Graft Copolymerization of 2-Acrylamido-2-methyl-1-propanesulphonic Acid onto Carboxymethylcellulose (Sodium Salt) Using Bromate/Thiourea Redox Pair

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ABSTRACT: Unreported graft copolymer of 2-acrylamido-2-methyl-1-propanesulphonic acid (AMPS) with sodium carboxymethylcellulose (Na-CMC) was synthesized and reaction conditions were optimized using a bromate/thiourea redox pair under an inert atmosphere at 40°C. Grafting ratio, add on, and conversion increase as the concentration of thiourea and $[H^+]$ increases up to 3.6×10^{-3} and 0.6×10^{-2} mol dm^{-3}, respectively, while on increasing the concentration of bromate ion and Na-CMC, grafting ratio, add on, and conversion decrease. The samples of Na-CMC and grafted Na-CMC with AMPS were subjected to thermogravimetric analysis, with the objective of studying the effect of grafting of AMPS on the thermal stability of graft copolymer. The graft copolymer was found to be more thermally stable than pure Na-CMC. Comparing the IR spectra of pure with grafted Na-CMC confirm the evidence of grafting. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 100: 26–34, 2006

Key words: graft copolymer; thermal degradation; carboxymethylcellulose; redox pair

INTRODUCTION

Graft copolymerization of vinyl monomers onto natural and synthetic polymers is a fascinating field of research with unlimited potential application for industrial production of various materials. Sodium carboxymethylcellulose (Na-CMC), also known as cellulose gum, water-soluble cellulose ether, is manufactured by reacting sodium monocholoroacetate with alkali on cellulose. Carboxymethyl group increases the swellability of polysaccharides,[1] which gives their unique applications in various industries, e.g., paper, textile processing, pharmaceuticals and cosmetic industries, etc. In light of its versatile applications, attempts have been made to prepare its derivatives (graft copolymer of it with vinyl monomers like acrylamide, methacrylate, acrylic acid, etc.) for specific application viz. oil field drilling,[2] biomedical applications,[3] etc.

On the other hand, polymer based on 2-acrylamido-2-methyl-1-propanesulphonic acid (AMPS) is characterized by its hydrophilicity and ionic character. Consequently, it has been used to prepare high swelling capacity polymer hydrogels[4,5] with vinyl monomers.

Its usages range from water treatment to enhanced oil recovery.[6] Copolymers of AMPS with acrylamide,[4,7] sodium acrylate, sodium 3-acrylamido-3-methyl butanoate,[5] etc. are reported, and have great potential in industry for viscosity modifying agents to enhance oil recovery, but these copolymers have a drawback that they are not biodegradable materials, while graft copolymers of Na-CMC are biodegradable in nature.[3] Prompted by fascinating applications of Na-CMC and its derivatives with other polymer, an attempt has been made to graft hitherto unreported poly AMPS on to Na-CMC; it was thought that Na-CMC-*g*-AMPS would be more environment friendly, biodegradable, and cost effective than copolymer of AMPS and would hold better properties of enhanced oil recovery, metal ion uptake, flocculation, etc. with biodegradable nature. Thus, we have investigated grafting of AMPS onto Na-CMC using KBrO$_3$/thiourea redox pair.
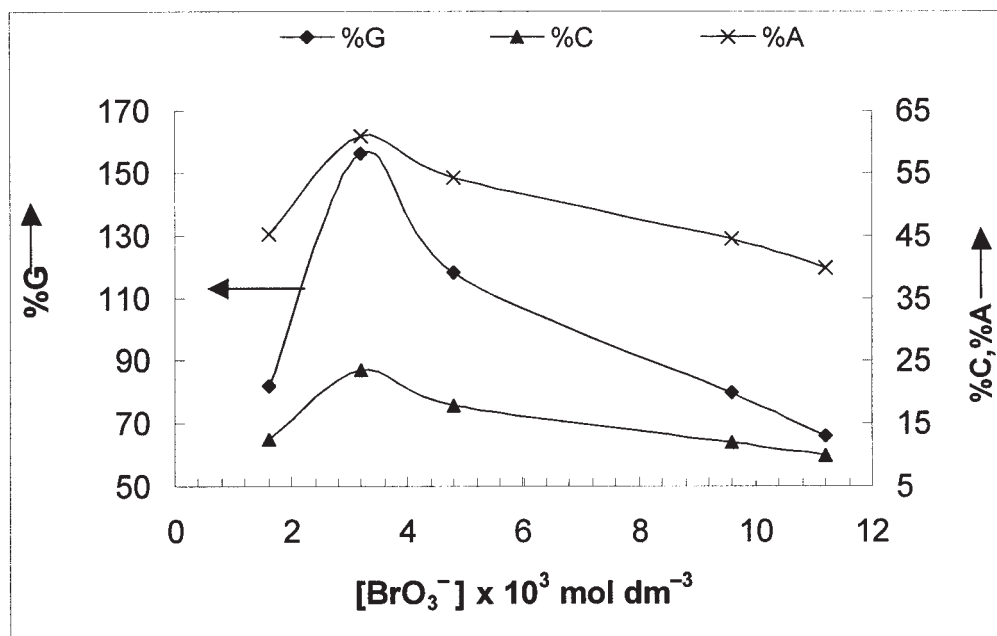
EXPERIMENTAL

Materials

AMPS (Aldrich Co. USA), Na-CMC (BDH), Potassium Broamte(E. Merck), Thiourea (E. Merck), and sulfuric acid (E. Merck). All solutions were prepared in triple distilled water.

Procedure for grafting

For each experiments, Na-CMC solution was prepared by slow addition of weighed amount of Na-CMC to

Figure 1 Effect of bromate ion concentration. [Thiourea] = 2.8×10^{-3} mol dm^{-3}; [AMPS] = 3.2×10^{-2} mol dm^{-3}; [Na-CMC] = 1.0 g dm^{-3}; [H$^+$] = 0.8×10^{-2} mol dm^{-3}; Temp. = 40°C; Time = 120 min. %A, add on; %C, conversion; %G, grafting ratio.

triple distilled water, with rapid stirring in reactor. Then a stream of purified nitrogen gas was passed for at least 30 min to remove the oxygen from the reaction mixture. A calculated amount of AMPS, thiourea, and sulfuric acid were added into the reactor. The reaction was initiated by addition of deoxygenated potassium bromate. Throughout the reaction period, the mixture was purged with the stream of purified nitrogen gas and kept at constant temperature. After a desired interval of time, the reaction was stopped by letting air into the reactor. The grafted sample was precipitated by pouring the reaction mixture into methanol. The precipitate was separated, dried, and weighed.

RESULTS AND DISCUSSION

The graft copolymer was characterized according to Fanta's[8] definition:

Grafting ratio (%G)

$$= \frac{\text{weight of grafted polymer}}{\text{weight of substrate}} \times 100$$

Add on (%A)

$$= \frac{\text{weight of synthetic polymer}}{\text{weight of polymer formed}} \times 100$$

Conversion (%C)

$$= \frac{\text{weight of graft copolymer}}{\text{weight of monomer charged}} \times 100$$

The effect of variation of concentration of BrO$_3^-$, thiourea, hydrogen ion, AMPS, Na-CMC along with the effect of time and temperature on grafting parameters was studied.

Determination of optimum reaction condition

Effect of bromate ion concentration

The effect of bromate ion concentration on grafting parameters was studied by varying its concentration from 1.6 to 11.2×10^{-2} mol dm^{-3} (Fig. 1). Grafting ratio, add on, and conversion increase with increase in bromate ion concentration up to 3.2×10^{-2} mol dm^{-3}. The same behavior of bromate ion was also observed in our laboratory, with acrylamide monomer.[9] The enhancement in above grafting parameters is due to the formation of greater number of primary free radicals, but as the concentration of
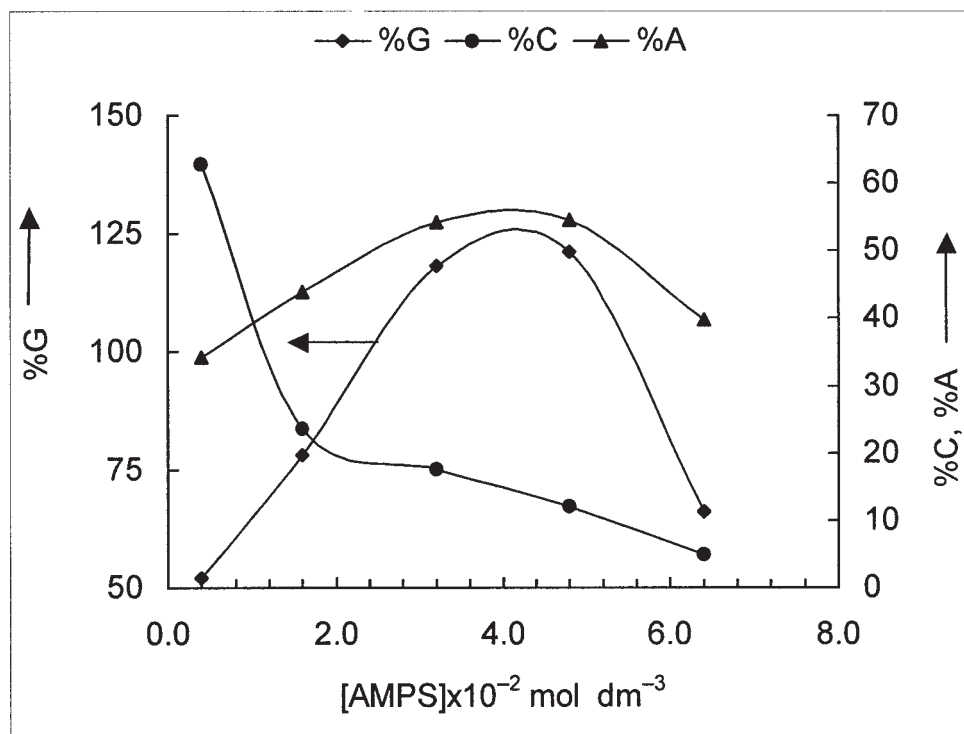
TABLE I
Effect of Thiourea Concentration

[Thiourea] $\times 10^3$ mol dm^{-3}	%G	%A	%C
1.2	66.0	39.7	9.9
2.0	96.0	49.0	14.5
2.8	118.0	54.1	17.8
3.6	140.0	58.3	21.1
4.4	74.0	44.6	11.2

[BrO$_3^-$] = 4.8×10^{-3} mol dm^{-3}, [AMPS] = 3.2×10^{-2} mol dm^{-3}, [Na-CMC] = 1.0 g dm^{-3}, [H$^+$] = 0.8×10^{-2} mol dm^{-3}, Temp = 40°C, Time = 120 min.
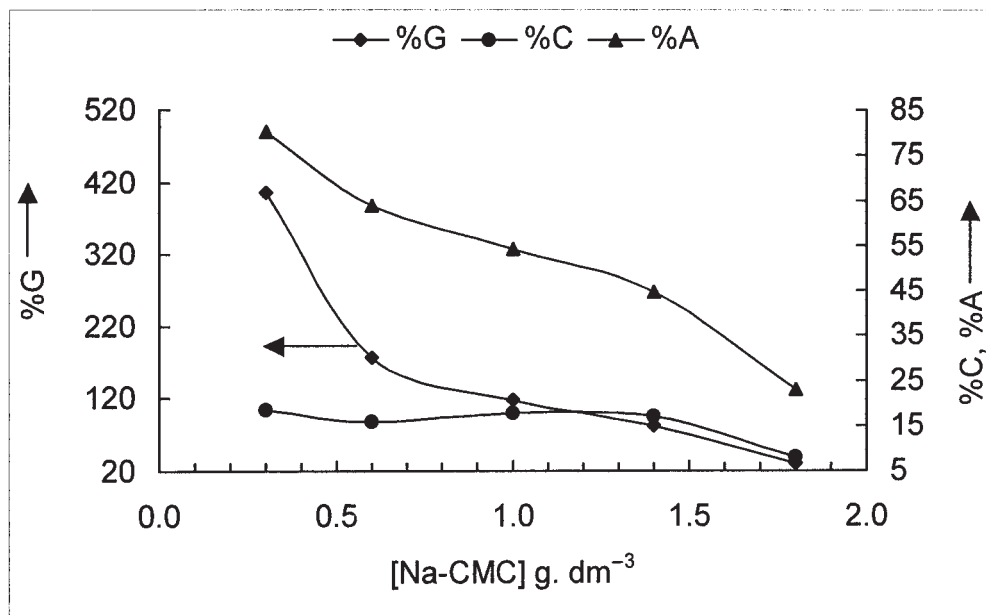
Figure 2   Effect of Na-CMC concentration. [Thiourea] = 2.8×10^{-3} mol dm^{-3}; [AMPS] = 3.2×10^{-2} mol dm^{-3}; [BrO$_3^-$] = 4.8×10^{-3} mol dm^{-3}; [H$^+$] = 0.8×10^{-2} mol dm^{-3}; Temp. = 40°C; Time = 120 min. %A, add on; %C, conversion; %G, grafting ratio.

Figure 3   Effect of AMPS concentration. [thiourea] = 2.8×10^{-3} mol dm^{-3}; [Na-CMC] = 1.0 g dm^{-3}; [BrO$_3^-$] = 4.8×10^{-3} mol dm^{-3}; [H$^+$] = 0.8×10^{-2} mol dm^{-3}; Temp. = 40°C; Time = 120 min. %A, add on; %C, conversion; %G, grafting ratio.

TABLE II
Effect of Hydrogen Ion Concentration

$[H^+] \times 10^2$ mol dm^{-3}	%G	%A	%C
0.4	106.0	51.5	16.0
0.6	142.0	58.7	21.4
0.8	118.0	54.1	17.8
1.0	102.0	50.5	15.4
1.2	78.0	43.8	11.8

[Thiourea] = 2.8×10^{-3} mol dm^{-3}, [BrO$_3^-$] = 4.8×10^{-3} mol dm^{-3}, [Na-CMC] = 1.0 g dm^{-3} [AMPS] = 3.2×10^{-2} mol dm^{-3}, Temp = 40°C, Time = 120 mm.

TABLE III
Effect of Time Period

Time (min)	%G	%A	%C
60	26.0	20.6	3.9
90	58.0	36.7	8.7
120	118.0	54.1	17.8
150	82.0	45.1	12.4
180	38.0	27.5	5.7

[Thiourea] = 2.8×10^{-3} mol dm^{-3}, [BrO$_3^-$] = 4.8×10^{-3} mol dm^{-3}, [Na-CMC] = 1.0 g dm^{-3} [AMPS] = 3.2×10^{-2} mol dm^{-3}, [H$^+$] = 0.8×10^{-2} mol dm^{-3}, Temp = 40°C.

bromate ion was increased beyond 3.2×10^{-2} mol dm^{-3}, grafting parameters were found to decrease because there might be large number of free radicals, which may terminate the growing grafted chains by oxidative path.

Effect of thiourea concentration

The variation in thiourea concentration from 1.2 to 4.4 $\times 10^{-3}$ mol dm^{-3} revealed that grafting ratio, add on, and conversion increased on increasing the thiourea concentration up to 3.6×10^{-3} mol dm^{-3}, but thereafter it showed a decreasing trend (Table I). The increasing trend of grafting parameters may be due to the increase in number of primary free radicals, and beyond 3.6×10^{-3} mol dm^{-3}, the decrease in grafting parameters may be due to premature termination of growing grafted chain.

Effect of Na-CMC

The grafting parameters were studied by varying the concentration of Na-CMC from 0.3 to 1.8 g dm^{-3} (Fig. 2). As the concentration of Na-CMC was increased, grafting ratio, add on, and conversion were found to decrease continuously. The above trend can be explained by the fact that as the concentration of Na-CMC increased, the viscosity of the reaction medium also increased, which hinders the movement of free radicals, thereby decreasing the grafting parameters.

Effect of AMPS

The effect of AMPS concentration on grafting parameters was studied by varying the concentration of AMPS from 0.4 to 6.4×10^{-2} mol dm^{-3} (Fig. 3). The grafting ratio and add on were found to increase up to 4.8×10^{-2} mol dm^{-3}. The increasing trend of grafting parameters with monomer concentration may be attributed to the greater availability of monomers at the close proximity of polymer backbone. The monomer molecule, which is at the immediate vicinity of the reaction sites, become ac-

ceptor of carboxymethylcellulose radicals resulting in chain initiation, and thereafter, it becomes free radical donor to the neighboring molecule, leading to lowering of termination. The decreasing trend of grafting parameters beyond the concentration of AMPS (4.8×10^{-2} mol dm^{-3}) may be attributed to greater solubility of poly AMPS in the water.

Effect of hydrogen ion concentration

The effect of hydrogen ion concentration has been studied by varying the concentration of hydrogen ion from 0.4 to 1.2×10^{-2} mol dm^{-3} (Table II). As the hydrogen ion concentration increased from 0.4 to 0.6 $\times 10^{-2}$ mol dm^{-3}, grafting ratio, add on, and conversion increased, but decreased thereafter with increase in hydrogen ion concentration.

Effect of time period

On varying the time period from 60 to 180 min, it was found that grafting ratio, add on, and conversion increased up to 120 min and thereafter showed decreasing trend. (Table III). The increase in grafting parameters may be attributed to the addition of monomer molecules to the growing grafted chains, but further increase in time period decreases these parameters because of mutual annihilation of growing grafted chains occurs.

TABLE IV
Effect of Temperature

Temp (°C)	%G	%A	%C
30	60.0	37.5	9.1
35	84.0	45.7	12.7
40	118.0	54.1	17.8
45	94.0	48.5	14.2
50	54.0	35.1	8.1

[Thiourea] = 2.8×10^{-3} mol dm^{-3}, [BrO$_3^-$] = 4.8×10^{-3} mol dm^{-3}, [Na-CMC] = 1.0 g dm^{-3} [AMPS] = 3.2×10^{-2} mol dm^{-3}, [H$^+$] = 0.8×10^{-2} mol dm^{-3}, Time = 120 mm.
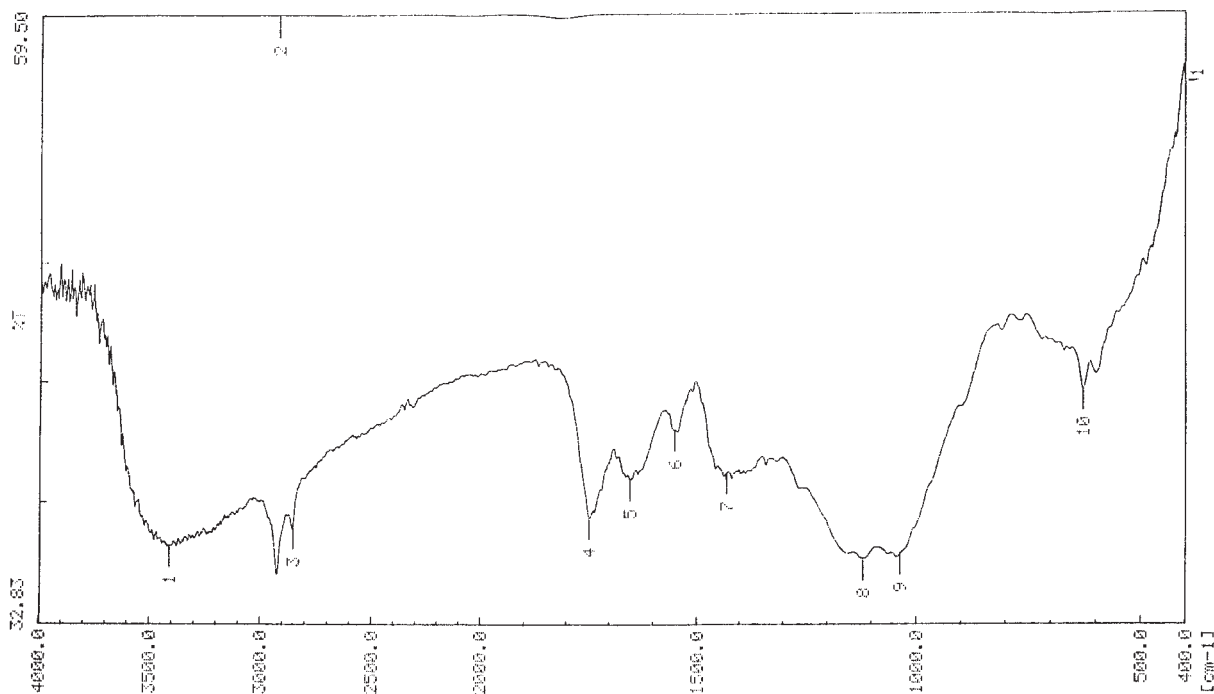
Figure 4   IR spectra of Na-CMC.

Effect of temperature

The effect of temperature on grafting parameters was studied by varying the temperature from 30 to 50°C (Table IV). The grafting parameters showed an increasing trend on increasing the temperature up to 40°C, but decrease in these parameters was observed as the temperature was raised from 45 to 50°C. The increase in parameters up to 40°C might be due to the increase in active sites on account of enhanced production of primary free radicals, with increase in temperature. The decrease in grafting parameters after 40°C may be attributed to the premature termination of growing grafted chains by excess of free radicals at higher temperature.
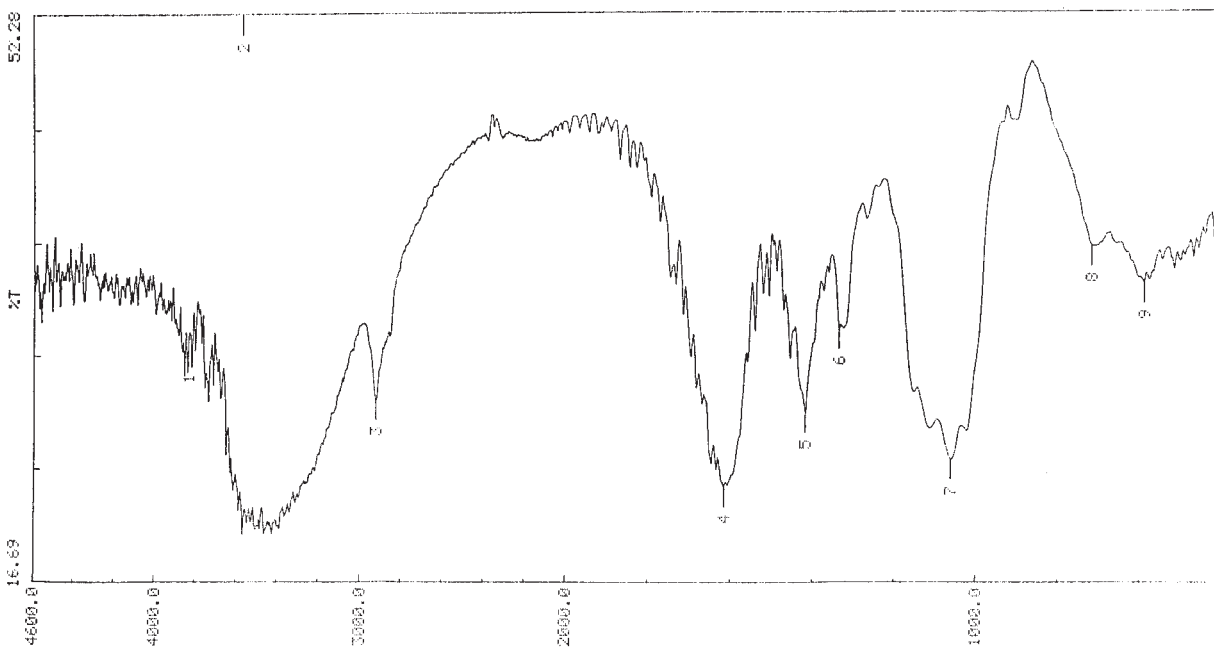
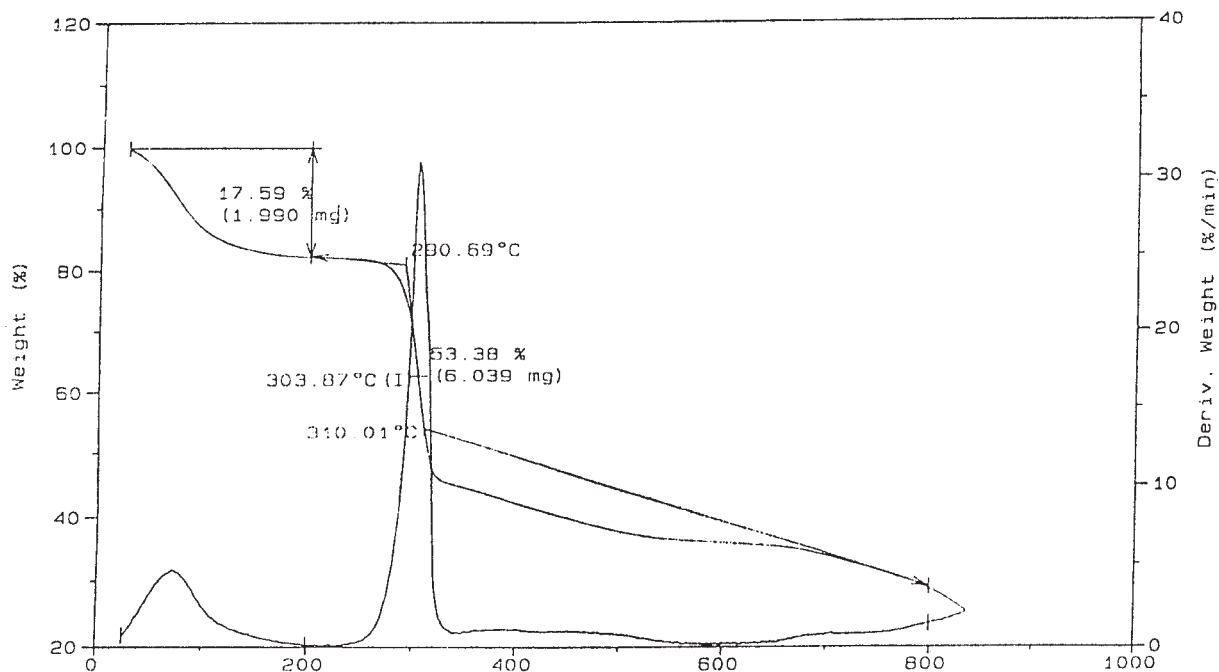

Figure 5   IR spectra of Na-CMC-*g*-AMPS.

Figure 6 Thermogravimetric trace of Na-CMC.

Evidence of grafting

IR Spectra

IR spectra was recorded using a Bruker IFS66U spectrophotometer. Polymeric samples were examined as KBr pellets. For IR of graft copolymer 118%G sample was taken.

On comparing the IR spectra of Na-CMC (Fig. 4) and Na-CMC-g-AMPS (Fig. 5), following additional peaks appeared in the spectra of Na-CMC-g-AMPS:

Amide-I band appeared at 1651.22 cm^{-1} due to C=O stretching vibration. Amide-II band due to bending and C—N stretching of the C—N—H group appeared at 1548.98 cm^{-1}. Band at 626.92 cm^{-1} appeared due to C—S stretching vibration. The disappearance of O—H bending vibration from the spectra of Na-CMC-g-2-acrylamido-2-methyl-1-propane gave an indication that grafting might have taken place on O—H sites.

Thermal analysis

Graft copolymer and Na-CMC were subjected to thermal analysis using Netzsch Geratebau GmbH STA 409 thermal analyzer with heating rate 15°C min^{-1}, starting from 90°C for an hour.

Grafting of AMPS onto Na-CMC seemed to be a fruitful attempt as it increases the thermal stability of Na-CMC-g-AMPS (118%G sample was taken for thermal analysis).

Na-CMC

The degradation of polymer started at about 200°C. Weight loss of 6.84 at 97.18°C was due to desorption of water (Fig. 6). The degradation occurred in a single step. The rate of weight loss increased with increase in the temperature from 200°C and reached a maximum at 303.87°C and thereafter, decreased and attained a constant value. There was almost 50% weight loss at 318.16°C temperature. The polymer decomposition temperature (PDT) has been found to be at 290.69°C and the temperature at which maximum degradation occurred, i.e., T_{max}, was found to be at 303.87°C. This was also confirmed from DSC analysis, which showed sharp exothermic peak at 297.46°C with an enthalpy value of 367.2 J g^{-1} (Table V), which also confirmed that maximum degradation has taken place at this temperature range. The final decomposition temperature (FDT) and integral procedural decomposition temperature (IPDT) were obtained at 310 and 194.83°C (Table VI). A char yield of 25.3°C has been obtained at 836.3°C.

Na-CMC-g-AMPS

The PDT was found at 206.8°C the rate of weight loss increased with increase in temperature and reached a

TABLE V
Thermogravimetric Analyses of Na-CMC and Na-CMC-g-AMPS

Sample code	Exo peak (°C)	Enthalpy (J/g)	Endo peak (°C)	Enthalpy (J/g)
UC	297.46	367.20	—	—
CTH	243.91	10.13	185.49	1.759

UC, sodium carboxymethyl cellulose; CTH, sodium carboxyrnethyl cellulose-g-AMPS

TABLE VI
Thermogravimetric Analyses of Na-CMC and Na-CMC-g-AMPS

Sample code	PDT (°C)	FDT (°C)	T_{max} (°C)	IPDT (°C)
UC	290.69	310.01	303.87	194.83
CTH	200.00	818.80	259.00	402.20
			358.32	
			640.90	
			740.90	

Char yield for UC at 836.3°C = 25.3%; char yield for CTH at 836.3°C = 48.8%; UC, sodium carboxymethyl cellulose; CTH, sodium carboxyrnethyl cellulose-g-AMPS.

maximum value at 259°C and then decreased again. It showed an increasing trend from 300°C and reached a maximum value at 358.32°C and then decreased and attained a minimum value at nearly 500°C. The maximum degradation of grafted copolymer took place at four temperatures, i.e., four T_{max} were obtained at 259, 358.32, 640.9, and 740.9°C (Table VI). The weight loss of grafted polymer in the lower temperature range, i.e., from 200 to 337.88°C, might be due to the elimination of CO_2 molecule from Na-CMC-g-AMPS. It was confirmed by the T_{max} of ungrafted Na-CMC value, which was nearly same as grafted Na-CMC. This was also supported by DSC analysis of grafted polymer, which showed an exothermic peak at 243.91°C, with an en-

thalpy value of 10.13 J g^{-1} (Table V). The second, third, and fourth T_{max} may be attributed to the elimination of H_2O, SO_3, and SO_2 molecule from the grafted polymer, as reported in following steps. At 772.72°C there was only 50% weight loss (Fig. 7). The FDT and IPDT were found to be at 818 and 402.2°C. A char yield of 48.8% was obtained at 836.3°C the high value of T_{max}, FDT, IPDT (Table VI), and char yield indicate that grafted polymer was thermally more stable than the parent polymer.
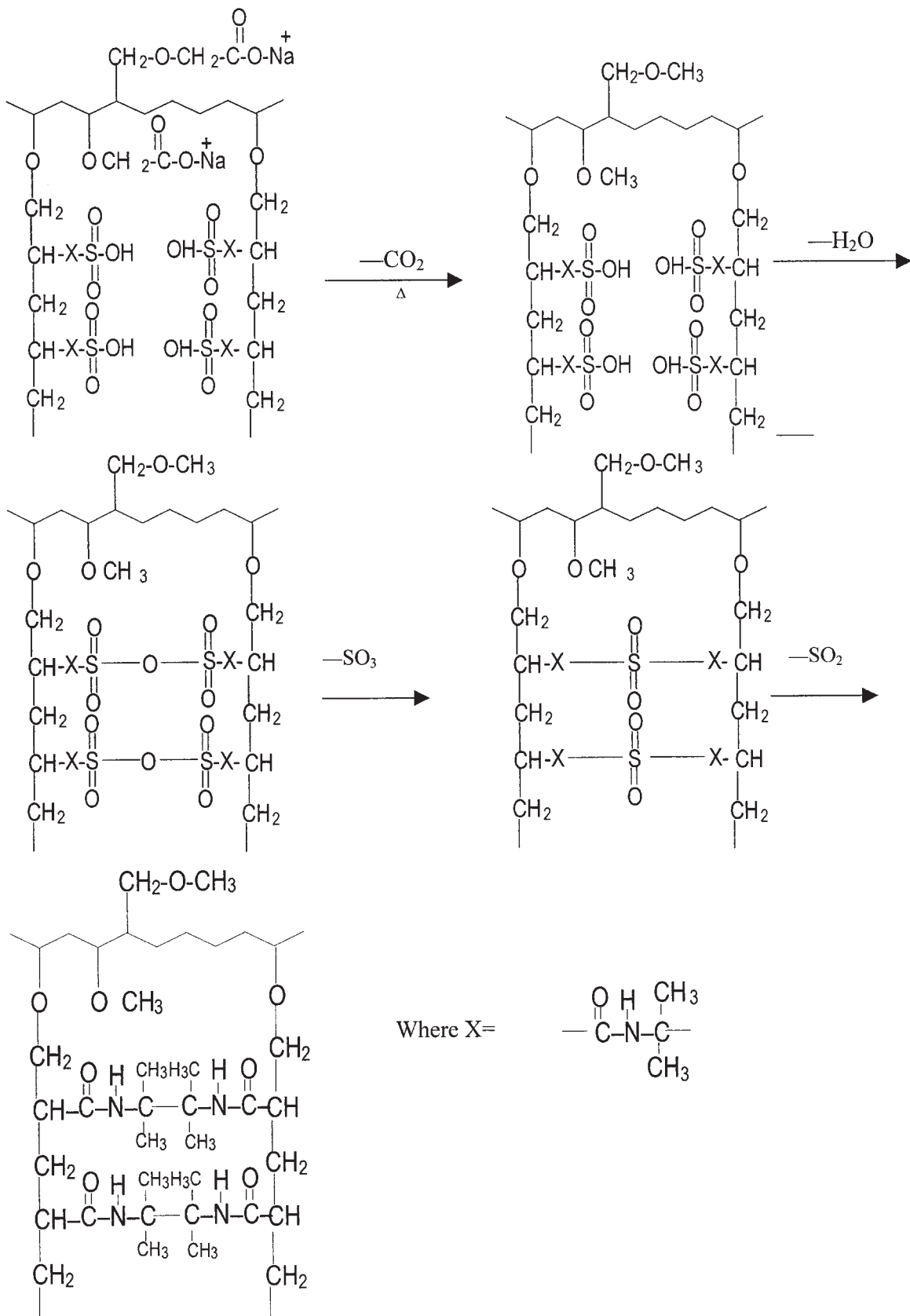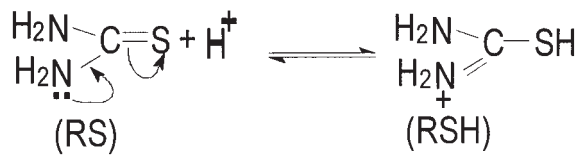
Mechanism

On the basis of the experimental results, the following tentative mechanism is proposed. Thiourea reacts with H^+ ion to give protonated species, which further react with BrO_3^- to give $RS^{\bullet}$, $OH^{\bullet}$, and $Br^{\bullet}$ radicals. These radicals represented by $R^{\bullet}$, abstract hydrogen atom from Na-CMC molecule(C—OH) to give Na-CMC free radical (C—$O^{\bullet}$). The monomer molecule that are in close vicinity of the reaction sites become acceptors of the Na-CMC radicals, resulting in chain initiation, and thereafter they themselves become free radical donor to the neighboring molecules. In this way grafted chains grow. These grafted chains terminate by coupling to give graft copolymers.

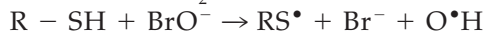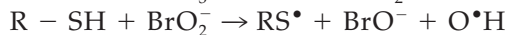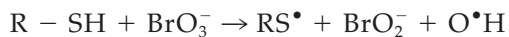The reaction mechanism can be represented by following steps:
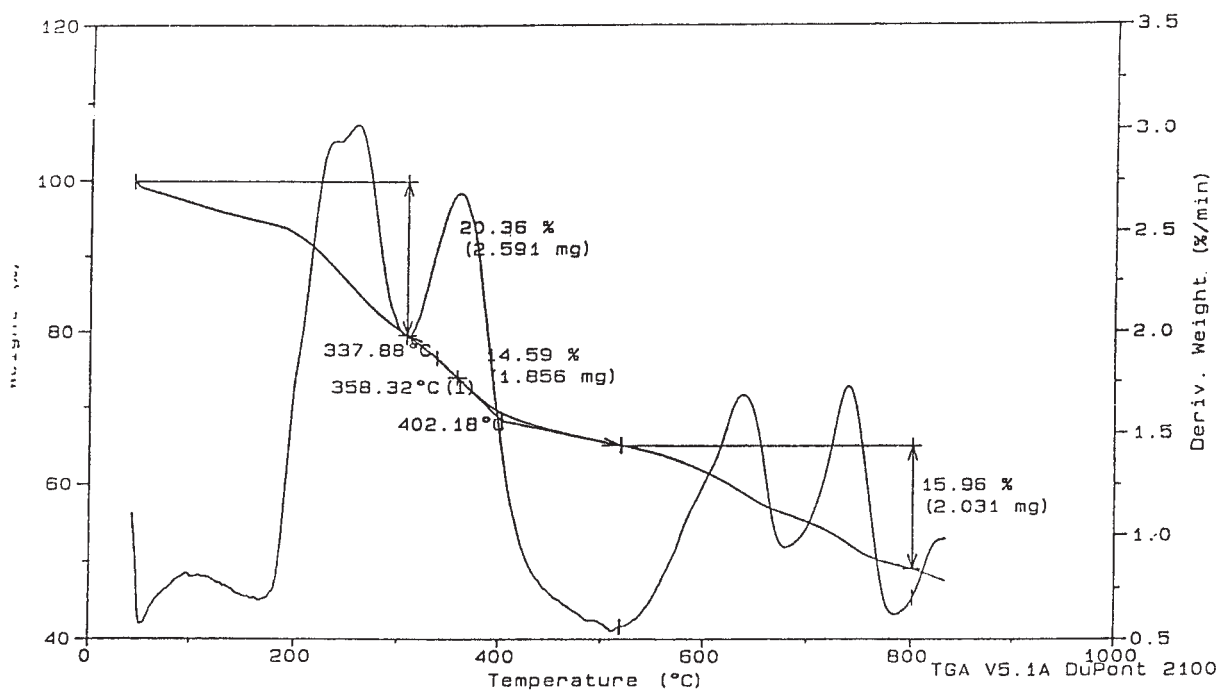
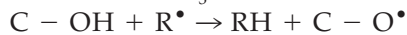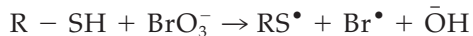**Figure 7** Thermogravimetric trace of Na-CMC-g-AMPS.

Scheme 1

Primary free radical formation
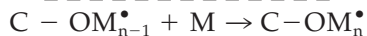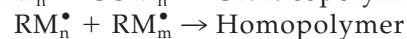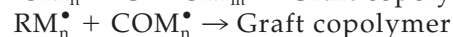
$$R - SH + BrO_3^- \rightarrow RS^\bullet + BrO_2^- + O^\bullet H$$
$$R - SH + BrO_2^- \rightarrow RS^\bullet + BrO^- + O^\bullet H$$
$$R - SH + BrO^- \rightarrow RS^\bullet + Br^- + O^\bullet H$$
$$\text{or}$$
$$R - SH + BrO_3^- \rightarrow RS^\bullet + Br^\bullet + \bar{O}H$$
$$C - OH + R^\bullet \rightarrow RH + C - O^\bullet$$

$$\{\text{where } R^\bullet = Br^\bullet, RS^\bullet, O^\bullet H\} M + R^\bullet \rightarrow RM^\bullet$$

Initiation

$$M + C - O^\bullet \rightarrow COM_1^\bullet$$

Propagation

$$C - OM_1^\bullet + M \rightarrow C - OM_2^\bullet$$
$$C - OM_2^\bullet + M \rightarrow C - OM_3^\bullet$$
$$- - - - - - - - - - - - -$$
$$- - - - - - - - - - - - -$$
$$C - OM_{n-1}^\bullet + M \rightarrow C - OM_n^\bullet$$
$$RM^\bullet + M \rightarrow RM_1^\bullet$$
$$RM_2^\bullet + M \rightarrow RM_2^\bullet$$
$$- - - - - - - - - - -$$
$$- - - - - - - - - - -$$
$$RM_{n-1}^\bullet + M \rightarrow RM_n^\bullet$$

Termination

$$C - OM_n^\bullet + C - OM_m^\bullet \rightarrow \text{Graft copolymer}$$
$$RM_n^\bullet + COM_n^\bullet \rightarrow \text{Graft copolymer}$$
$$RM_n^\bullet + RM_m^\bullet \rightarrow \text{Homopolymer}$$

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