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Study of carboxymethyl chitosan based polyampholyte superabsorbent polymer I Optimization of synthesis conditions and pH sensitive property study of carboxymethyl chitosan-g-poly(acrylic acid-co-dimethyldiallylammonium chloride) superabsorbent polymer

Chen Yu*, Liu Yun-fei, Tang Huan-lin, Tan Hui-min

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

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ABSTRACT

A novel polyampholyte superabsorbent polymer-carboxymethyl chitosan-g-poly(acrylic acid-co-dimethyldiallylammonium chloride) (CMCTS-g-(PAA-co-PDMDAAC)) has been prepared through the graft copolymerization of acrylic acid (AA) and dimethyldiallylammonium chloride (DMDAAC) onto the chain of carboxymethyl chitosan. The optimal conditions for synthesizing the polymer with the highest swelling ratio has been identified by studying the water absorption of the polymer prepared under different conditions. The swelling ratio of the prepared polyampholytic polymer was found to be pH dependent, and in particular, the prepared polymer showed peaks in swelling capacity at both acidic condition (pH 3.5) and basic condition (pH 9.5). The effects of the interactions between the charged groups on the polymer backbone as well as the counter ion screening on the non-freezable water content have also been studied by measuring the DSC curve of the swollen hydrogel at different pH values.

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1. Introduction

Superabsorbent polymers are lightly crosslinked hydrophilic functional polymers (Zohuriaan-Mehr & Kabiri, 2008). Such polymers are able to absorb large quantities of water, ranging from hundreds to thousands of times of their mass. These polymers have been extensively applied as sorbents in personal-care products, including infant diapers, feminine hygiene products, and incontinence products (Liu, Zhang, & Zhu, 2008). Meanwhile, these polymers also attract the attention for a variety of more-specialized applications (Hua and Wang, 2009; Mudiyanselace and Neckers, 2008), such as matrices for enzyme immobilization, the biosorbents in preparative chromatography, as materials for agricultural mulches, and matrices for controlled release devices.

Chitosan is an important natural polymer exhibiting several favorable properties, including good biodegradability, biocompatibility, antibacterial property and low toxicity (Hein, Wang, Stevens, & Kjems, 2008; Prabaharan, 2008). However, the strong intermolecular and intramolecular hydrogen bonds between the hydroxyl groups as well as the amino groups along the chain backbone not only limit the water solubility of chitosan (Enescu & Olteanu, 2008) but also complicate the preparation of the superabsorbent polymer from chitosan. In recent years, our research group has prepared a series of superabsorbent polymers from the water soluble derivatives of chitosan (Chen & Tan, 2006; Chen, Liu, Tan, & Jiang, 2009; Yan, Chen, Liu, & Tan, 2008), such as carboxymethyl chitosan, hydroxyethyl chitosan, etc. Particularly, we found that the preparation routes can be significantly simplified by using this water soluble polysaccharide while the swelling ratio of the prepared polymers was reasonably high. However, because the copolymerizaiton monomers were usually the anionic acrylic acid as well as the non-ionic vinylpyrrolidone, acrylamide, etc., the prepared superabsorbent polymers were all polyanions.

On the other hand, many studies have been reported recently on the synthesis and characterization of synthetic polyampholyte superabsorbent polymers (Kakinoki et al., 2003; Xu et al., 2007). Polyampholyte superabsorbent polymers are crosslinked macromolecular networks containing both positively and negatively charged repeating units. Compared with traditional polyelectrolyte polymers that contain only one kind of charge, polyampholyte superabsorbent polymers can show very unusual properties (Mohan & Geckeler, 2007). For instance, the swelling capacity of polyampholyte superabsorbent polymers depends on a delicate balance between the attractive and repulsive ionic interactions as well as the solvent mediated effects. In addition, the counter ion dissociation and the presence of other small ions also play a crucial role in facilitating their absorption capacity (Anthony, Toyoichi, & Elazer, 1998; Xu et al., 2008). Particularly, the swelling and

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* Corresponding author. Tel.: +86 10 68912370.
E-mail address: cylsy@163.com (C. Yu).

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shrinking of the polyampholyte superabsorbent polymers exhibit unique pH dependant properties (Chen, Tian, & Du, 2004; Sutani, Kaetsu, Uchida, & Matsubara, 2002), being essentially different from those of traditional polyelectrolyte superabsorbent polymers. Polyampholyte superabsorbent polymers have shown widespread applications such as selective sorbents, drug delivery carriers, fertilizer coating, etc. The synthesis and study of polyampholyte superabsorbent polymers have drawn significant attentions.

In the present work, we report the preparation of a novel polyampholyte superabsorbent polymer by graft copolymerization of acrylic acid and dimethyldiallylammonium chloride onto the chain of the carboxymethyl chitosan. The swelling behaviors of the prepared polymer as well as its interactions with water have been studied at different pH levels. The results indicated that the prepared polymer showed unique swelling properties, and the applications of superabsorbent polymers can be expanded by combing the unique properties of chitosan and polyampholyte.

2. Experimental

2.1. Materials

Chitosan (CTS) was supplied by Zhejiang Yuhuan Biochemical CO. Ltd. (China) with a deacetylation degree 76%, as determined by the alkalimetry method, and an average molecular weight 1.05×10^6, as determined by the viscosity method. Carboxymethyl chitosan was synthesized in our lab according to a method reported in the literature (Chen & Tan, 2006). The substitution degree of the carboxymethyl was found to be 0.67 using elemental analysis.

Acrylic acid (AA, A.R.) was purchased from Tianjin Chemical Reagent Institute (China) and purified by reduced pressure distillation before the polymerization. Dimethyldiallylammonium chloride (DMDAAC, 60 wt.% aqueous solution) was supplied by Jiangsu Feixiang Chemical Co., Ltd. (China). Ammonium persulfate (APS, A.R.) and *N*,*N*′-methylene diacrylamide (MBAM, A.R.) were used as the initiator and the crosslinking agent, respectively. The alcohol, hydrochloric acid and sodium hydroxide were all analytical grade reagents and used as received.

2.2. Preparation of the novel superabsorbent polymer

Carboxymethyl chitosan (1.0 g) was first dissolved into 50 mL deionized water and then added into a three-necked flask equipped with a stirring apparatus and a reflux condenser. The resulting solution was stirred for 30 min under the protection of nitrogen and then heated in a water bath. The graft polymerization was initiated by slowly adding a certain amount of APS dispersed in 20 mL distilled water into the flask, then the suitable amounts of DMDAAC, MBAM and acrylic acid neutralized to a certain degree were dissolved into the total 80 mL distilled water and were added into the flak 30 min later. After a certain reaction period, the reactor was cooled down and the reaction was stopped. The product was then precipitated by pouring alcohol into the reaction mixture. The precipitate was filtered, washed thoroughly with the alcohol/water mixture (4:1, v/v) for several times under high-speed stirring, and then soaked with the alcohol/water mixture (4:1, v/v) for 24 h. The product was collected by filtration and dried under vacuum. Finally, the dried products were sieved and the particles of the sizes ranging from 150 μm to 250 μm were used for the water absorption test.

2.3. FTIR spectroscopy

FTIR spectrum was obtained on a NEXUS-470 series FTIR spectrometer (Nicolet Co., USA). KBr pellets of the samples were used.

2.4. SEM examination

The surface morphology of the carboxymethyl chitosan and the superabsorbent polymers were examined using a scanning electron microscope (SEM) (QUANTA 200 series, FEI Co., USA). The samples were coated with Au prior to the SEM examination.

2.5. Test of the water absorption capability

To test the water absorption capability, 0.100 g of the superabsorbent polymer was placed into a net. The net was then immersed into the distilled water to swell. After a suitable period, the sample was taken out of the water. After removing the excess water, the weight of the swollen polymer was measured. The swelling ratio (Q, g/g) is calculated by:

$$Q = \frac{m_2 - m_1}{m_1} \tag{1}$$

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

When comparing the water absorption capability of the polymers prepared at different conditions, the polymers were swollen in the distilled water or normal saline for 12 h and the swelling ratio Q_d and Q_n was calculated, respectively.

2.6. DSC characterization

The prepared superabsorbent polymers were first allowed to swell in the test solution until the swelling equilibrium was reached. Then, the samples were taken out form the solution and wiped with a filter paper to remove the excess surface water and sealed in the aluminum pans. The weight of swollen samples were normally in a range of 5–10 mg. To conduct DSC characterization, the samples were heated between −40 °C and 40 °C at a heating rate of 5 °C/min under a dynamic N_2 atmosphere in Perkin-Elmer DSC-7.

The equilibrium water content (W_{EWC}) is calculated by:

$$W_{EWC} = \frac{m_2 - m_1}{m_2} \times 100\% \tag{2}$$

In which m_1 and m_2 are the weight of the dried and swollen samples, respectively.

The freezable-water content (W_f) is calculated by:

$$W_f = \frac{\Delta H}{\Delta H_0} \times 100\% \tag{3}$$

where ΔH is the fusion enthalpy of the sample per unit mass calculated by integrating of the endothermic peaks, ΔH_0 is the fusion enthalpy of pure distilled water (334.3 J/g).

Finally, the non-freezable water content (W_{nf}) is calculated by:

$$W_{nf} = W_{EWC} - W_f. \tag{4}$$

3. Results and discussion

3.1. Preparation of the superabsorbent polymer

3.1.1. FTIR spectroscopy

After the graft copolymerization of acrylic acid and dimethyldiallylammonium chloride onto carboxymethyl chitosan, obvious changes in FTIR spectrum (Fig. 1) have been observed. Specifically, the intensity of the absorption peak at 2920 cm^{-1} from the stretching vibration of C–H of carboxymethyl chitosan increased significantly after introducing the long carboxymethyl chitosan chain. Meanwhile, the peak at 793 cm^{-1} from the rocking vibration of C–H also increased. Particularly, both the absorption peak at 1710 cm^{-1} that was attributed to –COOH of PAA and the absorption

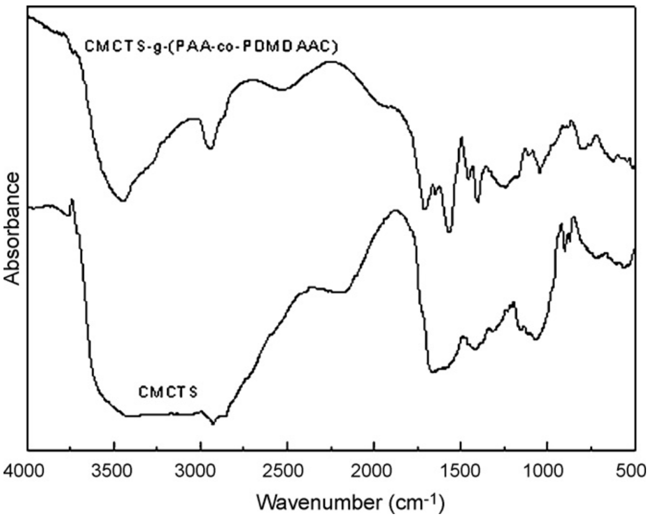


Fig. 1. FTIR spectrum of CMCTS and CMCTS-g-(PAA-co-PDMDAAC) superabsorbent polymer.

peak at 1570 cm^{-1} assigned to the asymmetric extension vibration of –COO$^-$ increased, which can be used as the evidence of the formation of PAA segments. Similarly, the characteristic absorption peaks of the quaternary ammonium salt appeared after the formation of the PDMDAAC segments. In addition, both the absorption peak at 1570 cm^{-1} that can be assigned as the bending vibration of the methylene coupled to N$^+$ and the absorption peak at 1420 cm^{-1} that was attributed to the in-plane asymmetric bending and stretching of the double-methyl coupled to N$^+$, increased greatly after the reaction, while the absorption peak at 1260 cm^{-1} that was assigned to the bending and stretching vibration of C–N bond of amide III increased significantly as a large amount of the quaternary ammonium group were introduced. It was clear that the FTIR spectrum of the superabsorbent polymer can provide a definite evidence for the occurrence of graft copolymerization of acrylic acid and dimethyldiallylammonium chloride onto the chain of carboxymethyl chitosan.

3.1.2. SEM examination

The surface morphology of carboxymethyl chitosan as well as the prepared superabsorbent polymer was examined by SEM (Fig. 2). As shown in Fig. 2, the surface of the carboxymethyl chitosan was very smooth. However, after the modification, the surface morphology changed significantly and became porous. The change in the surface morphology can also be used as an evidence for the occurrence of the graft copolymerization.

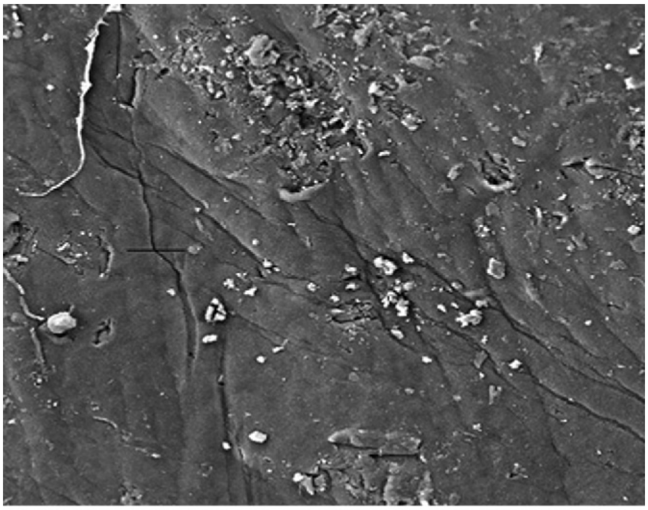
3.2. Effects of the synthesis conditions on the properties of the superabsorbent polymer

There is great difference between the structures of the superabsorbent polymers synthesized at different conditions and the water absorption capacities of the polymer was influenced greatly (Pourjavadi, Amini-Fazl, & Barzegar, 2008; Zhang, Li, & Wang, 2006). In this paper, the effects of the synthesis conditions on the water absorption capacities of the superabsorbent polymers were studied.

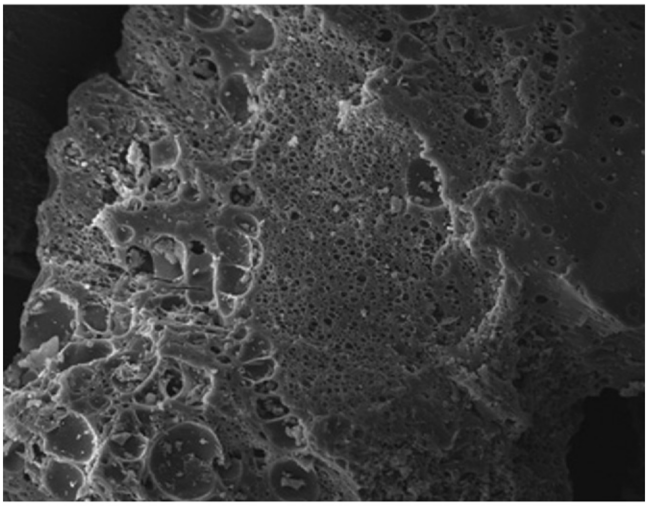
3.2.1. Effects of the amount of crosslinking agent

To study the effects of the amount of crosslinking agent on the water absorption capacity of the polymer, graft polymerizations were studied at various $n_{\mathrm{MBAM}}/n_{\mathrm{AA}}$ ratios while keeping other reaction conditions constant. When the amount of the crosslinking agent was relative low, the water absorption capacity of the polymer was low. As DMDAAC has two double bonds with the same reactivity and can also be acted as crosslinker itself, it was found that the swelling ratio was 92.1 g/g in distilled water and 10.6 g/g in normal saline for the polymer without MBAM added. For the traditional superabsorbent copolymer prepared through copolymer of the vinyl monomers with single double bond, the swelling ratio was sharply decreased without additional crosslinker being added. However, the reactivity of DMDAAC was lower and the effectiveness of crosslinking was not as high as MBAM. The water absorbency of the polymer was gradually enhanced on increasing the amount of MBAM. When the mass ratio was around 0.0081, the swelling ratio reached its maximum value (Fig. 3). When the amount of the crosslinking agent was increased further, the water absorption capacity began to decrease. 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 be seen from Flory equation (Eq. (5)) that if the crosslinking density ν_e/V_0 is high, the equimbium swelling ratio q_{m} is decreased.

$$q_{\mathrm{m}}^{5/3} \cong \frac{\left[(i/2\nu_u S^{*1/2})^2 + (1/2 - \chi_1)/\nu_1\right]}{(\nu_e/V_0)} \tag{5}$$



CMCTS ×500



CMCTS-g-(PAA-co-PDMDAAC) ×500

Fig. 2. SEM images of carboxymethyl chitosan and CMCTS-g-(PAA-co-PDMDAAC) superabsorbent polymer.

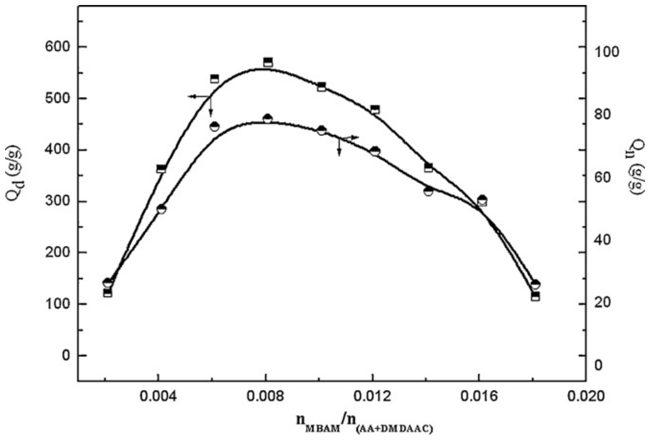


Fig. 3. Effects of the amount of crosslinking agent on the swelling ratio of the polymer. *Reaction conditions*: $n_{DMDAAC}/n_{(AA+DMDAAC)}$, 0.079; $n_{(AA+DMDAAC)}/n_{CMCTS}$, 24.22; $n_{APS}/n_{(AA+DMDAAC)}$, 0.007; neutralization degree, 50%.

Table 1
Effects of the vinyl monomers on the swelling ratio of the polymer.

$n_{DMDAAC}/n_{(AA+DMDAAC)}$	$n_{AA+DMDAAC})/n_{CMCTS}$	Q_d (g/g)	Q_n (g/g)
0.000		92.1	10.6
0.020		138.6	23.1
0.042		172.3	29.6
0.060		326.8	56.9
0.079	24.22	481.3	66.2
0.114		306.9	53.8
0.159		222.7	36.8
0.204		134.5	25.9
0.340		59.8	8.2
	14.91	15.1	2.0
	18.64	16.0	7.3
	22.36	315.3	45.7
0.079	24.22	570.2	78.9
	26.09	538.9	75.7
	29.82	353.2	59.4

Reaction conditions: $n_{MBAM}/n_{(AA+DMDAAC)}$, 0.0081; $n_{APS}/n_{(AA+DMDAAC)}$, 0.007; Neutralization degree, 50%.

3.2.2. *Effects of amount of initiator*

When the $n_{APS}/n_{(AA+DMDAAC)}$ ratio was low, the swelling ratio of polymer was low because the graft points initiated on the chain of carboxymethyl chitosan were low, the reaction rate was slow, and the formation of the network structure was difficult. With the increase of the amount of APS, both the reaction rate and the active groups initiated on the chain of carboxymethyl chitosan was increased, the three dimensional network could be formed more easily and the water absorption capacity of the polymer was increased. However, in the radical polymerization, the mean kinetic chain length was decreased as the increase of the initiator concentration while other conditions were kept constant (Flory, 1953). Similarly, the molecular weight of the branched chains was low too and the formation of the network was incomplete. As a result, the swelling ratio of the polymer decreased. When the molar ratio was around 0.007 (Fig. 4), the water absorption capacities of the polymer reached its highest value.

3.2.3. *Effects of two monomers*

The effects of the molar ratio and total amount of two monomers on the swelling ratio of the polymer were studied, respectively.

The effects of the molar ratio of two monomers on the water absorption capacity of the polymer was studied by changing the ratio of $n_{DMDAAC}/n_{(AA+DMDAAC)}$ while keeping the total amount of two monomers constant. As shown in Table 1, when the molar ratio was less than 0.079, the swelling ratio was increased. However, the swelling ratio was decreased when the molar ratio was higher than 0.079. The electrostatic attraction between the anionic carboxylate groups of PAA segments and the cationic quaternary ammonium groups of PDMDAAC segments was increased as enhancing the content of quaternary ammonium salt. The crosslinking degree of the network structure was increased and the swelling capacity of the polymer was decreased. If the molar ratio of DMDAAC was increased further, the water absorption capability of the polymer was decreased to a very low level because the molecular volume of DMDAAC was larger and the reactive activity of it was low, and so the polymerization degree of the polymer chain was low at this time and the swelling ratio was significantly reduced. Furthermore, As DMDAAC is also acted as crosslinker itself, the crosslinking density of the network structures was increased as promoting the amount of DMDAAC, this can also lead to a decrease in the swelling ratio.

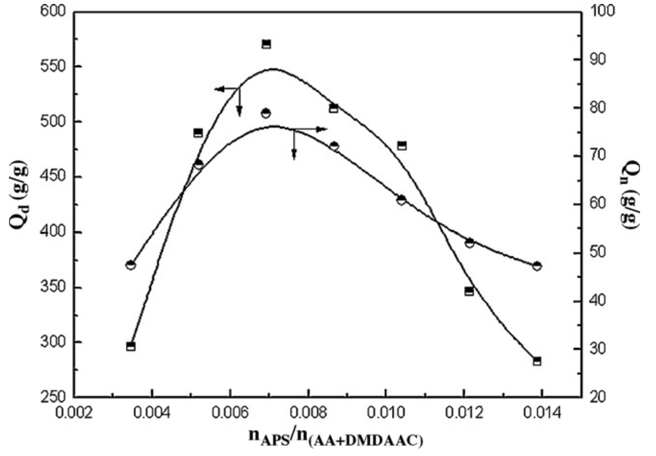


Fig. 4. Effects of the amount of initiator on the swelling ratio of the polymer. *Reaction conditions*: $n_{DMDAAC}/n_{(AA+DMDAAC)}$, 0.079; $n_{(AA+DMDAAC)}/n_{CMCTS}$, 24.22; $n_{MBAM}/n_{(AA+DMDAAC)}$, 0.0081; neutralization degree, 50%.

Table 1 also shows the effects of the total amount of two monomers on the swelling ratio of the polymer. When the molar ratio of $n_{(AA+DMDAAC)}/n_{CMCTS}$ was smaller than 24.22, the swelling ratio of the polymer increased with the increase of the molar ratio. This can be explained by the fact that there were more monomers available when the molar ratio was increased; therefore, the rate of graft polymerization was increased. Under these conditions, the polymerization was sufficient and the number of the hydrophilic groups in the network was increased. However, the swelling ratio began to decrease with the increase of the mass ratio when the ratio was higher than 24.22. At this time, the molecular weight of the branched polymer chains was so high that the viscosity of the system was sufficiently high to effectively hinder the movement of the radicals and monomers. The polymerization rate decreased and the three dimensional network structures formed were less than ideal. In addition, because the degree of crosslinking of the polymer was increased by the entanglement of the high molecular weight branched chains, the swelling of the network was reduced. All of these effects made the swelling ratio of the polymer low at the high mass ratios. The swelling ratio reached the maximum value when $n_{(AA+DMDAAC)}/n_{CMCTS}$ was around 24.22.

3.2.4. *Effects of neutralization degree of acrylic acid*

Fig. 5 shows that when the neutralization degree of acrylic acid was around 50%, the water absorbency of the polymer reached a maximum value. At lower neutralization degree, the dissociation of AA is very weak and many of $-COO^-$ groups interacted with the cationic quaternary ammonium groups. Consequently the value of i/v_u (the concentration of the fixed charges of the unswollen network) in Eq. (5) is low and the swelling of the network was limited.

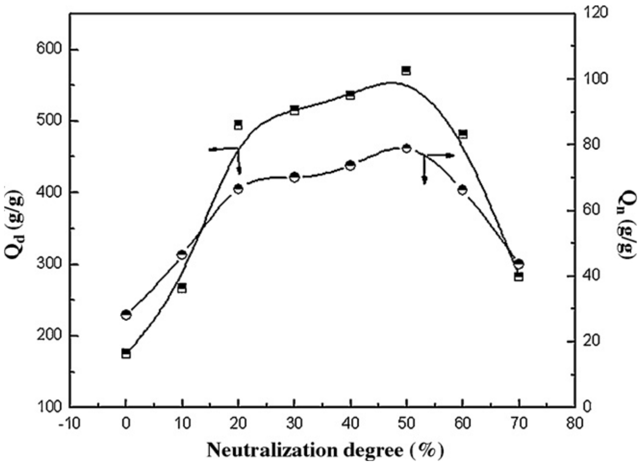


Fig. 5. Effects of the neutralization degree of acrylic acid on the swelling ratio of the polymer. *Reaction conditions*: $n_{\mathrm{DMDAAC}}/n_{\mathrm{(AA+DMDAAC)}}$, 0.079; $n_{\mathrm{(AA+DMDAAC)}}/n_{\mathrm{CMCTS}}$, 24.22; $n_{\mathrm{MBAM}}/n_{\mathrm{(AA+DMDAAC)}}$, 0.0081; $n_{\mathrm{APS}}/n_{\mathrm{(AA+DMDAAC)}}$, 0.007.

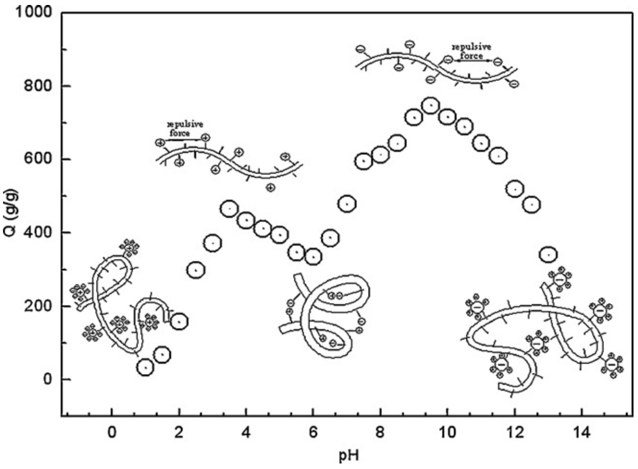


Fig. 6. Effects of the pH of the solution on water absorption capacity of the superabsorbent polymers.

If the degree of neutralization is increased, the content of –COO$^-$ groups increased and the difference in osmotic pressure between the inside and outside of the network is increased and the swelling ratio of the polymer was enhanced. However at a higher neutralization degree of AA, reduced swelling was observed, for various reasons. The charge-screening effect of excess Na$^+$ ions shielded the carboxylate anions on the chains of PAA and inhibits effective anion–anion repulsive forces. Furthermore, with increase of the NaOH concentration, the ionic strength of the swollen solution (S^* in Eq. (5)) is increased. As a result, the osmotic pressure of the gel phases was reduced and the swelling ratio was consequently decreased.

By studying the water swelling ratio of the polymer synthesized at different conditions, we found that the optimal conditions to synthesize the polymer with the highest swelling ratio was as follows: $n_{\mathrm{DMDAAC}}/n_{\mathrm{(AA+DMDAAC)}}$ was around 0.079 and $n_{\mathrm{(AA+DMDAAC)}}/n_{\mathrm{CMCTS}}$ was around 24.22, the molar ratio of the crosslinking reagent and the initiator to monomers was 0.0081 and 0.007, respectively, the neutralization degree of acrylic acid was around 50%. The polymer synthesized at this condition could absorb over 612 g/g distilled water and over 81 g/g normal saline.

3.3. *Effects of pH on the swelling capacities and structure of the polymer*

In polyampholyte superabsorbent polymers, the interactions between the counter ions have significant influences on the shrinking and expansion of the network and hence the absorption capacity of the polymer. The concentration of both the counter anions and counter cations are essentially controlled by the dissociation of charged groups along the polymer backbone and are expected to be significantly affected by the pH value in the solution. In this work, the equilibrium swelling of the prepared superabsorbent polymer has been studied in a pH value range from 1.0 to 13.0. In addition, because the water absorption capacity of the superabsorbent polymer is very sensitive to the ionic strength of the solution, great care must be taken to avoid the introduction of additional ions into the system. Here, the pH value of the medium was set by using a buffer solution, and both the stock NaOH and HCl solution were diluted with distilled water to the desired basic and acidic pH values.

As shown in Fig. 6, CMCTS-g-(PAA-co-PDMDAAC) superabsorbent polymer exhibited a pH-dependent swelling capacity. Specifically, unlike conventional polyanionic superabsorbent polymers that only showed a single swelling peak over the entire pH region, the swelling curve of the prepared polyampholyte polymer exhibited two swelling peaks: one was at pH 3.5 (acidic condition) while the other was at pH 9.5 (basic condition), and the swelling capacity decreased to a low value around pH 6.0 between the two peaks. The observed pH dependence of the swelling capacity can be attributed to the polyampholytic nature of CMCTS-g-(PAA-co-PDMDAAC) superabsorbent polymer.

Under the strong acid conditions ($\mathrm{pH} < 2$), the electric charge of the quaternary ammonium cations can be effectively screened by Cl$^-$ ions thereby the repulsion between the cations became negligible. Consequently, an obvious decrease in equilibrium swelling has been observed in the prepared superabsorbent polymer under strong acidic conditions. With a slight increase in pH value ($\mathrm{pH} < 3.5$), the screening effect of the Cl$^-$ counter ions gradually decreased while the attractive interaction between anions and cations was still weak due to the low ionization degree of –COOH group. Under such circumstances, the swelling ratio of the prepared polymer reached to the maximum around pH 3.5 because of the increase in repulsive interaction between the cations. However, increasing pH value further, the ionization degree of –COOH group started to increase. Consequently, the number of the hydrogen bonds between the quaternary ammonium and carboxylic acid groups increased, leading to an increase in crosslinking. As a result, the swelling ratio decreased until reaching a very low value around pH 6.0, which is just the isoelectric point of the polyampholyte. At still higher pH values, the number of carboxylic acid group outweighed that of the quaternary ammonium group, for the ionization degree of –COOH group increased with the pH value. Consequently, the properties of prepared superabsorbent polymer began to be dominated by those of polyanions, and its swelling ratio increased due to the increase of repulsive interaction between the –COO$^-$ anions. Meanwhile, the osmotic pressure inside the network also increased due to the increase of Na$^+$ concentration. The swelling capacity finally reached another maximum value at pH 9.5. Further increasing the pH value to the strong basic conditions ($\mathrm{pH} > 10$), however, the network structure of the prepared polymer collapsed. Simultaneously, the swelling ratio of the prepared polymer decreased sharply (it was not as obvious as that under the strong acidic conditions), which is very likely due to the screening of the repulsive interaction between the –COO$^-$ groups by the counter ion Na$^+$. The osmotic pressure inside the network was still high because of the high Na$^+$ concentration. The interaction between anions and cations were showed schematically in Fig. 6 to illuminate the pH$^-$ dependence of the swelling ratio

Table 2
Effects of pH value on non-freezable water content in the swollen CMCTS-g-(PAA-co-PDMDAAC) hydrogel.

pH	W_{EWC} (%)	W_f (%)	W_{nf} (%)
2.0	99.26	47.89	51.37
3.5	99.65	69.87	29.78
6.0	99.63	85.29	14.34
9.5	99.70	77.63	22.07
13.0	99.59	88.67	10.92

of the prepared CMCTS-g-(PAA-co-PDMDAAC) superabsorbent polymer.

The specific polymer–water interactions could reflect the special structures–properties relationship of the hydrogel and many researchers have reported the studies on this (Qu, Wirsen, & Albertsson, 2000; Yoshida, Hatakeyama, & Hatakeyama, 1993). There are two kinds of bound water inside the network of the superabsorbent hydrogel: freezable and non-freezable water. Particularly, the non-freezable water is commonly thought to be the water closely associated with (bound or immobilized by) the hydrophilic groups of the polymer. The content of the non-freezable water can be affected by the amount of hydrophilic groups, and the types of hydrophilic groups due to their different interactions with water molecules. Therefore, the change in the content of the non-freezable water can provide significant information about the structure–property relationship of the superabsorbent polymer network.

Since the physical properties of the superabsorbent hydrogel apparently depend on water content of various states, characterization of the amount of adsorbed water in the swollen superabsorbent hydrogel is essential (Kim, Park, & Kim, 2003). Different analytical techniques have been employed to study water structure in superabsorbent hydrogels, such as NMR (Capitani, Crescenzi, DeAngelis, & Segre, 2001), dilatometry and electrical conductivity (Jhon, Hattori, Ma, Gregonis, & Andrade, 1975), dielectric relaxation spectroscopy (Kyritsis, Pissis, & Grammatikakis, 1995), dynamic-mechanical spectroscopy (Lustig, Caruthers, & Peppas, 1991) and differential scanning calorimetry (Kim et al., 2003), etc. Differential scanning calorimetry (DSC) has proved to be very useful in determining the state of water in hydrogels.

In the present work, the influence of pH value on the water content of various states in the CMCTS-g-(PAA-co-PDMDAAC) superabsorbent hydrogel was investigated by DSC for the purpose of revealing the unique properties of the polyampholyte network. The results are summarized in Table 2. As shown in Table 2, the content of the non-freezable water changed with the pH value of the solution. Specifically, the non-freezing water content decreased gradually with the pH value of the absorbed solution in a pH range 2.0–6.0. It can be explained as follows. At low pH values, the dissociation of –COOH groups are rather limited. As a result, a significant amount of water molecules can be associated with the abundant –COOH groups as well as the quaternary ammonium groups via hydrogen bond. The non-freezable water content is therefore high. However, with the increase of pH value, more and more –COOH groups are dissociated to form $-COO^-$ groups. The amount of the hydrophilic groups decreases simply because of the combination between the $-COO^-$ and quaternary ammonium groups. Consequently, the non-freezable water content decreases. Particularly, when the amount of $-COO^-$ groups reached its maximum at the isoelectric point, the content of the non-freezable water became very low. With the further increase of pH value, the dissociation degree of –COOH continued to increase to produce more highly hydrophilic $-COO^-$ groups. As a result, the content of the non-freezable water reached another maximum around pH 9.5. However, the non-freezable water content at pH 9.5 was lower than that around pH 3.5, which is probably due to the interaction of some $-COO^-$ with quaternary ammonium groups. At still higher pH values, the non-freezing water content kept decreasing due to the screening of the $-COO^-$groups by Na^+ counter ions.

4. Conclusion

A novel superabsorbent polymer has been prepared by graft copolymerization of acrylic acid and dimethyldiallylammonium chloride onto the chain of carboxymethyl chitosan. The water swelling behavior of the prepared polymer has been studied at different conditions. The optimal conditions to synthesize the polymer showing the highest swelling ratio has been identified, at which the swelling ratio of the prepared polymer in distilled water and normal saline water can be as high as 612 g/g and 81 g/g, respectively. In addition, the swelling ratio of the prepared polymer was found to be pH dependent, which can be attributed to the polyampholytic nature of CMCTS-g-(PAA-co-PDMDAAC) superabsorbent polymer. Finally, the effects of the interactions between the charged groups on the polymer backbone as well as the effects of counter ion screening on the non-freezing water content have also been studied by studying the DSC curve of the swollen hydrogel at different pH values.

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