

# Ceric-Initiated Free Radical Graft Copolymerization of Acrylonitrile onto kappa Carrageenan

Hossein Hosseinzadeh

Department of Chemistry, University of Payame Noor, West Azerbaijan Miandoab, Iran

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**ABSTRACT:** The polysaccharide, kappa carrageenan (kC), was modified using ceric-initiated graft copolymerization of acrylonitrile (AN) under inert atmosphere in a homogeneous aqueous medium. Grafting was confirmed using FTIR spectroscopy, solubility test, elemental analysis, acid hydrolysis, and thermogravimetric analysis (TGA). kC-graft-poly(AN) products had a higher thermal stability than kC as revealed by TGA analysis. The polyacrylonitrile branches were isolated by acidic degradation of the carrageenan main chains and characterized by size exclusion chromatography (SEC). Residual monomers were not found by HPLC in graft copolymers stored even for longer periods. The effect of various factors affecting on grafting, i.e., concentration of the initiator, monomer,

and polysaccharide as well as the reaction time and temperature were studied by conventional methods to achieve the optimum grafting parameters. The graft copolymerization reactions were kinetically investigated using semi-empirical expressions and a suitable rate expression has been derived. According to the empirical rates of the polymerization and the graft copolymerization of AN onto kC backbone, the overall activation energy of the graft copolymerization reaction was estimated to be 20.96 kJ/mol. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 404–412, 2009

**Key words:** carrageenan; acrylonitrile; graft copolymerization; ceric ammonium nitrate

## INTRODUCTION

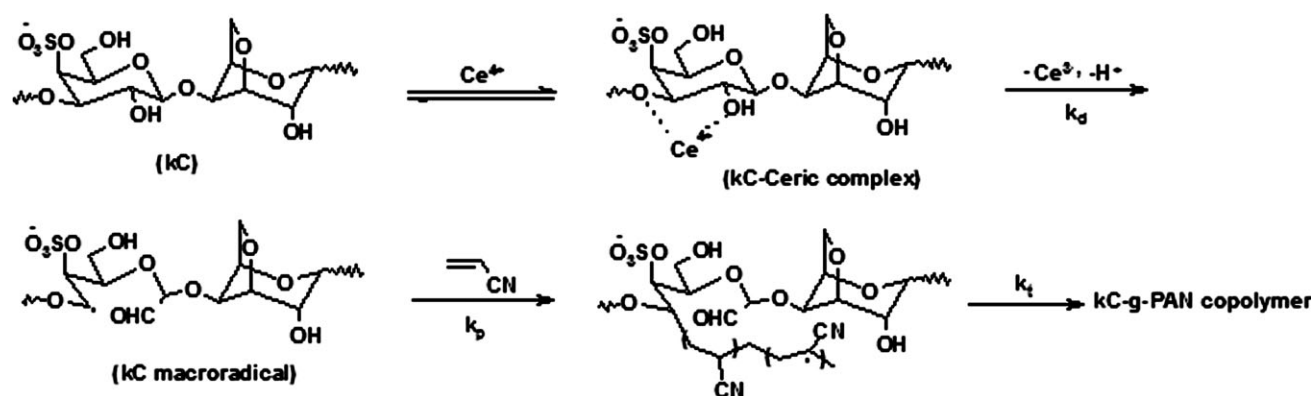
Graft copolymerization of hydrophilic and hydrophobic vinyl monomers is a useful technique for modifying the properties of the synthetic and natural polymers. In the area of natural polymer modification through graft copolymerization, various vinyl monomers were grafted onto polysaccharides such as starch, chitosan, and sodium alginate.<sup>1–4</sup> Graft copolymers are prepared by first generating free radicals on the polysaccharide backbone and then allowing these radicals to serve as macroinitiators for the vinyl monomers. These biodegradable and low-cost graft copolymers, with new properties can be used in many applications such as textiles, paper industry, agriculture, medical treatment, in petroleum industry as flocculants and thickening agents,<sup>5–11</sup> and also development of selective permeable membranes,<sup>12</sup> sorption agents,<sup>13</sup> and in fabrication of drug delivery systems.<sup>14,15</sup>

Free radical graft copolymerization was usually carried out using various initiators such as ammonium persulfate, benzoyl peroxide, and azoisobutyronitrile. Mino and Kaizerman for the first time utilized ceric

ammonium nitrate (CAN) as a very effective redox initiator.<sup>16</sup> Since then,  $Ce^{4+}$  has been widely employed as an initiator in redox graft copolymerization of a variety of vinyl monomers. For example, methyl acrylate was grafted onto starch using Ce (IV) as an initiator.<sup>17,18</sup> Ceric ions have been also used to graft copolymerized some vinyl monomers including acrylonitrile,<sup>19</sup> methyl acrylate and methyl methacrylate,<sup>20</sup> and acrylamide<sup>21,22</sup> onto sodium alginate. In addition, ceric ion was used to graft copolymerization of acrylamide onto carboxymethyl starch<sup>23</sup> and carboxymethylcellulose.<sup>24</sup> Starch-g-poly(methacrylonitrile)<sup>25</sup> and cyanoethylcellulose-g-poly(acrylonitrile)<sup>26</sup> were also prepared by this method. Although much work has been reported on the grafting of acrylonitrile onto various polysaccharides, but a literature survey reveals that no article has been reported in the case of acrylonitrile (AN) grafting onto kappa-carrageenan (kC). Therefore, in the present work, we attempted to modify kC by free radical graft copolymerization of acrylonitrile. The effect of concentration of kC, AN, and CAN as well as the reaction time and temperature on the graft copolymerization was studied by determining the grafting parameters.

Carrageenan is a collective term for linear sulfated polysaccharides that are obtained commercially by alkaline extraction of certain species of red seaweeds.<sup>27</sup> kC is the most well known and most important type of carrageenan family. Schematic

Correspondence to: H. Hosseinzadeh (h\_hosseinzadeh@pnu.ac.ir).



**Scheme 1** A brief proposed mechanism for ceric-induced grafting of polyacrylonitrile (PAN) onto kappa carrageenan (kC).

diagram of the idealized structure of the repeat units for the kC, is framed in Scheme 1.

## EXPERIMENTAL

### Materials

The polysaccharide, kappa carrageenan (kC, from Condinson Co., Denmark) was of analytical grade and was used as received. CAN was purchased from Merck and was used without purification. It was as freshly prepared 0.1 M solution in 1 mol/L HNO<sub>3</sub>. Acrylonitrile (AN, Merck) was used after distillation for removing inhibitor.

### Graft copolymerization method

Variable amounts of kC (0.5–3.5 g) were dissolved in 50 mL of distilled water in a three-necked 100 mL round-bottomed flask fitted with a magnetic stirrer, immersed into a thermostated water bath, and preset at desired temperature (30–90°C). An inert gas (argon) was gently bubbled into the reactor to remove the oxygen during the graft copolymerization reaction. After complete dissolution of the kC, a given amount of monomer, AN (0.5–5.0 g), was added to the flask and the mixture was stirred for 10 min. Then, the initiator solution (1.0–7.0 mL of 0.1 mol/L acidic solution of CAN) was added to the mixture and continuously stirred for certain times (30–180 min). Finally, the product was precipitated by pouring the reaction mixture solution into 200 mL of ethanol. Then, the precipitate was filtered and repeatedly washed with ethanol and dried in oven at 50°C for 10 h.

### Homopolymer extraction

The graft copolymer, namely kC-g-PAN, was freed from polyacrylonitrile (PAN) homopolymer, by pouring 0.50 g of the product in 50 mL of dimethyl

formamide solution. The mixture was stirred gently at room temperature for 24 h. After complete removal of the homopolymer, the kC-g-PAN was filtered, washed with ethanol and dried in oven at 50°C to reach a constant weight.

### Isolation and characterization of polyacrylonitrile branches

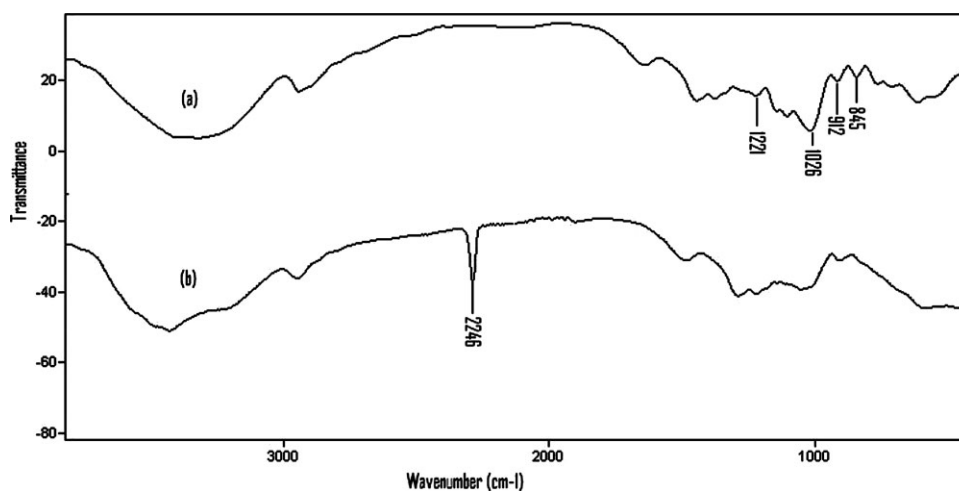
An accurately weighed sample of the graft copolymer in 20 mL of 1 mol/L hydrochloric acid was heated at 100°C for 8 h. Hydrochloric acid was removed from the resulting solution with a rotary evaporator, and the residue was extracted with warm DMF. The extract was evaporated, filtered, and the residue was dried to give polyacrylonitrile whose IR spectrum was virtually identical with that of polyacrylonitrile. The number and weight average molecular weights,  $\overline{M}_n$  and  $\overline{M}_w$ , were determined by size exclusion chromatography (SEC).

### Size exclusion chromatography

Molecular weights were determined with a SEC equipped with a Waters 590 HPLC pump, Dawn DSP multiangle laser light scattering (MALLS) detector, and a Waters 410 differential refractometer (DRI). The dried polymers were dissolved in THF and eluted at a flow rate of 0.9 mL/min through two Phenogel columns from Phenomenex. SEC calibration was performed using polystyrene standards.

### High performance liquid chromatography

Residual monomers of graft copolymers were analyzed by a reverse phase Shim-Pack C18 (ODS) column (Shimadzu, Japan, 15 cm × 4.6 mm i.d.) in a Shimadzu HPLC system consisting of an LC 6A pump equipped with UV-Vis spectrophotometric detector, according to the procedure of Saroja et al.,<sup>28</sup> which involves separation using 0.05 M KH<sub>2</sub>PO<sub>4</sub>, pH



**Figure 1** FTIR spectra of (a) kC and (b) homopolymer-free kC-g-PAN.

5.5 at  $1 \text{ mL min}^{-1}$  at  $30^\circ\text{C}$ . A 10 mL volume of standard acrylonitrile, diluted in glass distilled water, was injected onto the column and detected at 220 nm. Their minimum detection limit varied from 1 to 10 ng.

### Infrared spectroscopy

FTIR spectra of finely powdered grafted and ungrafted kC were run in the form of KBr pellets using an ABB Bomem MB-100 FTIR spectrophotometer.

### Elemental analysis

The elemental composition of the polymer product was determined with an elemental analyzer (Heraeus CHN-O-Rapid Analyzer Instrument).

### Thermal analysis

Thermogravimetric analyses (TGA) were performed on a Universal V4.1D TA Instruments (SDT Q600) with 8–10 mg samples on a platinum pan under nitrogen atmosphere. Experiments were performed at a heating rate of  $20^\circ\text{C/min}$  until  $600^\circ\text{C}$ .

## RESULTS AND DISCUSSION

### Proof of grafting

Evidence of grafting was obtained by comparison of FTIR spectra of kC and the graft copolymer, TGA, solubility characteristics, and elemental analysis of the products.

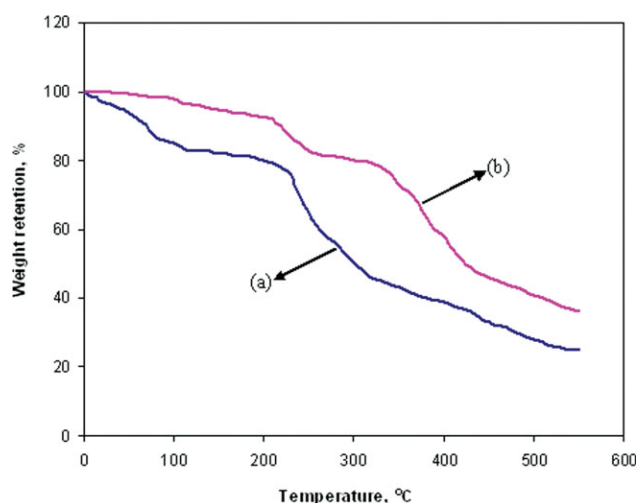
### Infrared spectroscopy

Infrared spectroscopy is the best tool to confirm the grafting reaction. The IR spectra of pure kC and the graft copolymer, kC-g-PAN, was shown in Figure 1.

In the IR spectrum of kC, the peaks observed at 845, 912, 1026, and  $1221 \text{ cm}^{-1}$  could be related to D-galactose-4-sulfate, 3,6-anhydro-D-galactose, glycosidic linkage, and ester sulfate stretching of kC, respectively [Fig. 1(a)]. The broad band at  $3200\text{--}3400 \text{ cm}^{-1}$  is due to stretching of  $\text{—OH}$  groups of kC. An additional sharp characteristic peak in the graft copolymer at  $2246 \text{ cm}^{-1}$  [Fig. 1(b)] which is attributed to  $\text{—C}\equiv\text{N}$  stretching absorption can be used for confirming the grafting of PAN onto the substrate, kC.

### Thermogravimetric behavior

The grafting was also supported by TGA (Fig. 2). TGA of kC (Fig. 2a) shows a weight loss in two distinct stages. The first stage ranges between 15 and  $120^\circ\text{C}$  and shows about 17% loss in weight. This may correspond to the loss of adsorbed and bound water.<sup>29</sup> No such inflexion was observed in the TGA



**Figure 2** TGA curves of (a) kC and (b) kC-g-PAN. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**TABLE I**  
Yield, Molecular Weight, and Polydispersities of PAN Grafts From Acidic Degradation of kC-g-PAN Copolymers

kC-g-PAN (g)	Yield of PAN		SEC of PAN		
	mg	%	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w \times 10^{-5}$	$\frac{\overline{M}_w}{\overline{M}_n}$
0.1	65	75	3.2	3.8	1.18
0.3	76	81	4.8	6.7	1.39
0.5	81	94	5.2	9.4	1.81

curve of kC-g-PAN. This indicated that the grafted copolymers were resistant to moisture absorption. The second stage of weight loss starts at 230°C and continues up to 380°C during which there was 60% weight loss due to the degradation of kC. Grafted samples, however, show almost different behavior of weight loss between 15 and 550°C (Fig. 2b). The first stage of weight loss starts at 210°C and continues up to 270°C, during which there was 19% weight loss due to the degradation of kC. The second stage from 340 to 440°C may contribute to the decomposition of different structure of the graft copolymer. The appearance of these stages indicates the structure of kC chains has been changed, which might be due to the grafting of PAN chains. In general, the copolymer had lower weight loss than kC. This means that the grafting of kC increases the thermal stability of kC in some extent.

### Solubility test

The existence of poly(AN) grafting was also confirmed by the difference between solubility of the graft copolymer and the non-grafted homopolymer. The classic method for separating homopolymer from graft copolymer is to extract the reaction product with a solvent that is capable of dissolving homopolymer and not trunk polymer. kC and PAN are soluble in water and DMF, respectively. However, the graft copolymer is insoluble in DMF as well as in water. When a reaction product was extracted with DMF and alternatively with water for 24 h, an insoluble solid still remained. A physical mixture of kC and PAN was treated in the same way and was found to dissolve completely. Therefore, it is obvious that the resulted graft copolymer was not a simple physical mixture, but some chemical bonds must exist between the kC substrate and PAN macromolecules.

In addition to the formation of graft copolymers, crosslinking between the chains of kC may also take place. This was evident by the reaction between kC and the initiator, in the absence of monomers, giving

a product with reduced solubility (unpublished data).

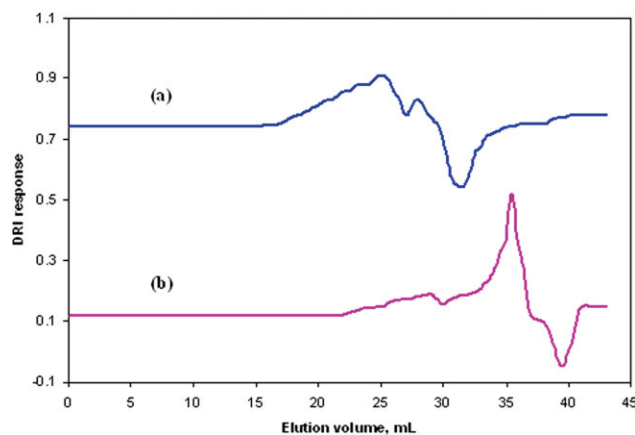
Moreover, because of insolubility of the graft copolymer and PAN in water and in the AN monomer, respectively, the polymerization reaction proceeds as a heterogeneous process and the formed copolymer precipitate during the process. This observation practically proves that the grafting reaction was performed. However, this phenomenon affect efficiency of the grafting and, moreover, molecular weight of the grafts. Although, it should be also pointed out the residual AN monomer, with progress of polymerization reaction, is very low (next section) and therefore the amount of precipitated PAN homopolymer is negligible.

### Residual monomer detection

The residual monomers if any, in the graft copolymers were extracted with water and subjected to an isocratic reverse phase-HPLC separation. No detectable monomers were revealed even in kC-g-PAN, although acrylonitrile is known for degradation if kept for long time, to acrylamide and acrylic acid.<sup>30</sup> Even a sample of kC-g-PAN stored for 3 months did not show any residual monomers.

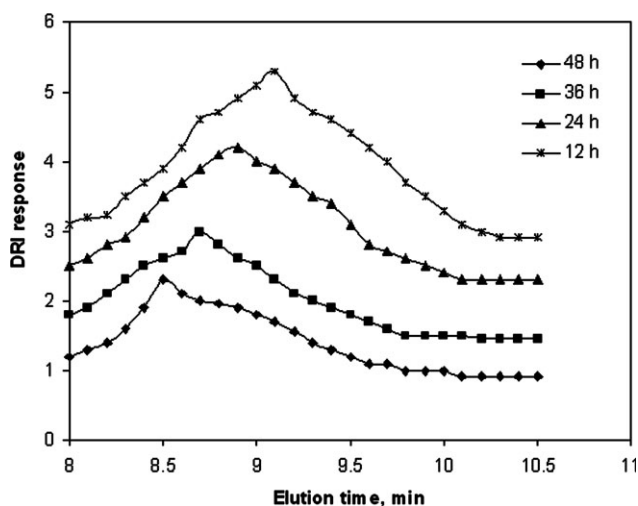
### Acid hydrolysis and SEC analysis

To separate the grafted side chain polymers, i.e., PAN, from kC backbone, the grafted copolymer was subjected to acid hydrolysis. The precipitated obtained in the acid hydrolysis study was then analyzed using SEC. The results are listed in Table I. The polydispersities were 1.18, 1.39, and 1.81 indicating that fairly narrow distributions were obtained with the graft copolymerization in a partially dissolved, highly swollen state. Also, a typical SEC of a



**Figure 3** Size exclusion chromatographs of (a) kC-g-PAN and (b) polyacrylonitrile grafts recovered from acidic hydrolysis. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]





**Figure 4** Size exclusion chromatographs of polyacrylonitrile grafts recovered from acidic hydrolysis of kC-g-PAN at various polymerization times.

kC-graft-polyacrylonitrile along with the SEC of the corresponding polyacrylonitrile grafts is shown in Figure 3. The molecular weights of the copolymers estimated by SEC appear relatively low due to the compact and the branched structures of the graft copolymers.

Moreover, size exclusion chromatographs of polyacrylonitrile grafts recovered from acidic hydrolysis of the grafted copolymer show that  $M_n$  for the grafts increased with polymerization time as shown in Fig. 4.

#### Estimation of acrylonitrile content in copolymerizate

The acrylonitrile proportion in the copolymerizate was calculated from the total nitrogen content (N-content) of the sample using the following equation:

$$AN_p, \text{wt}\% = \frac{N_p, \text{wt}\%}{N_m, \text{wt}\%} \times 100 \quad (1)$$

where  $AN_p$ ,  $N_p$ , and  $N_m$  denote acrylonitrile content in the copolymer, nitrogen content in the copolymer, and nitrogen content in the initial acrylonitrile monomer, respectively. The acrylonitrile content of the chemically synthesized copolymer was 81.5%. In the kC tested no nitrogen content was detectable.

#### Graft copolymerization mechanism

The suggested mechanism of the AN grafting onto kC in the presence of CAN as free radical initiator can be seen in the Scheme 1. Duke and Froist<sup>31,32</sup> have shown that ceric salts form complexes with alcohols, and these complexes are disproportionate via single electron transfer with the formation of free

radicals on the reducing agent. However, it has been shown that the anhydroglucose units are predominantly oxidized through C2–C3 bond cleavage induced by Ce (IV) ions.<sup>33</sup> Therefore, a general reaction mechanism for graft copolymerization reaction, in analogy with that previously mentioned<sup>34</sup> may be as follows (Scheme 1): the first step of the mechanism is a complex formation of the  $Ce^{4+}$  ion with the oxygen atom at the C-3 position and the hydroxyl group at the C-2 position. This kC- $Ce^{4+}$  complex are then reduced to a  $Ce^{3+}$  ion and consequently a free radical is formed onto kC backbone. These radicals are responsible for the initiation of acrylonitrile grafting onto polysaccharide backbone.

The 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>35</sup>

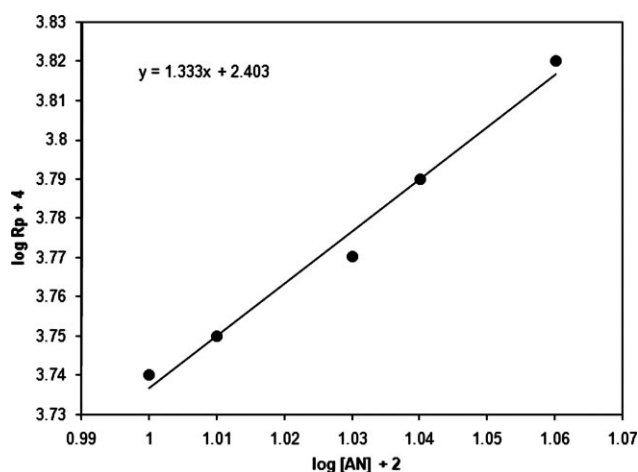
$$R_p (\text{mol.L}^{-1}.\text{s}^{-1}) = \frac{1000TP}{MTV} \quad (2)$$

$$R_g (\text{mol.L}^{-1}.\text{s}^{-1}) = \frac{1000GS}{MTV} \quad (3)$$

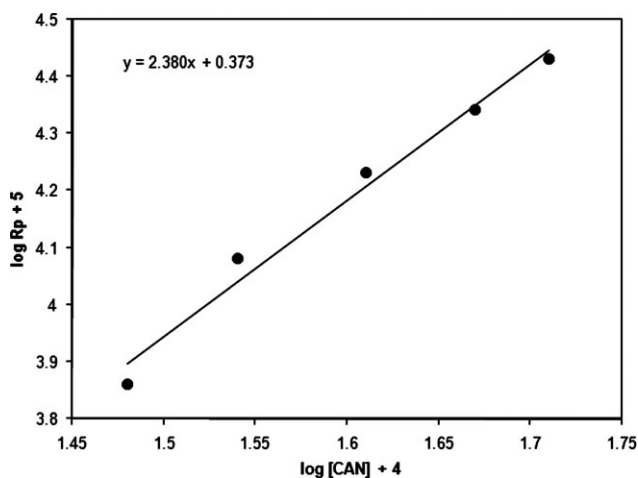
$TP$  (g) stands for weight of total polymer formed.  $M$  (g/mol) is the molecular weight of the monomer used (i.e., AN, 53.0).  $T$  and  $V$  denote total reaction time (s) and total volume (mL) of the reaction mixture.

The calculation of  $R_p$  values may be of significant importance in confirming a proposed reaction mechanism and kinetics. Therefore, we investigated the relation between rate of graft copolymerization and concentration of CAN, AN, and kC.

In general, the relation between the rate of polymerization ( $R_p$ ) and the monomer, initiator, and polysaccharide concentrations can be written as<sup>36</sup>



**Figure 5** The change of rate of grafting with monomer concentration.



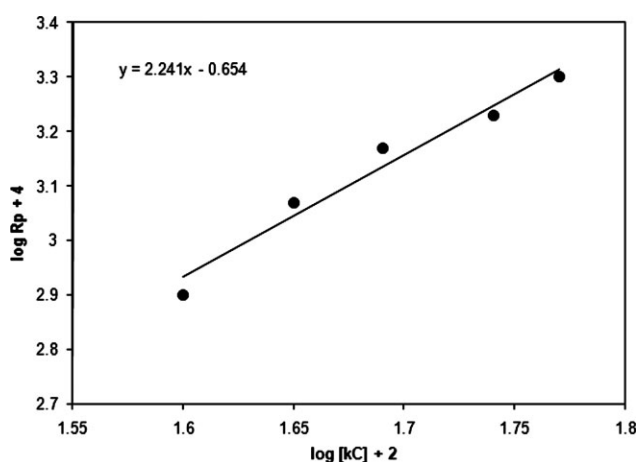
**Figure 6** The change of rate of grafting with initiator concentration.

$$R_p = k[\text{monomer}]^a[\text{initiator}]^b[\text{polysaccharide}]^c$$

where  $a$ ,  $b$ , and  $c$  can be experimentally determined by the logarithmic form of the equation given above:

$$\log R_p = \log k + a(\log[\text{monomer}]) + b(\log[\text{initiator}]) + c(\log[\text{polysaccharide}])$$

The changes in the initial rate of grafting with AN concentration, by keeping the CAN and kC concentrations constant, are given in Figure 5. The slope of the  $\log R_p$  vs.  $\log [\text{AN}]$  graph reflects that the rate of grafting is proportional to the 1.33 power the of AN concentration. Similarly, the changes in the initial rate of grafting were separately determined for CAN and kC concentrations, keeping the concentrations of other reactants constant (Figs. 6 and 7). Thus, from



**Figure 7** The change of rate of grafting with polysaccharide concentration.

these experimental results, the grafting rate of AN onto kC backbones using CAN initiator can be written as:

$$R_p = k[\text{AN}]^{1.33}[\text{CAN}]^{2.38}[\text{kC}]^{2.24}$$

The overall activation energy ( $E_a$ ) of the graft polymerization reaction was calculated using of the eq. (3) and the slope of the plot  $\text{LnRg}$  versus  $1/T$  (Fig. 8) based on Arrhenius relationship [ $k_p = A\exp(-E_a/RT)$ ]. Therefore,  $E_a$  for the graft copolymerization was found to be 20.96 kJ/mol.

### Evaluation of grafting parameters

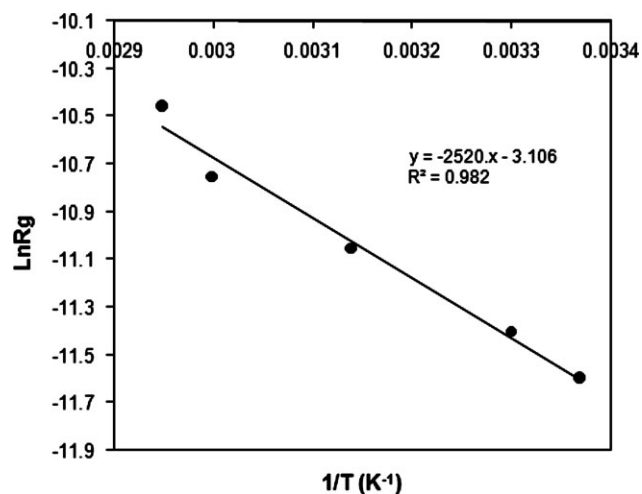
The graft copolymerization parameters used in the present study were calculated according to Fanta's definition:<sup>5</sup>

$$\text{Grafting ratio (\%Gr)} = \frac{\text{Weight of grafted polymer}}{\text{Weight of substrate}} \times 100 \quad (4)$$

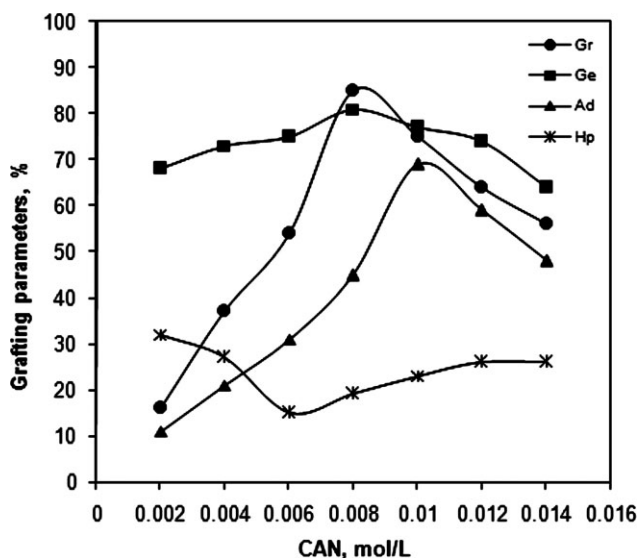
$$\text{Grafting efficiency (\%Ge)} = \frac{\text{Weight of grafted polymer}}{\text{Weight of polymer formed}} \times 100 \quad (5)$$

$$\text{Add on (\%Ad)} = \frac{\text{Weight of grafted polymer}}{\text{Weight of graft copolymer}} \times 100 \quad (6)$$

$$\text{Homopolymer (\%Hp)} = 100 - \%Ge \quad (7)$$



**Figure 8** Plot of  $\text{LnRg}$  versus  $1/T$  for estimating the activation energy of the graft polymerization reaction.



**Figure 9** Grafting parameters as functions of initiator concentration. Reaction conditions: kC solution 2 wt %, AN 0.5 mol/L, temperature 50°C, time 70 min.

The percentage of grafting ratio (%Gr) is the weight percent of the graft copolymer synthetic part (PAN grafted) formed from initial kC used. The grafting efficiency percent (%Ge) stands for the grafted PAN formed from initial monomer charged. The percentage of add-on (%A) is the weight percent of the grafted PAN of the graft copolymer kC-g-PAN. Finally, homopolymer content (%H) denotes the weight percent of the homopolymer, PAN, formed from initial monomer used.

### Optimization of the reaction conditions

#### Effect of initiator concentration

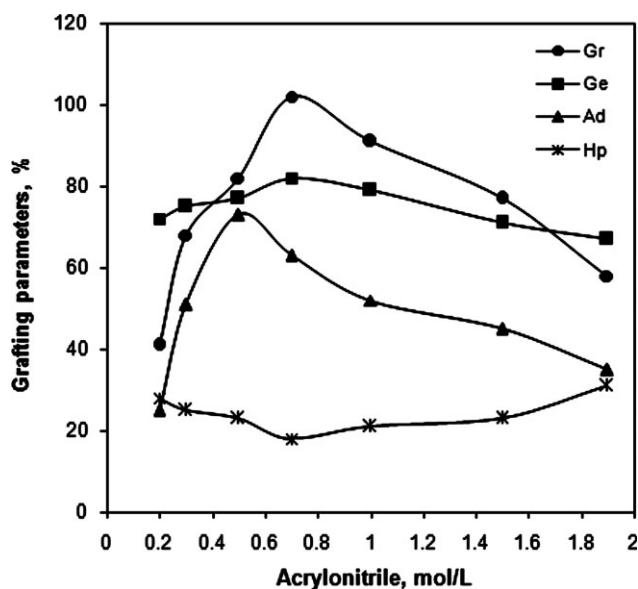
Graft copolymerization was studied at various CAN concentrations by keeping other reaction conditions constant. As shown in Figure 9, the %Ge and %Gr increase with increasing in the initiator concentration and reach at a maximum value. Further increase of concentration of CAN beyond 0.008 mol/L disfavored the grafting parameters. A relatively high concentration of the initiator may cause a reduction of %Ge and %Gr due to increase in the number of kC free radicals terminated before AN addition. Furthermore, homopolymer formation at higher CAN concentrations which compete with the grafting reaction for available monomer could lead to decrease in the %Ge and %Gr. Oxidative degradation of kC chains by excess  $Ce^{4+}$  ions may be other possible reason for the diminished grafting at higher initiator concentrations. Similar oxidative degradation behaviors were already reported by other workers.<sup>37,38</sup>

#### Effect of monomer concentration

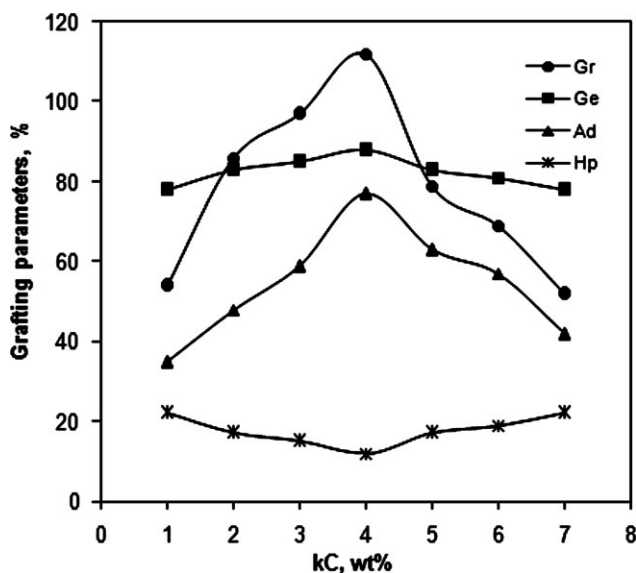
The effect of AN concentration on the grafting parameters is presented in Figure 10. In the initial stages, though both %Ge and %Gr rise with increase in AN concentration, but beyond certain concentration of monomer, the grafting parameters decrease. The optimum values for %Ge of 82% and %Gr of 102% were obtained at 0.7 mol/L of monomer. The initial increase in grafting parameters could be associated with the greater availability of monomer molecules in the vicinity of kC macroradicals. The decrease of %Gr and %Ge with further increase in the AN concentration may be explained as follows: (a) preferential homopolymerization over graft copolymerization, (b) increasing the viscosity of reaction medium, which hinders the movement of free radicals, and (c) increase in the chance of chain transfer to monomer molecules.

#### Effect of polysaccharide concentration

Figure 11 shows the effect of kC concentration on the grafting parameters. With increasing the kC amount, more reactive grafting sites are formed which are favorable for grafting. This can account for initial increment in grafting parameters up to 4.0 wt % of kC value. Beyond this amount, the grafting values were diminished. This may be ascribed to the increase in viscosity that restricts the movement of the monomer molecules in a relatively small volume of the reaction mixture of 50 mL, and the termination reaction between macroradical-macroradical



**Figure 10** Effect of the monomer concentration on the grafting parameters. Reaction conditions: kC solution 2 wt %, CAN 0.008 mol/L, temperature 50°C, time 70 min.

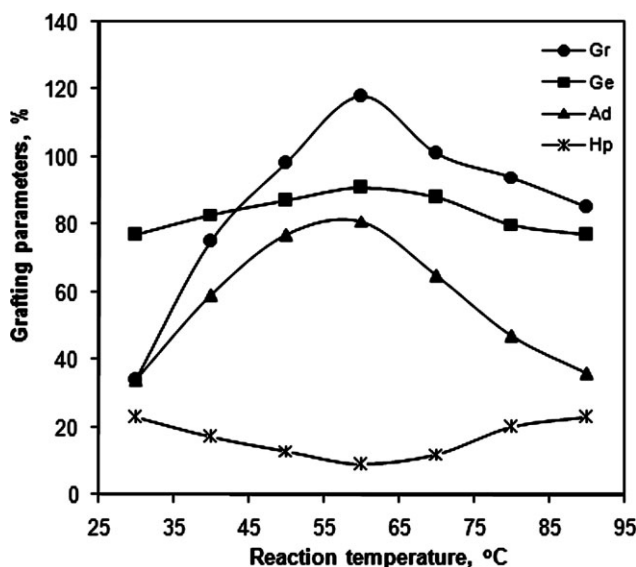


**Figure 11** Effect of kC concentration on the grafting parameters. Reaction conditions: CAN 0.008 M, AN 0.7 mol/L, temperature 50°C, time 70 min.

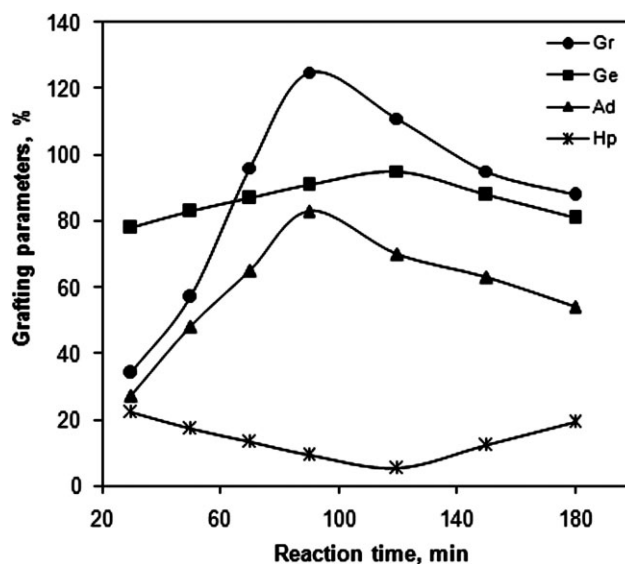
and macroradical-primary radicals as well. This observation is in close agreement with the results obtained by other investigators.<sup>39–41</sup>

#### Effect of reaction temperature

The results obtained by changing the reaction temperature for the graft copolymerization are presented in Figure 12. The %Ge and %Gr were increased with increasing of temperature up to 60°C and then declined. The initial increase was owing to the higher rate of diffusion of monomer molecules



**Figure 12** Effect of the reaction temperature on the grafting parameters. Reaction conditions: kC solution 4 wt %, CAN 0.008 mol/L, AN 0.7 mol/L, time 70 min.



**Figure 13** Effect of the reaction time on the grafting parameters. Reaction conditions: kC solution 4 wt %, CAN 0.008 mol/L, temperature 60°C, AN 0.7 mol/L.

to kC macroradicals. In addition, higher temperatures increase the solubility of the reactants. Moreover, the favorable effect of temperature on grafting could be ascribed to increased rate of decomposition of the complex formed between  $Ce^{4+}$  and kC. The decrease in %Ge and %Gr may be attributed to the substantial increase in the rate of chain transfer and chain termination reactions between grafted chains and monomer molecules. Additionally, above 60°C, the monomer is volatilized out to some extent. Similar behaviors were observed in the case of grafting of methacrylic acid onto carboxymethyl chitosan<sup>42</sup> and buthyl acrylate onto *N*-maleamic acid-chitosan.<sup>43</sup>

#### Effect of reaction time

Figure 13 depicts the effect of reaction time on graft copolymerization of acrylonitrile onto kC backbones. It is obvious that the higher the contact time of monomer molecules with the kC macroradicals, the higher will be grafting. The decrease in %Ge and %Gr with time could be attributed to decrease in concentrations of initiator and monomer as well as a reduction in the number of free macroradicals accessible for grafting as reaction proceeds. Similar time-dependency of grafting parameters was reported by others.<sup>44,45</sup>

It should be pointed out that, as shown in Figures 9–13, the magnitudes of changes of Gr and Ge differ drastically, i.e., the changes of Gr is much more than Ge in the case of every reaction variable. This difference implies that the physical significance of the grafting parameters is more influenced by the initial substrate rather than the initial monomer charged.



So, each reaction variable influences on Gr much more than on Ge. In other word, the parameter Gr is more sensitive to the initial reactants than Ge.

## CONCLUSIONS

kC was graft copolymerized with synthetic monomer, acrylonitrile, in the presence of CAN as an efficient free radical initiator in acidified aqueous medium, under inert atmosphere. The study of FTIR spectra and SEC analysis as well as solubility characteristics, acid hydrolysis, and TGA analysis provide the graft copolymerization do takes place. No residual monomers were found in the graft copolymers, even after storage for long periods. The optimum reaction conditions for an effective grafting of AN onto kC backbones have been worked out as follows: CAN 0.008 mol/L in 0.1 molar HNO<sub>3</sub>, AN 0.7 mol/L, kC 4 wt %, reaction temperature 60°C, and reaction time 90 min. Under the optimized conditions the grafting parameters were calculated to be Gr 125%, Ge 95%, Ad 83%, and Hp 5%. The relation between the rate of polymerization ( $R_p$ ) and the concentrations of reactants was also investigated. Graft copolymers based on kC are of interest because of biodegradability and compatibility characteristics. Further works, such as investigation of thermal and mechanical properties and modification to prepare thickeners and flocculants for aqueous systems, is in progress on these grafting copolymers in our laboratory.

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