

Preparation and Characterization of Poly(2-acrylamido-2-methylpropane-sulfonic acid) Grafted Chitosan Using Potassium Persulfate as Redox Initiator

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ABSTRACT: A grafted material based on chitosan and 2-acrylamido-2-methylpropane-sulfonic acid (AMPS) has been successfully prepared in homogenous solution using potassium persulfate as a redox initiator. The grafted copolymer was precipitated during the reaction polymerization. The effects of the reaction temperature and chitosan–potassium persulfate contact time as well as concentrations of AMPS, potassium persulfate, and acetic acid on grafting yield were investigated. The percentage of grafting is gradually increased with the increasing of the AMPS concentration. The extent of grafting can be controlled by setting the appropriate reaction conditions. The maximum percentage of grafting was about 180% under the optimum conditions (1% v/v acetic acid, 50°C reaction temperature, 10 min chitosan–potassium persulfate mixing period, 0.37 mmol of potassium persulfate, and 28.96 mmol AMPS). The grafted chitosan was insoluble in the acid of the grafting. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2314–2318, 2000

Key words: graft copolymerization; chitosan; 2-acrylamido-2-methylpropanesulfonic acid

INTRODUCTION

Graft copolymerization of vinyl monomers onto chitosan and other natural polymers using free radicals initiation has attracted the interest of many scientists in the last two decades. This technique enables the production of new polymer materials with desired properties. Chitosan [(1(4) 2-amino-2-deoxy-D-glucan)] is a polyaminosaccharide of acid-soluble deacetylated derivative of chitin and obtained from N-deacetylation of chitin with a strong alkali.¹ Chitin naturally occurring polysaccharide is found in the shell of crustacea,

insect, and the cell walls of bacteria. Chitosan and chitin are known as a novel materials and have a wide range of applications in biomedical, pharmacology, agricultural, and flocculent.² Few papers have been published on the graft copolymerization of acrylonitrile, dimethylaminoethylmethacrylate, 2-hydroxyethyl methacrylate, ethylene glycol monomethylacrylate, acrylamide, and vinyl pyrrolidone onto chitosan backbone using ceric ammonium nitrate (CAN) as initiator.^{3–8} γ -Ray and photoinduced graft copolymerization of acrylamide, methyl methacrylate, styrene, and acrylonitrile onto chitosan backbone also have been reported.^{9–13} Potassium persulfate has been used as redox initiator for the grafting of methyl methacrylate, methyl acrylate and butyl acrylate onto chitosan.^{14,15} Kim and his co-workers^{16,17}

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have grafted 2-acrylamido-2-methylpropanesulfonic acid onto chitosan using CAN as redox initiator. The optimum reaction temperature and reaction period found were 40°C and 2 h, respectively. They have tested the use of the prepared chitosan-g-poly(2-acrylamido-2-methylpropanesulfonic acid) for chemical oxygen demand and suspended solid. Throughout the survey, no attempt has been apparently made to graft polymerize of 2-acrylamido-2-methylpropanesulfonic acid (AMPS) onto chitosan using potassium persulfate as initiator.

In this article, therefore, we report the homogenous reaction grafting of AMPS onto chitosan using potassium persulfate as redox initiator in acetic acid solution. The grafting reaction was studied by varying the temperature and free radical initiation period as well as concentration of AMPS, potassium persulfate, and acetic acid solutions. The solubility tests of the grafted copolymer in acid solutions of the graft copolymerization were also carried out.

EXPERIMENTAL

Materials

The chitosan sample was prepared from chitin powder¹⁸ and the degree of deacetylation was determined to be 88%. Chitin powder was prepared from dry crab shells according to the procedures mentioned in the literature.¹⁹ Chitosan was dissolved in 2% acetic acid solution and filtered to remove any undissolved material. The concentration of chitosan solution was determined by gravimetric analysis. AMPS was purchased from Fluka Chimica AG, Switzerland and used without any purification. Potassium persulfate (analytical grade reagent from BDH, England) was also used as received. All other chemicals were of analytical grade.

Graft Copolymerization

The graft copolymerization was carried out under nitrogen atmosphere in a 250 mL of two necked-flask equipped with reflux condenser and N₂ gas inlet. Seventy-five milliliters of chitosan solution containing 0.6135 g of chitosan and 1.85×10^{-3} mol of potassium persulfate were added into the flask. To control the reaction temperature, the flask was placed in thermostated water bath fitted with magnetic stirrer. The mixture was

heated to the desired temperature and stirred for 10 min before a chosen amount of AMPS dissolved in 20 mL distilled water was added. The reaction mixture was continuously stirred at the same temperature until the product was precipitated. The product was then filtered and soaked in 100 mL of distilled water. The water was replaced every 24 h for a week to remove ungrafted monomer and homopolymer. The chitosan-g-poly-(AMPS) was filtered, washed with acetone, and dried in an oven at 60°C to a constant weight.

Characterization of Chitosan-g-poly(AMPS)

The presence of the AMPS on the chitosan was studied by IR spectroscopy. The infrared spectra of the chitosan, AMPS, and chitosan-g-poly-(AMPS) sample were recorded by a Perkin Elmer (1600 series) Fourier transform IR (FTIR) spectrophotometer using the potassium bromide disk technique. Scanning was carried out from 4000 to 400 cm⁻¹.

Calculation of the Percentage of Grafting

The polymer yield was evaluated by the percentage of grafting (%G).

$$\%G = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 and W_2 are weights of chitosan and grafted chitosan, respectively.

RESULTS AND DISCUSSION

In this study, the grafting reaction of AMPS onto chitosan was carried out in a homogenous solution. This was achieved by dissolving the chitosan in dilute acetic acid solution followed by additions of initiator and the monomer solution. The graft chitosan [chitosan-g-poly(AMPS)] was precipitated during the grafting reaction. Since the poly-(AMPS) can only be precipitated in some organic compounds and was found to be soluble in water,²⁰ separation of the homopolymer from grafted chitosan was carried out by soaking the products in distilled water several times for a week.

The FTIR spectra of chitosan and the grafted chitosan [chitosan-g-poly(AMPS)] are shown in Figure 1. The FTIR spectrum (A) of chitosan shows the absorptions of around 900 cm and 1154 cm⁻¹ peaks, which assign the saccharide struc-

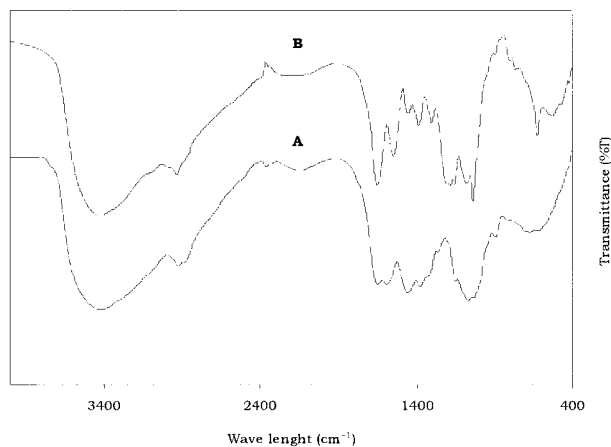
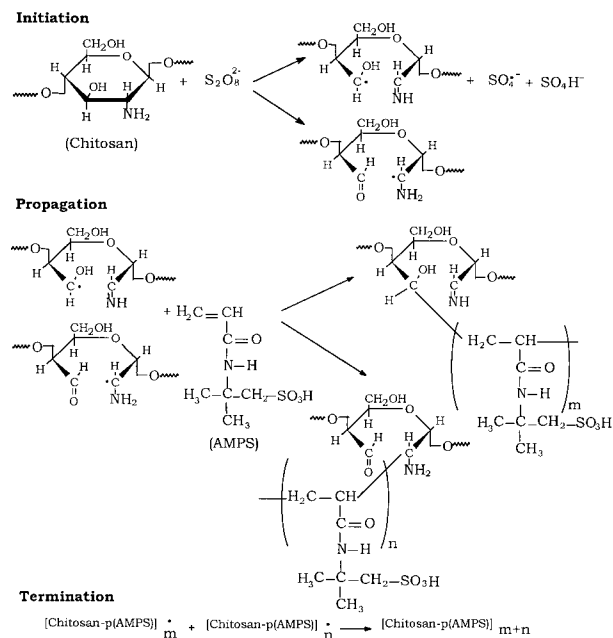


Figure 1 IR spectrum of (A) chitosan and (B) grafted chitosan.

ture.²¹ The vibration of the —NH_2 group is responsible for the absorption band at about 1560 cm^{-1} and the carbonyl absorption is seen at about 1640 cm^{-1} .²² Figure 1(B), which illustrates the new absorption bands at about 630 and 1040 cm^{-1} indicate the presence of the valent oscillation of S—O bonds and valent symmetric oscillation of SO_2 groups.²³ The presence of these absorptions on the purified grafted chitosan suggests that the AMPS has been successfully grafted onto the backbone polymeric. The mechanism of the graft copolymerization of AMPS onto chitosan is shown in Scheme 1. Potassium persulfate reacts directly with a polysaccharide to produce radicals on the polymer backbone.²⁴

Effect of the Reaction Temperature

The graft copolymerization of AMPS onto chitosan was carried out at four temperatures ranging from 40 to 70°C and the results are presented in Figure 2. It was observed that the $\%G$ was increased with increasing of the reaction temperature between 40 and 50°C . Further increase in the reaction temperature leads to the decrease the grafting yield. Increase of $\%G$ at 50°C could be ascribed to (1) increase in the number of the free radicals formed on the backbone, (2) increase propagation of chitosan grafts, (3) increase in the mobility of monomer molecules and their collision with backbone macroradicals, and (4) enhancement of diffusion of monomer and initiator into and onto backbone structure.²⁵ The decrease in the $\%G$ as the reaction temperature is increased beyond 50°C is probably owing to (1) the increase



Scheme 1 The mechanism of the graft copolymerization of AMPS onto chitosan.

of the free radical termination,²⁶ (2) instability of initiator salt, and (3) increased termination of grafted polymeric chains.²⁶ However, the optimum reaction temperature in our work of 50°C is 10°C higher than the optimum reaction temperature using CAN as initiator.¹⁶

Effect of Chitosan–Potassium Persulfate Contact Time

The effect of mixing period of chitosan and potassium persulfate on $\%G$ is given in Table I. These

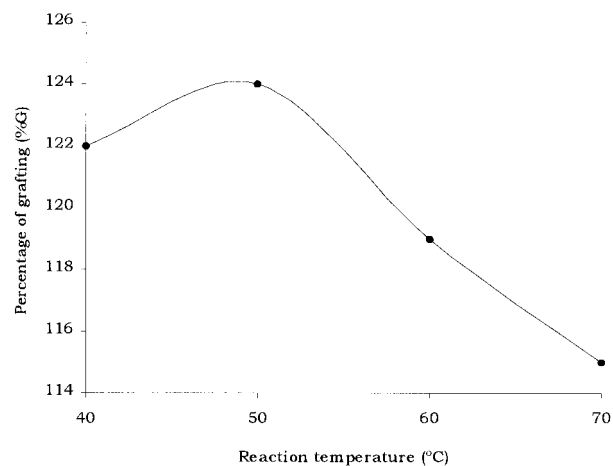


Figure 2 Effect of reaction temperature on the percentage of grafting ($\%G$); chitosan 0.6135 g ; initiator $1.85 \times 10^{-3}\text{ mol}$; AMPS $9.65 \times 10^{-3}\text{ mol}$; acetic acid 2% v/v.

Table I Effect of Chitosan–Potassium Persulfate Mixing Period on the %G

Time (min)	%G
2.5	117
5.0	122
7.5	119
10.0	121

results suggest that increase the mixing period beyond 5 min does not give any significant effect on %G.

Effect of Monomer Concentration

Figure 3 shows the changes of %G with the varying of the AMPS quantity over the range of $4.83\text{--}38.62 \times 10^{-3}$ mol. It is observed that by increasing the amount of AMPS in the grafting reaction, %G is gradually increased and reached 168% at 38.62×10^{-3} mol of AMPS. Increase of the %G of AMPS onto chitosan was attributed to the rising of grafting rate.²⁸

Effect of Initiator

The effect of the initiator concentration on %G is given in Figure 4. The %G is increased with the increase of the amount of initiator of the reaction mixture and reaches the maximum value at the amount of initiator of 1.85×10^{-3} mol. The increase trends of %G may be attributed to, as the

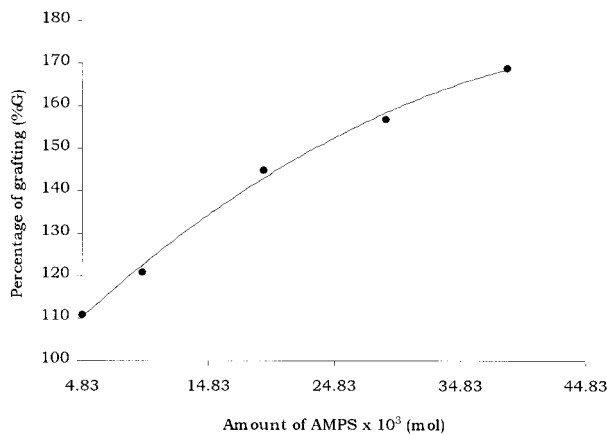


Figure 3 Effect of AMPS concentration on the percentage of grafting (%G); chitosan 0.6135 g; reaction temperature 50°C ; initiator 1.85×10^{-3} mol; acetic acid 2% v/v.

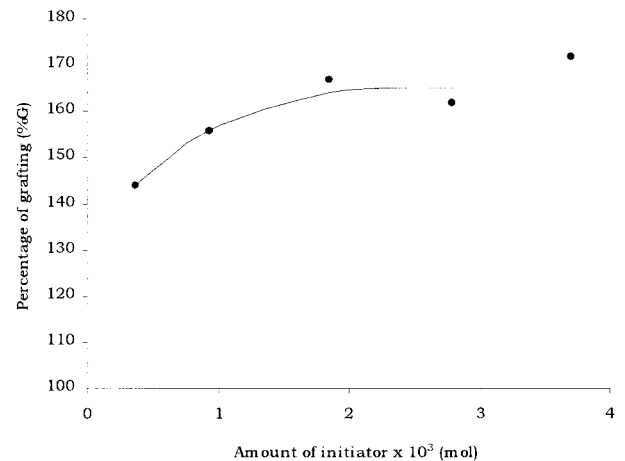


Figure 4 Effect of initiator concentration on the percentage of grafting (%G); chitosan 0.6135 g; reaction temperature 50°C ; AMPS 28.96×10^{-3} mol; acetic acid 2% v/v.

amount of potassium persulfate increases, the number of free radicals sites on the chitosan backbone is increased. However, further increasing of initiator concentrations did not lead to an increase of %G. This is may be due to the presence of oxides of the product, which are incapable of initiating polymerization.¹⁹

Effect of Acetic Acid

Acetic acid was used for grafting reaction to dissolve the chitosan in order to obtain a homogeneous solution. Figure 5 shows the effect of the

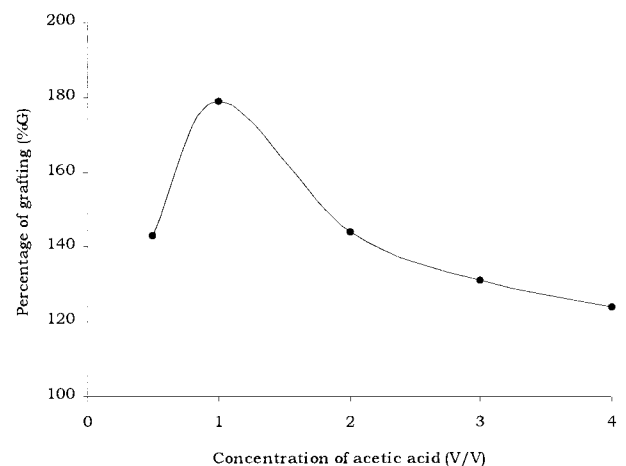


Figure 5 Effect of acetic acid on the percentage of grafting (%G); chitosan 0.6135 g; reaction temperature 50°C ; initiator 0.37×10^{-3} ; AMPS 28.96×10^{-3} mol.

acetic acid concentration on to the extend of the graft copolymerization. The grafting yield increases with increasing of acetic acid concentration between 0.5 and 1.0% and then decreases with further increase of acetic acid concentration. The maximum percentage of grafting (180%) obtained when the chitosan is dissolved in 1.0% acetic acid. The increase in the grafting yield with the increase of acetic acid concentration may be due to a kinetics that favors redox reaction between chitosan backbone macroradicals and the monomer units. Further increases of the acetic acid concentration maybe partially terminate the macroradicals on the chitosan backbone resulting in reducing the grafting yield.²⁷

CONCLUSION

2-Acrylamide-2-methyl propanesulfonic acid was successfully grafted onto chitosan backbone in a homogenous solution by using potassium persulfate as redox initiator. The chitosan-g-poly-(AMPS) was precipitated from the reaction solution. The optimum conditions for the grafting were as follows: reaction temperature, 50; chitosan-potassium persulfate mixing period, 5 min; amount of potassium persulfate, 0.37 mmol; amount of AMPS, 28.96 mmol; acetic acid concentration, 1% v/v. The maximum percentage of grafting obtained under these conditions was about 180%.

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