

# Modified Chitosan. I. Optimized Cerium Ammonium Nitrate-Induced Synthesis of Chitosan-graft-Polyacrylonitrile

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**ABSTRACT:** Chitin was extracted from shrimp shells and then deacetylated to obtain chitosan. The degree of deacetylation of the chitosan was determined to be 0.76 using pH-metric titration. A large number of cyanide functional groups were introduced onto chitosan by grafting with polyacrylonitrile as an efficient way of modification. The graft copolymerization reactions were carried out under argon atmosphere in a homogeneous aqueous phase (containing a small portion of acetic acid) by using ceric ammonium nitrate as an initiator. Evidence of grafting was obtained by comparing FTIR spectra of chitosan and the graft copolymer as well as solubility characteristics of the products. The synthetic conditions were systematically optimized through studying the influential factors, including temperature and concentrations of the initiator, acrylonitrile monomer (AN), acetic acid, and chitosan. The effect of individual factors was

investigated by calculating and monitoring the variations of the grafting parameters [i.e., grafting ratio ( $Gr$ ), grafting efficiency ( $Ge$ ), add-on value ( $Ad$ ), homopolymer content ( $Hp$ ), and total conversion ( $Ct$ )]. Under optimum conditions, the grafting parameters were achieved as 535, 98, 81, 2, and 102%, respectively. A mechanism for the free-radical grafting was proposed. As empirical rates of polymerization and graft copolymerization were plotted against  $[AN]$  and  $[Ce^{4+}]^{1/2}$ , the experimental kinetic data displayed a good match to a reported rate statement. The overall activation energy for the graft copolymerization was determined to be 44.9 kJ/mol. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2048–2054, 2003

**Key words:** chitosan; acrylonitrile; graft copolymer; ceric ammonium nitrate; kinetics

## INTRODUCTION

Chitosan [1(4)-2-amino-2-deoxy-D-glucan] is a polyaminosaccharide of the acid-soluble deacetylated derivative of chitin and obtained from N-deacetylation of chitin using a strong alkali. Chitin, a naturally occurring polysaccharide, is found in the shells of crustaceans, insects, and the cell walls of bacteria.<sup>1</sup> Chitin and chitosan are known as materials having a wide range of applications in biomedicine, pharmacy, agriculture, and flocculation.<sup>2,3</sup>

The modification of polysaccharides is a promising method for the preparation of new materials. This enables one to introduce special properties and enlarge the field of the potential applications of these biopolymers. Among the diverse modifications that are possible to achieve, grafting of synthetic polymer is a convenient method.<sup>4</sup> Graft copolymerization of

vinyl monomers onto chitosan and other natural polymers using free-radical initiation has attracted the interest of many scientists in the last three decades.

As a thermal initiator, azobis(isobutyronitrile) has been used to graft copolymerize some vinyl monomers including acrylonitrile (AN), methylmethacrylate (MMA), methylacrylate (MA), and vinylacetate (VAc) onto chitosan.<sup>5</sup> Generally, the grafting percentages have been low. Chitosan-graft-poly(vinyl alcohol) was previously prepared through hydrolysis of chitosan-graft-poly(VAc).<sup>6</sup> With Fenton's reagent as a redox initiator, MMA has been graft copolymerized onto chitosan.<sup>7,8</sup> In another work, MMA was also initiated by UV light to be grafted onto chitosan chains.<sup>9</sup> Gamma-ray irradiation was also used for graft copolymerization of styrene, VAc, and acrylamide (AAm) onto chitosan.<sup>10–12</sup> Potassium persulfate (KPS) has been used to graft poly(*N*-vinylpyrrolidone)<sup>13</sup> and poly(2-acrylamido-2-methylpropane-sulfonic acid)<sup>14</sup> onto the chitosan backbone. Acrylic acid (AA) was recently grafted onto chitosan using a KPS/ferrous ammonium sulfate initiator system.<sup>15</sup> Most recently, another redox initiator system, named thiocarbonation-KBrO<sub>3</sub>, was used for grafting hydroxyethyl methacrylate onto chitosan.<sup>16</sup> Ce(IV) is another efficient initiator to graft poly(AAm),<sup>17</sup> poly(AA),<sup>18</sup> and

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poly(*N*-isopropylacrylamide)<sup>19</sup> onto chitosan. To the best of our knowledge, there have been no previous reports on using the ceric ion for grafting of acrylonitrile onto chitosan, except a noninternational short paper.<sup>20</sup>

In the present work, we studied the chitosan modification by ceric-induced graft copolymerization of acrylonitrile. The combined effect of the principal reaction variables for the grafting process was systematically studied to achieve the optimum conditions. The grafting reaction was carried out in homogeneous phase by using ammonium cerium (IV) nitrate as a redox initiator in dilute acetic acid solution.

## EXPERIMENTAL

### Materials

The chitosan sample was prepared from chitin<sup>21</sup> and the degree of deacetylation was determined to be 76% by the titration method.<sup>1</sup> Chitin powder was prepared from dry shrimp shells by removing protein, inorganic materials, and pigments according to procedures reported in the literature.<sup>22</sup> Ceric ammonium nitrate (CAN) was purchased from Merck (Darmstadt, Germany) and was used without purification. It was used as freshly prepared solution in 1*N* HNO<sub>3</sub>. Acrylonitrile (AN; Merck) was used after distillation to remove the inhibitor. All other chemicals were of analytical grade.

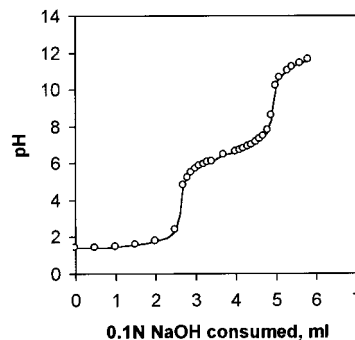
### Preparation of chitin

Shrimp shells were cleaned and dried in air. Clean dried shells were ground and digested with 40 wt % acetic acid for 2 h at room temperature, filtered, and washed to remove inorganic materials and pigments. Then, they were digested for 24 h with 2*N* NaOH at 55°C to remove the proteins, filtered, and washed with water. For complete removal of inorganic components, the shells were digested with 2*N* HCl at 30°C for 2 h, filtered, and thoroughly washed with water. Finally, pure chitin was washed with methanol and dried at 50°C.

### Preparation of chitosan

Chitosan was obtained by deacetylation of chitin.<sup>21</sup> Thus, chitin was treated with 47 wt % aqueous solution of sodium hydroxide at 100°C for 1.5 h under argon. After cooling, the mixture was filtered and washed with water to reach a neutral state and then washed with methanol and dried at 50°C.

The degree of deacetylation (DD) of chitosan was determined by acid–base titration. Chitosan (0.05 g) was dissolved in excess 0.1*N* HCl and the solution was titrated pH-metrically with a standardized solution of



**Figure 1** pH-metric titration curve of the prepared chitosan sample for determining its degree of deacetylation (DD).

0.1*N* NaOH. This yielded a titration curve having two equivalent points related to the excess HCl and to the protonated amino groups (Fig. 1). The degree of deacetylation was calculated from the amount of NaOH consumed between the two points by the following equation:

$$DD = 16.1(y - x)(f/w) \quad (1)$$

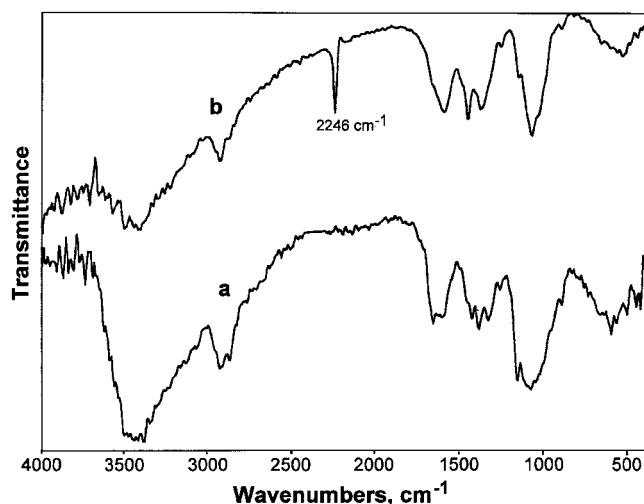
where  $f$  is molarity of the NaOH solution,  $y$  and  $x$  stand for the consumed NaOH volume at the equivalent points, and  $w$  is the sample weight (g). Therefore, DD was calculated as  $16.1 \times (2.4) \times 0.1/0.05 = 77$ . The chitosan preparation procedure was repeated three times and an average DD value was calculated to be 76%. This value was reconfirmed by a modified method based on quantitative FTIR spectroscopy<sup>23</sup> using the equation  $DD\% = 100 - [(31.92A_{1320}/A_{1420}) - 12.20]$ , where  $A_{1320}$  and  $A_{1420}$  are the areas under the peaks at 1320 and 1420  $\text{cm}^{-1}$ , respectively.

### Graft copolymerization

A CAN solution was prepared by dissolving 2.74 g ceric ammonium nitrate in 50 mL of 1*N* HNO<sub>3</sub>. Generally, 1.80 g of this stock solution (0.10*M*) was used for each experiment except for the experiments by which the effect of the initiator concentration was studied.

The chitosan solution was prepared in a 50-mL two-neck flask equipped with magnetic stirrer, gas inlet, and reflux condenser. Chitosan was dissolved in degassed distilled water containing 1 wt % of acetic acid. The total volume of the aqueous solution was 30 mL in all experiments. To control the reaction temperature, the flask was placed in a water bath preset at the desired temperature.

AN (1.60 g) was added to the flask and the mixture was heated at a given temperature and stirred for 5 min. Then a given volume of the initiator solution was added to the mixture. The mixture was continuously stirred at the desired temperature until completion of



**Figure 2** FTIR spectra of (a) chitosan and (b) chitosan-graft-polyacrylonitrile.

the reaction (2 h). The product was then precipitated by neutralization using 1N NaOH solution. The product was thoroughly washed with methanol and dried at 50°C for 1 h. To separate the polyacrylonitrile (PAN) homopolymer, 0.50 g of the crude product was poured in 50 mL of dimethylformamide (DMF) and stirred gently at 30°C for 24 h. After centrifugating and decanting the supernatant (PAN in DMF), the chitosan-g-polyacrylonitrile was precipitated in methanol, thoroughly washed with methanol, and dried at 50°C to reach a constant weight.

## RESULTS AND DISCUSSION

### Evidence of grafting

The simplest method to prove the formation of chitosan-g-PAN is based on the solubility difference of the graft copolymer and the nongrafted homopolymer PAN. Chitosan and PAN are soluble in 1 wt % acetic acid aqueous solution and DMF, respectively. When a reaction product was Soxhlet-extracted with DMF and alternately with 1 wt % acetic acid solution for 24 h, an insoluble solid still remained. A physical mixture of chitosan and PAN was treated in the same way and was found to dissolve completely. Therefore, it is obvious that the graft copolymer obtained was not a simple physical mixture but, rather, some chemical bonds must exist between the chitosan substrate and PAN macromolecules.

The existence of PAN grafting was also confirmed by the differences between FTIR spectra of the substrate and that of the graft copolymer (Fig. 2). An obvious difference corresponds to the intense sharp characteristic peak in the copolymer at 2246 cm<sup>-1</sup> that is assigned to CN stretching absorption. The bands 3435–3295 cm<sup>-1</sup> (O—H and N—H stretching), 2911

and 2866 cm<sup>-1</sup> (C—H stretching), 1400–1100 cm<sup>-1</sup> (C—O stretching of secondary alcohol), and 1070–1020 cm<sup>-1</sup> (C—O stretching of the primary alcohol) are common in both spectra because of the chitosan backbone.<sup>24</sup> The similar bands of the polysaccharide main chain of the graft copolymer mainly overlap the C—C and C—H vibrational bands of the synthetic part of the copolymer.

### Grafting parameters

Grafting parameters [i.e., total conversion (*Ct*), grafting ratio (*Gr*), grafting efficiency (*Ge*), add-on (*Ad*), and homopolymer content (*Hp*)] were determined according to known weight-basis expressions<sup>4,25</sup>:

$$Ct = W_2/W_1 \quad (2)$$

$$Gr = W_3/W_0 \quad (3)$$

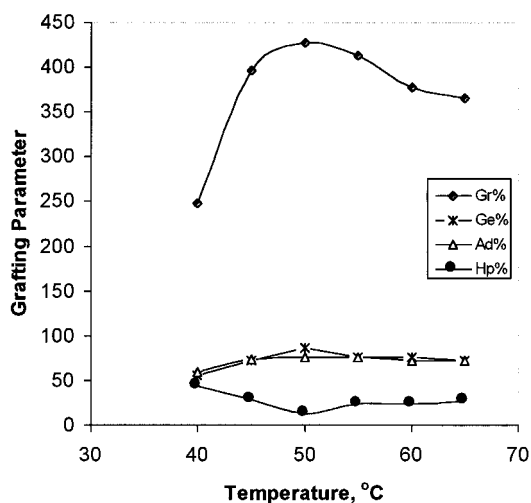
$$Ge = W_3/W_2 \quad (4)$$

$$Ad = (W_3 - W_0)/W_3 \quad (5)$$

$$Hp = (W_2 - W_3)/W_2; \text{ or } Hp = 1 - Ge \quad (6)$$

where  $W_0$ ,  $W_1$ ,  $W_2$ , and  $W_3$  are weight of the initial substrate, the monomer charged, total product (i.e., copolymer and homopolymer), and pure graft copolymer (after DMF extraction), respectively.

In this work, acrylonitrile was grafted onto chitosan in a homogeneous solution under an inert atmosphere. Unlike some other polysaccharides, such as gelatinized starch<sup>25</sup> and gum tragacanth<sup>26</sup> that recently were grafted by PAN using the same initiator in the presence of oxygen, the present CAN-initiated process does not proceed under normal atmospheric conditions. Thus, all solutions were previously degassed and the reactions were run under a gentle stream of argon. After dissolving the chitosan in diluted acetic acid solution, the monomer and initiator were in turn added to the solution. Because polymerization variables determine the extent of grafting and homopolymer amount, certain factors affecting the grafting parameters were investigated to achieve the optimum condition of polymerization. Therefore, we optimized the grafting of acrylonitrile onto chitosan in homogeneous aqueous media by changing temperature, the initial concentration of monomer, initiator, acetic acid, and the relative amount of chitosan. Within the range of the amount of the reactants used, our preliminary studies showed no considerable dependency between the reaction time and the grafting extent.



**Figure 3** Effect of the bath temperature on the grafting parameters. Reaction conditions: chitosan 0.3 g, acetic acid 1% w/w, AN 1.6 g, CAN 0.006 mol/L, time 2 h.

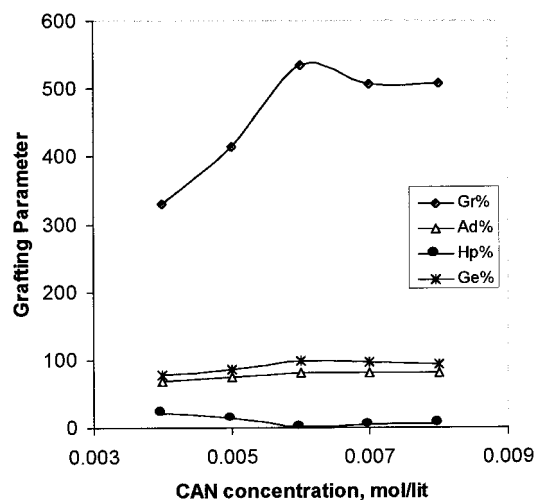
**Effect of the bath temperature**

To study the influence of temperature on the grafting parameters, the grafting of AN onto chitosan was carried out at six different temperatures, ranging from 40 to 65°C, and the results are presented in Figure 3. Grafting percentage (%Gr) increased by increasing the temperature from 40 to 50°C, and then decreased. At 50°C, maximum grafting ( $Gr = 428\%$ ) and minimum homopolymer content ( $Hp = 13\%$ ) were obtained. No considerable change was observed in add-on value beyond 45°C.

The corresponding increase in %Gr up to 50°C could be attributable to the following factors: increased number of free radicals formed on the chitosan backbone, increased propagation of the graft copolymerization onto chitosan, enhanced diffusion of monomer and initiator into and onto backbone structure, and increased mobility of the monomer molecules and their higher collision probability with the backbone macroradicals.<sup>27</sup> However, Gr decreased as the bath temperature was raised beyond 50°C. This can be accounted for in terms of chain radical termination at higher temperatures. Premature termination of growing chains and instability of the ceric-saccharide complex<sup>28</sup> are presumably other reasons for reduced amount of grafting beyond 50°C. The PAN homopolymer formation is minimal at the bath temperature of 50°C.

**Effect of initiator concentration**

Gr dependency on CAN concentration can be seen in Figure 4. Maximum grafting ratio (535%) was achieved at 0.006M of CAN where homopolymer content was only 2%. Increased CAN concentration resulted in more radical sites on the chitosan backbone

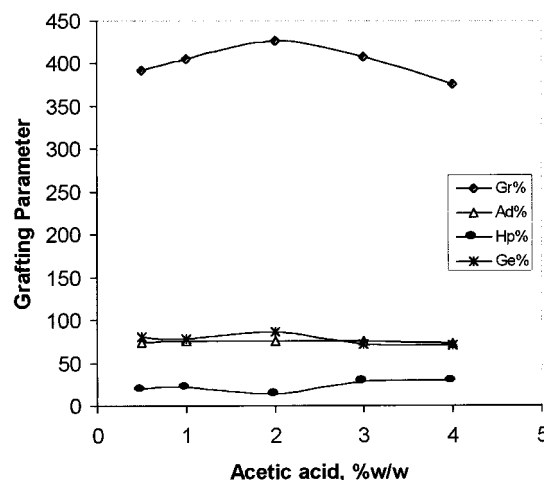


**Figure 4** Effect of the initiator concentration on the grafting parameters. Reaction conditions: chitosan 0.3 g, acetic acid 1% w/w, AN 1.6 g, temperature 50°C, time 2 h.

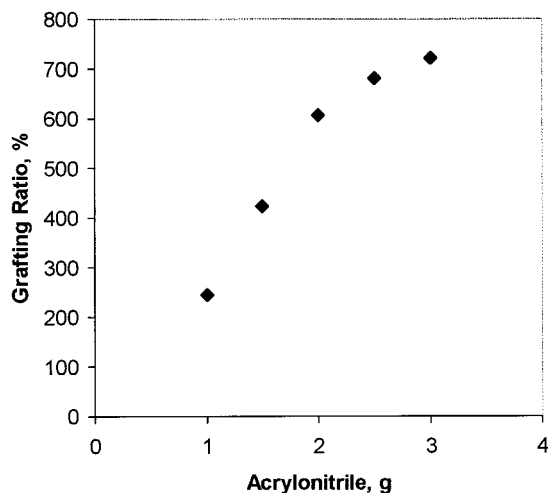
that in turn led to higher Gr and add-on values and lower homopolymer formation. However, because the CAN initiator solution is used as dilute HNO<sub>3</sub>, at CAN concentrations higher than 0.006 mol/L, a more acidic pH probably causes partial termination of the macroradicals on the chitosan. As a result, increased amounts of free radicals on chitosan are compensated by partial termination of the macroradicals. Thus Gr and add-on values remain at constant levels (i.e., 507 and 81%, respectively).

**Effect of acetic acid concentration**

Diluted acetic acid was used to dissolve chitosan and to obtain a homogeneous reaction medium. Figure 5 shows the effect of acetic acid concentration on the grafting ratio. With increasing the acetic acid concen-



**Figure 5** Effect of acetic acid concentration on the grafting parameters. Reaction conditions: chitosan 0.3 g, AN 1.6 g, CAN 0.006 mol/L, temperature 50°C, time 2 h.

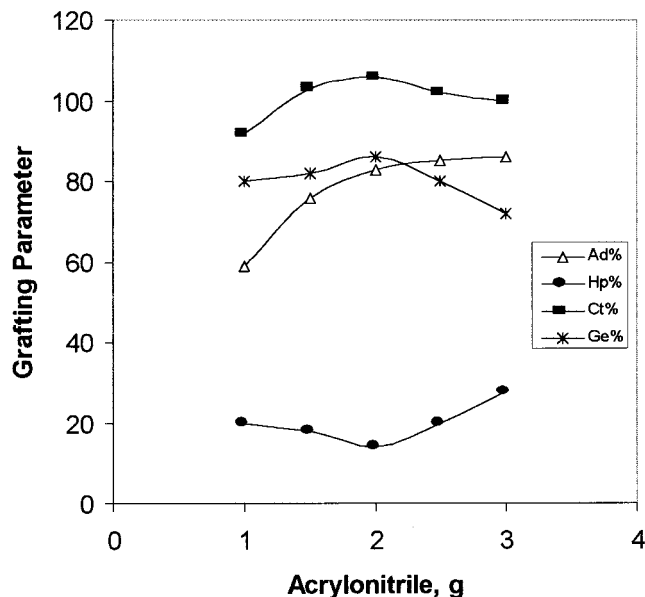


**Figure 6** Effect of the monomer amount on grafting ratio. Reaction conditions: chitosan 0.3 g, acetic acid 1% w/w, CAN 0.006 mol/L, temperature 50°C, time 2 h.

tration between 0.5 and 2%,  $Gr$  increases and then decreases with further increase in acetic acid concentration. The maximum grafting (426%) and minimum homopolymer formation (13%) were obtained when the chitosan was dissolved in 2.0% w/w acetic acid. The increase in the grafting yield with the increase of acetic acid may be attributable to a kinetics that favors a redox reaction between chitosan backbone macroradicals and the monomer units. Further increases in the acetic acid concentration may partially terminate the macroradicals, resulting in reduced grafting ratio.<sup>29</sup>

#### Effect of monomer concentration

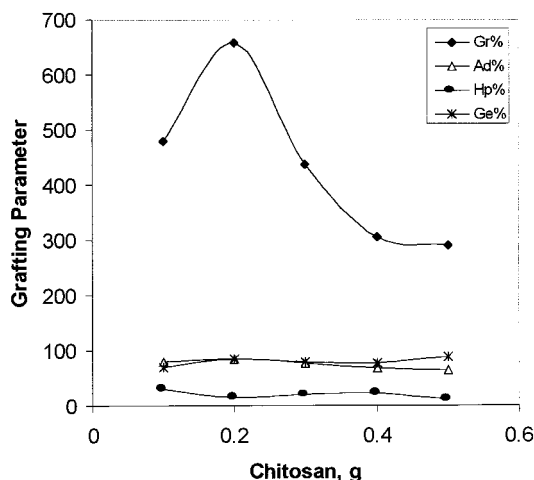
The effect of monomer amount on the grafting reaction was studied at various concentrations of AN while other influential factors were kept constant. The grafting parameter variations were changed by the amount of charged monomer, as shown in Figures 6 and 7. As can be clearly seen in Figure 6, the grafting extent significantly increases because of the increased availability of monomer for grafting. However, beyond a certain  $Gr$  value (i.e., 607% at 2 g AN), the trend slope inverses, whereas the add-on values remain approximately unchanged ( $Ad \sim 85\%$ ), total conversion ( $Ct$ ) and the grafting efficiency ( $Ge$ ) are decreased, and homopolymer content is increased noticeably from 14 to 28% (Fig. 7). Thus, acrylonitrile in an amount of 2 g was recognized as an optimum monomer concentration. Once the monomer units are added, an excess of monomer can only increase the optimum volume of the reaction mixture. The resulting reduced relative concentration of the initiator and substrate leads to decreased conversion and grafting efficiency.



**Figure 7** Effect of the monomer amount on total conversion ( $Ct$ ), grafting efficiency ( $Ge$ ), add-on ( $Ad$ ), and homopolymer content ( $Hp$ ). Reaction conditions as given in Figure 6.

#### Effect of chitosan amount

The grafting dependency on chitosan amount is shown in Figure 8. The maximum grafting ratio ( $Gr$  659%) was observed at 0.20 g chitosan, whereas others, including acetic acid, monomer, initiator, and temperature, were kept constant. Beyond this value, both grafting ratio and add-on values are considerably reduced ( $Gr$  decreases from 659 to 29% and  $Ad$  decreases from 84 to 65%). This behavior is attributed to the availability of more grafting sites for initiation of graft copolymerization at higher chitosan concentrations (Fig. 8, from 0.10 to 0.20 g chitosan). However, upon



**Figure 8** Effect of chitosan amount on the grafting parameters. Reaction conditions: acetic acid 1% w/w, AN 1.6 g, CAN 0.006 mol/L, temperature 50°C, time 2 h.

further increase in the substrate concentration, an increase in the reaction medium viscosity restricts the movements of macroradicals, thereby decreasing the grafting ratio and add-on values. It also may be attributed to deactivation of the macroradical growing chains (e.g., by transfer reactions, combination, and/or interaction with the primary radicals) soon after their formation.

**Reaction rate and mechanism**

Rates of polymerization ( $R_p$ ) and graft copolymerization ( $R_g$ ) may be evaluated as measures of the rate of monomer disappearance by using the following equations<sup>25</sup>:

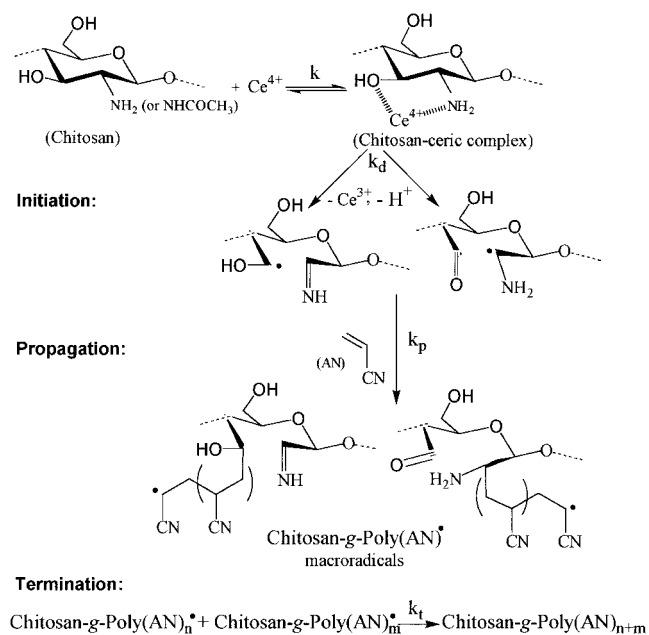
$$R_p \text{ (mol L}^{-1} \text{ s}^{-1}\text{)} = 1000W_2/MTV \quad (7)$$

$$R_g \text{ (mol L}^{-1} \text{ s}^{-1}\text{)} = 1000W_3/MTV \quad (8)$$

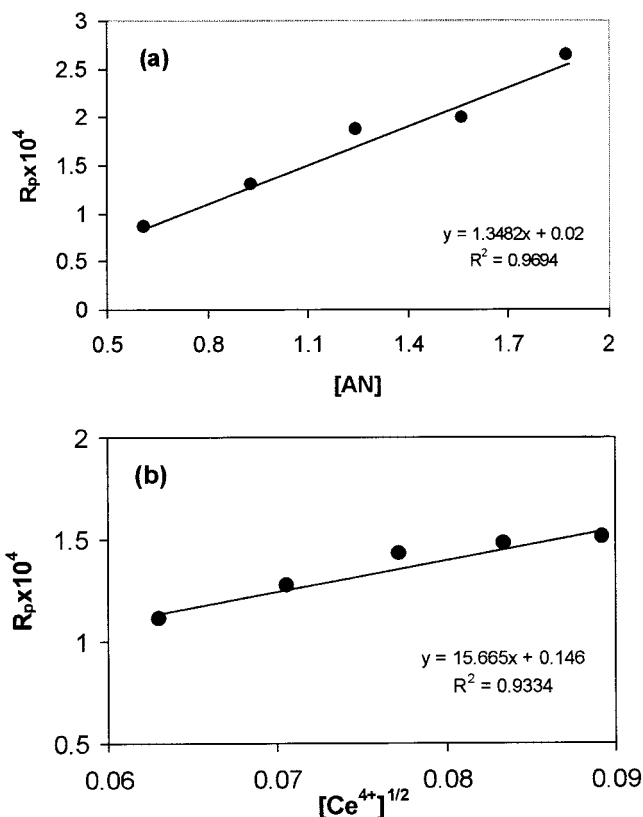
where  $M$  (g mol<sup>-1</sup>) is the molecular weight of the monomer;  $T$  and  $V$  stand for total reaction time (s) and total volume (mL) of the reaction mixture, respectively. The simply calculated rate values may be of significant importance in confirming a proposed reaction mechanism and kinetics.

It has been shown that the anhydroglucose units are predominantly oxidized through C<sub>2</sub>-C<sub>3</sub> bond cleavage induced by Ce<sup>4+</sup> ions.<sup>30</sup> Therefore, a general reaction scheme for grafting, in analogy with that previously mentioned,<sup>31</sup> may be as follows (Scheme 1).

In the case of chitosan, the reactive vicinal OH and NH<sub>2</sub> groups may form a complex with ceric ion. The



**Scheme 1** General mechanism for ceric-initiated graft copolymerization of acrylonitrile onto chitosan.



**Figure 9** Plots of  $R_p$  versus (a)  $[AN]$  and (b)  $[Ce^{4+}]^{1/2}$ .

complex may dissociate, giving rise to free-radical sites onto the polysaccharide backbone. As in Figure 9, both plots of  $R_p$  versus the monomer concentration  $[AN]$  and half-order of the initiator concentration  $1/[Ce^{4+}]$  are linear. This is in agreement with a modified kinetic scheme recently explored for CAN-initiated methylacrylate grafting onto sago starch.<sup>32</sup> The statement of rate of polymerization according to the scheme is as follows:

$$R_p = k_p(kk_d/k_t)^{1/2} [\text{Substrate}]^{1/2} [Ce^{4+}]^{1/2} [AN] \quad (9)$$

where the coefficient  $k$  is the equilibrium constant and  $k_p$ ,  $k_d$ , and  $k_t$  are the rate constants for propagation, chitosan-ceric complex dissociation, and termination reactions, respectively. Therefore, we preliminarily conclude that the CAN-initiated grafting of acrylonitrile onto chitosan is also fitted with this kind of rate statement.

Finally,  $\ln R_g$  versus  $1/T$  was plotted for the initial portion of the curve related to the temperature series shown in Figure 3. This Arrhenius plot (Fig. 10) results in an estimation of the overall activation energy of the graft copolymerization ( $E_a$ ) using the relationship  $\tan(\text{slope}) = -E_a/R$ , where  $R$  is the universal gas constant. Therefore,  $E_a$  was found to be 44.9 kJ/mol (10.7 kcal/mol).

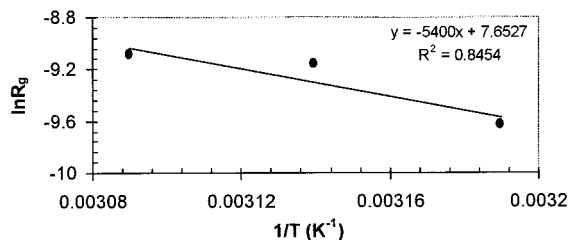


Figure 10 Plot of  $\ln R_g$  versus  $1/T$ .

## CONCLUSIONS

Polyacrylonitrile was successfully grafted onto chitosan in a homogeneous phase under inert atmosphere using CAN as an initiator. The grafting changes by varying the reaction conditions. The optimum conditions for graft copolymerization were determined to be the following: chitosan amount 0.20 g; acetic acid 2% w/w; reaction temperature 50°C; AN 1.60 g; CAN concentration 0.006M; time 2 h. The maximum grafting ratio and add-on value obtained under these conditions were 535 and 81%, respectively. The grafting efficiency was recognized to remain almost unchanged with the reaction time. The independence of grafting on time can be attributed to a decrease in concentration for both initiator and monomer and also to a reduction of the number of sites on the chitosan backbone accessible for grafting as the reaction proceeds. This observation is similar to such leveling observed in grafting of some vinyl monomers onto cellulose initiated with ceric ion.<sup>33</sup> The empirical polymerization rate ( $R_p$ ) showed a first-order dependency on the monomer concentration and a half-order dependency on the initiator concentration. According to the slope of the  $R_p$  plots (Fig. 9), the polymerization rate is much more sensitive to concentration of the ceric initiator than it is to the concentration of the acrylonitrile monomer. Further investigation on modified chitosan is in progress in our laboratory.

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