# Synthesis and swelling properties of a pH- and temperature-dual responsive hydrogel by inverse microemulsion polymerization

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**ABSTRACT:** A novel pH- and temperature-dual responsive hydrogel was synthesized by inverse microemulsion polymerization, using itonic acid (IA) as pH-responsive monomer, N-isopropylacrylamide (NPAM) as thermo-responsive monomer and acrylamide (AM) as the nonionic hydrophilic monomer. Factors affecting water and salt absorption, as well as swellability of the dual responsive hydrogels, such as IA/NPAM mass ratio and crosslinker amount, were investigated. pH- and temperature-sensitivity and dynamic viscoelasticity behaviors of the dual responsive hydrogels were also studied. The dual responsive responsive hydrogels showed suitable water and salt absorbency, remarkable pH-, and temperature-sensitivity, adjustable swellability and enhanced viscoelastic behaviors under high stress. Water absorbency and pH-sensitivity increased while salt absorbency and temperature- sensitivity decreased with increasing IA/NIPAM mass ratio. Both water absorbency and salt absorbency increased first with crosslinker amount increased to 0.2 wt %, and then decreased with increasing crosslinker amount. Temperature-induced shrinkage range of the dual responsive hydrogels was higher and broader than that of the conventional poly(N-isopropylacrylamide) hydrogel. TEM indicated that the as-synthesized hydrogel particles were regular and spherical-like in shape and had the mean particle size of 49nm in the range of 30–78 nm. FTIR indicated the structure of the dual responsive hydrogels. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42139.

## INTRODUCTION

Intelligent hydrogels, which can undergo significant changes in their physicochemical properties in response to minor changes in external stimuli, such as temperature,[1] pH,[2] solvent composition,[3] light,[4] magnetic fields,[5] and ionic strength,[6,7] have attracted much attention because of their potential applications in the areas of drug delivery,[8–10] microlenses,[11] sensors,[12,13] artificial organ,[14] and enhanced oil recovery (EOR).[15]

Multiresponsive hydrogels that are both temperature- and pH-sensitive are the most widely investigated because these two stimuli are the most common used external stimuli. Poly(N-isopropylacrylamide) (PNIPAAm) is the most popular temperature-responsive hydrogel since it has a volume phase transition temperature (around 32°C) close to normal body temperature. PNIPAAm has been extensively studied due to its thermal sensitive property and can react with acrylic acid or other polymers to design new multifunctional materials.[16–21]

Much research has also been dedicated on the preparation of temperature- and pH-sensitive hydrogels.[22–29] Serrano-Medina *et al.*[30] prepared a pH and temperature sensitive core–shell nano/microgels by soapless emulsion polymerization, introducing 2-methacryloyloxybenzoic acid to PNIPAAm crosslinked core to produce pH sensitivity. The inclusion of ionizable groups allows for small increase in the transition temperature and gives anchoring sites for loading of solutes of opposite charge by ionic interactions. Durand and Hourdet[22,23] prepared a well-defined graft copolymer hydrogel according to a two-steps method, involving the synthesis of functionalized PNIPAM followed by their grafting onto a poly(acrylic acid) backbone. The PAA-*g*-PNIPAM hydrogel exhibited very interesting thermothickening properties in aqueous solution. Zhao *et al.*[24] synthesized novel intelligent hydrogels composed of biodegradable and pH-sensitive poly(L-glutamic acid) (PGA) and temperature sensitive poly(N-isopropylacrylamide-*co*−2-hydroxyethyl methacrylate). The swelling ratios of hydrogels increased with the pH increase and these processes were reversible, and the

temperature had great influence on the optical transmittance of hydrogels. Ju et al.[25] prepared semi-IPN hydrogels composed of alginate and amine-terminated PNIPAAm with various compositions by crosslinking with calcium ions. The semi-IPN hydrogels exhibited a change in swelling ratio at around 32°C. Zhang et al.[26] prepared a series of temperature- and pH-sensitive semi-IPN hydrogels composed of crosslinked PNIPAAm and linear sodium alginate (SA) by solution polymerization. The semi-IPN hydrogels show suitable mechanical strength and improved sensitivity to alternating changes in pH and temperature because of the incorporation of SA. Zhang and Peppas[27] prepared hydrogels of an interpenetrating polymeric network (IPN) composed of the temperature-sensitive PNIPAAm and the pH-sensitive poly (methacrylic acid) (PMAA) by a sequential UV polymerization. The IPN hydrogels exhibited a combined pH- and temperature-sensitivity at a temperature range of $31-32$°C and a pH value of $\sim5.5$. Zhao et al.[28] prepared thermo- and pH-sensitive hydrogels by UV light irradiation, using a biodegradable crosslinker derived from poly(L-glutamic acid). The hydrogels shrank under acidic condition or at temperature above their collapse temperature and swelled in neutral or basic media or at lower temperature.

Up to now most of the multiresponsive hydrogels are prepared by precipitation polymerization, emulsion polymerization and photopolymerization. Although some research has been done on the pH- or temperature-responsive hydrogels by inverse microemulsion polymerization,[31–37] there have been no previous reports on the pH- and temperature-dual responsive hydrogels via inverse microemulsion polymerization.

On the basis of our previous research on superabsorbent hydrogels and microemulsion polymerization,[38–54] in this article, a new pH- and temperature-dual responsive hydrogel was prepared by inverse microemulsion polymerization, using itonic acid (IA) as pH-responsive monomer, N-isopropylacrylamide (NIPAM) as thermo-responsive monomer and acrylamide (AM) as the nonionic hydrophilic monomer. Possible mechanism of the dual responsive hydrogels formation was discussed. Structure and morphologies of resulting hydrogels were investigated by Fourier transformation infrared spectra (FTIR) and transmitting electronic microscopy (TEM). Effects of IA/NIPAM mass ratio and crosslinker amount on water and salt absorption, as well as time- dependent swellability behaviors of the dual responsive hydrogels were investigated. In addition, pH- and temperature-sensitivity and dynamic viscoelasticity behaviors of the dual responsive hydrogels were also evaluated.

## EXPERIMENTAL

### Materials

Itaconic acid (IA), analytical grade, was purchased from Guangzhou Zhengtong Chemical (China) and purified by recrystallization. Acrylamide (AM), analytical grade, was purchased from Chengdu Kelong Chemical (China) and purified by recrystallization. N-isopropyl acrylamide (NIPAM), N-methylene-bis-acrylamide (MBA), analytical grade, were purchased from Chengdu Best Reagent (China) and purified by recrystallization. Ammonium persulfate (APS), sodium bisulfite (SBS),

sorbitan monooleate (Span-80), polyoxyethylene sorbitan monooleate (Tween 80), cyclohexane, analytical grade, were all purchased from Chengdu Kelong Chemical (China) and used without further purification.

### Synthesis of pH- and Temperature-Dual Responsive Hydrogels

A series of pH- and temperature-dual responsive hydrogels with different components were prepared by microemulsion polymerization according to the following procedure: Typically,3 g IA was dissolved in 10 mL distilled water and neutralized with 20% sodium hydroxide solution in an ice bath, and then 4 g acrylamide, 2 g N-isopropyl acrylamide and 0.036 g N-methylene-bis-acrylamide were added to the above monomer solution and the mixed solution was stirred at room temperature for 30 min. Subsequently, the solution was added dropwise to the inverse microemulsions formed by 100 g cyclohexane, 6 g Span80, and 4 g Tween 80. The water bath was heated slowly to 45–55°C with mild stirring after redox initiator APS (55 mg) and sodium bisulfite (15 mg) were introduced to the above inverse microemulsions. After 3–5 h of the reaction, the resulting product was washed several times with ethanol and acetone, respectively, dried at 60°C to a constant weight, and then milled and screened.

### Water Absorbency of pH- and Temperature-Dual Responsive Hydrogels Using Filtration Method

Approximately 100 mg of dried, milled and sifted hydrogels were dispersed in 100 mL of deionized water for 300 min. Then, excess water was allowed to drain through a 300 mesh wire gauze (with 48 $\mu$m in pore size). The weight of the hydrogels containing absorbed water was measured after draining for 30min, and water absorbency was calculated according to the following equation:

$$\text{Absorbency (g/g)} = (W_2 - W_1)/W_1 \qquad (1)$$

where $W_1$ and $W_2$ are the weight of the dry and swollen hydrogels, respectively. All the experiments were carried out in triplicate, and the average values were reported.

### Saline Solution Absorbency of pH- and Temperature-Dual Responsive Hydrogels Using Filtration Method

Approximately 20 mg of dried, milled, and sifted hydrogels were dispersed in 50 mL 5% NaCl solution for 300 min. Then, excess 5% NaCl solution was allowed to drain through a 300 mesh wire gauze (with 48 $\mu$m in pore size). The weight of the hydrogels containing absorbed 5% NaCl solution was measured after draining for 30 min, and the saline solution absorbency was calculated according to the following equation:

$$\text{Saline solution absorbency (g/g)} = (W_2 - W_1)/W_1 \qquad (2)$$

where $W_1$ and $W_2$ are the weight of the dry and swollen hydrogels, respectively. All the experiments were carried out in triplicate, and the average values were presented.

### Determination of Swellability of pH- and Temperature-Dual Responsive Hydrogels

Particle sizes of the pH- and temperature-dual responsive hydrogels swollen at different time were determined by a
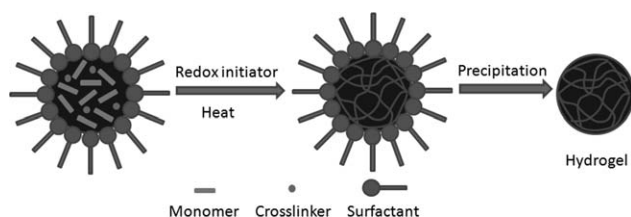
**Scheme 1.** Illustration of the formation of pH- and temperature-dual responsive poly (NIPAM/IA/AM) hydrogels via microemulsion polymerization.

OMEC LS-POP(III) laser particle size analyzer (Zhuhai OMEC instrument, China).

### Dynamic Viscoelasticity Measurements

Dynamic viscoelasticity measurements were performed with a Rheometric Fluids RFR 7800 rheometer. The applied frequency ($\omega$) was changed from 0.1 to 10 rad/s. The storage ($G'$) and loss ($G''$) moduli were obtained from oscillatory measurements with stress of 50, 100, and 200 Pa, respectively.

### Characterization of the pH- and Temperature-Dual Responsive Hydrogels

FTIR spectrum was carried out on a Perkin–Elmer 1750 spectrophotometer, equipped with an Epson Endeavour II data station. The dried samples were crushed with KBr to get pellets. The micrographs of pH- and temperature-responsive hydrogels were taken using TEM (Tecnai G2 F20S-TWIN, FEI). Before TEM observation, inverse microemulsion samples were diluted with cyclohexane, stained with phosphotungstic acid, and then dipped onto the copper grid and allowed to evaporate at room temperature.

### RESULTS AND DISCUSSION

### Synthesis, Morphology, and Structure of the pH- and Temperature-Dual Responsive Hydrogels

A new facile one-pot route to synthesize poly (NIPAM/IA/AM) hydrogels via microemulsion polymerization under mild reaction conditions is shown in Scheme 1. A possible synthesis mechanism is as follows: First, NIPAM and AM monomers and crosslinker MBA are dissolved in IA solution (partially neutralized with 20% sodium hydroxide solution) to form a water phase, and Span 80/Tween 80 used as complex surfactants are dissolved in cyclohexane to form an oil phase. Then two phases
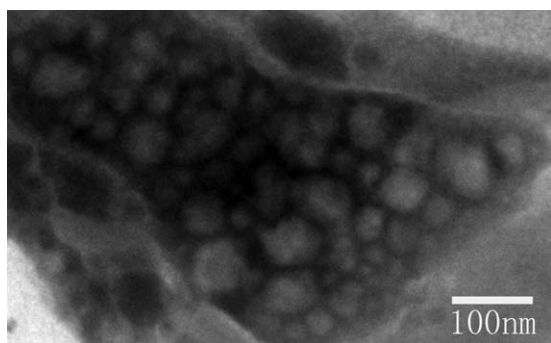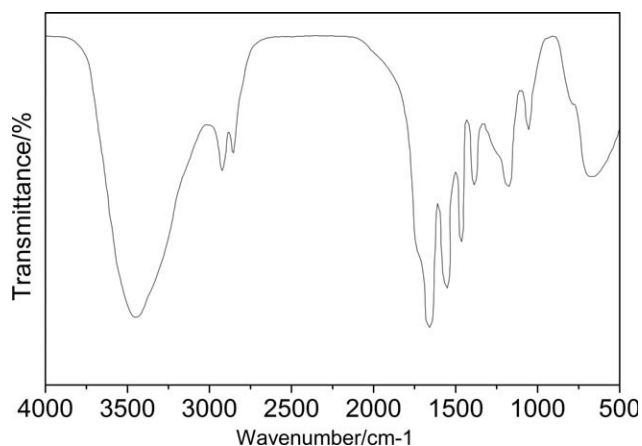


**Figure 2.** FTIR spectrum of the pH- and temperature-dual responsive hydrogels.

are mixed together to form stable inverse microemulsion. Finally, water soluble redox initiators are added into the formed inverse microemulsion and they enter into the nanosized monomer droplets by diffusion from oil phase and decomposed into free radicals when heated to initiate microemulsion polymerization. After disappearance of monomer droplets, the growing latex particles can still propagate via diffusion of monomers from oil phase into them. After 3–5 h inverse microemulsion polymerization, pH-, and temperature-dual responsive hydrogels are formed, and then they are precipitated via cooling at low temperature and washed with ethanol and acetone, respectively.

The morphology and size of the as-synthesized dual responsive hydrogels were characterized by TEM and the results were shown in Figure 1. Hydrogel particles are regular and spherical-like in shape and have the mean particle size of 49 nm in the range of 30–78 nm, indicating that dual responsive hydrogels with nanoscale size, have been successfully synthesized by microemulsion polymerization.

FTIR spectroscopy was used to confirm the chemical structure of poly (NIPAM/IA/AM) hydrogels and the result was demonstrated in Figure 2. As shown in Figure 2, the peak at
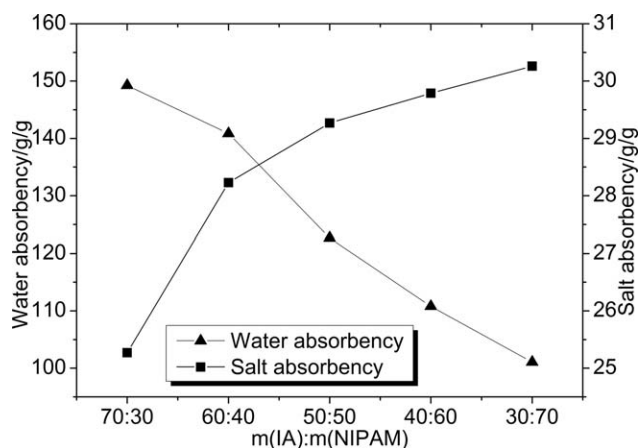


**Figure 1.** TEM picture of the as-synthesized pH- and temperature-dual responsive hydrogels.



**Figure 3.** Effects of IA and NIPAM mass ratio on the water absorbency and salt absorbency of the pH- and temperature-dual responsive hydrogels.

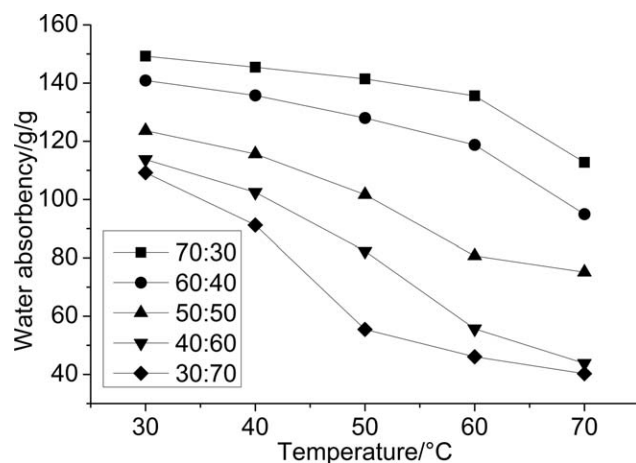**Figure 4.** Temperature-sensitivity of the pH- and temperature-dual responsive hydrogels at different IA/NIPAM mass ratio.



**Figure 5.** pH-sensitivity of the pH- and temperature-dual responsive hydrogels at different IA/NIPAM mass ratio.

$3445$ cm$^{-1}$ is attributed to OH and NH stretching vibrations. The peaks at 2920 and 2854 cm$^{-1}$ are ascribed to the CH2 asymmetric and CH2 symmetric stretch, respectively.[55] The absorption bands at 1720 cm$^{-1}$ are assigned to carboxylic acid.[56] The bands at 1660 and 1550 cm$^{-1}$ represents amide group stretching.[57] The absorption peak at 1385 cm$^{-1}$ is attributed to isopropyl group. The peak at 1050 cm$^{-1}$ arises from C—O stretching vibration. All the above results revealed the formation of dual responsive poly (NIPAM/IA/AM) hydrogels.

### Effects of IA/NIPAM Mass Ratio on the Water Absorption and Salt Absorption of the pH- and Temperature-Dual Responsive Hydrogels

Effects of IA/NIPAM mass ratio on water absorbency and salt absorbency of dual responsive hydrogels were shown in Figure 3. Water absorbency and salt absorbency of dual responsive hydrogels increased and decreased as the IA/NIPAM mass ratio increased from 30 : 70 to 70 : 30, respectively. NIPAM is a nonionic monomer and poly(NIPAM) has a good salt-resistance at the temperature under LCST. In the fully hydrated state (T < LCST, 32°C),[58] NIPAM segments of the dual responsive hydrogels are still completely surrounded by water molecules in the presence of salt solution. However, the salt-induced dehy-
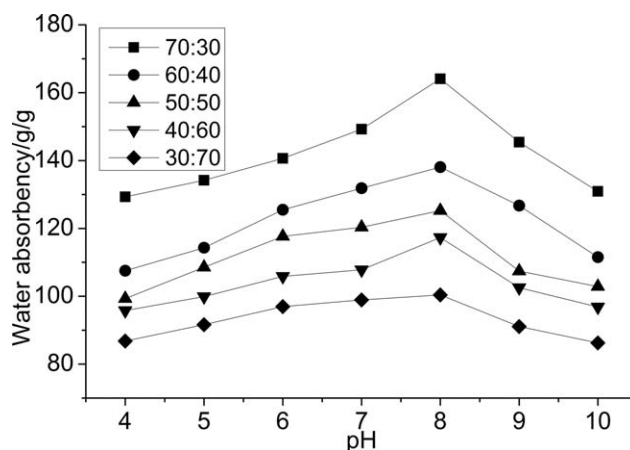
dration (salt-out) of NIPAM segments over the LCST leaves the NIPAM chains in a collapsed state.[59–61] Meanwhile, IA, as an ionic monomer, holds a better adsorption capability in water. With increase in IA amount, the amount of COO$^-$ increase, which increases the electrostatic repulsion force between COO$^-$ groups, inducing an expansion of the polymer chains within the network structure, causing an extensive chain relaxation process within the network. On the other hand, the amount of Na$^+$ ions also rises, which leads to the enhancement of the ionic strength in the polymeric network and the improvement of osmotic pressure difference. Hence, water absorbency increases with increasing IA/NIPAM mass ratio. However, in salt solution, Na$^+$ ion concentration will increase with increasing IA amount and reduce the electrostatic repulsions by screening the negative charges of COO$^-$ groups. As a result, both the osmotic pressure of the gel phases and the chain relaxation process within the network are reduced and thus the salt absorbency decreases with increasing IA/NIPAM mass ratio.

### Effects of IA/NIPAM Mass Ratio on the Temperature-Sensitivity of the pH- and Temperature-Dual Responsive Hydrogels

The swelling behavior of dual responsive hydrogels was investigated as a function of temperature and IA/NIPAM mass ratio.
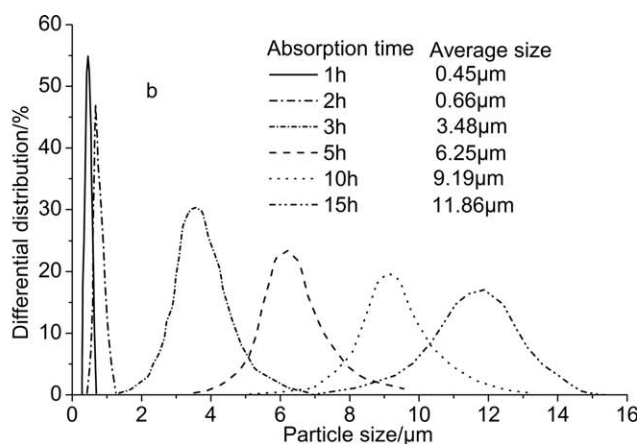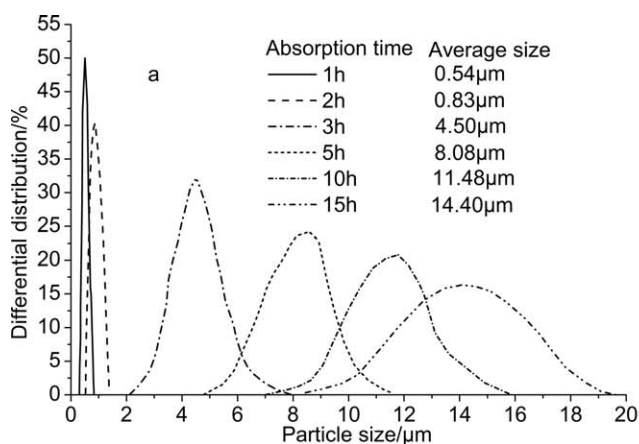


**Figure 6.** Water swellability of the pH- and temperature-dual responsive hydrogels synthesized by different IA/NIPAM mass ratio, (a) 70 : 30 and (b) 30 : 70.
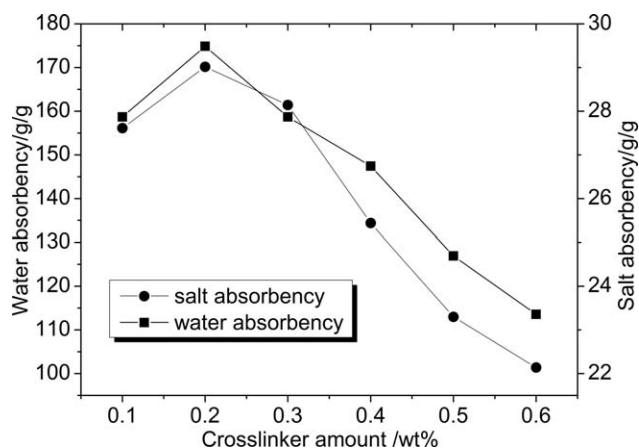
**Figure 7.** Effects of crosslinker amount on the water absorbency and salt absorbency of the pH- and temperature-dual responsive hydrogels.

As shown in Figure 4, swelling capacities of all hydrogels decreased with temperature increasing from 30 to 70°C, and the swelling behavior of hydrogels around 30–50°C displayed an increasing sharp decrease with decreasing IA/NIPAM mass ratio, indicating an increased temperature-sensitivity of the pH- and temperature-responsive hydrogels with decreasing IA/NIPAM mass ratio. The NIPAM moieties become dehydrated (and effectively hydrophobic in nature) when heated above their LCST (i.e., $T > 32°C$),[58] and will associate and form thermoreversible aggregates, resulting in the shrinkage of the polymeric network, release of the absorbed water and decrease of swelling capacity. It is of interest to note that the shrinkage temperature range (around 30–50°C) of the dual responsive hydrogels was higher and broader than that of the conventional PNIPAM hydrogel (around 32°C). This might be ascribed to the fact that LCST can be enhanced by the copolymerization of NIPAM with hydrophilic or ionized monomers.[62]

### Effects of IA/NIPAM Mass Ratio on the pH-Sensitivity of the pH- and Temperature-Dual Responsive Hydrogels
pH-dependent swelling behaviors of the dual responsive hydrogels under room temperature were investigated with changes in pH and IA/NIPAM mass ratio, as shown in Figure 5. It can be seen that water absorbency increased as pH increased to 8, and

then decreased with further increase of pH value. In addition, pH-sensitivity of the dual responsive hydrogels increased with increasing IA/NIPAM mass ratio. According to previous works, the swelling capacity of hydrogels were influenced by the rubbery elasticity, ionic osmotic, and affinity of polymer toward water.[63] At a low pH region, most carboxylic acid groups in dual responsive hydrogels are in the form of COOH. As the pH of the medium increases, the carboxylic acid groups become ionized, and the resulting electrostatic repulsion in the network causes the hydrogels to swell. Besides, the amount of $Na^+$ ions rises with increasing pH value, leading to the enhancement of the ionic strength in the polymeric network, and thereby the improvement of osmotic pressure difference and water absorption capacity. However, more $Na^+$ ions will be introduced into the hydrogels with the pH value over 8, reducing the repulsion by screening the negative charges of $COO^-$ groups.[64] As a result, both the osmotic pressure of the gel phases and the chain relaxation process within the network are reduced and consequently the water absorption capacity decreases.

### Effects of IA/NIPAM Mass Ratio on Swellability of the pH- and Temperature-Dual Responsive Hydrogels
Swellability of the dual responsive hydrogels synthesized at different IA/NIPAM mass ratio under room temperature was shown in Figure 6. The dual responsive hydrogels became expanding rapidly with increasing swelling time, accompanied with increasing mean particle size and broadening particle size distribution. Mean particle size of the dual responsive hydrogels synthesized at IA/NIPAM mass ratio of 70 : 30 and 30 : 70, increased from 0.54 and 0.45 $\mu$m to 14.40 and 11.86 $\mu$m, respectively, with swelling time increasing from 1 to 15 h. This indicated the good swellability of the dual responsive hydrogels.

### Effects of Crosslinker Amount on the Water Absorption and Salt Absorption of the pH- and Temperature-Dual Responsive Hydrogels
Crosslinking density plays a major role in modifying the swelling properties of hydrogels. The amount of crosslinker dependence of water absorbency and salt absorbency of the dual responsive hydrogels was investigated and indicated in Figure 7. Both water absorbency and salt absorbency increased with crosslinker amount increased to 0.2 wt %, and then decreased
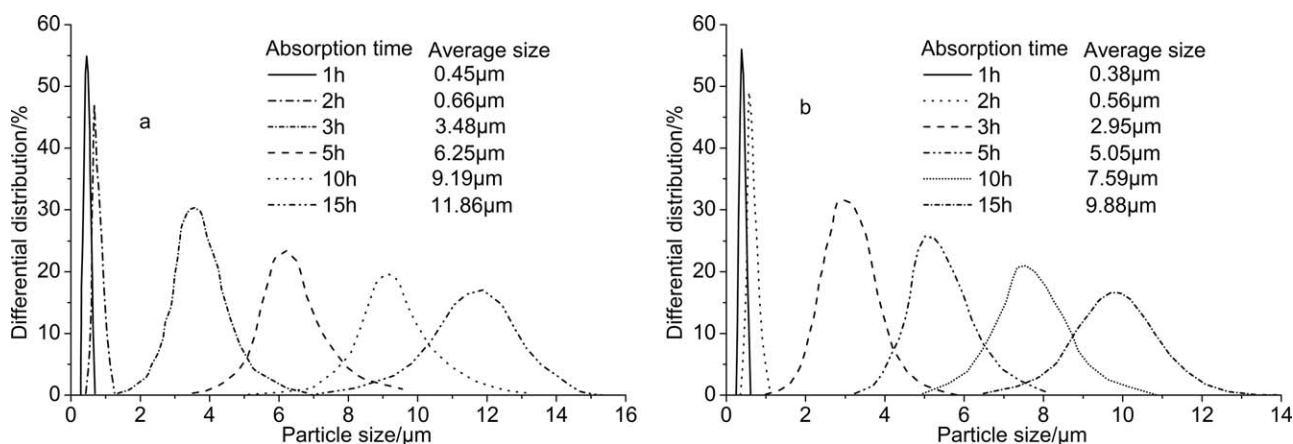


**Figure 8.** Water swellability of the pH- and temperature-dual responsive hydrogels synthesized by different crosslinker amount, (a) 0.2% and (b) 0.6%.
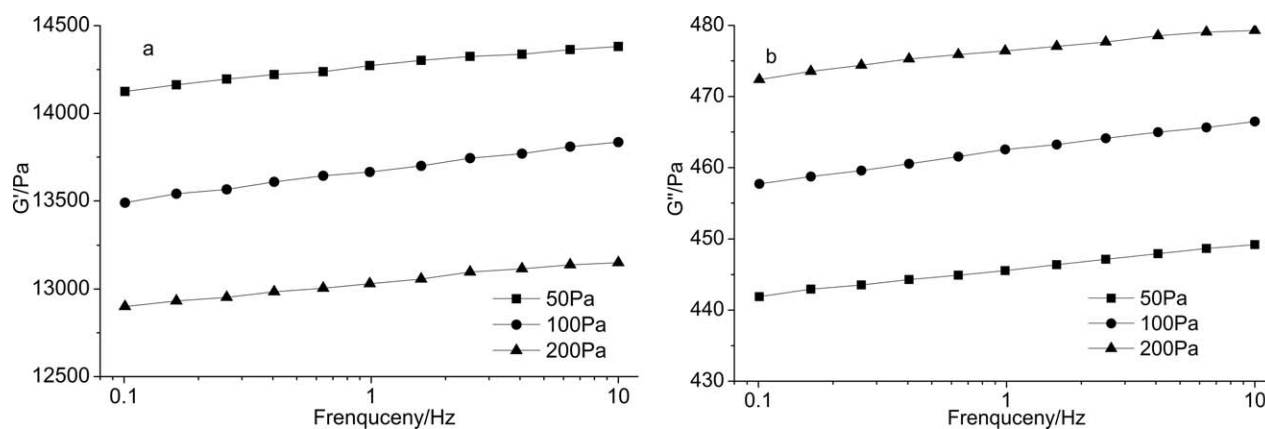
**Figure 9.** Variation of the storage modulus $G'$ (a) and the loss modulus $G''$ (b) with the oscillation frequency for the pH- and temperature-dual responsive hydrogels at different stress.

with increasing crosslinker amount. As we known, crosslinker amount determines the crosslinking density of the hydrogels, accordance to the theory of Flory.[65] When crosslinker amount is below 0.2 wt %, both water and salt absorbencies decrease because of the increase of soluble materials and incomplete network structure. On the other hand, higher crosslinking agent will result in more crosslink points, decreasing both the space among the grids of the three-dimensional network and the elasticity of the polymeric network. This will make it more difficult for the network to be swollen by water or salt solution and therefore decrease both water and salt absorbency.

### Effects of Crosslinker Amount on Swellability of the pH- and Temperature-Dual Responsive Hydrogels

Swellability of the dual responsive hydrogels synthesized at different crosslinker amount under room temperature and pH value of 7 was shown in Figure 8. As indicated in Figure 8, mean particle size of the dual responsive hydrogels synthesized at crosslinker amount of 0.2 and 0.4 wt %, increased from 0.45 and 0.38 $\mu$m to 11.86 and 9.88 $\mu$m, respectively, with swelling time increasing from 1 to 15 h. This indicated the good adjustable swellability of the dual responsive hydrogels via changing the amount of crosslinker.

### Dynamic Rheology of the Swollen pH- and Temperature-Dual Responsive Hydrogels

Rheology measurements under oscillating dynamic conditions were carried out on the swollen dual responsive hydrogels, and the results were in Figure 9. As indicated in Figure 9, both storage moduli $G'$ and loss moduli $G''$ of the swollen dual responsive hydrogels changed little with increasing oscillation frequency under stress of 50 Pa, 100 Pa, and 200 Pa, respectively. Solid-like behaviors (storage moduli $G' >$ loss moduli $G''$) were observed in the whole oscillation frequency region, due to the three-dimensional network structure. With the increase of stress, $G'$ decreased, whereas $G''$ gradually increased, indicating enhanced viscoelastic behaviors of the swollen dual responsive hydrogels under high stress. As we know, polymeric chains of the hydrogels are more liable to stretch, twist and relax under high stress, resulting in an increasing liquid-like behavior and decreasing solid-like behavior. Therefore, the dual responsive

hydrogels show remarkable viscoelastic behaviors under high stress.

### CONCLUSIONS

A novel pH- and temperature-dual responsive poly (NIPAM/IA/AM) hydrogels was synthesized by facile inverse microemulsion polymerization. The dual responsive hydrogels showed suitable water and salt absorbency, distinct pH-, and temperature-sensitivity, adjustable swellability, solid-like behaviors and enhanced viscoelastic behaviors under high stress. Water absorbency and pH-sensitivity increased while salt absorbency and temperature- sensitivity decreased with increasing IA/NIPAM mass ratio. Both water absorbency and salt absorbency increased with crosslinker amount increased to 0.2 wt %, and then decreased with increasing crosslinker amount. Temperature-induced shrinkage range (around 30–50°C) of the dual responsive hydrogels was higher and broader than that of the conventional PNIPAM hydrogel (around 32°C). TEM indicated that the as-synthesized regular and spherical-like hydrogel particles had the mean particle size of 49 nm in the range of 30–78 nm. FTIR spectrum revealed the formation of dual responsive poly (NIPAM/IA/AM) hydrogels.

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