One-Pot Synthesis of a Polysaccharide-Based Graft Copolymer with an Efficient Redox Pair (Fe^{2+}/BrO_3^-)

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ABSTRACT: A graft copolymer based on a polysaccharide (sodium salt of carboxymethylcellulose) and a vinyl monomer (acrylamide) has been synthesized in a nitrogen atmosphere, and its reaction conditions have been optimized for a better yield with ferrous sulfate and potassium bromate as a redox initiator. The effects of ferrous ion, bromate ion, hydrogen ion, sodium carboxymethylcellulose, and acrylamide along with the reaction time and temperature have been studied through the determination of the grafting parameters: the grafting ratio, add-on, conversion, efficiency, homopolymer, and rate of grafting. The maximum yield has been found to occur when the acrylamide concentration is 8.0×10^{-2} mol/dm³, whereas the maximum conversion occurs at a minimum concentration of acrylamide, that is, at 3.0×10^{-2} mol/dm³. The grafting parameters have been found to increase with an increasing concentration of the redox initiator (Fe^{2+}, from 2.0×10^{-3} to 10.0×10^{-3} mol/dm³; BrO_3^-, from 2.2×10^{-3} to 4.0×10^{-3} mol/dm³). The maximum efficiency occurs with a reaction time of 210 min. The rate of grafting has been found to be maximum up to 60 min; after that, it decreases rapidly. In this article, it is shown that the hydrogen ion leads to a very clear decrease in the grafting parameters as its concentration increases from 2.1×10^{-3} to 11.3×10^{-3} mol/dm³. Grafted gum and ungrafted gum have been characterized with Fourier transform infrared spectroscopy and thermogravimetric analysis. A probable mechanism has been suggested for graft copolymerization. It has been observed that the graft copolymer is thermally more stable than the parent backbone. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2883–2891, 2008

Key words: biodegradable; FT-IR; graft copolymers; polysaccharides; thermal properties

INTRODUCTION

Among the various methods for modifying polymers, graft copolymerization appears to be highly attractive and has made a paramount contribution toward improved industrial and biomedical applications.[1–3] Sodium carboxymethylcellulose is a naturally occurring polysaccharide consisting of substituted anhydroglucose units and is also known as cellulose gum. The carboxymethyl group increases the swellability of polysaccharides,[4] which leads to their unique applications in various industries, such as the paper[5] and textile processing industries.[6]

Usually, water-based muds for oil-field drilling are effective water-soluble polymers used to perform such main functions as shale inhibition, viscosity, and filtration control.[7,8] Up to now, conventional anionic polymers such as carboxymethylcellulose and partially hydrolyzed polyacrylamide and recently developed cationic polymers such as quaternary poly-

amine and cationic polyacrylamide have been widely used for these purposes.[9–11] Both exhibit inherent advantages and disadvantages. The anionic polymers possess good filtration control and viscosity-building properties but weak shale inhibition. The cationic polymers exhibit effective shale inhibition but suffer from weak mud performance, bad compatibility, and high toxicity to aquatic organisms. Therefore, there has been increasing demand in the oil-field industry to develop environmentally acceptable polymeric additives that can combine cationic and anionic polymer behavior advantageously and overcome the limitations inherent in the aforementioned additives.[12–14] On the other hand, polymers based on acrylamide are the most widely commercially used water-soluble products.[15] Their uses range from paper manufacturing[16] and water treatment[17] to oil recovery,[18] soil modification,[19] and medical applications.[20]

Thus, polysaccharide (sodium carboxymethylcellulose)-based graft copolymers have been found to have multifunctional characteristics as oil-field-drilling mud additives with respect to shale inhibition, viscosity building, and filtration control.[21,22] Therefore, it was thought to be worthwhile to graft acrylamide onto carboxymethylcellulose with the Fe^{2+}/BrO_3^- redox pair.

EXPERIMENTAL

Materials

Acrylamide (Sigma) (ST. Louis, USA) was recrystallized twice from methanol (E. Merck; Mumbai, India) and dried *in vacuo*; ferrous sulfate (Anala R.; BDH West Chester, Pennsylvania, USA), potassium bromate (E. Merck), and sodium carboxymethylcellulose (BDH) were used as received. For the variation of the hydrogen-ion concentration, sulfuric acid (E. Merck) was used.

Procedure for graft copolymerization

For each experiment, a sodium carboxymethylcellulose solution was prepared by the slow addition of a calculated amount of sodium carboxymethylcellulose into a reactor containing triple-distilled water. Calculated amounts of acrylamide, sulfuric acid, and ferrous sulfate were added to the reactor, and a slow stream of oxygen-free nitrogen gas was passed for 30 min. A known amount of a deoxygenated potassium bromate solution was added to initiate the reaction. The reaction was performed under a continuous flow of oxygen-free nitrogen gas. After the desired time, the reaction was stopped by air being allowed into the reactor. The grafted sample was precipitated by the pouring of the reaction mixture into a water/methanol mixture, from which grafted carboxymethylcellulose precipitated. The precipitate was separated, dried, and weighed, and polyacrylamide remained in the solution.

Separation of the homopolymer

To the filtrate, a pinch of hydroquinone was added and concentrated by distillation under reduced pressure. The polyacrylamide was precipitated by the pouring of the concentrated filtrate into pure methanol. The polyacrylamide thus obtained was separated, dried, and weighed.

RESULTS AND DISCUSSION

The graft copolymer has been characterized according to Fanta's definition,[23] and the rate of grafting[24,25] has also been calculated:

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

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

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

$$\text{Conversion (\%)} = \frac{\text{Weight of polymer formed}}{\text{Weight of monomer charged}} \times 100$$

$$\text{Homopolymer (\%)} = 100 - \text{Grafting efficiency (\%)}$$

$$\text{Rate of grafting} =$$
$$\frac{1000 \times \text{Weight of grafted polymer}}{\text{Volume} \times \text{Time} \times \text{Molecular weight of ACM}} \text{mol L}^{-1}\text{S}^{-1}$$

The effects of variations in the concentration of Fe^{2+}, BrO_3^-, hydrogen ion, carboxymethylcellulose, and acrylamide along with the effects of time and temperature on the grafting parameters have been studied.

Effect of the ferrous ion concentration

The effect of ferrous ion on the grafting parameters has been studied through the variation of the concentration of ferrous sulfate from 2.0×10^{-3} to 10.0×10^{-3} mol/dm^3, and the results are summarized in Table I. The grafting ratio, efficiency, add-on, conversion, and rate of grafting increase continuously with an increasing ferrous ion concentration; however, a reverse trend has been observed for homopolymer formation. The enhancement of the grafting parameters might be attributed to the increase in the production of primary free radicals ($^\bullet$OH and Br$^\bullet$) produced by the Fe^{2+}/BrO_3^- redox pair, which increase

TABLE I
Effect of the Ferrous Sulfate Concentration

$[Fe^{2+}]$ ($\times 10^3$ mol/dm^3)	Grafting ratio (%)	Grafting efficiency (%)	Add-on (%)	Conversion (%)	Homopolymer (%)	Rate of grafting ($\times 10^7$ mol L^{-1} s^{-1})
2.0	45.8	56.1	31.4	22.0	43.9	9.0
3.0	53.0	60.7	34.6	22.7	39.6	10.3
4.0	53.01	63.1	34.7	23.7	34.9	10.4
6.0	67.2	73.7	40.1	24.6	26.3	13.1
10.0	131.2	85.0	56.8	41.7	15.0	25.6

$[BrO_3^-] = 4.0 \times 10^{-3}$ mol/dm^3; $[H^+] = 4.2 \times 10^{-3}$ mol/dm^3; acrylamide concentration = 5.0×10^{-2} mol/dm^3; sodium carboxymethylcellulose concentration = 96.0×10^{-2} g/dm^3; time = 120 min; temperature = 35°C.

TABLE II
Effect of the Potassium Bromate Concentration

$[BrO_3^-]$ ($\times 10^3$ mol/dm^3)	Grafting ratio (%)	Grafting efficiency (%)	Add-on (%)	Conversion (%)	Homopolymer (%)	Rate of grafting ($\times 10^7$ mol L^{-1} s^{-1})
2.2	86.1	79.8	46.3	29.1	20.3	16.8
2.5	87.5	77.6	46.7	30.5	22.4	17.1
3.3	127.6	74.8	56.0	46.1	25.2	24.9
4.0	131.2	85.0	56.6	41.7	15.0	25.6
5.0	116.4	83.5	53.9	37.6	16.2	22.7

$[Fe^{2+}] = 10.0 \times 10^{-3}$ mol/dm^3; $[H^+] = 4.2 \times 10^{-3}$ mol/dm^3; acrylamide concentration $= 5.0 \times 10^{-2}$ mol/dm^3; sodium carboxymethylcellulose concentration $= 96.0 \times 10^{-2}$ g/dm^3; time $= 120$ min; temperature $= 35°C$.

the number of grafting sites on the substrate, that is, sodium carboxymethylcellulose.

Effect of the bromate ion concentration

The variation of the bromate ion concentration has been studied in the range of 2.2×10^{-3} to 5.0×10^{-3} mol/dm^3. Table II shows that the grafting ratio, add-on, and rate of grafting increase with an increase in the bromate ion concentration up to 4.0×10^{-3} mol/dm^3, whereas the conversion is maximum at 3.3×10^{-3} mol/dm^3. The enhancement in these grafting parameters might be due to the formation of a greater number of primary free radicals, but as the concentration of the bromate ion is increased beyond 4.0×10^{-3} mol/dm^3, the grafting parameters decrease, and this is due to the formation of a large number of free radicals that terminate the growing grafted chain by oxidative termination.

Effect of the acrylamide concentration

The effect of the acrylamide concentration on the grafting parameters has been studied through the variation of the concentration of acrylamide from 3.0×10^{-2} to 8.0×10^{-2} mol/dm^3, and the results are summarized in Table III. The grafting ratio, add-on, and conversion decrease up to 5.0×10^{-2} mol/dm^3; thereafter, the values of the grafting ratio, add-on, conversion, and rate of grafting increase. The increment in the grafting parameters might be attributed to the fact that an increase in the acrylamide concen-

tration leads to the accumulation of acrylamide molecules in close proximity to sodium carboxymethylcellulose. The acrylamide molecules that are in the immediate vicinity of reaction sites become acceptors of sodium carboxymethylcellulose macroradicals, resulting in chain initiation; thereafter, they become free-radical donors to the neighboring molecules, lowering termination, whereas decreases in the grafting ratio, efficiency, add-on, conversion, and rate of grafting can be attributed to an increase in the viscosity of the medium due to preferential formation of polyacrylamide at a lower concentration.

Effect of the sulfuric acid concentration

The extent of grafting of acrylamide onto sodium carboxymethylcellulose with the Fe^{2+}/BrO_3^- redox couple has been found to highly dependent on the hydrogen-ion concentration. The effect of the change in the hydrogen-ion concentration from 2.1×10^{-3} to 11.3×10^{-3} mol/dm^3 reveals that the grafting ratio, efficiency, add-on, conversion, and rate of grafting decrease continuously as the hydrogen-ion concentration increases up to 11.3×10^{-3} mol/dm^3 (Figs. 1 and 2), whereas the reverse trend has been observed in the case of polyacrylamide formation. The decrease in the grafting parameters can be explained on the basis of the fact that the high concentration of hydrogen ion does not favor the oxidation of Fe^{2+} to Fe^{3+} by BrO_3^-, which affects the formation of primary free radicals ($^\bullet OH$ and $Br^\bullet$), thereby reducing the value of all the grafting parameters.

TABLE III
Effect of the Acrylamide Concentration

Acrylamide concentration ($\times 10^2$ mol/dm^3)	Grafting ratio (%)	Grafting efficiency (%)	Add-on (%)	Conversion (%)	Homopolymer (%)	Rate of grafting ($\times 10^7$ mol L^{-1} s^{-1})
3.0	154.9	73.7	60.8	90.2	26.3	30.2
4.0	151.0	77.3	60.2	79.1	22.7	29.3
5.0	131.2	85.0	56.8	41.7	15.0	25.6
6.0	186.0	75.2	65.0	43.0	24.8	36.3
8.0	186.9	68.0	65.1	61.5	32.0	36.5

$[Fe^{2+}] = 10.0 \times 10^{-3}$ mol/dm^3; $[BrO_3^-] = 4.0 \times 10^{-3}$ mol/dm^3; $[H^+] = 4.25 \times 10^{-3}$ mol/dm^3; sodium carboxymethylcellulose concentration $= 96.0 \times 10^{-2}$ g/dm^3; time $= 120$ min; temperature $= 35°C$.
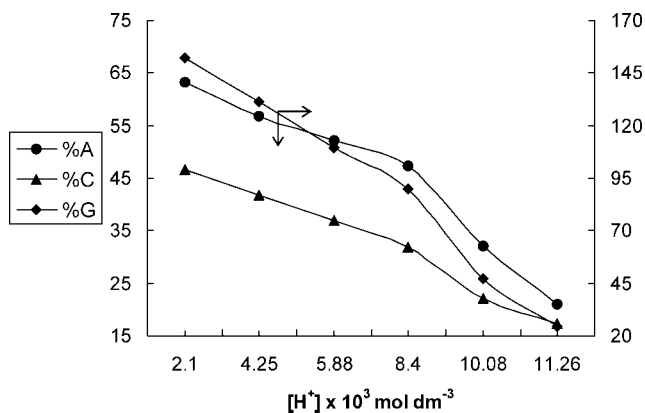
Figure 1 Effect of the hydrogen-ion concentration ($[Fe^{2+}]$ = 10.0×10^{-3} mol/dm^3; $[BrO_3^-]$ = 4.0×10^{-3} mol/dm^3; acrylamide concentration = 5.0×10^{-2} mol/dm^3; sodium carboxymethylcellulose concentration = 96.02×10^{-2} g/dm^3; time = 120 min; temperature = 35°C; %A = add-on; %C = conversion; %G = grafting ratio).

Figure 3 Effect of the sodium carboxymethylcellulose concentration ($[Fe^{2+}]$ = 10.0×10^{-3} mol/dm^3; $[BrO_3^-]$ = 4.0×10^{-3} mol/dm^3; acrylamide concentration = 5.0×10^{-2} mol/dm^3; $[H^+]$ = 4.25×10^{-3} mol/dm^3; time = 120 min; temperature = 35°C; %A = add-on; %C = conversion; %G = grafting ratio).

Effect of the sodium carboxymethylcellulose concentration

The effects of sodium carboxymethylcellulose on grafting parameters have been studied through the variation of the concentration of sodium carboxymethylcellulose from 73.0×10^{-2} to 188.8×10^{-2} g/dm^3. As the concentration of sodium carboxymethylcellulose increases from 73.0×10^{-2} to 188.8×10^{-2} g/dm^3, the grafting ratio, add-on, and efficiency decrease continuously (Figs. 3 and 4), whereas the conversion increases from 73.0×10^{-2} to 143.0×10^{-2} g/dm^3; with respect to the aforementioned grafting parameters, the rate of grafting increases continuously with increasing concentration. These results can be explained by the fact that as the con
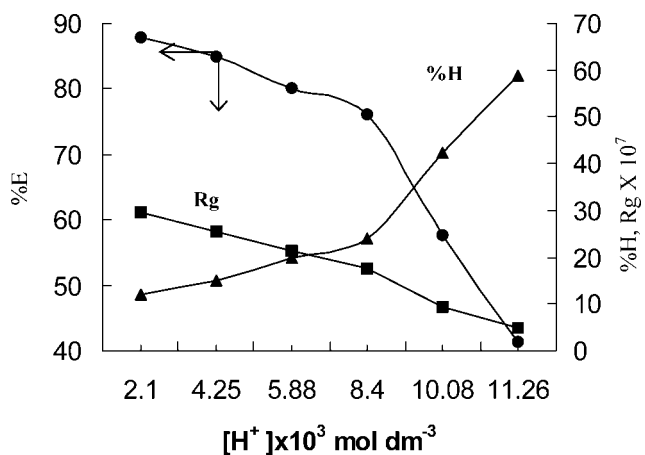
centration of sodium carboxymethylcellulose increases, the viscosity of the reaction medium increases, and this hinders the movement of free radicals, thereby reducing the grafting parameters.

Effect of time

The graft copolymerization of acrylamide onto carboxymethylcellulose has been studied through changes in the time interval of the reaction from 60 to 210 min, and the results are shown in Figures 5 and 6. The grafting ratio, add-on, conversion, and homopolymer increase with an increase in the time interval of reaction from 60 to 150 min, whereas the efficiency decreases. With a further increase in the time, the grafting ratio, add-on, and conversion decrease. It has also been observed that the rate of

Figure 2 Effect of the hydrogen-ion concentration ($[Fe^{2+}]$ = 10.0×10^{-3} mol/dm^3; $[BrO_3^-]$ = 4.0×10^{-3} mol/dm^3; acrylamide concentration = 5.0×10^{-2} mol/dm^3; sodium carboxymethylcellulose concentration = 96.02×10^{-2} g/dm^3; time = 120 min; temperature = 35°C; %E = efficiency; %H = homopolymer; Rg = rate of grafting).
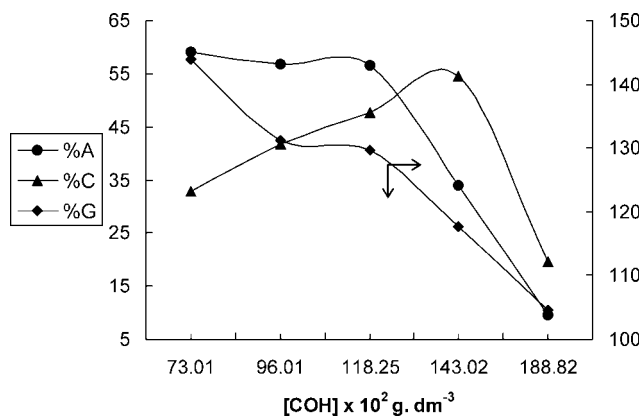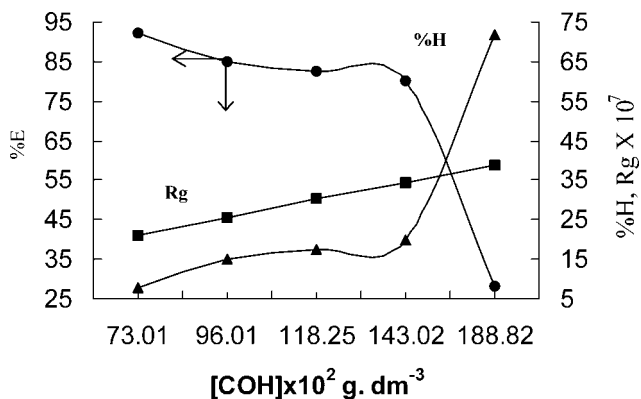

Figure 4 Effect of the sodium carboxymethylcellulose concentration ($[Fe^{2+}]$ = 10.0×10^{-3} mol/dm^3; $[BrO_3^-]$ = 4.0×10^{-3} mol/dm^3; acrylamide concentration = 5.0×10^{-2} mol/dm^3; $[H^+]$ = 4.25×10^{-3} mol/dm^3; time = 120 min; temperature = 35°C; %E = efficiency; %H = homopolymer; Rg = rate of grafting).

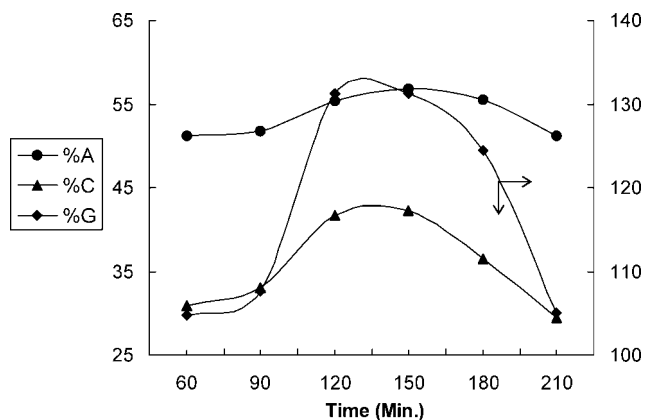**Figure 5** Effect of time ($[Fe^{2+}]$ = 10.0 × 10^{-3} mol/dm³; $[BrO_3^-]$ = 4.0 × 10^{-3} mol/dm³; acrylamide concentration = 5.0 × 10^{-2} mol/dm³; $[H^+]$ = 4.25 × 10^{-3} mol/dm³; sodium carboxymethylcellulose concentration = 96.02 × 10^{-2} g/dm³; temperature = 35°C; %A = add-on; %C = conversion; %G = grafting ratio).

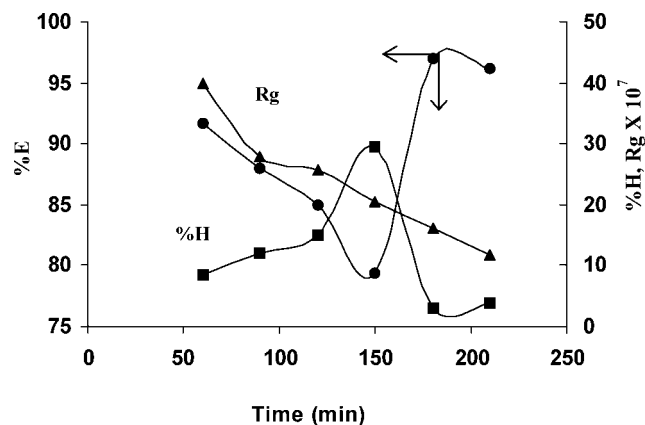**Figure 6** Effect of time ($[Fe^{2+}]$ = 10.0 × 10^{-3} mol/dm³; $[BrO_3^-]$ = 4.0 × 10^{-3} mol/dm³; acrylamide concentration = 5.0 × 10^{-2} mol/dm³; $[H^+]$ = 4.25 × 10^{-3} mol/dm³; sodium carboxymethylcellulose concentration = 96.02 × 10^{-2} g/dm³; temperature = 35°C; %E = efficiency; %H = homopolymer; Rg = rate of grafting).

grafting increases continuously as the time interval of reaction increases. The increase in the values of the grafting parameters might be attributed to the addition of more acrylamide molecules to the growing grafted chains, whereas the decrease in the values of the grafting parameters might be due to termination of free radicals and growing grafted chains.
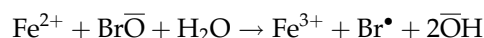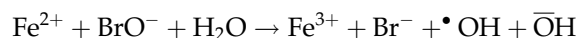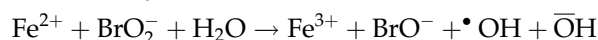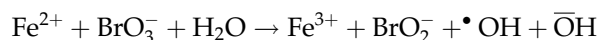
Effect of temperature

The effect of temperature on the grafting parameters has been studied through the variation of the temperature from 30 to 50°C (Table IV). The grafting ratio, efficiency, add-on, conversion, and rate of grafting decrease as the temperature increases from 30 to 45°C, whereas the homopolymer increases. This behavior might be explained by the fact that with an increase in the temperature up to the optimum value, there is an increase in the mobility of macro-radicals leading to termination, and therefore the values of the grafting parameters decrease. Similar

results have been observed for the grafting of acrylamide onto nylon-6 and silk fiber.[26,27]

Mechanism

Hydroxyl and bromide radicals have been generated by the interaction of Fe^{2+} and BrO_3^- ions as suggested by Thomas et al.:[28]

$$Fe^{2+} + BrO_3^- + H_2O \rightarrow Fe^{3+} + BrO_2^- + {}^\bullet OH + \overline{O}H$$

$$Fe^{2+} + BrO_2^- + H_2O \rightarrow Fe^{3+} + BrO^- + {}^\bullet OH + \overline{O}H$$

$$Fe^{2+} + BrO^- + H_2O \rightarrow Fe^{3+} + Br^- + {}^\bullet OH + \overline{O}H$$

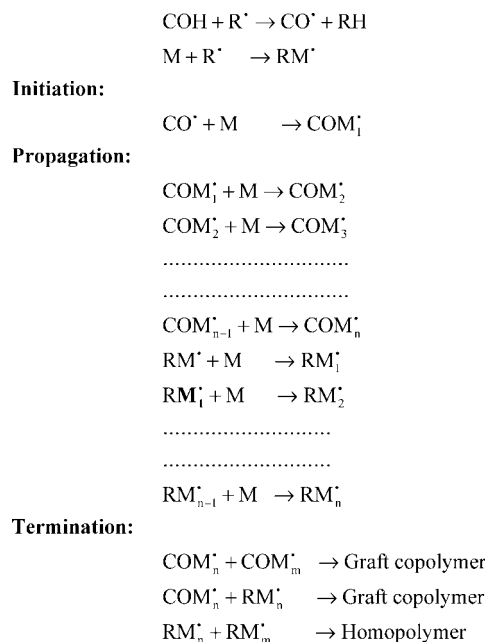$$Fe^{2+} + Br\overline{O} + H_2O \rightarrow Fe^{3+} + Br^\bullet + 2\overline{O}H$$

The hydroxyl and bromide free radicals, represented by $^\bullet R$, abstract a hydrogen atom from sodium carboxymethylcellulose, producing a sodium carboxymethylcellulose free radical ($CO^\bullet$). The acrylamide molecules, which are in close vicinity to the reaction sites, become acceptors of the sodium carboxyme-

TABLE IV
Effect of the Temperature

Temperature (°C)	Grafting ratio (%)	Grafting efficiency (%)	Add-on (%)	Conversion (%)	Homopolymer (%)	Rate of grafting (×10^7 mol L^{-1} s^{-1})
30	149.8	86.2	60.0	46.9	13.8	29.3
35	131.2	85.0	56.8	41.7	15.0	25.6
40	120.8	84.2	54.7	38.3	15.8	23.6
45	119.2	70.4	54.1	37.8	29.6	23.3
50	117.9	86.2	54.4	45.2	13.8	23.0

$[Fe^{2+}]$ = 10.0 × 10^{-3} mol/dm³; $[BrO_3^-]$ = 4.0 × 10^{-3} mol/dm³; acrylamide concentration = 5.0 × 10^{-2} mol/dm³; $[H^+]$ = 4.2 × 10^{-3} mol/dm³; sodium carboxymethylcellulose concentration = 96.0 × 10^{-2} g/dm³; time = 120 min.

$$COH + R^\bullet \rightarrow CO^\bullet + RH$$
$$M + R^\bullet \rightarrow RM^\bullet$$

Initiation:

$$CO^\bullet + M \rightarrow COM_1^\bullet$$

Propagation:

$$COM_1^\bullet + M \rightarrow COM_2^\bullet$$
$$COM_2^\bullet + M \rightarrow COM_3^\bullet$$
$$\cdots\cdots\cdots\cdots\cdots\cdots$$
$$\cdots\cdots\cdots\cdots\cdots\cdots$$
$$COM_{n-1}^\bullet + M \rightarrow COM_n^\bullet$$
$$RM^\bullet + M \rightarrow RM_1^\bullet$$
$$RM_1^\bullet + M \rightarrow RM_2^\bullet$$
$$\cdots\cdots\cdots\cdots\cdots$$
$$\cdots\cdots\cdots\cdots\cdots$$
$$RM_{n-1}^\bullet + M \rightarrow RM_n^\bullet$$

Termination:

$$COM_n^\bullet + COM_m^\bullet \rightarrow \text{Graft copolymer}$$
$$COM_n^\bullet + RM_n^\bullet \rightarrow \text{Graft copolymer}$$
$$RM_n^\bullet + RM_m^\bullet \rightarrow \text{Homopolymer}$$

Scheme 1

thylcellulose radicals, resulting in chain initiation, and thereafter they themselves become free-radical donors to the neighboring molecules. In this way, grafted chains grow. These grafted chains may terminate by coupling to produce a graft copolymer, as shown in Scheme 1 (which depicts the reaction mechanism), whereas acrylamide free radicals may attack acrylamide to generate polyacrylamide.

Evidence of grafting: IR spectra

The Fourier transform infrared (FTIR) spectra of sodium carboxymethylcellulose and sodium carboxy-methylcellulose-g-acrylamide were recorded with a Bruker IFS 66v FTIR spectrophotometer in the range of 500–4000 cm^{-1}. On comparing the IR spectra of sodium carboxymethylcellulose (Fig. 7) and sodium carboxymethylcellulose-g-acrylamide (Fig. 8), we have found that the additional absorption bands corresponding to the amide group appear in the spectra of sodium carboxymethylcellulose-g-acrylamide. The band at 1663.44 cm^{-1} is due to the overlapping of C=O stretching and N—H bending vibrations. The C—N stretching band of the amide group appears at 1421 cm^{-1}. The frequencies due to N—H stretching and O—H stretching vibrations overlap, and this results in the broad band in the region of 2900–3400 cm^{-1}. Thus, the disappearance of O—H bending vibrations and the appearance of additional bands in the spectrum of the graft copolymer prove that grafting has taken place on the —OH site of the parent polymer.

Thermal analyses

The thermograms were recorded on a Netzsch–Geratebau GmbH thermal analyzer up to 1000°C at a heating rate of 10°C/min in an atmosphere of nitrogen.

Sodium carboxymethylcellulose

The degradation of sodium carboxymethylcellulose starts at about 135.3°C. The degradation occurs in two stages, that is, from 135.3 to 283.1°C and from 283.1 to 385.2°C. An approximately 40% weight loss occurs between 200 and 400°C. The rate of weight loss increases as the temperature increases up to 285.0°C but decreases thereafter. The polymer decomposition temperature (PDT), final decomposi-
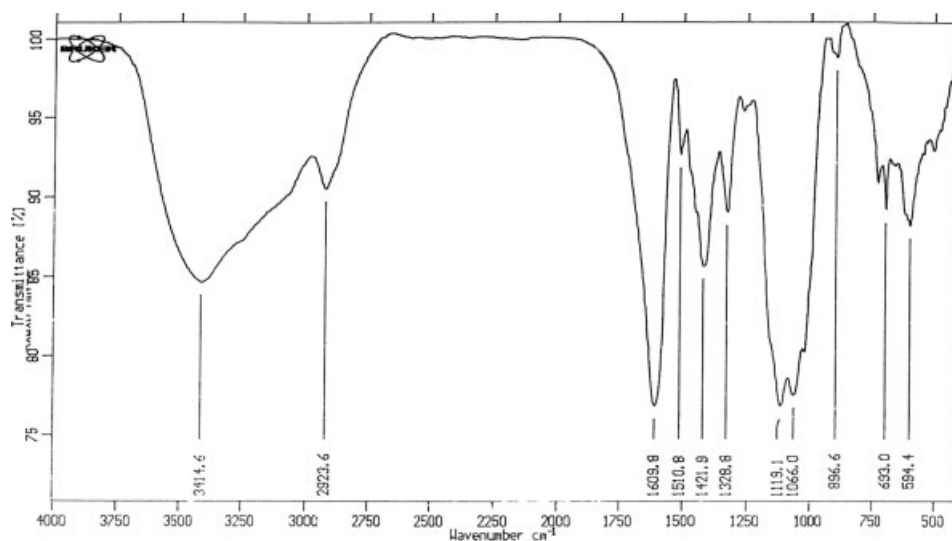

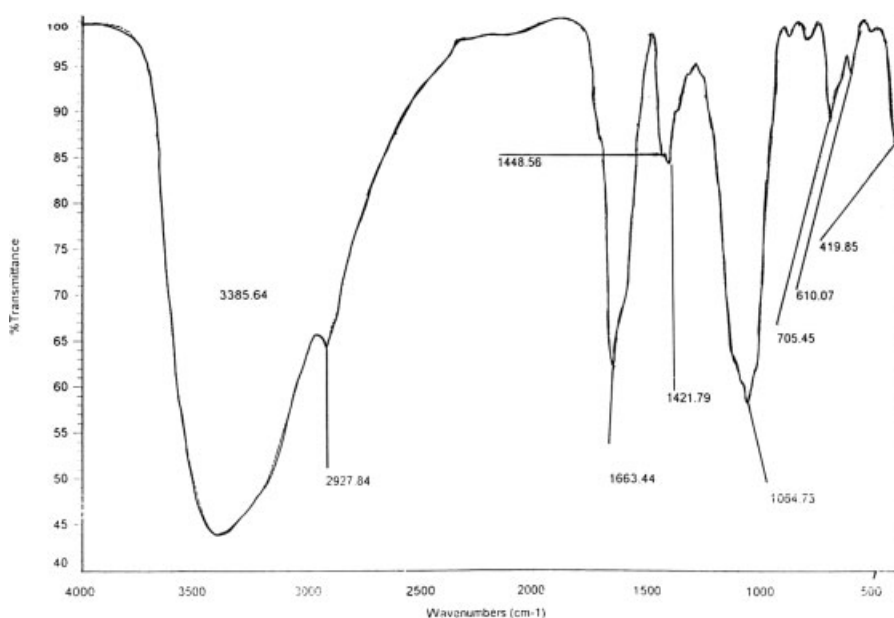**Figure 7** IR spectra of sodium carboxymethylcellulose.

Figure 8 IR spectra of sodium carboxymethylcellulose-*g*-acrylamide.

tion temperature (FDT), temperature at which maximum degradation occurs (T_{max}), and integral procedural decomposition temperature (IPDT) have been found to be 135.3, 385.2, 283.1, and 294.5°C, respectively (Table IV). Tables V and VI reveal that the weight loss in the temperature range of 400–700°C is almost constant. A char yield of 38% has been obtained at 924°C (Fig. 9). The dynamic thermal analysis curve of sodium carboxymethylcellulose shows an endothermic peak with a gradual decrease in the weight and a broad band with fluctuations at 304 and 413.1°C. This may be due to decarboxylation of sodium carboxymethylcellulose of the carboxyl group.

Sodium carboxymethylcellulose-*g*-acrylamide

The graft copolymer begins to degrade at about 180°C (Fig. 10). However, a 10% weight loss is observed up to 100°C and might be due to the absorbed water. The degradation appears to be a two-stage process, that is, from 233.9 to 312.7°C and from 312.7 to 462.2°C. The rate of weight loss increases with an increase in the temperature up to 268.7°C and gradually decreases thereafter. Again, an increase in the rate of weight loss has been observed from 325 to 377.1°C, and it decreases thereafter (Tables V and VI). Therefore, two T_{max} values have been obtained: 268.7 and 377.1°C. PDT is 233.92°C,

TABLE V
Decomposition Temperatures

Sample	Temperature (°C)							
	10% weight loss	20% weight loss	30% weight loss	40% weight loss	50% weight loss	60% weight loss	70% weight loss	80% weight loss
C_1	270.0	284.0	296.0	382.0	740.0	904.0	—	—
C_2	109.8	259.8	315.5	362.2	400.2	461.8	712.5	876.2

C_1 = sodium carboxymethyl cellulose; C_2 = sodium carboxymethylcellulose-*g*-acrylamide.

TABLE VI
Amount of Decomposition

Sample	Weight loss (%)								
	100°C	200°C	300°C	400°C	500°C	600°C	700°C	800°C	900°C
C_1	1.2	2.9	29.4	38.8	42.9	43.0	44.7	52.3	62.3
C_2	9.0	14.6	32.4	54.2	63.6	67.7	68.0	76.0	81.8

C_1 = sodium carboxymethyl cellulose; C_2 = sodium carboxymethylcellulose-*g*-acrylamide.
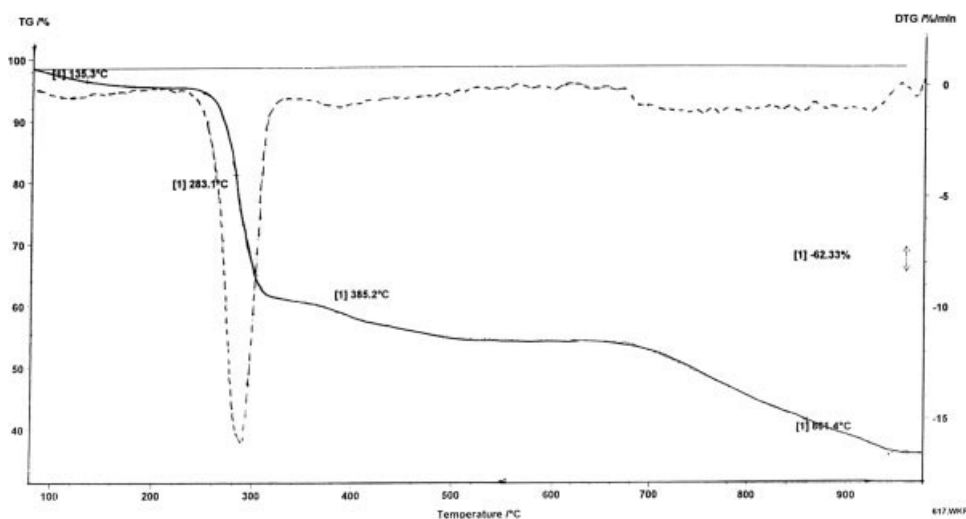
Figure 9 Thermogravimetric analysis/and differential thermogravimetry traces of sodium carboxymethylcellulose.
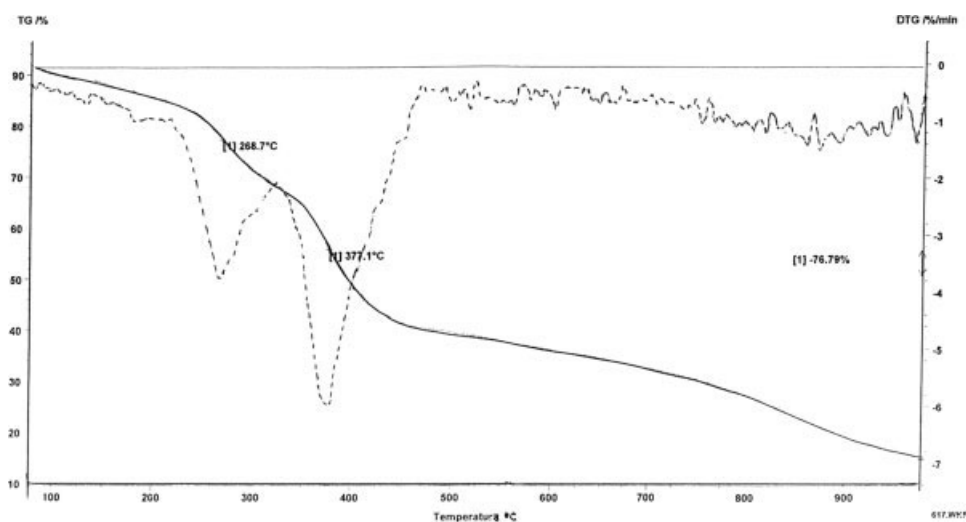

Figure 10 Thermogravimetric analysis/and differential thermogravimetry traces of sodium carboxymethylcellulose-*g*-acrylamide.

that is, 98.62°C (Table VII) higher than that of sodium carboxymethylcellulose, and FDT of sodium carboxymethylcellulose-*g*-acrylamide is also higher than that of sodium carboxymethylcellulose. The weight loss of sodium-carboxymethylcellulose-*g*-acrylamide in a lower temperature range, that is, 180–268.7°C, is due to the elimination of the CO_2 molecule from the sodium carboxymethylcellulose backbone (Scheme 2). The second T_{max} is attributed to the formation of a $-\overset{O}{\underset{}{C}} - \overset{H}{\underset{}{N}} - \overset{O}{\underset{}{C}} -$ group with elimination of the ammonia molecule from the two neighboring amide groups of the grafted chain. At 975°C, a char yield of 15% has been obtained. The high values of the IPDT, FDT, and char yield of sodium carboxymethylcellulose-*g*-acrylamide suggest that it is

TABLE VII
Thermogravimetric Analyses of the Graft Copolymer

Sample	PDT (°C)	FDT (°C)	T_{max} (°C)	IPDT (°C)	Dynamic thermal analysis curves	
					Exo peaks (°C)	Endo peaks (°C)
C_1	135.3	385.2	283.1	294.5	—	711.5
C_2	233.9	432.1	268.7 and 377.1	370.1	—	789.4

C_1 = sodium carboxymethyl cellulose; C_2 = sodium carboxymethylcellulose-*g*-acrylamide.
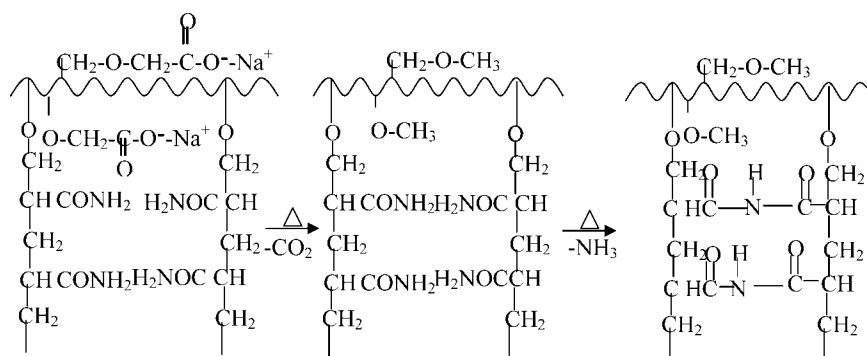
Scheme 2

thermally more stable than sodium carboxymethyl-cellulose.

CONCLUSIONS

1. Carboxymethylcellulose-grafted acrylamide has been synthesized with an efficient redox system, that is, Fe^{2+}/BrO_3^-. The effects of various factors on graft copolymerization have been studied in detail

2. The grafting ratio (%) increases continuously as the ferrous ion concentration increases. The hydrogen ion retards the grafting ratio very effectively. A high concentration of polysaccharides does not favor grafting, and a high temperature and a long duration also do not favor the extent of grafting.

3. The spectroscopic data confirm that the acrylamide has been grafted at the hydroxyl group of the parent gum.

4. The thermal analysis data show that the grafted gum is more thermally stable than the ungrafted gum on the basis of the values of the IPDT, FDT, and char yield.

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