



# Synthesis and characterization of a novel superabsorbent polymer of *N,O*-carboxymethyl chitosan graft copolymerized with vinyl monomers

Chen Yu <sup>a,\*</sup>, Liu Yun-fei <sup>a</sup>, Tan Hui-min <sup>a</sup>, Jiang Jian-xin <sup>b</sup>

<sup>a</sup>School of Material Science and Engineering, Beijing Institute of Technology, No. 5. South Street Zhongguancun, Beijing 100081, PR China

<sup>b</sup>State Key Laboratory of Trauma Burns and Combined Injury, The Third Military Medical University, Chongqing 400042, PR China

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## ABSTRACT

A novel superabsorbent polymer was prepared by graft copolymerization of sodium acrylate and 1-vinyl-2-pyrrolidone onto the chain of *N,O*-carboxymethyl chitosan. The molecular structure of the product was confirmed by FTIR. The surface morphologies before and after the polymerization were examined by SEM. By studying the water absorption of the polymer synthesized under different conditions, the optimal conditions for synthesizing the polymer with the highest swelling ratio was defined. We showed that the water absorption rates of the prepared polymers were high, the swelling processes of the polymers showed first-order kinetics, and the swelling ratio of the polymer was pH dependent.

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## 1. Introduction

Superabsorbent polymers are polymers with a network structure and an appropriate degree of crosslinking (Omidian, Rocca, & Park, 2005) which can absorb a large amount of water. These polymers have been extensively used as absorbents in personal care products, matrices for enzyme immobilization, materials for agricultural mulches, and matrices for controlled release devices (Hany, 2007; Marcos et al., 2005).

Some natural polymers such as celluloses or starches can be prepared as superabsorbent polymers through radical graft polymerization with vinyl monomers and crosslinking (Li, Zhang, & Wang, 2007; Peng, Xu, Peng, Wang, & Zheng, 2008; Suo, Qian, Yao, & Zhang, 2007; Zhang, Li, & Wang, 2006). Chitosan is another important natural polymer. Because of the abundant hydroxyl groups and amino groups distributed along its chain, chitosan can be easily modifying chemically. Graft polymerization is a very important method for modify chitosan (Jenkins & Hudson, 2001; Mochalova et al., 2007; Park et al., 2003). Chitosan based superabsorbent polymers could be prepared by graft polymerization with vinyl monomers along the chitosan chain and crosslinking (Liu, Wang, & Wang, 2007; Zhang, Wang, & Wang, 2007). Because of its very good biocompatibility and antibacterial property, chitosan based superabsorbent polymers are expected to be widely used in many applications (Sun et al., 2006) such as medical materials, sanitary materials, controlled release devices, and matrices for enzyme immobilization. Carboxy-

methyl chitosan is a very important chitosan derivative showing very good water solubility and biocompatibility (Pang, Cheng, Park, Cha, & Kennedy, 2007). In this paper, we report the preparation of a novel superabsorbent polymer by graft copolymerization of sodium acrylate and 1-vinyl-2-pyrrolidone along the chains of *N,O*-carboxymethyl chitosan. Because 1-vinyl-2-pyrrolidone is a nonionic monomer, poly(1-vinyl-2-pyrrolidone) (PVPD) segments were introduced to increase the water affinity of the polymers and therefore control the haloduric property of the superabsorbent polymers. In addition, because the PVPD segments can be easily modified, the introduction of PVPD segments provides the possibilities to further functionalize superabsorbent polymers (Cui, Yi, & Liao, 2001).

## 2. Experimental

### 2.1. Materials

Chitosan (CTS) with a deacetylation degree of 76% and a molecular weight of about  $6.7 \times 10^4$  was supplied by Zhejiang Yuhuan Biochemical CO. Ltd. (China). Acrylic acid (AA, A.R.) was purchased from Tianjin Chemical Reagent Institute (China) and purified by reduced pressure distillation before polymerization. 1-vinyl-2-pyrrolidone (VPD, A.R.) was supplied by MERCK-Schuchardt Co., of Germany and purified by reduced pressure distillation before the reaction. Azobis(isobutylamine) hydrochloride (AIBA, A.R.) was used as the initiator and *N,N*-methylene diacrylamide (NNMBA A.R.) was used as the crosslinking agent. Isopropyl alcohol, chloroacetic acid, alcohol and sodium hydroxide are analytical grade reagents and used as received.

\* Corresponding author. Tel.: +86 10 68912370.

E-mail address: [cylsy@163.com](mailto:cylsy@163.com) (C. Yu).

## 2.2. Preparation of *N,O*-carboxymethyl chitosan (CMCTS)

10 g chitosan of meshes was added into 38 g 40 wt% NaOH aqueous solution in a three-necked flask, which was equipped with a stirring apparatus and a reflux condenser. Then, 100 mL isopropyl alcohol and 17 g chloroacetic acid were added into the flask. After reacting at 65 °C for 4 h, the mixture was filtered and the solid product was washed with 80 wt% alcohol until the pH was neutral. The product was then dried under vacuum. The substitution degree of the *N,O*-carboxymethyl chitosan was determined as 0.81 by elemental analysis.

## 2.3. Preparation of the novel superabsorbent polymer

*N,O*-Carboxymethyl chitosan (1.5 g) was dissolved in various amounts of 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 by a water bath. Various amounts of AIBA dispersed in moderate amount of deionized water were slowly added into the flask to initiate the graft polymerization. The suitable amounts of VPD, sodium acrylate and NNMB were added 30 min later. The total volume of the water in the system was controlled at a certain level whereas the stirring speed was fixed. After a certain period, air was introduced into the reactor to cool down the flask and stop the reaction. The product was precipitated by pouring alcohol into the reaction mixture. The precipitate was filtered, washed thoroughly with alcohol/water mixture (4:1, v/v) 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. The fractions with a size range from 150 to 250  $\mu\text{m}$  was used for the water absorption experiments.

## 2.4. FTIR spectroscopy

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

## 2.5. SEM examination

The surface morphologies of the *N,O*-carboxymethyl chitosan as well as the superabsorbent polymers were examined by a scanning electron microscope (CSM950 series, OPTON Co., Germany). The samples were coated with Au prior to SEM examination.

## 2.6. Determination of the water absorption capability

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

$$Q = (m_2 - m_1)/m_1 \quad (1)$$

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

## 3. Results and discussion

### 3.1. Preparation of the superabsorbent polymer

Diazo salt is a kind of common initiator of radical polymerization. It can be used as the initiator of the graft copolymerization

of chitosan or carboxymethyl chitosan with the vinyl monomer. Qurashi, Blair, and Allen (1992) reported the initiation of the graft copolymerization of methylacrylic acid onto the chitosan chain by diazo salt. In their study, they concluded that the reaction was initiated at the amino groups of chitosan by the fact the products were not soluble in 2% acetic acid solution. They have also shown that the reaction was initiated at the amino groups when the vinyl acetate was graft copolymerized with chitosan initiated by diazo salt. Therefore, according to this mechanism, the primary radicals were initiated at the amino groups of *N,O*-carboxymethyl chitosan. Then, after the chain propagation and crosslinking reaction, the network structure was formed and the superabsorbent polymer was obtained.

#### 3.1.1. FTIR spectroscopy

The structure changes of chitosan and *N,O*-carboxymethyl chitosan were confirmed by FTIR spectroscopy (Fig. 1). In the spectrum of carboxymethyl chitosan, the absorption peak at 1620  $\text{cm}^{-1}$  that attributed to the asymmetric extension vibration of  $\text{—COO}^-$  coincided with the extension vibration of  $\text{C=O}$  of amide I band at 1660  $\text{cm}^{-1}$ ; therefore, a wide peak was observed. The peak at 1450  $\text{cm}^{-1}$  from the symmetrical extension vibration of  $\text{—COO}^-$  and the peak at 1308  $\text{cm}^{-1}$  that assigned to the extension vibration of  $\text{C—O}$  increased greatly after the reaction. Meanwhile, compared with the spectrum of chitosan, the absorption peak at 1323  $\text{cm}^{-1}$  that was assigned to the stretching vibration and bending vibration of  $\text{C—N}$  bond of amide III band was obviously increased after the reaction, whereas the absorption peak at 898  $\text{cm}^{-1}$  from the out-plane bending vibration of  $\text{N—H}$  of the primary amino group was decreased to 873  $\text{cm}^{-1}$ . All of these indicated that the carboxymethyl groups have substituted the hydrogen on the  $\text{—NH}_2$ . Moreover, the absorption peak at 1156  $\text{cm}^{-1}$  and 1071  $\text{cm}^{-1}$  showed the existence of  $\text{C—O—C}$  bond, confirming that the  $\text{—OH}$  of the chitosan has been substituted by the carboxymethyl group. From all these IR peak changes, we conclude that the *N,O*-carboxymethyl chitosan has been produced.

After the graft copolymerization of *N,O*-carboxymethyl chitosan with sodium acrylate and 1-vinyl-2-pyrrolidone, the absorption peak at 1650  $\text{cm}^{-1}$  from the stretching vibration of  $\text{C=O}$  appeared and it was coincided with the wide peak around 1660  $\text{cm}^{-1}$  attributed to the *N,O*-carboxymethyl chitosan mentioned above. The intensity of this peak was strong. The absorption peak at 1586  $\text{cm}^{-1}$  attributed to the bending vibration of  $\text{N—H}$  bond of amide II was overlapped with the peak at 1592  $\text{cm}^{-1}$  that was as-

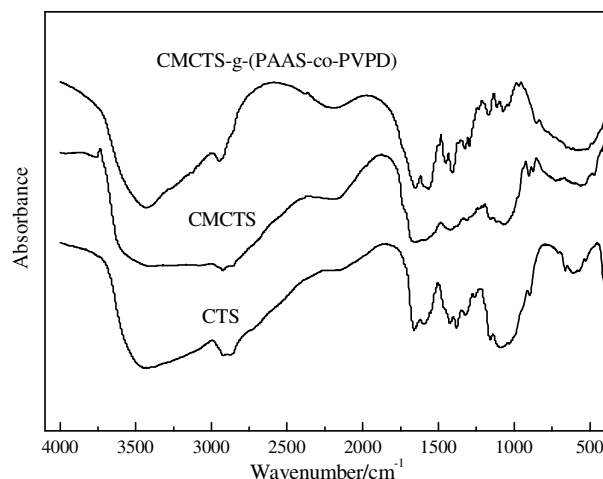


Fig. 1. The FTIR spectrum of chitosan (CTS), *N,O*-carboxymethyl chitosan (CMCTS) and CMCTS-g-(PAAS-co-PVPD) superabsorbent polymers.

signed to the asymmetric extension vibration of  $\text{—COO}^-$ . The intensity of this peak was increased greatly after the reaction. The peak at  $1441\text{ cm}^{-1}$  from the symmetrical stretching vibration of  $\text{—COO}^-$  and the absorption peak at  $1290\text{ cm}^{-1}$  assigned to the extension vibration of  $\text{C—O}$  was increased greatly too after the reaction. Furthermore, the absorption peak at  $1323\text{ cm}^{-1}$  that was attributed to the bending vibration and stretching vibration of  $\text{C—N}$  bond of amide III band was increased significantly as a result of the cyclization of the acylamide group. Meanwhile, the intensity of the absorption peak at  $2920\text{ cm}^{-1}$  from the stretching vibration of  $\text{C—H}$  of *N,O*-carboxymethyl chitosan was increased greatly after the introduction of the long polymer chain. It was therefore clear that the FTIR spectrum of the superabsorbent polymer revealed the existence of not only the PAAS and PVPD segments but also the saccharide unit of *N,O*-carboxymethyl chitosan, indicating the occurrence of graft polymerization.

### 3.1.2. SEM examination

The surface morphologies of *N,O*-carboxymethyl chitosan and the superabsorbent polymer were examined by SEM (Fig. 2). As shown in Fig. 2, the surface of the *N,O*-carboxymethyl chitosan was very smooth. However, after the modification, their surface morphology changed dramatically. The surface became porous. This change in surface morphology supported the occurrence of graft polymerization.

### 3.2. Effects of the synthesis conditions on the water absorption properties of the superabsorbent polymer

It was reported that the structures of the superabsorbent polymers synthesized at different conditions were quite different and so were their water absorption capacities (Liang & Liu, 2006; Xu, Wu, Huang, Cao, & Wang, 2006). We therefore investigated the effects of the synthesis conditions on the water absorption capacities of the superabsorbent polymers.

#### 3.2.1. Effects of the reaction time and temperature

Varying the reaction time from 3–7 h while keeping other reaction conditions constant, the change in water absorption capacity was summarized in Table 1. The swelling ratio of the polymer was increased first with the reaction time, reached a maximum value at about 5 h, and then decreased at longer reaction times. With a short reaction time, the vinyl monomers probably did not polymerize completely and the crosslinking reaction was also not complete. When the reaction time increased, more three-dimensional network structure was formed and the swelling ratio was increased gradually increased. However, if the reaction time was too long, more and more branched chains were formed, which could entangle with each other and prohibit the expansion of the polymer. Therefore, it was difficult for water to enter into the network and the water absorption capacity of the polymer decreased.

The swelling ratio of the polymer was also affected greatly by the reaction temperature. As shown in Table 1, when the temperature was lower than  $60^\circ\text{C}$ , the swelling ratio was increased with the increase of the temperature. However, the water absorption capacity was decreased when the temperature was increased further. Chemically, it is easy to understand that increased temperature enhanced the radical formation and polymerization reaction, and lead to more graft polymerization and water absorption capacity. However, too high temperature likely led to chain termination and less graft polymerization, and thus lower swelling ratio. In our case, the swelling ratio of the polymer reached the maximum at  $60^\circ\text{C}$ .

#### 3.2.2. Effects of the ratios of the reagents

The effects of the amounts of the crosslinking agent, initiator, monomer, the molar ratio of the two monomers, and the volume

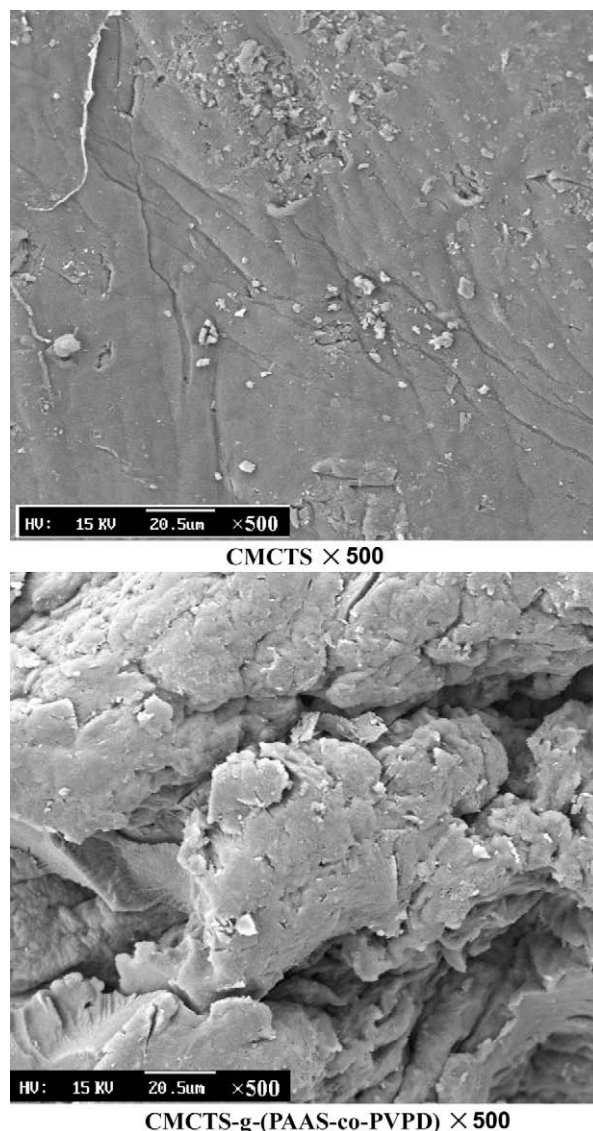


Fig. 2. The SEM images of *N,O*-carboxymethyl chitosan and CMCTS-g-(PAAS-co-PVPD) superabsorbent polymer.

Table 1

Effects of the reaction time and temperature on the water absorption capacities of the polymer

Temperature ( $^\circ\text{C}$ ) and time (h)	$Q_d/\text{g/g}$	$Q_n/\text{g/g}$
60, 3	433	99
60, 4	579	109
60, 5	656	126
60, 6	451	118
60, 7	412	101
40, 5	209	68
50, 5	389	101
70, 5	585	115
80, 5	488	103

Other reaction conditions:  $n_{\text{NNMBA}}/n_{\text{AAS}} = 0.0146$ ;  $n_{\text{AIBA}}/(n_{\text{AAS}} + n_{\text{PVPD}}) = 0.0175$ ;  $(n_{\text{AAS}} + n_{\text{PVPD}})/n_{\text{CMCTS}} = 24.01$ ;  $n_{\text{AAS}}/(n_{\text{AAS}} + n_{\text{PVPD}}) = 0.73$ ; water volume = 125 mL.  $Q_d$  is the equilibrium swelling ratio of the polymer in the distilled water;  $Q_n$  is the equilibrium swelling ratio of the polymer in the normal saline.

of the water in the reaction system on the water absorption capacities of the polymers were studied. The results were listed in Table 2.

To study the effect of the amount of crosslinking agent on the water absorption capacity of the prepared polymers, various  $n_{\text{NNMBA}}/n_{\text{AAS}}$  ratios were used and the other reaction conditions were kept the same. When the amount of the crosslinking agent was low, the water absorption capacity 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. We found that with the increase of the amount of NNMBA, the water absorption capacity of the prepared polymer gradually increased. When the molar ratio was around 0.0208, the swelling ratio reached its maximum. When the amount of the crosslinking agent was increased further, the water absorption capacity began to decrease. It is predicted by the Flory equation Eq. (2) that when the crosslinking density  $v_e/V_0$  is high, the equilibrium swelling ratio  $q_m$  is decreased.

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

Similarly, the effects of the amount of initiator on the water absorption capacity of the prepared polymers were studied with various  $n_{\text{AIBA}}/(n_{\text{AAS}} + n_{\text{VPD}})$  ratios. The water absorption ratio increased with increased amount of initiator AIBA, likely because more graft polymerization occurred and more stable network structures formed. However, in the radical polymerization, the mean kinetic chain length was decreased with the increase of the initiator concentration when other reaction conditions were kept the same (Flory, 1953). As a result, the swelling ratio of the polymer was decreased. When the ratio was around 0.0230, the water absorption capacities of the polymer reached its highest value.

The effects of the amount of the monomer were investigated with various ratios of  $(n_{\text{AAS}} + n_{\text{VPD}})/n_{\text{CMCTS}}$  ( $n_{\text{CMCTS}}$  represents the

substantial number of the carboxymethyl pyran rings). When the molar ratio was smaller than 27.45, the swelling ratio of the polymer was increased with the increase of the molar ratio, likely due to more graft polymerization. However, the swelling ratio began to decrease with the increase of the molar ratio when the ratio was higher than 27.45. The increased amount of monomers formed long polymer chains and less than ideal network structures. The swelling ratio reached the maximum value when  $(n_{\text{AAS}} + n_{\text{VPD}})/n_{\text{CMCTS}}$  was around 27.45.

The effects of the molar ratio of monomers on the water absorption capacity of the polymer were studied by changing the ratio of  $n_{\text{AAS}}/(n_{\text{AAS}} + n_{\text{VPD}})$  while keeping the total amount of the monomer constant. When the molar ratio was less than 0.73, the swelling ratio was increased with the increase of the amount of the AAS. However, the swelling ratio started to decrease when the molar ratio was increased further. Because the PVPD segment is less hydrophilic than that of PAAS, the water absorption capacity of the polymer was low at the low AAS concentration. When the amount of the AAS was increased further, the osmotic pressure difference between the inside and outside the network was increased because of the increase of the fraction of the  $-\text{COONa}$  group. However, the polymerization rate was decreased as the result of the low activity of AAS (Ma, Duo, & Tan, 2003). As a result, the water absorption capacity of the polymer decreased.

The concentration of the reactants also affected the water absorption capacity of the polymer. When the volume of the water in the reaction system was increased, the concentrations of the crosslinking agent, the initiator, and the monomer were all decreased. As a result, the rates of polymerization and crosslinking reaction were slowed and the water absorption capacity of the

**Table 2**  
Effects of the ratios of reagents on the water absorption capacities of the polymer

$n_{\text{MBAM}}/n_{\text{AAS}}$	$n_{\text{AIBA}}/n_{(\text{AAS}+\text{VPD})}$	$n_{(\text{AAS}+\text{VPD})}/n_{\text{CMCTS}}$	$n_{\text{AAS}}/n_{(\text{AAS}+\text{VPD})}$	$C_{\text{reactants}}/\text{mol/L}$	$Q_d/\text{g/g}$	$Q_n/\text{g/g}$
0.0085					126	28
0.0116					232	75
0.0146					451	118
0.0177	0.0175	24.01	0.73	1.28	485	123
0.0208					535	146
0.0262					473	110
0.0292					388	96
	0.0115				218	66
	0.0145				235	68
	0.0175				268	76
0.0146	0.0200	24.01	0.73	1.28	380	86
	0.0230				451	118
	0.0260				439	101
	0.0290				382	88
		17.17			328	69
		20.60			368	82
0.0146	0.0175	24.01	0.73	1.28	451	118
		27.45			545	125
		30.88			473	116
		34.31			362	88
		37.72			278	63
			0.44		312	58
			0.54		407	91
			0.64		438	103
			0.83		442	118
			0.91		229	108
0.0146	0.0175	24.01	0.73	1.28	451	64
			1.00		199	31
				1.60	328	98
				1.28	451	118
				1.06	491	125
0.0146	0.0175	24.01	0.73	0.91	592	146
				0.80	960	162
				0.71	714	138
				0.64	537	132

Reaction temperature: 60 °C, reaction time: 5 h  $C_{\text{reactants}} = n_{(\text{AAS}+\text{VPD}+\text{CMCTS})}/V_{\text{H}_2\text{O}}$ .



polymer was decreased. However, at low water volume, the concentrations of the reactants were very high and the rate of polymerization was actually slowed down. The swelling ratio of the polymer obtained at low water volume was low too. As shown in Table 2, the swelling ratio of the polymer reached the maximum when the molar concentration of the reactants was around 0.80 mol/L.

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: the reaction time was 5 h and the reaction temperature was 60 °C, the molar ratios of the crosslinking reagent and the initiator to sodium acrylate were 0.0208 and 0.0230, respectively,  $(n_{AAS} + n_{VPD})/n_{CMCTS}$  was around 27.45 and  $n_{AAS}/(n_{AAS} + n_{VPD})$  was around 0.73, and the water volume of the system was 200 mL. The polymer synthesized at this condition absorbed over 1268 g/g distilled water, over 165 g/g normal saline, over 112 g/g artificial blood and over 121 g/g artificial urine.

### 3.3. Swelling property of the superabsorbent polymer

#### 3.3.1. Swelling rate of the polymer

A preliminary study was conducted on the water absorption rate of the superabsorbent polymers. Fig. 3 shows the time course of the swelling of the two types of superabsorbent polymers synthesized at different conditions. The water uptake was fast and the equilibrium was achieved in 10 min. So the absorption rate of the polymers was high.

On the assumption that the swelling of the polymer fits the process of first-order dynamics (Liu, Cheng, & Qian, 1996), the swelling rate at a given temperature is:

$$dQ_i/dt = k(Q_e - Q_t) \quad (3)$$

where  $t$  is the swelling time,  $Q_t$  is the swelling ratio at that time,  $Q_e$  is the equilibrium swelling ratio. Eq. (1) is integrated:

$$\int_{Q_t}^{Q_e} dQ_i/(Q_e - Q_t) = \int_0^t k dt \quad (4)$$

The result is:

$$\ln[(Q_e - Q_0)/(Q_e - Q_t)] = kt \quad (5)$$

Then the following equation is gained:

$$Q_t = Q_e - (Q_e - Q_0)/e^{kt} \quad (6)$$

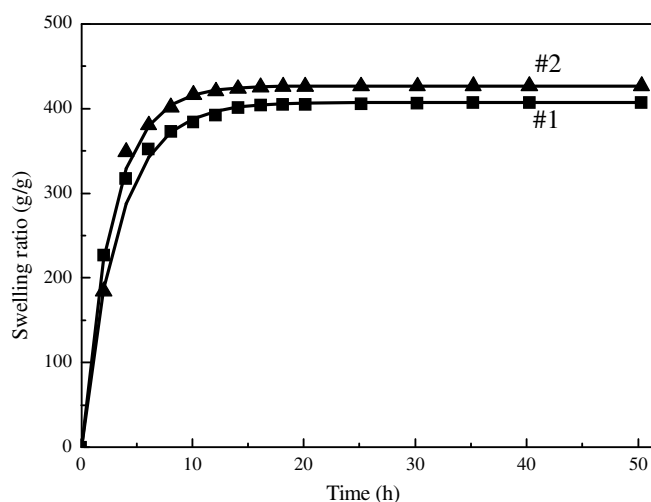


Fig. 3. The time courses of water absorption. The square and triangle represent the experimental data. The solid lines are the theoretical calculations.

The swelling rate constant  $k$  was obtained by plotting  $\ln[(Q_e - Q_0)/(Q_e - Q_t)]$  versus  $t$ . Then the theoretical swelling curve Eq. (6) of the polymer was drawn. As shown in Fig. 3, the theoretical calculations and experiment results agreed well. Therefore the hypothesis that the swelling processes of the polymers fit the processes of first-order dynamics was likely correct.

#### 3.3.2. Effect of pH on the swelling capacity

The swelling of the superabsorbent polymer was studied at various pHs from 2.0 to 12.0. As the water absorption capacities of the superabsorbent polymer was affected greatly by the ionic strength of the solution, great care was taken to make sure no additional ions were introduced into the medium. Distilled water was used to make all solutions.

Fig. 4 shows the swelling capacities of the polymers at different pH values. Curves 1 and 2 were the swelling curves of the polymers prepared from the above described method. Curve 3 was that of the polymer prepared from graft polymerization of *N,O*-carboxymethyl chitosan with acrylic acid initiated with ammonium persulfate. There was a maximum swelling ratio at pH = 4 in curve 3. A similar phenomenon was observed by Mahdavinia, Pourjavadi, Hosseinzadeh, and Zohuriaan (2004) for the superabsorbent hydrogel prepared from graft copolymerization of chitosan with acrylic acid and acrylamide initiated with potassium persulfate. However, the peak at the acidic condition in curve 1 and 2 was not obvious.

When the graft polymerization of chitosan was initiated with persulfate, the primary radicals were formed on the C<sub>2</sub> and C<sub>3</sub> positions of the pyran ring (Najjar, Yunus, Ahmad, & Rahman, 2000; Samgameesh, Kumbhar, & Tejraj, 2003) and most primary amino groups remained intact. The protonation of the amine group under different pHs would affect the swelling ratio of the polymer as our data indicated. Under acidic conditions, as the basic amine groups were protonated, the charge density on the polymer was increased and the osmotic pressure inside the network was enhanced because of the electrostatic repulsion of the NH<sub>3</sub><sup>+</sup> ions. The increased osmotic pressure enhanced the swelling of the polymer and the swelling ratio was the highest around pH = 4. This phenomenon has also been observed by the authors (Chen & Tan, 2006). However, for the superabsorbent polymer prepared from graft polymerization of *N,O*-carboxymethyl chitosan initiated with AIBA, the radicals were formed on the amino groups of the polysaccharide. After polymerization, there were less amino groups to be protonated and therefore the peak swelling ratio at the acidic pH was

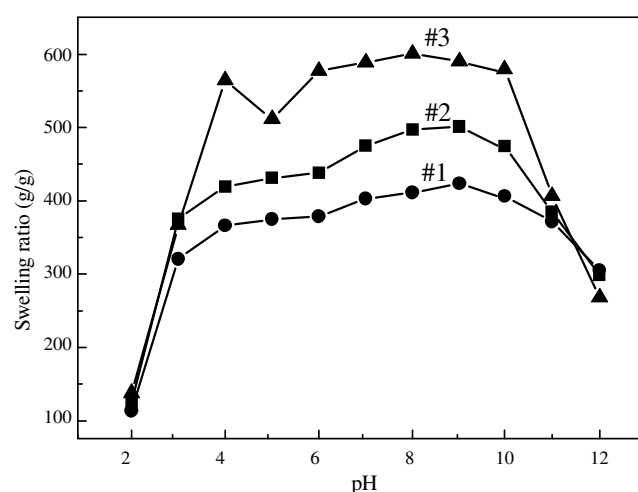


Fig. 4. Effect of the pH of the solution on the water absorption capacities of the superabsorbent polymers.

not obvious. This pH effect also supported the proposed reaction mechanism.

For the superabsorbent polymers we prepared, under acidic conditions (pH < 4), as the pH was decreased, the Na<sup>+</sup> of the —COONa group was replaced with H<sup>+</sup>. As a result, the concentration of the Na<sup>+</sup> inside the network was decreased and the osmotic pressure was decreased greatly. Therefore, low equilibrium swelling ratio was observed. With the increase of pH from 4 to about 9, as the ionization of the —COOH to —COO<sup>−</sup> groups were enhanced gradually and the osmotic pressure of the network structure was also increased. The swelling reached the maximum ratio at a pH of around 9. However, when the pH was higher than 10, the network structure began to collapse and the swelling ratio decreased sharply. A similar observation was recently reported for the saponified chitosan-g-polyacrylonitrile hydrogels and chitosan-g-poly(acrylic acid-co-acrylamide) hydrogels (Pourjavadi, Mahdavinia, & Zohuriaan-Mehr, 2003).

#### 4. Conclusion

A novel superabsorbent polymer was prepared by graft copolymerization of sodium acrylate and 1-vinyl-2-pyrrolidone onto the chain of N,O-carboxymethyl chitosan. By studying the water swelling ratio of the polymer synthesized at different conditions, the optimal conditions to synthesize the polymer with the highest swelling ratio was found. The polymer synthesized at this condition absorbed over 1268 g/g distilled water, over 165 g/g normal saline, over 112 g/g artificial blood and over 121 g/g artificial urine. The water absorption rates of the polymers were high and the swelling processes of the polymers fit of first-order dynamics. We also found that the swelling ratio of the polymer was pH dependent.

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