

# Graft Copolymerization of Itaconic Acid onto Sodium Alginate Using Ceric Ammonium Nitrate as Initiator

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**ABSTRACT:** Graft copolymers of sodium alginate (NaAlg) with itaconic acid (IA) were prepared in aqueous solution using ceric ammonium nitrate (CAN) as the redox initiator under N<sub>2</sub> atmosphere. The carboxylic acid groups of IA were neutralized with sodium hydroxide before grafting process. Grafted copolymers as sodium salts (NaAlg-g-PIA) were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, intrinsic viscosity measurement, differential scanning calorimetry, and thermogravimetric analysis. The graft yield (GY %) of the graft copolymer and the grafting efficiency (GE %) of the reaction were evaluated comparatively. The effects of the reaction variables such as the reaction time, temperature, percentage of NaAlg, monomer and initiator

concentrations on these parameters were studied. It was observed that GY% and GE% increased and then decreased with increasing concentrations of IA and polymerization temperature. The optimum grafting conditions for maximum GY were obtained with a reaction time of 5 h, reaction temperature of 30°C, IA concentration of 0.23 M, CAN concentration of  $9.12 \times 10^{-2}$  M and percentage of NaAlg 0.5 g/dL. The overall activation energy for the grafting was also calculated to be 1135 cal/mol. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 40–48, 2009

**Key words:** graft copolymerization; sodium alginate; itaconic acid; free radical copolymerization

## INTRODUCTION

Natural polymers are extensively used in recent years in chemical engineering, medicine pharmaceuticals, food, and agriculture because of their non-toxic, low cost, free availability, and biodegradability characteristics.<sup>1–3</sup> Among such natural polymers, alginates are obtained mainly from brown algae belonging to the Phaeophyceae and composed of two monomeric units,  $\beta$ -D-mannuronic acid and  $\alpha$ -L-guluronic acid.<sup>3</sup> The uses of alginates are based on three main properties. The first is their ability, when dissolved in water, to thicken the resulting solution. The second is their ability to form gels. The third property of alginates is the ability to form film. For these abilities, alginates are used in variety of areas such as in textile printing, food, immobilized biocatalysts, paper industry, pharmaceutical, and medical uses. However, several natural polymers, especially the class of polysaccharides, have some inherent disadvantages, such as poor mechanical strength, uncontrolled water uptake, and microbial contamination.<sup>2</sup> To overcome these problems, efforts have

been made to develop chemically modified matrices by grafting or blending with other polymers. The grafting technique can be considered a useful tool for the new properties of polymer.

Grafting is a well established and powerful method for the development of natural-synthetic polymer hybrid materials. Among chemical initiation methods, redox-initiated grafting offers advantages because in the presence of a redox system, grafting can be carried out under milder conditions and side reactions are at a minimum. So far, the grafting of vinyl monomers such as acrylamide,<sup>4</sup> acrylonitrile,<sup>5</sup> and methyl acrylate<sup>6</sup> with redox initiators has gained considerable attention and proved of value in preparing new polymeric materials with special properties and enlarging the range of its utilization. However, grafting of hydrophilic itaconic acid (IA) onto sodium alginate (NaAlg) has not been studied up to now.

IA is one of the monomers, which is readily available at low cost. It is obtained from renewable resources by fermentation with *Aspergillus terreus*.<sup>7</sup> It is very hydrophilic and is expected to show high biocompatibility because of its nature source. The application of IA can be considered important. Because commercial availability of IA gives it a clear advantage over monomers, that have to be synthesized via a multiple-step reaction sequence. The presence of carboxylic acid groups in the structure

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of IA is another advantage of this monomer. This could help in designing copolymers with specific characteristics, which is a hot research field in both industrial and academic fields. Double ionization of IA at different pH values provides stepwise release behavior of specially adsorbed drugs or other adsorbents by controlling pH of the medium. Doubly-ionized carboxylic groups bring additional capability of chelate formation under certain cases.<sup>8</sup> A few workers have carried out grafting reactions of IA onto low density polyethylene,<sup>9</sup> polypropylene,<sup>10</sup> and chitin.<sup>11</sup> It was therefore decided to graft IA onto NaAlg.

In the previous study,<sup>12</sup> *N*-vinyl-2-pyrrolidone was grafted onto NaAlg using azobisisobutyronitrile (AIBN) as the initiator, and beads of these copolymers were prepared for controlled release study of indomethacin. In the present work, we carried out the grafting of IA onto NaAlg with ceric ammonium nitrate (CAN), and we evaluated optimized reaction conditions of grafting to form pH sensitive drug delivery systems. The graft copolymer was also characterized with different techniques.

## EXPERIMENTAL

### Materials

NaAlg with a viscosity of 3500 cps (2% solution, 25°C) was purchased from Sigma Chemical Co (Louis). IA and CAN were supplied from Fluka Chemie AG (Buchs, Switzerland). Other reagents were Merck products and used as supplied.

### Graft copolymerization

The grafting reactions were carried out under a nitrogen atmosphere in a 250-mL three-necked flask equipped with a reflux condenser, a stirrer, and a gas inlet system, immersed in a constant temperature bath. In a typical reaction, NaAlg (0.5–1.75 g) was dissolved in distilled water (50 mL) at room temperature with constant stirring. The solution was immediately placed into the water bath adjusted to the polymerization temperature. The required amount of IA was dissolved in 10 mL of distilled water and neutralized with saturated NaOH solution. After that, this solution was mixed with NaAlg solution and stirred a slow stream of nitrogen for 30 min. Then CAN at the required concentration in distilled water was added slowly to the reaction mixture and the total volume of the reaction mixture was made up to 100 mL with distilled water. A continuous supply of nitrogen was maintained throughout the reaction period. The grafting reactions were carried out for various time (1–6 h) and temperature (20–60°C). At the end of the predetermined polymer-

ization time, the reaction was terminated by adding a saturated solution of hydroquinone. The products were precipitated in an excess of acetone, separated by filtration, and then extracted with methyl alcohol to remove the homopolymer (PIA) for 24 h. After the complete removal of PIA, the pure graft copolymer was dried at 40°C under vacuum to a constant weight. The grafting parameters, including graft yield (GY) and grafting efficiency (GE), were calculated as follows:

$$\text{GY}(\%) = [(w_g - w_o)/w_o] \times 100 \quad (1)$$

$$\text{GE}(\%) = [(w_g - w_o)/(w_g - w_o) + w_h] \times 100 \quad (2)$$

where  $w_o$ ,  $w_g$ , and  $w_h$  denote the weights of the original (ungrafted) NaAlg, grafted NaAlg, and homopolymer, respectively.

The rate of grafting ( $R_g$ ) was calculated with the formula as follows:

$$R_g = [(w_g - w_o) \times 1000]/[M \times t \times V] \quad (3)$$

where  $M$  is the molar weight of the monomer;  $t$  is the polymerization time (s); and  $V$  is the volume (mL) of the overall reaction medium.

### Fourier transform infrared measurements

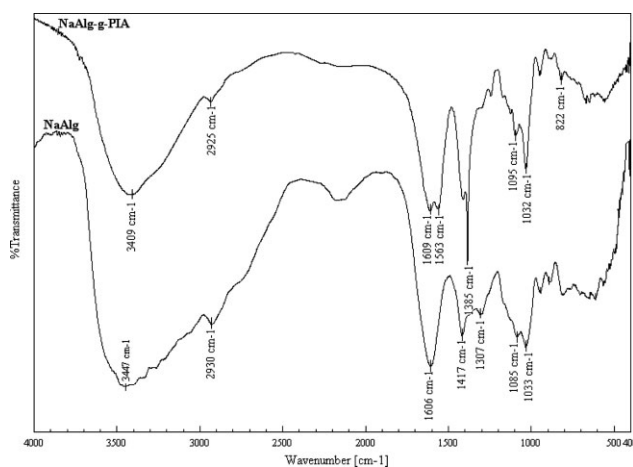
Fourier transform infrared (FTIR) spectra of NaAlg and NaAlg-*g*-PIA were taken in the wavelength region between 400 and 4000  $\text{cm}^{-1}$  at the ambient temperature, using Jasco FTIR-480 Plus spectrophotometer (Japan) with KBr discs. Completely dried samples were prepared by dispersing the samples in FTIR grade KBr (Sigma-Aldrich Chemical Co.) and then pressed using a hydraulic pressure of 70 MPa to form pellets of 2.0 cm of diameter.

### Differential scanning calorimetry

Thermal analyses were performed with Differential Scanning Calorimeter (PerkinElmer, Sapphire DSC). The sample weights ranged from 3.0 to 9.0 mg. The samples were initially heated from  $-100^\circ\text{C}$  to  $100^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ , then cooled to  $-100^\circ\text{C}$  and heated to  $300^\circ\text{C}$  at same heating rate. Second scans are reported. The intercept points of slopes were taken as the glass transition temperatures ( $T_g$ ).

### Thermal analysis

Thermogravimetric analysis was carried out with Setaram Instrument (SETSYS-1750 Simultaneous TG/DTA). Analyses were performed with 8–10 mg



**Figure 1** FTIR spectra of NaAlg and NaAlg-g-PIA (GY of 85.6%).

samples on a platinum pan under nitrogen atmosphere at a heating rate of 10°C/min until 900°C.

### Scanning electron microscopy

SEM photographs were taken with JSM 5600 Scanning Microscope (JEOL, Tokyo, Japan) to examine the morphology and surface structure of NaAlg and IA grafted NaAlg at the required magnification at room temperature. The polymers were deposited on a brass hold and sputtered with a thin coat of gold under vacuum. The acceleration voltage was 20 kV with the secondary electron image as a detector.

### Determination of intrinsic viscosity

Intrinsic viscosity measurements were carried out for grafted NaAlg in 0.2 M NaCl solution, using an Ubbelohde capillary flow viscometer mounted in a water bath maintained at 25.0 ± 0.1°C. Intrinsic viscosity,  $[\eta]$ , was determined by extrapolating the lin-

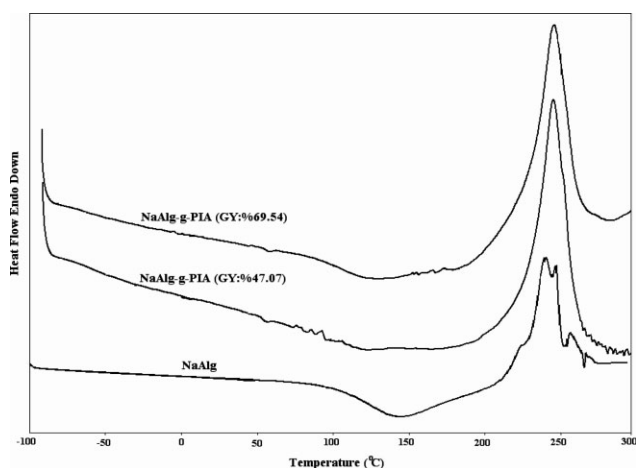
ear portion of the reduced viscosity vs. concentration plot to the zero concentration. From the values of  $[\eta]$ , the viscosity average molar mass,  $M_{\eta}$ , was calculated using the Mark Houwink-Sakurada (MHS) equation.

## RESULTS AND DISCUSSION

### Characterization of the graft copolymers of NaAlg with IA

The FTIR spectra of NaAlg and its graft copolymer with a GY (%) of 85.6 are shown in Figure 1. Grafted and ungrafted NaAlg showed a broad band between 3000 and 3800  $\text{cm}^{-1}$ , which was attributed to O—H stretching vibrations. The spectrum of NaAlg showed the peaks at around 2930, 1606, 1417, and 1033  $\text{cm}^{-1}$ , indicating the stretching vibrations of aliphatic C—H,  $\text{COO}^-$  (asymmetric),  $\text{COO}^-$  (symmetric), and C—O, respectively, which are characteristics of the polysaccharide (Fig. 1).<sup>6</sup> The spectrum of the NaAlg-g-PIA showed the peaks at around 2925, 1609, 1417, and 1032  $\text{cm}^{-1}$ , indicating the stretching of aliphatic C—H,  $\text{COO}^-$  (asymmetric),  $\text{COO}^-$  (symmetric), and C—O, respectively. Moreover, new strong band compared to NaAlg spectrum at around 1563 and 1385  $\text{cm}^{-1}$  were assigned to carboxylate ions as sodium salt of NaAlg-g-PIA, which confirmed the grafting of the monomer. This is in good agreement with the results reported in the literature.<sup>13,14</sup> The band at 1563  $\text{cm}^{-1}$  is also evidences a neutralization reaction as reported Krivoguz et al.<sup>9</sup>

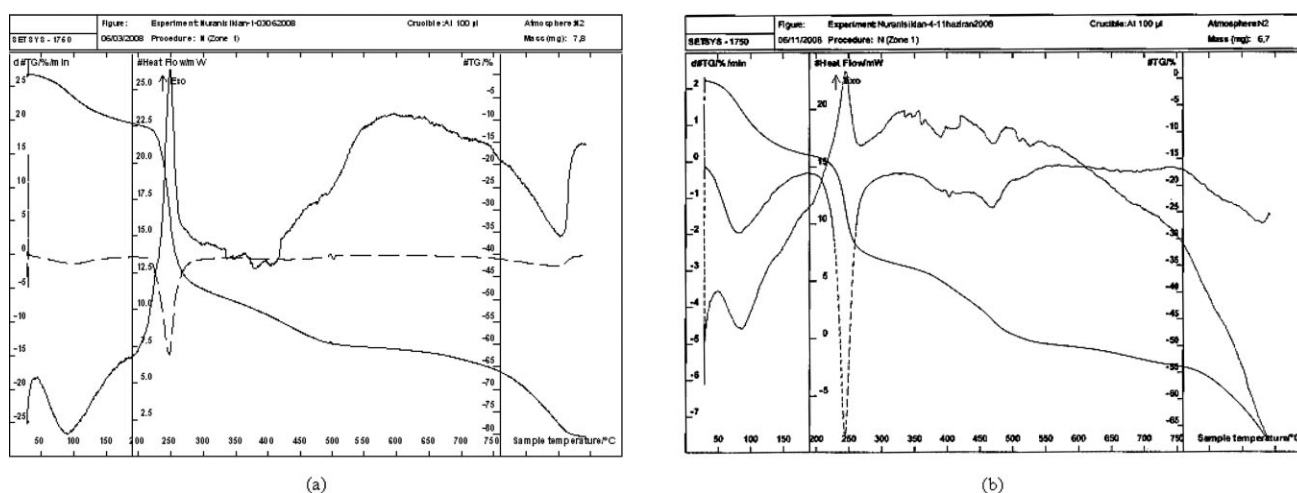
DSC analyses were performed to understand the thermal behavior of the graft copolymers and results are illustrated in Figure 2. As it reflected from the figure, the temperature of the end points of the endotherm peaks shifted to lower temperatures with the grafting of IA monomer.  $T_g$  values of NaAlg-g-PIA copolymers were lower than that of NaAlg as shown in the Table I. This is attributed to the fact that grafted chains might act as internal plasticizers. Similar observations can also be found in the literature and earlier study.<sup>15,16</sup> In the earlier study,<sup>16</sup> *N*-vinyl-2-pyrrolidone (*N*-VP) was grafted onto another natural polymer, sodium carboxymethyl cellulose (NaCMC), using AIBN. In this study, it was observed that  $T_g$  value decreased from 69.5 (NaCMC) to 52.0 (NaCMC-g-PVP with the 113% GY) with the grafting of *N*-VP onto NaCMC.



**Figure 2** DSC thermograms of NaAlg (a), NaAlg-g-PIA with 47.07% GY (b), NaAlg-g-PIA with 69.54% GY (c).

**TABLE I**  
 $T_g$  Values of NaAlg and Grafted NaAlg Obtained from DSC Analysis

Polymer	Graft yield (%)	$T_g$ (°C)
NaAlg	—	104
NaAlg-g-PIA1	47.07	89
NaAlg-g-PIA2	69.54	84



**Figure 3** TG/DTA thermograms of NaAlg (a), NaAlg-g-PIA with 85.6% GY (b).

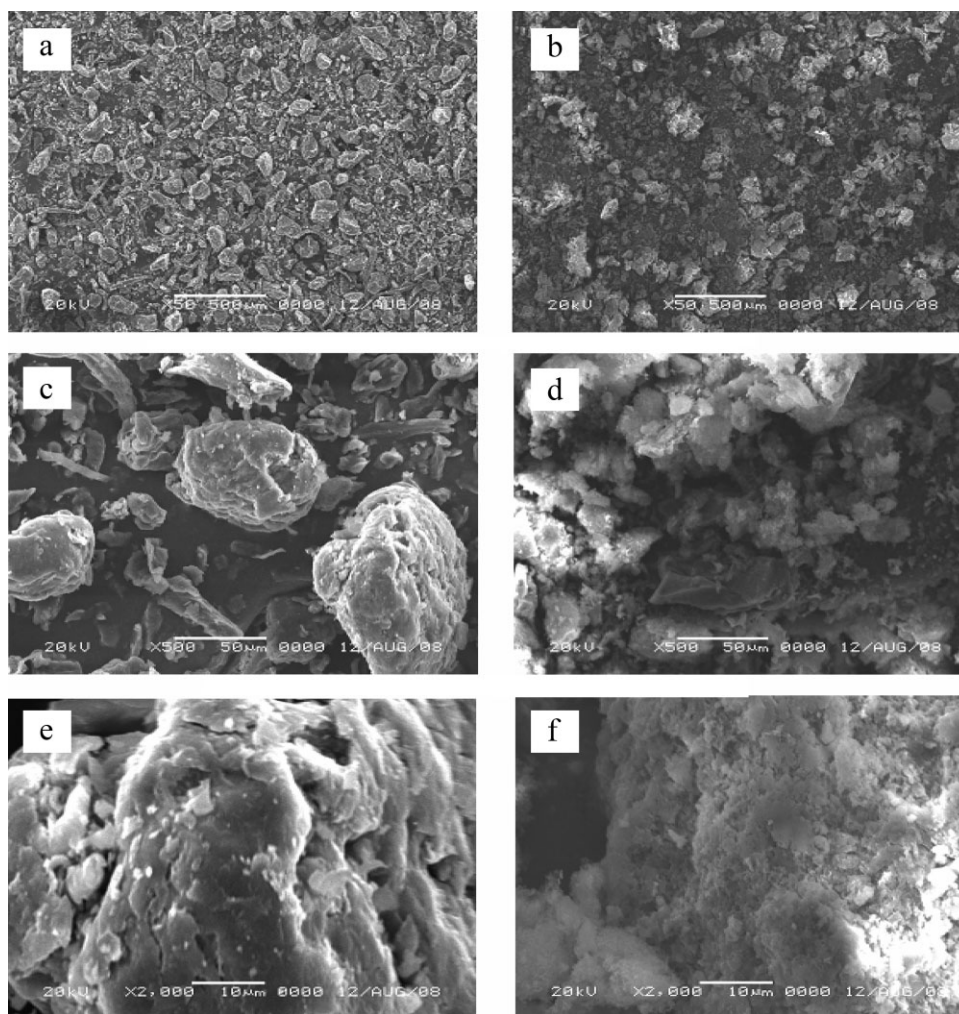
Thermogravimetric curves of NaAlg and NaAlg-g-PIA in a nitrogen atmosphere are displayed in Figure 3. The thermogram of NaAlg exhibited two distinct stages. One in the range of 0–160°C with a maximum decomposition rate at 104°C was assigned to elimination of water adsorbed to the hydrophilic polymer. The other in the range of 210–310°C with a maximum decomposition rate at 248°C was ascribed to a complex process including dehydration of the saccharide rings, depolymerization with the formation of water, CO<sub>2</sub>, and CH<sub>4</sub>.<sup>17</sup> Temperature of 50% weight loss was found to be 340°C for NaAlg. The differential thermogravimetric curve of the grafted NaAlg showed three degradation steps. The first in the range of 30–190°C with a maximum decomposition rate at 86°C was attributed to elimination of water adsorbed to the NaAlg-g-PIA structure. The second in the range of 200–300°C with a maximum decomposition rate at 245°C was assigned to depolymerization with the formation of water, CO<sub>2</sub>, sodium carbonate, and CH<sub>4</sub>. The third in the range of 395–505°C with a maximum decomposition rate at 471°C was attributed to chain degradation of PIA as sodium salt.<sup>13</sup> Temperature of 50% weight loss was also found to be 581°C for grafted NaAlg. TG/DTA thermogram was also in consistency with the results of DSC curve. From the DTG curves, it can be concluded that the grafting of PIA chains onto the polysaccharide backbone enhances the thermal stability of the polysaccharide, which can indicate that the grafted copolymer was synthesized successfully. This phenomenon has been also reported by Mostafa et al.<sup>11</sup> They have indicated that grafting of IA onto chitin improved thermal stability of the natural polymer.

The scanning electron micrographs of ungrafted and IA grafted NaAlg (with 80.7% GY) are shown in Figure 4. By comparing the surface morphology of

the grafted NaAlg [Fig. 4(b,d,f)] with ungrafted NaAlg [Fig. 4(a,c,e)] we found that the grafted chains drastically changed to the morphology of NaAlg. As shown in Figure 4, the surface of the NaAlg-g-PIA copolymer was more grained structure than that of NaAlg, and this is another proof of grafting.

The results of viscosity measurements along with the viscosity average molecular masses are presented in Table II, assuming the  $k$  and  $\alpha$  values do not change with the grafting. The observed decrease in intrinsic viscosity and molecular mass of the NaAlg can be attributed to the grafting. Intrinsic viscosity of a polymer is a measure of its hydrodynamic volume in solution, which in turn, depends on its molar mass and structure, the nature of the solvent and temperature of the medium. In general, the intrinsic viscosity of polysaccharide increases with grafting. This behavior has been observed for starch, carboxymethyl cellulose, and guar gum.<sup>18</sup> However, opposite behavior was reported for xanthan and NaAlg. Similarly, intrinsic viscosity and molecular mass of the NaAlg decreased with the grafting of NaAlg. Table II also reflected that the intrinsic viscosity decreases with the increasing of GY due to reduction of hydrodynamic volume. Similar findings were also reported in the study of Tripathy et al.<sup>4</sup> They have prepared polyacrylamide-grafted NaAlg and indicated that intrinsic viscosity of the grafted polymers decreases from 6.75 dL/g (conversion% = 83.76) to 6.00 dL/g (conversion% = 85.88) with the increasing cerium ammonium nitrate concentration from  $1.003 \times 10^{-4}$  to  $3.009 \times 10^{-4}$  mol, respectively.

The grafting mechanism of IA monomer onto NaAlg using CAN as the initiator in a manner similar to the one proposed by Lin et al.<sup>19</sup> Accordingly, Ce(IV) salts functioned as a powerful oxidizing



**Figure 4** SEM micrographs of ungrafted (a, c, e) and IA grafted (b, d, f) NaAlg (GY of 80.7%) with 50, 500, 2500 magnifications.

agent while alginate itself acted as a reducing component in the redox system. The active centers are directly produced on the alginate backbone and no charge transfer mechanism is necessary to initiate alginate graft copolymer formation. Cerium (IV) ions form chelates with the hydroxyl groups on carbons C-2 and C-3 of the mannuronic or guluronic acid units of NaAlg. Transfer of electrons from NaAlg to Ce (IV) gives Ce (III), which dissociates from the chelate, and short-living radical is formed. In the presence of IA monomer, grafting reaction is initiated to produce graft copolymer. Postulated reaction is presented in the Figure 5.

#### Determination of the optimum reaction conditions

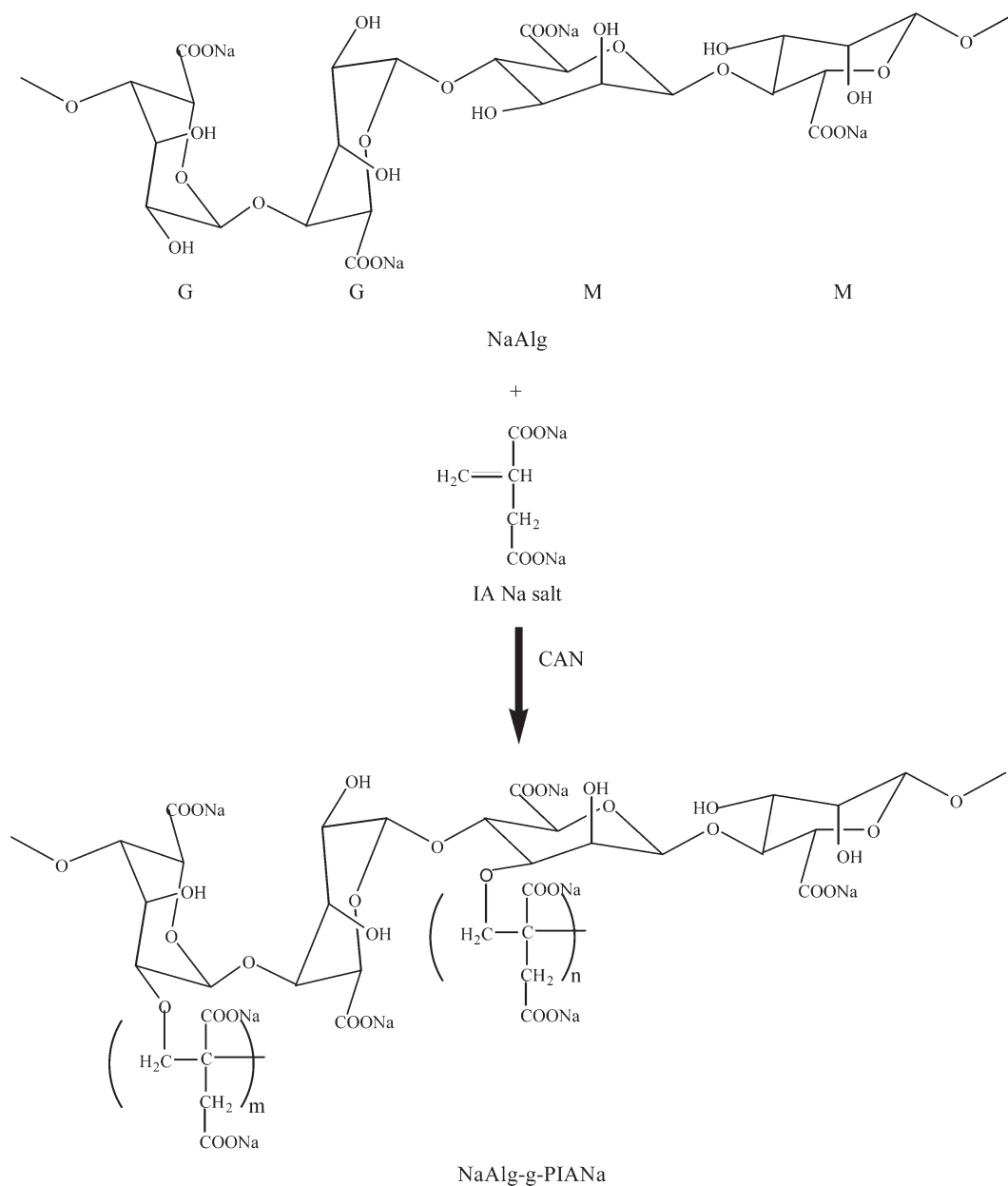
To optimize the reaction conditions for grafting, reaction time, temperature, concentrations of monomer, initiator, and the percentage of NaAlg were varied.

#### Effect of the reaction time

The reaction time plays an important role in the graft copolymerization. Grafting of NaAlg was carried out at various polymerization times, with the temperature, monomer and initiator concentrations

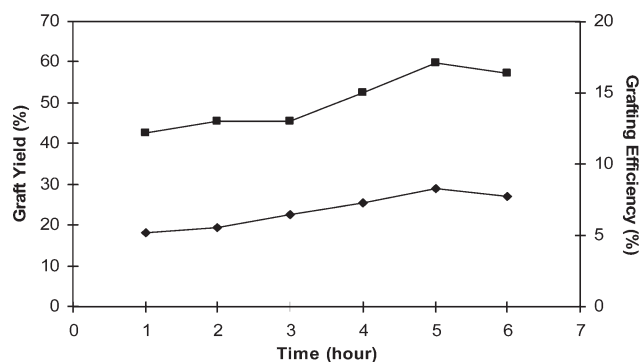
**TABLE II**  
Variation of Intrinsic Viscosity and Viscosity Average Molar Mass of Copolymers With the Graft Yield

Graft yield (%)	Intrinsic viscosity, $[\eta]$ , dL/g	$M_v$
–	8.1096	101,751
47.07	7.1873	90,179
56.10	6.0343	75,712
57.22	5.869	73,639
59.73	5.409	67,867
69.54	4.6338	58,141
106.51	4.0013	50,204
125.99	3.2682	41,006
164.42	2.4377	30,585
314.58	1.2025	15,087

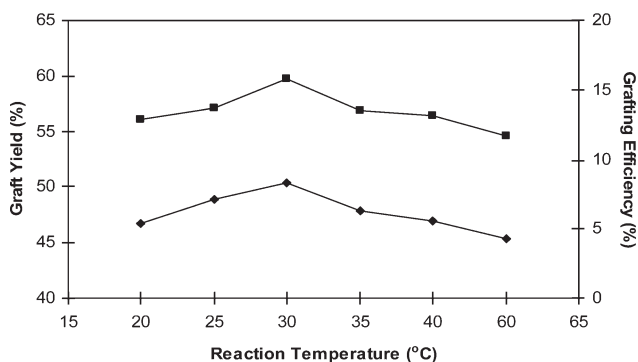


**Figure 5** Possible reaction of NaAlg with IA sodium salt.

kept constant, and the results are shown in Figure 6. GY and grafting efficiency progressively increased with the increase in polymerization time up to 5 h then leveled off reaching a 59.73% saturation grafting value was reached. The increase in the grafting parameters could be attributed to the increase in the number of grafting sites on the NaAlg backbone and the addition of monomer molecules to the growing grafted chains. The following trend of almost leveling off was due to the decrease in monomer, initiator concentrations, a reduction in the number of active sites on the NaAlg backbone and an increase in the medium viscosity, and thus the formation of a diffusion barrier. Similar results were found for the graft copolymerization of methacrylamide onto agar



**Figure 6** Variation of the graft yield (■) and grafting efficiency (◆) with the reaction time. Reaction conditions: Percentage of NaAlg (%) = 1.0; [IA] = 0.46 M; [CAN] =  $9.12 \times 10^{-3}$  M;  $T = 30^\circ\text{C}$ .



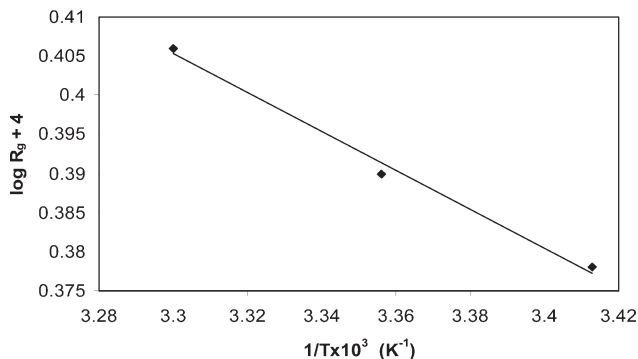
**Figure 7** Variation of the graft yield (■) and grafting efficiency (◆) with the temperature. Reaction conditions: Percentage of NaAlg (%) = 1.0; [IA] = 0.46 M; [CAN] =  $9.12 \times 10^{-3}$  M;  $t = 5$  h.

using CAN.<sup>20</sup> They have reported same trend in the effect of the reaction time and found to be 3 h for the optimum reaction time.

Joshi and Sinha,<sup>21</sup> have studied grafting of 2-hydroxyethylmethacrylate onto another polysaccharide carboxymethyl chitosan using CAN. They have obtained the same trend in the effect of the reaction time on the grafting parameters. The optimum reaction time has been reported to be 4.5 h in their study.

### Effect of the temperature

To investigate the effect of the temperature on the graft copolymerization of IA onto NaAlg was studied by the variation of the temperature between 20 and 60°C, and the results are presented in Figure 7. As can be seen from the Figure, the GY increased with increasing the temperature from 20°C to 30°C. a further increase in the temperature, values of it decreased. However, grafting efficiency increased very rapidly in the beginning and then decreased with a further increase in the temperature. The highest GY and grafting efficiency values obtained were 59.73% and 8.28 %, respectively, at 30°C. The enhancement in the grafting with the rising the poly-



**Figure 8** Arrhenius plot of  $\log R_g$  versus  $1/T$ .

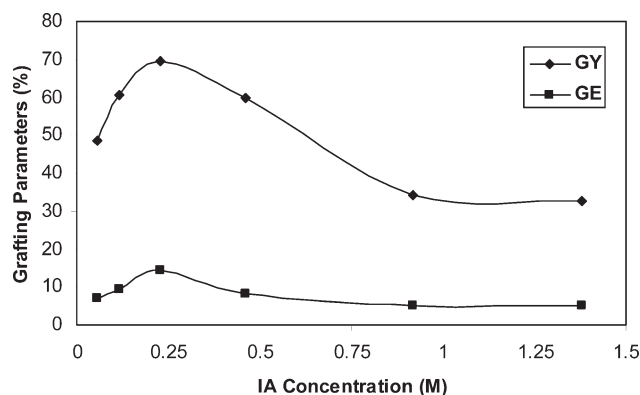
merization temperature could be ascribed to a higher rate of redox reaction between the CAN and NaAlg. The increase in the reaction temperature also enhanced the mobility of the NaAlg backbone, monomer and initiator molecules. Hence, the diffusion of monomer and initiator into the NaAlg backbone increased with the increasing temperature. Therefore, rates of grafting increased. However, the lowering of grafting parameters by an increase in the temperature above 30°C could be due to the favored chain termination reactions, chain transfer reactions, and an increase in the formation of homopolymer, as reflected from the grafting efficiency curve in Figure 6. Similar results have been obtained by many workers who have studied graft copolymerization.<sup>6,11,21–23</sup>

Gupta and Khandekar<sup>23</sup> studied the graft copolymerization of acrylamide and ethyl acrylate onto cellulose using CAN and reported that the grafting parameters increased with an increase in the temperature up to 35°C and then decreased up to 50°C.

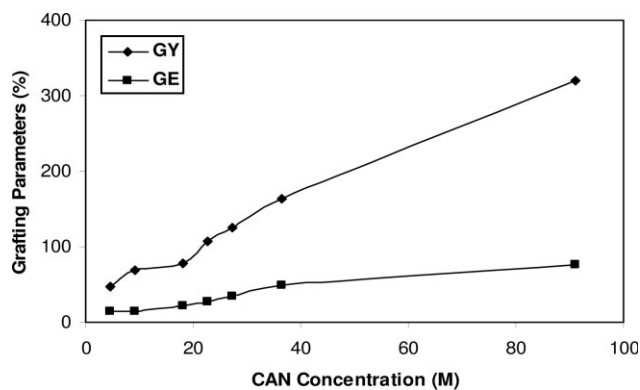
The grafting rate of copolymerization at different temperatures has been used to determinate activation energy of the graft copolymerization. The overall activation energy for grafting was found to be 1135 cal/mol from the Arrhenius plot of  $\log R_g$  versus reciprocal of the temperature ( $1/T$ ) as shown in Figure 8. In our previous work, the overall activation energy was calculated similarly to be 10.5 kcal/mol for the grafting of N-VP onto sodium carboxymethylcellulose.<sup>16</sup> The small value of the obtained activation energy shows that the grafting reaction between IA and NaAlg is thermodynamically favored and needs little energy.

### Effect of the monomer concentration

The monomer concentration has a remarkable effect on the GY and grafting efficiency. For this purpose,



**Figure 9** Effect of the monomer concentration on the grafting parameters. Reaction conditions: Percentage of NaAlg (%) = 1.0; [CAN] =  $9.12 \times 10^{-3}$  M;  $t = 5$  h,  $T = 30^\circ\text{C}$ .



**Figure 10** Effect of the initiator concentration on the grafting parameters. Reaction conditions: percentage of NaAlg (%) = 1.0; [IA] = 0.23 M;  $t = 5$  h,  $T = 30^\circ\text{C}$ .

monomer concentration was changed from 0.0575 M to 1.38 M with all the other conditions kept constant. Results obtained are presented in Figure 9. The grafting parameters increased steadily with the monomer concentration up to 0.23 M and then decreased with a further increase in the IA concentration. As the monomer concentration increased, the diffusion of the monomer molecules into the NaAlg backbone increased, and this led to a higher GY. The decrease in the grafting after this value could be associated with the depletion of the available IA due to the simultaneous increase in the homopolymerization rate (as shown by the GE values) with the growing IA concentration in the polymerization medium. With a higher monomer concentration, the concentration of PIA macroradicals increased, and the rates of their combination and disproportionation were faster than the rate of their combination with NaAlg molecules. Therefore, the homopolymer and a lower percentage of grafting were produced. In addition, the homopolymer that accumulated in the reaction medium increased the medium viscosity, and the monomer diffusion into the NaAlg backbone became more difficult. Such behaviors were also obtained in other studies in the literature.<sup>11,24-26</sup> In the study of Liu et al.,<sup>25</sup> they investigated the grafting of methyl methacrylate onto NaAlg, and observed that the grafting percentage increased as the monomer concentration increased from 0.4 mL to 1.6 mL and after that decreased with a further increase in the monomer concentration to 2.8 mL.

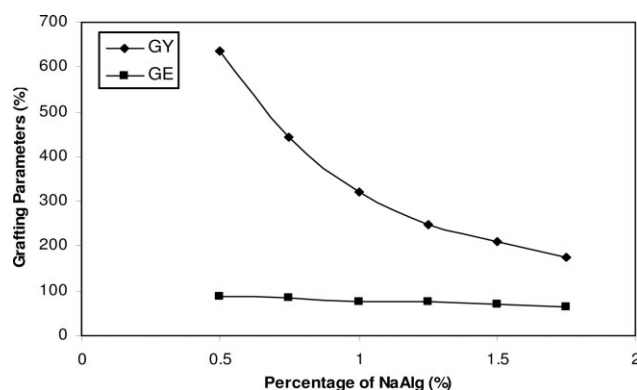
#### Effect of the initiator concentration

Another parameter that affects the grafting parameters is the initiator concentration. Figure 10 shows the effect of CAN concentration on the grafting parameters as the CAN concentration increased. As can be seen from the figure, an important impact on

grafting of IA on the NaAlg formed as increase in CAN concentration. The GY and grafting efficiency increased significantly as the CAN concentration increased from  $4.56 \times 10^{-3}$  M to  $9.12 \times 10^{-2}$  M. The best GY and grafting efficiency were obtained to be 320.56% and 77.2 %, respectively, in the  $9.12 \times 10^{-2}$  M CAN concentration. The enhancement of the grafting by increasing the CAN concentration implies that free-radical species may participate essentially in the direct abstraction of a hydrogen atom from the NaAlg backbone to yield a NaAlg macroradical capable of initiating the grafting. The increase in the grafting parameters with a increase in initiator concentration is consistent with the results of other studies.<sup>27,28</sup> Sangramsingh et al.,<sup>28</sup> carried out graft copolymerization of methyl methacrylate onto starch using Ce(IV)-glucose initiator system in aqueous media and observed that GY increased with an increase in the concentration of Ce(IV) from 0.005 to 0.045 M.

#### Effect of the NaAlg percentage

The effect of the NaAlg percentage on the grafting parameters was studied by the variation of the concentration of NaAlg from 0.5 to 1.75 g/dL and obtained results are presented in Figure 11. The highest GY value in the study was obtained to be 635.28% at 0.5 g/dL NaAlg concentration as seen in the figure. As the percentage of NaAlg was increased, the GY was found to decrease continuously. It can also be seen from the figure, grafting efficiency decreases slowly with the increase in percentage of NaAlg. These trends can be explained by the fact that as the percentage of NaAlg increased, the viscosity of the reaction medium also increased, which hinders the movement of CAN, thereby reducing the grafting parameters. Moreover, a high NaAlg percentage could produce more NaAlg macroradicals, which could interact with one



**Figure 11** Effect of the NaAlg concentration on the grafting parameters. Reaction conditions: [CAN] =  $9.12 \times 10^{-2}$  M; [IA] = 0.23 M;  $t = 5$  h,  $T = 30^\circ\text{C}$ .



another to terminate the reaction, thus lowering both the GY and the grafting efficiency values. Similar findings have also been found in the literature and previous study.<sup>16,22,24–26,28</sup>

### CONCLUSIONS

In this study, IA as a sodium salt was successfully grafted onto NaAlg under N<sub>2</sub> atmosphere with CAN as the initiator. The graft copolymerization was confirmed by FTIR, DSC, TG/DTA, and SEM. On the basis of the TGA results we found the grafted NaAlg to be more thermally stable than the ungrafted one due to incorporation of PIA. Results obtained showed that control of the grafting parameters was possible by varying the reaction conditions such as reaction time, temperature, concentration of monomer, and initiator. The optimum conditions for the maximum grafting parameters (GY of 635.28% and GE of 87.87%) were obtained when the polymerization was carried under the following conditions: [CAN] =  $9.12 \times 10^{-2} M$ ; [IA] = 0.23 M; [NaAlg] = 0.5 g/dL; time = 5 h, and temperature = 30°C. The overall activation energy for grafting was calculated to be 1135 cal/mol. Furthermore, it was observed that the intrinsic viscosity of grafted NaAlg decreased with the increase in the GY.

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