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Xylan-rich Hemicelluloses-*graft*-Acrylic Acid Ionic Hydrogels with Rapid Responses to pH, Salt, and Organic Solvents

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ABSTRACT: Exploitation of biomaterials derived from renewable resources is an important approach to address environmental and resource problems in the world today. In this paper, novel ionic hydrogels based on xylan-rich hemicelluloses were prepared by free radical graft copolymerization of acrylic acid (AA) and xylan-rich hemicelluloses (XH) by using *N*,*N*-methylene-bis-(acrylamide) (MBA) as cross-linker and ammonium persulfate/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (APS/TMEDA) as redox initiator system. The network characteristics of the ionic hydrogels were investigated by Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM), as well as by determination of mechanical properties, swelling, and stimuli responses to pH, salts, and organic solvents. The results showed that an increase in the MBA/XH or AA/XH ratio resulted in higher cross-linking density of the network and thus decreased the swelling ratio. Expansion of the network hydrogels took place at high pH, whereas shrinkage occurred at low pH or in salt solutions as well as in organic solvents. The ionic hydrogels had high water adsorption capacity and showed rapid and multiple responses to pH, ions, and organic solvents, which may allow their use in several areas such as adsorption, separation, and drug release systems.

KEYWORDS: xylan-rich hemicelluloses, hydrogel, acrylic acid, graft copolymerization

INTRODUCTION

Hydrogels, which are three-dimensional, hydrophilic, polymeric networks capable of imbibing large amounts of water or biological fluids, receive ever-increasing attention due to their many favorable properties, such as hydrophilicity, soft tissue-mimicking consistency, high permeability to metabolites and oxygen, and resilience.[1−3] Another interesting feature is that different functionalities can easily be incorporated in the physical or chemical cross-linked network to produce "intelligent" or "smart" hydrogels. These hydrogels exhibit multiple responses to changes in external conditions, such as temperature, pH, salt, electric field, and chemical environment,[4−8] and thus are highly attractive materials in various fields of medicine, biotechnology, and environmental protection.[9−12]

Among the numerous macromolecules used for hydrogel formation, polysaccharides are particularly advantageous as compared with synthetic polymers, due to their economical, biocompatible, nontoxic, and biodegradable properties. Hemicelluloses, comprising the noncellulose cell-wall polysaccharides of plants, are the second most abundant polysaccharides in biomass. Recently, the importance of hemicelluloses-based macromolecules[13−16] and materials[17−19] has been increasingly emphasized. They are suitable for different applications in tissue engineering and drug delivery systems because of their peculiar physicochemical properties, such as biocompatibility.[20,21] Thus, increasing research activities have been directed to prepare hemicelluloses-based hydrogels for applications. Hemicelluloses-based hydrogels could be prepared by radical polymerization of 2-hydroxyethyl methacrylate or poly(ethylene glycol) dimethacrylate with oligomeric hydrosoluble hemicelluloses modified with methacrylic functions.[22,23] A series of galactoglucommanan-based hydrogels were successfully developed for drug delivery systems.[24,25] The drug release kinetics of hydrogels could be regulated and quicker release kinetics and higher swelling capabilities could be achieved by protonation of carboxylic functionalities.[25] Hydrogel microspheres based on acetylated galactoglucomannan were also prepared for drug release purposes.[26] The speed of drug release was found to depend on the pore mesh size of network of the hydrogels. Furthermore, glucomannan hydrogel was found to have potential application in protein loading and release and colon-specific delivery.[27,28] In addition, carboxylic acid functionalized deacetylated konjac glucomannan was prepared and used to remove metal ions from aqueous solution.[29] Therefore, hemicelluloses-containing hydrogels have promising future prospects in drug release formulations and adsorption of liquid and metal ions or dyes.

Xylan-type hemicelluloses are the main hemicellulosic components of the cell walls of hardwoods and herbaceous plants (constituting about 20−35 wt % of the biomass) and thus are available in huge amounts as byproducts from forestry, agriculture, and pulp and paper industries. Although xylan-rich hemicelluloses (XH)-based hydrogels were prepared by blending hemicelluloses and chitosan in acidic conditions,[30,31] related studies are very limited. Furthermore, there were few studies directly on the preparation of hemicelluloses-based hydrogels with multistimulus response properties.

Acrylic acid (AA) is an important monomer that is widely used for the preparation of functional hydrogels. By incorporation of AA into the network, hydrogels can find important applications

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in water adsorption and selective removal of heavy metal ions or dyes.[29,32,33] Especially, the incorporation of carboxyl groups imparts hydrogel responses to various external stimuli, such as pH and salts,[34,35] and thus allows their use in drug release systems. Variations in pH are known to occur at several body sites, such as the gastrointestinal tract, vagina, and blood vessels, and such hydrogels can provide a suitable base for pH-responsive drug release.[4] In the present study, we prepared novel ionic hydrogels based on XH by introducing carboxyl groups into the network hydrogels. The incorporation of carboxylic acid groups into hemicelluloses can improve the chemical and physical features of the hydrogels. The network structures of the prepared hydrogels were characterized, and the multistimulus responses to pH, salt, and organic solvents were also investigated.

MATERIALS AND METHODS

Materials. XH was isolated from bamboo (*Dendrocalamus membranaceus* Munro, *Dm*M) holocellulose using 10% KOH at 23 °C for 10 h with a solid to liquid ratio of 1:20 (g/mL). The holocellulose was obtained by delignification of the extractive-free *Dm*M (40−60 mesh) with sodium chlorite in acidic solution (pH 3.7−4.0, adjusted by 10% acetic acid) at 75 °C for 2 h.

N,*N*,*N*′,*N*′-Tetramethylethylenediamine (TMEDA) was purchased from Aldrich Chemical Co. *N*,*N*-Methylene-bis(acrylamide) (MBA) and ammonium persulfate (APS) were purchased from Shanghai Chemical Reagent Corp., China. All of these chemicals were used without any further purification. AA (Xi'an Chemical Reagent Factory, China) was purified by distillation under reduced pressure to remove the inhibitor hydroquinone before use. All other reagents used were of analytical grade, and all solutions were prepared with distilled water.

Sugar Composition. The sugar composition in the *Dm*M was determined by using a high-performance anion exchange chromatography (HPAEC) system (Dionex ISC 3000) with an amperometric detector, an AS50 autosampler, and a Carbopa PA1 column (4 mm × 250 mm, Dionex). Calibration was performed with standard solutions of L-arabinose, D-glucose, D-xylose, D-glucose, D-mannose, D-galactose, glucuronic acid, and galacturonic acid. The sugar analysis showed the following sugar composition (relative weight percent, w/w): 89.38% xylose, 5.75% arabinose, 1.87% glucose, 0.66% galactose, 1.78% glucuronic acid, and 0.55% galactose acid.

Preparation of Ionic Xylan-rich Hemicelluloses-*graft*-Acrylic Acid Hydrogels (XH-*g*-AA Hydrogels). Ionic XH-*g*-AA hydrogels were prepared by free radical graft copolymerization of XH and AA in the presence of cross-linker (MBA) and a redox initiator system (APS/TMEDA). The typical procedure to prepare ionic XH-*g*-AA hydrogels was as follows. One gram of XH was dissolved in 30.0 mL of distilled water in a three-necked flask with a magnetic stirrer at 85 °C for 60 min before the solution was cooled to room temperature. The XH solution was continuously purged with gaseous N_2 for 10 min, and 0.05 g of APS and 0.05 mL of TMEDA as an initiator system were then added to the solution; the mixture was allowed to stir for 10 min to generate radicals in nitrogen gas atmosphere. Thereafter, variable amounts of AA (2.0−16.0 g) and cross-linker MBA (0.050−0.25 g) were subsequently added, and stirring was continued for 2 h under nitrogen gas atmosphere. Then the reaction was allowed to proceed at room temperature for 24 h without stirring. Continuous purging with nitrogen was used throughout the reaction period. The hydrogels were carefully removed and washed thoroughly in distilled water for 7 days. During this period, the distilled water was replaced with fresh distilled water at least four times daily to leach out the unreacted chemicals. To obtain ionic hydrogels with high swelling capacity and rapid response behaviors, the XH-*g*-AA hydrogels were immersed in 1 M NaOH solution for 24 h. During the process, COOH groups in the network hydrogels were converted to COO^- groups. The ionic hydrogels were again carefully washed thoroughly in distilled water for another 7 days and then were dried to a constant mass at 50 °C. These samples are summarized in Table 1.

Table 1. Stress and Modulus of Xylan-rich Hemicelluloses-*graft*-Acrylic Acid Hydrogels

sample	MBA/XH[a] (g/g)	AA/XH[b] (g/g)	stress (kPa)	modulus (kPa)
1	0.05	4	13.6 ± 1.5	38.4 ± 5.8
2	0.10	4	17.3 ± 2.1	95.7 ± 9.6
3	0.15	4	24.4 ± 2.7	119.5 ± 12.3
4	0.20	4	32.3 ± 3.5	156.2 ± 18.1
5	0.25	4	38.6 ± 4.1	202.4 ± 26.5
6	0.10	2	8.9 ± 1.1	31.3 ± 3.7
7	0.10	4	17.1 ± 1.9	97.9 ± 7.8
8	0.10	8	22.4 ± 2.6	110.6 ± 9.5
9	0.10	12	28.5 ± 2.9	142.7 ± 15.4
10	0.10	16	33.2 ± 3.6	187.4 ± 17.1

[a] *N*,*N*-Methylene-bis(acrylamide)/xylan-rich hemicelluloses ratio (by weight). [b] Acrylic acid/xylan-rich hemicelluloses ratio (by weight).

FT-IR Analysis. FT-IR spectra of XH and ionic XH-*g*-AA hydrogels were performed by Nicolet 750 spectrophotometer within the frequency range of 400−4000 cm^{-1} by the method of transmission. The 1% finely ground hydrogel samples were mixed with KBr to press a plate for measurement.

Morphology of Ionic Hydrogels. For the morphological study, the hydrogels were first immersed in distilled water to reach equilibrium swelling, and the swollen hydrogel samples were then freeze-dried. The morphology of the hydrogels was investigated by scanning electron microscopy (SEM, Hitachi S3700). Specimens were coated with gold for 30 s in SEM coating equipment.

Mechanical Testing. Compression stress and modulus were measured to evaluate the density of the ionic hydrogel network.[36] Compression measurement was carried out using an electromechanical material testing machine (Instron Universal Testing Machine, 5565) fitted with a 200 N load cell. The testing was performed at room temperature (25 °C and 50% humidity) with a cross head speed of 2 mm/min. The samples with dimensions of 5 cm × 5 cm × 4 cm were preloaded with 1 N load to reduce the influence of surface artifacts. Stress and modulus at failure were recorded. The stress and modulus were calculated on the basis of the initial cross section.

Swelling Characterization of Ionic Hydrogels in Distilled Water. Preweighed dry ionic hygrogels (m_0) were immersed into excessive distilled water to reach a state of equilibrium swelling. The weight gain of the samples was monitored gravimetrically. The mass of the wet hydrogels (m_{eq}) was determined after removal of the surface water by gently dabbing the hydrogels with filter paper. The equilibrium swelling ratio (Q_{eq}) was determined by the equation

$$Q_{eq} = (m_{eq} - m_0)/m_0 \quad (1)$$

where m_0 and m_{eq} are the masses of the preweighed dry hydrogel and the swollen hydrogel, respectively.

Evaluation of pH, Salt, and Organic Solvent Response Behaviors. The buffer solutions with various pH values were prepared by combining KH_2PO_4, K_2HPO_4, H_3PO_4, and NaOH properly, and the pH values were determined by a pH-meter (DELTA-320) at room temperature. The ionic strengths of all the buffer solutions were controlled to 0.1 M using NaCl. Salt solutions (0.005, 0.01, 0.05, 0.1, 0.5, and 1.0 M) were adjusted with NaCl and $CaCl_2$. The equilibrium water absorption (Q_{eq}) of the hydrogels in various pH buffer solutions and salt solutions were measured according to a method similar to that for distilled water.

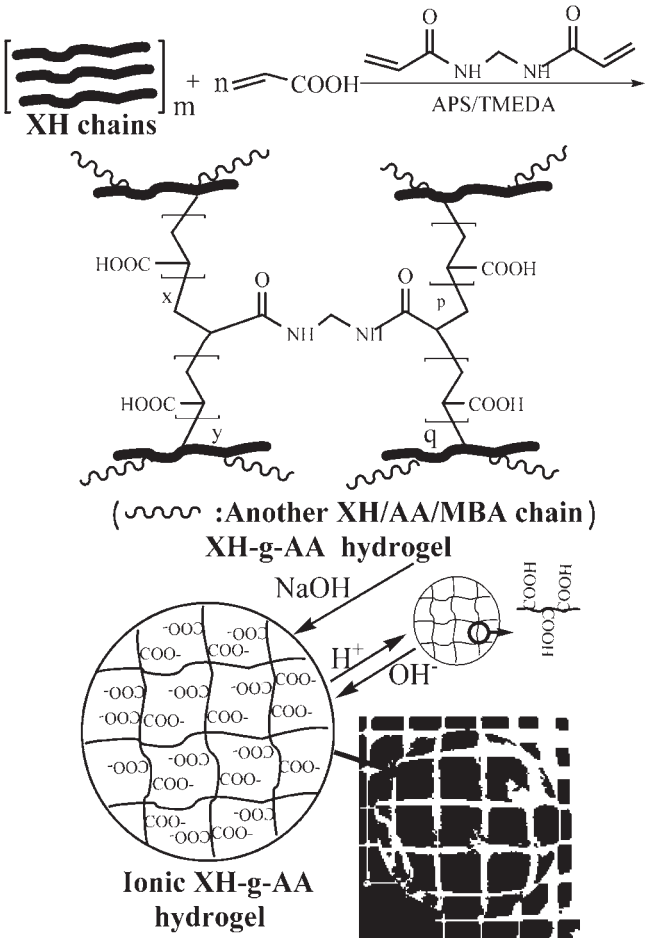

Figure 1. Proposed mechanistic pathway in the formation of xylan-rich hemicelluloses-*graft*-acrylic acid hydrogels (x, y, q, or $p \geq 1$).

pH and organic solvent swelling reversibilities of the ionic hydrogels were carried out in response to repeated changes in buffer solutions (pH 2.0 and 7.4 or 12.0) and organic solvents (ethanol or acetone). Typically, the swelling samples in water were first immersed in buffer solution of pH 2.0 or organic solvents (ethanol or acetone). The swollen samples were then soaked in pH 7.4 or 12.0 buffer solution and distilled water for set time intervals (10 min) and then were weighed. The time evolution of hydrogel swelling at pH 2.0 or organic solvents was measured again after swelling at pH 12.0 and distilled water for 30 min, and the procedure was repeated. After every measurement, each solution was renewed. In all cases, three parallel samples were used in this paper. All of the measurements were carried out in triplicates, and standard deviations were <4.0%.

RESULTS AND DISCUSSION

Synthesis and Spectral Characterization of Ionic XH-*g*-AA Hydrogels. In this paper, various ratios of MBA/XH and AA/XH in the reaction mixture were employed to investigate their influences on the network structure of the hydrogels. The mechanism of free radical graft copolymerization of polysaccharides, such as konjac glucomannan, chitosan, carrageenan, and cellulose, with AA was described elsewhere.[28,35,37,38] Briefly, sulfate anion radical generated from APS abstracts hydrogen from the hydroxyl group of the XH backbone to form alkoxy radicals, resulting in active centers on the XH backbone to radically initiate

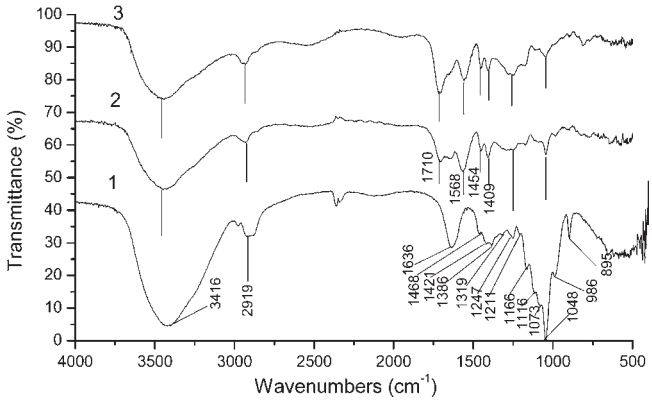

Figure 2. FT-IR spectra of xylan-rich hemicelluloses (spectrum 1) and xylan-rich hemicelluloses-*graft*-acrylic acid hydrogel sample 2 (spectrum 2) and sample 9 (spectrum 3) in Table 1.

polymerization. The presence of cross-linking reagent (MBA) results in a copolymer network comprising a chemical cross-linked structure to prevent dissolution of the hydrophilic polymer chains in an aqueous environment. The proposed mechanistic pathway in the formation of XH-*g*-AA hydrogels is shown in Figure 1.

During the treatment of the NaOH solution, COOH groups were converted to COO^- groups in aqueous solution. The presence of COO^- groups, which were converted from COOH groups by NaOH treatment, localized negative charges on the polymer network and enhanced electrostatic repulsion, which favors the expansion of the chain network, as also shown in Figure 1.

Figure 2 illustrates the FT-IR spectra of XH (spectrum 1) and ionic XH-*g*-AA hydrogels sample 2 (spectrum 2) and sample 9 (spectrum 3). In spectrum 1, the absorbances at 3416, 2919, 1468, 1421, 1386, 1319, 1247, 1166, 1116, 1073, 1048, 986, and 895 cm^{-1} are associated with XH. A sharp band at 895 cm^{-1} is assigned to β-glucosidic linkages between the sugar units, indicating that the xylose residues forming the backbone of the macromolecule are linked by β-form bonds.[39] The low intensity of the bands at 986 and 1166 cm^{-1} suggests the presence of arabinosyl units, which are attached only at position 3 of the xylopyranosyl constituents.[40] The region between 1468 and 1048 cm^{-1} relates to the C—H and C—O bond stretching frequencies. A strong broadband caused by hydrogen-bonded hydroxyls occurs at 3416 cm^{-1}, and a symmetric C—H vibration band appears at 2919 cm^{-1}.[41] In spectra 2 and 3, new peaks at 1710, 1568, and 1454 cm^{-1} are related to the stretching vibration of C═O, asymmetrical stretching vibration, and symmetrical stretching vibration of $-COO^-$, respectively, indicating the presence of COO^- groups in the hydrogel network.[37] These results indicate that AA monomers were actually grafted onto the backbone of XH.

Equilibrium Swelling Ratio in Distilled Water and Network Structure of Ionic XH-*g*-AA Hydrogels. The swelling ratio is a very important parameter because it describes the amount of water stored within the hydrogel network and is a function of water retention for hydrogels. Electrostatic repulsion generating from the negatively charged carboxylic groups in the ionic XH-*g*-AA hydrogels results in the expanded network and high swelling capacity. The effects of cross-linker (MBA) or monomer (AA) to XH ratio on the swelling capacity of the hydrogels in distilled water are shown in Figure 3. The swelling ratio decreased from

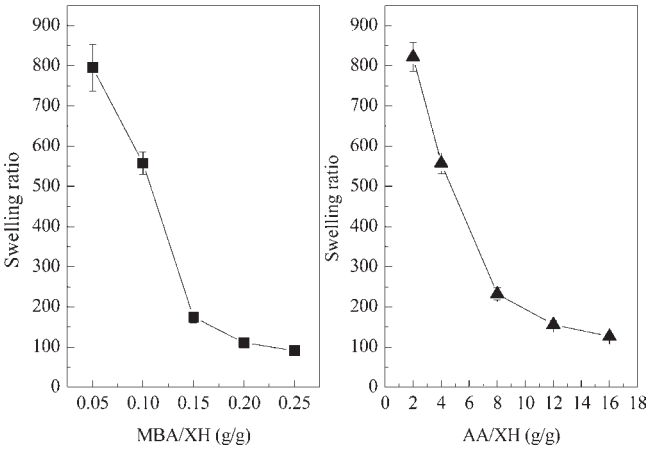

Figure 3. Effects of *N*,*N*-methylene-bis(acrylamide)/xylan-rich hemicelluloses ratio (by weight) and acrylic acid/xylan-rich hemicelluloses ratio (by weight) on the swelling ratio of ionic hydrogels in distilled water.

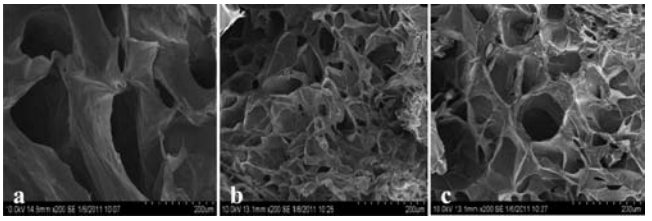

Figure 4. SEM images of xylan-rich hemicelluloses-*graft*-acrylic acid hydrogels: (a) sample 2; (b) sample 5; (c) sample 9.

795 to 91 when the MBA/XH ratio increased from 1:20 to 1:4, which is indicative of a less expanded network. SEM images (Figure 4) indicate that all of the hydrogels show a macroporous structure. It is supposed that these pores are the regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the graft copolymers. As compared with sample 2 (Figure 4a, MBA/XH ratio of 1:10), sample 5 (Figure 4b, MBA/XH ratio of 1:4) shows a network with smaller pores, which is indicative of a less expanded or denser network. Higher cross-linking reagent concentration is reasoned to produce higher cross-linking density and decrease the spaces between the copolymer chains, and consequently the resulting highly cross-linked structure is less expanded. In all hydrogels, an increase in cross-linking reagent causes a higher cross-linking density and an appreciable decrease in swelling capacity.[35,37]

In the case of samples with different AA/XH ratios, a lower swelling ratio could be observed at a higher AA/XH ratio, which also indicates a denser network. SEM images indicate that sample 9 (Figure 4c) has a less expanded network than sample 7 does (Figure 4a). Therefore, a higher AA/XH ratio also results in a denser network structure with smaller pores or space for water storage. This may originate from (a) the increase in viscosity of the reaction solution, which restricts the movement of the reactants and deactivates the macroradical growing chains soon after their formation, and (b) the enhanced homopolymerization reaction over graft copolymerization.[42,43] Similar results were also reported in the literature.[24,28,44] Table 1 demonstrates the mechanical properties of the ionic hydrogels. The compress

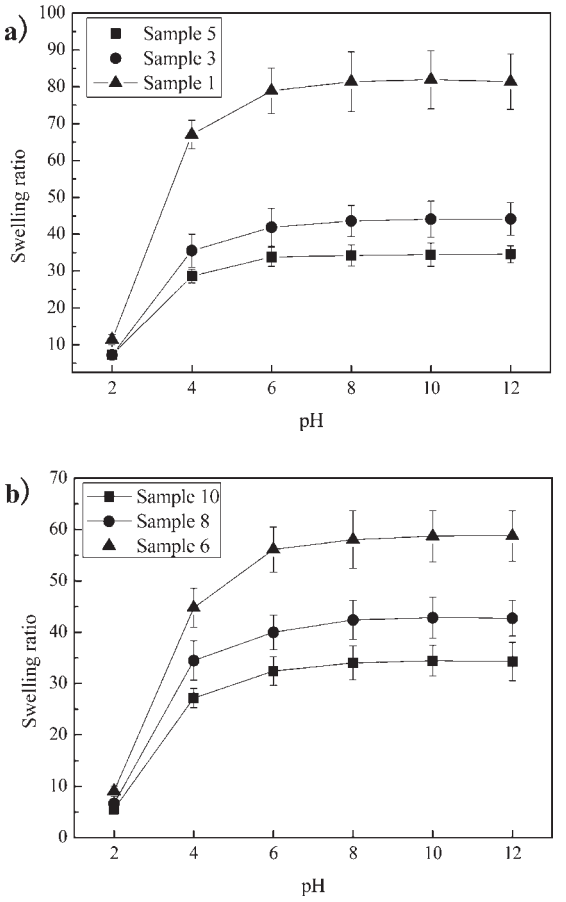

Figure 5. Swelling ratio of xylan-rich hemicelluloses-*graft*-acrylic acid hydrogels as a function of pH in buffer solutions at room temperature: (a) hydrogels with different *N*,*N*-methylene-bis(acrylamide)/xylan-rich hemicelluloses ratio (by weight); (b) hydrogels with different acrylic acid/xylan-rich hemicelluloses ratio (by weight). Ionic strengths of all buffer solutions were controlled to 0.1 M using NaCl.

stress and modulus increased with increasing MBA/XH or AA/XH ratio. Obviously, a denser network is less easily collapsed when the hydrogels are subjected to compression load and, thus, shows stronger compression strength. This well agrees with the results obtained from swelling ratio and SEM. Although a lower MBA/XH or AA/XH ratio gives rise to higher swelling capacity, the hydrogel is too weak to be handled.

pH Response Behaviors of Ionic XH-*g*-AA Hydrogels. One of the important properties of ionic hydrogels is their response to pH. Figure 5 shows the dependence of the equilibrium swelling ratio of the ionic hydrogels (samples 1, 3, 5, 6, 8, and 10) on solutions of various pH ranging from 2 to 12 at room temperature. The ionic strength in all solutions was adjusted to 0.1 M with NaCl. It is found that the swelling ratios of the samples were <15 at pH 2 and then rapidly increased to pH 6. Small changes in swelling ratio occurred in the pH range between 6 and 12. Because the pK_a value of the carboxylic group is 4.6, COO^- groups are gradually protonated and converted to COOH groups at low pH (<4.6). The protonation of COO^- groups results in a decrease in the electrostatic repulsion among negatively charged COO^- groups and an increase in the hydrogen bonding interaction among COOH groups and, thus, the collapse of the network.[34] For this reason, the polymer network has a low swelling

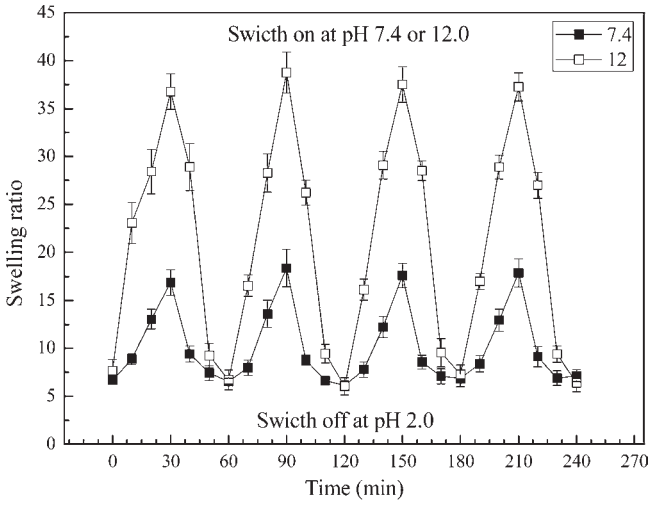

Figure 6. On−off reversible switch behaviors of the xylan-rich hemicelluloses-*graft*-acrylic acid hydrogel (sample 9) when the hydrogel was repeatedly immersed in buffer solutions of pH 2.0 and 7.4 (12.0).

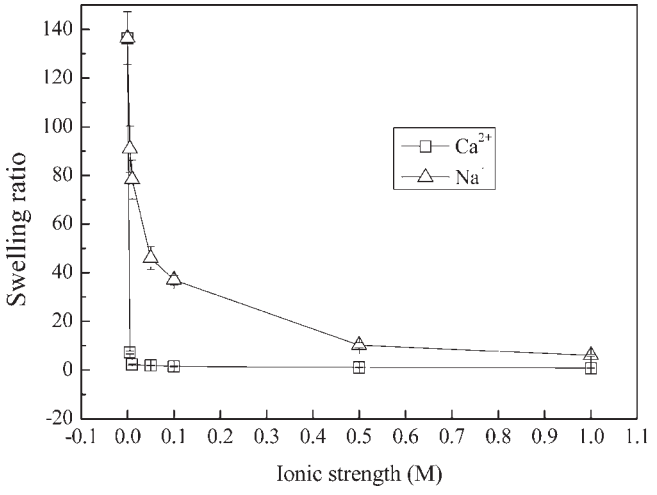

Figure 7. Swelling ratio of xylan-rich hemicelluloses-*graft*-acrylic acid hydrogel (sample 9) as a function of ionic composition (Na^+ and Ca^{2+}) and ionic strength (molar concentration).

ratio at low pH. On the other hand, the ionization of COOH groups occurs at pH >4.6 and is enhanced at higher pH. The presence of COO^- groups leads to strong electrostatic repulsion, leading to an expanded network, as illustrated in Figure 1. Small changes in pH in acid environment (pH <4.0) may result in significant changes in the polymeric network structure.

A higher MBA/XH or AA/XH ratio results in less swelling capacity in all buffer solutions, which is also due to the denser network. It should be noted that all of the hydrogels show lower swelling ratios in these buffer solutions than do those in distilled water (Figure 3), which is mainly due to the presence of salt (Na^+) in the buffer solutions.

Figure 6 shows the reversible pH-controlled switch when the ionic hydrogels were exposed to buffer solutions of pH 2.0 (off) and 7.2 or 12.0 (on). The sample was transferred between buffer solution of pH 2.2 and buffer solution of pH 7.4 or 12.0 at room temperature. The ionic strengths of all the buffer solutions were controlled to 0.1 M using NaCl. In acidic medium (pH 2)

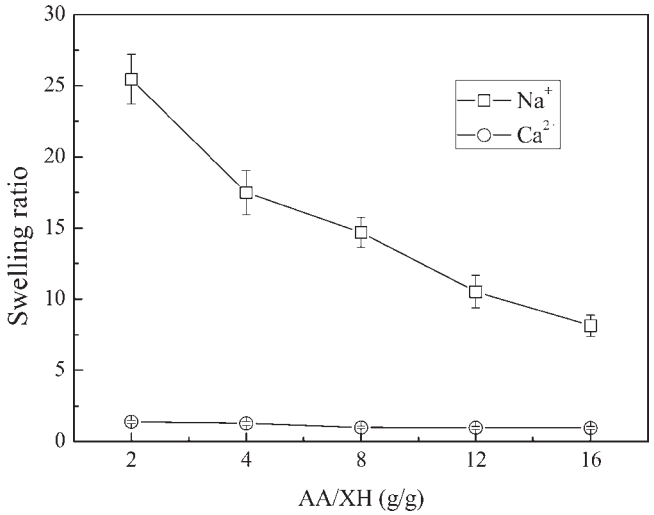

Figure 8. Swelling ratio of xylan-rich hemicelluloses-*graft*-acrylic acid hydrogel (sample 9) as a function of acrylic acid/xylan-rich hemicellulose ratio (by weight) in 0.5 M NaCl solution and $CaCl_2$ solution.

carboxylic groups are fully protonated, and the decreasing electrostatic repulsion causes network collapse. Whereas carboxylic groups are ionized at pH 7.4 or 12.0, the increasing electrostatic repulsion induces expansion of the network. This intriguing on−off switch is still observed after four swelling−deswelling cycles. A more prominent reversible switch can be achieved in a short period (within 30 min) between pH 2.0 and 12.0, which is attributed to the faster and more complete ionization of carboxylic groups at pH 12.0 within 30 min. This interesting behavior was reported in other AA-containing hydrogels.[35,45]

Saline Response Behavior of Ionic XH-*g*-AA Hydrogels. Reversible swelling and deswelling in response to the change of pH and ionic strength or composition are typical of polyelectrotyte hydrogels. The swelling ratios of the ionic XH-*g*-AA hydrogels in aqueous solutions of low molecular weight electrolytes are shown in Figures 7 and 8. It is observed that the swelling ratio strongly depends on the "concentration" and "type" of salt added to the swelling medium. The swelling ratio decreased as the concentrations of Na^+ or Ca^{2+} increased and then reached a relatively constant value. This indicates that the hydrogel network shrinks when it is exposed to electrolyte solutions with counterions (e.g., Na^+ or Ca^{2+}). It is well-known that an osmotic pressure difference exists between the internal and external solutions of the gel network in aqueous solution.[44,46] Increasing the total amount of counterions (Na^+ or Ca^{2+}) decreases the ratio of ions between the interior of the hydrogel and the surrounding solution due to the interaction between COO^- groups and counterions, and thus the osmotic pressure difference decreases, resulting in shrinkage of the network.[44,47] Also, the increasing concentration of electrolytes results in the screening of anionic groups (COO^-) of the polymer network by Na^+ or Ca^{2+}, which leads to a decrease in electrostatic repulsion.[48] These effects induce the deswelling of the hydrogel in salt solutions. This discrete phase transition of hydrogels affected by counterions was also reported for collagen-based hydrogels[49] and poly(acrylamide/maleic acid) hydrogels[50] and can be taken into account in designing hydrogels for practical purposes.

Furthermore, ion composition shows a significant influence on the network of the ionic hydrogels, as shown in Figures 7 and 8.

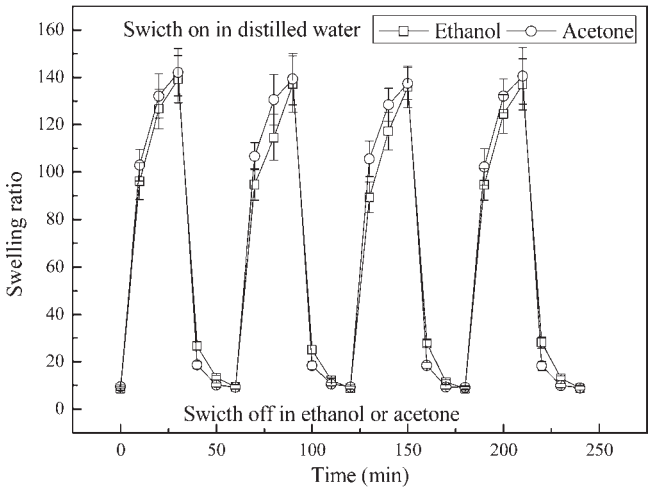

Figure 9. On−off reversible switch behaviors of xylan-rich hemicelluloses-*graft*-acrylic acid hydrogel (sample 9) when the hydrogel was repeatedly immersed in distilled water and ethanol (acetone).

Serious shrinkage occurrs to the hydrogel network even at very low ion strength in $CaCl_2$ solution. The swelling ratio of the hydrogels reached a relatively constant value at 0.005 M $CaCl_2$ solution and 0.5 M NaCl solution. The swelling ratio was only 7.2 at 0.005 M ion strength in $CaCl_2$ solution, which was much lower than that in NaCl solution (90.9) at 0.005 M ion strength. This indicates that the network of the ionic hydrogels is more sensitive to divalent Ca^{2+}, which is due to stronger ionic cross-linking and a more prominent charge screening effect.[35,51,52] Serious collapse of the network also occurs in the presence of Mg^{2+}, Cu^{2+}, and Al^{3+} in aqueous solution.[52−54] In addition, the swelling ratio of the hydrogels decreased with increasing AA/XH ratio (Figure 8) in 0.5 M NaCl solution, which is mainly due to the denser network at higher AA/XH ratio. However, there is no significant difference among the hydrogels with different AA/XH ratios in 0.5 M $CaCl_2$ solution due to the much stronger ionic cross-linking and charge screening effect.

Hydrophilic Organic Solvent Response Properties of Ionic XH-*g*-AA Hydrogels. Phase transitions of hydrogels have drawn much attention since the collapse of polyacrylamide hydrogels in an aqueous solution of acetone was observed by Tanaka.[55] Figure 9 shows the swelling−deswelling behavior of ionic XH-*g*-AA hydrogels between distilled water and ethanol or acetone. The swollen hydrogel in distilled water rapidly deswells in ethanol or acetone, and then the shrunken network expands again in distilled water within a short period. This organic solvent-controlling switch and reversibility are more prominent as compared with the pH-controlling switch in Figure 6, which is reflected by the lower and higher swelling ratios with the switch off and on, respectively.

The swelling capacity of the network of the hydrogels in organic solvents closely relates to the solubility parameter and dielectric constant of solvent as well as the interaction between the polar groups of solvents and the ionic groups in the polymer network.[56] The decrease in solubility parameter of solvent will cause shrinkage of solvent absorption.[57] A lower dielectric constant of solvent gives rise to a lower osmotic pressure of the network, resulting in decreasing swelling ratio.[56] Both the solubility parameter and dielectric constant of ethanol or acetone are lower than those of water; thus, the swelling ratio decreases in ethanol or acetone. In addition, ethanol or acetone has lower polarity and can interact more easily with the ionic groups of the hydrogel network, which results in water being extracted from the polymeric network in ethanol or acetone.[58] It can also be found from Figure 9 that no obvious slack is observed after four on−off cycles.

It has been observed in some cases that ionic hydrogels show better swelling behavior in distilled water than nonionic hydrogels due to stronger electrostatic repulsion.[59] Ionic groups can be introduced into the network either by direct copolymerization of macromolecules with AA salts or by hydrolysis in the alkali medium. Poly(*N*-isopropylacrylamide-*co*-acrylic acid) hydrogels obtained in alkaline solution showed extremely expanded networks and exhibited improved oscillating swelling−deswelling properties.[59] Ionic alginate-*g*-polyacrylamide hydrogels obtained by alkaline hydrolysis also showed high swelling capacity.[60] Furthermore, ionic hydrogels were found to respond rapidly to a changing environment, such as pH and ions, and were designed as drug delivery systems.[25,28,48] In this work, we also developed ionic hydrogels based on XH by introducing ionic groups in a hydrogel network. Ionic groups (COO^-) in XH-*g*-AA hydrogels enable an expanded network, which has high water absorbency capacity. These hydrogels also show multiple responses to pH, ions (strength and composition), and organic solvents. A swelling ratio range between 91 and 822 could be achieved in distilled water, which is much higher than that of nonionic galactoglucomannan hydrogels,[24,27,28] methacryloylated hemicelluloses hydrogels,[22] and xylan/chitosan hydrogel.[30,31] The stimulus-response behaviors indicate that the expansion and shrinkage of the network can be easily controlled by changing environmental conditions, such as pH, ionic composite, and strength, and solvent type to realize more specific applications in many areas and complex environments such as adsorption, separation, and drug release.

In summary, novel ionic hydrogels based on XH were prepared by free radical graft copolymerization and consecutive alkaline neutralization. The ionic XH-*g*-AA hydrogels show expanded network in water due to strong electrostatic repulsion among anion (COO^-) groups. Swelling ratios ranging between 91 and 822 could be achieved in distilled water by changing the amount of cross-linker (MBA) or monomer (AA). Higher MBA/XH or AA/XH ratios resulted in denser cross-linking networks and, thus, decreased swelling ratios. The ionic hydrogels prepared were sensitive to pH, ionic strength and composition of the medium, and organic solvents. The network of hydrogels became more expanded in the solutions at high pH, whereas shrinkage occurred when the hydrogel was exposed to salts and ethanol or acetone. In addition, the hydrogels showed reversible on−off switching behavior in acidic−basic solutions or water−ethanol or acetone solutions. The multistimulus response properties may allow the ionic XH-*g*-AA hydrogels to be applied in removal of heavy metal ions and medicine delivery systems.

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