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Thermal preparation of chitosan–acrylic acid superabsorbent: Optimization, characteristic and water absorbency

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ABSTRACT

Chitosan–acrylic acid superabsorbent polymer was successfully prepared by the thermal reaction without using initiator and crosslinker in air. The effects of some reaction variables on the water absorbency of this polymer were investigated by orthogonal tests, and the optimal conditions were described. The influences of temperature, time, ratio of the reactants and neutralization degree of acrylic acid on the reaction were further studied. These polymers were also prepared in nitrogen atmosphere and by using a radical initiator and compared against thermal reaction obtained polymers. The structures of the polymers were characterized by FT-IR, TGA, XRD, ^{13}C NMR and elemental analyses. The results showed that the thermal reaction product of acrylic acid with chitosan might form *N*-carboxyethyl grafted and amide-linked polymer and this product could absorb water 644 times its own dry weight. The possible mechanism for the thermal reaction was further suggested. The purpose of this research was to explore the friendly synthesized method of the superabsorbent.

1. Introduction

Superabsorbent polymer (SAP) materials are hydrophilic networks that can absorb and retain huge amounts of water or aqueous solutions (Zohuriaan-Mehr, Omidian, Doroudiani, & Kabiri, 2010). They can uptake water as high as 100,000%. SAPs are mainly used in infant diapers, feminine hygiene products, agriculture, and other specialized areas as medical materials (Dutkiewicz, 2002; Laftah, Hashim, & Ibrahim, 2011; Zohuriaan-Mehr & Kabiri, 2008).

Among the recently developed superabsorbents, acrylic acid (AA)-based superabsorbents have been extensively studied because AA is cheap and easily polymerized to a higher molecular weight polymer (Raju & Raju, 2001). However, it was not so good to fit the ecological requirements, which brings the idea to graft with biodegradable natural polymers. One of the natural polymers that has attracted great attention is chitosan (Liu, Wang, & Wang, 2011; Yazdani-Pedram, Retuert, & Quijada, 2000; Yin, Fei, Cui, Tang, & Yin, 2007). Chitosan is a highly deacetylated derivative of chitin, one of the most abundant natural and biodegradable polymers. It is nonpoisonous and has excellent biocompatibility and bacteriostasis character (Muzzarelli et al., 2012; Raju, Raju, & Mohan, 2003). It has been widely applied in the biomedical, pharmaceutical, environmental and agricultural fields (Dash, Chiellini, Ottenbrite, & Chiellini, 2011; Ge & Fan, 2011; Muzzarelli, 2009, 2011, 2012; Rinaudo, 2006). It has both reactive amino and hydroxyl groups that can be used to chemically alter its properties under mild reaction conditions. It is a bio-adsorber with gel forming ability (De Morais, Pereira, & Fonseca, 2012). The superabsorbent resins grafted with chitosan can absorb aqueous solutions up to hundreds of times their own dry weight (Ge, Pang, & Luo, 2006; Nge, Hori, Takemura, & Ono, 2004) and should have the antibacterial activities (El-Mekawy, Hudson, El-Baz, Hamza, & El-Halafawy, 2010). An effective approach to modify swelling behavior of chitosan resin in various pHs is graft polymerization of vinylic monomers such as acrylic acid, acrylamide, acrylonitrile onto chitosan (Borzacchiello et al., 2001; Mahdavinia, Pourjavadi, Hosseinzadeh, & Zohuriaan, 2004; Sing, Tiwari, & Tripathi, 2006). The superabsorbent composites of chitosan have been widely studied (Kabiri, Omidian, Zohuriaan-Mehr, & Doroudiani, 2011; Spagnol et al., 2012; Yu, Liu, Kong, Zhang, & Liu, 2011).

The acrylic acid (AA)-based superabsorbents are mainly prepared by the radical copolymerization under redox initiators and crosslinkers (Liu et al., 2011; Yin et al., 2007; Zohuriaan-Mehr & Kabiri, 2008). However, the use of the initiator and crosslinker increases production cost and they are harmful or toxic substances. As medical and agricultural supplies, the trace of them in SAPs may be not friendly (Kosemund et al., 2009; Rai et al., 2009). Therefore,

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the preparation of superabsorbents with no use of chemical catalyst or promoter is important for personal care products and medical materials. Some articles were published on the effect of the temperature on the structural modification of chitosan by acrylic acid and related compounds, essentially via amide formation (Gallardo, Aguilar, Elvira, Peniche, & Roman, 2005; Jeung & Mishra, 2011; Qu et al., 1997) that evolved into methods for the regeneration of chitin and chitin analogs from chitosan (Qu, Wirsen, & Albertsson, 1999; Toffey & Glasser, 1999). In these studies, however, acrylic acid or poly acrylic acid (aqueous) was usually used directly as a solvent of chitosan and the products were water-soluble or hydrophilic gels with smaller water absorbing capacities (Sashiwa, Yamamori, Ichinose, Sunamoto, & Aiba, 2003; Skorik, Pestov, Kodess, & Yatluk, 2012). In our paper, formic acid solution was used as a solvent of chitosan and the thermal reaction of chitosan with acrylic acid was carried out with no use of initiators, catalysts or crosslinkers, with a view at the production of indisputably safe superabsorbents offering enhanced performances.

2. Experimental

2.1. Materials

Biochemical reagent grade chitosan (viscosity average molecular weight: 400 kDa) was purchased from China National Medicine Corporation Ltd. (Shanghai, China). The deacetylation degree of chitosan (90%) was determined by the acid–base titration (Jia & Li, 2002). Analytical-grade acrylic acid purchased from Kemiou Chemical Reagent Corporation Ltd. (Tianjin, China) was used without further purification. Other chemical agents used were all analytical grade and all solutions were prepared with distilled water.

2.2. Thermal preparation of chitosan–acrylic acid superabsorbent

1 g of chitosan powder and 44 mL water were added to a three-neck reactor with stirring. After 1 h, 6 mL of 5%(w/w) formic acid solution was added into the reactor and the mixture was stirred until to form the uniform solution. Meanwhile, 28 mL of 5% (w/w) sodium hydroxide solution was added dropwise to the acrylic acid solution (3 mL) in a 100 mL beaker cooled with an ice bath for partial neutralization. Then, the reactor with stirring was placed in a thermostated oil bath preset at the desired temperature (70–90 °C) under atmospheric pressure. The neutralized acrylic acid was dropwise added to the reactor. After reacting for some time in an air atmosphere, the mixture was allowed to cool to room temperature and neutralized into the week alkalinity by adding 5% NaOH solution. The flocculent product was filtered with a 100-mesh steel screen and washed with diluted hydrochloric acid (pH = 4–5) to be neutral. After soaking for 24 h in 75% aqueous alcohol to remove the unreacted materials and dehydrated for 2 h in pure alcohol, the specimen was vacuum dried at 60 °C until the weight became constant. After being grounded and sieved with a 100-mesh steel screen, a powdered superabsorbent was obtained.

Some variables of the above thermal reaction exposed to air were optimized. Using these optimized variables which the reaction temperature, time, ratio of volume of acrylic acid to mass of chitosan, neutralization degree of acrylic acid were 80 °C, 1 h, 3 mL/g, 80%, respectively, the thermal preparation in a nitrogen atmosphere was also done.

The reaction yield was calculated according to the following equation:

$$\text{Yield}\,(\%) = \frac{W_2}{W_1} \times 100 \quad (1)$$

where W_1 and W_2 are the weights of the raw chitosan and the product, respectively.

2.3. Radical inducing preparation of chitosan–acrylic acid polymer

In order to compare with the thermal prepared products, the radical inducing product was prepared and the optimized variables of the thermal preparation exposed to air were referred in the radical inducing reaction. 1 g of chitosan powder and 44 mL water were added to a three-neck reactor with stirring. After 1 h, 6 mL of 5%(w/w) formic acid solution was added and the mixture was stirred until to form the uniform solution. Then, the reactor with stirring was placed in a thermostated oil bath preset at 80 °C and filled with the nitrogen. 5 mL of 0.056 mol/L potassium peroxydisulfate (radical initiator) solution was slowly added to the reactor under nitrogen atmosphere. Meanwhile, 3 mL of acrylic acid was neutralized with 28 mL of 5% NaOH solution. The partial neutralized acrylic acid and 5 mL of 0.0043 mol/L *N*,*N*-methylenebisacrylamide (crosslinker) solution were added to the reactor, respectively. After reacting for 1 h in the nitrogen atmosphere, the mixture was allowed to cool to room temperature and neutralized into the week alkalinity by adding 5% NaOH solution. The product was filtered with a 100-mesh steel screen and washed with diluted hydrochloric acid (pH = 4–5) to be neutral. After soaking for 24 h in 75% aqueous alcohol to remove the unreacted materials and dehydrated for 2 h in pure alcohol, the specimen was vacuum dried at 60 °C until the weight became constant. After being grounded and sieved with a 100-mesh steel screen, a powdered superabsorbent was obtained.

2.4. Characterization

Infrared spectra (IR) were recorded on a Bruker FT-IR spectrometer (Vector 33). Thermogravimetric analysis (TGA) was carried out on a Universal V4.1 DTA instrument (SDTQ600) under nitrogen atmosphere. X-ray diffraction patterns (XRD) were determined with a Rigaku diffractometer (D/max-IIIA). Solid-state ^{13}C nuclear magnetic resonance (NMR) was performed on a Bruker NMR spectrometer (Avance AV–400 MHz). Elemental analysis was done on a Bruker element analyzer (Vario ELCube).

2.5. Measurement of water absorbency

The powdered superabsorbent resin (0.1 g) was dispersed in distilled water (100 mL) for at least 4 h at room temperature (20–24 °C) to reach swelling equilibrium, which resulted in the absorption of water inside the network of the resin and the formation of swelled sample. The residual water was removed by filtrating with 100-mesh stainless steel screen and until water ceased to dropped. The weight of the resin containing absorbed water was measured after draining for 10 min, and the water absorbency was calculated according to the following equation:

$$\text{Absorbency}\,(\text{g/g}) = \frac{W' - W}{W} \quad (2)$$

where W and W' are the weights of the dry and swollen superabsorbent resin, respectively.

3. Results and discussion

3.1. Optimization of thermal prepared conditions of chitosan–acrylic acid polymer in air atmosphere

In order to select the optimization factor of the reaction, several preliminary experiments have been carried out. The experimental results showed that the reaction time needed 1 h to obtain the higher yield and water absorbency.

Table 1
Orthogonal experimental arrangement and test result.

Experiment number		Variables and their levels (values)				Absorbency (g/g)
		A-Reaction temperature	B-Reaction time	C-Ratio of volume of acrylic acid to mass of chitosan	D-Neutralization degree of acrylic acid	
1		1 (70 °C)	1 (1 h)	1 (1 mL/g)	1 (40%)	5.31
2		1 (70 °C)	2 (1.5 h)	2 (3 mL/g)	2 (60%)	19.31
3		1 (70 °C)	3 (2 h)	3 (4 mL/g)	3 (80%)	307.6
4		2 (80 °C)	1 (1 h)	2 (3 mL/g)	3 (80%)	**644.3**
5		2 (80 °C)	2 (1.5 h)	3 (4 mL/g)	1 (40%)	83.1
6		2 (80 °C)	3 (2 h)	1 (1 mL/g)	2 (60%)	205.8
7		3 (90 °C)	1 (1 h)	3 (4 mL/g)	2 (60%)	161.1
8		3 (90 °C)	2 (1.5 h)	1 (1 mL/g)	3 (80%)	403.3
9		3 (90 °C)	3 (2 h)	2 (3 mL/g)	1 (40%)	0
Average	Levels 1	110.7	**270.2**	204.8	29.5	Total average=203.3
	Levels 2	**311.1**	168.6	**221.2**	128.7	
	Levels 3	188.1	171.1	183.9	**451.7**	
Variance (average)		200.3	101.7	37.3	422.3	

The bold values represent the maximum values of the variables.

The best condition of the reaction was selected from the orthogonal tests. Four independent variables: reaction temperature (°C), reaction time (h), ratio of volume of acrylic acid to mass of chitosan (mL/g), neutralization degree of acrylic acid (%) were chosen, each at three levels. The investigated variables and their test levels are listed in Table 1. Reference to the experimental design theory, the orthogonal array $L_9(3^4)$ was selected to arrange the test program. The water absorbency of the product was a criterion of each test. The test results are also listed in Table 1.

The order of influence of each variable on the water absorbency appears to be D » A > B > C. Thus, the neutralized degree of acrylic acid has the greatest influence and the ratio of volume of acrylic acid to mass of chitosan has the smallest influence. The optimum level of each variable is A-2, B-1, C-2, D-3. Therefore, the optimum reaction conditions were as follows: reaction temperature, 80 °C; reaction time, 1 h; ratio of volume of acrylic acid to mass of chitosan, 3 mL/g; neutralized degree of acrylic acid, 80%. Under these conditions, the product could absorb water 644.3 times its own dry weight.

3.2. Single variable analysis of thermal prepared conditions

3.2.1. Effect of reaction temperature

To study the effect of reaction temperature on the reaction, the other reaction variables were adopted as the optimal levels: reaction time, 1 h; ratio of volume of acrylic acid to mass of chitosan, 3 mL/g; neutralized degree of acrylic acid, 80% and reaction temperature was adjusted. The impact of reaction temperature on reaction yield and water absorbency of the product is given in Fig. 1(a). The reaction yield and water absorbency increase with the increase of the reaction temperature till a maximum value at 80 °C and then decrease with further increase of temperature. Based on the later suggested mechanism, thermal preparation includes the reactions of auto-polymerization and grafting of acrylic with chitosan. Higher temperature can assist the auto-polymerization of the acrylic acid which leads to reduce the grafting yield. At the same time, the chitosan grafted with the shorter or longer chain of acrylic autopolymer weakens the flexible extension of the polymer network which leads to reduce the water absorbency. Therefore, the more proper reaction temperature should be 80 °C. Under these conditions, the reaction yield was 89% and the resin could absorb water 644 times its own dry weight.

3.2.2. Effect of reaction time

The effect of reaction time was examined while keeping the other reaction variables on the above mentioned conditions: reaction temperature, 80 °C; ratio of volume of acrylic acid to mass of chitosan, 3 mL/g; neutralized degree of acrylic acid, 80%. The impact of reaction time on reaction yield and water absorbency of the product is given in Fig. 1(b). The reaction yield and water absorbency increase with the increase of the reaction time till a maximum value at 1 h and then decrease with further increase of time. These could be explained that increase of reaction time assists the auto-polymerization reaction of acrylic acid. Therefore, the more proper reaction time should be 1 h, and the reaction yield and water absorbency were 89% and 644 g/g, respectively.

3.2.3. Effect of ratio of reactants

The effect of ratio of reactants was also investigated while the other variables were kept on the above mentioned conditions: reaction temperature, 80 °C; reaction time, 1 h; neutralized degree of acrylic acid, 80%. The impact of ratio of volume of acrylic acid to mass of chitosan on reaction yield and water absorbency of the product is given in Fig. 1(c). The results indicate that the effects of the ratio on the yield and water absorbency are slightly different. With the increase of the ratio, the reaction yield increases remarkably, however, increases slightly when the ratio exceeds 3 mL/g. The water absorbency increases with the increase of the ratio till a maximum value at the ratio of 3 mL/g and then decreases with further increase of the ratio. These might be explained that increase of the ratio leads to fierce competition between auto-polymerization of acrylic acid and the grafting or linking of chitosan with acrylic acid. Therefore, the more proper ratio of volume of acrylic acid to mass of chitosan should be 3 mL/g, and the reaction yield and water absorbency were 89% and 644 g/g, respectively.

3.2.4. Effect of neutralization degree of acrylic acid

The effect of neutralized degree of acrylic acid was also investigated while the other variables were kept on the above mentioned conditions: reaction temperature, 80 °C; reaction time, 1 h; ratio of volume of acrylic acid to mass of chitosan, 3 mL/g. The impact of neutralization degree on reaction yield and water absorbency of the product is given in Fig. 1(d). The results indicate that the effects of the neutralization degree on reaction yield and water absorbency are similar. The reaction yield and the water absorbency increase with the increase of the neutralization degree till a maximum value at neutralization degree of 80% and then decrease with further increase of the neutralization degree. In fact, when the neutralization degrees of acrylic solution are 40%, 60%, 80% and 100%, the pH of the solution are 4.5, 4.9, 5.7 and 12.7, respectively. The increase of the neutralization degree from 40% to 80% causes little increase of solution pH but more carboxylic acid anions are got. The increase of the carboxylic acid anions would enhance the repulsive

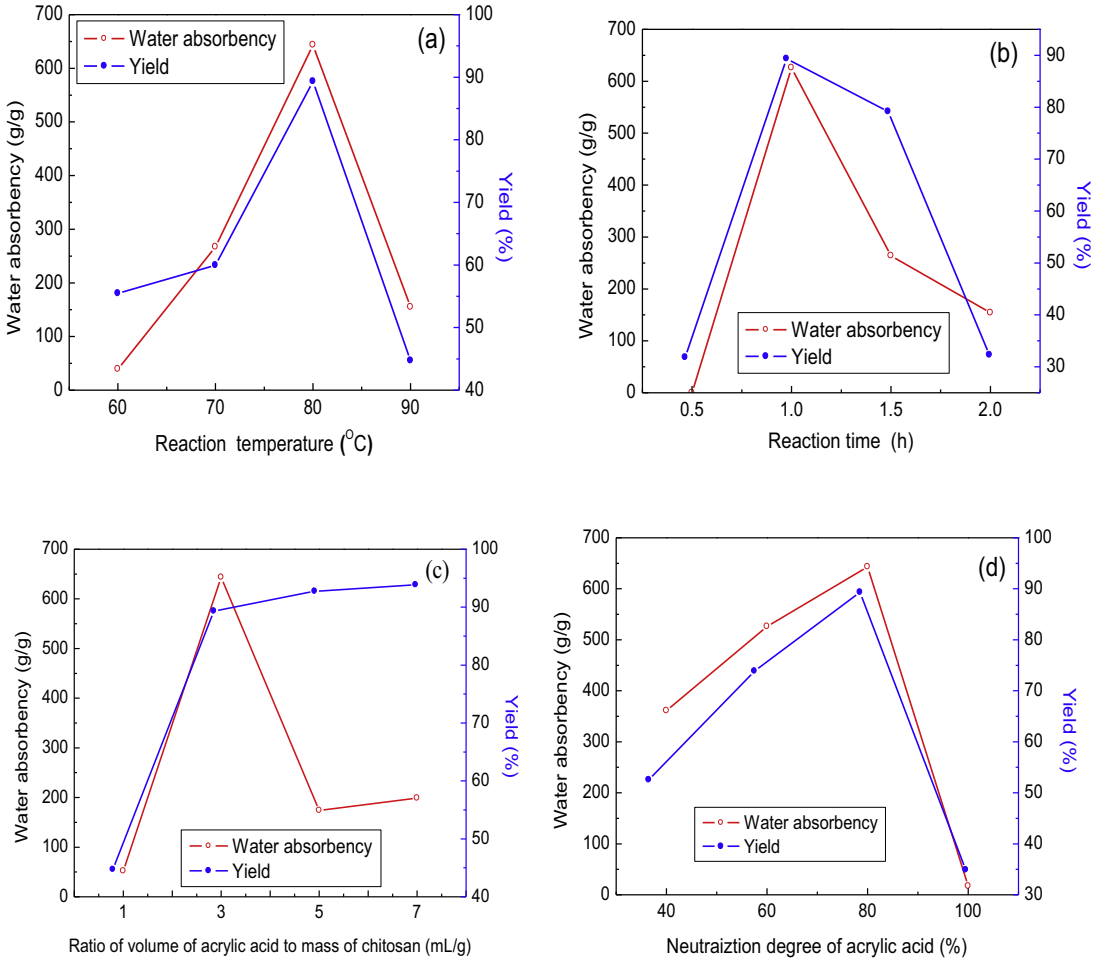

Fig. 1. Effect of reaction temperature (a), reaction time (b), ratio of reactants (c) and neutralization degree of acrylic acid (d) for water absorbency and yield.

force among chains, which strengthen the impetus of the extension of polymer network (Yu et al., 2011). Therefore, the yield and water absorbency increase. However, when excess NaOH is added into the reaction solution, excess Na cations shield the charge of the carboxylate anions and thus prevent effective repulsion between carboxylate anions. So, the yield and water absorbency decrease. Hence, the more proper neutralization degree of acrylic acid should be 80%, and the reaction yield and water absorbency were 89% and 644 g/g, respectively.

3.3. Comparison of water absorbency of products prepared by different methods

The three products were prepared by thermal reactions in atmospheric pressure air, in nitrogen atmosphere and radical inducing reaction and named as SAP-A, SAP-N and SAP-R, respectively in following discussion. The reaction yields were 89%, 87% and 300%, respectively. The water absorbency of the three products was 644, 621 and 321 g/g, respectively. Apparently, the two thermal reactions have almost same yields and corresponding products have similar water absorbency. However, the yield of thermal reaction was lower than that of the radical inducing reaction and the water absorbency of thermal prepared product was larger than that of radical inducing product. In fact, the water absorbency of 704 g/g for the similar product prepared by the radical inducing had been reported (Ge et al., 2006). These mean that the chitosan–acrylic acid resin prepared by the thermal reaction had water absorbency equivalent to that prepared by the traditional radical inducing reaction.

3.4. Characterization of products

3.4.1. FT-IR analysis

The FT-IR spectra of the raw chitosan, SAP-R, SAP-N and SAP-A before and after acid treatment with 0.1 mol/L HCl aqueous are shown in Fig. 2. Fig. 2(a) shows that the main characteristic peaks of chitosan are at 3446 cm^{-1} (O—H stretch), 2920 cm^{-1} (CH_2 asymmetric stretch), 2875 cm^{-1} (C—H stretch), 1656 (amide band), 1599 cm^{-1} (NH_2 band), 1322 cm^{-1} (C—N stretch), 1156 cm^{-1}

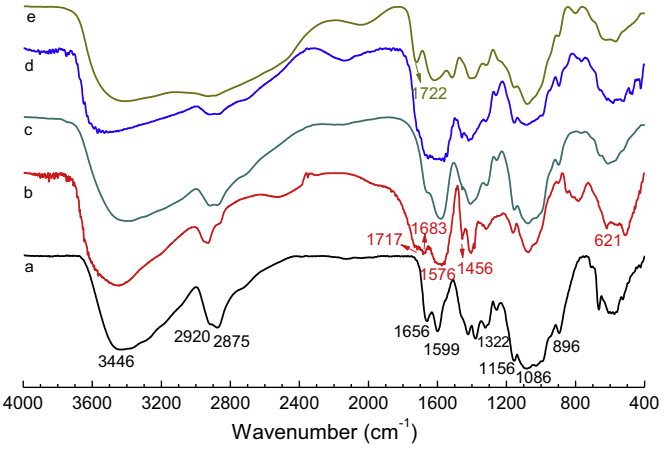

Fig. 2. FT-IR spectra of chitosan (a), SAP-R (b), SAP-A (c), SAP-N (d) and acidified SAP-A (e).

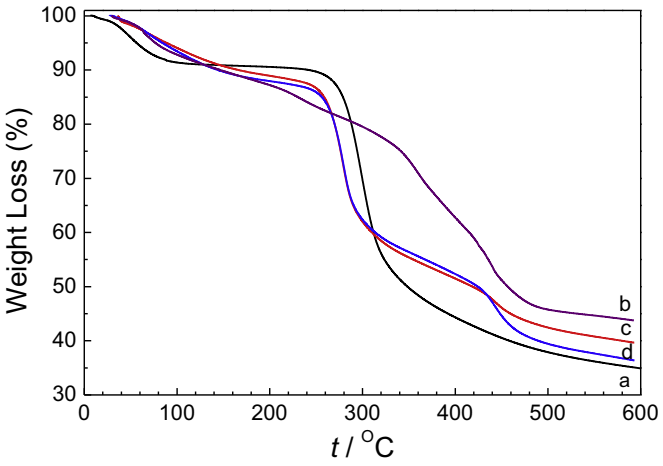

Fig. 3. TGA of chitosan (a), SAP-R (b), SAP-A (c) and SAP-N (d).

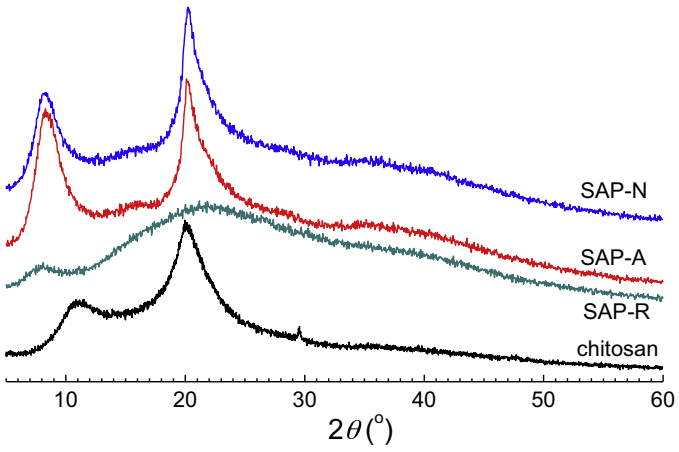

Fig. 4. XRD of chitosan and three products.

(bridge O stretch), 1086 cm^{-1} (C—O stretch) and 896 cm^{-1} (pyranoid ring stretch). In the spectra of three products, in addition to the chitosan characteristic peaks, some new absorption peaks appear. For the radical inducing product SAP-R (Fig. 2(b)), the peaks at 1717, 1683, 1576, 1456 and 621 cm^{-1} are the characteristic peaks of poly (acrylic acid) (Ge et al., 2006) and the peaks at 1717 and 1683 cm^{-1} correspond to COOH and COO^- groups. For the thermal prepared products SAP-A and SAP-N (Fig. 2(c) and (d)), the peaks near 1576, 1456 and 621 cm^{-1} have not been changed. However, the peaks at 1716 and 1683 cm^{-1} become unapparent. For the thermal product SAP-A (Fig. 2(e)) after the acid treatment, the COOH group peak at 1722 cm^{-1} becomes very apparent. Therefore, the structures of the three products should be similar in some way and the acrylic acid in polymer was linked on chitosan.

3.4.2. TGA analysis

The change of chitosan structure before and after chemical modification was also supported by thermogravimetric analysis (Fig. 3). TGA of chitosan shows a weight loss in two stages. The first stage ranges between 20 and 100 °C and shows about 8% loss in weight. This may correspond to the loss of adsorbed and bound water. The second stage of weight loss starts at 210 °C and continues up to 440 °C during which there was 48% weight loss due to the degradation of chitosan. However, the TGA of the radical inducing product SAP-R is slightly different and shows three stages of weight loss. The first stage of weight loss starts at 30 °C and continues up to 130 °C, during which there was 9% weight loss due to the loss of adsorbed and bound water. The second stage from 190 to 330 °C and the third stage from 330 to 500 °C may contribute to the degradation of chitosan and the decomposition of different structure of the graft copolymer, respectively. For the thermal prepared products SAP-A and SAP-N, their TGAs are very similar and show three stages of weight loss. The first and third stages of weight loss are similar to ones of SAP-R. The second stage of weight loss is similar to that of chitosan. Therefore, the alteration of chitosan structure in two thermal reactions was less than that in the radical inducing reaction.

3.4.3. XRD analysis

The change of chitosan structure before and after chemical modification was further investigated by means of powder X-ray diffraction (Fig. 4). The XRD pattern of chitosan represents the distinct crystalline peaks at 2θ 11.5° and 20.0°. This is because plenty of hydroxyl and amino groups of the chitosan structure could form stronger intermolecular and intramolecular hydrogen bonds. In addition, the structure of chitosan molecules has certain regularity. As a result, chitosan molecules can form crystalline regions very easily (Ge, Chen, & Huang, 2012). For the radical inducing product SAP-R, however, the characteristic peaks decrease obviously and are shifted to 8.1° and 21.2°. The less peak intensity means that large amount of acrylic had been grafted on chitosan. For the thermal prepared products SAP-A and SAP-N, the two characteristic peaks at 8.1° and 20.1° are strong. These further indicate that the chitosan structure of the thermal reaction was less changed than that of the radical inducing reaction.

3.4.4. Elemental analysis

Elemental analyses were used to estimate the deacetylation degree or grafting degrees of chitosan. Because the water contents in the chitosan and products were difficult to be accurately determined, the molar ratios of atoms C to N were used to calculate the possible formulas $(Chitin)_{1-x}$ (Chitosan-y AA)$_x$ where x was the deacetylation degree of chitosan and y was the grafting (polymerization) degree of acrylic acid (AA) in products. The results are listed in Table 2. The deacetylation degree of chitosan is 86.8% which was approached the value (90%) determined by the acid–base titration. The grafting degrees for three products are 0.592, 0.993 and 3.436, respectively. For the two thermal products SAP-A and SAP-N, the grafting degrees are less than 1. These mean that the acrylic acid units in the products were linked to chitosan mainly in monomer and dimer. For the radical initial product SAP-R, however, higher grafting degree (3.436) indicates that the acrylic acid units in the product were linked to chitosan mainly in copolymer.

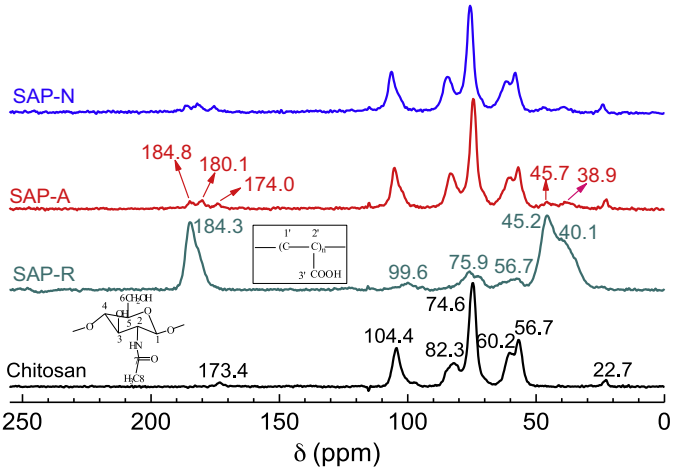

Fig. 5. Solid-state ^{13}C NMR of chitosan and three products.

Table 2
The results of elemental analyses for chitosan and three products.

Material	wt (%)				Molar ratio of C/N	Deacetylation degree	Grafting degrees
	C	N	H	O			
Chitosan	39.75	7.40	7.09	47.42	6.26	0.868	
SAP-A	38.89	5.81	7.42	52.1	7.81		0.592
SAP-N	38.4	5.06	7.71	53.93	8.85		0.993
SAP-R	37.95	2.91	7.03	54.66	15.21		3.436

3.4.5. NMR analysis

Solid-state ^{13}C NMR spectra were used to confirm the graft structure of the products (Fig. 5). For chitosan, the chemical shift values 56.7, 60.2, 74.6, 82.3, 104.4, 173.4 and 22.7 ppm correspond to C2, C6, C3 (C5), C4, C1, C7 and C8, respectively. For the radical inducing product SAP-R, the chemical shift values 56.7,75.6 and 99.6 ppm correspond to C2 (C6), C3 (C4, C5), C1 of the chitosan structure and the chemical shift values 40.1,45.2 and 184.3 ppm

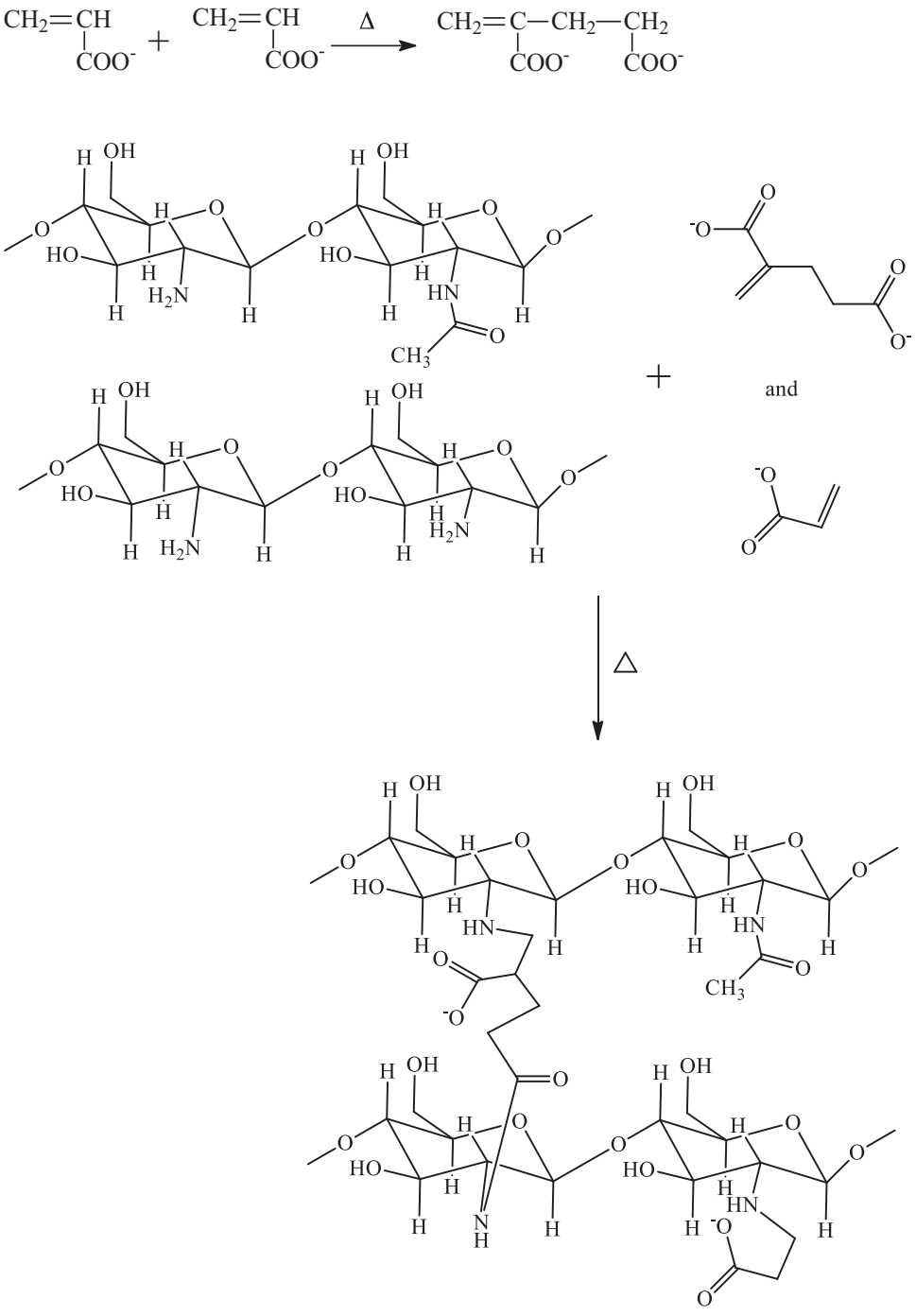

Fig. 6. Possible mechanism for the thermal preparation of chitosan–acrylic acid superabsorbent.

correspond to C1′, C2′ and C3′ of the graft poly (acrylic acid). For the thermal prepared products SAP-A and SAP-N, their NMR spectra are similar and have the main characteristic peaks of chitosan and graft poly (acrylic acid) units. However, the main characteristic peaks of the graft poly (acrylic acid) units are weak. Hence, the grafting degrees of chitosan in two thermal prepared products should be smaller than that of the radical inducing product. These should be in agreement with the results of elemental analyses. In addition, two different C3′ (184.8 and 180.1 ppm) in SAP-A indicate that the thermal reaction of acrylic acid with chitosan might form *N*-carboxyethyl grafted and amide-linked polymer.

3.5. Thermal prepared mechanism of the superabsorbent

The thermal reaction of acrylic acid with chitosan can be carried out in air and N_2 atmospheres without using initiator and the yields and the structures of the products were similar. The pH of the reacting systems kept near 5–6 in whole reaction processes. About 0.05% radical inhibitor existed in the acrylic acid reagent would not also support the radical reaction. Without catalyst, however, chitosan could react with acrylic acid to form the soluble *N*-carboxyethyl chitosan by the Michael reaction (Sashiwa et al., 2003; Skorik et al., 2012) when the temperature was about 50–70 °C. In addition, we found that the acrylic acid or partly neutralized solutions could fastly auto-polymerized to form the solids in air atmosphere when the temperature was higher than 110 °C. These results indicate that the reaction should not be by the radical mechanism. Under out experimental conditions, the acrylic acid (salts) could form the dimer by the ionic chain or Diels–Alder cycloaddition ways (Hall & Padias, 2009). The monomer and dimer of acrylic acid (salts) with chitosan might form *N*-carboxyethyl grafted and amide-linked polymers which have higher water absorbing capacity. The possible mechanism is given in Fig. 6.

4. Conclusions

A superabsorbent polymer was successfully synthesized by the thermal reaction of chitosan with acrylic acid without using radical initiator and crosslinker in air at atmospheric pressure. The reaction conditions were optimized. Under the optimized conditions, the reaction yield was 89% and the water absorbency of product was 644 g/g. The reactions in nitrogen atmosphere and induced using radical initiator were also done. The results showed that the reaction in air was similar that in nitrogen and the yield of thermal reaction was lower than that of the radical inducing reaction. However, the thermal prepared products had water absorbency equivalent to the radical inducing product. FT-IR, TGA, XRD, ^{13}C NMR and elemental analyses indicated that the thermal prepared materials might form *N*-carboxyethyl grafted and amide linked polymers and the grafting degrees were low. The possible mechanism for the thermal reaction was suggested. Because the thermal preparation of the superabsorbent did not use any one radical initiator and crosslinker which are harmful or toxic for human body and natural environment, this would be a friendly synthesized method and might be extended to the copolymerization reactions of acrylic monomer with other molecules. For the applications in the biomaterials area, the thermal prepared resin would be safer than the traditional radical inducing.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.06.078.

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