Journal of Colloid and Interface Science 377 (2012) 137–144

Contents lists available at SciVerse ScienceDirect

Journal of Colloid and Interface Science

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Nano-gel containing thermo-responsive microspheres with fast response rate owing to hierarchical phase-transition mechanism

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ARTICLE INFO

Article history:
Received 17 January 2012
Accepted 4 April 2012
Available online 11 April 2012

Keywords:
Thermo-responsive microspheres
Rapid response
Composite structure
Hierarchical phase-transition
Poly(*N*-isopropylacrylamide)

ABSTRACT

A new strategy is developed in this study to achieve thermo-responsive microspheres with fast response rates by designing a hierarchical phase-transition mechanism. The proposed thermo-responsive microspheres are composed of poly(*N*-isopropylacrylamide-*co*-acrylic acid) (PNA) microsphere matrixes and embedded poly(*N*-isopropylacrylamide) (PNIPAM) nano-gels, which have different volume phase-transition temperatures (VPTTs). The VPTT of PNIPAM nano-gels ($VPTT_1$) is lower than that of PNA microsphere matrixes ($VPTT_2$). Upon heating-up, the temperature increases across the $VPTT_1$ first and then the $VPTT_2$, as a result the PNIPAM nano-gels shrink earlier than the PNA microsphere matrixes. Upon cooling-down, the temperature decreases across the $VPTT_2$ first and then the $VPTT_1$, as a result the PNA microsphere matrixes swell earlier than the PNIPAM nano-gels. Consequently, large amounts of voids and channels form around the nano-gels inside the microsphere matrixes when the temperature changes across the range between $VPTT_1$ and $VPTT_2$, which are beneficial to the enhancement of water transport rate inside the microsphere matrixes. The experimental results show that, compared with normal homogeneous PNA (N-PNA) microspheres, the nano-gel containing PNA (C-PNA) microspheres exhibit remarkably fast response rate due to the hierarchical phase-transition mechanism attributed to different VPTT values of the embedded nano-gels and the microsphere matrixes.

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1. Introduction

Environmental stimuli-responsive microspheres can swell or shrink significantly by taking in or expelling large amounts of water or solvent in response to environmental changes, such as temperature, pH, ionic strength, light, electric, or magnetic fields [1–3]. Such responsive swelling/shrinking behaviors make those microspheres promising in numerous applications [4–6], including drug delivery systems [7–11], chemical separations, and sensors [12–14] and gene carriers [15].

Because temperature change is one of the most important factors in the natural environment and can be easily designed and artificially controlled, much attention has been focused on thermo-responsive functional materials. Poly(*N*-isopropylacrylamide) (PNIPAM) is one of the most popular thermo-responsive materials [5,16]. It has a transition temperature or volume phase-transition temperature (VPTT) around 33 °C [1,17,18], which is close to the physiological temperature. At temperatures below the VPTT, PNIPAM hydrogels keep abundant water within their matrixes and exhibit swollen states; while at temperatures above the VPTT, PNIPAM hydrogels expel water from their matrixes and dramatically shrink. PNIPAM hydrogels undergo a completely reversible swelling/shrinking volume transition in response to temperature change across the VPTT. So, PNIPAM hydrogels are highly potential in various applications such as controlled release systems, smart actuators, and on–off switches [19,20]. In most cases, fast response rates are desired for the responsive materials. For example, ideal drug delivery systems are expected to control the release of drugs in a site-specific and rate- and time-programmed manner to ensure targeting and security. Therefore, stimuli-responsive material systems with fast response rate are more preferable. However, homopolymerized PNIPAM hydrogels have limited response rate due to the resistance of water molecules diffusing through the cross-linked polymer networks. To improve the response rate of PNIPAM-based hydrogels, several approaches have been reported as follows.

One simple strategy to speed up the response kinetics of hydrogels is diminishing the dimension of hydrogels [21,22], because the swelling and shrinking rates (*i.e.*, response rate) of hydrogels have been verified to be inversely proportional to the square of a linear dimension of the hydrogels [23,24]. So, the smaller the hydrogel dimension is, the faster the response rate. The bulk homogenous hydrogels take a long time to reach the equilibrium swelling/shrinking state (from several hours to days), whereas the hydrogel microspheres can achieve the equilibrium swelling/shrinking state much faster because of the small size and large surface area.

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0021-9797/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcis.2012.04.009

Another effective method to accelerate the response rate is chemically grafting linear side chains onto the cross-linked polymeric hydrogel networks [25–29]. Such hydrogels are called comb-type grafted hydrogels. Attributed to the freely mobile chains grafted on the backbones, the molecular mobility of the hydrogel networks is improved and therefore the response rate of the hydrogel is enhanced.

Another simple method to improve the response rate of hydrogels is fabricating porous structures in the hydrogels. When the temperature increases above the VPTT, the periphery of the hydrogels responds to the environmental stimuli prior to the interior and thus a dense polymer layer typically forms on the surface of homogenous hydrogels. The so-called "skin effect" significantly decelerates the shrinking of hydrogels because the dense "skin" layer becomes less permeable for water transport. Therefore, PNIPAM hydrogels with porous structures are developed to provide more water channels and to eliminate the "skin effect". The incorporation of pore-forming agents is often used to prepare the porous hydrogels. The pore-forming agents are either organic linear polymers and microspheres such as poly(ethylene glycol) [30,31], poly(ethylene oxide) [32], dodecyl dimethyl benzyl ammonium bromide [33], polystyrene microspheres [34] and other polymers [35], or inorganic compounds such as silica particles [36–38]. To avoid the subsequent extraction of the pore-forming agents, some methods are also developed to prepare porous hydrogels without adding of pore-forming agents, including freeze-drying [36,39], hydrogen bond interaction [40], and phase separation [41,42].

Recently, a type of PNIPAM nanoparticle-incorporated PNIPAM hydrogels with fast shrinking kinetics has been reported [43]. Because the response rate is inversely proportional to the square of a linear dimension of the hydrogels, the embedded PNIPAM nanoparticles shrink much faster than the bulky PNIPAM hydrogel when the temperature increases across the VPTT; therefore, water channels form between the PNIPAM hydrogel matrixes and the PNIPAM nanoparticles to promote the water expelling from PNIPAM hydrogels. As a result, the response rate of the PNIPAM nanoparticle-incorporated PNIPAM hydrogels is faster than that of the homogeneous PNIPAM hydrogels upon heating-up. However, the fast response rate of the PNIPAM nanoparticle-incorporated PNIPAM hydrogels could be achieved merely in heating-up process but not in cooling-down process. When the temperature decreases across the VPTT, because the response rate of PNIPAM nanoparticles is always faster than that of the bulky PNIPAM hydrogels, the fast swelling of nanoparticles in the bulky hydrogels will try to clog the water channels inside the hydrogels and therefore could not contribute to the fast swelling of the bulky hydrogels.

In this study, a new strategy is developed to achieve fast response rate of PNIPAM-based microspheres by designing a hierarchical phase-transition mechanism. The proposed PNIPAM-based microspheres are composed of poly(*N*-isopropylacrylamide-*co*-acrylic acid) (PNA) microsphere matrixes and embedded PNIPAM nano-gels, which have different volume phase-transition temperatures (the $VPTT_1$ of PNIPAM nano-gels is lower than the $VPTT_2$ of PNA microsphere matrixes, as shown in Fig. 1). Upon heating-up, the temperature increases across the $VPTT_1$ first and then the $VPTT_2$. When the temperature increases to the range from $VPTT_1$ to $VPTT_2$, the PNIPAM nano-gels are already in the shrunken state while the PNA microsphere matrixes are still in the swollen state. As a result, large amounts of voids and channels form around the nano-gels inside the microsphere matrixes due to the shrinkage of nano-gels (Fig. 1c). Consequently, the porous structure of microsphere matrixes will facilitate the water to escape from the microsphere matrixes when the temperature increases to higher than the $VPTT_2$ (Fig. 1c and d). More importantly, the composite microspheres can also exhibit fast response rate upon cooling-down. When the temperature decreases to the range from $VPTT_2$ to $VPTT_1$, the PNA microsphere matrixes are already in the swollen state while the PNIPAM nano-gels are still in the shrunken state. So, large amounts of voids and channels also form around the nano-gels inside the microsphere matrixes during the cooling-down process (Fig. 1c), and the porous structure of microsphere matrixes will enhance the water intake from the environment for the fast swelling of the microspheres. The hierarchical phase-transition of the microspheres, which is achieved due to the different VPTTs of embedded nano-gels and the microsphere matrixes, leads to rapid response rate upon either the heating-up or the cooling-down process. To obtain the different VPTTs, hydrophilic monomer acrylic acid (AAc) is introduced and PNA homogenous microsphere matrixes are prepared, while nano-gels are still made of PNIPAM. The nano-gel containing PNA (C-PNA) microspheres consist of homogenous PNA microsphere matrixes and embedded PNIPAM nano-gels, and they are expected to be featured with fast response rate to temperature stimuli compared with normal homogenous microspheres. The morphology, and the equilibrium and dynamic volume shrinking as well as swelling behaviors of the prepared C-PNA microspheres will be investigated systematically in this study. Such C-PNA microspheres would be highly attractive for developing micro-scale responsive hydrogel systems with fast response characteristics.

2. Experimental

2.1. Materials

N-isopropylacrylamide (NIPAM) monomer was kindly provided by Kohjin Co. Ltd., Japan, and used after purification by recrystallization twice in hexane and acetone and then dried in vacuum at room temperature. Comonomer acrylic acid (AAc), crosslinker *N*,*N*-methylenebisacrylamide (BIS), accelerator *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED), initiator ammonium persulfate (APS), and isopropanol were purchased from Chengdu Sitong Chemicals, China. Polyglycerol polyricinoleate (PGPR 90) was purchased from Danisco Co. Ltd., Denmark. Edible soybean oil (Class A refining, Arawana®, Yihai Kerry Oils & Grains (Sichuan) Ltd., China) was bought from supermarket. Deionized water (18.2 MΩ, Millipore, Milli-Q) was used in the experiments.

2.2. Synthesis of PNIPAM nano-gels

PNIPAM nano-gels were prepared by precipitation polymerization [44,45]. Before starting the experiment, 350 ml of deionized water was bubbled with pure nitrogen for 10 min and heated to 65 °C. Then, NIPAM (1.5 g) and BIS (the mass ratio of [BIS]/[NIPAM] is 1:10) were dissolved into the deionized water, and the nitrogen bubbling was continued for another 5 min. As soon as 1 ml of APS aqueous solution (0.105 g APS) was added to the monomer solution, the polymerization was initiated and lasted 4 h under stirring (300 rpm) at 65 °C. The resultant PNIPAM nano-gels were purified five times by centrifugation (Biofuge Primo R, SORVALL, Germany; 8000 rpm, 15 min each time) to remove the unreacted monomers, initiator, and crosslinker. After purification, the PNIPAM nano-gel suspension was obtained.

2.3. Synthesis of nano-gel containing microspheres

Monodisperse nano-gel containing PNA (C-PNA) microspheres with PNA microsphere matrixes and embedded PNIPAM nano-gels were prepared by using capillary microfluidic technology and emulsion template method. Microfluidic technology can produce emulsions with excellent monodispersity [46–49]. With those monodisperse emulsions as templates, monodisperse micro-

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