

# Synthesis and properties of a dual responsive hydrogel by inverse microemulsion polymerization

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MS received 4 July 2014; revised 24 August 2014; accepted 30 August 2014

**Abstract.** A novel dual responsive hydrogel was synthesized by inverse microemulsion polymerization, using itaconic acid as pH-responsive monomer and N-isopropylacrylamide as thermo-responsive monomer. pH- and temperature-sensitivity and dynamic viscoelasticity behaviour of the dual responsive hydrogels were investigated. Dual responsive hydrogels showed remarkable pH- and temperature-sensitivity and enhanced viscoelastic behaviour under high stress. Temperature-induced shrinkage range of the dual responsive hydrogels was higher and broader than that of the conventional poly(N-isopropylacrylamide) hydrogel. FTIR revealed the structure of dual responsive hydrogels. The as-synthesized regular and sphere-like hydrogel particles had the average particle size of 49 nm in the range of 30–78 nm.

**Keywords.** Hydrogel; microemulsion polymerization; sensitivity; N-isopropylacrylamide.

## 1. Introduction

Intelligent hydrogels undergoing significant changes in their physicochemical properties in response to minor changes in external stimuli, such as temperature,<sup>1,2</sup> pH,<sup>3</sup> solvent composition,<sup>4,5</sup> light,<sup>6</sup> magnetic field,<sup>7</sup> and ionic strength,<sup>8</sup> have attracted much attention because they can serve as functional materials with potential applications in the areas of drug delivery,<sup>9</sup> microlenses,<sup>10</sup> sensors<sup>11</sup> and artificial organ,<sup>12</sup> etc.

Dual responsive hydrogels that are both temperature- and pH-sensitive are the most widely investigated because these two stimuli are the most commonly used external stimuli.<sup>13</sup> Poly(N-isopropylacrylamide) (PNIPAM) is the most popular temperature-responsive hydrogel due to its volume phase transition temperature (around 32°C) close to normal body temperature. PNIPAM has been extensively studied due to its thermal sensitive property and can react with acrylic acid or other polymers to design new multifunctional materials.<sup>14–19</sup>

On the basis of our previous research on super-absorbent hydrogels and microemulsion polymerization,<sup>20–31</sup> a novel dual responsive hydrogel with

average particle size of 49 nm was prepared by inverse microemulsion polymerization, using itaconic acid as pH-responsive monomer, N-isopropylacrylamide as thermo-responsive monomer and acrylamide as the non-ionic hydrophilic monomer. The dual responsive hydrogel showed good pH- and temperature-sensitivity and water swellability.

## 2. Experimental

### 2.1 Materials

Itaconic acid (IA) was purified by recrystallization. Acrylamide (AM), N-isopropyl acrylamide (NIPAM) and N-methylene-bis-acrylamide (MBA) were purified by recrystallization. Ammonium persulfate (APS), sodium bisulfite (SBS), sorbitan mono-oleate (Span-80), polyoxyethylene sorbitan monooleate (Tween 80), cyclohexane were used without further purification.

### 2.2 Synthesis of dual responsive hydrogels

Dual responsive hydrogel was synthesized according to the following steps. Typically, 3 g IA was dissolved

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in 10 mL distilled water and neutralized with 20% sodium hydroxide solution in an ice bath, and then 4 g AM, 2 g NIPAM and 0.036 g MBA 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 Span 80, 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 SBS (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.

### 2.3 Water absorbency of 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. The weight of the hydrogels containing absorbed water was measured after draining for 30 min, and water absorbency was calculated according to the following equation:

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

where  $W_1$  and  $W_2$  are the weight of the dry and swollen hydrogels, respectively.

### 2.4 Dynamic viscoelasticity measurements of the dual responsive hydrogels

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 Pa, 100 Pa and 200 Pa, respectively.

### 2.5 Characterization of the dual responsive hydrogels

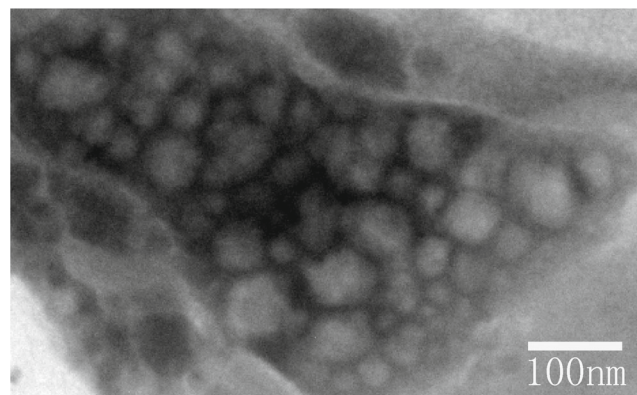
The micrographs of dual responsive hydrogels were taken using TEM (Tecnai G2 F20S-TWIN, FEI). Before TEM observation, inverse microemulsion samples were diluted with cyclohexane, stained with phosphotungstic acid, and then dipped onto the copper grid and allowed to evaporate at room temperature. FT-IR 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.

## 3. Results and Discussion

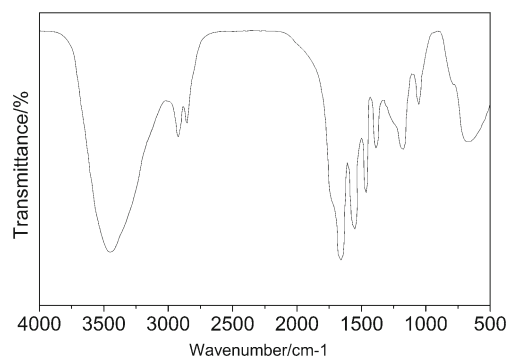
### 3.1 Morphology and structure of the as-synthesized dual responsive hydrogels

Morphology of the as-synthesized dual responsive hydrogels was characterized by TEM and the result was shown in figure 1. The hydrogel particles are regular and spherical-like in shape, and have the average 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 spectrum of dual responsive hydrogels was demonstrated in figure 2. The peak at  $3445 \text{ cm}^{-1}$  is attributed to OH and NH stretching vibrations. The peaks at  $2920$  and  $2854 \text{ cm}^{-1}$  are ascribed to the  $\text{CH}_2$  asymmetric and  $\text{CH}_2$  symmetric stretch, respectively.<sup>32</sup> The absorption bands at  $1720 \text{ cm}^{-1}$  are assigned to carboxylic acid.<sup>33</sup> The bands at  $1660 \text{ cm}^{-1}$  and  $1550 \text{ cm}^{-1}$  represent amide group stretching.<sup>34</sup> The absorption peak at  $1385 \text{ cm}^{-1}$  is attributed to isopropyl group. The peak at  $1050 \text{ cm}^{-1}$  arises from C- O stretching



**Figure 1.** TEM image of the dual responsive hydrogels synthesized at IA/ NIPAM mass ratio of 70:30.



**Figure 2.** FTIR spectrum of the dual responsive hydrogels synthesized by inverse microemulsion polymerization.

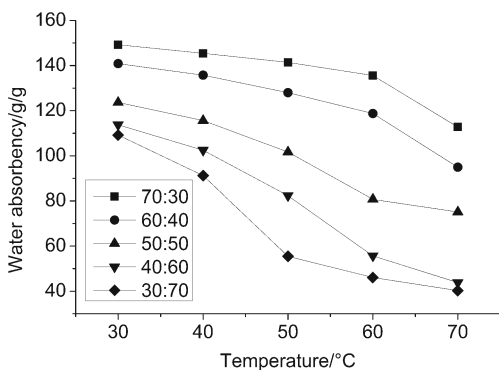
vibration. All the above results revealed the formation of dual responsive poly (NIPAM/IA/AM) hydrogels.

### 3.2 Temperature-sensitivity of the dual responsive hydrogels

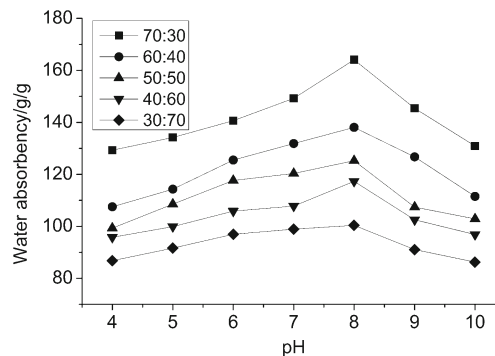
Temperature-dependent swelling behaviours of the dual responsive hydrogels were investigated with different temperatures and IA/NIPAM mass ratio, and the results were shown in figure 3. Swelling capacities of all hydrogels decreased with temperature increasing from 30 to 70°C, and the swelling behaviour of hydrogels around 30–50°C displayed an increasing sharp decrease with decreasing IA/NIPAM mass ratio, indicating an increased temperature sensitivity of the dual 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.,  $T > 32^\circ\text{C}$ ),<sup>35</sup> associate and form thermoreversible aggregates, decreasing Flory-Huggins interaction parameter  $\chi$  between the solvent and the hydrogel, thus inducing changes in the osmotic pressure. This results 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.<sup>36</sup>

### 3.3 pH-sensitivity of the dual responsive hydrogels

pH-dependent swelling behaviours of the dual responsive hydrogels were investigated with changes in pH and IA/NIPAM mass ratio, as shown in figure 4. Water



**Figure 3.** Temperature sensitivity of the dual responsive hydrogels synthesized at different IA/ NIPAM mass ratio.

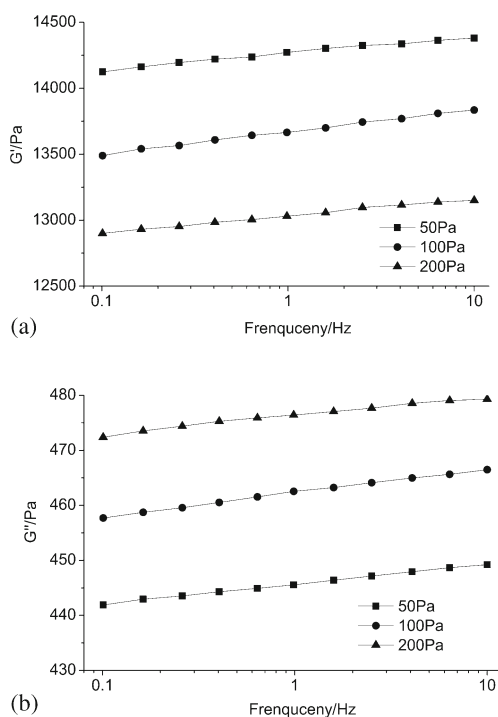


**Figure 4.** pH sensitivity of the dual responsive hydrogels synthesized at different IA/ NIPAM mass ratio.

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. 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  $\text{Na}^+$  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  $\text{Na}^+$  ions will introduce into the hydrogels with the pH value exceeding 8, reducing the repulsion by screening the negative charges of  $\text{COO}^-$  groups.<sup>37</sup> 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.

### 3.4 Dynamic rheology of the dual responsive hydrogels

Dynamic rheology behaviours of the dual responsive hydrogels were shown in figure 5. Both storage moduli  $G'$  and loss moduli  $G''$  of the dual responsive hydrogels changed little with increasing oscillation frequency under stress of 50 Pa, 100 Pa and 200 Pa, respectively. Solid-like behaviours (storage moduli  $G' > \text{loss moduli } G''$ ) were observed due to the three-dimensional network structure. With the increase of stress,  $G'$  decreased, whereas  $G''$  gradually increased, indicating enhanced viscoelastic behaviours of the dual responsive hydrogels under high stress. Polymeric chains of the hydrogels are more liable to stretch, twist and relax under high stress, resulting in an increased liquid-like behaviour and decreased solid-like behaviour. Therefore the dual responsive hydrogels



**Figure 5.** Variation of the storage modulus  $G'$  (a) and the loss modulus  $G''$  (b) with the oscillation frequency for the dual responsive hydrogels at different stress.

show remarkable viscoelastic behaviours under high stress.

#### 4. Conclusions

For the first time, a new dual responsive hydrogel was synthesized by facile inverse microemulsion polymerization, using IA as pH-responsive monomer and NIPAM as thermo-responsive monomer. pH-sensitivity and temperature-sensitivity of the dual responsive hydrogels increased and decreased with increasing IA/NIPAM mass ratio, respectively. 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). Dual responsive hydrogels show enhanced viscoelastic behaviour under high stress. FTIR demonstrated the formation of dual responsive poly(NIPAM/IA/AM) hydrogels. TEM indicated that the as-synthesized hydrogel particles were regular and sphere-like in shape and had average particle size of 49 nm in the range of 30–78 nm.

#### Acknowledgements

The authors are grateful to the support of PetroChina Innovation Foundation, China (2012D-5006-0212),

Sichuan Provincial Science & Technology Pillar Program, China (2013GZ0149, 2014GZX0010), Opening fund of State Key Laboratory of Geohazard Prevention and Geoenvironment Protection, Chengdu University of Technology, China (SKLGP2012K004) and the Sichuan Youth Science and Technology Innovation Research Team Funding Scheme, China (2013TD0005).

#### References

1. Kiler J, Scranton A B and Peppas N A 1990 *Macromolecules* **23** 4944
2. Xue F F, Yuan D D, Sahasrabudhe A, Biswas S, Wang P, Tang X Y, Chen D Y, Yuan R X and Roy S 2012 *New J. Chem.* **36** 2541
3. Chiu H C, Lin Y F and Hung S H 2002 *Macromolecules* **35** 5235
4. Roy S G, Haldar U and De P 2014 *ACS Appl. Mater. Interfaces* **6** 4233
5. Kokufata E, Zhang Y Q and Tanaka T 1991 *Nature* **351** 302
6. Mamada A, Tanaka T, Kungwachakun D and Irie M 1990 *Macromolecules* **23** 1517
7. Xulu P M, Filipcsei G and Zrinyi M 2000 *Macromolecules* **33** 1716
8. Park T G and Hoffman A S 1993 *Macromolecules* **26** 5045
9. Ward M A and Georgiou T K 2011 *Polymers* **3** 1215
10. Dong L and Jiang H 2007 *Soft Matter* **3** 1223
11. Hoare T and Pelton R 2007 *Macromolecules* **40** 670
12. Shiino D, Murata Y, Kataoka K, Koyama Y, Yokoyama M, Okano T and Sakurai Y 1994 *Biomaterials* **15** 121
13. Zhao C W, Zhuang X L, He P, Xiao C S, He C L, Sun J R, Chen X S, Jing X B 2009 *Polymer* **50** 4308
14. Zhang X, Yang Y, Wang F and Chung T 2002 *Langmuir* **18** 2013
15. Zhang J, Xu S and Kumacheva E 2004 *J. Am. Chem. Soc.* **126** 7908
16. Muratalin M and Luckham P F 2013 *J. Colloid. Interf. Sci.* **396** 1
17. Stile R A, Burghardt W R and Healy K E 1999 *Macromolecules* **32** 7370
18. Nishio T, Ayano E, Suzuki Y, Kanazawa H and Okano T 2011 *J. Chromatogr. A* **1218** 2079
19. Burova T V, Grinberg N V, Lozinskii V I, Moiseeva S P, Kotelnikov G V, Grinberg V Y and Khokhlov A R 2010 *Polym. Sci. Ser. A* **52** 356
20. Wan T, Xiong L, Huang R Q, Zhao Q H, Tan X M, Qin L L and Hu J Y 2014 *Polym. Bull.* **71** 371
21. Wan T, Huang R Q, Zhao Q H, Xiong L, Luo L, Zhang H B and Cai G J 2014 *J. Compos. Mater.* **48** 2341
22. Wan T, Huang R Q, Zhao Q H, Xiong L, Luo L, Tan X M and Cai G J 2013 *J. Appl. Polym. Sci.* **130** 698
23. Wan T, Huang R Q, Zhao Q H, Xiong L, Qin L L, Tan X M and Cai G J 2013 *J. Appl. Polym. Sci.* **130** 3404
24. Wan T, Yao J, Sun Z S, Wang L and Wang J 2011 *J. Petrol. Sci. Eng.* **78** 334
25. Wan T, Zang T S, Wang Y C, Zhang R and Sun X C 2010 *Polym. Bull.* **65** 565

26. Wan T, Wu C, Ma X L, Yao J and Lu K 2009 *Polym. Bull.* **62** 801
27. Wan T, Yao J and Ma X L 2008 *J. Appl. Polym. Sci.* **110** 3859
28. Wan T, Wang L, Yao J, Ma X L, Yin Q S and Zang T S 2008 *Polym. Bull.* **60** 431
29. Wan T, Hu Z W, Ma X L, Yao J and Lu K 2008 *Prog. Org. Coat.* **62** 219
30. Wan T, Wang X Q, Yuan Y and He W Q 2006 *Polym. Int.* **55** 1413
31. Wan T, Wang X Q, Yuan Y and He W Q 2006 *J. Appl. Polym. Sci.* **102** 2875
32. Mendelsohn R, Flach C R and Moore D J 2006 *BBA-Biomembranes.* **1758** 923
33. Chen G, Zhang Y and Zhou X 2006 *Appl. Surf. Sci.* **253** 1107
34. Krishnan M and Flanagan D R 2000 *J. Control. Release.* **69** 273
35. Zhao C W, Gao X Y, He P, Xiao C S, Zhuang X L and Chen X S 2011 *Colloid. Polym. Sci.* **289** 447
36. Gil E S and Hudson S M 2004 *Prog. Polym. Sci.* **29** 1173
37. Ma J H, Xu Y J, Zhang Q S, Zha L S and Liang B R 2007 *Colloid Polym. Sci.* **285** 479