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Freezing as a path to build macroporous structures: Superfast responsive polyacrylamide hydrogels

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Abstract

Macroporous polyacrylamide (PAAm) hydrogels were prepared from acrylamide monomer and *N*,*N*′-methylene(bis)acrylamide (BAAm) crosslinker in frozen aqueous solutions. It was found that the swelling properties and the elastic behavior of the hydrogels drastically change at a gel preparation temperature of −6 °C. The hydrogels prepared below −6 °C exhibit a heterogeneous morphology consisting of pores of sizes 10–70 μm, while those formed at higher temperatures have a non-porous structure. PAAm networks with largest pores were obtained at −18 °C. The pore size of the networks increased while the thickness of the pore walls decreased by decreasing the monomer concentration. The hydrogels formed below −6 °C exhibit superfast swelling and deswelling properties as well as reversible swelling–deswelling cycles in water and in acetone, respectively.
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1. Introduction

Responsive hydrogels are soft and smart materials, capable of changing volume and/or shape in response to specific external stimuli, such as the temperature, solvent quality, pH, electric field, etc. [1]. Depending on the design of the hydrogel matrices, this volume change may occur continuously over a range of stimulus values, or, discontinuously at a critical stimulus level. These properties of the hydrogels received considerable interest in last three decades and, a large number of hydrogel-based devices have been proposed, including artificial organs, actuators, and on-off switches. However, the practical design and control of these devices still present some problems. In particular, hydrogel-based devices are limited in their response rate by diffusion processes, which are slow and even slower near the critical point [2]. In order to increase the response rate of hydrogels, several techniques were proposed, such as reducing the size of the gel particles [3], creating dangling chains on the gel samples [4], or, constructing an interconnected pore structure within the hydrogel matrices [5].

As is well known, in sea ice, pure hexagonal ice crystals are formed and the various impurities, e.g., salts, biological organisms, etc. are expelled from the forming ice and entrapped within the liquid channels between the ice crystals [6,7]. This natural principle was used by Lozinsky for the preparation of porous gels [8]. As in nature, during the freezing of a monomer solution, the monomers expelled from the ice concentrate within the channels between the ice crystals, so that the polymerization reactions only take place in these unfrozen liquid channels. After polymerization and, after melting of ice, a porous material is produced whose microstructure is a negative replica of the ice formed [9–12]. Recently, we have shown that by conducting the copolymerization–crosslinking reactions below −8 °C, hydrogels based on 2-acrylamido-2-methylpropane sulfonic acid (AMPS) monomer with superfast swelling properties could be

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obtained [13]. This was achieved by using gelation reactions occurring in the apparently frozen reaction system, which allowed for the formation of a bicontinuous morphology in poly(AMPS) (PAMPS) networks. It was shown that the free water freezing in the gel causes the network chains to gather and condense so that a heterogeneous network forms after removing the ice [13]. The PAMPS network maintains a honeycomb structure upon drying.

In this report, we apply this procedure for the preparation of polyacrylamide (PAAm) hydrogels. The copolymerization–crosslinking reactions of acrylamide (AAm) monomer and *N*,*N*′-methylenebis(acrylamide) (BAAm) crosslinker were carried out in aqueous solutions. We systematically varied the gel preparation temperature, the initial monomer concentration as well as the crosslinker content of the monomer mixture in order to obtain the optimum reaction conditions for the preparation of fast responsive PAAm hydrogels with a two-phase morphology. As will be seen below, PAAm hydrogels prepared below −6 °C swell immediately upon contact with water, regardless of their crosslinker contents. The size-independent superfast swelling and deswelling kinetics of the hydrogels is accounted for by their interconnected pore structure which is stable against the volume changes.

2. Experimental section

2.1. Materials

Acrylamide (AAm, Merck), *N*,*N*′-methylenebis(acrylamide) (BAAm, Merck), ammonium persulfate (APS, Merck), and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED, Merck) were used as received. Stock solutions of APS and TEMED were prepared by dissolving 0.16 g of APS and 0.50 mL of TEMED each in 20 mL of distilled water. Stock solution of BAAm was prepared by dissolving 0.132 g of BAAm in 10 mL of distilled water.

Polyacrylamide (PAAm) hydrogels were prepared by free-radical crosslinking–copolymerization of AAm with BAAm in aqueous solution at various temperatures (T_{prep}) between −25 °C and +25 °C. The initial concentration of the monomer (AAm + BAAm), C_o, as well as the crosslinker ratio X, which is the mole ratio of the crosslinker BAAm to the monomer AAm, was also varied in our experiments. The reaction time was set to 24 h. APS (3.51 mM) and TEMED (0.25 mL/100 mL reaction solution) were used as the redox initiator system. To illustrate the synthetic procedure, we give details for the preparation of hydrogels at $C_o = 5$ w/v% and $X = 1/80$.

AAm (0.4868 g), stock solutions of BAAm (1 mL), TEMED (1 mL), and distilled water (7 mL) were first mixed in a graduated flask of 10 mL in volume. The solution was cooled to 0 °C in ice-water bath, purged with nitrogen gas for 20 min and then, APS stock solution (1 mL) was added. Portions of this solution, each 1.5 mL, were transferred to glass tubes of 4 mm in diameter; the glass tubes were sealed, immersed in a thermostated bath at T_{prep} and the polymerization was conducted for one day. After polymerization, the gels were cut into specimens of approximately 10 mm in length and immersed in a large excess of water to wash out any soluble polymers, unreacted monomers and the initiator.

2.2. Methods

For the equilibrium swelling measurements, hydrogel samples after preparation in the form of rods of 4 mm in diameter and about 10 mm length were placed in an excess of water at room temperature (21 ± 0.5 °C). In order to reach swelling equilibrium, the hydrogels were immersed in water for at least two weeks replacing the water every other day. The swelling equilibrium was tested by measuring the diameter of the gel samples by using an image analyzing system consisting of a microscope (XSZ single Zoom microscope), a CDD digital camera (TK 1381 EG) and a PC with the data analyzing system Image-Pro Plus. The swelling equilibrium was also tested by weighing the gel samples. Thereafter, the equilibrium swollen hydrogel samples in water were carefully deswollen in a series of water–acetone mixtures with increasing acetone contents. This solvent exchange process facilitated final drying of the hydrogel samples. They were then washed several times with acetone and dried at 80 °C to constant weight. The equilibrium volume and the equilibrium weight swelling ratios of the hydrogels, q_v and q_w, respectively, were calculated as

$$q_v = \left(D_w/D_{dry}\right)^3 \tag{1a}$$

$$q_w = \left(m_w/m_{dry}\right) \tag{1b}$$

where D_w and D_{dry} are the diameters of the equilibrium swollen and dry gels, respectively, m_w and m_{dry} are the weight of gels after equilibrium swelling in water and after drying, respectively.

For the deswelling kinetics measurements, the equilibrium swollen hydrogel samples in water were immersed in acetone at 21 °C. The weight changes of the gels were measured gravimetrically after blotting the excess surface solvent at regular time intervals. For the measurement of the swelling kinetics of gels, the collapsed gel samples in acetone were transferred into water at 21 °C. The weight changes of gels were also determined gravimetrically as described above. The results were interpreted in terms of the relative weight swelling ratio $m_{rel} = m/m_w$, where m is the mass of the gel sample at time t. The swelling kinetics measurements were also conducted in situ by following the diameter of the hydrogel samples under microscope using the image analyzing system mentioned above.

Uniaxial compression measurements were performed on equilibrium swollen gels in water. All the mechanical measurements were conducted in a thermostated room of 21 ± 0.5 °C. The stress–strain isotherms were measured by using an apparatus previously described [14]. Briefly, a cylindrical gel sample of 4–8 mm in diameter and 7–15 mm in length was placed on a digital balance (Sartorius BP221S, readability and reproducibility: 0.1 mg). A load was transmitted vertically to the gel through a rod fitted with a PTFE end-plate. The compressional force acting on the gel was calculated from the readings in the

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