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SHORT COMMUNICATION

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Synthesis and characterization of a novel thermosensitive gel with fast response

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Abstract A gel is a kind of water-swellable but water-insoluble, crosslinked polymer. Some kinds of gels can respond to external temperature changes. This specific property is useful in biomedical and other technological fields. In this paper the synthesis of a novel, thermosensitive gel by the copolymerization of *N*-isopropylacrylamide or *N*,*N*-diethylacrylamide with 3-methacryloxypropyltrimethoxy silane (MPTMS) is reported. The formation of the gel is caused through the interaction of MPTMS under acidic condition. This thermosensitive gel can deswell and reswell quickly in response to the external temperature changes, this behavior probably being due to the heterogeneous structure of the gel produced. This fast-response gel may be useful both in biomedical and biotechnological fields.

Key words Thermosensitive · Gel · Lower critical solution temperature · Fast response

Introduction

Thermosensitive polymers show thermoreversible hydration-dehydration changes in response to external temperature changes and exhibit lower critical solution temperatures (LCST) [1]. Correspondingly, crosslinked gels are swellable below this temperature and undergo abrupt changes in volume, precipitating from solution suddenly as the temperature is increased above the LCST. This property of discontinuous phase separation of gels has been used in biomedical and biotechnological fields, for instance, controlled drug release [2], absorption of proteins [3], immobilization of enzymes [4] and recyclable absorbents [5], etc.

The temperature response rate of a normal thermosensitive gel is slow and this restricts some potential applications of this kind of gel, such as on–off switches. Several successful attempts have been made to increase the response rate. For example, Hirasa et al. [6] synthesized poly (vinyl methyl ether) gel by radiation crosslinking. Kabra and Gehrke [7] synthesized poly(*N*-isopropylacrylamide) (PNIPA) by using a phase-separation technique to create fast-temperature-response gels. Wu et al. [8] used a new method, which is based on a modification of the original method used by Kabra and Gehrke to prepare fast-response, macroporous PNIPA gels. Recently, Kaneko and coworkers [9–11] prepared a comb-type grafted PNIPA gel which showed a rapid deswelling rate at high temperature (above its LCST).

This paper reports a new approach to preparing a fast-temperature-response gel by using 3-methacryloxypropyltrimethoxy silane (MPTMS) during the polymerization/crosslinking reaction. PNIPA and poly(*N*,*N*-diethylacrylamide) (PDEAA) gels are typical thermosensitive gels, and *N*-isopropylacrylamide (NIPA) and *N*,*N*-diethylacrylamide (DEAA) were chosen as the monomers.

Experimental

Materials

NIPA and DEAA were synthesized and purified according to Refs. [4, 12], respectively. MPTMS was a gift from Wuhan University Chemical Plant (Wuhan, China) and was used as supplied. Ammonium persulfate (APS), sodium bisulfite (SBS) and glacial acetic acid (HAc) were all analytical grade and were used as received.

Synthesis of PNIPA and PDEAA gels

The monomers NIPA and MPTMS were dissolved in distilled water/HAc (0.5 ml/0.5 ml) mixed solvent. APS and SBS were used as a pair of redox initiators (5.0 wt% based on NIPA). The polymerization/crosslinking was carried out at 26 °C for 15 h in a glass vessel. After the reaction, the gel was cut into discs (10 mm in diameter and 3 mm in thickness) and then the gel discs were immersed in ethanol at 5 °C for 24 h. During this period, the ethanol was replaced every 4–5 h with fresh ethanol in order to leach out the chemical residues. The gel thus obtained was further purified by immersing it in distilled water at 5 °C for 72 h. Likewise, the distilled water was also refreshed at regular time intervals as in the procedure described for ethanol in order to leach out the ethanol. The gel thus obtained was defined as PNIPA gel.

The synthesis of the PDEAA gel was carried out at 20 °C for 15 h and the other polymerization conditions and treatment procedures were the same as those for the PNIPA gel. The feed compositions of monomers and other reactants are listed in Table 1.

Measurement of the swelling ratios of the PNIPA and PDEAA gels

The swelling ratios (SR) of these two kinds of gels were measured gravimetrically after blotting the excess surface water with moistened filter paper. The gels were incubated in distilled water for at least 24 h at every particular temperature. The SR is defined as follows:

$$\mathrm{SR} = W_\mathrm{s}/W_\mathrm{d} \ , \tag{1}$$

where W_s is the weight of water in the swollen gel after the equilibrium in distilled water at a particular temperature and W_d is the dry weight of the gel dried in vacuum overnight.

Measurement of the deswelling kinetics of the PNIPA and PDEAA gels

The deswelling kinetics of the PNIPA and the PDEAA gels were measured gravimetrically at 50 °C and 42 °C, respectively, after blotting the excess surface water with moistened filter paper. The weight changes of the gels were recorded during the course of the deswelling process at regular time intervals. The water retention (WR) is defined as follows:

$$\mathrm{WR} = 100 \times (W_\mathrm{t} - W_\mathrm{d})/W_\mathrm{s} \ , \tag{2}$$

where W_t is the weight of the gel at regular time intervals, W_s is the weight of the water in the swollen gel after reaching equilibrium in distilled water at 5 °C and W_d is the dry weight of the gel.

Measurement of the reswelling kinetics of the PNIPA and PDEAA gels

The reswelling kinetics of the PNIPA and the PDEAA gels were measured gravimetrically at 20 °C and 15 °C, respectively, after blotting the excess surface water with moistened filter paper. The weight changes of the gels were recorded during the course of the reswelling process at regular time intervals. The water uptake (WU) is defined as follows:

$$\mathrm{WU} = 100 \times (W_\mathrm{t} - W_\mathrm{d})/W_\mathrm{s} \ , \tag{3}$$

where the symbols W_t, W_d and W_s are the same as defined previously.

Results and discussion

Formation of the PNIPA and PDEAA gels

The formation of a gel is caused by the subsequent reaction of MPTMS under acidic conditions. First, it is quickly copolymerized with the monomers NIPA or DEAA through redox radical polymerization. This copolymerization process is quick and the MPTMS reacted as a usual monomer at this moment. Then, the trimethoxy silane groups of MPTMS hydrolyzed to give silanol. Finally, silanol condensed to form a siloxane linkage, thus causing the crosslinking of the polymer chains. This process is complicated and the details of it are under investigation. The formation of the gel is shown in Fig. 1.

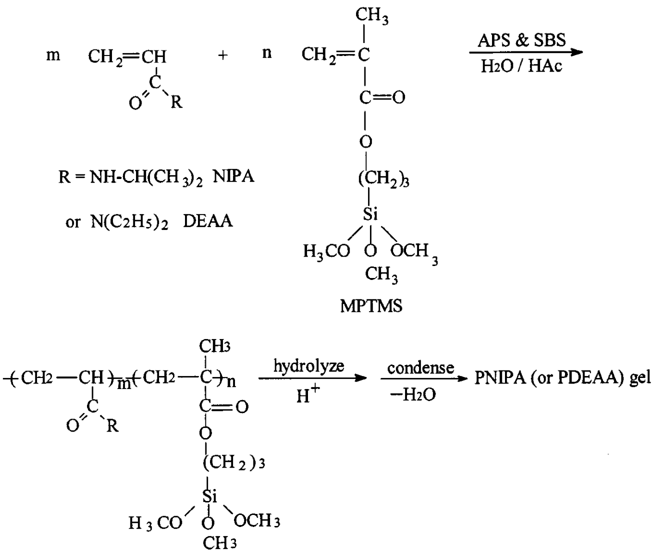

Fig. 1 The formation process of the poly(*N*-isopropylacrylamide) (*PNIPA*) and poly(*N*,*N*-diethylacrylamide) (*PDEAA*) gels

Table 1 Feed composition for the preparation of poly(*N*-isopropylacrylamide) (*PNIPA*) and poly(*N*,*N*-diethylacrylamide) (*PDEAA*) gels

Component	Sample code							
	N1	N2	N3	N4	D1	D2	D3	D4
N-isopropylacrylamide (mg)	100	100	100	100				
N,*N*-diethylacrylamide (mg)					100	100	100	100
3-methacryloxypropyltrimethoxy silane (ml)	6	8	12	20	8	10	14	20

Table 2 Physical properties of the PNIPA and PDEAA gels

Physical property	Sample code							
	N1	N2	N3	N4	D1	D2	D3	D4
Appearance below/above lower critical solution temperature	translucent/ opaque	translucent/ opaque	opaque/ opaque	opaque/ opaque	translucent/ opaque	translucent/ opaque	opaque/ opaque	opaque/ opaque
Mechanical strength	poor	normal	strong	fragile	poor	normal	strong	fragile

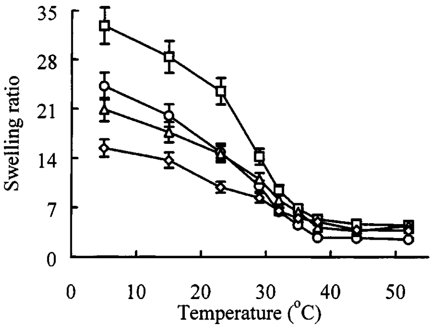

Fig. 2 Temperature dependence of equilibrium swelling ratios of the PNIPA gels (□-N1, ○-N2, Δ-N3, ◇-N4)

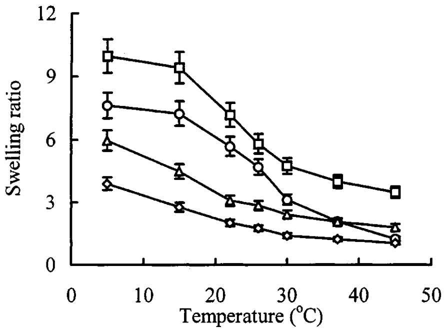

Fig. 3 Temperature dependence of equilibrium swelling ratios of the PDEAA gels (□-D1, ○-D2, Δ-D3, ◇-D4)

Physical properties of the PNIPA and PDEAA gels

The appearance and the mechanical properties of these two kinds of gels are summarized in Table 2. At temperatures below the LCST of the corresponding gel, when the content of MPTMS is increased, the gels change from translucent to opaque. As the temperature is increased above their LCST, all the gels turn opaque. At the same time, the mechanical properties of the gels change according to the different MPTMS contents. When the MPTMS content is very low, the gel is too soft to take up a shape and the mechanical strength is poor. As the MPTMS content is increased, the mechanical strength of the gel is sufficient for the gel to be handled with forceps; however, if the MPTMS content is too high, the gel becomes fragile.

Swelling ratio of the PNIPA and PDEAA gels

Figures 2 and 3 show the temperature dependence of the equilibrium swelling ratio of the PNIPA and PDEAA gels, respectively. These figures illustrate that the SR of both the PNIPA and the PDEAA gels decrease as the MPTMS content is increased at temperatures below the LCST. However, the SR of the PNIPA gel is larger than that of the corresponding PDEAA gel at low temperature. This is attributed to the different nature of the isopropylamino and diethylamino substituent groups.

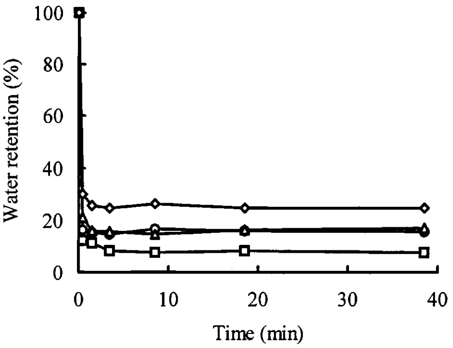

Fig. 4 Deswelling kinetics of the PNIPA gels at 50 °C (□-N1, ○-N2, Δ-N3, ◇-N4)

Deswelling kinetics of the PNIPA and PDEAA gels

Figures 4 and 5 show the deswelling kinetics of the PNIPA and the PDEAA gels, respectively. It is evident that all the gels can shrink and lose the water in them quickly. The gels shrink to the equilibrated water content in a few minutes and the equilibrated water content is higher the greater the MPTMS content, with the exception of D4.

Reswelling kinetics of the PNIPA and PDEAA gels

The reswelling kinetics of these two kinds of gels are shown in Figs. 6 and 7. All the gels reswell and absorb water quickly, but the equilibrated WU is different. This shows that the reswelling rate is faster when the

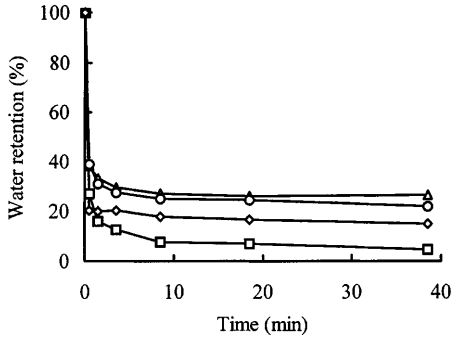

Fig. 5 Deswelling kinetics of the PDEAA gels at 42 °C (□-D1, ○-D2, Δ-D3, ◇-D4)

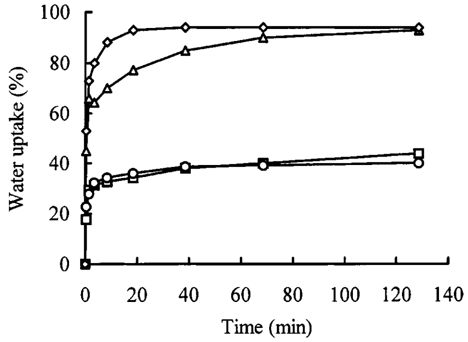

Fig. 7 Reswelling kinetics of the PDEAA gels at 15 °C (□-D1, ○-D2, Δ-D3, ◇-D4)

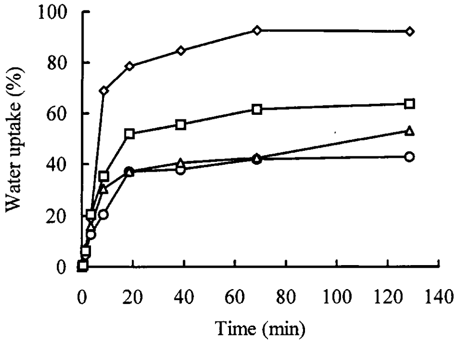

Fig. 6 Reswelling kinetics of the PNIPA gels at 20 °C (□-N1, ○-N2, Δ-N3, ◇-N4)

MPTMS content is increased, although this trend is not always true. On comparing the reswelling kinetics and deswelling kinetics, we found that the shrinkage process is faster than the reswelling process.

Under the experimental conditions adopted, the gels obtained are translucent or opaque at room temperature and the reported dense, thick skin layer [13, 14], which is believed to be impermeable to water, did not form during the deswelling process. We infer that the network structure of the gel obtained is heterogeneous, which leads to the rapid response rate in response to external temperature changes. During the deswelling process, the trapped water molecules are easily freed and released to the outer aqueous solution as the temperature is increased above the LCST. As in the case of the reswelling process, the polymer chains can relax/expand immediately into the surrounding bulk aqueous medium with hydration [15] and the fast reswelling rate is achieved.

Conclusion

Through copolymerizing NIPA or DEAA with MPTMS, we prepared a novel thermosensitive gel. This gel was crosslinked through the condensation of silanols under acidic condition, not by the usual crosslinker. This gel exhibits a fast response rate to temperature changes and may be useful both in biomedical and biotechnological fields.

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