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Fast responsive poly(*N*-isopropylacrylamide) hydrogels prepared in phenol aqueous solutions

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Abstract

Fast responsive poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogels with improved properties were prepared in phenol aqueous solutions with different concentrations. Due to the expanded network structure in water, the resulted hydrogels are capable of absorbing a large amount of water, i.e. exhibits a much increased swelling ratio at room temperature. Importantly, the hydrogels demonstrated much faster response rate than that of traditional PNIPAAm hydrogel upon external temperature increase.

Keywords: Poly(*N*-isopropylacrylamide) hydrogel; Temperature sensitive; Volume transition; Response rate

1. Introduction

Poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogel is temperature sensitive in water and exhibits the unique volume transition at temperature around 33 °C, termed as the volume transition temperature (T_{tr}) [1–3]. At a temperature below the T_{tr}, PNIPAAm hydrogel is swollen in aqueous media. When the temperature is raised above the T_{tr}, phase separation occurs and the volume of PNIPAAm hydrogel shrinks dramatically. Due to the special properties, PNIPAAm hydrogel has been widely used for many applications, including macromolecular solution concentrating [4,5], column packing materials for chromatography [6], recyclable absorbents [7] and micro-scale actuators [8]. As a temperature sensitive hydrogel, the response rate upon external temperature changes is critically important, especially in some cases where the fast response rate is necessary when used as artificial organs [9], actuators [8,10] and on–off switches [11]. In order to improve the response dynamics, several strategies were reported during the last decade [12–16]. A widely used method reported involves the use of phase separation technique [12,13] to prepare a heterogeneous structure of the resulting PNIPAAm hydrogel. In this technique, a polymerization temperature above the T_{tr} is necessary for the formation of the heterogeneous matrix in the phase separation

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system. The other commonly used method is the porosigen technique [14–16]. With the presence of a porosigen or pore-forming agent, macroporous PNIPAAm hydrogel, which exhibits fast response upon heating, can be obtained. Recently, several other effective methods were also proposed in our previous investigations [17–20].

In this paper, a new method was employed to improve the response rate of PNIPAAm hydrogels by using phenol aqueous solution as the polymerization solvent. The effect of the phenol concentration on the property of resulting PNIPAAm hydrogels was examined in terms of morphology via scanning electron microscopy (SEM) and swelling capability at room temperature as well as deswelling kinetics upon temperature increase.

2. Experimental

2.1. Materials

N,*N*′-Methylenebisacrylamide (BIS) was purified by ethanol. Phenol, *N*-isopropylacrylamide (NIPAAm), ammonium persulfate (APS) and sodium bisulfite (SBS) were used without further purification.

2.2. Hydrogel preparation

The hydrogels designated as Gel30, Gel50, Gel70, and Gel100 were prepared in aqueous phenol solutions with different concentrations (30, 50, 70 and 100 mM), respectively. Other fabrication conditions are the same. A typical fabrication procedure was depicted as follows. 565 mg (5×10^{-3} mol) monomer NIPAAm, 15.4 mg (1.0×10^{-4} mol) crosslinker BIS and 5.7 mg initiator APS were dissolved in 5 ml of aqueous phenol solution with a certain concentration. Then 2.6 mg of SBS was added and used as the catalyst to accelerate the polymerization. The polymerization was carried out at 18 °C for 30 min. The resulting hydrogel was purified by immersing in distilled water for one week to remove un-reacted chemicals and phenol. The water was replaced 3–4 times every day and the purified hydrogel was stored in distilled water for the characterization. The control hydrogel (CGel) was prepared in pure water with the same recipe and fabrication condition. All the purified hydrogels were cut into disc-like pieces approximately 10 mm in diameter and 4 mm in thickness for further studies.

2.3. FT-IR

The hydrogel samples were analyzed by FT-IR (Perkin Elmer Spectrum One, USA) spectrophotometer. Before the measurement, the originally swollen samples were quickly frozen in liquid nitrogen and further freeze-dried in a Freeze Drier (Labconco CA, USA) for three days to completely remove water.

2.4. Surface morphology observation

Scanning electron microscopy (SEM, Hitachi-X650, Japan) was used to study the surface morphology of the PNIPAAm hydrogels. To prepare samples for SEM, the swollen hydrogels at room temperature (22 °C) were freeze-dried and then sputter coated with gold.

2.5. Measurement of swelling ratio

The swelling ratio of hydrogels was measured gravimetrically after carefully blotting surface water with moistened filter paper in the temperature range from 22 to 50 °C. Hydrogel samples were immersed in distilled water for at least 24 h at each predetermined temperature. The average value of three measurements was taken for each sample, and the swelling ratio (SR) is defined as follows:

$$\text{Swelling ratio} = W_s/W_d,$$

where W_s is the weight of water in swollen hydrogel at the particular temperature (wet weight − dry weight) and W_d is the dry weight of the hydrogel.

2.6. Measurement of deswelling kinetics

The deswelling kinetics of hydrogels was measured gravimetrically at 50 °C. The hydrogel samples were first immersed in distilled water at room temperature until equilibrium was reached. Then, the equilibrated hydrogels were quickly transferred to a water bath at a temperature of 50 °C. At specified time intervals, the samples were removed from the hot water and weighted after wiping off the excess surface water with moistened filter paper. The average value of three measurements was taken for each sample, and the water retention is defined as follows:

$$\text{Water retention} = [(W_t - W_d)/W_s] \times 100,$$

where W_t is the weight of hydrogel at regular time intervals, W_d is the same as above and W_s is the weight of water in swollen hydrogel at 22 °C.

3. Results

3.1. Fabrication of hydrogels

From the procedure of polymerization, it was found that the presence of phenol in the polymerization solvent significantly influenced the formation of PNIPAAm hydrogels. CGel, Gel30 were formed in 2–3 min and appeared to be transparent. Gel50 was generated in about 5 min, while Gel70 and Gel100 were generated in 10 min or more, and all these three samples (Gel50, Gel70 and Gel100) were opaque in appearance. Fig. 1 presents the optical photos of CGel prepared in pure water, Gel50 and Gel100 prepared in phenol aqueous solutions with the concentrations of 50 mM and 100 mM respectively, after the polymerization.

3.2. FT-IR

The FT-IR spectra of PNIPAAm hydrogels are displayed in Fig. 2. The spectra of different hydrogels are similar. Each spectrum shows a broad band in the range of 3100–3700 cm^{-1}, which belongs to N–H stretching vibration. The typical amide I and II bands in the NIPAAm are evident at ~1650 cm^{-1} and 1550 cm^{-1} (bands b and c in Fig. 2). Besides, there is no typical absorbent peak of phenol (~1580 cm^{-1}, ~1500 cm^{-1} stretching vibration of phenyl) in Fig. 2, indicating the phenol was totally removed or the amount of residual phenol was too little to be detected after the purification.

3.3. Surface morphology of hydrogels

SEM micropictures of freeze-dried hydrogels are exhibited in Fig. 3. The surface morphology of CGel and Gel30 is dense and smooth, while the Gel50, Gel70 and Gel100 exhibit a porous microstructure. In comparison with the surface morphology of Gel50 and Gel70, Gel100 exhibits a little constrained network with small pores.

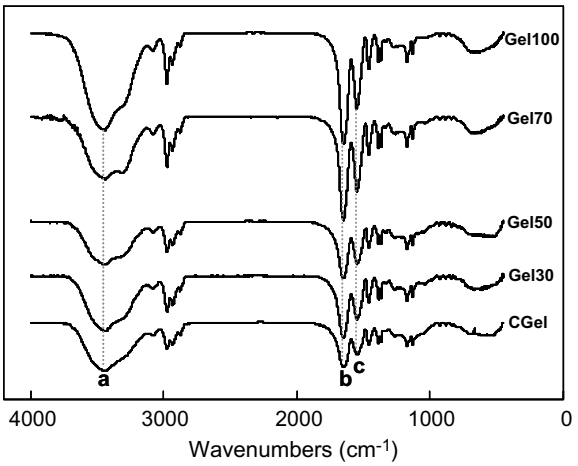

Fig. 2. FT-IR spectra of PNIPAAm hydrogels prepared in pure water (CGel) and phenol aqueous solutions with different concentrations of 30 mM (Gel30), 50 mM (Gel50), 70 mM (Gel70) and 100 mM (Gel100). (a: 3100–3700 cm^{-1}, b: ~1650 cm^{-1} and c: 1550 cm^{-1}).

3.4. Swelling ratio of hydrogels

Fig. 4 indicates the equilibrium swelling ratio of hydrogel in the temperature range from 22 to 50 °C. At room temperature, the equilibrium swelling ratios of the conventional hydrogel (CGel) and Gel30 are almost the same and smaller than the one of the other three. For example, equilibrium swelling ratio of CGel and Gel30 is around 15, while that of Gel50, Gel70 and Gel100 are around 21, 37 and 25 respectively at room temperature.

Upon heating, all the hydrogels exhibit a temperature-stimulant decreasing in swelling ratio, but with different magnitudes of the thermo-induced decreasing in swelling ratio. As the temperature

Fig. 1. Optical photos of the PNIPAAm hydrogels prepared in pure water (CGel) and phenol aqueous solutions with different concentrations of 50 mM (Gel50) and 100 mM (Gel100).

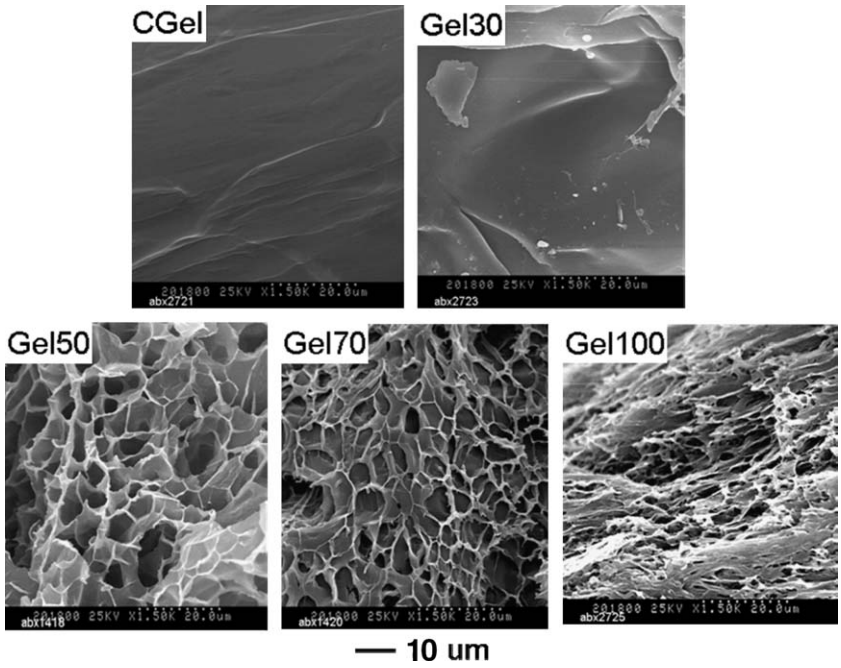

Fig. 3. Surface morphologies of the PNIPAAm hydrogels prepared in pure water (CGel) and phenol aqueous solution with different concentrations of 30 mM (Gel30), 50 mM (Gel50), 70 mM (Gel70) and 100 mM (Gel100).

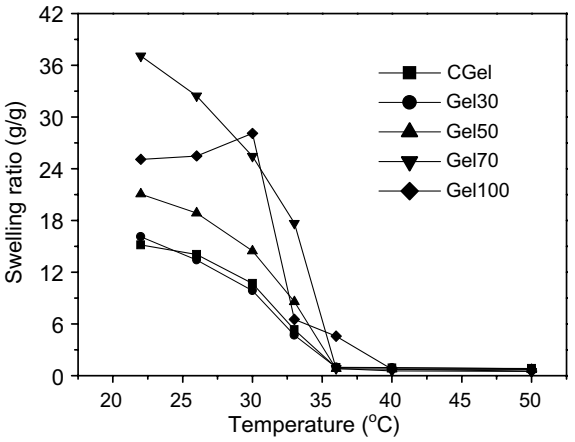

Fig. 4. Temperature dependence of equilibrium swelling ratio of the PNIPAAm hydrogels in the temperature range of 22–50 °C.

changes from 22 to 36 °C, the swelling ratio of the traditional PNIPAAm hydrogel (CGel) reduces from 15 to be around 1, with a ΔSR ($\Delta SR = SR_{22\,^\circ C} - SR_{36\,^\circ C}$) of around 14. In the case of Gel70, the swelling ratio reduces from 37 to around 0.8, with a ΔSR of around 36. The increased ΔSR observed in Gel50, Gel70 and Gel100 hydrogels appears to be attributed to the expanded network structure and subsequently the larger amount of contained water at 22 °C. Thus, more water would be extruded upon heating, which results in the increased ΔSR.

3.5. Deswelling kinetics of hydrogels

Above data indicate the improved equilibrium swelling ratios of the hydrogels prepared in phenol solutions. Another concern for hydrogels is the

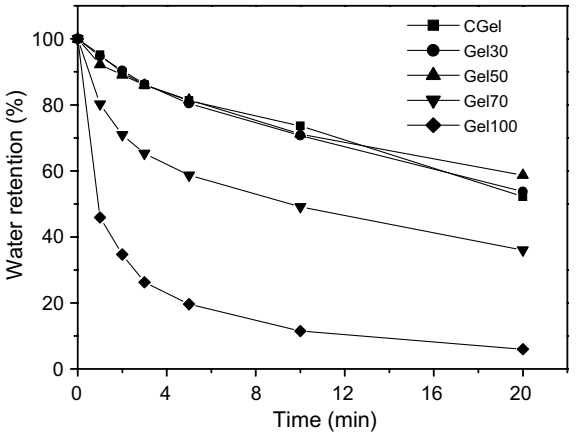

Fig. 5. The deswelling kinetics of the PNIPAAm hydrogels upon temperature jumping from 22 to 50 °C.

response rate since the response rate upon external temperature changes is a critical factor for their potential applications. In this study, the deswelling kinetics of hydrogel upon temperature jumping from 22 to 50 °C was further studied and the data are shown in Fig. 5. It is obvious that Gel100 exhibits the fastest shrinking rate and lost water dramatically, and the water retention reduces from 100% to about 20% within 5 min, and 6% within 20 min. Gel70 also shows a fast deswelling rate. However, CGel, Gel30 and Gel50 exhibit almost the same slow deswelling rate, reducing from 100% to about 81% within 5 min and 54% within 20 min.

4. Discussion

It was reported that due to the selective solvation, phenol exhibits an excess equilibrium concentration inside the swollen hydrogels and PNIPAAm hydrogels swollen at 20 °C in phenol aqueous solutions display a volume transition at the concentration close to 50 mM [21]. Similar findings were also reported that the volume phase transition of PNIPAAm hydrogel was induced by a degree of the hydrogen-bond-driving alkylphenol binding of alkylphenols to *N*-alkylacrylamide hydrogel and the complexes of *N*-alkylamide with alkylphenol were condensed to form the ordered microstructures [22,23]. In this paper, when PNIPAAm hydrogels were fabricated in phenol aqueous solutions with the concentrations below 50 mM, the binding interactions between phenols and the monomeric units of PNIPAAm chains were not strong enough to induce the condense of PNIPAAm chains. Resulting PNIPAAm hydrogels (Gel30) still displayed a similar property as the traditional PNIPAAm hydrogel fabricated in pure water (CGel). Once the concentration of phenol aqueous solution reached 50 mM or above, owing to the increased equilibrium concentration inside the resulting hydrogels [21], relative binding interactions turned to be strong enough to induce the condense of PNIPAAm chains and resulted hydrogels appeared to be opaque as seen in Fig. 1. After the gelation, resulted PNIPAAm hydrogels were immersed in pure water for purification purpose to remove the phenol inside the network. The condensed PNIPAAm chains would expand and the porous network was expanded correspondingly. As a result, Gel50, Gel70 and Gel100 exhibited an expanded network. Obviously, increasing the phenol concentration from 50 mM to 100 mM would result in an increased binding interaction between phenols and PNIPAAm chains as well as an expanded network. From the SEM observation (Fig. 3), Gel50 and Gel70 did exhibit increased expanding network. However, compared with Gel50 and Gel70, Gel100 exhibited a little compacted porous structure as shown in Fig. 3. This exception of Gel100 was attributed to the extremely strong binding interactions between phenols and PNIPAAm chains, which induced the condensed structure.

Above speculation is also supported by the swelling ratio data in Fig. 4. At room temperature, the equilibrium swelling ratios of Gel50, Gel70 and Gel100 were much increased compared with the one of CGel and Gel30 since more volume was provided to contain water in their relative expanded networks. Among Gel50, Gel70 and Gel100, Gel70 exhibited the largest swelling ratio at room temperature, while Gel100 exhibited an intermediate swelling ratio due to its condensed structure caused by the extremely strong binding interactions between phenols and PNIPAAm chains.

It is important to point out, as the temperature was increased in the range below T_{tr}, the swelling ratio of Gel100 got a little increased. The slight increase in swelling ratio with increasing temperature is attributed to the destruction of hydrogen bonding interactions between the residual phenol and water in Gel100. As temperature increased slightly above the room temperature, the driving force for network expansion resulting from the destruction of the hydrogen bonds overwhelmed the driving force for breakdown of the hydrophobic interactions between the hydrophobic groups in PNIPAAm chains. As a result, the network was expanded as the swelling temperature increased slightly above the room temperature. However, with a further increase in the temperature above T_{tr}, the much strengthened hydrophobic interactions between the hydrophobic groups of PNIPAAm chains overwhelmed the hydrogen bonding interactions and the networks of Gel100 exhibited a dramatically decreased swelling ratio, thus, Gel100 shrank quickly.

With respect to the deswelling kinetics, the PNIPAAm hydrogels with an expanded network would demonstrate improved deswelling rate when transferred into hot water [13–15]. It is regarded that, when the PNIPAAm hydrogel was transferred into the hot water, the surface layer of the hydrogel was the first region to be affected, and a dense skin layer was generated due to hydrophobic interactions

among the isopropyl groups of PNIPAAm chains. Such a dense skin layer would greatly restrict the outward permeation of water from the hydrogel interior [24,25]. In our study, the expanded PNIPAAm network prepared in this report retarded the formation of such a dense skin layer during the deswelling process and the freed water might diffuse out quickly. As a result, PNIPAAm hydrogels with expanded network (Gel70 and Gel100) exhibited a fast response rate upon heating.

5. Conclusions

In summary, a new concept was provided to prepare fast responsive PNIPAAm hydrogels by using the phenol aqueous solution with different concentrations. Attributed to the strong hydrogen-bonding interactions between the phenol and producing PNIPAAm chains, an expanded network structure was constructed after phenol was removed and replaced by water during the purification process. The resulting PNIPAAm hydrogels with expanded network exhibited improved swelling capabilities as well as fast deswelling rates upon temperature increase.

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