Journal of Colloid and Interface Science 336 (2009) 162–170

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Effects of surface wettability and roughness of microchannel on flow behaviors of thermo-responsive microspheres therein during the phase transition

Ming-Yu Zhou, Rui Xie, Ya-Lan Yu, Gang Chen, Xiao-Jie Ju, Lihua Yang, Bin Liang, Liang-Yin Chu *

School of Chemical Engineering, Sichuan University, Chengdu, Sichuan 610065, China

ARTICLE INFO

Article history:
Received 21 January 2009
Accepted 20 March 2009
Available online 5 April 2009

Keywords:
Thermo-responsive microspheres
Flow characteristics
Phase transition
Surface wettability
Surface roughness

ABSTRACT

The flow characteristics of monodisperse thermo-responsive poly(*N*-isopropylacrylamide) (PNIPAM) microspheres during the phase transition in microchannels with different surface wettabilities and roughnesses are investigated systematically. Glass microchannels are modified by hydroxylation treatment to achieve hydrophilic surface, by self-assembly of chlorotrimethylsilane to realize hydrophobic surface, and by coating with silica nanoparticles to generate rough surface. The phase transition of PNIPAM microspheres in microchannels is induced by local heating. The results show that the surface wettability and roughness of microchannel significantly affect the flow behaviors of PNIPAM microspheres during the phase transition. It is much easier for the PNIPAM microspheres in microchannel with hydrophobic surface to stop right after the phase transition than those in microchannel with hydrophilic surface, and it is also much easier for the PNIPAM microspheres in microchannel with rough surface to stop right after the phase transition than those in microchannel with smooth surface. These results indicate that hydrophobic and rough surface properties of the microchannel can enhance the site-specific targeting of PNIPAM microspheres caused by the phase transition. The results in this study provide valuable information for the application of thermo-responsive drug carriers in site-specific targeting therapy.

1. Introduction

Environmental stimuli-sensitive microspheres are getting more and more attention from both technological and scientific aspects, because of their promising application potentials in the fields of controlled drug delivery [1–6], enzyme immobilization [7–9], chemical separation [10–13], catalysis [14–16], sensor [17–20], and so on. Such microspheres can response to fluctuations in environmental conditions including temperature [21–29], pH [30–33], magnetic field [34–36] and other stimuli signals [37,38]. There are many cases where environmental temperature fluctuations either occur naturally or are artificially designed and controlled. Thus, much recent attention has been focused on thermo-responsive microspheres.

For applications of thermo-responsive microspheres, one important factor is the kinetic characteristics of their movement. However, there are very few reports on their movement characteristics during their phase transition processes. In our previous reports, we investigated the flow and aggregation behaviors of millimeter-scale thermo-responsive spheres in a transparent Pyrex glass pipe with an inner diameter of 6.4 mm [39], and also the flow and aggregation behaviors of thermo-responsive microspheres in unmodified glass microchannel with an inner diameter of 520 μm [40]. However, the effects of surface wettability and roughness of microchannel on flow behaviors of thermo-responsive microspheres during the phase transition have not been investigated yet. For the patients with diabetes or hyperlipidemia [41–43], hydrophobic fattiness in the blood can easily deposit onto the inner surface of blood vessels, which turns the inner surface of blood vessels from hydrophilic and smooth to hydrophobic and rough. Therefore, for thermo-responsive microspheres to achieve applications as thermo-responsive drug carriers specifically targeting such pathologically changed sites in blood vessels, it is necessary and essential to study the flow and aggregation behaviors of such thermo-responsive microspheres in the microchannel with different surface wettabilities and roughnesses.

Here we report our investigations on how surface wettability and roughness of microchannel affect the flow behaviors of thermo-responsive microspheres during the phase transition. In this study, we achieve different surface properties of glass microchannels by modifying their inner surfaces using the following three methods: by hydroxylation treatment to achieve hydrophilic surface, by self-assembly of chlorotrimethylsilane to realize hydrophobic surface, and by coating with silica nanoparticles to generate rough surface [44]. The thermo-responsive microspheres in this study are monodisperse poly(*N*-isopropylacrylamide) (PNIPAM) microspheres prepared by utilizing a simple microfluidic device [40,45]. The phase transition of PNIPAM microspheres in microchannels is induced by local heating. Flow and aggregation

* Corresponding author. Fax: +86 28 8540 4976.
E-mail address: chuly@scu.edu.cn (L.-Y. Chu).

0021-9797/$ - see front matter © 2009 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2009.03.048

behaviors of monodisperse PNIPAM microspheres in differently modified glass microchannels are recorded by a digital pickup camera equipped on an optical microscope. We characterize the thermo-responsive phase transition of the PNIPAM microspheres by measuring their temperature-dependent volume variation. Using such a simple strategy, we systematically investigated how changes in surface wettability and roughness of microchannel affect the average velocity of fluid phase and the behaviors of PNIPAM microspheres in the following four aspects: aggregation configuration, flow velocity variation during the phase transition, stop probability, and stop position inside the microchannels.

2. Materials and methods

2.1. Materials

N-Isopropylacrylamide (NIPAM) was kindly provided by Kohjin Co., Japan, and was used after being further purified by recrystallization for three times in the mixture of hexane and acetone. *N*,*N*′-Methylene-bis-acrylamide (MBA) and ammonium persulfate (APS) were purchased from Chengdu Kelong Chemicals (Chengdu, China). Tetramethylethylenediamine (TEMED) was purchased from Tianhua Chemicals (China). Kerosene, ethanol, hexane, NH_4OH (30% in water), sulfuric acid (98% (w/w)), hydrogen dioxide, chlorotrimethylsilane (CTMS), tetraethylorthosilicate (TEOS), sodium dodecyl sulfate (SDS), glass capillaries with an inner diameter of 520 μm used as microchannels were all purchased from Chengdu Sitong Chemicals, China. Polyglycerol polyricinoleate (PGPR 90) was purchased from Danisco, Denmark. All reagents were used as supplied without further purification unless otherwise specified.

2.2. Modification of inner surface of glass microchannel

The inner surfaces of glass microchannels were modified using the following three methods: by hydroxylation treatment to achieve hydrophilic surface, by self-assembly of chlorotrimethylsilane to realize hydrophobic surface, and by coating with silica nanoparticles to generate rough surface via sol–gel method [44] (Fig. 1).

Hydroxylation treatment was carried out by immersing unmodified glass microchannels into piranha solution (70 vol% of sulfuric acid and 30 vol% of hydrogen dioxide) at 90 °C for 30 min. Then, we picked the glass microchannels out, washed them with de-ionized water to remove residual piranha solution, and dried them by blowing with nitrogen gas. After the hydroxylation treatment, the inner surfaces of glass microchannels were modified to be hydrophilic and smooth.

In order to obtain hydrophobic and smooth inner surface, we employed the self-assembly of chlorotrimethylsilane to modify the inner surface of glass microchannel. Briefly, we immersed one of the microchannels pretreated by hydroxylation treatment into 0.2 M of CTMS hexane solution at room temperature for 2 h and then cleaned and dried it as in the hydroxylation treatment.

To generate rough inner surface of glass microchannel, we used sol–gel method to coat the surface with silica nanoparticles. The sol was prepared in two steps: firstly, adding 3 ml of NH_4OH (30% in water) into 50 ml ethanol and stirring the mixture vigorously at 60 °C for 30 min; secondly, adding 3 ml TEOS dropwise into the NH_4OH/ethanol mixture and stirring for another 90 min. The prepared sol consists of monodisperse spherical silica nanoparticles with diameter of about 100 nm [46]. We injected the prepared sol into some of the microchannels pretreated by hydroxylation treatment and then heated the channels at 210 °C for 1 h. The heating helps remove the solvent in injected sol and, as a result, a layer of SiO_2 nanoparticles was formed on the inner surfaces of microchannels. We subsequently immersed the microchannels into H_2O_2 solution at room temperature for 30 min in order to generate the hydroxyl groups on their inner surfaces. Thus, the inner surfaces of the glass microchannels have been modified to be hydrophilic and rough.

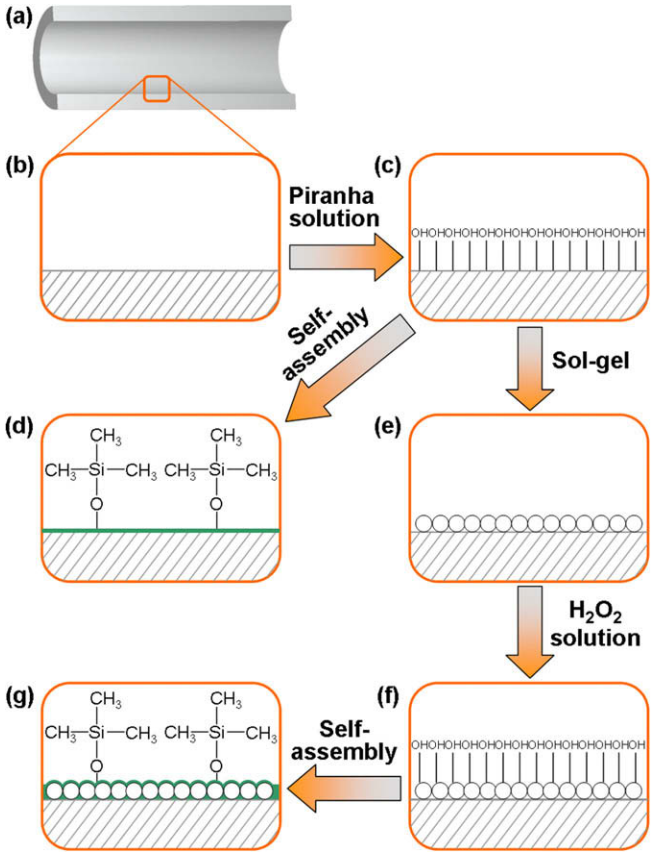

Fig. 1. Schematic illustration of the process of surface modification of glass microchannel. (a) Unmodified glass microchannel; (b) inner surface of unmodified glass microchannel; (c) hydrophilic and smooth surface of glass microchannel; (d) hydrophobic and smooth surface of glass microchannel; (e) rough surface of glass microchannel with a layer of silica nanoparticles; (f) hydrophilic and rough surface of glass microchannel; and (g) hydrophobic and rough surface of glass microchannel.

To prepare hydrophobic and rough inner surface, we employed the self-assembly of chlorotrimethylsilane. Briefly, we further immersed one of the glass microchannels with hydrophilic and rough inner surfaces into 0.2 M of CTMS hexane solution at room temperature for 2 h.

2.3. Characterization of the wettability and roughness of modified glass microchannels

The wettability of modified glass microchannels can be determined by characterizing aqueous static contact angle (θ) of their inner surfaces. The aqueous static contact angle was typically calculated by using following formula [47]:

$$\cos\theta = \frac{rh\rho g}{2\sigma} \tag{1}$$

where r is the inner radius of the modified microchannel (m), h is the liquid-meniscus height (m), ρ is the liquid density (kg/m^3), and σ is the liquid surface tension coefficient (N/m). At constant temperature, water has constant ρ (1000 kg/m^3) and σ (0.073 N/m). By assuming r to be the same as the inner radius of unmodified microchannel (0.00026 m), the aqueous static contact angles of microchannel inner surfaces can be determined by measuring water-meniscus heights within the microchannels.