The microfluidic device consists of a circular quartzitic capillary nested within a square quartzitic capillary. To make sure the co-flow focusing geometry, the inner side length of the outer square capillary is equal to the outer diameter of the inner circular capillary. A PTFE tube and a PU tube are respectively connected with the circular capillary and the square capillary, in order to conveniently transport fluids.

2.3. Synthesis and characterization of P(AA-grad-TFEMA)

Typically, 0.469 g (6×10^{-4} mol) RAFT agent was dissolved in 32.8 g deionized water under magnetic stirring. After deoxygenation by bubbling with nitrogen for 15 min, 2.88 g (4×10^{-2} mol) AA and 5.04 g (3×10^{-2} mol) TFEMA were added to the solution and mixed well. Reaction system was heated in a water bath to