

Synthesis and Study of Metal Ion Sorption Capacity of Xanthan Gum-g-2-Acrylamido-2-Methyl-1-Propane Sulphonic Acid

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ABSTRACT: In this study, xanthan gum-g-2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) was synthesized by free radical polymerization using bromate/thiourea redox pair in inert atmosphere. Various studies have been conducted to observe the effect of reactants on grafting parameters by varying the reactant concentration and to understand the physical-chemical properties. Grafting ratio, add on, and conversion showed a decrease on increasing the concentration of xanthan gum. The grafting parameters increased on increasing the concentration of AMPS from 3×10^{-2} to 6×10^{-2} mol dm⁻³, BrO₃ from 2×10^{-3} to 8×10^{-3} mol dm⁻³, and thiourea from 1×10^{-3} to 2.8×10^{-3} mol dm⁻³, respec-

tively. Optimum temperature and time for grafting of AMPS on xanthan gum were found to be 35°C and 120 min. Water swelling capacity, swelling ratio, metal ion uptake, and metal retention capacity were also studied, and it was found that grafted polymer shows better enhancement in these properties than substrate. Graft copolymer was characterized by FTIR and thermal analysis. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 470–478, 2007

Key words: xanthan gum; graft copolymer; thermal analysis; bromate/thiourea redox pair; 2-acrylamido-2-methyl-1-propane sulfonic acid; metal ion uptake

INTRODUCTION

In the present scenario, the work on natural polymers is the most fascinating and hence more advanced studies on their properties and biomedical applicability are in progress, and for this purpose polysaccharides and proteins have been extensively investigated.^{1,2} One of them is xanthan gum, which is an extracellular heteropolysaccharide of xanthomonas campestris. Its structure consists of a β-(1 to >4)-linked D-glucopyranosyl backbone chain. Its relatively high viscosity permits its economical use. It can be used in food and pharmaceutical industry because of properties like thickening, emulsion stabilization, water binding, suspending, and acid compatibilities.³ It is widely used in enhanced oil recovery,⁴ drug delivery system for poor water-soluble drugs,⁵ and good stabilizer in eye make up.⁶ Beside these uses it has a drawback: it is susceptible to microbial attack, which limits its uses. Modification of xanthan gum by graft copolymerization technique allows one to chemically change the polysaccharide chain by introducing polymer chain that configures different structural characteristics to the initial material. Several monomers like acrylamide, acrylic acid,⁷ etc, have been

grafted on xanthan gum to make use of its properties in many areas.

Polymer derived from 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) was found to be highly useful. Its high swelling capacity was used in making ionic hydro gel,^{8,9} and it is also used in synthesis of offset ink¹⁰ as well as in cosmetics, etc. In the light of fascinating applications of xanthan gum and its derivatives, an attempt has been made to graft hitherto unreported AMPS onto xanthan gum. The effect of redox components, hydrogen ion, xanthan gum, and AMPS, along with time and temperature on the grafting parameters, has been studied. Properties like metal ion uptake and swelling behavior were also studied. The synthesized graft copolymer is characterized by FTIR spectroscopy and thermogravimetric analysis.

EXPERIMENTAL

Materials

Xanthan gum (Sigma), AMPS (Aldrich Chemical, St. Louis, MO), thiourea (Merck, Mumbai, India), and bromate (Sigma) were used without any further purification. Sulfuric acid (Merck) was used for maintaining hydrogen ion concentration. All the solutions were prepared in triple distilled water.

Procedure for graft copolymerization

For each experiment, xanthan gum solution was prepared by addition of weighed amount of xanthan

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gum into reactor containing triple distilled water. The calculated amount of thiourea, AMPS, and sulfuric acid solution was added to the reactor at constant temperature, and a slow stream of oxygen-free nitrogen was passed. After 30 min, a known amount of deoxygenated potassium bromate solution was added to initiate the reaction, and reaction was carried out under inert atmosphere. After desired time period the reaction was stopped by letting air into the reactor, and the graft copolymer was precipitated by pouring the reaction mixture into the water methanol mixture. The precipitate was separated, dried, and weighed. Separate experiment was performed for homopolymerization, and it was found that by employing this redox pair no homopolymer was formed.

RESULTS AND DISCUSSION

The graft copolymers were characterized according to the definition by Fanta.¹¹

$$\text{Grafting ratio}(\%G) = \frac{\text{Grafted Polymer}}{\text{Weight of Substrate}} \times 100$$

$$\text{Add on}(\%A) = \frac{\text{Synthetic Polymer}}{\text{Graft copolymer}} \times 100$$

$$\text{Conversion}(\%C) = \frac{\text{Polymer formed}}{\text{Monomer charged}} \times 100$$

The effect of concentration of xanthan gum, AMPS, thiourea, bromate, along with the time and temperature on grafting parameters, was studied. Besides, the swelling ratio percentage of swelling and metal retention capacity of graft copolymer for different toxic metals were also studied by using the following definition.^{12,13}

Percent Swelling

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

Swelling Ratio

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

Percent uptake

$$= \frac{\text{Amount of metal ion in the polymer}}{\text{Amount of metal ion in feed}} \times 100$$

Partition coefficient

$$= \frac{\text{Amount of metal ion in the polymer}}{\text{Amount of metal ion left in the solution}} \times \frac{\text{Volume of solution (ml)}}{\text{Weight of dry polymer (gm)}}$$

Retention capacity

$$= \frac{\text{Amount of metal ion in the polymer (meq.)}}{\text{Weight of dry polymer (gm)}}$$

Effect of bromate concentration

The bromate–thiourea system is a novel initiator for the aqueous polymerization of vinyl monomers. It was tested that neither potassium bromate nor thiourea when used alone initiates polymerization. On the other hand, thiourea coupled with bromate ion can initiate vinyl polymerization. So, the effect of bromate ion concentration on grafting reaction was studied, and the result is summarized in Table I. It was observed that grafting ratio, conversion, and add on increases on increasing the bromate ion concentration from 2.0×10^{-3} to 8×10^{-3} mol dm⁻³, but beyond this concentration range grafting parameters decrease. The enhancement of grafting parameter within the cited range of bromate ion concentration is due to the progressive reduction of bromate, with thiourea producing bromite ion and isothiocarbamide free radical that attack on the xanthan gum molecules and create more free radicals site onto which monomer addition takes place. The grafting ratio, conversion, and add on decreases on increasing the bromate ion concentration because of one of following reason:

1. At higher bromate ion concentration, it might react with the gum macroradical or with the growing radical, thus inhibiting the extent of grafting.
2. Oxidation of the active groups on the backbone takes place, thereby preventing the formation of free radicals.
3. Inhibition due to the liberation of appreciable amount of oxygen takes place, which acts as a scavenger.

Effect of thiourea concentration

Increment in the concentration of thiourea from 1.0×10^{-3} to 2.8×10^{-3} mol dm⁻³ show the increment in

TABLE I
Effect of Bromate (BrO₃⁻) Ion Concentration

[BrO ₃ ⁻] × 10 ³ mol dm ⁻³	%G	%A	%C
2.0	104.0	50.98	10.00
4.0	120.0	54.54	11.53
5.0	140.0	58.33	13.46
8.0	196.0	66.21	18.84
10	120.0	54.54	11.53

[Thiourea] = 2.8×10^{-3} mol dm⁻³, [AMPS] = 5.0×10^{-3} mol dm⁻³, [XOH] = 1.0 g dm⁻³, [H⁺] = 5.0×10^{-3} mol dm⁻³, time = 120 min, temp. = 35°C.

TABLE II
Effect of Thiourea Concentration

[Thiourea] $\times 10^3$ mol dm ⁻³	%G	%A	%C
1.0	106.0	51.63	10.26
2.0	136.5	57.71	13.12
2.8	140.0	58.33	13.46
4.0	124.0	55.35	11.92
5.0	102	50.49	9.80

[BrO₃⁻] = 5.0 $\times 10^{-3}$ mol dm⁻³, [AMPS] = 5.0 $\times 10^{-2}$ mol dm⁻³, [H⁺] = 5.0 $\times 10^{-3}$ mol dm⁻³, [XOH] = 1.0 g dm⁻³, time = 120 min, temp. = 35°C.

grafting parameters, but beyond the 2.8 $\times 10^{-3}$ mol dm⁻³ the grafting ratio, add on, and conversion were decreased. The increment in grafting parameters within cited range of thiourea concentration is due to the production of more primary free radicals that are produced from the reaction of protended species of thiourea with bromate ion, and on higher concentration grafting parameters show decrease, which might be due to the premature termination of growing grafted chain (Table II).

Effect of AMPS concentration

The result of AMPS variation is presented in Figure 1. It was clear from Figure 1 that grafting ratio and add on increase on increasing the concentration of AMPS up to 6 $\times 10^{-2}$ mol dm⁻³, and thereafter the values of these grafting parameters decrease. This behavior could be explained by the fact that the increase of AMPS concentration leads to accumulation of monomer molecules that are in close proximity to the polymer backbone molecules, which at immediate vicinity of reaction sites become acceptors of xanthan gum macroradicals, resulting in chain initiation, and thereafter themselves become free radical donor to neigh-

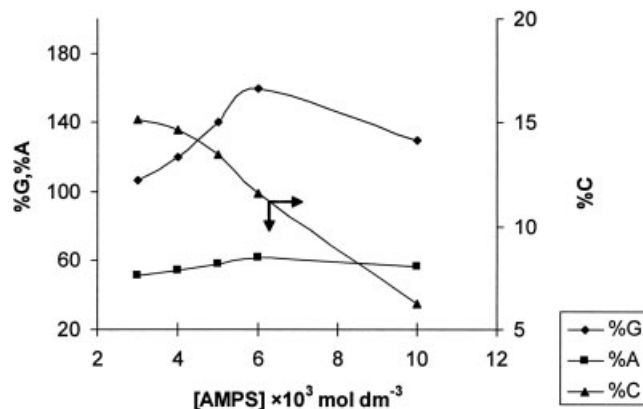


Figure 1 Effect of AMPS. [XOH] = 1 g dm⁻³, [thiourea] = 2.8 $\times 10^{-3}$ mol dm⁻³, [BrO₃⁻] = 5 $\times 10^{-3}$ mol dm⁻³, [H⁺] = 5 $\times 10^{-3}$ mol dm⁻³, temp. = 35°C, time = 120 min.

TABLE III
Effect of Xanthan Gum (XOH) Concentration

[XOH] g dm ⁻³	%G	%A	%C
0.6	273	73.19	15.75
0.8	200	66.66	15.38
1.0	140	58.33	13.46
1.4	102	50.35	13.65
1.8	90	47.37	15.57

[BrO₃⁻] = 5.0 $\times 10^{-3}$ mol dm⁻³, [AMPS] = 5.0 $\times 10^{-2}$ mol dm⁻³, [Thiourea] = 2.8 $\times 10^{-3}$ mol dm⁻³, [H⁺] = 5.0 $\times 10^{-3}$ mol dm⁻³, time = 120 min, temp. = 35°C.

boring molecules, causing the lowering of termination. The decrease in grafting ratio and add on could be interpreted in terms of increase in viscosity of the medium.

Effect of xanthan gum concentration

The effect of xanthan gum concentration on grafting parameters was studied by varying the concentration of xanthan gum from 0.6 to 1.8 g dm⁻³ (Table III). Grafting ratio and add on decrease with the increase in concentration of xanthan gum. This may be due to the increase in viscosity, which may restrict the accessibility of monomer to the growing polymeric chain at the active sites, leading to the decrease in grafting ratio.

Effect of sulfuric acid concentration

The results obtained because of the variation of hydrogen ion concentration on grafting parameters are summarized in Figure 2. From Figure 2 it is clear that grafting ratio add on and conversion increase upto 12 $\times 10^{-3}$ mol dm⁻³, which can be explained by increasing [H⁺] ion. The formation of thiourea proto-

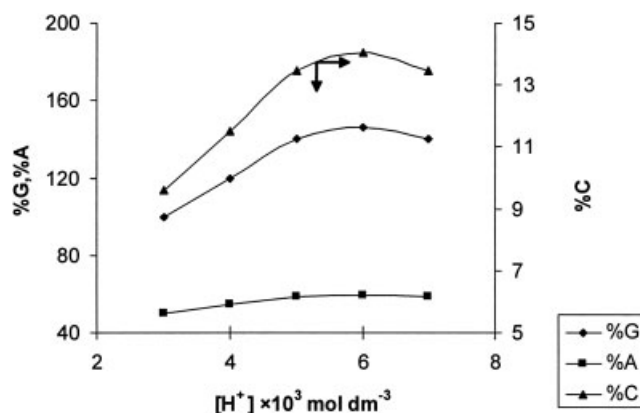
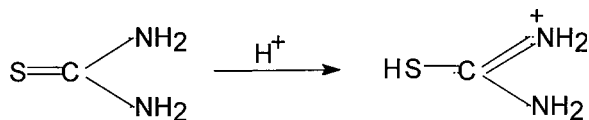
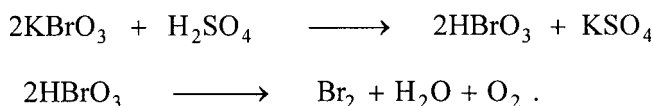


Figure 2 Effect of [H⁺]. [XOH] = 1 g dm⁻³, [thiourea] = 2.8 $\times 10^{-3}$ mol dm⁻³, [BrO₃⁻] = 5 $\times 10^{-3}$ mol dm⁻³, [AMPS] = 5 $\times 10^{-3}$ mol dm⁻³, temp. = 35°C, time = 120 min.

nated species also increases, which react with bromate ion and give rise to primary free radicals; these primary free radicals react with xanthan gum and give rise to more active sites.



But on further increasing the $[\text{H}^+]$ ion, i.e., beyond $12 \times 10^{-3} \text{ mol dm}^{-3}$, the grafting, ratio, add on, and conversion was found to decrease, which might be due to the fact that excess hydrogen ion react with bromate ion to form HBrO_3 . This species is further decomposed to give oxygen, which acts as scavenger, and grafting parameters show decreasing trend



Effect of time period

The effect of time duration of grafting reaction was studied by varying time period from 60 to 180 min (Fig. 3). Grafting parameters increase with increasing the time period from 60 to 150 min, but beyond this time period grafting ratio, efficiency, and add on decrease. On increasing the time period, propagation of grafted chain takes place because of the availability of more active species, which results in the increase of grafting parameters. But on further increase in time period, these parameters decrease; this may be due to the termination of growing grafted chain with increase in time period.

Effect of temperature

The effect of temperature on grafting parameters was studied by varying the temperature from 25 to 45°C, and results are summarized in Figure 4. Grafting ratio, add on, and conversion show increase on increas-

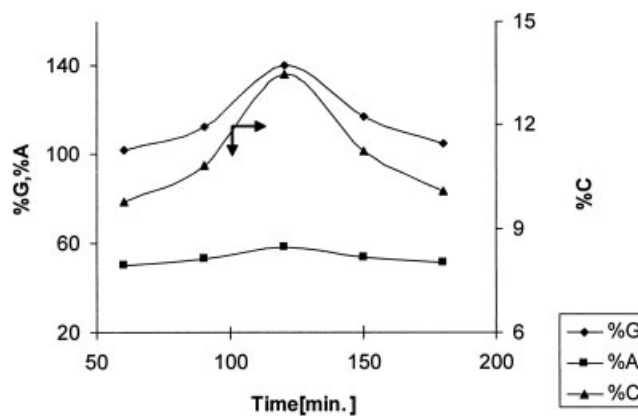
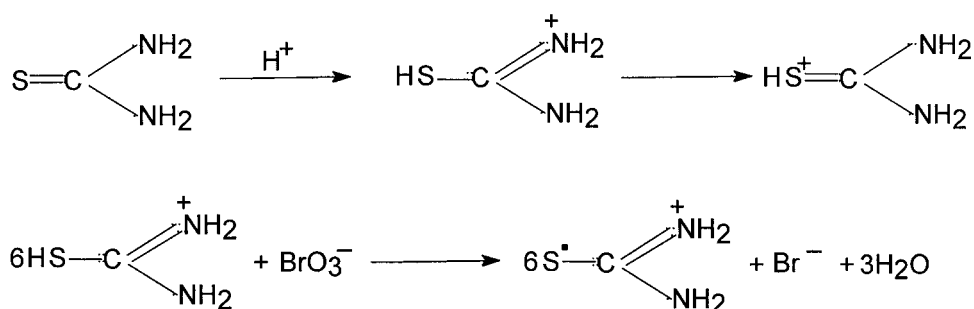


Figure 3 Effect of time (min). $[\text{XOH}] = 1 \text{ g dm}^{-3}$, $[\text{thiourea}] = 2.8 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{BrO}_3^-] = 5 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 5 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{AMPS}] = 5 \times 10^{-3} \text{ mol dm}^{-3}$, $\text{temp} = 35^\circ\text{C}$.

ing the temperature upto 40°C, but on further increasing the temperature these parameters showed a decreasing trend. The increase in the grafting ratio, add on, and conversion up to cited range may be attributed to the fact that with increase in temperature, rate of production of primary free radicals increases, causing an increase in these parameters and also diffusion of AMPS molecules into the domain of xanthan gum free radicals. However, further increase in temperature could result in the decreasing of grafting parameter. This is due to the destruction of the primary free radicals because of higher temperature.

Mechanism

It is assumed that in presence of hydrogen ion, thiourea is present as protonated species, which reacts with bromate ion to give isothiocarbamido radicals. These radicals extract hydrogen atom from the xanthan gum molecule producing xanthan gum free radicals. The monomer molecules that are in near vicinity of the reaction sites become acceptor of xanthan gum radicals, resulting in chain initiation, and thereafter themselves become free radicals donors to neighboring molecules; thus, grafted chains grow. Termination of chain by coupling yields graft copolymer.



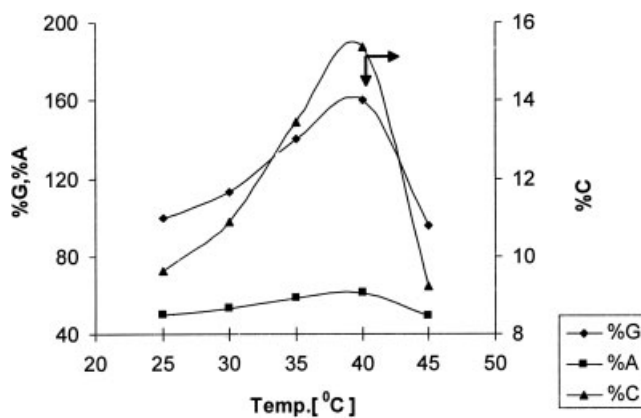
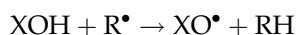
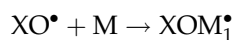


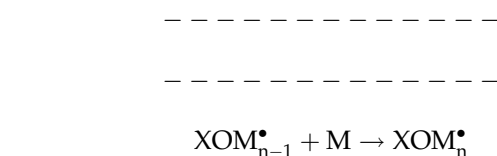
Figure 4 Effect of temp (°C). [XOH] = 1 g dm⁻³, [thiourea] = 2.8 × 10⁻³ mol dm⁻³, [BrO₃⁻] = 5 × 10⁻³ mol dm⁻³, [H]⁺ = 5 × 10⁻³ mol dm⁻³, [AMPS] = 5 × 10⁻³ mol dm⁻³, time = 120 min.

Initiation

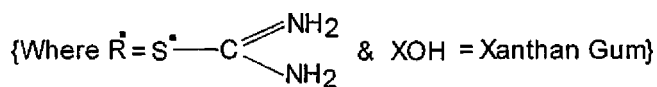
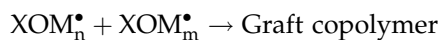
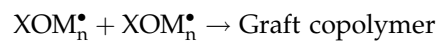


Propagation





Termination



{M = Monomer}

Evidence of grafting

FTIR spectra

FTIR spectra of pure and grafted xanthan gum (%G = 140) has been recorded on PERKIN ELMER FTIR. On comparing the FTIR of pure xanthan gum and xanthan gum-g-AMPS, following additional band appeared in the spectra of xanthan gum-g-AMPS: C=O stretching of amide at 1630 cm⁻²; the band at 617 cm⁻¹ is due to C-S stretching vibration; the sharpness of O-H stretching vibration might be due

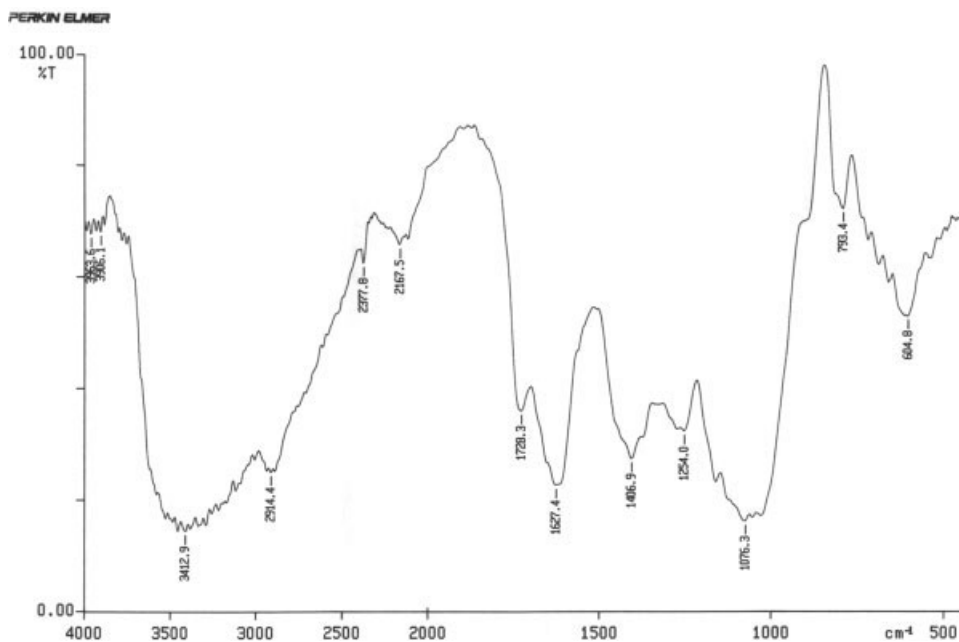


Figure 5 IR spectra of xanthan gum.

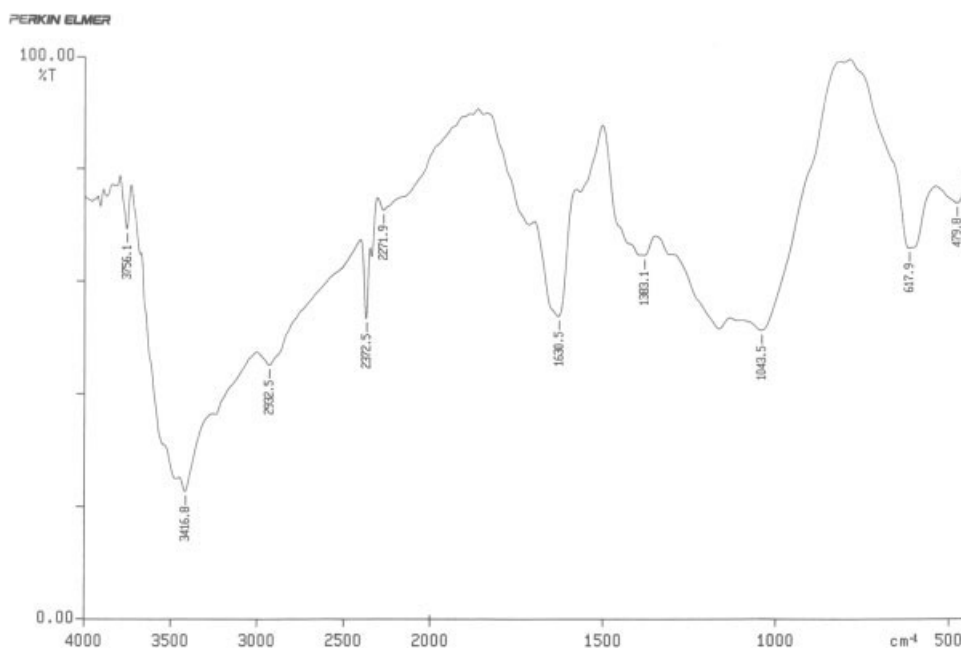


Figure 6 IR spectra of xanthan gum-g-2-acrylamido-2-methyl-1-propane sulfonic acid.

reduction of number of OH stretching vibration, which indicates the grafting might have taken place at O—H site. (Figs. 5 and 6).

Thermogravimetric analysis

Thermal analysis of xanthan gum and xanthan gum-g-AMPS (%G = 140) was carried out in inert atmosphere at heating rate of 15°C/min.

Xanthan gum

The degradation of xanthan gum (XOH) started at about 200°C and occurred in single step. The weight loss about 10% at 100°C was due to the loss of absorbed water. Almost 50% weight loss was found at 300°C. The rate of weight loss increases initially with temperature and reached a maximum value at 700°C. Polymer decomposition temperature (PDT), temperature at which maximum degradation occurred (T_{max}),

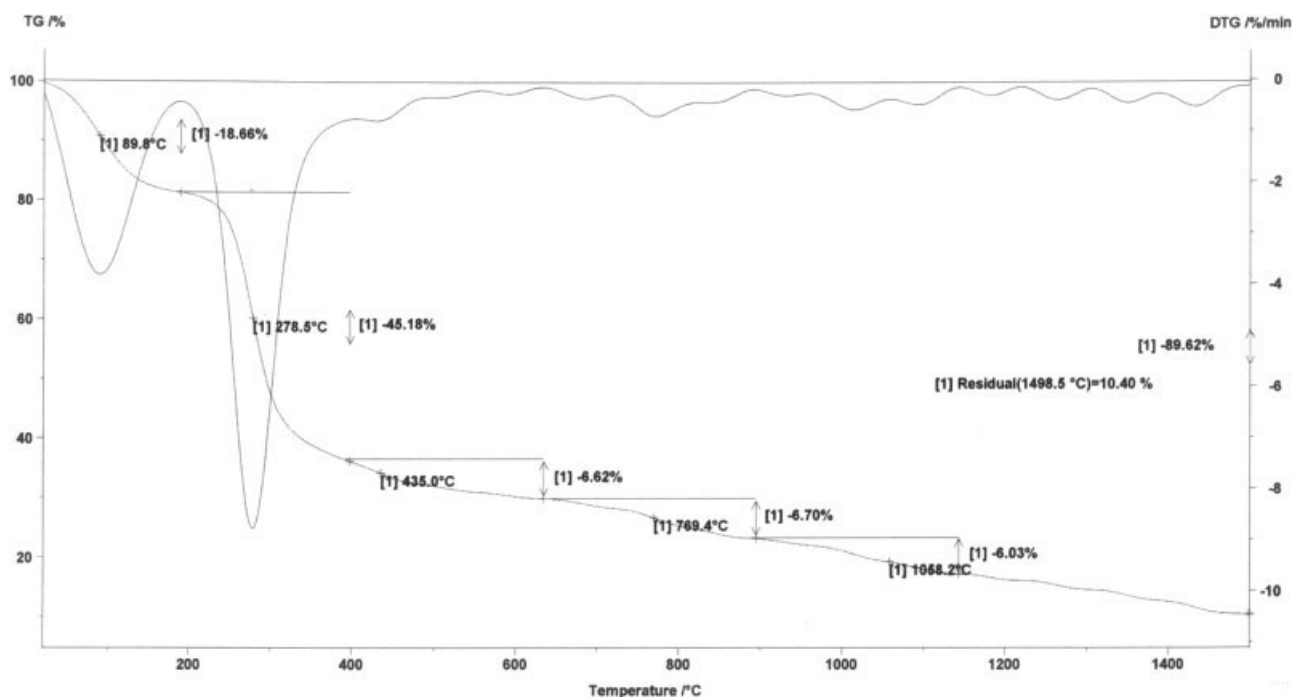


Figure 7 Thermogravimetric trace of xanthan gum.

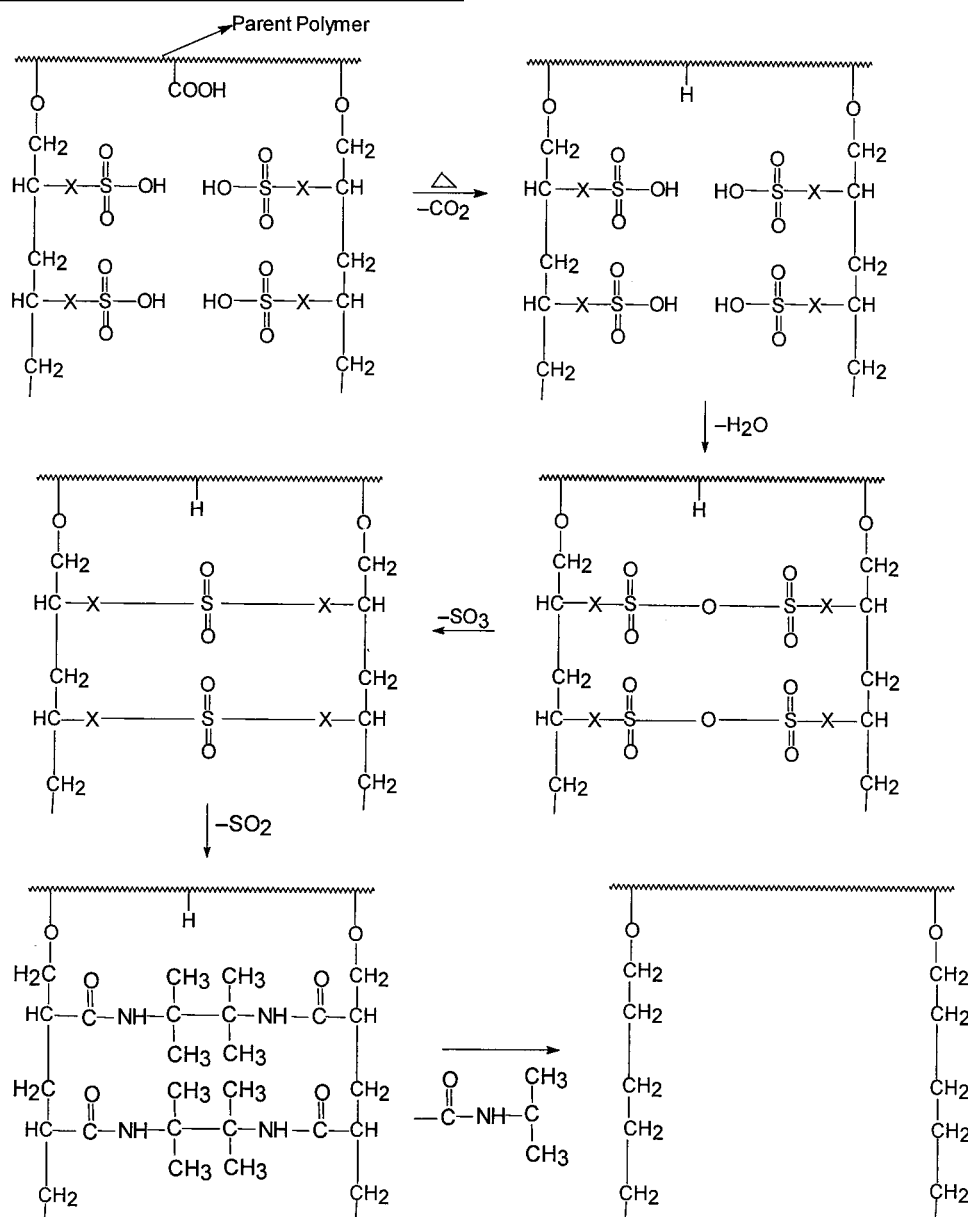
TABLE IV
Thermo Gravimetric Analysis

Sample	PDT(°C)	FDT(°C)	T_{max} (°C)	IPDT
Xanthan gum	250.00	825.00		
Xanthan gum-g-AMPS	218.75	1104	216 566 661 810 1101	366.18

and integral procedural decomposition temperature (IPDT) were obtained at 250°C, 278.5°C, and 274.68°C, respectively. The final decomposition temperature (FDT) was found at 825°C and char yield of 25% was obtained at 900°C. (Fig. 7, Table IV).

Xanthan gum-g-AMPS

The graft copolymer began to degrade at about 150°C and degradation occurred in five steps. Weight loss of 6.36% due to desorption of water occurred at 100°C. PDT was found at 218.75°C. The temperature at which T_{max} appeared at 216°C, 566°C, 661°C, 810°C, and 1101°C might be due to elimination of CO₂, H₂O, SO₃, and SO₂ group and structure breaking from the grafted molecules. There is 50% weight loss at 661°C. The FDT and IPDT have been found at 1087°C and 360.18°C, respectively. A char yield of about 30% was obtained at 1105°C. The high value of T_{max} , FDT, IPDT, and char yield indicated that grafted polymer is thermally more stable than parent polymer. (Fig. 8, Table IV).



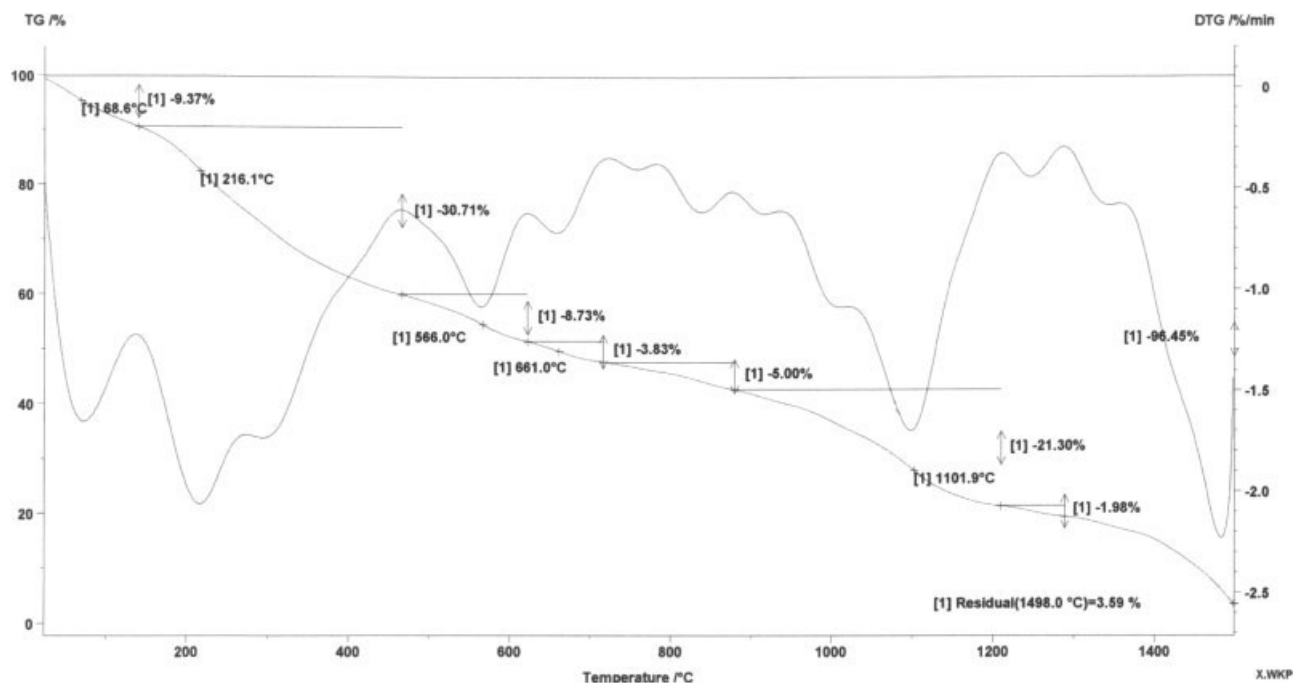


Figure 8 Thermogravimetric trace of xanthan gum-g-2-acrylamido-2-methyl-1-propane sulfonic acid.

Swelling studies

Swelling studies were carried out on graft copolymer and samples were prepared by varying the monomer concentration. For the swelling studies we took 0.020 g of graft copolymer and this was kept undisturbed for 24 h in triple distilled water. After this time period the graft copolymer was taken out, and surface water on the swollen graft copolymer was removed by softly pressing the graft copolymer in between the folds of filter paper. After this, an increase in weight was recorded. Percent swelling and swelling ratio were calculated.

The results of swelling studies are summarized in Table V, and from the data it reveals that with the increase in percent grafting the percent swelling and swelling ratio increase up to a certain limits. This character might be certified by the fact that AMPS is hydrophilic in nature and with the increase in percent grafting the percent of AMPS character is also increased.

TABLE V
Swelling Behavior

Sample	[AMPS] $\times 10^{-3}$ mol dm ⁻³	%G	Percent swelling	Swelling ratio
A	3	106	455	4.5
B	4	120	605	6.05
C	5	140	680	6.8
D	6	160	690	6.9
E	10	130	470	4.7

Metal ion sorption studies

Structural aspects of polymers and sorption behavior of metal ions. Hydrophilic–hydrophobic balance, nature of monomer, and extent of crosslinking of macromolecular supports are major factors that affect metal ion uptake.¹⁴ Further, ligand function dictates reactivity, complexion ability, and efficiency of polymer-supported ligands.¹⁵ This functionality can be tailored and incorporated by grafting to retain ions by polymer analogous reaction or by simple chelation or absorption due to opening of polymer matrix or pores created by crosslinking. Out of these possibilities, all may contribute in metal ion sorption though extent of contribution of any factor may be different. However, functional group incorporated by grafting is its ability to interact with metal ion may play more important role in determination of selectivity and quantum of metal ion uptake.

Sorption behavior of xanthan gum and its graft copolymer. The metal ion sorption studies have been carried out on graft copolymer of different compositions (which has been synthesized by varying the concentration of monomer) by taking its 0.020 g in 10 mL of metal ion solution of known concentration and kept undisturbed for 24 h. For the metal ion sorption studies five metals have been chosen (Cu, Zn, Ni, Pb, and Hg) and the amount of metal ion uptake is calculated by titrating the unabsorbed metal ion. The results are summarized in Table IV. From data it is clear that graft copolymer show better metal ion uptake behavior than substrate (xanthan gum).

TABLE VI
Absorption of Metal Ion on Xanthan Gum and its Graft Copolymer

Sample	[AMPS] × 10 ⁻³ mol dm ⁻³	%G	Percent uptake				Partition coefficient				Retention capacity						
			Cu ²⁺	Pb ²⁺	Ni ²⁺	Zn ²⁺	Hg ²⁺	Cu ²⁺	Pb ²⁺	Ni ²⁺	Zn ²⁺	Hg ²⁺	Cu ²⁺	Pb ²⁺	Ni ²⁺	Zn ²⁺	Hg ²⁺
XOH	-	-	4.5	1.3	3.7	2.5	0.69	39.1	6.9	19.3	13	3.5	2.2	0.6	1.8	1.4	0.3
A	3	106	18.3	5.1	14.2	8.6	1.69	112.2	27.1	83.0	43.3	8.6	8.9	2.3	7.1	4.9	0.8
B	4	120	19.7	5.5	15.0	9.2	1.84	122.7	29.6	88.8	46	9.4	9.6	2.5	7.5	5.2	0.9
C	5	140	19.7	5.6	15.9	9.6	2.4	123.3	29.9	94.7	48	12.5	9.6	2.5	8.0	5.5	1.2
D	6	160	21.7	5.9	16.9	9.8	2.5	138.9	31.7	102.2	49.3	13.3	10.6	2.7	8.5	5.6	1.2
E	10	130	19.7	5.6	15.6	9.3	2.04	123.1	29.7	92.4	46.8	10.4	9.6	2.5	7.8	5.3	1.0

XOH, xanthan gum and A, B, C, D are graft copolymer.

The effect of percent grafting on sorption behavior of graft copolymer was studied in terms of percent ion uptake, partition coefficient, and retention capacity. From Table VI, it is observed that these parameters have directly proportional relationship with percent grafting. It might be due to the fact that with the increase in percent grafting the percent of AMPS concentration was also increased and the AMPS have the pendent groups that can hold the metal ions.

References

- Jeong, B.; Bae, Y. H.; Lee, D. S.; Kim, S. W. *Nature* 1997, 388, 860.
- Younes, H.; Cohn, D. *J Biomed Mater Res* 1987, 213, 1301.
- Kang, K. S.; Cottrell, I. In *Microbial Technology*, 2nd ed.; Pessler, H. J.; Perlman, D., Eds.; Academic press: New York, 1979; Vol. 1, p 417.
- Sandvick, E. I.; Merker, J. M. In *Extra cellular Microbial Polysaccharides*; Sandford, P.; Laskin, A., Eds.; American Chemical Society: Washington, DC, 1977; ACS Symposium series No. 45, p 242.
- Charnet, E.; Ishizawa, C.; Dumitriu, S. *PCT Int Appl WO* 0203, 962(CI A61K9/20), 2003.
- Collin, N.; Bichon, Y.; Pays, K. *Fr. Demands FR* 2,834,457 (Cl. A61K7/032), 2003.
- Pandey, P. K.; Behari, K. *Carbohydr Polym* 2001, 42, 185.
- Mc Cormic, C. L.; Chen, G. S. *J Polym Sci Polym Chem* 1982, 20, 817.
- Mehmet, M. O.; Okay, O. *Eur Polym Mater* 2003, 39, 877.
- Sawamura, K.; Chosupake, H.; Urapi, H.; Nagawe, T. *Jpn Pat* 2002, 201, 377.
- Fanta, G. F. In *Block and Graft Copolymerization*; Ceresa, R. J., Ed.; Wiley Interscience: New York, 1973; p 1.
- El-Rahim Abd, H. A.; Hegazy El-sayeed, A.; Ali, A. M. *J Appl Polym Sci* 2000, 76, 125.
- Rivas, B. L.; Maturana, H. A.; Molina, M. J.; Gomez-Anton, M. R.; Pierola, I. F. *J Appl Polym Sci* 1998, 67, 1109.
- Lehto, J.; Vaaramaa, K.; Vesterinen, E.; Tenhu, H. *J Appl Polym Sci* 1988, 68, 355.
- Jose Pillai, V. N. R. *J Appl Polym Sci* 1996, 60, 1855.