

# Modification of Natural Polymer Via Free Radical Graft Copolymerization of 2-Acrylamido-2-Methyl-1-Propane Sulfonic Acid in Aqueous Media and Study of Swelling and Metal Ion Sorption Behavior

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**ABSTRACT:** In the present article, the graft copolymer of xanthan gum with 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) was synthesized using potassium bromate/ascorbic acid as a redox initiator in aqueous medium; reaction conditions were optimized to obtain maximum % grafting ratio (%G). The optimum concentration of  $\text{BrO}_3^-$  ion, ascorbic acid,  $\text{H}^+$  ion, and AMPS for maximum %G were  $8.0 \times 10^{-3}$ ,  $2.8 \times 10^{-3}$ ,  $4.0 \times 10^{-3}$ , and  $33.2 \times 10^{-3}$  mol  $\text{dm}^{-3}$ , respectively. The maximum %G (433.0) occurred at a minimum concentration of xanthan gum, i.e.,  $0.6 \text{ g dm}^{-3}$ . The optimum time duration and temperature of the reaction for maximum % of grafting were 180 min and  $45^\circ\text{C}$ , respectively. The graft copolymer was characterized by FTIR spectroscopy. The thermal analysis of xanthan gum and prepared graft copolymer was performed in a nitrogen

atmosphere to study their thermal behavior. It was observed that the PDT (polymer decomposition temperature) of graft copolymer is lower than that of xanthan gum, whereas the IPDT (integral procedural decomposition temperature) of graft copolymer is higher than that of xanthan gum, making the former more thermally stable. The swelling and metal ion sorption capability of graft copolymer was investigated. The metal ion sorption behavior of graft copolymer was studied for five metal ions ( $\text{Cu}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Pb}^{++}$ ,  $\text{Hg}^{++}$ ). Our results show that the grafted sample absorbs a good amount of water and the metal ion. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1426–1434, 2009

**Key words:** polysaccharide; graft copolymer; biodegradable; thermal properties; FTIR

## INTRODUCTION

Nowdays, more emphasis is given to biodegradable polymers such as polysaccharides and proteins, which are extensively used and investigated for industrial applications. One of them is xanthan gum, which is an extracellular heteropolysaccharide<sup>1</sup> of *Xanthomonas campestris*, which exists as a double helix in solution. In solution, this polymer is known to tolerate high concentrations of electrolytes, and its viscosity is nearly independent of pH and temperature.<sup>2</sup> The structural unit of xanthan gum consists of  $\beta$ -(1→4)-D-glucopyranose glucan (as cellulose) backbone with side chains of  $-(3\rightarrow1)\text{-}\alpha$ -linked D-mannopyranose-(2→1)- $\beta$ -D-glucuronic acid-(4→1)-

$\beta$ -D-mannopyranose on alternating residues. Slightly less than half ( $\approx 40\%$ ) of the terminal mannose residues are 4,6-pyruvated, and the inner mannose is mostly 6-acetylated.<sup>3</sup> Each molecule consists of 7000 pentamers and the gum is more polydisperse than most hydrocolloids. Due to its biocompatibility, high thickening efficiency,<sup>4</sup> hydrogen bonding properties,<sup>5</sup> good electrolytic compatibility, and low cost, it has a wide range of applications, viz, in food,<sup>6</sup> cosmetics,<sup>7</sup> and additives<sup>8</sup> and also is employed as matrices for prolonged drug delivery systems.<sup>9</sup> Kuniharan et al. (1985) used its graft copolymer in adsorption of heavy metal ions. Although it possesses various industrial applications, it is susceptible to microbial attack and can be improved by grafting of different vinyl monomers. Therefore, in the present work, the main aim was the modification of gum through the grafting of 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS); this vinyl monomer was chosen for grafting because polymers derived from AMPS have been found to be highly useful in preparing high swelling-capacity polymer hydrogel,<sup>10</sup> temperature-sensitive hydrogel,<sup>11</sup> and sensor and electrochromic cells.<sup>12</sup> Furthermore, graft copolymer of AMPS has been reported as widely

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used in enhanced oil recovery<sup>13</sup> because of its solubility in water by increasing the viscosity of treated muds. Therefore, synthesized graft copolymer of xanthan gum and AMPS would be a good drag-reducing agent and a better flocculent.

## EXPERIMENTAL

### Materials

AMPS (Aldrich, USA), potassium bromate (Merck, Mumbai, India), ascorbic acid (Merck), and xanthan gum (Sigma, USA) were used without further purification. For maintaining hydrogen ion concentration, sulfuric acid (Merck) was used. The other chemical reagents were of analytical grade and were used without further purification. All solutions were prepared in triple-distilled water.

### Procedure for grafting

For each experiment, xanthan gum solution was prepared by adding the desired amount of xanthan gum to 50 mL of triple-distilled water in a reactor. The reaction was carried out under nitrogen atmosphere at a constant temperature. A calculated amount of AMPS, sulfuric acid, and ascorbic acid solutions were added to the known amount of the gum solution in the reactor. To initiate the reaction, a known amount of deoxygenated potassium bromate solution was added into the reactor containing the reaction mixture. After a desired interval of time, air was let into the reactor to stop the reaction. The graft copolymer was precipitated by pouring the reaction mixture into a water-methanol mixture and kept overnight. The precipitate was separated by filtration, dried, and weighed. Under reaction conditions, there was no formation of homopolymer. Similar observations were made in our laboratory.<sup>14</sup>

### FTIR analysis

The FTIR spectra of the sample in KBr Pellets was recorded using the JASCO FT/IR-5300 model.

### Thermogravimetric analysis

The thermal behavior of xanthan gum and xanthan gum-g-AMPS were recorded on a NETZSCH Geratebau GmbH thermal analyzer within a temperature range of 0–1500°C in an N<sub>2</sub> atmosphere at a heating rate of 20°C min<sup>-1</sup>.

## RESULTS AND DISCUSSION

Graft copolymer was characterized according to Fanta's definition.<sup>15</sup>

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

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

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

The rate of grafting was calculated according to the following formula, which has been reported elsewhere.<sup>16,17</sup>

$$\text{Rate of grafting (R}_g\text{)} = \frac{1000 \times W}{V \times t \times M} \text{ mol/L/s}$$

where  $W$  is weight of grafted gum minus the weight of ungrafted gum;  $V$ , the volume of reaction mixture;  $t$ , the time of reaction in seconds; and  $M$ , the molecular weight of monomer (AMPS).

### Determination of optimum reaction condition

To determine the optimum reaction condition for the grafting of AMPS onto xanthan gum using a BrO<sub>3</sub>/ascorbic acid redox pair, graft copolymerization was carried out under different conditions of the reaction components (reaction time and temperature and concentration of bromate ion, ascorbic acid, xanthan gum, hydrogen ion, AMPS).

#### Effect of bromate ion concentration

The effects of [BrO<sub>3</sub><sup>-</sup>] on grafting parameters and rate of grafting were studied by varying the concentration of potassium bromate from 2.0 × 10<sup>-3</sup> to 14.0 × 10<sup>-3</sup> mol dm<sup>-3</sup> (Table I). It has been observed that the % grafting ratio, % add on, % conversion, and rate of grafting increase on increasing the concentration of potassium bromate from 2.0 × 10<sup>-3</sup> to

TABLE I  
Effects of Bromate Ion Concentrations

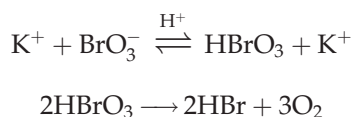
[BrO <sub>3</sub> <sup>-</sup> ] × 10 <sup>3</sup> mol dm <sup>-3</sup>	%G	%A	%C	R <sub>g</sub> × 10 <sup>7</sup> mol L <sup>-1</sup> S <sup>-1</sup>
2.0	180	64.4	26.2	12.0
5.0	230	69.7	33.4	15.4
8.0	250	71.4	36.3	16.7
11.0	197	66.3	28.6	13.2
14.0	120	54.5	17.4	8.0

[XOH] = 1.0 g dm<sup>-3</sup>; [AMPS] = 33.2 × 10<sup>-3</sup> mol dm<sup>-3</sup>; [AA] = 2.8 × 10<sup>-3</sup> mol dm<sup>-3</sup>; [H<sup>+</sup>] = 3.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>; Time = 120 min; Temp = 35°C.

$8.0 \times 10^{-3} \text{ mol dm}^{-3}$ . The enhancement in grafting parameters might be attributed to the progressive reduction of bromate ion with ascorbic acid producing  $\text{OH}^\bullet$ ,  $\text{AA}^\bullet$ , and  $\text{Br}^\bullet$  radicals, which interact with xanthan gum molecules to produce the xanthan gum macroradicals. The AMPS molecules then attach to xanthan gum macroradicals to propagate the growing grafted chains.

The decrement in grafting parameters has been observed at higher concentrations of potassium bromate, i.e., beyond  $8.0 \times 10^{-3} \text{ mol dm}^{-3}$ , and it might be due to the following reasons, which have been supported by Nayak and coworkers.<sup>18</sup>

1. At higher concentrations of bromate ion, it might react with xanthan gum macroradicals or with the growing radicals, thus a decrease in the parameters is observed that is due to decrease in active sites of xanthan gum macroradicals or by termination between growing grafted chains.
2. Decrement is due to the liberation of appreciable amounts of oxygen,<sup>19</sup> which acts as a scavenger for free radicals and is represented as



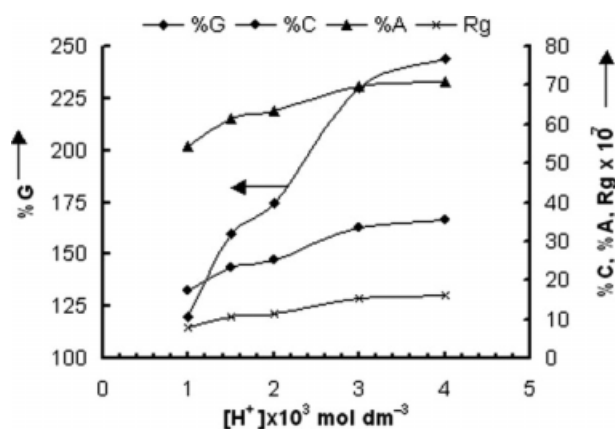
#### Effect of ascorbic acid concentration

The increase in ascorbic acid concentration from  $1.2 \times 10^{-3}$  to  $2.8 \times 10^{-3} \text{ mol dm}^{-3}$  (Table II) shows increment in % grafting ratio, % add on, % conversion, and rate of grafting, and it might be due to the formation of sufficient amounts of active species ( $\text{AA}^\bullet$ ,  $\text{OH}^\bullet$ ,  $\text{Br}^\bullet$ ). On further increase in concentrations of ascorbic acid ( $2.8 \times 10^{-3}$  to  $4.4 \times 10^{-3} \text{ mol dm}^{-3}$ ), the grafting parameters and rate of grafting decreased. The decrement in grafting parameters might be due to production of excess primary free radicals by progressive oxidation of ascorbic acid,

**TABLE II**  
Effects of Ascorbic Acid Concentrations

$[\text{AA}] \times 10^3$ $\text{mol dm}^{-3}$	%G	%A	%C	$R_g \times 10^7$ $\text{mol L}^{-1} \text{S}^{-1}$
1.2	160	61.5	23.3	10.7
2.0	180	64.2	26.2	12.0
2.8	230	69.6	33.4	15.4
3.6	120	54.5	17.4	8.0
4.4	80	44.4	11.6	5.4

$[\text{XOH}] = 1.0 \text{ g dm}^{-3}$ ;  $[\text{AMPS}] = 33.2 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{BrO}_3^-] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{H}^+] = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$ ; Time = 120 min; Temp = 35°C.



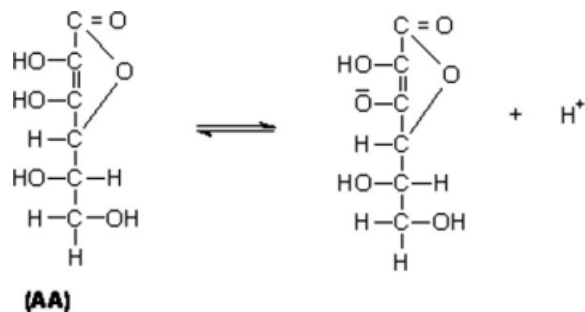
**Figure 1** Effect of hydrogen ion concentration  $[\text{XOH}] = 1.0 \text{ g dm}^{-3}$ ;  $[\text{AMPS}] = 33.2 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{BrO}_3^-] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{AA}] = 2.84 \times 10^{-3} \text{ mol dm}^{-3}$ ; Time = 120 min; Temp = 35°C; %G = Grafting ratio; %A = Add on; %C = Conversion;  $R_g$  = Rate of grafting.

which terminates the growing xanthan gum radicals.

#### Effect of hydrogen ion concentration

The effect of  $[\text{H}^+]$  on grafting parameters and rate of grafting has been studied by varying the concentration of sulfuric acid from  $1.0 \times 10^{-3}$  to  $4.0 \times 10^{-3} \text{ mol dm}^{-3}$ , and results are shown in Figure 1. The % grafting ratio, % add on, % conversion, and rate of grafting have been found to increase continuously on increasing the concentration of hydrogen ions. This behavior can be explained as follows (Scheme 1), which has been reported by others.<sup>20</sup>

On increasing the concentration of hydrogen ions, the concentration of AA species increases, which reacts with bromate ion, giving rise to primary free radicals. The primary free radicals react with xanthan gum molecules, giving rise to more xanthan gum macro free radicals, which are responsible for propagation of growing grafted chains, which results in the increased value of % grafting ratio, % conversion, % add on, and rate of grafting.



**Scheme 1** Ionization of ascorbic acid in the presence of hydrogen ion.

Effect of 2-acrylamido-2-methyl-1-propane sulfonic acid

Figure 2 shows that % grafting ratio, % add on, and rate of grafting increase up to  $33.2 \times 10^{-3} \text{ mol dm}^{-3}$  after that decrease, whereas conversion increases continuously on increasing the concentration of AMPS. The increment in grafting parameters and rate of grafting might be due to greater availability of monomer at the close proximity of xanthan gum. The monomer molecules, which are at the immediate vicinity of the reaction sites, becomes the acceptor of xanthan gum radicals ( $\text{XO}^*$ ), resulting in chain initiation; thereafter, it becomes free radical donor to the neighboring molecule (monomer), leading to lowering the termination. The decrement in grafting parameters and rate of grafting beyond  $33.2 \times 10^{-3} \text{ mol dm}^{-3}$  might be attributed to the increase in the viscosity of the reaction medium.

Effect of xanthan gum concentration

The results of variation of xanthan gum concentration on grafting parameters and rate of grafting are shown in Figure 3. The % grafting ratio and % add on have been found to decrease continuously from 0.6 to  $2.2 \text{ g dm}^{-3}$ . This behavior can be explained on this basis, when the concentration of xanthan gum increases the viscosity of reaction medium increases, which hinders the movement of free radicals, thereby decreasing the grafting parameters.

Effect of time

The effect of time on grafting parameters and rate of grafting has been studied by changing the time of reaction from 60 to 180 min (Fig. 4). It has been

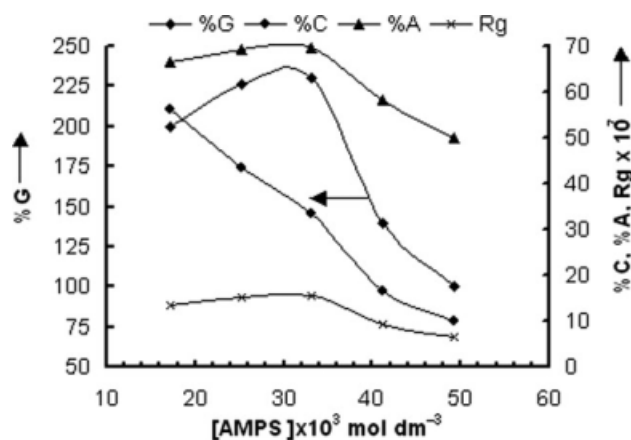


Figure 2 Effect of 2-acrylamido-2-methyl-1-propane sulfonic acid Concentration.  $[\text{XOH}] = 1.0 \text{ g dm}^{-3}$ ;  $[\text{H}^+] = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{BrO}_3^-] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{AA}] = 2.84 \times 10^{-3} \text{ mol dm}^{-3}$ ; Time = 120 min; Temp. =  $35^\circ\text{C}$ ; %G = Grafting ratio; %A = Add on; %C = Conversion;  $R_g$  = Rate of grafting.

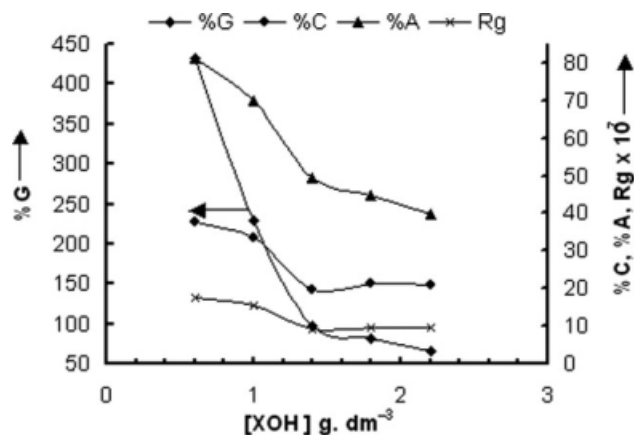


Figure 3 Effect of xanthan gum concentration.  $[\text{AMPS}] = 33.2 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{H}^+] = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{BrO}_3^-] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{AA}] = 2.84 \times 10^{-3} \text{ mol dm}^{-3}$ ; Time = 120 min; Temp. =  $35^\circ\text{C}$ ; %G = Grafting ratio; %A = Add on; %C = Conversion;  $R_g$  = Rate of grafting.

observed that the % grafting ratio, % add on, % conversion, and rate of grafting increase on increasing the duration of grafting reaction. The increment in grafting parameters and rate of grafting might be attributed due to the addition of more and more monomer molecules to the growing grafted chains.

Effect of temperature

The grafting parameters and rate of grafting have been found to increase continuously on increasing the temperature from 25 to  $45^\circ\text{C}$ ; results are summarized in Table III. This may be explained on the basis that with an increase in temperature, the rate of production of primary free radicals increased and diffusion of AMPS molecules to xanthan gum macroradicals also increased, thereby increasing %

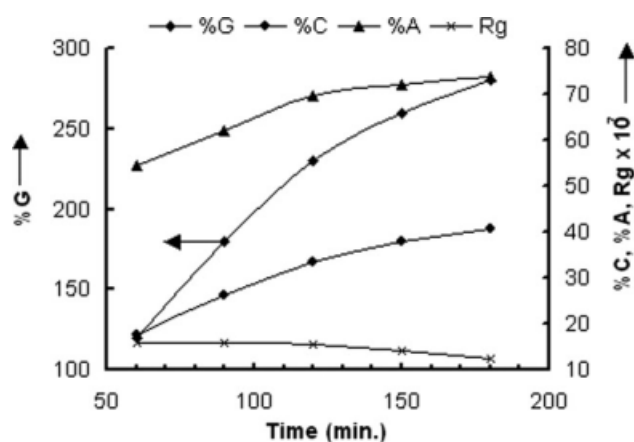


Figure 4 Effect of time.  $[\text{AMPS}] = 33.2 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{H}^+] = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{BrO}_3^-] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{AA}] = 2.84 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{XOH}] = 1.0 \text{ g dm}^{-3}$ ; Temp. =  $35^\circ\text{C}$ ; %G = Grafting ratio; %A = Add on; %C = Conversion;  $R_g$  = Rate of grafting.

TABLE III  
Effects of Temperature

Temp (°C)	%G	%A	%C	$R_g \times 10^7 \text{ mol L}^{-1} \text{ S}^{-1}$
25	160	61.5	23.2	10.7
30	200	67.8	29.0	13.4
35	230	69.7	33.4	15.4
40	240	70.5	33.8	16.0
45	260	72.2	37.8	17.4

[XOH] = 1.0 g dm<sup>-3</sup>; [AMPS] = 33.2 × 10<sup>-3</sup> mol dm<sup>-3</sup>;  
[BrO<sub>3</sub><sup>-</sup>] = 8.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>; [AA] = 2.8 × 10<sup>-3</sup> mol dm<sup>-3</sup>;  
[H<sup>+</sup>] = 3.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>; Time = 120 min.

grafting ratio, % add on, % conversion, and rate of grafting.

### Swelling studies

The swelling studies were carried out by taking 0.05 g (50 mg) of the sample in 20 mL of triple-distilled water and kept undisturbed for 24 h. The surface water on the swollen graft copolymer was removed by safely pressing between the folds of filter paper; an increase in weight was recorded. Percent swelling ( $P_S$ ) and swelling ratio ( $S_R$ ) were calculated by using the following expressions.<sup>21</sup> Results are given in Table IV.

$$P_S = \frac{\text{Weight of swollen polymer} - \text{Weight of dry polymer}}{\text{Weight of dry polymer}} \times 100$$

$$S_R = \frac{\text{Weight of swollen polymer} - \text{Weight of dry polymer}}{\text{Weight of dry polymer}}$$

It was observed that percent swelling and swelling ratio of graft copolymer increase on increasing the percent grafting ratio up to certain limit. This behavior can be explained by the fact that AMPS is hydrophilic

TABLE IV  
Swelling Studies

Sample code	[AMPS] × 10 <sup>3</sup> mol dm <sup>-3</sup>	%G	$P_S$	$S_R$
XA <sub>1</sub>	17.2	200	136	1.36
XA <sub>2</sub>	25.2	226	164	1.64
XA <sub>3</sub>	33.2	230	180	1.80
XA <sub>4</sub>	41.2	140	152	1.52
XA <sub>5</sub>	49.2	100	122	1.22

[XOH] = 1.0 g dm<sup>-3</sup>; [AA] = 2.84 × 10<sup>-3</sup> mol dm<sup>-3</sup>;  
[BrO<sub>3</sub><sup>-</sup>] = 8.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>; [H<sup>+</sup>] = 3.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>;  
Time = 120; Temp = 35°C; X, xanthan gum; X<sub>A</sub>, xanthan gum-g-2-acrylamido-2-methyl-1-propane sulfonic acid.

in nature, and with the increase in percent grafting the amount of AMPS is also increased, thereby increasing percent swelling and swelling ratio.

### Metal ion sorption studies

The metal ion sorption studies were carried out on graft copolymer at different compositions (which was synthesized by varying the concentration of monomer) by taking 0.02 g (20 mg) in 10 mL of a metal ion solution of known concentration and keeping it undisturbed for 24 h. For metal ion sorption studies, we chose five metal ions like Cu<sup>+2</sup>, Zn<sup>+2</sup>, Ni<sup>+2</sup>, Pb<sup>+2</sup>, and Hg<sup>+2</sup>. The strength of unabsorbed metal ions was determined by standard methods.<sup>22</sup> Percent uptake, partition coefficient, and retention capacity were calculated using the following expressions.<sup>23</sup>

$$\text{Percent uptake } (P_u) = \frac{\text{Amount of metal ion in polymer}}{\text{Amount of metal ion in feed}} \times 100$$

$$\text{Partition coefficient } (K_d) = \frac{\text{Amount of metal ion in polymer}}{\text{Amount of metal ion left in solution}} \times \frac{\text{Volume of solution (mL)}}{\text{Weight of dry polymer (g)}}$$

TABLE V  
Metal Ion Sorption Studies

Sample code	[AMPS] × 10 <sup>3</sup> mol dm <sup>-3</sup>	%G	Percent uptake ( $P_u$ )					Partition coefficient ( $K_d$ ) (g g <sup>-1</sup> )					Retention capacity ( $Q_r$ ) (mequiv g <sup>-1</sup> )				
			Cu <sup>2+</sup>	Ni <sup>2+</sup>	Zn <sup>2+</sup>	Pb <sup>2+</sup>	Hg <sup>2+</sup>	Cu <sup>2+</sup>	Ni <sup>2+</sup>	Zn <sup>2+</sup>	Pb <sup>2+</sup>	Hg <sup>2+</sup>	Cu <sup>2+</sup>	Ni <sup>2+</sup>	Zn <sup>2+</sup>	Pb <sup>2+</sup>	Hg <sup>2+</sup>
X	—	—	4.17	3.0	1.7	1.07	0.45	21.7	15.7	8.7	5.42	2.30	0.4	0.58	0.22	0.62	0.29
XA <sub>1</sub>	17.2	200	16.85	3.7	3.44	3.53	1.28	101.3	19.5	17.9	7.07	6.49	1.7	0.72	0.45	1.99	0.81
XA <sub>2</sub>	25.2	226	17.3	4.8	3.9	3.84	1.42	104.3	25.2	20.7	19.9	7.10	1.8	0.92	0.52	2.24	0.90
XA <sub>3</sub>	33.2	230	18.5	7.3	4.5	4.8	1.51	113.8	39.5	23.5	25.21	7.67	1.9	1.42	0.59	2.80	0.96
XA <sub>4</sub>	41.2	140	6.4	5.4	3.6	2.35	1.19	34.6	28.8	18.8	12.05	6.02	0.6	1.04	0.47	1.37	0.75
XA <sub>5</sub>	49.2	100	4.8	5.2	3.1	1.67	0.91	25.2	27.6	16.0	8.53	4.62	0.5	1.0	0.40	0.98	0.58

[XOH] = 1.0 g dm<sup>-3</sup>; [AA] = 2.84 × 10<sup>-3</sup> mol dm<sup>-3</sup>; [BrO<sub>3</sub><sup>-</sup>] = 8.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>; [H<sup>+</sup>] = 3.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>;  
Time = 120; Temp = 35°C; X, xanthan gum; X<sub>A</sub>, xanthan gum-g-2-acrylamido-2-methyl-1-propane sulfonic acid.

**TABLE VI**  
Thermogravimetric Analysis

Sample code	PDT (°C)	FDT (°C)	$T_{max}$ (°C)	IPDT (°C)	DTA peaks	
					Exopeaks (°C)	Endopeaks (°C)
X	250.0	825.0	278.5	235.8	-	297.3 648.3
X <sub>A</sub>	225.0	1205.0	204.3, 562.1 679.0, 933.8 1171.9	322.1	-	547.7 872.8

X, xanthan gum; X<sub>A</sub>, xanthan gum-g-2-acrylamido-2-methyl-1-propane sulfonic acid.

Retention capacity ( $Q_r$ )

$$= \frac{\text{Amount of metal ion in polymer (meq)}}{\text{Amount of dry polymer (g)}}$$

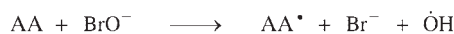
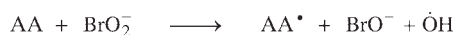
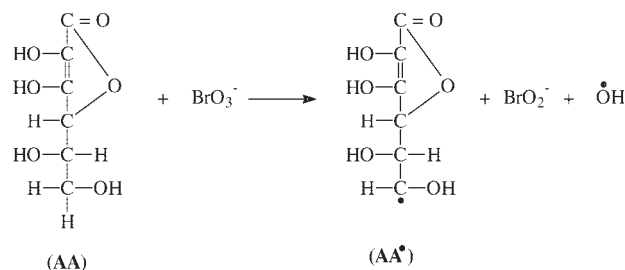
The effect of percent grafting on sorption behavior of graft copolymer was studied in terms of percent ion uptake ( $P_u$ ), partition coefficient ( $K_d$ ), and retention capacity ( $Q_r$ ); results are summarized in Table V. It was observed that the percent ion uptake, partition coefficient, and retention capacity increase with increase in value of percent grafting, which may be due to increased pendent poly(AMPS) chain onto xanthan gum. Results also showed that  $Hg^{++}$  was the least uptakable ion, whereas other metal ions ( $Cu^{++}$ ,  $Zn^{++}$ ,  $Ni^{++}$ , and  $Pb^{++}$ ) showed better uptake results.

**Mechanism**

Initially  $AA^\bullet$ ,  $\bullet OH$ , and  $Br^\bullet$  radicals are generated by the interaction of  $BrO_3^-$  and ascorbic acid. These radicals extract hydrogen atoms from the xanthan gum molecules, producing xanthan gum macro free radicals. The monomer molecules that are at close prox-

imity of the reaction sites become acceptors of the xanthan gum radicals, resulting in chain initiation and thereafter themselves become free radical donors to neighboring molecule. In this way, grafted chains propagate and these grafted chains terminate by coupling to produce graft copolymer.

**Free radical formation**

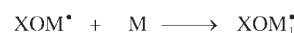


**Initiation**



Where  $R^\bullet = AA^\bullet, Br^\bullet, \bullet OH$

**Propagation**



where XOH is xanthan gum and M is monomer.

**Termination**

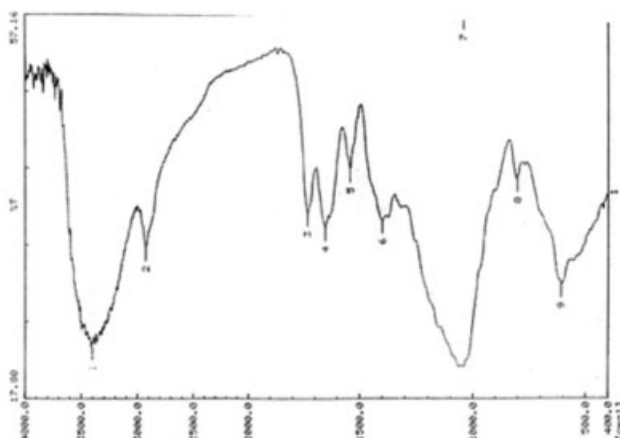


Figure 5 IR spectra of xanthan gum-g-AMPS.

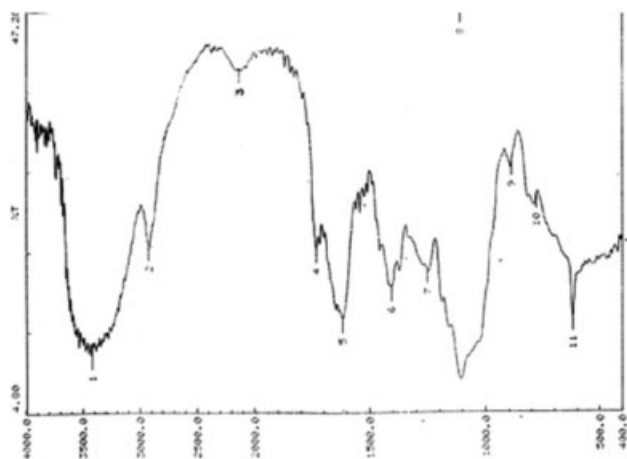


Figure 6 IR spectra of xanthan gum.

### Evidence of grafting

#### IR spectra

IR spectral analyses were utilized to prove the grafting. For this purpose, the IR spectra of xanthan gum and xanthan gum-g-AMPS were taken in the range of 400–4000  $\text{cm}^{-1}$ . From Figure 5 it has been observed that the graft copolymer shows absorption bands related to xanthan gum (Fig. 6) and also the additional bands at 1655, 1543, 1400, 1043, and 607  $\text{cm}^{-1}$ , which are attributed to C=O stretching vibration (Amide I band), C–N–H bending vibration (Amide II band), C–N stretching vibration of amide band, S–O stretching vibration of  $-\text{SO}_3\text{H}$  and C–S stretching vibration, respectively; these bands are characteristics of poly AMPS. Amide II band results from the interaction between N–H bending and C–N stretching of the C–N–H group. Thus the presence of these additional bands in spectra of the graft copolymer indicates that the grafting has taken place on xanthan gum. The absence of O–H bending vibrations from the spectra of xanthan gum-g-AMPS indicates that grafting might have taken place on the –OH sites of the xanthan gum, which is the probable site for grafting.

### Thermogravimetric analysis

#### Xanthan gum

Thermogravimetric analysis of xanthan gum showed that degradation of xanthan gum started at about 200°C. It was observed that the rate of weight loss increased with increases in temperatures up to 290°C, but after 40% weight loss, the decreased; therefore it is a single-step degradation process. The polymer decomposition temperature (PDT), temperature at which maximum weight loss occurred ( $T_{\text{max}}$ ) and integral procedural decomposition temperature (IPDT) were 250.0, 278.5, and 235.8°C, respectively

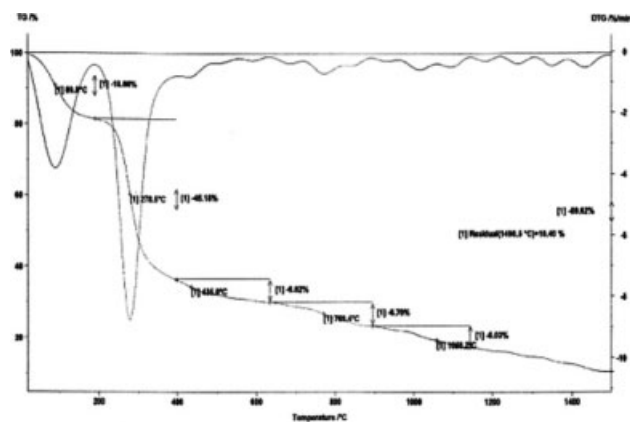


Figure 7 Thermogravimetric analysis curve of xanthan gum.

(Table VI). About 70% of xanthan gum was lost at about 700°C; therefore FDT was 825°C. The  $T_{\text{max}}$  was also confirmed by the differential thermal analysis (DTA) curve in which a endothermic broad peak was observed at 297.3°C, and it may be due to elimination of  $\text{CO}_2$  and  $\text{CH}_3\text{COOCH}_2$  groups from the xanthan gum chain. A char yield of about 25% occurred at 900°C (Fig. 7).

#### Xanthan gum-g-2-acrylamido-2-methyl-1-propane sulfonic acid

From Figure 8, it was observed that the graft copolymer starts to degrade at about 150.0°C. However, 4.15% weight loss was observed at 100°C, which might be due to loss of absorbed water. Thermogravimetric analysis curve (TGA) showed multistep degradation process, i.e., degradation completed in five steps. Therefore, five  $T_{\text{max}}$  values are obtained. The polymer decomposition temperature (PDT) was found to be 225°C, which is lower than that of

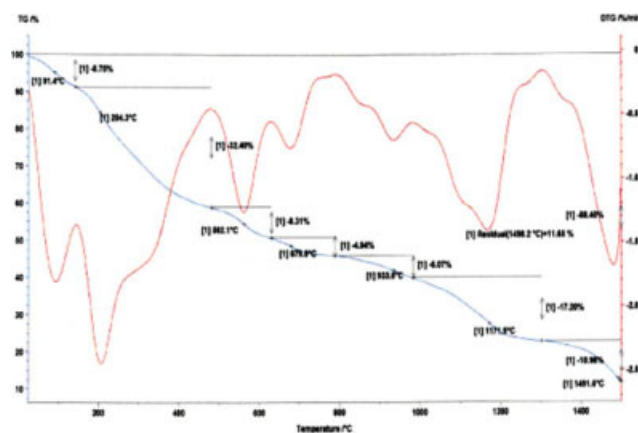
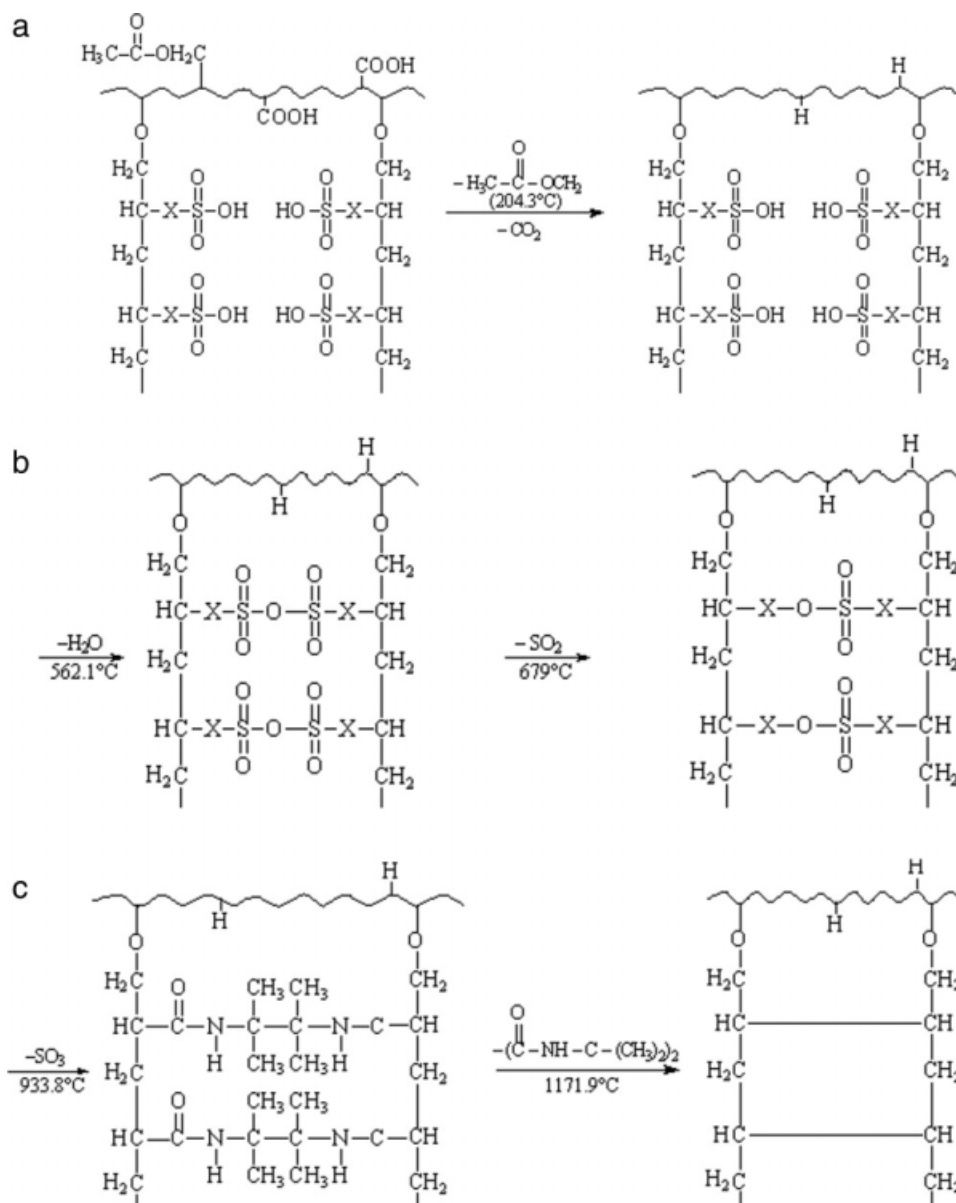


Figure 8 Thermogravimetric analysis curve of xanthan gum-g-AMPS. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



Scheme 2 Thermodegradative pathway of graft copolymer.

xanthan gum, and it might be due to the elimination of groups from graft copolymer. The degradation in the first step was almost the same as in the parent polymer, and first  $T_{max}$  occurred at  $204.3^\circ C$ ; second, third, fourth, and fifth occurred due to the elimination of  $H_2O$ ,  $SO_2$ ,  $SO_3$ , and  $((O=CH-NH-CH-(CH_3)_2)_2$  at  $562.0$ ,  $679.0$ ,  $933.8$ , and  $1171.9^\circ C$ , respectively, from pendent poly(AMPS) chain and is represented in Scheme 2.

About 70% of xanthan gum was lost at  $1175^\circ C$ ; hence, final decomposition temperature (FDT) of graft copolymer was higher than that of xanthan gum, i.e., at  $1205^\circ C$ . The integral procedural decomposition temperature (IPDT) and char yield were  $322.4^\circ C$  and

20% at  $1443.7^\circ C$ . Thus, the high value of FDT, IPDT, and char yield confirmed that the xanthan gum-g-AMPS is thermally more stable than xanthan gum.

## CONCLUSION

- Xanthan gum grafted with AMPS was synthesized by employing efficient redox system, i.e.,  $BrO_3^-$  / ascorbic acid.
- The percent-grafting ratio increases continuously on increasing the time and temperature, and it was observed that the conversion decreases continuously on increasing the monomer concentration.



- The spectroscopic data confirm that the grafting of AMPS occurred at the hydroxyl group of xanthan gum.
- The thermal analysis data show that the grafted xanthan gum is more thermally stable than the ungrafted xanthan gum, considering the value of IPDT, FDT, and char yield.
- The synthesized graft copolymers absorbed a good amount of water.
- Grafted samples showed better metal ion absorption in comparison to ungrafted gum. Therefore, synthesized graft copolymer can be used as absorbent for metal ion sorption and has applicability to the method of separation of various metals for analytical and technological purposes such as the treatment of waste water, ground water, and sea water.

## References

1. Daskalakis, S. A. *Handbook of Pharmaceutical Excipients*, 3rd ed.; American Pharmaceutical Association: Washington, DC, 2000.
2. Talukdar, M. M.; Plaizier-Vercammen, J. *Drug Dev Ind Pharm* 1993, 19, 1037.
3. Kang, K. S.; Pettitt, D. In *Industrial Gums: Polysaccharides and Their Derivatives*, 3rd ed.; Whistler, R. L., BeMiller, J. N. Eds.; Academic Press, 1993; p 341.
4. Goda, S. *Jpn. Kokai Tokkyo Koho JP 169, 624* (2003).
5. Sakai, T.; Kojima, M.; Uzuhashi, Y. *Jpn. Kokai Tokkyo Koho JP 192, 703* (2003).
6. Uesugi, M.; Shizu, K. *Jpn. Kokai Tokkyo Koho JP, CI A2321/16* (2003).
7. Hongjie, C.; Gary, T. M.; Richardson, P. H. *FR. Demande Fr, U.S. Appl 198, 469*, (2003); p 43.
8. Burdick, C. L.; Podlas, T. J. *U.S. Pat.* (2003); p 6.
9. El-Gazayerly, O. N. *Drug Dev Ind Pharm* 2003, 29, 241.
10. Murat, O. M.; Okay, O. *Eur Polym J* 2003, 39, 877.
11. Delongehemp, D. M.; Hommond, P. T. *Chem Mater* 2003, 15, 1165.
12. Zhang, L. M.; Chen, D. Q. *Macromol Mater Eng* 2003, 288, 252.
13. Kulick, W. M.; Nottlemann, H.; Aggour, Y. A.; Elsabee, M. Z. *Polym Mater Sci Eng* 1989, 61, 393.
14. Srivastava, A.; Banerjee, J.; Srivastava, A.; Behari, K. *Des Monom Polym* 2005, 8, 335.
15. Fanta, G. F. In *Block and Graft Copolymerization*; Ceresa, R. J., Ed.; Wiley Inter Sciences: New York, 1973; p 1.
16. Xiaoyan, Y.; Jing, S.; Ningxiang, S. *J Appl Polym Sci* 1998, 69, 1917.
17. Mohanty, E.; Singh, B. C. *J Appl Polym Sci* 1998, 69, 2569.
18. Nayak, P. L.; Lenka, S.; Pati, N. C. *Angew Makromol Chem* 1980, 85, 29.
19. Rastogi, S. C.; Agrawal, S. K. In *A Text Book on Advanced Inorganic Analysis (Qualitative and Quantitative)*, 9th ed.; Pragati Prakashan: India, 1993; p 256.
20. Hakon, N. *Acta Chem Scand* 1983, 9, 442.
21. El-Rehim Abd, H. A.; El-Sayed, A. H.; Ali, A. M. *J Appl Polym Sci* 2000, 6, 1.
22. Basset, J.; Denny, R. C.; Jeffery, G. H.; Mendham, J. *Vogel's Textbook of Quantitative Inorganic Analysis*, 4th ed.; William Clowes & Sons Limited: Becaes and London, 1978; p 324.
23. Rivas, B. L.; Maturana, H. A.; Molina, M. J.; Gomez-Anton, M. R.; Pierola, I. F. *J Appl Polym Sci* 1998, 67, 1109.