

Preparation and characterization of hydrophobically modified polyacrylamide hydrogels by grafting glycidyl methacrylate

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Abstract A modified polyacrylamide (PAM-g-GMA) has been prepared by ring-opening reaction of glycidyl methacrylate (GMA) monomer grafted onto the COO^- groups of partially hydrolytic polyacrylamide (PAM) chain. The modified polyacrylamide hydrogels were obtained via a free radical polymerization of PAM-g-GMA without adding any a crosslinker using potassium persulfate (KPS), as initiator, and triethanolamine (TEA), as a coupling agent in aqueous solution. The molecular structure of PAM-g-GMA was characterized by FT-IR, $^1\text{H-NMR}$, and the thermal behaviors of hydrogels were studied by DSC. Furthermore, the swelling property and compressive properties of PAM-g-GMA hydrogels were investigated. The results show that the modified polyacrylamide hydrogels exhibit a remarkable hydration-dehydration change in response to pH in aqueous media and also undergo dramatic increase in volume with increasing temperature. So the modified polyacrylamide hydrogels will have promising and wide applications such as pharmaceutical use, water retention, electrophoretic media and so on.

Introduction

Polyacrylamide is a very good water-soluble functional polymer used extensively in a variety of applications including paper chemicals, mineral processing, water treatment, oil-wells stimulation, friction retion and the like [1]. Moreover, hydrogels of polyacrylamide also have a broad applications like as electrophoretic media for the separation or purification of biomolecules, as model drug delivery systems due to having random morphologies with a wide distribution of pore sizes [2, 3], and as matrix for enzymes and living cells immobilization owing to its controllable pore size and no need for enzyme reactive groups for the attachment to an insoluble support, high residual activity etc [4]. More recently, hydrogels of PAM are exploited in metal speciation techniques such as diffusion gradient in thin films (DGT) [5, 6]. In addition, high swelling capacity of PAM hydrogel [7] is very useful for water retention as grouting agents.

In the past several years, intelligent hydrogels that have the capability to respond to small external stimulus changes, such as temperature [8], pH [9], photo field [10], and antigen [11], have attracted significant attention from both academia and industry. Adding pendant acidic and basic functional groups to the polymer backbone produces pH-sensitive polymers; these groups either accept or release protons in response to appropriate pH changes in aqueous media [12]. Kumares S. Soppimath have previously reported polyacrylamide grafting guar gum based no crosslinked anionic microgels as pH-sensitive drug delivery systems [13], and some other scientists also studied the copolymer of acrylamide and acrylic acid as drug devices [14]. And Tanaka once reported the acrylamide/bis(acrylamide) hydrogel

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undergo dramatic change in volume with the change of volume of acetone in an acetone/water mix [15, 16]. However, the work on hydrogels based on hydrolytic polyacrylamide was scarce. In our present work, we prepare a new modified polyacrylamide hydrogel, which exhibits a remarkable hydration-dehydration change (volume phase transition) in response to pH in aqueous media. So the modified polyacrylamide hydrogels will have promising and wide applications such as pharmaceutical use, water retention, electrophoretic media and the like.

Experimental

Material

Partially hydrolytic polyacrylamide (PAM) ($M_n 50 \times 10^4$; Hydrolytic degree 20%) was purchased from Jiangsu Nantian flocculants Co. Ltd and purified before modification using water/isopropyl alcohol. Glycidyl methacrylate (GMA) was supplied by Guangzhou Shuangjian Trade Co.Ltd and distilled under reduced pressure before use. Benzoquinone was purchased from Changzhou Xinhua Institute of Active materials and used without further purification. The other materials such as isopropyl alcohol, acetone, potassium persulfate (KPS), as an initiator; triethanolamine (TEA), as a coupling agent, dodecyl sulfonic acid sodium salt (SDS) were of analytical grade.

Preparation of modified polyacrylamide

Modified polyacrylamide was prepared as follows: an amount of partially hydrolytic polyacrylamide (PAM), was dissolved in deionized water to make the concentration 5 wt%, and a proportional (1:1 mol/mol) of glycidyl methacrylate (GMA) was added, the solution was heated to 80 °C. Subsequently, the reaction was allowed to continue for another 15 h at 80 °C. After the reaction completed, the solution was poured into cold isopropyl alcohol (1:2 v/v), then the precipitate of

modified PAM was filtrated and washed by acetone for three times, dried in vacuum desiccators at 60 °C overnight. The reaction of PAM with GMA was shown in Fig. 1.

Preparation of modified polyacrylamide hydrogels

Procedures of preparing PAM-g-GMA hydrogels were as follows: Firstly, the modified PAM was dissolved in an amount of double distilled water to obtain different concentration water solution over a range of 2–10 wt%, Whereafter, a certain mass proportion (2 w/w) of KPS/TEA initiator system was charged into the solutions, whisked equably then radical polymerization carried out immediately. And then, the solutions were placed at room temperature for 24 h to make the gels gain the best properties. Lastly, hydrogels were immersed in distilled water, with the relative volume of distilled water to gel was 2/1, for a week to remove unreacted agents (KPS and TEA). The water was renewed every day. The preparation reaction of PAM-g-GMA hydrogel was shown in Fig. 1.

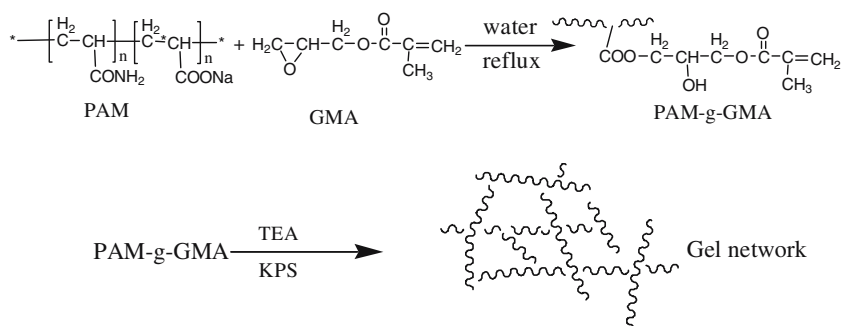
Determination of degree of GMA grafting (dg)

The average degree of grafting (dg, the percentage of methacrylate groups with respect to mono acrylamide units of PAM-g-GMA) was calculated by the $^1\text{H-NMR}$ spectra of PAM-g-GMA as $[(142.2a)/(142.2a + 71.08b)] \times 100$, where a is the integrated area of one vinylproton peak at about 6.05 ppm, while b is the integrated area of acrylamido proton peak at about 1.54 ppm; 142.2 and 71.08 are the mole molecular weight of GMA and PAM, respectively. And the average number of chain section between any two crosslink points (n) can be easily calculated by dg.

Characterization of modified polyacrylamide

Molecular Structure of modified polyacrylamide was determined by FT-IR and $^1\text{H-NMR}$. Both FT-IR and

Fig. 1 Reaction of PAM with GMA and preparation reaction of PAM-g-GMA hydrogel



$^1\text{H-NMR}$ spectrum confirmed that GMA were grafted onto the side groups of PAM chains successfully. The polymer sample was crushed to make the KBr pellet and FT-IR (China, WQF-410) spectra was taken in the wavelength region $400\text{--}4,000\text{ cm}^{-1}$ with a resolution of 2 cm^{-1} . $^1\text{H-NMR}$ spectrums of PAM, PAM-g-GMA and GMA were recorded on a Germany BRUKER DRX-400 spectrometer (400 MHz for hydrogen) in D_2O and DMSO solvent, respectively.

Thermal behaviors of hydrogels

DSC characterized thermal behaviors of PAM-g-GMA hydrogels. The DSC analysis was carried out using Perkin-Elmer DSC-2C by scanning in the temperature range of $25\text{--}300^\circ\text{C}$ at a rate of $10^\circ\text{C}/\text{min}$ under a N_2 atmosphere. And DSC of different concentration hydrogels for modified polyacrylamide (prepared at 2.3.): 3, 5, 7 and 10 wt% were carried out. The glass transition temperature (T_g) was determined as the temperature at the midpoint of the endothermic rise, measured from the extension of the post-transition baselines.

Swelling properties

The above hydrogels prepared were dried in vacuum at 353 K for about 24 h to obtain extracted xerogels which were weighed as m_d , the swelling hydrogels were obtained by making xerogels completely swollen to equilibrium in distilled water and weighed m_s . It was considered that the equilibrium was achieved if the mass of sample did not change more than 0.01 g during 24 h [17, 18].

To study the dynamic swelling properties of xerogels, each xerogel was immersed in distilled water at 298 K. At given times the gels were removed from water, excess surface liquid was removed by blotting with filter paper and were weighed m_t . The water uptake (S_w) was calculated using Eq. (1), and S_w is the exponential function of time (t) shown in Eq. (1).

$$S_w = \frac{m_t - m_d}{m_d} \times 100\% \quad (1)$$

According to Vervoort et al. [15] and Reis et al. [17], the equilibrium swelling ratio (Q_{eq}) was, for each case, calculated according to Eq. (2).

$$Q_{\text{eq}} = \frac{m_s}{m_d} \quad (2)$$

Compression measurements

Compression measurements of the hydrogels were performed on a SN-06 Universal Test Machine made in Shenzhen China, and the speed was 0.25 mm/s and the height of all samples was 40 mm. The compressive stress was a function of stain and was expressed in units of MPa.

Results and discussion

Structure determination of modified polyacrylamide

Infrared spectra characterization

FT-IR spectrums of the PAM and PAM-g-GMA were shown in Fig. 2. A broad band, attributed to $-\text{OH}$ and $-\text{NH}_2$, may be observed at $3,440\text{--}3,100\text{ cm}^{-1}$ from the spectra of PAM-g-GMA. Band at $1,666\text{ cm}^{-1}$ was assigned to the composite band of the acryloyl groups conjugated system and carboxamido groups. The band at $1,200\text{--}1,040\text{ cm}^{-1}$, assignable to C-O and/or C-O-C groups from alcohol and ethers were also present in the spectra of PAM-g-GMA. In addition, an absorption band at 887 cm^{-1} , attributed to the out-of-plane bending wagging of $=\text{C-H}$ may also be observed. And yet, the bands could not be observed in FT-IR spectra of the PAM. All of changes indicated that GMA molecule was successfully grated onto the side groups of PAM chains.

$^1\text{H-NMR}$ characterization

From $^1\text{H-NMR}$ spectrums of GMA, PAM and PAM-g-GMA, shown in Fig. 3, the presence of signals at $\delta 6.05$

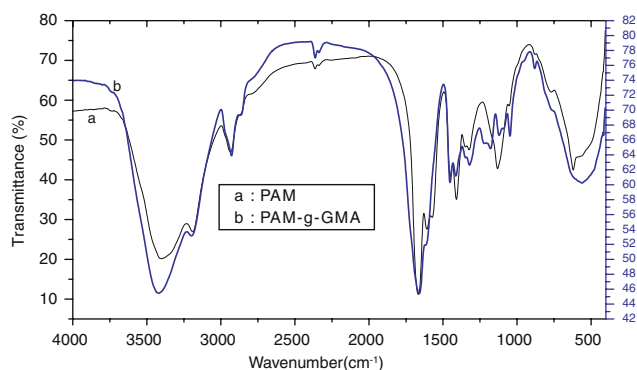
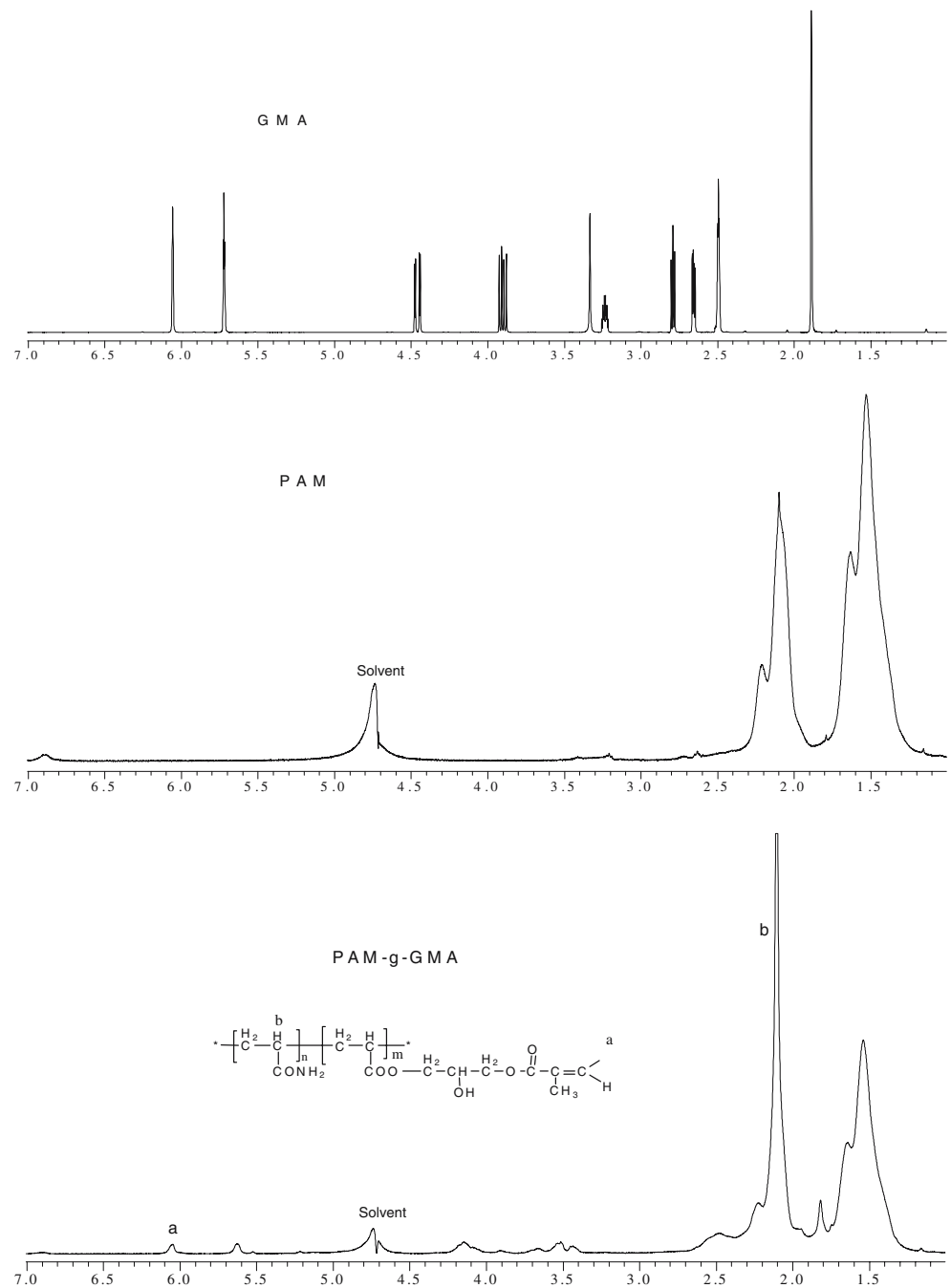


Fig. 2 FT-IR spectra of PAM and PAM-g-GMA

Fig. 3 $^1\text{H-NMR}$ spectrums of GMA (top), PAM (midst) and PAM-g-GMA (bottom) (unit:ppm)



and 5.63 ppm attributed to the vinyl protons and at δ 1.83 ppm attributed to the methyl protons were observed both in the spectrums of GMA and PAM-g-GMA, and not observed in the spectrum of PAM. δ 1.5 and 2.12 ppm were assigned as the signals of $-\text{CH}_2-$ and $-\text{CH}-$ in PAM chains. The appearance of these signals confirmed the presence of methacryl groups on PAM-g-GMA molecules.

Characterization of modified polyacrylamide hydrogels

Thermal behaviors characterization

The thermal behaviors of dry PAM-g-GMA hydrogels were characterized by determining the glass transition temperature (T_g) of 3, 5, 7 and 10 wt% hydrogels. As

shown in Table 1, the glass transition temperature (T_g) increased (from 440 °C to 461 °C) with increasing PAM-g-GMA concentration such as from 3 wt% to 10 wt%. This could be explained that effective crosslink density increased as polymer concentration increased; and more energy will be inevitably consumed to destroyed the molecules interaction force such as hydrogen bonds inside PAM-g-GMA molecules. So the increased modified PAM (PAM-g-GMA) concentration resulted in an increased T_g .

Swelling properties

The swelling behaviors of xerogels in different pH value and different temperature were studied and The swelling dynamics of xerogels in neutral aqueous solution at 25 °C was also investigated.

The swelling behaviors of xerogels were measured in response to pH change by adjusting the pH value. Figure 4 shows the swelling behaviors of xerogels over a pH range of 1–14.0. From the graph, it was obviously observed equilibrium swelling ratio changed a fat lot over a pH range of 1–7.0 for three dried gels, as pH value above 8.0, equilibrium swelling ratio (Q_{eq}) increased dramatically, and Q_{eq} value changed from 18 to 150 for 8 wt% gel. This phenomenon may be attributed to the existence of –COOH groups on the side chains of partly hydrolytic PAM. At higher pH (above 7), the –COOH groups may dissociate, thereby increasing the osmotic pressure inside the gels resulting in a higher swelling.

Table 1 Glass transition temperature (°C) of dry PAM-g-GMA hydrogel powder samples

Polymer concentration	3 wt%	5 wt%	7 wt%	10 wt%
T_g (°C)	440.2	450.3	456.2	461.5

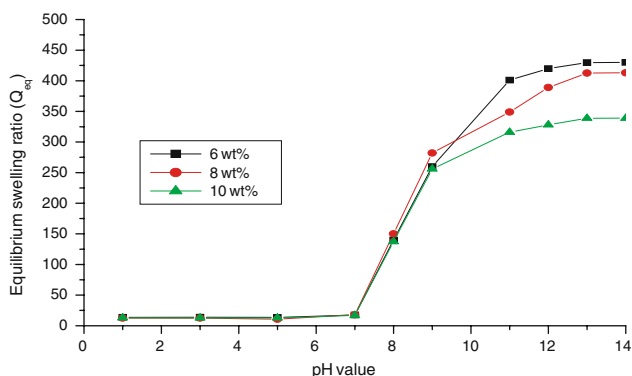


Fig. 4 Swelling behaviors of xerogels in varied pH value at 25 °C

The effect of temperature on swelling behavior of xerogels was also studied, as shown in Fig. 5. As a whole, equilibrium swelling ratio (Q_{eq}) became high by raising the temperature of the aqueous media. This fact could be explained as that partially hydrogen bonds destroyed due to the increase in temperature directly leading to the swelling process endothermic, greater hydrodynamic free volume was produced owing to the network of gels being looser as the partly hydrogen bonds were destroyed, so the capacity of uptaking water viz. equilibrium swelling ratio became greater.

As expected, Equilibrium swelling ratio of xerogels increased (from 2 wt% to 6wt%) and then decreased (from 6 wt% to 10 wt%) with the increasing PAM-g-GMA concentration in pH = 7.0 aqueous solution at 25 °C, as could be seen in Table 2. The possible causes of the results were that swelling of xerogels in aqueous media strongly depends upon the extent of effective crosslink density, since effective crosslink density increased with the increase in polymer chain concentration. At extremely low crosslink density, the network is too loose to uptake many water molecules, for instance, 2 wt% gel ($Q_{eq} = 83$), whereas as crosslink density a little higher, the network became close also with a enough great hydrodynamic free volume and so could accommodate more of the water molecules, such as 6 wt% gel ($Q_{eq} = 103$). However, as crosslink density was too high, the network was so close that it had not enough hydrodynamic free place to accommodate the solvent molecules resulting in a lower equilibrium swelling ratio like 10 wt% gel ($Q_{eq} = 68$).

Compression properties

Figure 6 presents the compression stress versus strain curves of several concentrations PAM-g-GMA hydrogels. From the curves, we could easily observe that

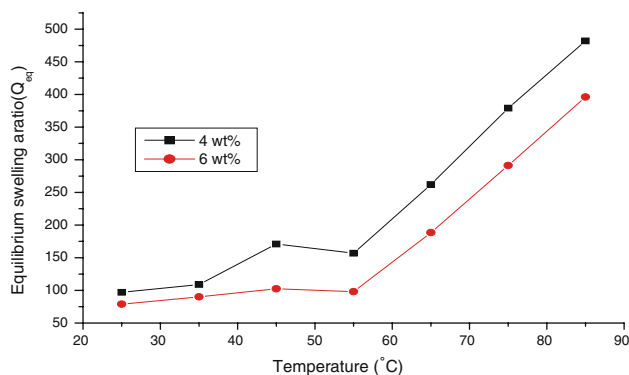
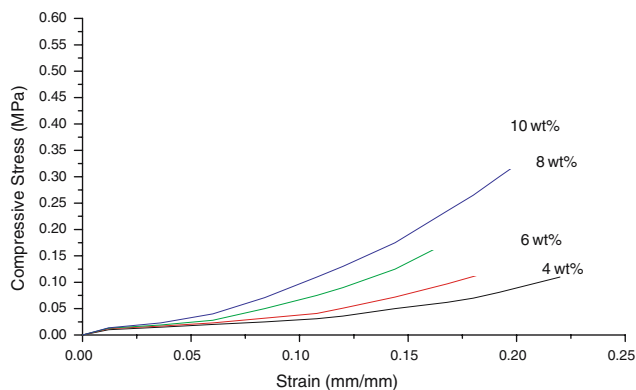


Fig. 5 Effect of temperature on swelling behaviors of gel at pH = 7.0

Table 2 Equilibrium swelling ratio (Q_{eq}) of several xerogels (from 2 wt% to 10 wt%)

Polymer concentration	2 wt%	4 wt%	6 wt%	8 wt%	10 wt%
Q_{eq}	83	95	103	76	68

**Fig. 6** Compression stress vs strain curves of several hydrogels

compressive strength increased slowly at first and very fast later with the increase in the concentration of PAM-g-GMA hydrogels (4–10 wt%), such as the compressive strength of 4, 6, 8 and 10 wt% were 0.1, 0.17, 0.32, 0.37 MPa, respectively. This outcome was absolutely consistent with the conclusions mentioned above. Meantime, great elasticity of hydrogels was also embodied and confirmed by the stress-strain curves. As the strain of four hydrogels was 0.22, namely, 22%, the elastic modulus of them could be calculated by the ratio value of compressive stress to strain [19], and gave their values: 0.45, 0.77, 1.45 and 1.68 MPa, respectively.

Molar mass per crosslink (M_c) and effective crosslink density (v_e)

According to the Flory's theory of rubber elasticity, Eqs. (4)–(6), referred to literatures [19, 20], but as for the special hydrogels system, Eqs. (7) and (8) could be deduced safely, so molar mass per crosslink (M_c) and effective crosslink density (v_e) could be calculated using the following equations.

$$\tau = RTv_e\phi_2^{1/3}(\lambda - \lambda^{-2}) \quad (3)$$

$$G = \tau/(\lambda - \lambda^{-2}) = E/3 \quad (4)$$

$$v_e = E\phi_2^{1/3}/3RT \quad (5)$$

$$\phi_2 = (m_d/\rho_d)/[m_d/\rho_d + (m_e - m_d)/\rho_{H_2O}] \quad (6)$$

$$M_c = \rho_d/v_e \quad (7)$$

$$M_c = 71.08n + 42.2 \times 2 \quad (8)$$

In Eqs. (3)–(8), m_e and m_d are the mass of hydrogels and xerogels, τ is the applied force per unit area, λ is the extension ratio, G is Young's modulus, Φ_2 is the volume fraction of polymer in hydrogel, R is the gas constant (8.314 J K^{-1}), T is the temperature in Kelvin, n is the average number of chain section between any two crosslink points and ρ_d is the density of xerogels.

According to the $^1\text{H-NMR}$ spectrum of modified PAM, we could calculate the grafting degree of PAM and the number of unsaturated bonds in 100-chain section of PAM molecule. As to the structure of modified PAM prepared by us, the average value of n is 25, so the average value of M_c is about 2,061, according to Eq. (8). As to 5 wt% and 7 wt% of xerogels, their densities (ρ_d) are 1.12×10^3 and $1.14 \times 10^3 \text{ kg/m}^3$, respectively; According to Eq. (7), the value of v_e will be 543 mol/m^3 and 553 mol/m^3 , respectively. From the values of v_e and M_c , it was obviously observed that the density (ρ_d) and effective crosslink density (v_e) increase with the increase in the concentration of PAM-g-GMA. These outcomes are good agreement with conclusion gained mentioned above (DSC results, swelling behaviors of xerogels and compression property measurements as well).

Conclusion

Modified polyacrylamide (PAM-g-GMA) was first prepared by the ring-opening reaction of glycidyl methacrylate grafted onto the side groups of partly hydrolytic polyacrylamide; its structure was confirmed by FT-IR and $^1\text{H-NMR}$. Then modified polyacrylamide hydrogel was synthesized through radical polymerization. The glass transition temperature, swelling properties, compressive strength of hydrogels were studied. And we observed that the glass transition temperature and compressive strength of the gels increased, the apertures of gels became smaller with the increase in concentration of PAM-g-GMA. But for the swelling properties of xerogels, the equilibrium swelling ratio (Q_{eq}) of several concentration xerogels all dramatically increased at about $\text{pH} = 7.5$. and it was more interesting that Q_{eq} values first increased and then decreased at about $45 \text{ }^\circ\text{C}$, then continued to increase after $55 \text{ }^\circ\text{C}$. The swelling behaviors of xerogels with the time change revealed that there existed an optimal polymer concentration at which the xerogel had a biggest Q_{eq} value, for instance, for the gels we

prepared, 6 wt% was the very optimal concentration, may because 6 wt% gel had the proper effective crosslink density.

Finally, for the modified PAM hydrogels we prepared in this paper, we employed the Eq. (7) and (8) to determine the molar mass per crosslink (M_c) and effective crosslink density (ν_e), and we arrived at a conclusion that the average value of M_c was about 2,061 and the ν_e value was approximately 550 mol/m³. The PAM-g-GMA hydrogels will have promising and wide applications such as pharmaceutical use, water retention, electrophoretic media and so on owing to their great properties. Of course, a lot of work remains to be done such as the polymer–water interaction parameter, entropy and enthalpy changes in the future. We will report them in the forthcoming paper.

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