



Study of Carboxymethyl Chitosan-based Polyampholyte Superabsorbent Polymer (Part II): Investigating the State of Water in CMCTS-*g*-(PAA-*co*-PTMAAC) Hydrogel

Chen Yu*, Yun-Fei Liu, Huan-Lin Tang, and Hui-Min Tan

School of Material Science and Engineering, Beijing Institute of Technology,
Beijing-100081, PR China

Received 9 August 2009; accepted 24 February 2010

ABSTRACT

Some specific structure-properties relationship of a polyampholyte carboxymethyl chitosan-*g*-poly(acrylic acid-*co*-trimethylallyl ammonium chloride) (CMCTS-*g*-(PAA-*co*-PTMAAC)) hydrogel and the properties of water in the hydrogel were investigated by DSC measurement. The freezing water and non-freezing water contents of the hydrogel were determined quantitatively by examining their relationship with the structure and constitutive parameters of the polyampholyte hydrogel. The experimental results showed that higher swelling ratio of the hydrogel could decrease the content of the non-freezing water. It was found that the shape of the exothermic or endothermic curves and the peak temperature were strongly influenced by the heating/cooling rate or heating/cooling cycling. A hysteresis loop was evident during the process of heating/cooling cycling and the temperature interval between T_{\max}^+ and T_{\max}^- was increased by higher heating/cooling rate. The cross-linking degree of the hydrogel, molar ratio of two monomers and the neutralization degree of the anionic acrylic acid also have a great influence on the water content at various states. The results showed that the amount of non-freezing water in the hydrogel increased gradually as the cross-linking degree increased, but it was reduced while the molar ratio of TMAAC increased. By increasing the neutralization degree of acrylic acid, the amount of the non-freezing water was also increased.

Key Words:

polyampholyte hydrogel;
DSC;
water state;
non-freezing water.

INTRODUCTION

Superabsorbent hydrogels with network structure and moderate cross-linking can absorb a large amount of water [1] and become much more bulky than their original state. The amount of the absorbed water can range from hundreds to thousands times of the polymer mass. These polymers have been extensively used as absorbents in personal care products, e.g., infant diapers, feminine hygiene products, and incontinence products [2,3]. They

have also received considerable attention for a variety of specialized applications, including matrices for enzyme immobilization, bioabsorbents in preparative chromatography, materials for agricultural mulches, and matrices for controlled release devices [4-6].

In our previous paper, we reported the synthesis of novel carboxymethyl chitosan-*g*-poly(acrylic acid-*co*-trimethylallyl ammonium chloride) (CMCTS-*g*-(PAA-*co*-PTMAAC)) polyampho-

(*) To whom correspondence to be addressed.
E-mail: cylsy@163.com

lyte superabsorbent hydrogel by graft copolymerization of acrylic acid with trimethylallyl ammonium chloride along the chain of the carboxymethyl chitosan [7]. The structure of the prepared hydrogel was characterized and the optimized synthetic conditions were applied to obtain polymer with the highest swelling ratio.

Chitosan is an important natural polymer exhibiting several favourable properties, including good biodegradability, biocompatibility, antibacterial property and low toxicity [8,9]. Meanwhile, the swelling and shrinking of the polyampholyte superabsorbent hydrogels exhibit unique pH dependant properties different from those of traditional polyelectrolyte superabsorbent hydrogels [10,11]. Thus, the prepared (CMCTS-g-(PAA-co-PTMAAC)) polyampholyte superabsorbent hydrogel bears special characteristics and wide application prospects.

To acquire such a wide range of uses, it is important to control physical properties of the hydrogels by changing their structures and polymerization conditions [12]. The properties of the hydrogels are decided not only by the cross-linking network structure of the constituent polymer, but also by the status and properties of the water in the network. The activity, freezing and melting behaviour of water present in the hydrogel are entirely different from that of free water [13-17]. The status of water in the hydrogel, interactions of hydrogel and water, the relationship between the stimulated conditions and the status of water have attracted great attentions in recent years [18-20].

Thus, characterization of the amount of absorbed water in the swollen hydrogel is essential [12]. Different analytical techniques, e.g., ^1H NMR [21,22], dilatometry and electrical conductivity [23], dielectric relaxation spectroscopy [24], dynamic-mechanical spectroscopy [25] and differential scanning calorimetry [12,26] have been employed to study water structure in hydrogels. The classification of water status in the hydrogels depends on the analytical techniques employed.

Differential scanning calorimetry (DSC) has proved to be a very useful technique in determining the state of water in hydrogels [27,28]. According to this method, the state of water in the polymer can be

distinguished from free water, freezing bound water and non-freezing water. The water portion which does not participate in hydrogen bonding with polymer molecules and has a similar transition temperature, enthalpy, and DSC curves as pure water, is defined as "free water". Freezing bound water or intermediate water indicates the water weakly interacting position with polymer molecules and has a phase transition temperature lower than 273 K.

Non-freezing water or non-freezing bound water includes water molecules which are bound to polymer molecules through hydrogen bond and has no detectable phase transition over the temperature range from 233 K to 273 K. The non-freezing water provides different energetic states depending on the associating strength of the water-water and water-polymer interactions. Therefore, the specific polymer-water interactions could reflect the special structure-properties relationship for the hydrogel on which there are numerous studies on this subject [29,30].

The purpose of the current study is to evaluate the different states of water in CMCTS-g-(PAA-co-PTMAAC) hydrogel using DSC technique and to examine the relationship between the water content in various states with constitutive parameters related to CMCTS-g-(PAA-co-PTMAAC) polyampholyte superabsorbent hydrogel.

EXPERIMENTAL

Materials

We synthesized carboxymethyl chitosan according to the method reported in literature [31]. The substitution degree of the carboxymethyl was 0.67 determined by elemental analysis. Acrylic acid (AA, analytical grade) was purchased from Tianjin Chemical Reagent Institute (China) and purified by reduced pressure distillation before polymerization process. Trimethylallyl ammonium chloride (TMAAC) was synthesized in our laboratory according to the method reported in literature [32]. Ammonium persulphate (APS, analytical grade) and sodium sulphite (analytical grade) were used as redox initiators. *N,N'*-Methylene diacrylamide (MBA, analytical grade) was used as a cross-linking agent.

Ethanol was also used as analytical grade reagent.

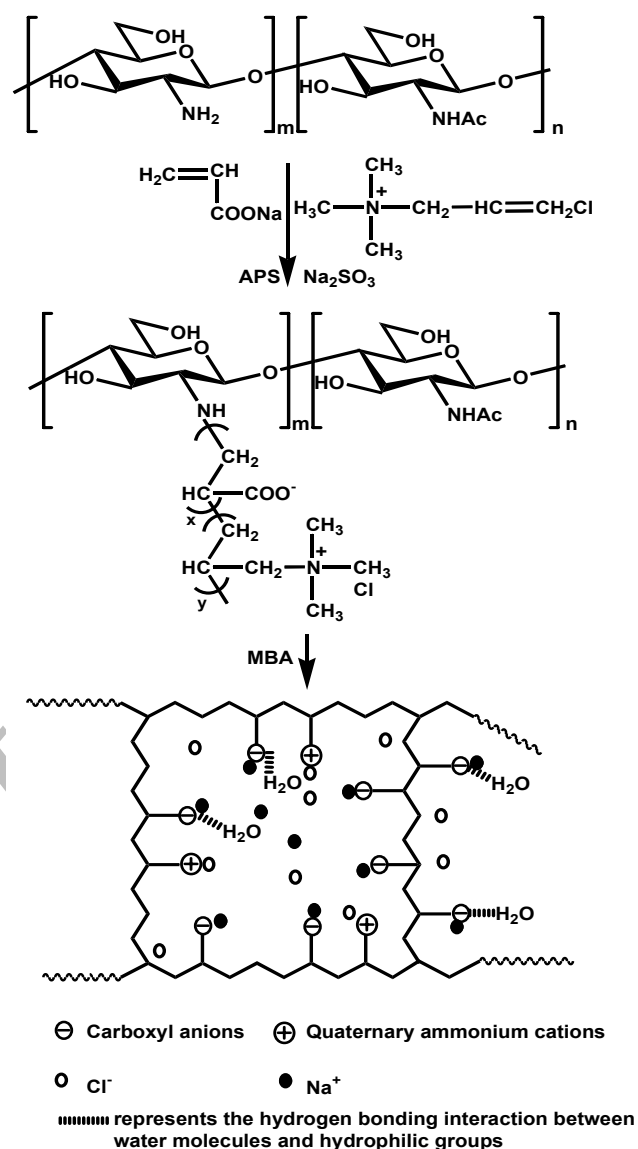
Preparation of CMCTS-*g*-(PAA-*co*-PTMAAC) Hydrogel

Carboxymethyl chitosan (1.5 g) was dissolved in 50 mL deionized water and then added into a three-necked flask which was equipped with a stirring apparatus and a reflux condenser. The solution was stirred for 30 min under the protection of nitrogen and heated in a water bath of 40°C. An exact amount of APS (0.00136 mol) and Na₂SO₃ (0.00136 mol) dispersed in 20 mL distilled water was slowly added into the flask to initiate the graft polymerization. Appropriate amounts of TMAAC, MBA and acrylic acid, neutralized to a desired degree by NaOH, were dissolved in 80 mL distilled water and the whole solution was added into the flask after 30 min. The total amount of two monomers was kept at 0.17 mol. After reacting for 5 h, air was introduced into the reactor to cool down the flask and stop the reaction.

The product was precipitated by pouring ethanol into the reaction mixture. The precipitate was filtered, washed thoroughly with an ethanol/water mixture (4/1, v/v) several times under high-speed stirring, and then soaked with ethanol/water mixture (4/1, v/v) for 24 h. The product was collected by filtration and dried under vacuum. The yields were in the range of 67% to 91%. Finally, the dried product was shivered and the particles with the size range between 150 μm and 250 μm were used for water absorption test. The structure of the CMCTS-*g*-(PAA-*co*-PTMAAC) hydrogel was characterized in the previous work [25] and the optimal conditions to synthesize the polymer with the highest swelling ratio had been qualified. The procedure for preparing CMCTS-*g*-(PAA-*co*-PTMAAC) hydrogel is shown in Scheme I.

DSC Characterization

DSC technique was used for quantitative determination of the exact contents of the freezing and non-freezing water in swollen hydrogels. The prepared hydrogels were allowed to swell in test solution until the equilibrium swelling was reached. The samples were wiped with a filter paper to remove the excess surface water and 5~10 mg swollen samples were sealed in aluminium pans. After cooling to 233 K to ensure that supercooled water was



Scheme I. Schematic CMCTS-*g*-(PAA-*co*-PTMAAC) hydrogel preparation.

completely frozen, the samples were then heated at a rate of 5 K/min to 313 K in a dynamic N₂ atmosphere by using Perkin-Elmer DSC-7 (USA).

The equilibrium water content (W_{EWC}) was calculated as follows:

$$W_{EWC}(\%) = \left(\frac{m_2 - m_1}{m_2} \right) \times 100 \quad (1)$$

where, m_1 and m_2 are weights of dry hydrogel and swollen hydrogel, respectively.

The fusion enthalpy (ΔH) calculated from the

integration of the area under the melting peak and the melting endothermic heat of fusion for pure water (ΔH_0 , 334.3 J/g) were used to calculate the percentage of freezing water (W_f) (the summation of both percentages of free water and the freezing bound water) in total water [33,26] by the following equation:

$$W_f = W_{free} + W_{freezing-bound} = (\Delta H / \Delta H_0) \times 100 \quad (2)$$

The amount of non-freezing water (W_{nf}) was obtained by subtracting the amount of free water from the equilibrium water content [34].

$$W_{nf} = W_{EWC} - W_f \quad (3)$$

RESULTS AND DISCUSSION

To study the relationship between the properties of the polyampholyte hydrogel with different states of water and the water content of each state, it is important to explore and test the states of water in the hydrogel and study the effect of external environments and test procedures on the performance of different states of water.

Figure 1 shows a set of typical endotherms for the polymer swollen at different water concentrations heated at a rate of 5 K/min from 233 K to 313 K. There is a stronger endothermic peak around 273 K in the DSC curve of the hydrogel which is similar to the melting curve of ice. However, the temperature at maximum melting velocity is lower than that of ice. This peak has been induced by two states of water immobilized in the hydrogel network, namely free water and freezing bound water. The melting behaviour of the free water coincided with the ice formed by the pure water, and yet the melting peak of the freezing bound water was lower than that of the ice formed by the pure water. As the contents of the free water and the freezing bound water of the CMCTS-*g*-(PAA-*co*-PTMAAC) superabsorbent hydrogel were relatively high, the endothermic peaks of different kinds of ice were wide and superimposed where they were hardly distinguished quantitatively. This is different from the split melting peaks of a hydrogel with which the water uptake is relatively

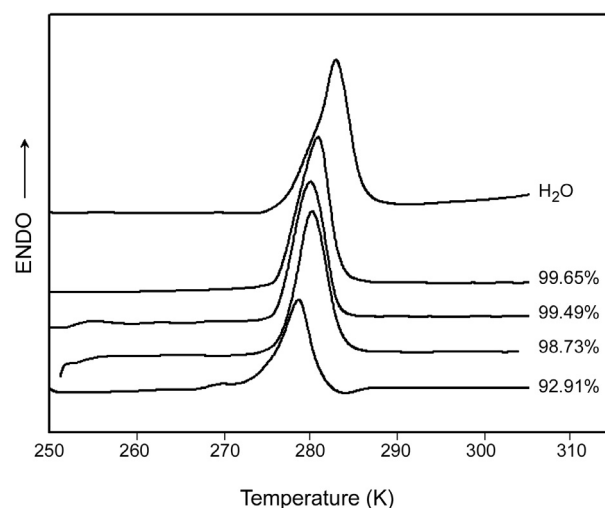


Figure 1. DSC Endotherms of CMCTS-*g*-(PAA-*co*-PTMAAC) superabsorbent hydrogel as function of different W_{EWC} values. The samples were heated at a rate of 5 K/min.

low around the same temperature range [35,36]. Thus, the total sum of free water and freezing bound water (W_f) in CMCTS-*g*-(PAA-*co*-PTMAAC) hydrogel were estimated by the ratio of integrated endothermic peak to the melting endothermic peak of the heat of fusion of pure water. It is shown in Table 1 that if W_{EWC} of the hydrogel increases gradually, the temperature at maximum melting velocity increases the same and approaches to the melting peak of the ice. This phenomenon indicates that the proportion of free water in W_f state increases gradually. The non-freezing water was commonly thought to be the water closely bound to or immobilized by the polymer. This represents a metastable supercooled state which is inhibited from attaining a true equilibrium state during freezing by motional

Table 1. Water content of different water states in the hydrogel with different W_{EWC} values.

W_{EWC} (%)	W_f (%)	W_{nf} (%)	T_{max} (K)
92.91	61.85	31.07	278.57
98.73	74.81	23.92	280.01
99.49	81.37	18.12	280.16
99.65	85.69	13.96	280.87

barriers [37]. Then, the non-freezing water shows no endothermic peak in the temperature range from 233 K to 313 K and its content cannot be calculated directly. Non-freezing water may be expressed as the difference in contents between the total water and total sum of free water and freezing bound water. The W_{EWC} values, the total amount of free water and freezing bound water and the non-freezing water content of the CMCTS-*g*-(PAA-*co*-PTMAAC) hydrogel at different swelling ratios were calculated and are listed in Table 1. It may be observed from these data that the content of the non-freezing water decreases gradually as the water content of the hydrogel increases.

For certain polymer structures, the absolute content of the non-freezing water bound by hydrophilic groups of the polymer chain may stay constant, and then the relative mass fraction of the non-freezing water decreases as the total water content of the hydrogel increases.

Exothermic curves of the hydrogel with different water contents which were recorded during the process of cooling are presented in Figure 2. Comparing with the melting processes, the exothermic peaks hystereses are much sharper than the endothermic peaks during the heating process. This corresponds to appreciable supercooling induced by the network structure of the hydrogel and the strong hydrogen bonding interaction of water

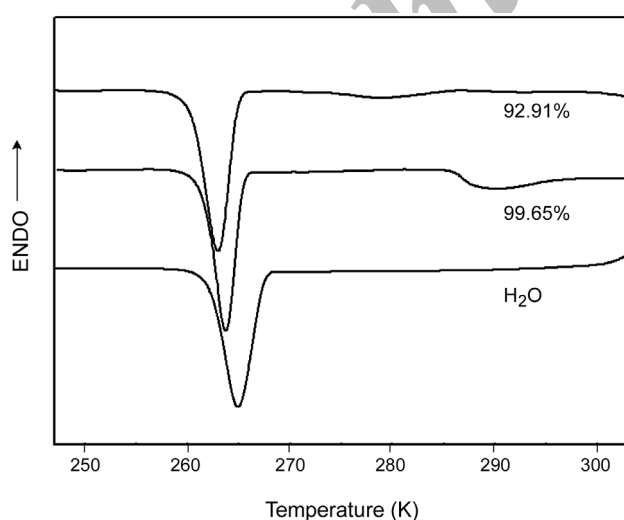


Figure 2. DSC Exotherms of CMCTS-*g*-(PAA-*co*-PTMAAC) superabsorbent hydrogel as function of different W_{EWC} values. The samples were cooled at a rate of 5 K/min.

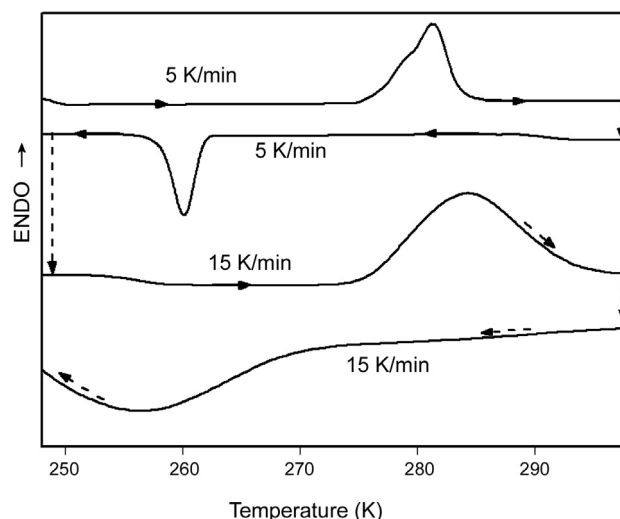


Figure 3. The thermodynamics of recurrent melting and crystallization processes of hydrogel at different heating/cooling rates.

molecules with hydrophilic acrylate and quaternary ammonium groups of CMCTS-*g*-(PAA-*co*-PTMAAC) hydrogel. Therefore, the onset of nucleation temperature is lower and the rate of nucleation is prompted to exothermic reaction during the freezing process.

Figure 3 displays the thermodynamics of recurrent melting and crystallization processes of hydrogel at different heating/cooling rates. There was an obvious hysteresis occurred during the process of heating/cooling cycling and the temperature interval (ΔT) between the temperature at maximum melting rate (T_{\max}^+) and the temperature at maximum crystallization rate (T_{\max}^-), which was also affected by the rate of heating and cooling. ΔT values were 28.07 K at 15 K/min heating/cooling rate and 21.08 K at 5 K/min heating/cooling rate.

The crystallization process of the freezing water was controlled by the onset of nucleation. At the lower cooling velocity, the time for crystallization was sufficient and the nucleation was able to start at higher temperature, followed by maximum crystallization velocity which occurred at higher temperature zone. In contrast, the crystallization peak was broader and T_{\max}^- was lower at higher cooling rate.

The peak shape of the melting curve of freezing water during the heating process was also controlled

by the heating rate. When the heating rate was higher, the hysteresis of molecular water dominating the intermolecular interaction was more evident, and then the melting peak was broader than those at lower heating rates. Because the peak shape and the maximum peak temperature of heating and cooling processes are severely dependent on the heating/cooling rate, the relative contents of water in various states were tested and calculated at constant heating/cooling rate (5 K/min).

It was previously found that the equilibrium water content of hydrogels is greatly influenced by the structure and polymer constituent [38,39]. In the present work, the effects of structure and constitutive parameters of the CMCTS-*g*-(PAA-*co*-PTMAAC) polyampholyte superabsorbent hydrogel on the water contents of various states were also investigated.

Figure 4 shows the effect of cross-linking agent concentration on the contents of water in various states. It was found that the amount of non-freezing water in the hydrogel was increased gradually as the cross-linking increased, while the free water and freezing water contents decreased. These results matched with the experimental data obtained by Bhardwaj et al. [40] on the effects of cross-linking agent on the water state of polyampholyte hydrogel prepared by polymerization of *p*-sodium styrene sulphonate and vinyl benzyl trimethyl ammonium chloride. This may be due to the increased water

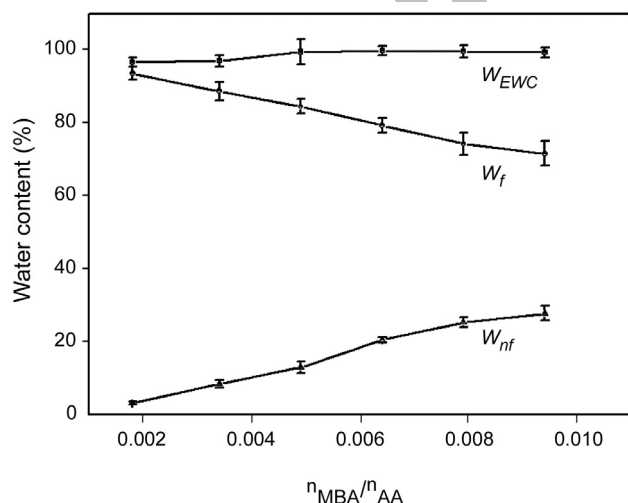


Figure 4. Water content of different water states in the hydrogel with different contents of cross-linking agent.

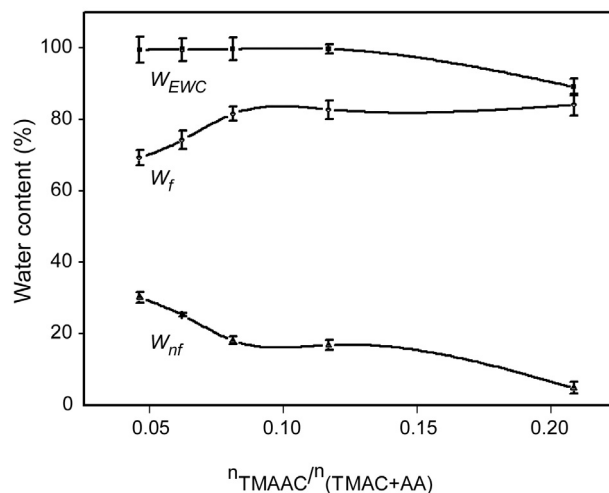


Figure 5. Water content of different water states in the hydrogel with different monomer contents.

binding sites generated by introduction of the MBA cross-linking agent with sites available for hydrogen bonding with water molecules.

The effect of molar ratio of the two monomers on the water contents of various states of the polymer is shown in Figure 5. If the molar ratio of TMAAC is increased, the content of non-freezing water of the hydrogel is decreased. As the interaction between the -COO^- groups and quaternary ammonium groups was enhanced by increased cation content, the free -COO^- groups with strong hydrophilicity was reduced and the content of $\text{-COO}^- \text{ } ^+\text{NR}_4$ with

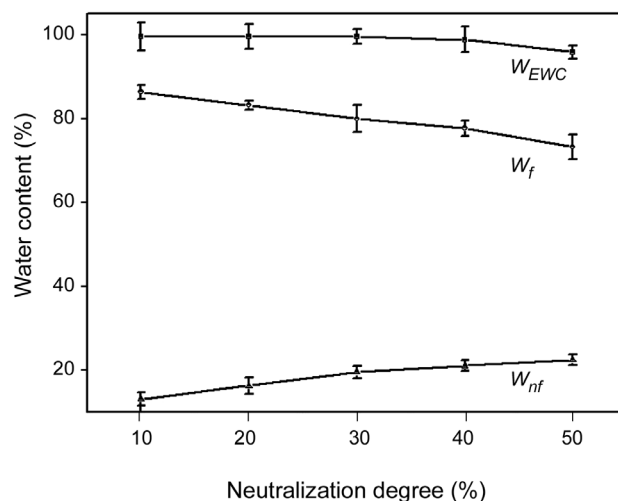


Figure 6. Water content of different water states in the hydrogel with different degrees of neutralization.

weaker water interaction was increased [8]. Thus, the hydrogen bonds between the hydrophilic groups and water molecules were weakened and then, the amount of non-freezing water was gradually decreased.

The influence of the neutralization degree of acrylic acid on the water content in various states is shown in Figure 6. The amount of non-freezing water is increased as the neutralization degree of acrylic acid is increased. By increasing the neutralization degree, the ionization of -COOH is enhanced and the amount of ionic -COO⁻ with stronger hydrophilicity is elevated. Then, the content of non-freezing water state is increased since it is combined with hydrophilic groups.

CONCLUSION

Differential scanning calorimetry (DSC) was used to investigate the state of water content in CMCTS-g-(PAA-co-PTMAAC) polyampholyte superabsorbent hydrogel, which was prepared by graft copolymerization of acrylic acid and trimethylallyl ammonium chloride onto the chain of carboxymethyl chitosan. It was found that by increasing the equilibrium water content the content of non-freezing water could decrease. Exothermic curves of the hydrogel during the cooling process displayed hystereses of much sharper than endothermic peaks during the heating process. By studying the thermodynamics of recurrent melting and crystallization processes of hydrogel at different heating/cooling rates, it was found that obvious hystereses loops occurred during the process of heating/cooling cycles and the temperature interval between T_{\max}^+ and T_{\max}^- increased as the heating/cooling rate increased. By studying the structure and constitutive parameters of the CMCTS-g-(PAA-co-PTMAAC) polyampholyte hydrogel and their effects on the content of various water states, it was found that the amount of non-freezing water in the hydrogel increased gradually as the cross-linking degree increased, while it decreased as the molar ratio of TMAAC increased. In this respect, the increased neutralization degree of the acrylic acid was accompanied by increased non-freezing water content.

ACKNOWLEDGEMENTS

This work was supported by the Natural Science Foundation of China (No. 50773005), and The Basic Study Program of Beijing Institute of Technology (20060442004).

REFERENCES

1. Mudiyansele TK, Neckers DC, Highly absorbing superabsorbent polymer, *J Polym Sci A Polym Chem*, **46**, 1357-1364, 2008.
2. Zhang JP, Liu RF, Li A, Wang AQ, Preparation, swelling behaviors and application of polyacrylamide/attapulgit superabsorbent composites, *Polym Adv Technol*, **17**, 12-19, 2006.
3. Zohuriaan-Mehr MJ, Kabiri K, Superabsorbent polymer materials: a review, *Iran Polym J*, **17**, 451-477, 2008.
4. Eming S, Smola H, Hartmann B, Malchau G, Wegner R, Krieg T, Smola-Hess S, The inhibition of matrix metalloproteinase activity in chronic wounds by a polyacrylate superabsorber, *Biomaterials*, **29**, 2932-2940, 2008.
5. Liu MZ, Liang R, Zhan FL, Liu Z, Niu AZ, Synthesis of a slow-release and superabsorbent nitrogen fertilizer and its properties, *Polym Adv Technol*, **17**, 430-438, 2006.
6. Flores G, Herraiz M, Ruiz del Castillo ML, Use of a superabsorbent polymer for the preconcentration of volatile components from complex matrices, *J Sep Sci*, **29**, 2677-2683, 2006.
7. Chen Y, Tang HL, Liu YF, Yu HP, Liu Y X, Tan HM, Study on preparation of the novel CMCTS-g-(PAA-co-PDMAAC) polyampholytic superabsorbent polymer (Chinese), *Ion Exc Adosopt*, **24**, 418-425, 2008.
8. Li CB, Hein S, Wang K, Biosorption of chitin and chitosan, *Mater Sci Technol*, **24**, 1088-1099, 2008.
9. Rinaudo M, Chitin and chitosan: properties and applications, *Prog Polym Sci*, **31**, 603-632, 2006.
10. Xu K, Wang JH, Xiang S, Chen Q, Yue YM, Su XF, Song CL, Wang PX, Polyampholytes superabsorbent nanocomposites with excellent gel strength, *Compos Sci Technol*, **67**, 3480-3486, 2007.

11. Mohan YM, Geckeler KE, Polyampholytic hydrogels: poly(*N*-isopropylacrylamide)-based stimuli-responsive networks with poly(ethyleneimine), *React Funct Polym*, **67**, 144-155, 2007.
12. Kim SJ, Park SJ, Kim SI, Synthesis and characteristics of interpenetrating polymer network hydrogels composed of poly(vinyl alcohol) and poly(*N*-isopropylacrylamide), *React Funct Polym*, **55**, 61-67, 2003.
13. Ostrowska-Czubenko J, Gierszewska-Druzynska M, Effect of ionic cross-linking on the water state in hydrogel chitosan membranes, *Carbohydr Polym*, **77**, 590-598, 2009.
14. Li JF, Lu JH, Li YM, Carboxymethylcellulose/bentonite composite gels: water sorption behavior and controlled release of herbicide, *J Appl Polym Sci*, **112**, 261-268, 2009.
15. Wang YJ, Tan GX, Zhang SJ, Guang YX, Influence of water states in hydrogels on the transmissibility and permeability of oxygen in contact lens materials, *Appl Surf Sci*, **255**, 604-606, 2008.
16. Ahmad MB, Huglin MB, DSC studies on states of water in cross-linked poly(methyl methacrylate-co-*N*-vinyl-2-pyrrolidone) hydrogels, *Polym Int*, **33**, 273-277, 1994.
17. Ahmad MB, O'Mahony JP, Huglin MB, Davis TP, Ricciardone AG, Application of dielectric spectroscopy and DSC to the study of relaxations in some copolymeric hydrogels, *J Appl Polym Sci*, **56**, 397-404, 1995.
18. Nakaoki T, Yamashita H, Bound states of water in poly(vinyl alcohol) hydrogel prepared by repeated freezing and melting method, *J Mol Struct*, **875**, 282-287, 2008.
19. Khurma JR, Nand AV, Temperature and pH sensitive hydrogels composed of chitosan and poly(ethylene glycol), *Polym Bull*, **59**, 805-812, 2008.
20. Khurma JR, Rohindra DR, Nand AV, Synthesis and properties of hydrogels based on chitosan and poly(vinyl alcohol) cross-linked by genipin, *J Macromol Sci Pure Appl Chem*, **43**, 749-758, 2006.
21. Capitani D, Crescenzi V, De Angelis AA, Segre AL, Water in hydrogels. An NMR study of water/polymer interactions in weakly cross-linked chitosan networks, *Macromolecules*, **34**, 4136-4144, 2001.
22. Imani M, Sharifi S, Mirzadeh H, Ziaee F, Monitoring of polyethylene glycol-diacrylate-based hydrogel formation by real time NMR spectroscopy, *Iran Polym J*, **16**, 13-20, 2007.
23. Jhon MS, Hattori S, Ma SM, Gregonis D, Andrade JD, The role of water in the osmotic and viscoelastic behavior of gel networks. In: *Hydrogels for Medical and Related Applications*, Andrade JD (Ed), *ACS Symp Ser*, **31**, Ch 4, 60-68, 1976.
24. Kyritsis A, Pissis P, Grammatikakis J, Dielectric relaxation spectroscopy in poly(hydroxyethyl acrylates)/water hydrogels, *J Polym Sci Pol Phys*, **33**, 1737-1750, 1995.
25. Lustig SR, Caruthers JM, Peppas NA, Dynamic mechanical properties of polymer-fluid systems. Characterization of poly(2-hydroxyethyl methacrylate) and poly(2-hydroxyethyl methacrylate-co-methyl methacrylate) hydrogels, *Polymer*, **32**, 3340-3353, 1991.
26. Wang CY, Yu BZ, Knudsen B, Harmon J, Moussy F, Moussy Y, Synthesis and performance of novel hydrogels coatings for implantable glucose sensors, *Biomacromolecules*, **9**, 561-567, 2008.
27. Onyari JM, Huang SJ, Synthesis and properties of novel polyvinyl alcohol-lactic acid gels, *J Appl Polym Sci*, **113**, 2053-2061, 2009.
28. Yamazaki Y, Matsunaga T, Ichinokawa A, Fujishiro Y, Saito E, Sato T, Analysis and evaluation of the ionic interaction of the novel soft contact lenses using the zwitterionic polymer gel, *J Appl Polym Sci*, **114**, 2764-2768, 2009.
29. Yoshida H, Hatakeyama T, Hatakeyama H, Characterization of water in polysaccharide hydrogels by DSC, *J Therm Anal Calorim*, **40**, 483-489, 1993.
30. Qu X, Wirsén A, Albertsson AC, Novel pH-sensitive chitosan hydrogels: swelling behavior and states of water, *Polymer*, **41**, 4589-4598, 2000.
31. Chen Y, Tan HM, Cross-linked carboxymethylchitosan-g-poly(acrylic acid) copolymer as a novel superabsorbent polymer, *Carbohydr Res*, **341**, 887-896, 2006.
32. Huang RH, Chen GH, Sun MK, Gao CJ, A novel

- composite nanofiltration (NF) membrane prepared from graft copolymer of trimethylallyl ammonium chloride onto chitosan (GCTACC)/ poly(acrylonitrile) (PAN) by epichlorohydrin cross-linking, *Carbohydr Res*, **341**, 2777-2784, 2006.
33. Wang CY, Yu BZ, Knudsen B, Harmon JL, Moussy F, Moussy Y, Synthesis and performance of novel hydrogels coatings for implantable glucose sensors, *Biomacromolecules*, **9**, 561-567, 2008.
34. Goda T, Watanabe JJ, Takai M, Ishihara K, Water structure and improved mechanical properties of phospholipid polymer hydrogel with phosphorylcholine centered intermolecular cross-linker, *Polymer*, **47**, 1390-1396, 2006.
35. Carena M, Cojazzi G, Bracci B, Lendinara L, Vitali L, Zinani M, Yoshida M, Katakai R, Takacs E, Higa OZ, Martellini F, The state of water in thermoresponsive poly(acryloyl-L-proline methyl ester) hydrogels observed by DSC and ¹H-NMR relaxometry, *Radiat Phys Chem*, **55**, 209-218, 1999.
36. Kim SJ, Lee CK, Lee YM, Kim IY, Kim SI, Electrical/pH-sensitive swelling behavior of polyelectrolyte hydrogels prepared with hyaluronic acid-poly(vinyl alcohol) interpenetrating polymer networks, *React Funct Polym*, **55**, 291-298, 2003.
37. McConville P, Pope JM, A comparison of water binding and mobility in contact lens hydrogels from NMR measurements of the water self-diffusion coefficient, *Polymer*, **41**, 9081-9088, 2000.
38. Li XM, Cui YD, Xiao JL, Liao LW, Hydrogel-hydrogel composites: the interfacial structure and interaction between water and polymer chains, *J Appl Polym Sci*, **108**, 3713-3719, 2008.
39. Lang YY, Jiang TY, Li SM, Zheng LY, Study on physicochemical properties of thermosensitive hydrogels constructed using graft-copolymers of poly(*N*-isopropylacrylamide) and guar gum, *J Appl Polym Sci*, **108**, 3473-3479, 2008.
40. Bhardwaj YK, Kumar V, Sabharwal S, Swelling behavior of radiation-polymerized polyampholytic two-component gels: dynamic and equilibrium swelling kinetics, *J Appl Polym Sci*, **88**, 730-742, 2003.