Synthesis and Properties of Chitosan-Modified Poly(acrylic acid)

Chung-Yang Chuang,[1] Trong-Ming Don,[2] Wen-Yen Chiu[1,3,4]

[1]*Institute of Polymer Science and Engineering, National Taiwan University, Taipei 106, Taiwan*
[2]*Department of Chemical and Materials Engineering, Tamkang University, Tamsui, Taipei 251, Taiwan*
[3]*Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan*
[4]*Department of Materials Science and Engineering, National Taiwan University, Taipei 106, Taiwan*

ABSTRACT: Potassium persulfate ($K_2S_2O_8$) was used to initiate the polymerization of acrylic acid (AA) monomer in a chitosan (CS) solution. Both a poly(acrylic acid) (PAA) homopolymer and a CS-*co*-PAA copolymer were produced. When the amount of AA was increased from 5 to 40 g with 5 g of CS, the total monomer conversion was found to increase from 89 to 98% after 2 h of reaction at 70°C. In addition, the percentage of reacted AA monomer being converted to the CS-*co*-PAA copolymer (copolymerization efficiency) and the weight composition of the PAA portion in the copolymer (copolymer composition) both increased with the amount of AA added. The structures and properties of the synthesized CS-modified PAA polymers were studied. In Fourier transform infrared spectra, the formation of a polyelectrolyte complex between CS chains and PAA chains could be observed. From the thermograms obtained via differential scanning calorimetry, we found that the presence of rigid CS chains increased the glass-transition temperature of PAA. Thermogravimetric analysis revealed three stages of degradation of the synthesized CS-modified PAA polymers. The swelling ratio of the CS-modified PAA polymers depended on the pH value and had a maximum value in a buffer solution at pH 7. This was due to the changes in the morphological structure with the pH value. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3382–3389, 2008

Key words: copolymerization; modification; radical polymerization; swelling; thermal properties

INTRODUCTION

Chitosan (CS) is a derivative obtained by partial deacetylation of chitin, which is the most abundant natural polysaccharide next to cellulose and can be found in the skeletal materials of crustaceans and insects and cell walls of bacteria and fungi. Because of several biological properties, including biodegradability, biocompatibility, antibactericity, and nontoxicity, CS can be used in the fields of wastewater treatment, food processing, cosmetics, pharmaceuticals, biomaterials, and agriculture.[1–3] Yet, CS is a low-acid-resistance material, and this limits its applications. To overcome this problem, hybridization of natural CS with synthetic polymers has been used to improve its antiacid property.[4–10] In our laboratory, we have found that CS chains undergo degradation in the presence of potassium persulfate (KPS or $K_2S_2O_8$) in a CS solution. At each scission, two shorter chains are produced with a free radical at one chain end and a terminal carbonyl at the end of the other chain. The reaction mechanism has been described in detail elsewhere.[11] From the reaction mechanism, it is expected that if KPS were used to initiate the polymerization of vinyl monomers in the presence of CS, not only would degradation of CS occur, but it would also affect the polymerization rate and structures. A CS copolymer, in addition to the homopolymer, is expected to be produced by the addition of vinyl monomers to CS chain radicals or a combination of growing polymer chain radicals with CS chain radicals. In this study, KPS was used to initiate the polymerization of acrylic acid (AA) monomer in the presence of CS, and a new material with desired properties was achieved. Both CS and poly(acrylic acid) (PAA) can absorb a great amount of water; therefore, the chemical combination of CS and PAA might have potential for superabsorbent materials with antibacterial and biodegradable properties. After polymerization, the thermal properties and swelling behaviors were examined, and they are reported in this article.

EXPERIMENTAL

Materials

CS was obtained from Tokyo Chemicals, Inc. (Tokyo, Japan). The degree of deacetylation was determined

by a colloid titration method[12] as well as a Fourier transform infrared (FTIR) method, which gave values of 86 and 84%, respectively. The viscosity-average molecular weight was found to be 616,000 by a viscometric method; the Mark–Houwink constants k and α were 1.38×10^{-2} and 0.85, respectively.[14] AA monomer from Tedia Chemical Co. (Fairfield, OH) was distilled under reduced pressure (<5 mmHg) at 60°C. Only the distillate obtained in the middle stage of distillation was used for polymerization. KPS (K$_2$S$_2$O$_8$) was a reagent grade from Janssen Chemicals (Geel, Belgium). The compositions of the different buffer solutions were as follows. The buffer solution at pH 4 was prepared by the addition of 10.12 g of anhydrous potassium hydrogen phthalate to 1000 mL of deionized water. The buffer solution at pH 7 was prepared by the addition of 3.387 g of potassium dihydrogen phosphate and 3.533 g of disodium hydrogen phosphate to 1000 mL of DI water. The buffer solution at pH 9 was prepared by the dissolution of 1.99 g of anhydrous sodium borate decahydrate in 1000 mL of DI water. All the other chemicals were analytical-grade or higher and were used as received without further purification.

Synthesis of CS-modified PAA

A specific amount of CS (5 g) was first dissolved in an aqueous solution of AA. The solution was purged with nitrogen and heated to 70°C in an isothermal water bath. KPS was dissolved in 20 mL of water and preheated to 70°C before it was poured into the solution. After 2 h of reaction, a dispersion aqueous solution containing the PAA homopolymer and CS-co-PAA copolymer was obtained, and it was called CS-modified PAA. The dispersion solution was taken out for dialysis for 96 h at room temperature with a dialysis membrane with a molecular weight cut-off of 6000 g/mol to remove the residual KPS and unreacted monomer. To prepare sample membranes for testing the properties, a drying process was employed. The dispersion solution was cast into a stainless mold and then dried for 48 h in a circulation oven; this was followed by another 48 h in a vacuum oven at 60°C with a pressure lower than 5 mmHg. The reaction conditions and sample codes of the membranes are listed in Table I. In addition, the total monomer conversion (X) was calculated by gravimetric analysis with the following equation:

$$X\ (\%) = \frac{(W_1 - W_{CS})}{(W_{AA})} \times 100 \qquad (1)$$

where W_{CS} and W_{AA} are the initial weights of the CS and AA monomer, respectively, and W_1 is the final weight of the drying product containing the

TABLE I
Reaction Conditions, Conversions, CC$_{PAA}$ Values, CE Values, and Sample Codes of the Final Samples from Different Reaction Systems

Reaction condition	System		
	CAK55	CAK520	CAK540
CS (g)	5	5	5
AA (g)	5	20	40
K$_2$S$_2$O$_8$ (mol)	2.77×10^{-3}	2.77×10^{-3}	2.77×10^{-3}
H$_2$O (g)	500	500	500
Temperature (°C)	70	70	70
Stirring speed (rpm)	300	300	300
Conversion (%)	89.4	91.4	97.5
CC$_{PAA}$	0.072	0.757	0.873
CE (%)	8.7	85	88.5

CAK55, CAK520, CAK540 are the sample codes of chitosan-modified poly(acrylic acid).

CS-co-PAA copolymer and PAA homopolymer. To calculate the percentage of the reacted AA being converted to form the CS-co-PAA copolymer [i.e., apparent copolymerization efficiency (CE)] and the composition of PAA in the CS-co-PAA copolymer [i.e., apparent copolymer composition (CC$_{PAA}$)], 0.1M aqueous NaOH was used to dissolve the PAA homopolymer from the drying product. After 48 h of dissolution, the remaining CS-co-PAA copolymer was washed repeatedly with DI water until it was neutral. Elemental analysis confirmed that no CS copolymer was dissolved in the NaOH solution. It was then dried, and the weight was measured (W_2). CC$_{PAA}$ and CE were calculated with the follow equations:

$$CC_{PAA} = \frac{\text{Weight of PAA in copolymer}}{\text{Weight of copolymer}}$$
$$= \frac{(W_2 - W_{CS})}{W_2} \qquad (2)$$

$$CE\ (\%) = \frac{\text{Weight of PAA in copolymer}}{\text{Total weight of PAA}}$$
$$= \frac{(W_2 - W_{CS})}{(W_1 - W_{CS})} \times 100 \qquad (3)$$

Structure and morphology

Structural analysis was carried out with an FTIR spectrophotometer (SPC3200, Bio-Rad, Cambridge, MA). For obtaining FTIR spectra, a sample was directly mounted on the sample holder and scanned from 4000 to 400 cm^{-1} 64 times to average the signal with a resolution of 4 cm^{-1}. A scanning electron microscope (S-800, Hitachi, Tokyo, Japan, or JSM-

6300, JEOL, Tokyo, Japan) was used to observe the surface morphology of sample membranes prepared with two different drying processes. In a direct oven-drying process, a sample solution was cast into a stainless mold and then dried for 48 h in a circulation oven followed by another 48 h in a vacuum oven at 60°C. To observe the morphology of a swollen sample, the sample was first swollen in a buffer solution at a specific pH value; it was then removed to a freezer at −20°C for 24 h, and this was followed by lyophilization. All samples were coated with a conductive layer of sputtered gold before scanning electron microscopy (SEM) observations.

Thermal properties

A differential scanning calorimeter (TA 2010, TA Instruments, New Castle, DE) was used to observe thermograms of the sample membranes. Nitrogen was purged into the cell. The samples were placed in aluminum pans and scanned from 25 to 250°C at a heating rate of 10°C/min. A midpoint method was employed to estimate the glass-transition temperature (T_g). A thermogravimetric analyzer (TGA-7, PerkinElmer, Shelton, CT) was employed to measure the weight loss of samples under heating. Samples were first held at 155°C for 15 min to remove moisture completely and then heated from 155 to 550°C at a heating rate of 10°C/min.

Swelling behaviors

The preweighed samples were immersed in several buffer solutions with different pH values at 30°C to observe the swelling behavior. The swollen samples were removed at various time intervals, and the water droplets on the surface were wiped off with filter paper. The weight of the swollen samples was measured, and the samples were reimmersed in the buffer solution. The procedure was repeated until there was no further increase in weight. The swelling ratio (SR) was calculated by the weight of a swollen sample at a specific time divided by the initial weight in the dry state.

## RESULTS AND DISCUSSION

Synthesis of CS-modified PAA

KPS is a thermally dissociated initiator. When heated, it dissociates into anionic sulfate radicals ($\cdot SO_4^-$), which can degrade CS chain into two fragments at each scission: one has a terminal carbonyl group, and the other has a free radical at the scission end.[11] From the reaction mechanism, it is expected that if KPS were used to initiate the polymerization of AA monomer in the presence of CS, not only

would degradation of CS occur, but it would also affect the polymerization. It is expected that the AA monomer could grow on the CS chain radical and thus produce the CS-*co*-PAA copolymer in addition to the PAA homopolymer. In all cases studied in this research, a dispersion was formed after the reaction. When CS was dissolved in an AA solution, some of the amino groups in CS became positively charged because of the reaction with the proton dissociated from the AA: $NH_2 + H^+ \rightarrow NH_3^+$. At the same time, the PAA chains became negatively charged from the carboxylate groups: $COOH \rightarrow COO^- + H^+$. As a result, an insoluble polyelectrolyte complex was produced between cationic CS chains and anionic PAA chains. In this reaction system, because the mobility of PAA segments in the copolymer was restricted by the covalently bonded CS, the polyelectrolyte complex existed mainly between CS and PAA homopolymer chains, and the formation of the polyelectrolyte complex among CS-*co*-PAA copolymer chains was difficult.

Table I shows X, CC_{PAA}, and CE values of various systems after 2 h of reaction at 70°C. The conversion was in the range of 89–98% and increased with an increase in the amount of the AA monomer. The increase in conversion occurred because increasing the AA concentration increased the probability of the AA monomer reacting with the growing chain radical. To calculate CC_{PAA} and CE, a $0.1M$ aqueous NaOH solution was used to extract the PAA homopolymer from the final product. Elemental analysis confirmed that no CS copolymer was dissolved in the $0.1M$ aqueous NaOH solution because no trace of the nitrogen element was detected in the extract. Both CC_{PAA} and CE values increased with an increase in the amount of added AA monomer as well. This occurred because increasing the AA concentration resulted in an increase in the probability of the AA monomer growing on the CS chain end radical, so both CC_{PAA} and CE values were increased.

Structural analysis

Figure 1 shows FTIR spectra of pure CS and PAA. The most important absorption peak in PAA is at 1715 cm^{-1}, caused by the C=O stretching vibration in the carboxylic acid group. The characteristic peaks used to describe CS are the N—H vibration at 1558 cm^{-1} (amide II) and the C=O vibration at 1650 cm^{-1} (amide I) from the acetamide group (—NHCOCH$_3$).[15] Figure 2 shows the FTIR spectrum of a CS-modified PAA sample, CAK520. In the spectrum, not only can the characteristic peaks of PAA and CS be observed, but the NH$_3^+$ absorption peak at 1630 cm^{-1} and COO$^-$ asymmetric stretching absorption at 1547 cm^{-1} can also be found. This evidence confirms that the carboxylic groups of PAA
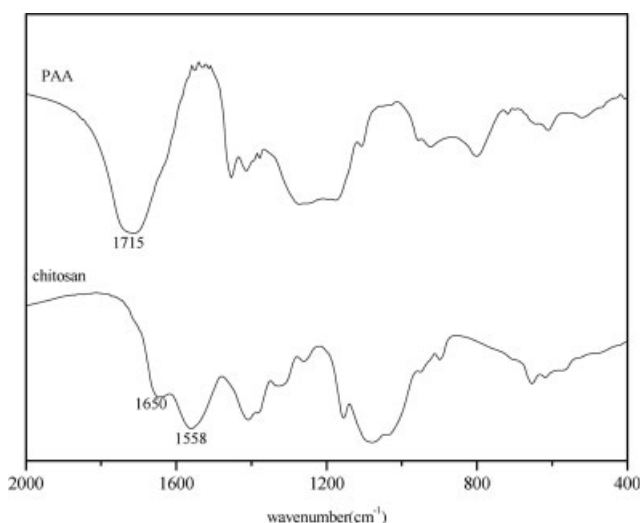
Figure 1 FTIR spectra of the pure PAA and CS.

were dissociated into COO^- groups, which complexed with protonated amino groups of CS through electrostatic interaction.[16–18] Figure 3 displays SEM images of CS and CS-modified PAA membranes prepared by different processes. By the direct oven-drying process, the surface morphologies of CS and CAK520 membranes were like dense, featureless films. By the lyophilization process, in which sample membranes were swollen in water and then freeze-dried, the surface morphologies of CS and CAK520 membranes revealed porous structures, and the CAK520 membrane showed numerous tiny holes in its structure. During the swelling process, water absorption and volume expansion of the sample membrane occurred. The absorbed water was then removed by a freeze-drying process, and this left voids. Because of these numerous voids, the CAK520 membrane could absorb a great amount of water.

Thermal properties

T_g of pure PAA was about 116°C according to the DSC thermogram. For pure CS, the first run in DSC revealed a broad endothermic peak centered at 150°C, which was due to the absorbed moisture and hydrogen bonding in the CS chain. This peak disappeared in the second run, and this indicated that this phenomenon was not reversible. T_g of CS could not be observed in the DSC thermogram because of its highly rigid chain. Table II lists the T_g values of the various samples from different reaction systems. When AA was polymerized in the presence of CS, the increase in T_g was observed. This was because the CS-modified PAA contained not only PAA homopolymer but also a copolymer of CS and PAA. Therefore, the chain segmental motion of PAA in the copolymer was retarded

by the rigid CS chain. Another reason for the large increase in T_g was the formation of the polyelectrolyte complex, especially for sample CAK55, in which the copolymer composition was only 0.072.

Figure 4 shows the TGA curves of CS and pure PAA. PAA started to degrade at 200°C and showed two-stage degradation behavior.[19,20] The first stage, between 200 and 350°C, was caused by the dehydration of carboxylic acid and decarboxylation. The second stage, mainly after 350°C, was due to chain scission in the main chain. CS started to degrade at 210°C and had a broad degradation temperature range with a high char yield at 550°C. The degradation mechanism was very complex, including dehydration, deacetylation, and chain scission.[16,21] The TGA curves of CS-modified PAA samples are shown in Figure 5, in which three stages can be observed. The first-stage degradation, from 200 to 250°C, was attributed to the loss of water due to amidation from the carboxylate group in PAA with the associated positively charged amino group in CS. This amidation was evidenced by FTIR, which is displayed in Figure 6. The CAK520 sample was heated at 250°C for about 1 min, and its FTIR spectrum shows that the NH_3^+ absorption peak at 1630 cm^{-1} and COO^- asymmetric stretching absorption at 1547 cm^{-1} disappeared. It thus proved the occurrence of amidation between CS and PAA chains. Deacetylation of CS and dehydration and decarboxylation of PAA chains caused the second-stage degradation from 250 to 350°C. The third-stage degradation behavior from 350 to 525°C was mainly due to the chain scission in both PAA and CS. It was found that the higher the AA feed was, the lower the char yield was at 550°C. This was because the char yield of pure PAA was much lower than that of pure CS.
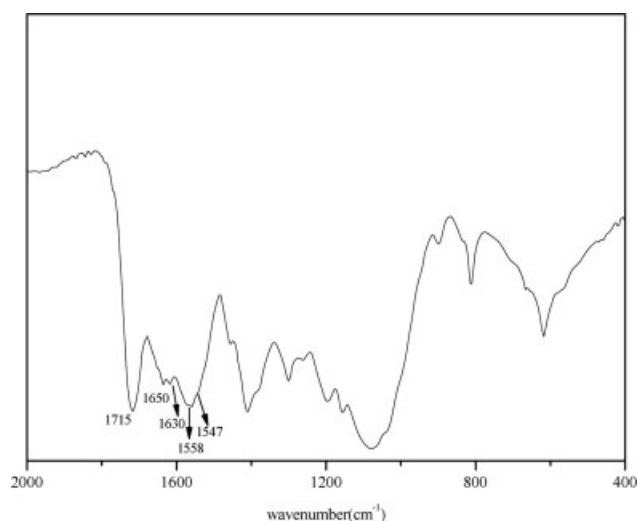
Figure 2 FTIR spectrum of a CS-modified PAA sample (CAK520).
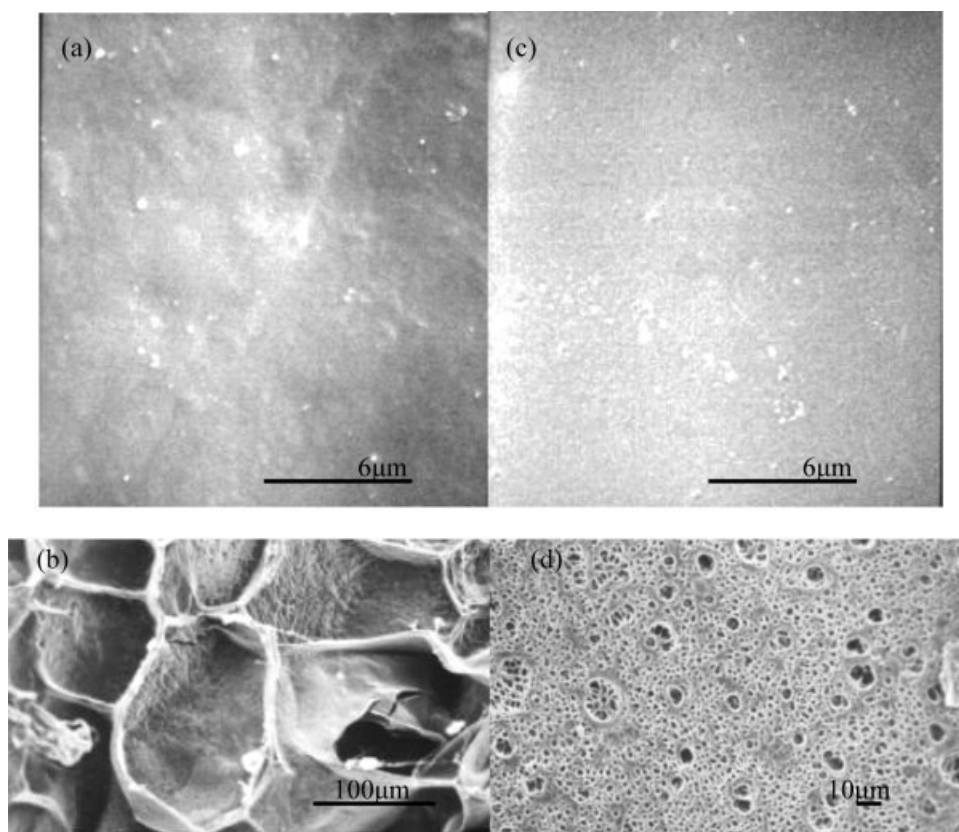
Figure 3 SEM micrographs of CS membranes (a) prepared by the direct oven-drying process, (b) preswollen in a pH 4 buffer and then freeze-dried and CS-modified PAA membranes (CAK520), (c) prepared by the direct oven-drying process, and (d) preswollen in DI water and then freeze-dried.

Swelling behaviors

Figure 7 shows the equilibrium SR of sample membranes in buffer solutions with different pH values. The SR depends on the pH value of the solution and the composition of CS-modified PAA. For the pure CS, the SR increased as the pH value decreased. This was because in a more acidic solution, more amino groups became protonated. At pH 4, 95% of the amino groups became positively charged (NH_3^+).[22] These positively charged groups along the CS chains exerted a repulsive force, which consequently extended the CS chains to a large extent. In addition, the charges in the CS chains resulted in an increase in the ion concentration, causing the water

to easily diffuse into the membrane because of the increasing osmotic pressure inside the structure. For these reasons, the SR of CS was higher in the acidic solution. In the literature, the SR of pure crosslinked PAA increased as the pH value increased. The SR

TABLE II
T_g Values of Various Samples from Different Reaction Systems After 2 h of Reaction at 70°C
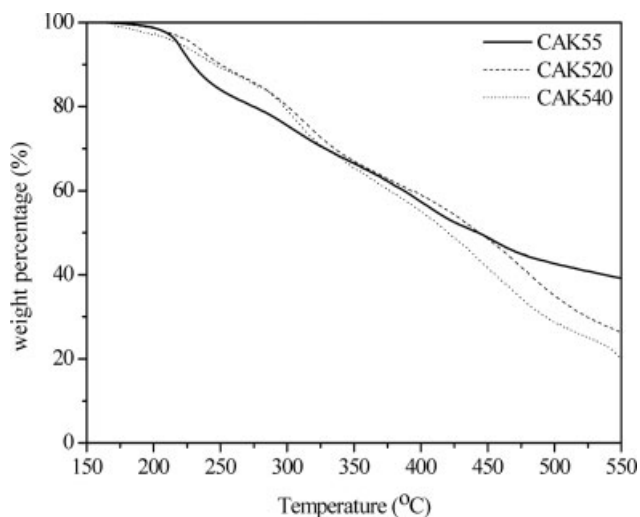
Sample	CAK55	CAK520	CAK540
T_g (°C)	144	142	141

Pure PAA had a T_g value of 116°C.
CAK55, CAK520, CAK540 are the sample codes of chitosan-modified poly(acryylic acid).
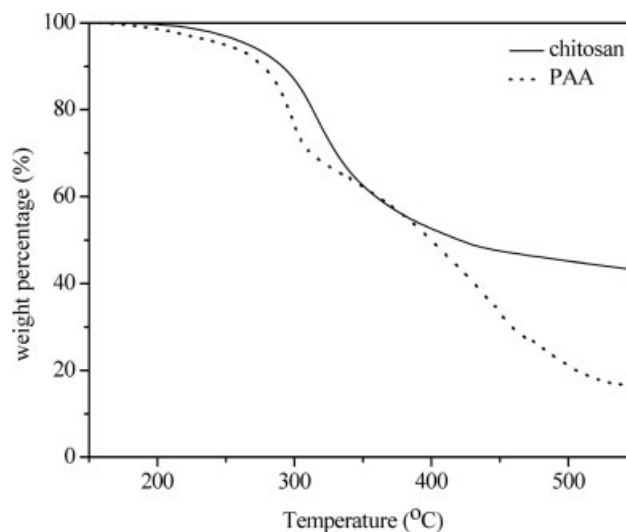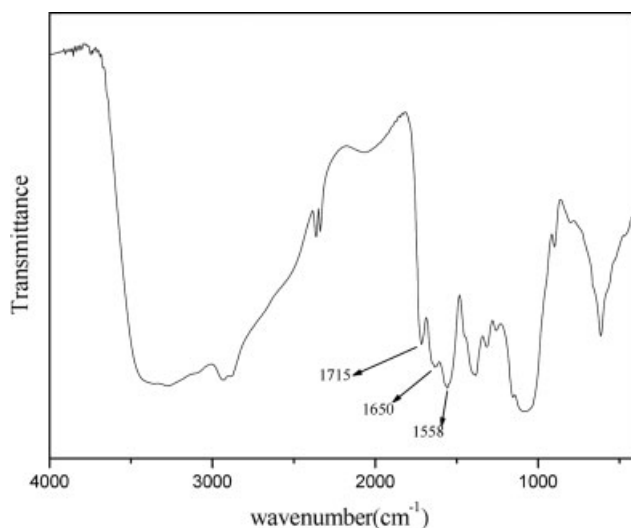

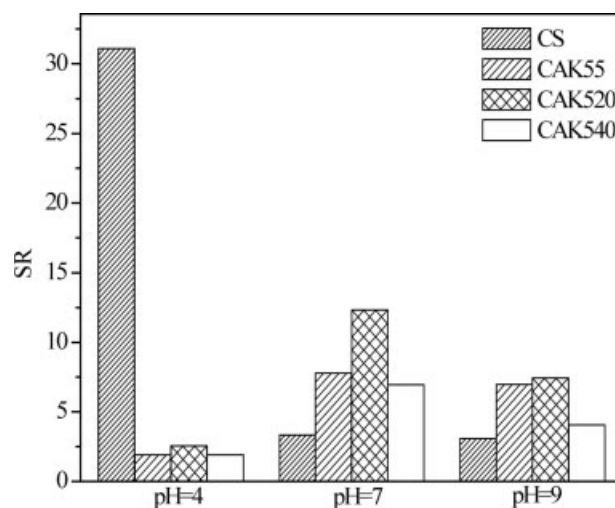**Figure 4** Thermal degradation curves of the PAA and CS.

Figure 5 Thermal degradation curves of the CS-modified PAA samples.

Figure 7 SR of the CS and CS-modified PAA samples in buffer solutions with different pH values.

values of crosslinked PAA were about 5 (in pH 4), 6.5 (in pH 7), and 9 (in pH 9).[23] This was because in a more basic solution, more carboxylic groups became ionized. Ionized carboxylic groups had a strong association with water molecules. The ionized carboxylic groups in the PAA chains also resulted in an increase in the ion concentration and thus the osmotic pressure. For these reasons, the SR of PAA was higher in the basic solution.

For the CS-modified PAA samples, the SR was also dependent on the structure of the sample, which could change with the pH value. In the buffer solution at pH 4, the polyelectrolyte complex was formed between CS and PAA, and the structure was thus more packed.[24–26] In addition, the ion concen-

Figure 6 FTIR spectrum of a CS-modified PAA sample (CAK520) after heating at 250°C for 1 min.

tration and thus the osmotic pressure inside the structure decreased, so the SR was lower. In the pH 7 buffer solution, part of the polyelectrolyte complex between CS and PAA collapsed, and thus the ion concentration increased (degree of ionization: CS, 17%, and PAA, 99%).[22,24,26] Therefore, the sample membrane at pH 7 could absorb more water. In the pH 9 buffer solution, the polyelectrolyte complex was no longer in existence (degree of ionization: CS, 0%, and PAA, 99%), and the structure of CS-modified PAA became so loose that the water-retaining ability decreased.[26] Therefore, the samples in the pH 7 buffer had the highest SR. In addition, the CS-modified PAA sample CAK520 had the highest SR in comparison with the other two samples under the same conditions. This was because the swelling behavior of a polymer depends on two factors: the polymer structure and the amount of the hydrophilic segment. If the crosslinking density is too high, it is difficult for polymer chains to expand so that water can diffuse into the structure. On the contrary, more water can diffuse into a low-crosslinking-density polymer, but it is difficult to retain it in the structure if only a few hydrophilic segments exist in the structure. It would have a high SR when the structure has an appropriate crosslinking density and sufficient hydrophilic segment. In this reaction system, the polyelectrolyte complex was mainly formed by the CS in the copolymer with the PAA homopolymer and served as the pseudocrosslinking point in the structure. The PAA segments in the CS-co-PAA copolymer had less probability of forming the polyelectrolyte complex with CS segments because of the restricted mobility. As a result, their carboxylic acid groups remained free and served as hydrophilic groups to attract water. As for those carboxylic acid groups in

TABLE III
CFI and HI Values of Various Samples

| | Sample | | |
	CAK55	CAK520	CAK540
Weight of the PAA homopolymer in the sample (g)	4.08	2.73	4.5
Weight of PAA in the CS-*co*-PAA copolymer (g)	0.39	15.55	34.5
Weight of CS in the CS-*co*-PAA copolymer (g)	5	5	5
CFI	0.96	0.33	0.22
HI	0.041	0.668	0.784

CAK55, CAK520, CAK540 are the sample codes of chitosan-modified poly(acrylic acid).

the PAA homopolymer, they no longer functioned as hydrophilic groups because they already formed an electrolyte complex with amino groups of CS. We thus defined two indices, the complex formation index (CFI) and hydrophilic index (HI), to illustrate the swelling ability of CS-modified PAA. The CFI and HI were calculated with the following equations:

$$CFI = \frac{\text{Weight of chitosan and weight of PAA homopolymer}}{\text{Total weight of CS} - \text{modified PAA}}$$
$$= \frac{(W_{CS} + W_1 - W_2)}{W_1} \quad (4)$$

$$HI = \frac{\text{Weight of PAA in copolymer}}{\text{Total weight of CS} - \text{modified PAA}}$$
$$= \frac{(W_2 - W_{CS})}{W_1} \quad (5)$$

Table III shows CFI and HI values in various CS-modified PAA systems. A higher value of CFI would lead to a tighter structure, which would limit the chain extensibility and thus the water absorption. On the other hand, if the value of CFI were too low, then the water diffusion into the structure would be easy, but the water storage ability would be decreased. Therefore, CFI has an optimal range of values. Second, the value of HI represents the percentage of the hydrophilic segment in a sample. The higher HI is, the better the ability of water absorption is. From the SR values shown in Figure 7, CAK520 apparently had appropriate CFI and HI values, and this indicated that the structure of CAK520 not only had enough hydrophilic segments for water absorption but also allowed effective diffusion and storage of water.

CONCLUSIONS

CS-modified PAA was successfully synthesized by the polymerization of 5–40 g of AA in the presence of 5 g of CS with KPS as the initiator. After 2 h of reaction at 70°C, a dispersion product was obtained,

and the monomer conversion was between 89 and 98%. Both CC_{PAA} and CE increased with the amount of AA added. From the analysis of the FTIR spectra, we found evidence for the formation of a polyelectrolyte complex between the CS and PAA chains. From the thermal analysis, we observed that the presence of CS increased T_g of PAA in the final CS-modified PAA polymers and that the thermal degradation of CS-modified PAA polymers started at 200°C and exhibited three stages of degradation. The SR of the CS-modified PAA polymer was measured in buffer solutions with different pH values and had a maximum value in the pH 7 buffer solution. Among all samples, the sample with the AA feed of 20 g with 5 g of CS (CAK520) had the highest SR, which reached 12 at pH 7.

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