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Metal-ion-mediated hydrogels with thermo-responsiveness for smart windows

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ABSTRACT

The poly(N-isopropylacrylamide-co-N-maleylgelatin) [P(NIPAAm-co-N-MAGEL)] hydrogel was prepared by the free radical polymerization of N-isopropylacrylamide (NIPAAm) and N-maleylgelatin (N-MAGEL) with N,N′-methylene bis(acrylamide) (BIS) as the cross linker in the complete aqueous environment. The hydrogel becomes opaque when the temperature exceeds lower critical solution temperature (LCST) and goes back to its original transparent state when it is cooled below the LCST which can be finely tuned as it shows a linear dependence on the concentration of Na^+, Mg^{2+} and Al^{3+}. Interestingly, different from Na^+ and Mg^{2+}, Al^{3+} could mediate the transparency of the hydrogel even when the temperature is below LCST and induce the formation of double-network (DN) hydrogel. Metal-ion-carboxylate supramolecular interactions are proposed to dominate this property through ionic cross-linking. The hydrogel could be used as the temperature and metal ions controlled smart window. Effects of metal ions on swelling characteristics, mechanical property and microstructures of the hydrogel were further investigated.

1. Introduction

Functional hydrogels composed of three-dimensional (3D) hydrophilic polymer can respond to environmental stimuli (e.g., temperature, ions, pH, light) and have diverse applications in many areas, such as biosensors, drug delivery, micro- or nano-reactors and tissue engineering [1–4]. Poly(N-isopropylacrylamide) (PNIPAAm) hydrogel, as a typical thermo-responsive system, has been most frequently studied [5–9]. PNIPAAm undergoes reversible hydrophilic/hydrophobic phase transitions at the lower critical solution temperature (LCST), which is close to ambient and human body temperatures [10–12]. Moreover, accompanying the heat/cool process, the reversible shifts between opaque state and transparent state with temperature could simply modify the passage of the light and make PNIPAAm hydrogel attractive material for smart window application [13–19]. By decorating the PNIPAAm polymer or hybridization with other additives, smart windows based on heat- [13–15,17,19], voltage- [13,19], light- [18] and solvent- [16] sensitive PNIPAAm hydrogels have been developed. The hydrogels show adjustable transparency in response to the external stimuli and could control the light transmission intelligently. Therefore, developing appropriate materials for smart window is of great importance for their contributions to reducing the energy consumption or protecting from strong sunlight and heat radiation [13–20]. Metal-ligand coordination is an important kind of supramolecular interactions, which is employed to construct and modulate properties of smart hydrogels facilely [21–24]. However, smart window based on PNIAAm hydrogel mediated by metal-ligand interaction hasn't been reported yet.

Double-network (DN) hydrogels which possess extraordinary mechanical strength and toughness are promising soft and tough materials [25]. Especially, developing DN hydrogels based on natural renewable biopolymers is still challenging [26].

Applications of PNIPAAm hydrogels are restricted by poor biocompatibility and cytotoxicity to some extent [27]. Gelatin is the natural polymer with excellent biocompatibility and biodegradability. It contains free amino groups in branch chain to make it possible to introduce other functional groups by acylation reaction [28]. Therefore, introducing the gelatin or derivative gelatin to PNIAAm hydrogel could open a new door for the smart window material and DN hydrogel.

In the work reported here, gelatin modified by maleic anhydride (MAH) was introduced to P(NIAAm) hydrogel to form P(NIPAAm-co-N-MAGEL) hydrogel. N-MAGEl could not only improve the

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biocompatibility of the hydrogel but afford carboxyl groups to coordinate with metal ions. Effects of different valent metal ions (Na^+, Mg^{2+}, Al^{3+}) on the transparency with varying temperature are studied using ultraviolet–visible (UV–vis) spectrophotometer. Swelling ratios, mechanical strength, thermostability and microstructures of the DN hydrogels induced by Al^{3+} were also investigated.

2. Experimental details

2.1. Materials

Gelatin (gel strength 225 bloom) was purchased from Qinghai Chem., China. NIPAAm was purchased from J&K Chem., China. BIS, N,N,N′,N′-tetramethylethylenediamine (TEMED), ammonium persulfate (APS), sodium chloride (NaCl), magnesium chloride hexahydrate ($MgCl_2{\cdot}6H_2O$), aluminum chloride ($AlCl_3$) and maleic anhydride were analytical grade purchased from Shanghai Fine Chemical Co. Ltd., China. All reagents were used without further purification. N-MAGEL was synthesized according to our previous literature [27] and the degree of substitution of amino groups in gelatin was 96.7%.

2.2. Preparation of P(NIPAAm-co-N-MAGEL) hydrogels with/without metal ions

The P(NIPAAm-co-N-MAGEL) hydrogel was synthesized via free radical polymerization [27]. N-MAGEL (0.3 g), NIPAAm (0.7 g) and BIS (0.012 g) were dissolved in deionized water (10 mL) by stirring. Nitrogen gas was bubbled into the solution for 10 min. TEMED (315 μL) as the accelerator and APS (4%, 210 μL) as the initiator were then added in. The obtained homogeneous and transparent solution reacted for 24 h to produce P(NIPAAm-co-N-MAGEL) hydrogel. The obtained hydrogel was washed three times to remove the unreacted compounds. Freeze drying was used to remove the water of the hydrogel to get xerogel. Hydrogels incorporated with metal ions were prepared by immersing the xerogel in the corresponding aqueous solution of NaCl, $MgCl_2$ and $AlCl_3$ at the onset temperature to swell and reach the equilibrium state.

2.3. Characterizations

Changes in transmittance of the hydrogel induced by temperature and metal ions were measured by UV–vis spectrophotometer (723P, Shanghai Spectrum Instruments, China) attached to high constant-temperature bath (CH-1015, the DC Instrument of Shanghai Precision Scientific Instrument, China) at visible light ($\lambda = 560$ nm, path length = 3 cm). The optical transmittance of each hydrogel sample was measured from 10 to 40 °C at the rate of 0.05–0.1 $°C\,min^{-1}$. Distilled water was used to calibrate the spectrophotometer. The equilibrium swelling ratios (ESR) of hydrogels were measured with the temperature ranging from 10 to 45 °C by a gravimetric method. At each particular temperature, hydrogel samples (5 mm × 5 mm × 2 mm) were incubated in an aqueous solution of NaCl, $MgCl_2$, or $AlCl_3$ for at least 24 h to reach an equilibrium state and weighed. ESR of hydrogels was calculated using the following equation:

$$ESR = (W_1 - W_0)/W_0 \tag{1}$$

where W_1 was the weight of the swollen hydrogel and W_0 is the weight of the xerogel. Swelling and deswelling experiments were measured gravimetrically by immersing the xerogel (5 mm × 5 mm × 2 mm) in 0.50 M $AlCl_3$ solution at 20 and 40 °C, respectively. The weight of the gels at intervals was determined. Swelling/deswelling ratio is defined as follows:

$$SR_t = (W_t - W_0)/W_0 \tag{2}$$

where W_t is the weight of the hydrogel at t time and W_0 is the initial weight of the xerogel.

The mechanical properties of hydrogels incorporated with NaCl, $MgCl_2$, or $AlCl_3$ were measured by compressive testing in a CT3 texture analyzer (Brookfield, US) using TA-10 as the analytical probe. A cylindrical swelling hydrogel sample was compressed up to 50% of its original height and the test speed was set at 1.0 mm/s with a trigger force of 4.5 g. During the experiment, the compressive strength was recorded as the maximum induction force (g, converted to Pa be used internationally). The thermal stability property of the freeze-dried hydrogel samples were assessed by thermogravimetric (TG) analysis, measuring the weight of the xerogels as a function of temperature in a controlled atmosphere. Thermogravimetry curves of freeze-dried hydrogel samples were performed on a thermo-gravimetric analyser (Q 600 SDT, TA instruments, US). A certain amount of xerogels were added to a crucible (Al_2O_3), which was heated from 20 to 600 °C at a heating rate of 10 $°C\,min^{-1}$ and nitrogen was the protective gas with flowing rate of 20 mL/min. Two xerogel samples were immersed in distilled water and 0.5 M $AlCl_3$ solution respectively to reach the equilibrium state. Two hydrogels with/without Al^{3+} were stained by Sudan and morphologies were monitored using an optical microscope (Olympus, IX71S1F-3).

3. Results and discussion

3.1. Thermo- and metal-ion-mediated transparency

Fig. 1 illustrates the adjustable transparency of the P(NIPAAm-co-N-MAGEL) hydrogel with temperature and metal ions. The hydrogel becomes opaque (Fig. 1b) abruptly when the temperature exceeds LCST. It becomes transparent (Fig. 1a) again when it is cooled down. After the addition of 0.15 M Al^{3+}, the transparent hydrogel turns to semi-opaque state (Fig. 1c), which becomes proximity to transparent state (Fig. 1d) with elevating the concentration of Al^{3+} to 0.5 M and the opaque state could be observed when the temperature is higher than LCST.

LCST of the P(NIPAAm-co-N-MAGEL) hydrogel is 33 ^{0}C, which could be obtained from the temperature dependence of transmittance plot shown in Fig. 2a–c (0 M). The hydrogel exhibits a sharp decrease in transmittance above LCST. When the temperature is higher than the LCST, the intramolecular interactions between C=O and N–H groups lead to a collapsed conformation of the polymer chains. So the polymers form a heterogeneous state and the transmittance decreases. The effects of Na^+, Mg^{2+} and Al^{3+} on the transmittance change of the P(NIPAAm-co-MAGEL) hydrogel are shown in Fig. 2. The transmittance of hydrogels incorporated with different metal ions decreases sharply, regardless of ions concentrations. Na^+, Mg^{2+} and Al^{3+} have the similar effect on LCST, that is, LCST shifts to a lower temperature with increasing concentrations of ions. For example, LCST decreased from 33 °C to 22 °C with Al^{3+} concentration increasing from 0 to 0.60 M. This LCST shift follows the so-called Hofmeister series [29]. The presence of different salts weakens the hydrogen bonds between the carboxylic groups and amide groups of the polymers with water, which makes P(NIPAAm-co-MAGEL) hydrogel easier to form volume phase transition that the

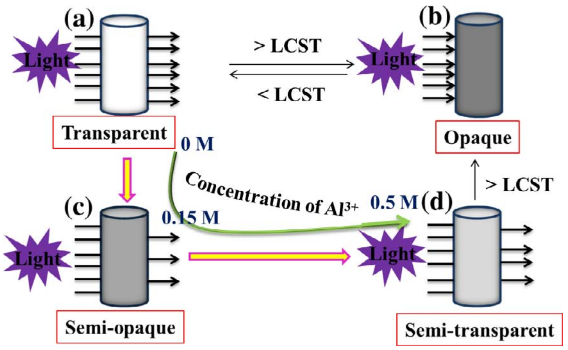

Fig. 1. Schematic representation of temperature and metal ions mediated transparency.