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Nonionic gelation agents prepared from hydroxypropyl guar gum

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ABSTRACT

Nonionic gels were prepared from hydroxypropyl guar gum (HPG) with different molar substitution degrees by crosslinking with ethylene glycol diglycidyl ether (EGDE). FTIR and solid-state NMR spectroscopy revealed that the crosslinking degree of HPG gels increased with the amount of EGDE used during the reaction; this result was also confirmed by the water mobility in the swollen gels. Rheological characterization revealed behaviors typical of true gels, and their viscoelastic behaviors strongly depended on the crosslinking degree. The HPG gels absorbed buffers, aqueous saline, and water, and the absorption was not affected by the ionic strength or pH of the solution. In addition, HPG gels with high crosslinking degrees and molar substitution degrees exhibited gelation ability toward protic organic solvents such as methanol, ethanol, and 1-propanol. These HPG gels may find application as gelation agents for many industrial uses.

1. Introduction

Hydrogels may generally be described as crosslinked hydrophilic polymers that are capable of absorbing large amounts of water, often as much as 100–500 times their own weight. These crosslinked polymers are widely used in many applications such as disposable diapers, sanitary napkins, and as soil additives in agriculture (Buchholz, 1998a). Among the many commercially available hydrogels, crosslinked sodium polyacrylates, synthesized by the copolymerization of acrylic acid with various monomers, are the most widely used superabsorbent polymers. A major drawback of crosslinked sodium polyacrylates is the drastic decrease or disappearance of absorption ability in acidic and ionic solutions, as well as in aqueous or neat organic solvents, because the ionization state of the sodium carboxylate groups in these materials has an important part to play in the absorption ability. The release of free sodium cations from the crosslinked polyacrylates in solution drives the osmotic pressure between the gel and solution, causing the gel to swell, while the electrostatic repulsion between the carboxylate anions increases the volume expansion of the gel, prompting further swelling (Buchholz, 1998b). In acidic solutions, however, the carboxylate anions are protonated, diminishing the electrostatic repulsion and thereby resulting in gel shrinkage. At higher ion concentrations, the osmotic pressure that arises from the difference in ionic concentration between the gel and medium is suppressed, which results in a drastic decrease in absorbency (Peppas & Hariharan, 1994). In pure or aqueous solutions of organic solvents, dissociation of the sodium cations and carboxylate anions does not occur, and the crosslinked sodium polyacrylates do not exhibit any absorption ability (Horkay, Basser, Hecht, & Geissler, 2000).

Guar gum (GG) is a polysaccharide consisting of a backbone of 1,4-linked β-D-mannopyranosyl units (Man) with branches of 1,6-linked α-D-galactopyranosyl units (Gal) (Dea & Morrison, 1975; Dey, 1980; Dierckx & Dewettinck, 2002; Maier, Anderson, Karl, Magnuson, & Whistler, 1993; Scherbukhin & Anulov, 1999). The Man-to-Gal ratio has been estimated at 1.5:1 to 2:1 (Crescenzi et al., 2004; Gamal-Eldeen, Amer, & Helmy, 2006). The molecular weight of GG has been reported as $\sim 2.8 \times 10^7$ g mol^{-1} (Barth & Smith, 1981; Vijayendran & Bone, 1984). Due to its low cost, nontoxicity, high viscosity, and high water-solubility, GG is now used in many industries as thickening, emulsifying, and stabilizing additives (Chudzikowski, 1971; Wang, Ellis, & Ross-Murphy, 2000). The various derivatives of GG, manufactured by reacting the hydroxyl groups with various chemicals, exhibit improved physical and chemical properties (Bahamdan & Daly, 2007; Das, Ara, Dutta, & Mukherjee, 2011; Kautharapu et al., 2009; Sinha & Kumria, 2001).

Among the derivatives of GG, hydroxypropyl guar gum (HPG) has drawn attention as an essential additive to fracturing fluids,

Abbreviations: HPG, hydroxypropyl guar gum; EGDE, ethylene glycol diglycidyl ether; GG, guar gum; DDMAS, dipolar-decoupled/magic angle spinning; SR, swelling ratio; CR, crosslinking degree; MS, molar substitution.

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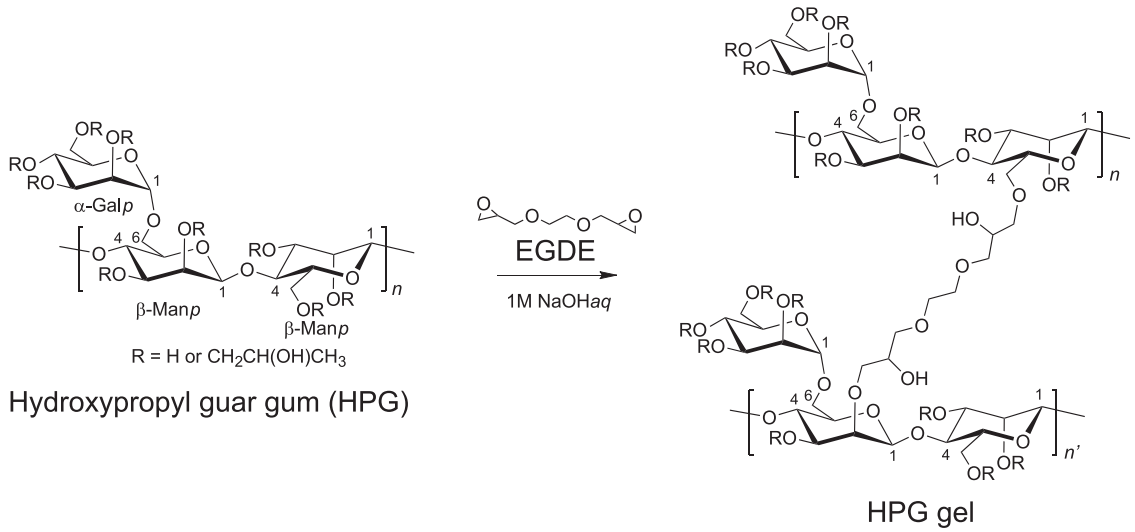

Fig. 1. Gel synthesis via crosslinking of HPG with EGDE. Although crosslinking can potentially occur at any hydroxyl group of GG, these possibilities were omitted in the figure for simplicity.

serving as a thickening agent to form concentrated muddy water in hydraulic fracturing for shale gas, tight gas, tight oil, and coal seam gas (Goel, Shah, & Grady, 2002). HPG is prepared from native guar gum via irreversible alkylation with propylene oxide in the presence of an alkaline catalyst (Prabhanjan, Gharia, & Srivastava, 1989). Compared to native guar gum, HPG shows better solubility toward alcohols such as methanol as well as water, and is thermally and chemically stable in solution (Prabhanjan, Gharia, & Srivastava, 1990). In the oil industry, for example, HPG can be easily dissolved in fracturing fluids, which normally contain many other chemical substances such as methanol, ethylene glycol, borate salts, and glutaraldehyde (Goel et al., 2002). Since HPG is soluble in various solvents, it was expected that chemically crosslinked HPG could potentially act as a versatile gelling agent for a variety of applications.

In this study, we prepared a series of gelling agents from HPG with various molar substitution (MS) values using ethylene glycol diglycidyl ether (EGDE) as a crosslinking agent (Kono, Onishi, & Nakamura, 2013). Structures of the obtained HPG gels were precisely determined through FTIR and solid-state ^{13}C NMR spectroscopies. The mobility of water in the swollen gels was investigated by analyzing the ^{1}H spin–spin relaxation time (T_2) of water, obtained by time-domain NMR spectroscopy. The viscoelastic behavior of the swollen HPG gels was characterized by rotational rheometry. Finally, the swelling behaviors of the crosslinked gels in various pH buffers, salines, and some organic solvents were investigated to determine their viability as gelling agents in different media. In addition, we discuss the relationship between the swelling behaviors and the structural parameters of the HPG gels.

2. Experimental

2.1. Materials

Three kinds of HPG with viscosity-average molecular weights of 1.9×10^5, 1.8×10^5, and 1.6×10^5 g mol^{-1} (the data of the molecular weights were provided from a manufacturer) and MS values of 1.2, 2.1, and 4.4 (described in Section 3.1), respectively, were kindly provided by Sansyo Co. Ltd., Japan. These HPGs are denoted as HPG1, HPG2, and HPG3, in order of sitincreasing MS value. EGDE was purchased from Tokyo Chemical Industry Co. Ltd., Japan. Deuterium oxide (99.9% isotopic purity) containing 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS) was purchased from Sigma-Aldrich Co., US. All other reagents were of analytical grade and were purchased from Kanto Chemicals, Japan.

2.2. Preparation of HPG gels

As shown in Fig. 1, a series of HPG gels was prepared from HPG1, 2, and 3 with EGDE in an organic synthesizer Process Station PPS-2511 with a Teflon stirring impeller (Tokyo Rikakikai Co., Ltd.). HPG gels were typically prepared as follows: HPG1 (2.0 g, 4.1 mmol per repeating unit of HPG) was completely dissolved in 1 mol L^{-1} NaOH solution (20 mL) at 4 °C using the Teflon impeller at 300 rpm. EGDE (4.1 g, 24 mmol) was added to the HPG solution, and the crosslinking reaction was carried out at 60 °C for 3 h with continuous stirring. Acetone (100 mL) was added to the reaction mixture to precipitate the gel. The gel was washed twice in 1:2 (v/v) water and acetone, dialyzed using dialysis tubing (Mw 1.2–1.3 × 10^4 cut-off, Thermo Fisher Scientific Inc., US) for 3 days until neutral, and then precipitated with acetone. The precipitate was dried under reduced pressure at 60 °C. The resultant solid particles were cut and screened through a 40 mesh filter using a PLC-2M plastic cutting mill (Osaka Chemical Co., Japan) to obtain a white granular product **1a**. The other HPG gels **1b**–**3c** were obtained using a similar method. The initial feed amounts of EGDE and the various HPGs used for the preparation of the HPG gels are listed in Table 1. All the gels were stored in a vacuum desiccator until further use.

2.3. Structural characterization

FTIR spectroscopy was carried out using a Spectrum Two spectrometer (PerkinElmer Inc., US) by the KBr disc method, as previously reported (Kono et al., 2013).

All NMR spectra were recorded on a Bruker AVIII 500 MHz spectrometer (Bruker BioSpin GmbH, Germany). ^{1}H NMR spectra were obtained by use of a 2-channel, 5 mm broadband observe probe incorporating a z-gradient coil at 353 K. The excitation pulse length (flip angle of 30°), data acquisition time, and repetition time were set to 4.5 μs, 3.17 s, and 6 s, respectively, and 16 scans were accumulated. The ^{1}H chemical shifts were calibrated by assigning the methyl peak of DSS as 0 ppm. Solid-state dipolar-decoupled/magic angle spinning (DDMAS) ^{13}C NMR spectra were recorded at 25 °C using a 4 mm dual-tuned MAS probe at a MAS frequency of 10 kHz. The details of the experimental conditions used for obtaining the solid-state ^{13}C NMR spectra were reported in our previous paper

Table 1
Initial feed amounts of HPG and EGDE used in HPG gels synthesis, and gel yields.

Sample no.	Used HPG	Initial feed amount		Yield (g)	Yield (%)[b]
		HPG (g mmol^{-1})[a]	EGDE (g mmol)		
1a	HPG1	2.0 (4.1 mmol)	1.0 (5.9 mmol)	2.0	86
1b	HPG1	2.0 (4.1 mmol)	2.1 (12 mmol)	2.4	92
1c	HPG1	2.0 (4.1 mmol)	4.1 (24 mmol)	2.7	94
2a	HPG2	2.0 (3.7 mmol)	1.0 (5.9 mmol)	1.9	85
2b	HPG2	2.0 (3.7 mmol)	2.1 (12 mmol)	2.1	90
2c	HPG2	2.0 (3.7 mmol)	4.1 (24 mmol)	2.4	94
3a	HPG3	2.0 (3.0 mmol)	1.0 (5.9 mmol)	1.8	84
3b	HPG3	2.0 (3.0 mmol)	2.1 (12 mmol)	2.1	92
3c	HPG3	2.0 (3.0 mmol)	4.1 (12 mmol)	2.2	91

(Yield, %) = [(Yield/g) × 10^3/(Mw_{rep} of each gel/g mol^{-1})] × 100/(initial feed amount of HPG/mmol), where the Mw_{rep} of each gel is summarized in Table 2.

[a] Molar amount of the repeating unit of HPG added to the reaction mixture for each gel synthesis. The amount was determined by the following equation, (molar amount of HPG/mmol) = 2.0 g × 10^3/Mw_{rep} g mol^{-1}, where the Mw_{rep} of each HPG is shown in Table S1.

[b] Yield of each gel was determined by the following equation.

(Kono, 2014). The spectra were typically accumulated over 4096 scans. ^{13}C chemical shifts of the DDMAS NMR spectra were calibrated based on the carbonyl carbon resonance of D-glycine, which was used as an external reference, at 176.03 ppm.

2.4. Time-domain ^{1}H NMR spectroscopy

^{1}H T_2 measurements were recorded at 298 K with a Bruker minispec mq20 (Bruker BioSpin GmbH, Germany) operating at 20 MHz. Each HPG gel (100 mg) was introduced into a 10 mm NMR tube, and 2 mL of deionized water was added. After 1 h at room temperature, the swelled HPG hydrogels were used for the NMR measurements. ^{1}H T_2 was measured by the Carr–Purcell–Meiboom–Gill method (Carr & Purcell, 1954; Meiboom & Gill, 1958). The $\pi/2$ and π pulse lengths and the delay time were set to 3 μs, 6 μs, and 15 s, respectively.

2.5. Rheological measurements

Each HPG gel (100 mg) was swelled in deionized water (2 mL) at room temperature for about 24 h, and then subjected to three rheological measurements at 298 K in a Physica MCR 301 rheometer (Anton Paar GmbH, Austria) equipped with a Rheoplus 32 data analyzer and a Peltier temperature controller. A 25-mm rough surface cone–plate measuring geometry was used to prevent sample slippage. The gap and strain were set at 1.0 mm and 1.0%, respectively. Oscillatory shear responses (storage modulus G' and loss modulus G'') were determined at 0.1 Pa over the angular frequency (ω) range of 0.063–63 rad s^{-1}. The test conditions were within the linearity range of the viscoelastic properties.

2.6. Swelling behaviors

Dried HPG gel (ca. 100 mg) was precisely weighed and then placed into a 15 mL polypropylene centrifuge tube. The desired solution was poured into the tube, and the tube was set in a shaker at 25 °C and shaken at 120 rpm. After 24 h, the tube was centrifuged at 8000 × g for 5 min and the supernatant was completely drained. The swelling ratio (SR) of the gel was determined using the following equation

$$\mathrm{SR} = \frac{(W_s - W_d)}{W_d},$$

where W_s and W_d are the weights of the swollen HPG gel and the dried HPG gel, respectively. The SRs were determined in deionized water, 1–26 (saturated) wt% NaCl solutions, 4 wt% LiCl solution, 4 wt% KCl solution, 4 wt% CsCl solution, 4 wt% $MgCl_2$ solution, 4 wt% $CaCl_2$ solution, 20 mM acetic acid–sodium acetate buffer (pH 4), 20 mM NaH_2PO_4–Na_2HPO_4 buffer (pH 7.0), 20 mM $NaHCO_3$–NaOH buffer (pH 10), methanol, ethanol, 1-propanol, acetone, and ethyl acetate.

3. Results and discussion

3.1. Preparation of HPG gels

Prior to preparing the HPG gels, the structures of the HPGs were characterized by ^{1}H NMR (Fig. S1). Three resonances were observed at 5.17, 5.02, and 4.74 ppm in the anomeric proton region. The protons at 5.02 and 4.74 ppm are due to H1 of the Gal and Man residues, respectively (Dodi, Hritsu, & Popa, 2011; van de Velde & Rollema, 2006), and the resonance at 5.17 ppm is due to H1 of Gal whose hydroxyl groups at the C2 position have been substituted by hydroxypropyl groups (Kono, 2013). The integral ratio of the ^{1}H resonance at 4.74 ppm to the sum of ^{1}H resonances at 5.17 and 5.02 ppm indicates that that the Man and Gal residues (moieties) were present in a 1.62:1 ratio. Table S1 summarizes the integral values of the methyl protons (I_{CH_3}) for each HPG at 1.3–0.9 ppm when the sum of integral values of the anomeric protons was set to 2.62. The MS value for each HPG gel could be determined by substituting the value of I_{CH_3} into the following equation:

$$MS = \frac{I_{CH_3}}{3}.$$

The MS values of HPG1, HPG2, and HPG3 were 1.2, 2.1, and 4.4, and the average molecular weights of the repeating units (Mw_{rep}) could be calculated to be 492, 545, and 679 g mol^{-1}, respectively (Table S1).

A series of HPG gels was prepared from HPG1 (**1a**–**1c**), HPG2 (**2a**–**2c**), and HPG3 (**3a**–**3c**) by varying the EGDE feed amount during etherification (Table 1). During the crosslinking reaction, the transparent HPG solution became increasingly viscous soon after the addition of EGDE, and the morphology of the mixture gradually changed from a solution to a gel after the onset of heating at 60 °C. The crosslinking reaction was allowed to proceed with stirring at 60 °C for 3 h, and the resulting gel was neutralized, purified, and dried under reduced pressure. The dried HPG gels were obtained as granular white powders. The yields were in the range 94–85%, and tended to increase with the amount of EGDE used, regardless of the HPG used for the gel syntheses. This suggests that the crosslinking of HPG progresses to a larger extent with an increase in EGDE concentration in the reaction mixture during gel synthesis. In addition, the yields were not slightly dependent on the MS of HPG because number of hydroxyl groups in HPG which becomes a crosslinking point was constant for all HPGs.

3.2. Structural characterization of HPG gels

Fig. 2 shows the FTIR spectra of HPG3 and the gels **3a**–**3c**, normalized by the peak intensity of the pyranose ring stretch at 1644 cm^{-1} (Mudgil, Barak, & Khatkar, 2012), and the characteristic absorptions of these gels are summarized in Table S2. The notable spectral differences between HPG3 and the gels were the peak intensities at 2924, 1371, and 1125 cm^{-1}, which are due to the asymmetric stretching vibration of CH_2, the scissoring deformation of CH_2, and the asymmetric bending vibration of the C—O—C, respectively (Kono, 2014; Mudgil et al., 2012). The intensities of these absorptions were enhanced with increasing initial feed amount of EGDE in the preparation of the gels, clearly indicating that the crosslinking degree (CD) of the gels was enhanced with increasing EGDE concentration.

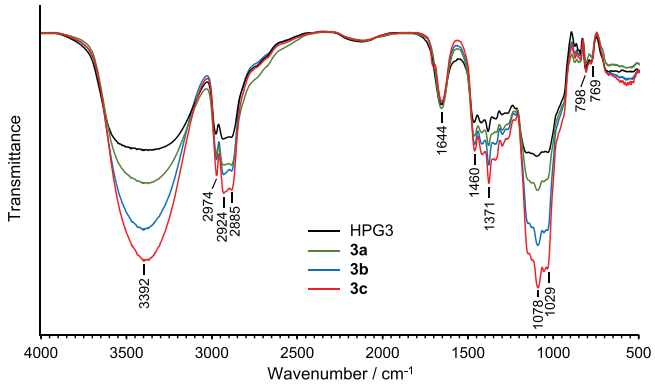

Fig. 2. FTIR spectra of HPG3 and HPG gels **3a**, **3b**, and **3c**. The assignments of the characteristic wavenumbers for the HPG gels and HPGs are summarized in Table S2.

The DDMAS ^{13}C NMR spectra of the HPGs and their gels are shown in Fig. 3. The ^{13}C resonances of the HPGs can be divided broadly into three regions: 110–90, 90–50, and 25–10 ppm. These regions can be assigned to the anomeric carbons of the Man and Gal residues, C2—C6 of the Man and Gal residues and the methine and methylene carbons of the hydroxypropyl groups, and the methyl carbons of the hydroxypropyl groups, respectively (Prashanth et al., 2006). Compared to the spectra of the HPGs, the spectra of the gels show a new resonance at 71 ppm due to the methylene carbons of EGDE crosslinked to HPG (Kono, 2013). The intensity of the resonance at 71 ppm increases with increasing EGDE concentration during gel preparation. Moreover, the methoxy carbon of the epoxide group in EGDE whose chemical shift is 45 ppm (Kono, 2014) could not be observed in the NMR spectra of HPG hydrogels. This indicates that the epoxy groups of EGDE reacted with the hydroxyl groups of HPG to form the ether crosslink in the hydrogels.

To quantitatively discuss the CD of HPGs, the integral values of the C1 resonances at 110–90 ppm (I_{C1}), the methyl carbon resonances at 25–10 ppm (I_{Me}), and the other carbon resonances at 90–50 ppm (I_{others}) of each HPG gel were determined (Table 2). The CD, defined in this study as the average number of EGDE molecules

Table 2
Structural parameters for each HPG gel determined by solid-state ^{13}C NMR.

Sample no.	HPG Used	Integral value of ^{13}C resonances[a]			Structural parameters	
		I_{C1} [a]	I_{others} [a]	I_{Me} [a]	CD[b]	Mw_{rep}[c] (g mol^{-1})
1a	HPG1	2.62	19.2	1.18	0.47	573
1b	HPG1	2.62	22.4	1.19	0.87	643
1c	HPG1	2.62	25.6	1.24	1.25	710
2a	HPG2	2.62	20.3	2.16	0.37	609
2b	HPG2	2.62	21.3	2.02	0.52	636
2c	HPG2	2.62	24.3	2.06	0.89	699
3a	HPG3	2.62	24.2	4.40	0.29	729
3b	HPG3	2.62	26.2	4.39	0.53	772
3c	HPG3	2.62	28.3	4.42	0.80	817

Mw_{rep}/g mol^{-1} = Mw_{rep} of used HPG/g mol^{-1} + n_{EGDE} × 174.2/g mol^{-1}, where the Mw_{rep} of the used HPG is summarized in Table S1.

[a] I_{C1}, I_{others}, and I_{Me} were the integral values of ^{13}C resonances for the sum of C1 resonances of Gal and Man residues, the sum of ^{13}C resonances of each gel except for C1 and methyl carbons, and the methyl carbons, respectively. I_{C1} was set to 2.62 for each gel.

[b] CD was defined as the average number of crosslinked EGDE molecules per repeating unit of the gel.

[c] The average molecular weight of the repeating unit of each gel was determined by the following equation: Mw_{rep} $\left(\text{g mol}^{-1}\right)$ = Mw_{rep} of used HPG (g mol^{-1}) + nEGDE × 174.2 (g mol^{-1}); where the Mw_{rep} of the used HPG is summarized in Table S1.

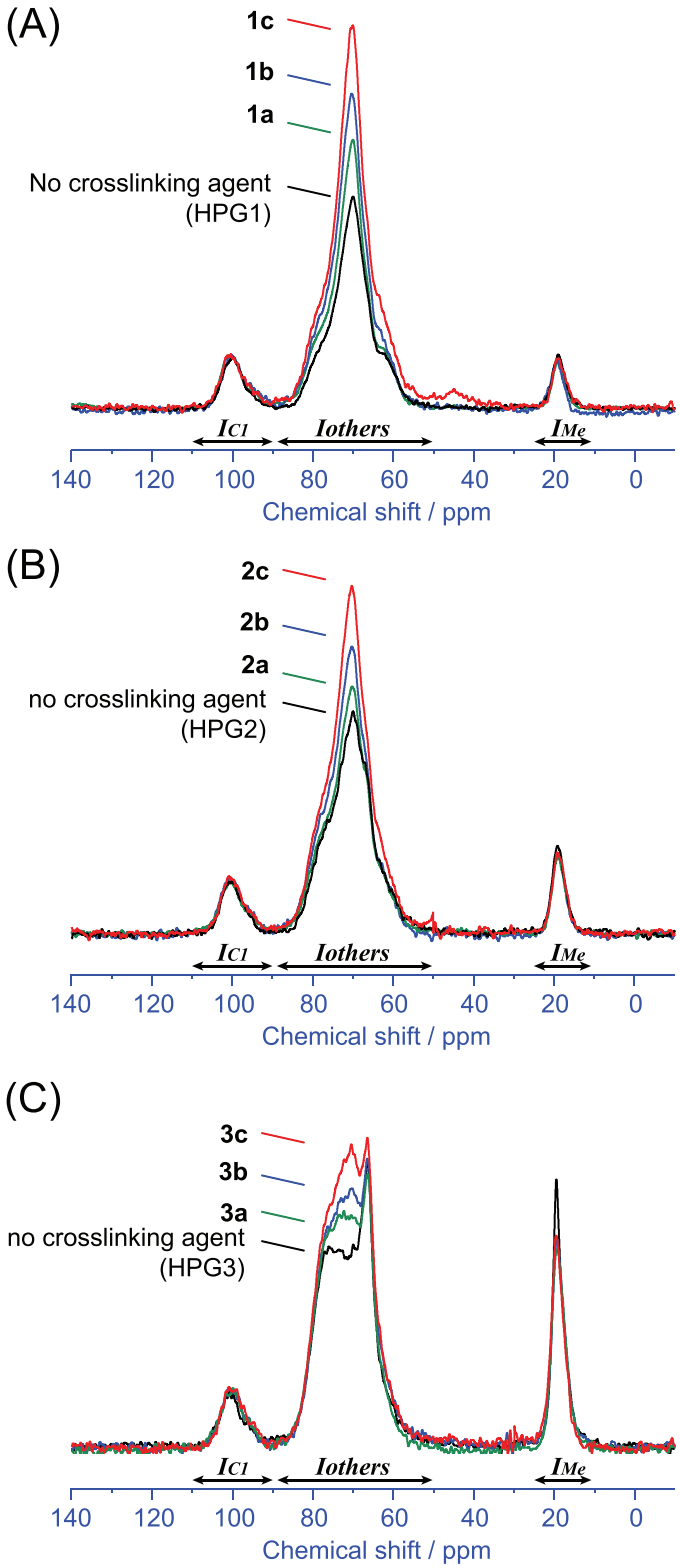

Fig. 3. Solid-state DDMAS ^{13}C NMR spectra of a series of HPGs and HPG gels. (A) HPG1 and HPG1 gels **1a**, **1b**, and **1c**; (B) HPG2 and HPG2 gels **2a**, **2b**, and **2c**; and (C) HPG3 and HPG3 gels;**3a**, **3b**, and **3c**. Integral values of the C1 resonances at 110–90 ppm (I_{C1}), methyl carbon resonances at 25–10 ppm (I_{Me}), and the other carbon resonances at 90–50 ppm (I_{others}) of each HPG gel were determined and are summarized in Table 2.

Table 3
^{1}H T_2 for H_2O in swollen HPG gels at 295 K.

Sample no.	T_2 (s)
1a	0.788
1b	0.489
1c	0.364
2a	0.820
2b	0.555
2c	0.534
3a	0.980
3b	0.622
3c	0.453
Deionized water	2.098

per repeating unit of HPG, could be determined by substituting I_{C1}, I_{others}, and I_{Me} into the following equation

$$CD = \frac{(I_{others} - I_{C1} \times 5 - I_{Me} \times 2)}{8}.$$

Thus, the Mw_{rep} of each HPG gel could be calculated by the following equation

$$Mw_{rep}\ (\mathrm{g\ mol^{-1}}) = (Mw_{rep}\ \text{of used HPG})\ (\mathrm{g\ mol^{-1}}) + CD \times 174\ (\mathrm{g\ mol^{-1}}),$$

where 174 g mol^{-1} is the molecular weight of EGDE. A comparison of the CDs of each series of gels reveals that an increase in the initial feed amount of EGDE enhances the CD of the obtained gels and that the CD of the gels depended on the MS value of the HPG used for the gel synthesis; for example, the CDs decreased in the following order: **1a** > **2a** > **3a**.

3.3. Molecular mobility of H_2O in HPG gels

Fig. 4 shows the ^{1}H T_2 relaxation decay of the swollen HPG gels and water as a reference. These relaxation decay curves could be completely fitted by a single exponential decay, as expressed by the following equation

$$I_{(t)} = I_0 \exp\left(-\frac{t}{T_2}\right),$$

where $I_{(t)}$ and I_0 are the amplitudes at $t = t$ and $t = 0$, respectively (Carr & Purcell, 1954; Meiboom & Gill, 1958). Compared with the ^{1}H T_2 of pure water (2.1 s), the ^{1}H T_2 values of the water in the HPG gels are considerably shorter, in the range 0.98–0.36 s, clearly indicating that the mobility of the water molecules in these HPG gels is restricted by the gel structure (Table 3). In addition, as shown in Fig. 5, plots of the ^{1}H T_2 of the water molecules in the HPG gels as a function of the CDs of the gels exhibit decreases in T_2 with increasing CD, which clearly proves that a higher CD enhances the strength of the HPG polymer networks, and that the networks suppress the mobility of the water contained in the gels.

3.4. Rheological properties

The G' and G'' of the swollen HPG gels were plotted as a function of angular frequency ω between 0.63 and 63 rad s^{-1} (Fig. 6). The swollen HPG gels exhibited similar trends for rheological properties during the ω sweeps; the G' values were always higher than those of G'', and there were no cross-over points for any of the HPG gels, indicating that the HPG hydrogels have characteristic gel structures. In addition, the G' and G'' of the **1b**, **1c**, **2b**, **2c**, **3b**, and **3c** hydrogels had almost no dependence on the number of frequency sweeps, and the G' values of these hydrogels were over an order of magnitude greater than those of G''. Thus, these HPG hydrogels exhibit properties characteristic of a string permanent gel network (Argüelles-Monal, Goycoolea, Peniche, & Higuera-Ciapara, 1998).

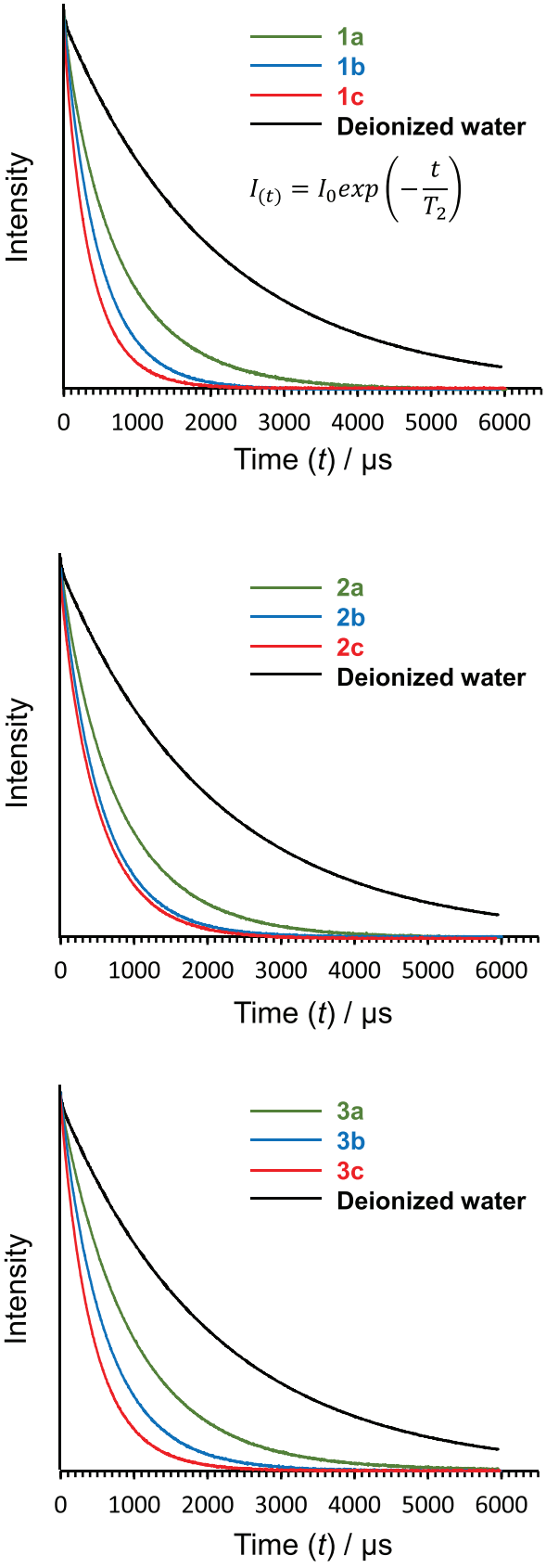

Fig. 4. ^{1}H T_2 Relaxation decay curves for water molecules in each HPG hydrogel at 298 K.

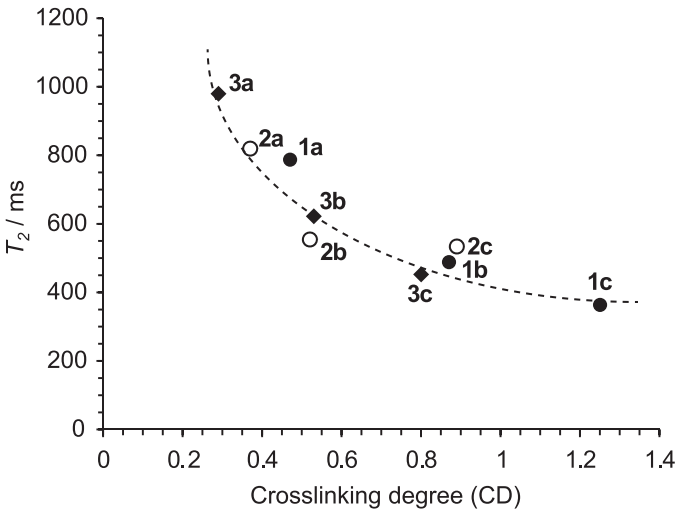

Fig. 5. Plots of the ^{1}H T_2 of water molecules in the HPG gels as a function of the CR of the gels. The ^{1}H T_2 values of water swelled in each HPG gel are summarized in Table 3.

The stiffness of these gel structures could be also confirmed by the slopes (~1) of the logarithmic plots of dynamic viscosity (η') over ω for these samples (Mitchell, 1980). On the other hand, the $G'$and $G''$of the other hydrogels, **1a**, **2a**, and **3a**, exhibited gradual increases with increase in ω, and the slopes of the logarithmic η' over ω plots were in the range 0.82–0.88. In addition, the loss tangents ($\tan\delta$) of the **1b**, **1c**, **2b**, **2c**, **3b**, and **3c** gels were about 0.1, whereas those of gels **1a**, **2a**, and **3a** were slightly higher, 0.12–0.14, indicating that hydrogels **1a**, **2a**, and **3a** exhibit a viscoelastic behavior weaker than those of other gels (Mitchell, 1980). From these observations, we conclude that the CD of the HPG gels was an important factor determining their rheological properties.

3.5. Swelling behaviors

3.5.1. Swelling in aqueous solutions

Fig. S2 shows the time-dependence of the SR of the HPG gels in deionized water. While general superabsorbent polymers composed of crosslinked sodium polyacrylate reach water-absorption equilibrium within a few minutes (Kono & Fujita, 2012), the rate of water absorption of the HPG gels was relatively slow. All the HPG gels reached absorption equilibrium after 4 h of soaking. This is because there are no ionic functional groups in the HPG gels, such as the sodium carboxylate groups in crosslinked sodium polyacrylates, to induce quick water absorption. Comparison of the SR of each HPG gel shows that the equilibrium SR was mainly affected by the CD of the gel; equilibrium SR values of HPG gels with lower CDs, such as **1a** and **2a**, were relatively high, ranging from ca. 70 to 85 g g-gel^{-1}. In contrast, the equilibrium SR values for gels with higher CD values, such as **1c**, **2c**, and **3c**, were in the range 25–40 g g-gel^{-1}. Thus, expansion of the HPG gels is suppressed when the CD is high, thereby resulting in low SR. In addition, the equilibrium SRs of the HPG gels are also affected by the MS value of the HPG used for the gel; the equilibrium SR value of each gel prepared from HPG3 with a high MS value is lower than the corresponding gels prepared from HPG1 and HPG2 under similar crosslinking conditions. For example, the equilibrium SR of gels **1a** and **2a** were in range of ca. 70–85 g g-gel^{-1}, whereas that of **3a** was ca. 50 g g-gel^{-1}. This indicates that a higher MS degree enhances the

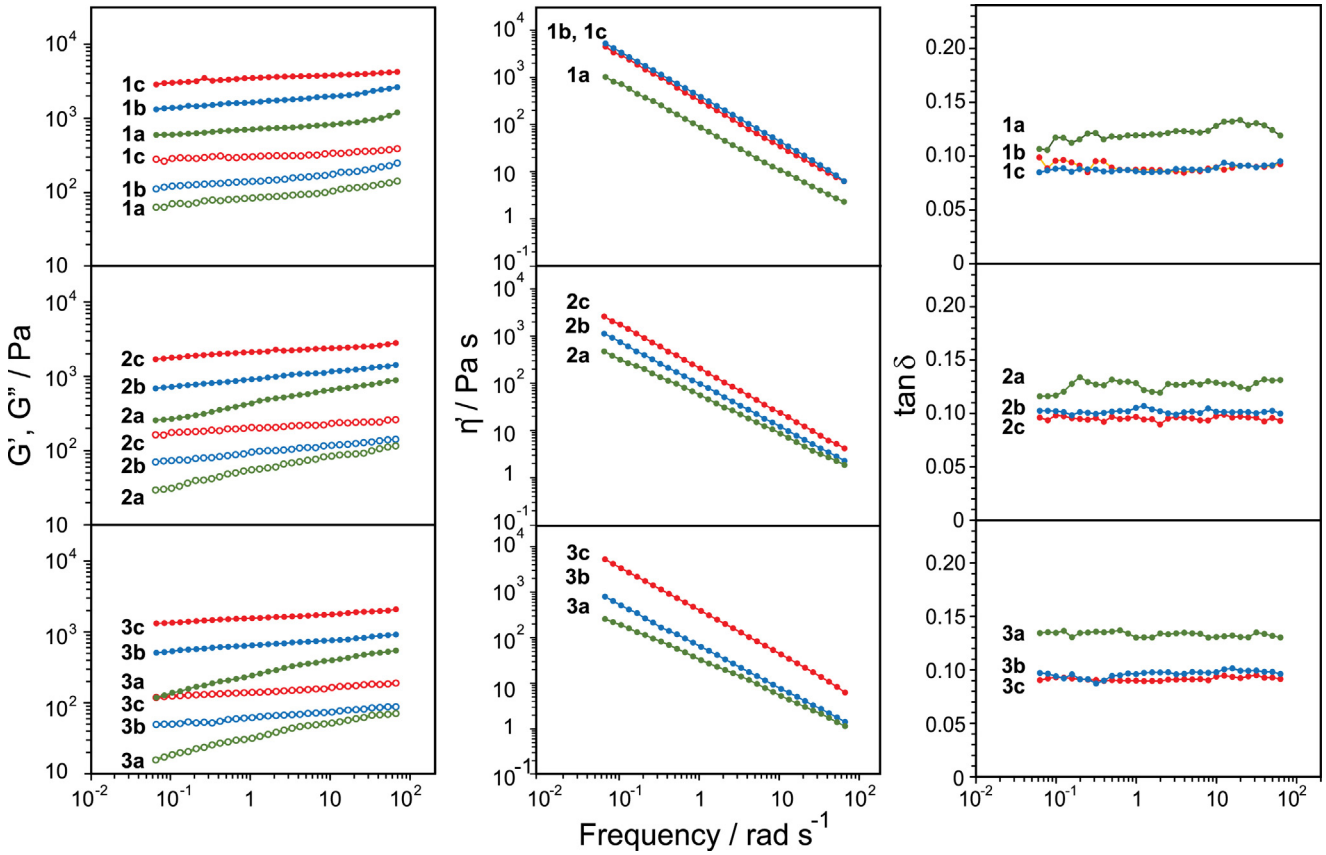

Fig. 6. Viscoelastic behavior of HPG gels (100 mg) swollen with deionized water (2 mL) at 298 K. (A) G' (solid circles) and G'' (open circles), (B) η', dynamic viscosity, and (C) $\tan\delta$, loss tangent.

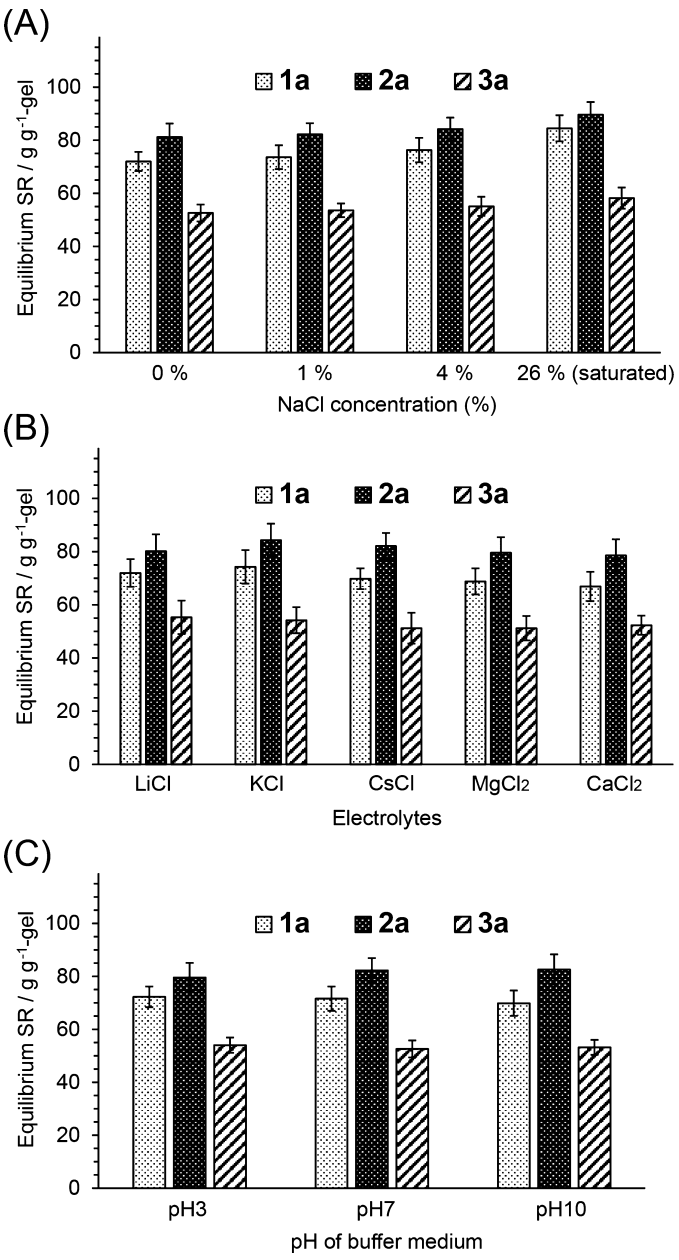

Fig. 7. Effects of (A) ionic strength, (B) electrolytes, and (C) pH on the equilibrium SR of HPG gels **1a**, **2a**, and **3a**.

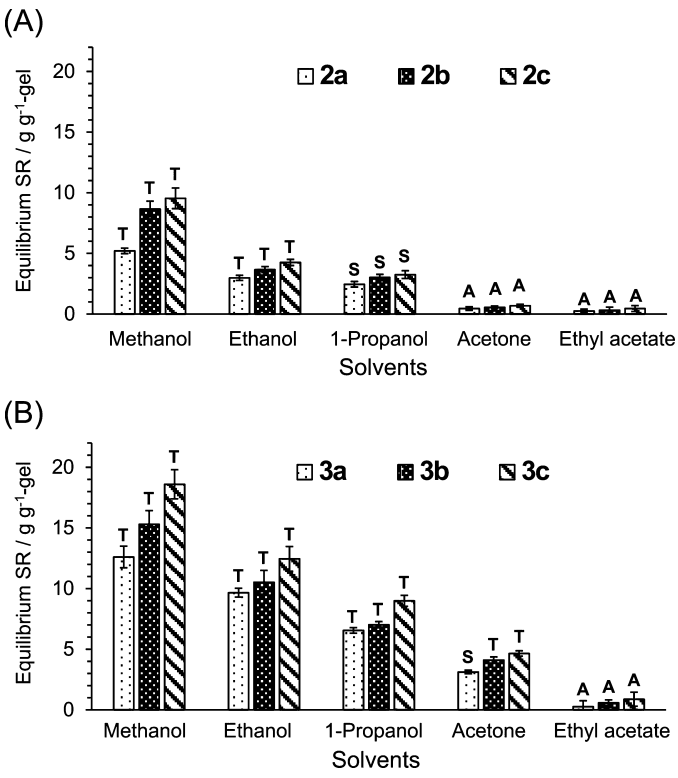

Fig. 8. Equilibrium SRs of a series of HPG gels from (A) HPG2 and (B) HPG3 in organic solvents. The notation on the column graph indicates the morphology of the HPG gels in the organic solvents: T: transparent gel; S: translucent gel; and A: aggregated solid particles.

hydrophobicity of the gel and lowers the equilibrium SR in deionized water.

Fig. 7(A) shows the effects of ionic strength on the equilibrium SR of HPG gels. The equilibrium SRs of each HPG gel in saline water are almost the same as that in deionized water, although the equilibrium SR of each gel is slightly enhanced with increasing NaCl concentration because of the gradual increment in the density of the solutions with increasing concentration. In addition, as shown in Fig. 7(B), each HPG hydrogel showed an almost constant of the equilibrium SR towards LiCl, KCl, CsCl, $MgCl_2$, and $CaCl_2$ solutions. Thus, the ionic strength as well as ionic species of the soaking medium has absolutely no influence on the SR of the HPG gels. In the case of ionic gels, water absorbency is drastically decreased in ionic solutions because the osmotic pressure, caused by the difference in cation concentration between the solution and gel, is suppressed (Kono & Fujita, 2012). On the other hand, the HPG gels have no ionic groups to induce osmotic pressure differences between the structure and medium, and thus, stable absorbency is retained in ionic solutions regardless of ionic strength.

Fig. 7(C) shows the equilibrium SRs of HPG gels in buffer solutions at pH 3, 7, and 10 after 24 h. The equilibrium SR of each gel is nearly constant in the different pH buffers, and corresponds to that in deionized water, indicating that the pH of the absorption medium has no influence on the SRs of the HPG gels.

3.5.2. *Swelling in organic solvents*

Equilibrium SRs of the HPG gels in organic solvents are shown in Fig. 8. The **1a**, **1b**, and **1c** gels were unable to absorb these solvents, and the gel morphologies after soaking were the same as those of the dried solid particles. The **2a**, **2b**, and **2c** gels absorbed and swelled in methanol, ethanol, and 1-propanol but could not absorb acetone and ethylacetate. The HPG2 gels were transparent in methanol and ethanol, but were hazy in 1-propanol. In addition, the SRs of these gels were enhanced with the increase in CD, indicating that the hydrophobicity of the HPG gels is enhanced by increasing CD. A similar tendency is observed in the **3a**, **3b**, and **3c** gels. A comparison of the SRs of the HPG2 gel series with those of the HPG3 gels indicates that gels with higher MS values can absorb organic solvents. This indicates that a higher MS enhances gel hydrophobicity and improves gel affinity toward organic solvents with lower polarities, thereby increasing the absorbency of the gel in the organic solvent. Therefore, if gels were prepared from HPGs with higher MS values, it would be expected that the obtained gels could absorb organic solvents with a wide range of polarities.

4. Conclusions

The equilibrium SR of each HPG gel is independent of the pH and ionic strength of the absorbed solution. In particular, it is notable that these materials absorb a saturated NaCl solution to form gels

without resulting in a lowering of the SRs. The gelation ability of the HPG gels in very highly concentrated ionic solutions could be applicable in electric devices such as solar cells, if the gels have the ability to solidify or gelate ionic liquids. In addition, the HPG gels are able to gelate some organic solvents. The HPG gels are therefore expected to be applicable in industrial applications as gelation agents for various kinds of solutions. Moreover, a significant expansion in its applicability could be realized if HPGs with higher MS values and/or more hydrophobic crosslinking agents were used for the preparation of HPG gels, as these materials would be expected to gelate various organic solvents.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.09.085.

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