

Properties of a Poly(acrylamide-*co*-diallyl dimethyl ammonium chloride) Hydrogel Synthesized in a Water–Ionic Liquid Binary System

Qian Zhao, Jianzhong Sun, Songwei Chen, Qiyun Zhou

State Key Laboratory of Chemical Engineering, Department of Chemical and Biochemical Engineering, Zhejiang University, Hangzhou 310027, China

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ABSTRACT: A novel copolymer hydrogel, poly(acrylamide-*co*-diallyl dimethyl ammonium chloride), was prepared by the radical copolymerization of acrylamide and diallyl dimethyl ammonium chloride in an ionic liquid (IL)–water binary system in the presence of the crosslinker *N,N'*-methylene bisacrylamide. The equilibrium swelling ratios of the hydrogels synthesized in the IL–water binary system increased with the content of IL and were remarkably higher than that of the gel synthesized in water. Differential scanning calorimetry measurements showed that the glass-transition temperatures of the dry hydrogels that were synthesized in the IL–water binary system were remarkably lower than that of the gel synthesized in pure

water. The mechanical properties of the gels synthesized in both water and the IL–water binary system were characterized with a universal material-testing machine. The results show that fracture toughness of the hydrogels was improved when they were synthesized in the IL–water binary system. The gel shrank under a direct-current electric field. The response rates of the gels that were synthesized with the IL–water binary system were faster than that of the gel synthesized in water. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2940–2945, 2010

Key words: hydrogels; stimuli-sensitive polymers; acrylamide; ionic liquid; electrostriction

INTRODUCTION

Hydrogels are able to absorb large amounts of water without losing their three-dimensional structures. Stimuli-sensitive hydrogels, so-called smart or intelligent hydrogels, exhibit responses to external stimuli, such as temperature,¹ electric fields,^{2,3} light,⁴ pressure,⁵ magnetic fields,⁶ pH,^{7,8} or specific molecular recognition events.⁹

Compared with the other external stimuli, there are some advantages when the hydrogels can respond to electric fields: the conditions of the stimulus, such as voltage, magnitude of current, duration of electric pulses, and intervals between pulses, can be controlled precisely without delay and transport resistance. Tanaka et al.¹⁰ reported that when partially hydrolyzed polyacrylamide gels were immersed in a water–acetone (50:50) mixture and fixed to one of the electrodes, 20% of the gel (adjacent to the anode) collapsed, whereas the rest of the gel remained in a swollen state. Sutani et al.¹¹ reported the controlled release of hyaluronic acid from a poly(acrylamide-*co*-2-hydroxyethyl methacry-

late) gel under the on–off switching of an electrical field. Most of the electroresponsive gels studied have been polyanions. Diallyl dimethyl ammonium chloride (DADMAC) is a kind of water-soluble compound, and its quaternary ammonium group can be a depressor of bacteria and fungi.¹² Poly(diallyl dimethyl ammonium chloride) (PDADMAC) is a typical cation polyelectrolyte. The crosslinked PDADMAC hydrogel is very fragile in the swollen state,^{13,14} which restricts its application. Kim and coworkers prepared alginate/PDADMAC¹⁵ and chitosan/PDADMAC¹⁶ semi-interpenetrating polymer network hydrogels. Both of the semi-interpenetrating polymer network hydrogels exhibited an electroresponse under a direct-current (dc) electric field. Chen et al.¹⁷ prepared a thermosensitive poly(*N*-isopropylacrylamide-*co*-diallyl dimethyl ammonium chloride) hydrogel and investigated its drug-release behavior at different temperatures.

Ionic liquids (ILs) are molten salts with melting points close to or below room temperature, high conductivity, nonvolatility, nonflammability, and low toxicity.^{18–20} Because of these properties, they are used to prepare gel polymer electrolytes to improve their performance with respect to the conductivity and mechanical properties.^{21–23} Moreover, Scott et al.²⁴ reported that imidazolium-salt-based ILs improved the thermal stability of poly(methyl

Correspondence to: J. Sun (bigwig@zju.edu.cn).

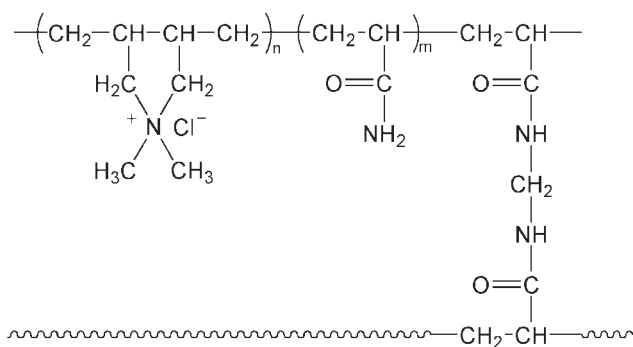


Figure 1 Chemical structure of the poly(AM-co-DADMAC) hydrogel.

methacrylate) and reduced its glass-transition temperatures (T_g 's). However, no authors have reported the properties of stimuli-sensitive hydrogels synthesized in ILs.

In this study, poly(acrylamide-co-diallyl dimethyl ammonium chloride) [poly(AM-co-DADMAC)] hydrogels were prepared in water and an IL-water binary system. The chemical structure of the hydrogel is shown in Figure 1. The differences in the swelling capability and mechanical properties between the two kinds of gels were investigated. The T_g values of the xerogels were also investigated by differential scanning calorimetry (DSC). Moreover, the deswelling behavior of the hydrogels was studied under a dc electric field.

EXPERIMENTAL

Materials

Acrylamide (AM; 99%, Shanghai Third Chemical Reagent Factory, China), 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim]BF₄; 97%, Hangzhou Chemer Chemical Co., Ltd., China), DADMAC (60% aqueous solution, Hangzhou Yinghu Chemical Co., Ltd., China), *N,N'*-methylene bisacrylamide (BIS; 98%, Fluka Chemika), *N,N,N',N'*-tetramethylethylenediamine (TEMED; 99%, Acros Organics, NJ), ammonium persulfate (APS; 98%, Yixing Second Chemical Reagent Factory, China) were used as received.

Synthesis of the poly(AM-co-DADMAC) gel

AM, BIS, and DADMAC were dissolved in the IL ([emim]BF₄)-deionized water binary system in glass vessels. Then, APS and TEMED were added to the glass vessels. Polymerization was carried out at room temperature for 8 h. After the reaction, the resulting hydrogels were immersed in excessive deionized water at ambient temperature for a week, during which the samples were refreshed by deionized

water every 12 h to remove the unreacted materials. The resulting gel was cut into pieces (20 × 20 × 10 mm³). The drying of the swollen gels was performed in an oven at 40°C for 48 h until there was no further weight decrease. The hydrogels prepared with various amount of IL were labeled IG0, IG1, IG2, IG3, and IG4. The feed compositions of the monomers and other reactants are summarized in Table I.

Measurement of the equilibrium swelling ratio (ESR)

The ESR values of the hydrogels were measured when the dry samples were immersed in deionized water, solutions with various pH values (the ionic strength of which were regulated to 0.5 mol/L with solutions of hydrochloric acid, sodium hydroxide, and sodium chloride), and IL-water binary system with various contents of IL to reach sufficient swelling. When the swelling was done in deionized water, The ESRs of the samples that were never dried were also measured for contrast. After the excessive water was wiped off of the sample surface with moistened filter paper, the weights of the swollen samples were measured. ESR was determined by $ESR = W_{eq}/W_d$, where W_{eq} and W_d are the weight of the gel after equilibrium swelling and the weight of dry gel, respectively.

DSC measurement of the xerogels

DSC studies were carried out on a PerkinElmer (USA) DSC 7 thermal analyzer with N₂ as a purge gas by nonisothermal scanning at a heating rate of 20°C/min from 50 to 200°C.

Mechanical properties of the gel

To investigate the effects of IL, the mechanical properties were tested with a universal material-testing machine (UMTM; Zwick/Roell Z020, Germany). The gel samples without any further treatment (the

TABLE I
Feed Compositions of the Poly(AM-co-DADMAC) Hydrogels

	Gel sample				
	IG0	IG1	IG2	IG3	IG4
AM (mg)	150	150	150	150	150
DADMAC (mL)	96	96	96	96	96
[emim]BF ₄ (mg)	0	150	300	450	600
BIS (mg)	5	5	5	5	5
4 wt % APS (mL)	100	100	100	100	100
TEMED (mL)	10	10	10	10	10
Water (mL)	1.5	1.5	1.5	1.5	1.5

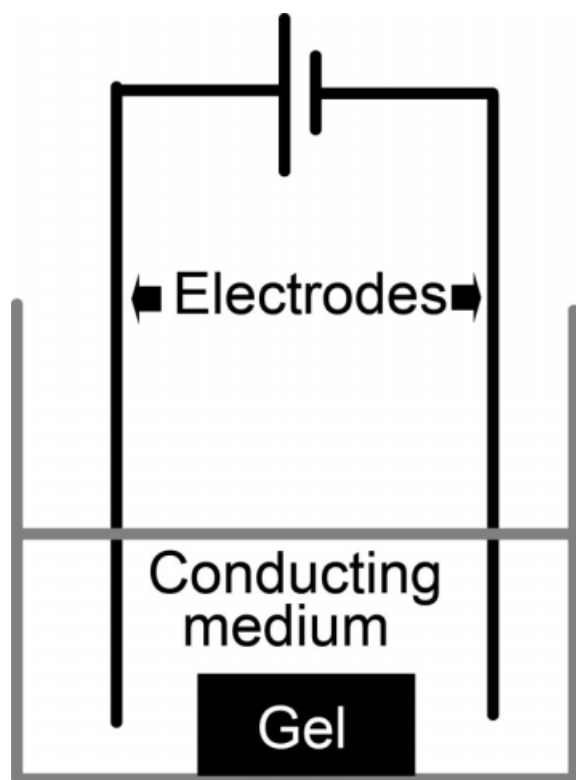


Figure 2 Schematic diagram showing gel electrostriction under an applied electrical field.

measurement was carried out as soon as the polymerization was complete) were cut into cylinders (15 mm thick, 12 mm in diameter). We measured the strength of the gels by compressing samples to 80% of their ordinary thickness between two parallel plates at a speed of 5 mm/min. The moduli of the samples were calculated from strains of 2–6% by the UTM software.

Deswelling behavior of the gel under an electrical field

The technique for measuring the deswelling behavior in the dc electric field is shown schematically in Figure 2.³ An aqueous solution of sodium chloride was poured in a mold equipped with two carbon electrodes. The distance between two parallel carbon electrodes was 20 mm. To measure the deswelling rate, the weight of the sample was measured at various time intervals after excessive water on the surface was removed with moistened filter paper. The electrorestrictive properties of the hydrogels under a dc electrical field were characterized by the deswelling ratio (DR). DR was determined by $DR = W_t/W_0$, where W_t and W_0 are the weight of the hydrogel at time t under an electric field and the initial weight of the hydrogel without an electric field, respectively.

RESULTS AND DISCUSSION

ESR of the hydrogels

ESR in water

Wet or dry gel samples IG0, IG1, IG2, IG3, and IG4 were immersed in deionized water until equilibrium swelling. The ESRs of the hydrogels are shown in Figure 3. Figure 3(a) was obtained from the swelling procedures of the xerogel samples, whereas Figure 3(b) was obtained from the swelling of the gel samples that were never dried. As shown in Figure 3(b), all of the ESRs of the gel samples were very high when the samples were not dried. As shown in Figure 3(a), which was measured through the swelling of the xerogels, the ESRs of the hydrogels that were synthesized in the IL–water binary system were much higher than that of the gels synthesized in water, and the ESR increased with increasing IL content in the IL–water binary system. Comparing the two curves, ESR of IG0, which was prepared in pure water, diminished greatly from 262 to 71 after the drying treatment. This indicated that the structure of the IG0 gel was partially destroyed during the drying procedure and could not recover when it was swollen again. On the other hand, ESR of IG4, which was prepared in the IL–water binary system with a high IL content, only changed from 329 to 310 after the drying treatment. This indicated that the synthesis of hydrogels in an IL–water binary system could prevent the original structure from damage during drying.

The swelling process of the gels was affected by two opposite forces:²⁵ one was the osmotic pressure, which drives the solvent, such as water, into the gel network to create the volume expansion, and the other was the elastic restrictive force of the polymer network due to the expansion of the gel network. When the two opposite forces reached the

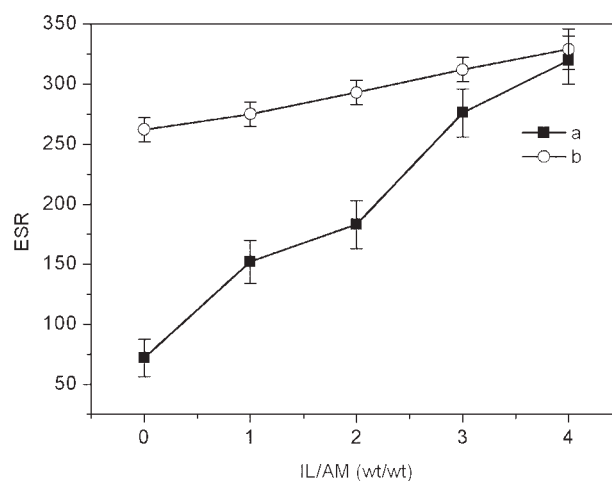


Figure 3 ESRs of the hydrogels in water obtained from (a) the swelling procedures of the xerogel samples and (b) the swelling of gel samples that were never dried.

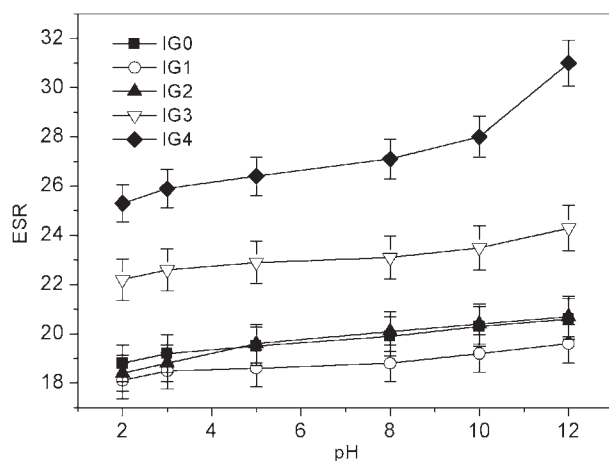


Figure 4 ESR of the hydrogels in solutions with various pH values.

equilibrium state, the swelling of the gel was in equilibrium. So, the swelling or shrinkage of the gel was caused by osmotic pressure due to the concentration gradient between the internal and external solutions of the gel. The IL existed between the polymer chains when the gel was synthesized in the IL–water binary system. The osmotic pressure of the gel inside was relatively larger because the IL was a compound of dissociated salts. Moreover, the IL, which was distributed within the gel network, decreased the elastic retractile force of the polymer network because of the increase in plasticity, so the ESR of the poly(AM-co-DADMAC) gels synthesized in the IL–water binary system were much higher than that of the gel synthesized in pure water.

ESR in solutions with various pH values

The dry gel samples were put into solutions with various pH values to measure the ESRs. The results are shown in Figure 4. As shown in Figure 4, The ESRs of gels IG3 and IG4, which were prepared in the IL–water binary system with high contents of IL, were significantly larger than those of the gels IG0, IG1, and IG2, which were prepared in water or aqueous solutions with low contents of IL. The ESR values of the gel IG4 were about twice that of the gel IG0. The enhancement of the swelling of the gels synthesized in the IL–water binary system was attributed to the introduction of IL with hydrophilic properties, which increased the osmotic pressure because of the distribution of free ionics within the gel. However, the ESRs in solutions with various pH values were much lower than that in pure water, which is shown in Figure 3, because the osmotic pressure of the solutions with various pH values was much larger than that of pure water. The resulting poly(AM-co-DADMAC) hydrogels were a kind of cation polyelectrolyte. Probably, this kind of qua-

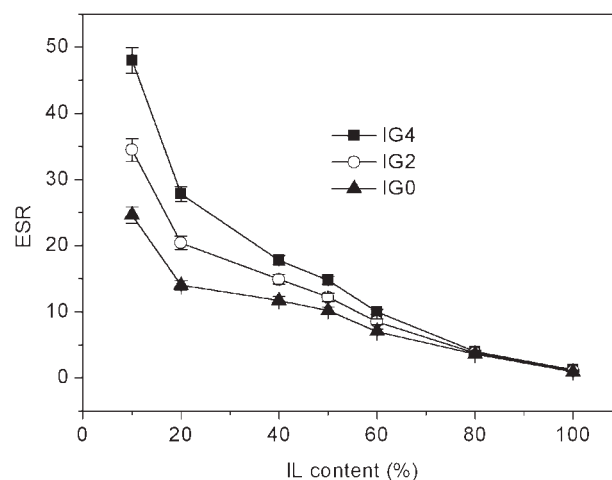


Figure 5 ESRs of the hydrogels in aqueous solutions of IL.

ternary ammonium could be ionized completely in solutions of various pH values so that the increase in ESR for a particular gel was not very significant. It has been proven that amide groups are hydrolyzed under alkaline conditions,²⁶ so the ESR of a polyacrylamide derivate hydrogels increases with an increase in the pH value, although the increase is not significant at room temperature.

ESR in aqueous solutions of IL

Figure 5 shows the ESR values of the hydrogels in aqueous solutions of IL. As shown in Figure 5, the ESR decreased with increasing IL content. Table II shows the ESR value of the gels in pure IL. As shown in Table II, the ESR value of the gel IG0 was less than 1. This demonstrates that the dry gel shrank in pure IL because the bound water was leached out of the gel. The bound water represented water molecules that interacted with the polymer network in a physical manner, which could not be removed during the drying procedure in an oven.²⁷ The mechanism of losing bound water is very complex; however, this phenomenon was explained by Kim et al.²⁸ Pure IL is composed of dissociated salts, which can be regarded as free ions. When a dry gel is immersed in pure IL, free ions distribute on the outside of the gel, and a difference in the ionic concentration between the internal and external solutions of the dry gel is generated. The internal solution exists in the form of bound water within the dry gel, the ion concentration of which is 0%, and

TABLE II
ESRs of the Gels in Pure IL

Gel sample	IG0	IG2	IG4
ESR	0.94	1.06	1.19

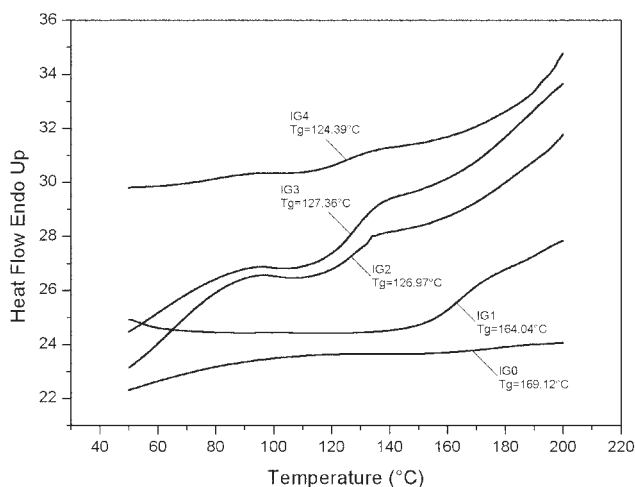


Figure 6 Nonisothermal DSC curves of the xerogels.

the external solution is pure IL with an ion concentration of 100%. A large osmotic pressure is induced by the large concentration gradient. Therefore, the osmotic pressure drives the water out of the dry gel and leads to shrinkage in the dry gel. However, the ESRs of gels IG2 and IG4 in pure IL were larger than 1. Possibly, the interaction between the polymeric matrix and water was reduced by the effect of IL when the hydrogels were prepared in the IL–water binary system. Further studies are required to obtain the exact reason.

DSC measurement of the xerogels

Figure 6 shows the results of DSC measurement of the dry gel samples. From the calculation of the curves, the T_g values of the gels were obtained. The T_g values of gels IG0, IG1, IG2, IG3, and IG4 were 169, 164, 127, 127, and 124°C, respectively. It has been reported that polymerization taking place in

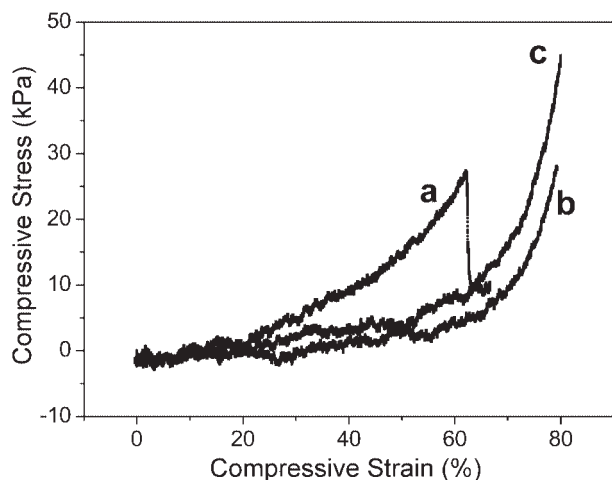


Figure 7 Compressive stress as function of the strain of gels: (a) IG0, (b) IG2, and (c) IG4.

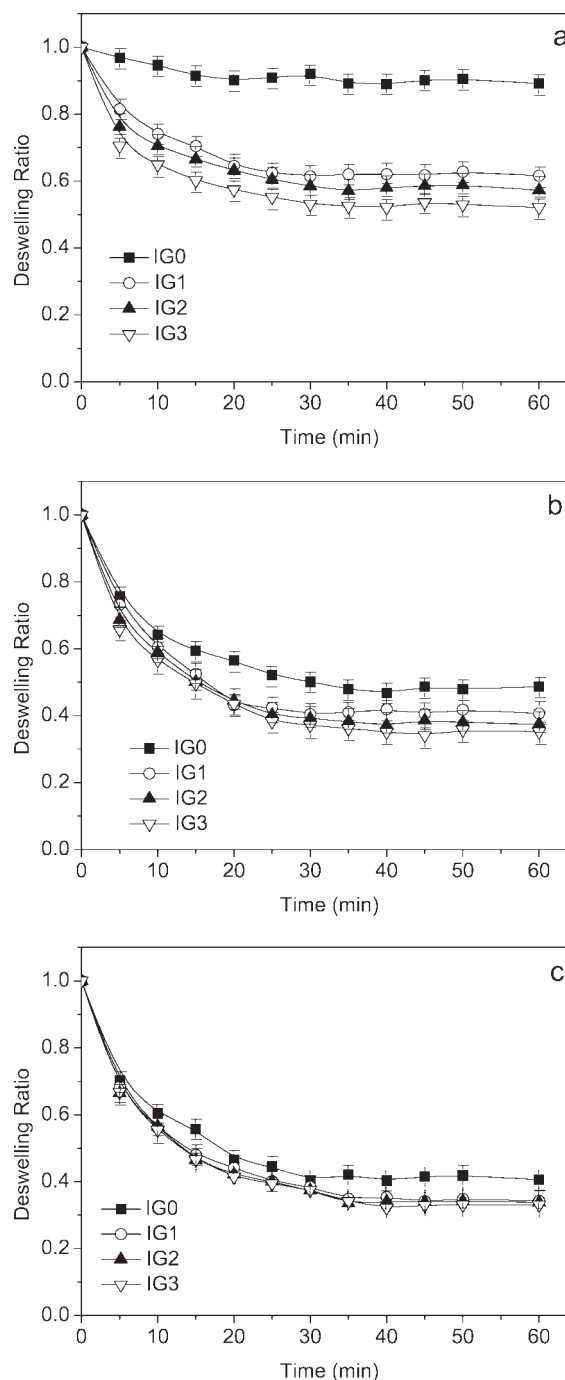


Figure 8 Deswelling kinetics of the poly(AM-co-DADMAC) gels containing IL at different constant voltages: (a) 5, (b) 15, and (c) 25 V.

the presence of IL would lead to a reduction in T_g of the resulting polymeric productions.²⁴ In this study, T_g of the gels decreased with increasing IL content in the binary system during the synthesis procedure. This implied that IL was a good plasticizer of poly(AM-co-DADMAC). Because of the nonvolatility properties of IL, the flexibility of the polymeric chains was enhanced, and the polymer was flexible and hard to break.

Strength of the gels

Figure 7 presents the stress–strain relation. Fluctuations existed in the curves during the process of compressing because the gels were soft and elastic. We calculated from strains of 2–6% by the UMTM software that the moduli of the samples IG0, IG2, and IG4 were 19.7, 14.6, and 15.5 kPa, respectively. The gel IG0 exhibited more rigidity compared with gels IG2 and IG4, and when the strain reached about 63% of ordinary height, the gel IG0 was cracked. However, gels IG2 and IG4 remained whole, even when the strain reached 80%. The result indicates that the IL in the gel network significantly influenced the rigidity and the flexibility of the gels. According to the results of DSC measurement, the polymeric chains became more flexible, and the resulting hydrogels were harder to break in the presence of IL than in the absence of IL. So, IL would be a promising plasticizer for the synthesis of hydrogels.

Electroresponse of the gels

The gels IG0, IG1, IG2, and IG3 were put into 0.1-mol/L aqueous solution of NaCl. Then, the equilibrium swollen gels were placed between two parallel electrodes full of an aqueous solution of NaCl under constant voltages of 5, 15, and 25 V. The results are shown in Figure 8. As shown in Figure 8(a), the deswelling rates of the gels synthesized in the IL–water binary system were faster than that of gels synthesized in water under a 5-V constant voltage. Moreover, the equilibrium DRs of the gels IG0, IG1, IG2, and IG3 were about 0.9, 0.61, 0.57, and 0.52, respectively. The equilibrium DR also showed a response sensitivity of the hydrogels toward the electric stimulus. The electroresponse of the gel without IL was very weak, and the response of the gels containing IL was significant. Comparing Figure 8(a) with Figure 8(b) and Figure 8(c), one can see that the hydrogels exhibited more volume change when the voltage increased. Under a 15-V constant voltage, the response rate and equilibrium DR of gel IG0, which was synthesized in water, improved further. The response behaviors of all of the gels were almost the same under 25 V. IL is a kind of compound with a high conductivity that dissociates completely in an aqueous solution regarded as free ions. When the gel contains IL, the effective ionic concentration increases a lot. So, the presence of IL can enhance the sensitivity of the electrorestrictive properties of hydrogels under low voltages.

CONCLUSIONS

There were obvious differences between the gel synthesized in water and that synthesized in the IL–

water binary system in swelling behavior, gel strength, and electroresponse. The ESRs of the hydrogels that were synthesized in the IL–water binary system increased with the content of IL and were remarkably higher than that of the gel synthesized in water when the hydrogels were swollen in deionized water, solutions with various pH values, and IL aqueous solutions. The T_g values of the xerogels decreased with the content of IL. The hydrogels were more flexible and harder to break in the presence of IL than in the absence of IL. Moreover, IL enhanced the sensitivity of the electrorestrictive properties of the hydrogels under low voltages.

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