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Crosslinked carboxymethylchitosan-g-poly(acrylic acid) copolymer as a novel superabsorbent polymer

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Abstract—A novel carboxymethylchitosan-g-poly(acrylic acid) (CMCTS-g-PAA) superabsorbent polymer was prepared through graft polymerization of acrylic acid onto the chain of carboxymethylchitosan and subsequent crosslinking. It was demonstrated by FTIR spectroscopy that acrylic acid had been graft polymerized with carboxymethylchitosan. The thermal stability of the polymer was characterized by thermogravimetric analysis. By studying the swelling ratio of the polymer synthesized under different conditions, optimization conditions were found for a polymer with the highest swelling ratio. The rate of water absorption of the polymer was high, and the swelling of the polymer fitted the process of first dynamics. The swelling ratio of the polymer was pH-dependent.

Keywords: Carboxymethylchitosan; Superabsorbent polymer; Swelling ratio

1. Introduction

Superabsorbent polymers have a network structure and suitable degree of crosslinking.[1] Such a polymer is able to absorb much more water than its mass, ranging from hundreds to thousands of times. These polymers have been extensively applied as sorbents in such personal-care products, as infant diapers, feminine hygiene products, and incontinence products. These polymers also attract attention for a variety of more-specialized applications, including matrices for enzyme immobilization, biosorbents in preparative chromatography, materials for agricultural mulches, and matrices for controlled-release devices.[2,3]

Extensive attention[4–7] has been directed toward superabsorbent polymers prepared through graft copolymerization of vinyl monomers onto the chain of such natural polymers as cellulose and starch. Chitin is another important natural polymer. Chitosan is N-deacetylated chitin, and is the only basic polysaccharide in nature. The abundant hydroxyl and amino groups distributed on its chain, allow chitosan to be modified via chemical reactions, graft copolymerization constituting one such modification for chitosan.[8–10] Introduction of macromolecular-branched chains affords various derivatives for enhanced applications for chitosan. After the vinyl monomers are graft polymerized with chitosan and properly crosslinked, superabsorbent polymers can be prepared. The excellent biocompatibility and antibacterial properties of chitosan suggest that superabsorbent polymers prepared from it would have application prospects,[11] as medical materials, sanitary materials, controlled-release devices, and matrices for enzyme immobilization. However, there are few reports on this aspect, mainly because the water solubility of chitosan is very low and the modification processes involved as complicated. Carboxymethylchitosan, an important derivant of chitosan, is water soluble and its biocompatibility is very good.[12] Preparation of a superabsorbent polymer from carboxymethylchitosan has not yet been reported. Here we describe, a novel superabsorbent

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polymer prepared through graft polymerization of acrylic acid onto the chain of carboxymethylchitosan and subsequently crosslinking.

The water absorbency of a superabsorbent polymer is greatly influenced by its composition, molecular weight, degree of crosslinking, the molecular conformation of the polymer, and also by the properties of liquids to be absorbed. In the present paper, the influence of the conditions for synthesis on the water absorbency of the superabsorbent polymer was examined and the optimized conditions for a synthetic polymer with the highest swelling ratio were found. The influence of pH of the solution on the swelling properties of the polymer was also studied.

2. Results and discussion

2.1. Preparation of the CMCTS-g-PAA superabsorbent polymer

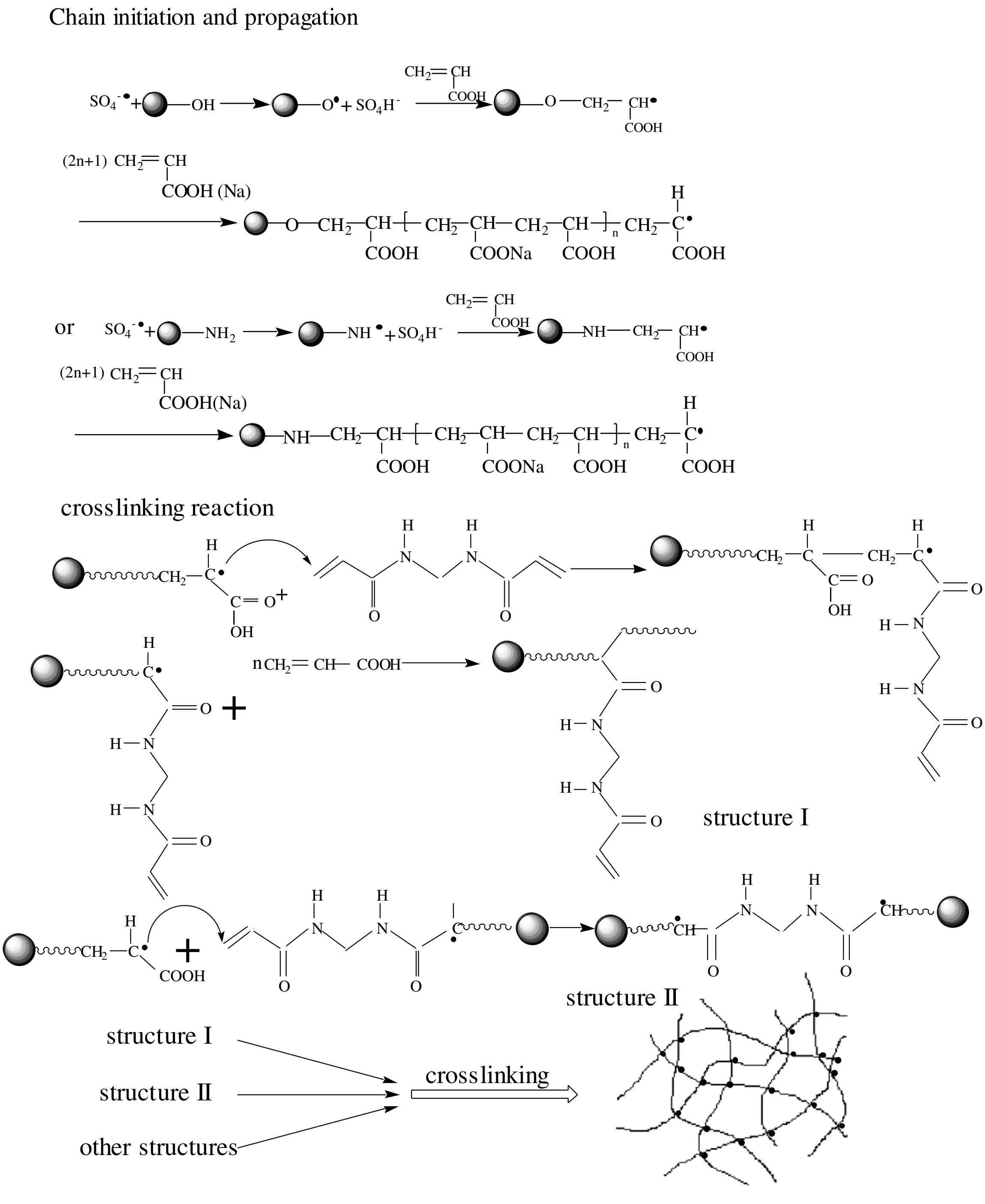
Synthesis of the CMCTS-g-PAA superabsorbent polymer includes three steps, namely chain initiation, chain propagation, and crosslinking, as described in Scheme 1. Peroxysulfate ion serves as a thermally dissociated initiator; it is readily dissociated to $SO_4^{-\bullet}$ and then the radicals abstract hydrogen from the amino and hydroxyl groups in the polysaccharide chain, affording macroradicals.[13] After the processes of chain propagation and crosslinking, the superabsorbent polymer is obtained.

It has been found by Hsu et al.[14,15] that as peroxysulfate ion is added to the chitosan solution, the viscosity decreases greatly. It is considered that the ammonium peroxysulfate (APS) free radicals attack at the C-1 or C-4 atoms of the pyranose rings and then cause breakage of the adjacent C–O–C glycosidic bonds in the main chain, creating free radicals at the chain ends. The process is shown in Scheme 2. As a result, when APS was used as an initiator, a block copolymer is also produced at the same time as acrylic acid is added to the solution of carboxymethylchitosan. The prepared superabsorbent polymer is thus a mixture of the graft copolymer of CMCTS and the block copolymer of CMCTS segments with poly(acrylic acid).

2.1.1. FTIR spectroscopy. The structural difference between chitosan and carboxymethylchitosan was confirmed by FTIR spectroscopy. In the spectrum of carboxymethylchitosan, the absorption peak at 1620 cm^{-1} is attributed to the asymmetric extension vibration of $–COO^-$, which coincided with the extension vibration of C=O of the amide I band at 1660 cm^{-1}, and a wide peak results. The strength of the peak at 1450 cm^{-1} contributed to the symmetrical extension vibration of $–COO^-$, and the peak at 1308 cm^{-1} assigned to the extension vibration of C–O is greatly increased. As compared with the spectrum of chitosan, the absorption peak at 1323 cm^{-1} should contribute to the stretching and bending vibrations of the C–N bond of the amide III band, and the intensity was notably increased after the reaction. The strength of the absorption peak at 898 cm^{-1}, assigned to the out-of-plane bending vibration of N–H of the primary amino group was decreased and moved to 873 cm^{-1}. All of these results demonstrated that a hydrogen atom of the $–NH_2$ group had been substituted by carboxymethyl groups. The absorption peaks of CMCTS at 1156 and 1071 cm^{-1} demonstrated the existence of a C–O–C bond, which confirmed that the hydroxyl groups of the chitosan were also substituted by the carboxymethyl group, indicating that an *N*,*O*-carboxymethylchitosan had been prepared.

After carboxymethylchitosan had been graft polymerized with acrylic acid, an absorption peak at 1720 cm^{-1} contributing to the C=O stretching vibration appeared and was overlapped by a wide peak around 1660 cm^{-1} attributed to carboxymethylchitosan as already mentioned, the intensity of the peak was strong. The absorption peak at 1586 cm^{-1} attributed to the bending vibration of the N–H bond of amide II band was overlapped by the peak at 1600 cm^{-1} assigned to the asymmetric extension vibration of $–COO^-$, and the intensity of the peak was greatly increased. The intensity of the peak at 1454 cm^{-1} contributed to the symmetrical $–COO^-$ stretching vibration, and the peak at 1290 cm^{-1} assigned to the extension vibration of C–O was greatly increased. The absorption peak at 2920 cm^{-1} contributing to the C–H stretching vibration of carboxymethylchitosan was moved to 2950 cm^{-1} and its intensity was greatly increased, as a result of the introduction of the long carbon chain; A strong absorption peak at 793 cm^{-1} attributed to the planar rocking vibration of C–H of the long carbon chain appeared, it coincided with the out-of-plane bending vibration of O–H at 901 cm^{-1} and the out-of-plane bending vibration of N–H at 873 cm^{-1}, the intensity was greatly increased. It is clear from the spectra that the CMCTS-g-PAA superabsorbent polymer had both characteristic peaks of PAA and the saccharide unit of carboxymethylchitosan, providing evidence of graft polymerization (Fig. 1).

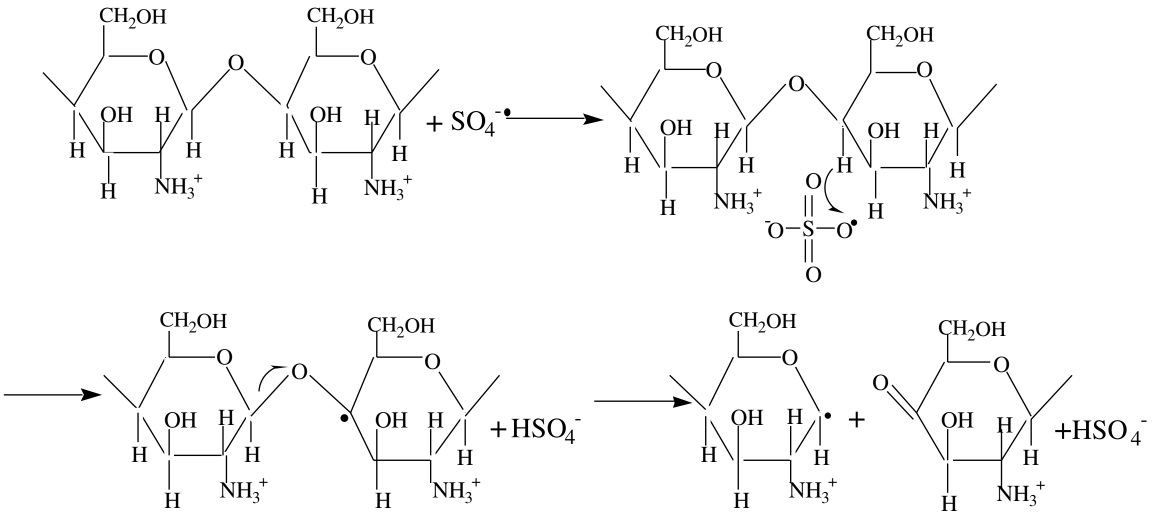
2.1.2. Thermal stability analysis. The thermal properties of carboxymethylchitosan, PAA, and CMCTS-g-PAA superabsorbent polymer were examined by thermogravimetric analysis (TGA). As shown in Figure 2 and Table 1, the weight loss of CMCTS in the range 221–361 °C is associated with a complex process, including dehydration of the saccharide rings and breaking of the C–O–C glycosidic bonds in the main chain of the polysaccharide.[16] The decomposition rate reached a maximum at 293 °C. The thermal decomposition process of PAA was divided into two steps, the first corresponding to decomposition of the carboxyl groups



Scheme 1. Synthesis of CMCTS-g-PAA superabsorbent polymer.

of PAA,[17,18] and the second step is attributed to the breakage of the chains of PAA.[18] The decomposition curves of two kinds of CMCTS-g-PAA superabsorbent polymer were divided into three steps. The first corresponded to the thermal degradation of CMCTS; the second step due to decomposition of the carboxyl groups of the PAA chain; and the third step was associated with breakage of PAA chain.

The following conclusions could be drawn from the experimental data: the total percentage weight loss of CMCTS-g-PAA superabsorbent polymer was higher than that of carboxymethylchitosan and PAA; for the superabsorbent polymer, the initial decomposition temperature and the temperature at the maximum decomposition rate of each step were obviously lower than that corresponding to carboxymethylchitosan and



Scheme 2. Mechanism of degradation of chitosan by ammonium peroxysulfate free radicals.

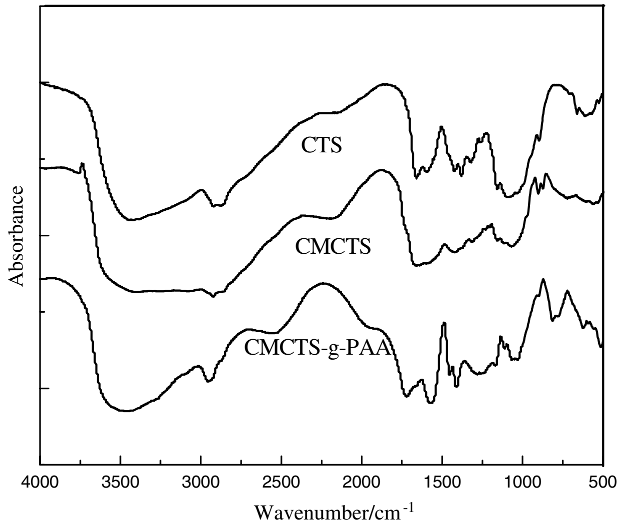


Figure 1. The FTIR spectra of CTS, CMCTS, and CMCTS-g-PAA superabsorbent polymers.

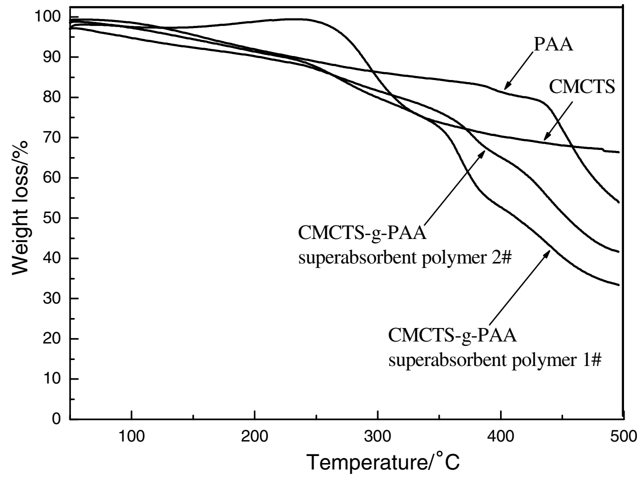


Figure 2. The TGA curves of PAA, CMCTS, and CMCTS-g-PAA superabsorbent polymers.

PAA; the temperatures for 5% and 10% weight loss for two kinds of superabsorbent polymer were distinctly lower than those corresponding to carboxymethylchitosan and PAA. All of these result demonstrate that the thermal stability of the CMCTS-g-PAA superabsorbent polymer was lower than that of carboxymethylchitosan and PAA.

2.2. Effect of synthesis conditions on the water absorbency of the superabsorbent polymers

The structures of the superabsorbent polymers and their water-absorption property are strongly affected by the conditions of synthesis.[19,20] The relationship between the swelling ratio and network structure can be described by the following Flory equation:[21]

$$q_m^{5/3} \cong [(i/2v_u S^{*1/2})^2 + (1/2 - \chi_1)/v_1]/(v_e/V_0) \qquad (1)$$

where q_m is the swelling ratio; i/v_u is the concentration of the fixed charges of the unswollen network; S^* is the ionic strength of the swollen solution; v_e/V_0 is the crosslinking density, which refers to the number of effective crosslinked chains in the unit volume. The term $(1/2 - \chi_1)/v_1$ stands for the network-medium affinity.

The influence of the conditions of synthesis on the water-absorption properties of superabsorbent polymers was studied according to Eq. 1.

2.2.1. Effect of crosslinking agent.

To find out the effect of the amount of crosslinking agent on the water absorbency of the polymer, graft polymerization was carried out at various mass ratio of *N*,*N*′-methylenediacrylamide (MBAM) to acrylic acid (AA) by keeping other

Table 1. Thermal decomposition data of CMCTS, PAA, and CMCTS-g-PAA superabsorbent polymer

Sample	Step of decomposition	Temperature range (°C)	$T_{\max}$[a] (°C)	Weight loss (%)	Total weight loss (%)	$T_{5\%}$[b] (°C)	$T_{10\%}$[c] (°C)
CMCTS	1	221–361	293	26.41	26.41	273.69	287.75
Superabsorbent 1#	1	223–308	268	11.10	54.58	141.69	223.88
	2	324–398	369	23.78			
	3	398–496	446	19.70			
Superabsorbent 2#	1	228–319	269	8.81	46.93	97.44	205.23
	2	319–403	378	15.23			
	3	403–495	440	22.89			
PAA	1	374–417	393	3.39	31.75	156.85	230.49
	2	417–493	447	25.70			

[a] Temperature at the maximum weight loss rate in the range.

[b] Temperature at weight loss = 5%.

[c] Temperature at weight loss = 10%.

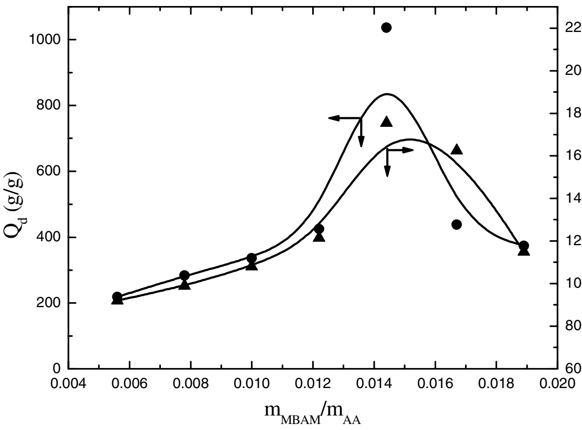


Figure 3. Effect of $m_{\text{MBAN}}/m_{\text{AA}}$ on the swelling ratio of the superabsorbent polymer. Reaction conditions: $m_{\text{APS}}/m_{\text{AA}}$, 0.04; $m_{\text{AA}}/m_{\text{CMCTS}}$, 6.0; time, 5 h; temperature, 60 °C; neutralization degree, 50%; water volume, 150 mL.

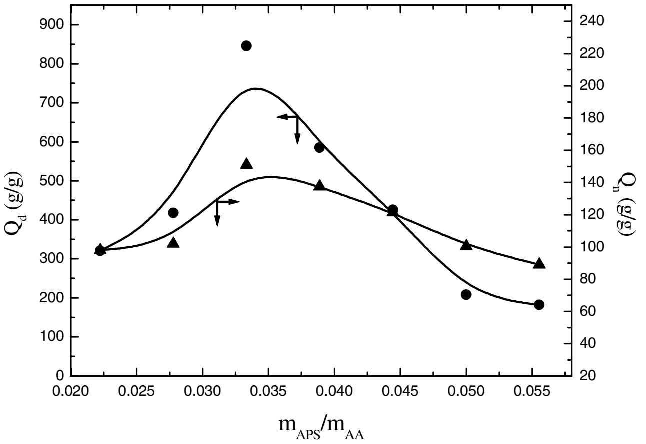


Figure 4. Effect of $m_{\text{APS}}/m_{\text{AA}}$ on the swelling ratio of the superabsorbent polymer. Reaction conditions: $m_{\text{MBAM}}/m_{\text{AA}}$, 0.012; $m_{\text{AA}}/m_{\text{CMCTS}}$, 6.0; time, 5 h; temperature, 60 °C; neutralization degree, 50%; water volume, 150 mL.

reaction conditions constant. As shown in Figure 3, when the amount of the crosslinking agent was small, the swelling ratio of the polymer was low, as the low crosslinking density is unable to maintain the absorbed water when measuring the swelling ratio by the filtration method. As increase of the amount of MBAM gradually enhanced the water absorbency of the polymer. When the mass ratio was around 0.014, the swelling ratio reached its maximum value. If the amount of the crosslinking agent was increased further, the water absorbency decreased. It is considered that the molecular weight between the crosslinking points was so low that stretching of the polymer chains was inhibited. It may also been seen from Eq. 1 that if v_e/V_0 is high, the q_m is decreased.

2.2.2. Effect of initiator.

Figure 4 shows the influence of $m_{\text{APS}}/m_{\text{AA}}$ on the swelling ratio of the polymer. The swelling ratio was changed upon increasing $m_{\text{APS}}/m_{\text{AA}}$ from 0.01 to 0.03. As the APS content increased, a large amount of radicals was produced, which in turn created more macroradicals in the main chain of CMCTS and the average kinetic chain length (v_e) of PAA becomes shorter. According to Eq. 1, as v_e, decreases the swelling capacity of the hydrogel increases. However, if the mass ratio is increased further, the water absorbency is decreased. This was attributed to the fact that more radicals would enhance the terminating step via bimolecular collision, and the molecular weights of the branched chains are thus decreased.[22] The available free volumes within the hydrogel are then reduced. When $m_{\text{APS}}/m_{\text{AA}}$ was around 0.02, the water absorbency of the polymer reached its highest value.

2.2.3. Effect of monomer concentration.

When $m_{\text{AA}}/m_{\text{CMCTS}}$ is less than 7.3, the swelling ratio of the polymer was raised with increase of the mass ratio. The higher monomer concentration would cause more AA molecules to be grafted onto the backbone of CMCTS. This

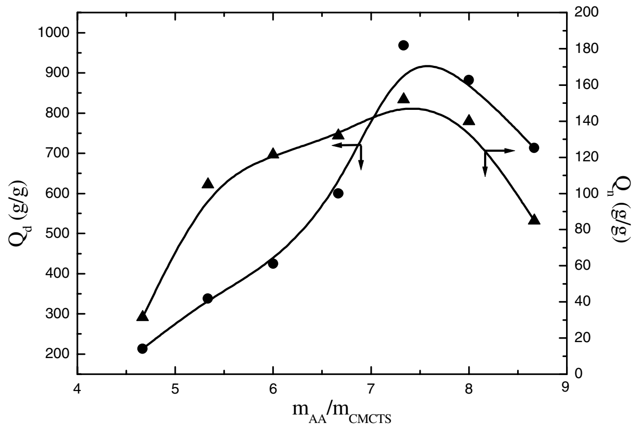


Figure 5. Effect of m_{AA}/m_{CMCTS} on the swelling ratio of the superabsorbent polymer. Reaction conditions: m_{APS}/m_{AA}, 0.04; m_{MBAM}/m_{AA}, 0.012; time, 5 h; temperature, 60 °C; neutralization degree, 50%; water volume, 150 mL.

increased the hydrophilicity in the hydrogel and consequently caused an increase in water absorbency. However, the swelling ratio was decreased if the mass ratio was increased above 7.3. There were many reason for this. As the concentration of AA increases, the viscosity of the system increases and the movement of the radicals and monomers is hindered. On the other hand, as the degree of crosslinking of the polymer is raised by entanglement of the PAA chains when its molecular weight is too high, the expansion of the networks is restricted. The effects of all of these reasons, is to decrease the swelling ratio of the polymer. The swelling ratio reached the maximum value when m_{AA}/m_{CMCTS} was around 7.3 (Fig. 5).

2.2.4. Effect of reaction temperature.

The swelling ratio of the polymer is also greatly influenced by the reaction temperature, as shown in Figure 6. When the temperature was lower than 50 °C, the swelling ratio increased with rise of the reaction temperature. However, the water absorbency decreased if the reaction temperature was increased further. Since APS is a thermal initiator, its dissociation efficiency is high at high temperature, and graft copolymerization is enhanced. In addition, the rate of diffusion of AA to the macroradicals is increased at higher temperature. This in turn resulted in a higher degree of graft polymerization and consequently higher water absorbency of the polymer produced. When the reaction temperature was too high, the rates of termination and chain transfer reaction are so fast that the absorbency is decreased instead. The swelling ratio of the polymer reached its maximum value when the reaction was carried at 50 °C.

2.2.5. Effect of reaction time.

By changing the reaction time from 3 to 8 h and keeping other reaction conditions constant, the influence of reaction time on the water absorbency is shown in Figure 7. The water absorbency of the polymer is first increased by extending the reaction time up to a maximum at about 6 h, but is decreased by further extension of the reaction time. When the time was too short, the polymerization and the crosslinking reactions are incomplete and the water absorbency is low. The swelling ratio is enhanced by prolonging the reaction time. However, when the reaction time was too long, the PAA chains become entangled, restricting expansion of the network, and the swelling ratio of the polymer is decreased.

2.2.6. Effect of the degree of neutralization of acrylic acid.

Figure 8 shows that when the degree of neutralization of acrylic acid was around 30%, the water absorbency of the polymer reached a maximum value. At lower degree of neutralization, the dissociation of AA is very weak and i/v_u in Eq. 1 is low. Consequently the

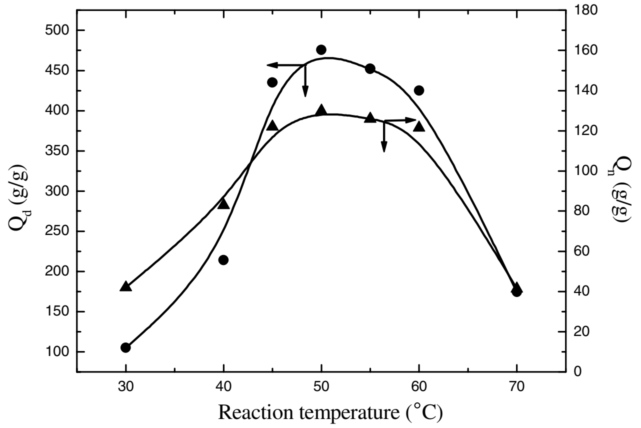


Figure 6. Effect of reaction temperature on the swelling ratio of the superabsorbent polymer. Reaction conditions: m_{APS}/m_{AA}, 0.04; m_{MBAM}/m_{AA}, 0.012; m_{AA}/m_{CMCTS}, 6.0; time, 5 h; neutralization degree, 50%; water volume, 150 mL.

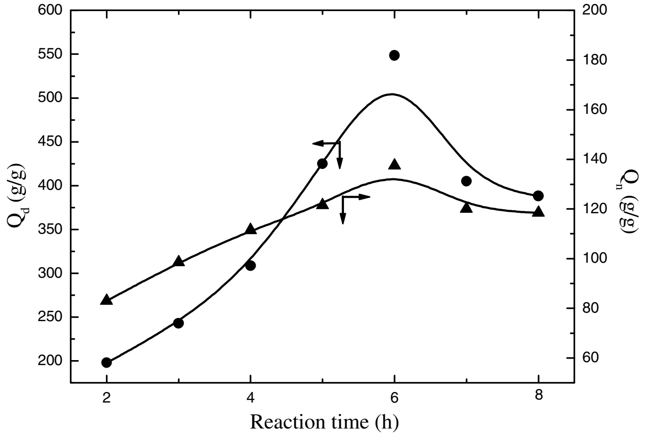


Figure 7. Effect of reaction time on the swelling ratio of the superabsorbent polymer. Reaction conditions: m_{APS}/m_{AA}, 0.04; m_{MBAM}/m_{AA}, 0.012; m_{AA}/m_{CMCTS}, 6.0; temperature, 60 °C; neutralization degree, 50%; water volume, 150 mL.

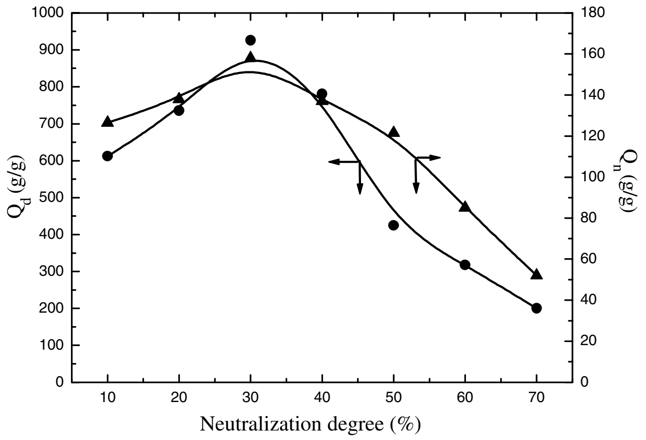


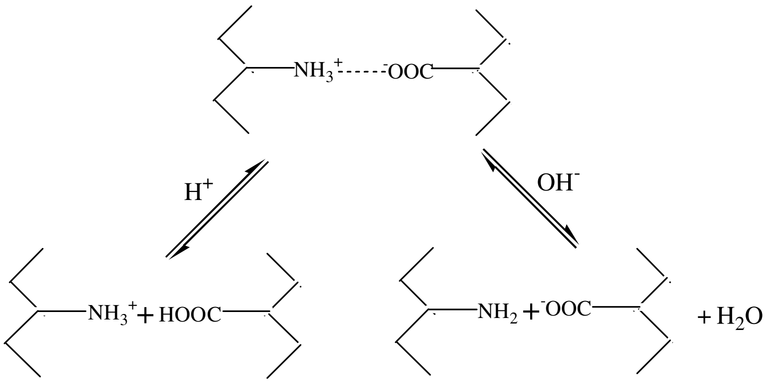
Figure 8. Effect of neutralization degree on the swelling ratio of the superabsorbent polymer. Reaction conditions: m_{APS}/m_{AA}, 0.04; m_{MBAM}/m_{AA}, 0.012; m_{AA}/m_{CMCTS}, 6.0; temperature, 60 °C; time, 5 h; water volume, 150 mL.

anion–anion repulsive forces are eliminated and the water absorbency of the polymer is thus decreased. If the degree of neutralization is increased, the content of $-CO_2Na$ groups is increased and the difference in osmotic pressure between the inside and outside of the network is increased and the swelling ratio of the polymer is enhanced. However at a higher neutralization degree of AA, reduced swelling is observed, because of various reasons. The charge-screening effect of excess Na^+ ions, shield the carboxylate anions on the chains of PAA and inhibit effective anion–anion repulsive forces. Furthermore, with increase of the NaOH concentration, the ionic strength of the swollen solution [S^* in Eq. 1] is increased. As a result, the osmotic pressure of the gel phases is reduced and the swelling ratio is consequently decreased.

Furthermore, the electrostatic attraction between the anionic carboxylate groups of PAA, the carboxymethylchitosan, and the residual cationic ammonium groups of CMCTS must be considered. Interaction between anions and cations is able to form a polyelectrolyte complex (PEC). Wu[23] and Li[24] have described the PEC formed by chitosan and poly(acrylic acid). When the degree of neutralization of acrylic acid is low, the ionization of $-CO_2H$ groups is very weak and the amino groups of the chitosan exist mainly in the $-NH_3^+$ form. The repulsive force between cations is so strong that the crosslinking structures caused by anion–cation charge attraction is broken down. The degree of crosslinking of the hydrogel is decreased and the measured water absorbency is low. On the other hand, if the degree of neutralization is high, the amino groups of the chitosan exist mainly in the $-NH_2$ form and the carboxyl groups are almost completely dissociated. The interaction between them is not very strong. The interaction between the anionic carboxylate and the cationic ammonium group is shown in Scheme 3.

2.2.7. Effect of the water volume of the system. Accompanying an increase of the water volume of the reaction system, the concentrations of the crosslinking agent, the initiator, and the monomer are decreased and the rates of polymerization and crosslinking are decreased, and the water absorbency of the polymer is decreased. However, when the water content of the system is low, the viscosity of the system becomes so high that the movement of free radicals and the monomers is hindered. The water absorbency of the polymer is low. As shown in Figure 9, the swelling ratio of the polymer reached a maximum value when the water volume of the system was around 125 mL.

2.2.8. Optimized synthetic conditions for a polymer with highest swelling ratio. By studies under different conditions, it was found that optimum synthetic conditions for a polymer with the highest swelling ratio are as follows: m_{AA}/m_{CMCTS} is around 7.3, the mass ratio of the initiator and the crosslinking reagent to acrylic acid are 0.02 and 0.014, respectively, the reaction time is 6 h and the reaction temperature is 50 °C, the degree of neutralization of the acrylic acid is around 30% and the water volume of the system is 125 mL. The polymer



Scheme 3. Interaction between anionic carboxylate and the cationic ammonium groups.

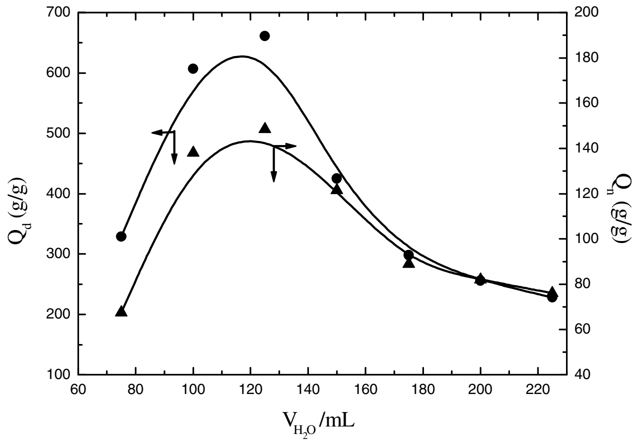


Figure 9. Effect of the water volume of the system on the swelling ratio of the superabsorbent polymer. Reaction conditions: $m_{\mathrm{APS}}/m_{\mathrm{AA}}$, 0.04; $m_{\mathrm{MBAM}}/m_{\mathrm{AA}}$, 0.012; $m_{\mathrm{AA}}/m_{\mathrm{CMCTS}}$, 6.0; temperature, 60 °C; time, 5 h; neutralization degree, 50%.

synthesized under these conditions is able to absorb over 1180 g/g of distilled water, over 162 g/g normal saline, over 116 g/g artificial blood, and over 108 g/g artificial urine.

2.3. Swelling properties of the superabsorbent polymer

2.3.1. Rate of swelling of the polymer. A preliminary study was conducted on the swelling kinetic of the CMCTS-g-PAA superabsorbent polymers. The dots in Figure 10 demonstrate the relationship between time and swelling ratio of three kinds of superabsorbent polymer synthesized under different conditions. The rate of swelling sharply increased initially, and equilibrium swelling could be achieved in 20 min for all of the polymers. The absorption rate of the polymers was thus very fast.

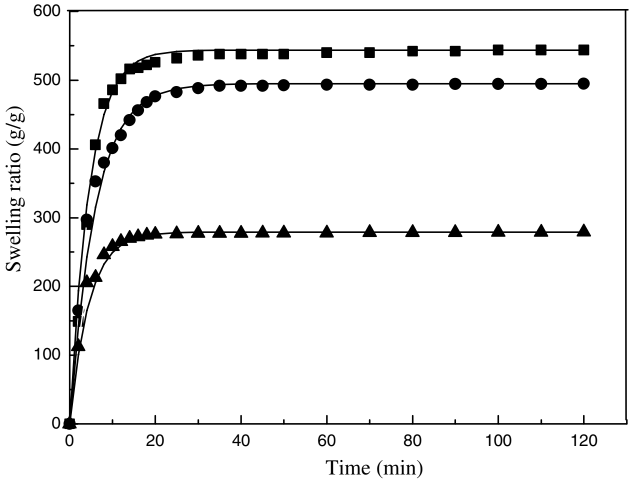


Figure 10. The curve of water-absorption rate before and after modification.

Assuming that the swelling of the polymers fits the process of first dynamics,[25] the swelling rate at a certain temperature is as follows:

$$dQ_t/dt = k(Q_e - Q_t) \tag{2}$$

where t is the swelling time; Q_t is the swelling ratio at the corresponding time; Q_e is the equilibrium swelling ratio.

Integration of Eq. 2

$$\int_{Q_0}^{Q_t} dQ_t/(Q_e - Q_t) = \int_0^t k\,dt \tag{3}$$

The result is

$$\ln[(Q_e - Q_0)/(Q_e - Q_t)] = kt \tag{4}$$

and the following equation is obtained:

$$Q_t = Q_e - (Q_e - Q_0)/e^{kt} \tag{5}$$

The curve between $\ln[(Q_e - Q_0)/(Q_e - Q_t)]$ and t was drawn and the value of slope k could be determined. This was introduced into Eq. 5 and the theoretical swelling curves of the polymers could be drawn (as the solid line in Fig. 10). It may be seen from the figure that the theoretical calculation and experimental results coincide very well, and so the hypothesis is reasonable. The swelling processes of all the polymers fits the processes of the first dynamics.

2.3.2. Effect of pH on the swelling properties. The equilibrium swelling of the CMCTS-g-PAA superabsorbent polymer was investigated at various pH values between 2.0 and 12.0. As the water absorbency of the superabsorbent polymer was greatly affected by the ionic strength of the solution, no additional ions (through use of a buffer solution) were introduced into the medium for setting pH, and stock NaOH and HCl solutions were diluted with distilled water to the desired basic and acidic pH values.

Figure 11 shows the swelling properties of the polymers at different pH values. Under acidic conditions, the swelling behavior was controlled mainly by the $-NH_2$ and $-NH-R$ groups at C-2 of carboxymethylchitosan. As the basic amine groups are readily protonated, the charge density on the polymer chains is increased and the osmotic pressure inside the network is enhanced by electrostatic repulsion between the NH_3^+ groups. The difference of osmotic pressure between the inside and outside of the network is balanced by the swelling of the polymer, and the swelling ratio was higher around pH 4. However, under conditions of high acidity (pH <4), the charge of the ammonium cations is shielded by the screening effect of the Cl^-, counter ions, and efficient repulsion is prevented. Thus a notable decrease in equilibrium swelling is observed. At the pH range of 5–6, most of the basic and acid groups exist in nonionized form, and so hydrogen bonding between amino and carboxylic acid groups can occur, leading to cross-

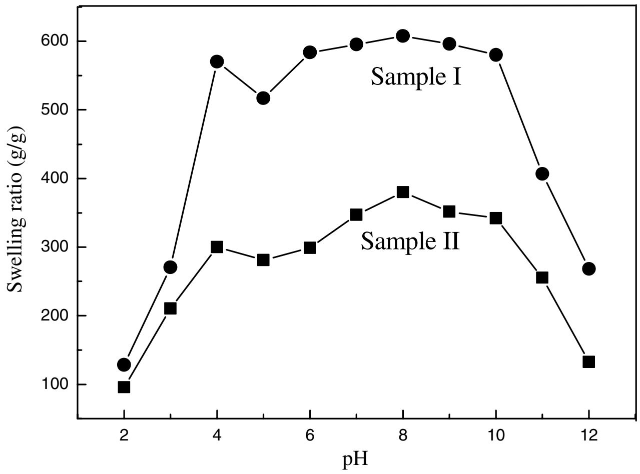


Figure 11. Effect of pH of the solution on the water swelling ratio of the superabsorbent polymers.

linking, and the swelling ratio is decreased. At higher pH values, the carboxylic acid groups become ionized, and electrostatic repulsion force between the $-CO_2^-$ anions increases the swelling ratio. However, the screening effect of the counterions (Na^+) limits the swelling at pH 9–10 and opposes the swelling at pH >11, so that the network is totally collapsed at pH 12. A similar observation was recently reported for saponified chitosan-g-polyacrylonitrile hydrogels[26] and chitosan-g-poly(acrylic acid-co-acrylamide) hydrogels.[27] In this system, a combination of attractive or repulsive electrostatic interactions and hydrogen bonding has been recognized as the main reason for the existence of several phases observed at various environmental conditions.

3. Experimental

3.1. Materials

Chitosan (CTS) was supplied by Zhejiang Yuhuan Biochemical Co., Ltd. (China), its degree of deacetylation was 76%. Acrylic acid (AA, AR grade) was purchased from Tianjin Chemical Reagent Graduate School (China) and purified by distillation under reduced pressure before polymerization. Ammonium peroxysulfate (APS, AR grade) was used as the initiator. *N*,*N*′-Methylenediacrylamide (MBAM, AR grade) was used as the crosslinking agent. Isopropyl alcohol, chloroacetic acid, ethyl alcohol, and sodium hydroxide were analytical-grade reagents and were used as supplied.

3.2. Preparation of carboxymethylchitosan

Chitosan (10 g) was added at room temperature to an aqueous solution of NaOH (38 g); with the mass concentration was 40%. To the solution, in a three-necked flask equipped with a stirrer and reflux condenser were added isopropyl alcohol (100 mL) and chloroacetic acid (17 g). After reaction at 65 °C for 4 h, the mixture was filtered and the solid product washed with 80% aqueous alcohol (mass concentration) to neutrality and then dried under vacuum. The degree of substitution of the carboxymethylchitosan was 0.635, as estimated by potentiometric titration.[28]

3.3. Preparation of the CMCTS-g-PAA superabsorbent polymer

Carboxymethylchitosan (1.5 g) was dissolved in a certain volume of water and introduced into a three-necked flask was equipped with a stirrer and reflux condenser. The solution was stirred for 30 min under high-purity nitrogen and heated with a water bath. A certain amount of APS dissolved in deionized water was then added slowly to initiate the graft polymerization. The desired quantities of MBAM and acrylic acid made neutral to extent degree by NaOH were added 30 min later. The total volume of the water in the system was controlled to a certain value and the rate of stirring was fixed. After the desired time, air was let into the reactor to cool it down and stop the reaction. The product was precipitated by pouring alcohol into the reaction mixture. The precipitate was filtered off, washed thoroughly by an alcohol–water mixture for several times with high-speed stirring. Then it was soaked with 4:1 (v/v) alcohol–water for 24 h, filtered off, and dried under vacuum at 60 °C.

3.4. FTIR spectroscopy

The samples were prepared into the form of KBr pellets and their FTIR spectra (NEXUS-470 series, Nicolet Co., USA) were obtained.

3.5. Thermal property analysis

Thermogravimetric analysis (TGA) of the samples was made using a TA-2000 thermogravimetric analyzer (Dupont Co., USA) at a heating rate of 15 °C/min with nitrogen as purge gas.

3.6. Test of water-absorption capability

Superabsorbent polymer (0.1000 g) was put into a sieve pouch, which was immersed in distilled water for swelling, and then taken out from the water at a certain time interval. The excess water was removed by absorption on filter paper. The weight of the swollen polymer was then measured by subtracting the weight of the wet pouch from the total weight. The swelling ratio (Q, g/g) is defined as

$$Q = (m_2 - m_1)/m_1$$

where m_1 is the weight of the dried superabsorbent polymer and m_2 is the weight of the swollen superabsorbent polymer.

To compare the water-absorption properties of the products prepared under different conditions, the polymers were swollen in distilled water or normal saline for 12 h to ensure that the equilibrium swelling ratio had been reached, and the swelling ratios Q_d and Q_n were calculated, respectively.

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