

Graft Copolymerization of Acrylic Acid onto Xanthum Gum Using a Potassium Monopersulfate/Fe²⁺ Redox Pair

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ABSTRACT: A previously unreported graft copolymer of xanthan gum (XOH) with acrylic acid was synthesized and the reaction conditions were optimized using a potassium monopersulfate (PMS)/Fe²⁺ redox pair. Grafting ratio, add on, and conversion increase with an increase in the ferrous ion concentration (2.0×10^{-3} to 5.0×10^{-3} mol dm⁻³) and PMS concentration (1.0×10^{-3} to 4.0×10^{-3} mol dm⁻³). It was observed that grafting takes place efficiently when the acrylic acid concentration and temperature were 5.0×10^{-2} mol dm⁻³ and 35°C, respectively. Samples of xanthan gum

and xanthan gum-g-acrylic acid were subjected to thermogravimetric analysis with the objective of studying the effect of grafting of acrylic acid on the thermal stability of xanthan gum. The graft copolymer was found to be more thermally stable than xanthan gum. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1341–1346, 2003

Key words: graft copolymers; synthesis; thermogravimetric analysis (TGA); thermal properties; xanthan gum

INTRODUCTION

Xanthan gum is an anionic heteropolysaccharide, which is a fermentation product of corn sugar.^{1,2} It enjoys a wide range of usage in industrial applications such as paper, mining, the textile industry, oil wells, and so forth. Similarly, acrylic acid also possesses some unique characteristics and reactivities and the polymers derived from it find many commercial applications, for example, as a thickener, ion-exchange resin, a suspending agent, and dispersants.^{6–10} Therefore, we investigated grafting acrylic acid onto xanthan gum using a potassium monopersulfate (PMS)/Fe²⁺ redox pair. The appeal of this redox pair is that no homopolymer is formed.

EXPERIMENTAL

Materials

Acrylic acid (Merck, Darmstadt, Germany) was distilled under reduced pressure in an inert atmosphere. Ferrous sulfate (AR; BDH, Toronto, Canada), potassium monopersulfate (Aldrich Chemical, Milwaukee, WI), and xanthan gum (Sigma, St. Louis, MO) were used as supplied.

Graft copolymerization

For each experiment, xanthan gum solution was prepared by adding a calculated amount of gum in triple-distilled water. The reaction was carried out under nitrogen atmosphere at constant temperature. A calculated amount of acrylic acid, sulfuric acid, and ferrous sulfate solutions were added to the known amount of gum solution in the reactor. To initiate the reaction, a known amount of potassium monopersulfate solution was added. 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 a methanol/water mixture and kept overnight. The precipitate was filtered, dried, and weighted.

Grafting parameters were calculated according to Fanta's definition¹¹:

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

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

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

RESULTS AND DISCUSSION

Effect of PMS concentration

The effect of PMS was studied by varying the concentration of PMS from 1.0×10^{-3} to 7.0×10^{-3} mol

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TABLE I
Effect of PMS Concentration^a

[PMS] ($\times 10^3$ mol dm ⁻³)	Grafting ratio (%G)	Add on (%A)	Conversion (%C)
1.0	135.9	57.6	38.8
2.5	154.0	60.6	44.0
4.0	192.3	65.8	54.9
5.5	181.4	64.5	51.8
7.0	171.5	63.2	49.0

^a Grafting parameters: $[\text{Fe}^{2+}] = 5.0 \times 10^{-3}$ mol dm⁻³, $[\text{H}^+] = 1.8 \times 10^{-3}$ mol dm⁻³; [acrylic acid] = 5.0×10^{-2} mol dm⁻³; [xanthan gum] = 1 g dm⁻³, time = 120 min; temperature = 35°C.

dm⁻³. It was observed that grafting ratio, add on, and conversion increase with increase in the concentration of PMS (1.0×10^{-3} to 4.0×10^{-3} mol dm⁻³), but decrease thereafter (Table I). The enhancement in grafting parameters may be attributed to the progressive reduction of PMS by the Fe²⁺ ion producing sulfate ion radical and hydroxyl free radical that attacks xanthan gum molecule, thus creating more free radicals sites to which monomer addition takes place. Retardation in grafting beyond 4.0×10^{-3} mol dm⁻³ concentration of PMS may be the result of (i) premature termination of growing grafted chain by the excess of sulfate ion radical and hydroxyl free radical; and (ii) production of excess Fe³⁺ ions, which become detrimental to grafting (i.e., in excess of Fe³⁺ ions causes premature termination of growing grafted chain because of its retarding effect). Fe³⁺ ions are known as the ideal retarder of radical polymerization.¹²⁻¹⁴

Effect of Fe²⁺ concentration

The effect of Fe²⁺ ion concentration is shown in Figure 1. With increasing Fe²⁺ ion concentration, the grafting ratio, add on, and conversion increase, with a maximum value of grafting (%G = 192.3) at Fe²⁺ ion concentration of 5.0×10^{-3} mol dm⁻³. Increasing the Fe²⁺

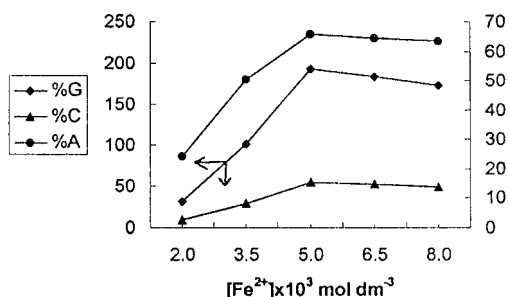


Figure 1 Effect of $[\text{Fe}^{2+}]$ on grafting parameters: $[\text{PMS}] = 4.0 \times 10^{-3}$ mol dm⁻³; $[\text{H}^+] = 1.8 \times 10^{-3}$ mol dm⁻³; [acrylic acid] = 5.0×10^{-2} mol dm⁻³; [xanthan gum] = 1.0 g dm⁻³; time = 120 min; temperature = 35°C.

TABLE II
Effect of Acrylic acid Concentration^a

[Acrylic acid] ($\times 10^2$ mol dm ⁻³)	%G	%A	%C
2.0	78.3	43.9	22.4
3.5	107.2	51.7	42.5
5.0	192.3	65.8	54.9
6.5	111.0	52.6	23.7
8.0	103.2	50.7	17.9

^a Grafting parameters: $[\text{PMS}] = 4.0 \times 10^{-3}$ mol dm⁻³, $[\text{Fe}^{2+}] = 5.0 \times 10^{-3}$ mol dm⁻³, $[\text{H}^+] = 1.8 \times 10^{-3}$ mol dm⁻³; [xanthan gum] = 1 g dm⁻³; time = 120 min; temperature = 35°C.

ion concentration results in the decrease of grafting. The increase in grafting may be attributed to the increase in the concentration of KHSO₅/Fe²⁺ transient adduct, which undergoes spontaneous decomposition at the xanthan gum surface, resulting in the generation of a number of free-radical sites at a faster rate to which monomer addition takes place. The decrease in grafting may be due to a detrimental factor arising out of excess of Fe³⁺ ions produced during the disproportionation of the KHSO₅/Fe²⁺ couple. That an excess of Fe³⁺ ions is detrimental to grafting has been reported by Rogovin and coworkers¹³ and Misra et al.¹⁴

Effect of acrylic acid concentration

The effect of monomer concentration on the grafting reaction was studied at various concentrations of acrylic acid. The grafting ratio, add on, and conversion increase with increasing acrylic acid concentration and a maximum value of grafting (%G = 192.3) is reached at an acrylic acid concentration of 5.0×10^{-2} mol dm⁻³ (Table II). A further increase in the acrylic acid concentration results in a decrease in the values of the grafting parameters. The enhancement in grafting results from the fact that acrylic acid exhibits Tromdorff's effect and, because of the gelation, the movement of growing polymeric chains is restricted, which lowers the termination.¹⁵ The retardation in grafting

TABLE III
Effect of Hydrogen Ion Concentration^a

$[\text{H}^+]$ ($\times 10^3$ mol dm ⁻³)	%G	%A	%C
0.90	230.4	69.7	65.8
1.35	212.3	67.9	60.7
1.80	192.3	65.8	54.9
2.25	145.3	59.2	41.5
2.70	113.4	53.1	32.4

^a Grafting parameters: $[\text{PMS}] = 4.0 \times 10^{-3}$ mol dm⁻³, $[\text{Fe}^{2+}] = 5.0 \times 10^{-3}$ mol dm⁻³, [acrylic acid] = 5.0×10^{-2} mol dm⁻³; [xanthan gum] = 1 gm dm⁻³; time = 120 min; temperature = 35°C.

TABLE IV
Effect of Gum Concentration^a

[Xanthan gum] (g dm ⁻³)	%G	%A	%C
0.60	129.1	56.3	22.1
0.80	139.2	58.2	31.8
1.00	192.3	65.8	54.9
1.20	152.3	60.4	52.2
1.40	135.2	57.5	54.1

^a Grafting parameters: [PMS] = 4.0×10^{-3} mol dm⁻³; [Fe²⁺] = 5.0×10^{-3} mol dm⁻³; [H⁺] = 1.8×10^{-3} mol dm⁻³; [acrylic acid] = 5.0×10^{-2} mol dm⁻³; time = 120 min; temperature = 35°C.

after the cited concentration of acrylic acid may be attributed to the decrease in the formation of new grafting sites because of inaccessibility of xanthan gum molecules to the primary free radicals arising from increased viscosity.

Effect of hydrogen ion concentration

The variation of H⁺ on the grafting parameters was studied by adding the requisite amount of sulfuric acid. The grafting ratio, add on, and conversion were found to decrease on increasing the H⁺ ion concentration (Table III). This behavior may be explained on the basis of the fact that with the increase in the hydrogen ion concentration, the concentration of reactive species HSO₅⁻ decreases, which results in reduced production of primary free radicals, thereby decreasing the grafting parameters.



Effect of xanthan gum concentration

Table IV reveals that the grafting ratio, add on, and conversion increase as the gum concentration is increased from 0.60 to 1.00 g dm⁻³ and thereafter grafting retarded with increasing gum concentration. The

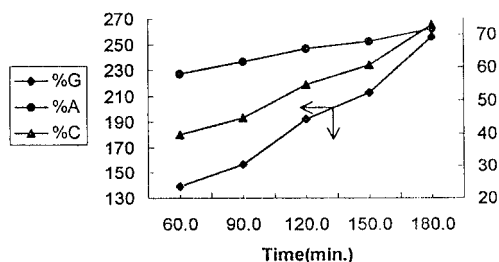


Figure 2 Effect of time period on grafting parameters: [PMS] = 4.0×10^{-3} mol dm⁻³; [Fe²⁺] = 5.0×10^{-3} mol dm⁻³; [H⁺] = 1.8×10^{-3} mol dm⁻³; [acrylic acid] = 5.0×10^{-2} mol dm⁻³; [xanthan gum] = 1.0 g dm⁻³; temperature = 35°C.

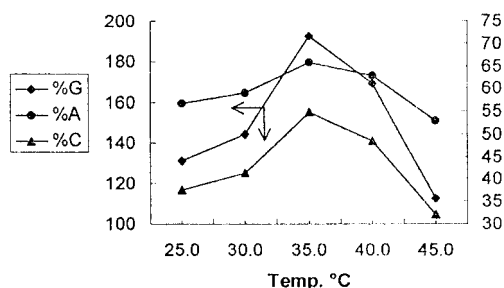


Figure 3 Effect of temperature on grafting parameters: [PMS] = 4.0×10^{-3} mol dm⁻³; [Fe²⁺] = 5.0×10^{-3} mol dm⁻³; [H⁺] = 1.8×10^{-3} mol dm⁻³; [acrylic acid] = 5.0×10^{-2} mol dm⁻³; [xanthan gum] = 1.0 g dm⁻³; time = 120 min.

enhancement of the grafting in the cited range may be attributed to availability of more grafting sites attributed to the sufficient presence of gum molecules. However, beyond the cited range the retardation in grafting may result from (i) an increase in the viscosity of reaction medium, which hinders the movement of the free radicals, and (ii) the fact that with an increase in the amount of xanthan gum, more graft radicals are formed; they may interact and lead to termination.

Effect of reaction time

The effect of the time period on grafting reaction was studied by varying the time period from 60 to 180 min (Fig. 2). There was an increase in the grafting ratio, add on, and conversion as the time period increased. With increasing reaction time, there may be addition of a greater number of monomer molecules to the growing grafted chains. A similar trend was observed in the case of grafting of acrylamide onto xanthan gum.¹⁶

Effect of temperature

The effect of temperature on grafting reaction is shown in Figure 3. The grafting ratio, add on, and conversion increase in the temperature range 25–35°C.

TABLE V
Weight Loss at Different Temperatures

Temperature (°C)	Weight loss (%)	
	Xanthan gum	Xanthan gum-g-acrylic acid
100	3.3	7
200	6.0	15.4
300	29.0	32.2
400	45.0	44.0
500	49.0	59.0
600	52.0	62.3
700	54.0	73.0
800	58.0	77.8

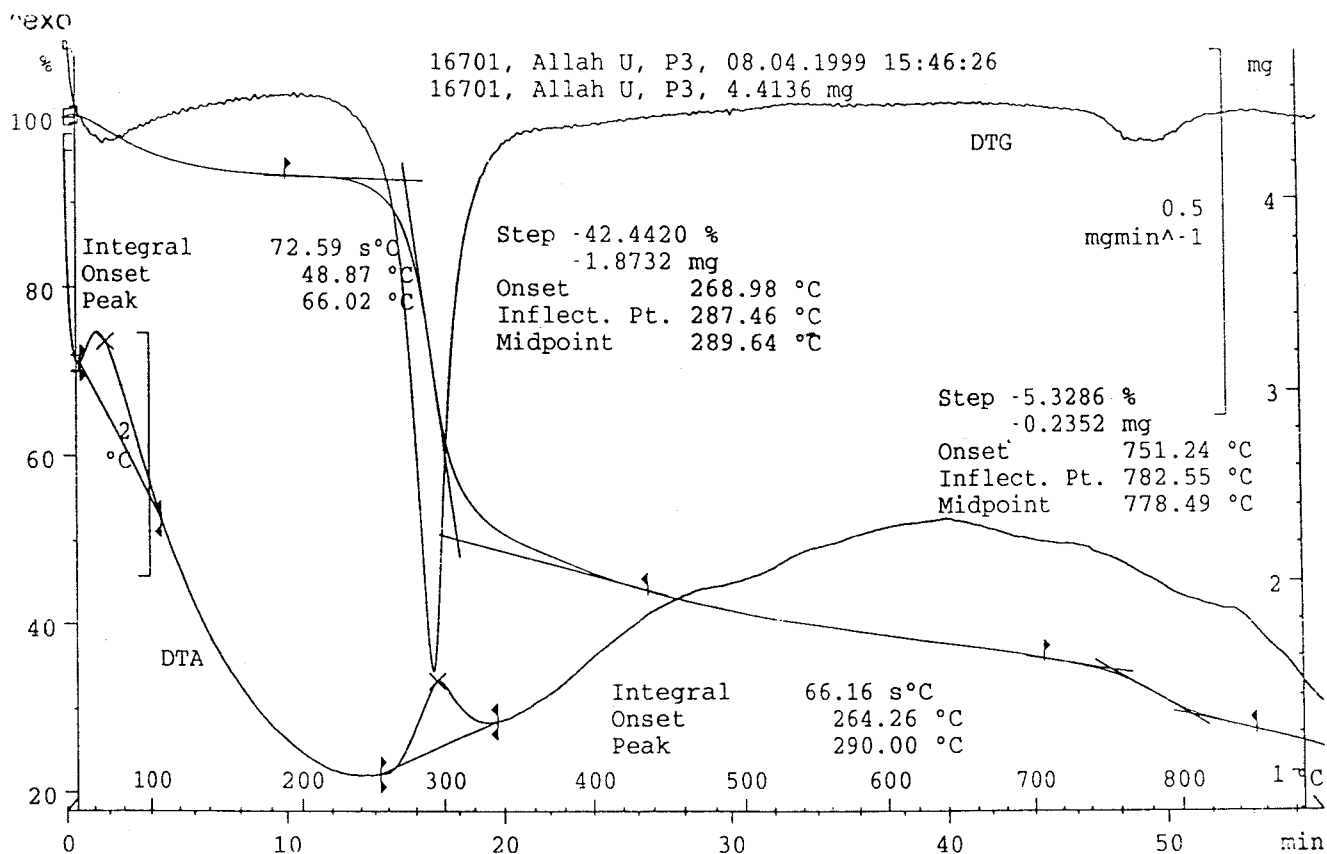


Figure 4 Thermogravimetric trace of xanthan gum.

These parameters show a decreasing trend beyond this range. This behavior may be explained on the basis of the fact that with the increase in temperature,

the rate of production of primary free radicals increases, thus generating the grafting sites at a greater rate and thereby increasing the values of grafting pa-

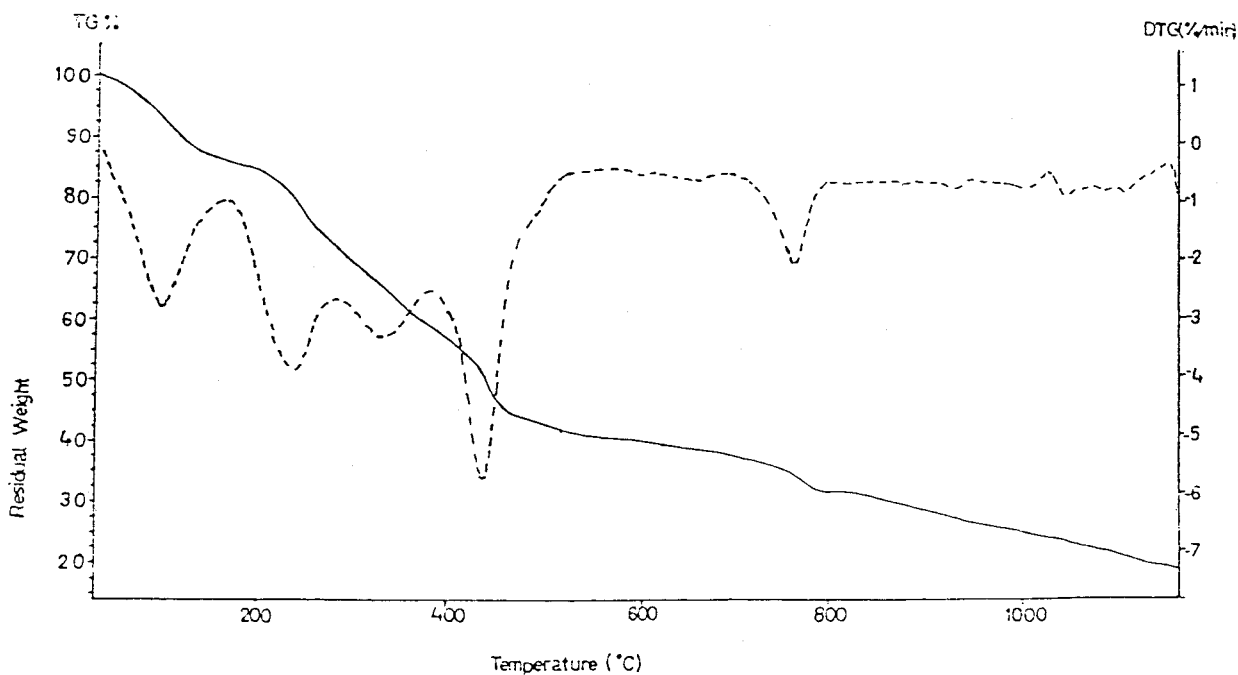
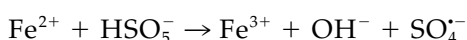


Figure 5 Thermogravimetric trace of xanthan gum-g-acrylic acid.

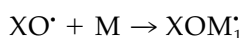
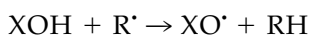
rameters. Beyond the optimum value, the decrease in grafting parameters may be attributed to the decreased concentration of active species arising from the decomposition of HSO_5^- into H_2O , HSO_4^- , and O_2 at higher temperature.¹⁷

Mechanism

The interaction of Fe^{2+} and KHSO_5 produces $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ free radicals, which abstract hydrogen atoms from xanthan gum, resulting in the formation of a xanthan gum macroradical (XO^{\cdot}). The monomer molecules that are in the close vicinity of the reaction sites become acceptors of the xanthan gum radicals, resulting in chain initiation and thereafter themselves become free-radical donors to the neighboring molecules; in this way, grafted chains grow. These grafted chains are terminated by disproportionation, coupling, or chain transfer to give the graft copolymer. On the basis of experimental results, the following reaction mechanism has been proposed:



Initiation

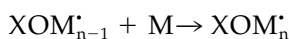


where $\text{R}^{\cdot} = \text{OH}^{\cdot}$ or $\text{SO}_4^{\cdot-}$.

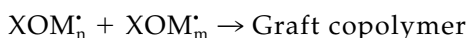
Propagation



⋮



Termination



Thermogravimetric analyses

Thermogravimetric analyses (TGA) of xanthan gum and graft copolymer were carried out using the Mettler Toledo star system in an inert atmosphere.

Xanthan gum

The thermogravimetric study of xanthan gum shows that decomposition of xanthan gum starts at 232°C, in a single-step degradation process (Table V). The polymer decomposition temperature (PDT) was found to be 281°C. The rate of weight loss increases initially but after 50% weight loss the rate was found to decrease. The temperature (T_{max}) at which maximum weight loss occurred was 296°C. The final decomposition temperature (FDT) and the integral procedural temperature (IPDT) was 316 and 287.6°C, respectively. A char yield at 30% was obtained at 800°C (Fig. 4).

Xanthan gum-g-acrylic acid graft copolymer

The graft copolymer starts to degrade at about 200°C. However 5% weight loss has been observed below 100°C, which may be attributed to the absorbed water (Table V). The degradation appears to be a three-stage process: from 236.9 to 337.1°C, from 337.1 to 436.5°C, and from 436.5 to 761.6°C. The maximum weight loss occurs at 436.5°C (T_{max}). The polymer decomposition temperature (PDT) was found to be 236.9°C. The final decomposition (FDT) was found to be 761.6°C, which is higher than that of xanthan gum. The PDT was found to be 294.5°C. About 55% weight loss occurred between 100 and 760°C and 33% char yield was obtained at 766°C (Fig. 5).

The grafting of acrylic acid lowers the PDT because of the formation of anhydride with elimination of water molecule from the two neighboring carboxylic groups of the grafted chains; after the formation of the anhydride ring, however, the thermal stability of the graft copolymer is greatly enhanced, resulting in the overall increment in the IPDT and thermal stability of the graft copolymer.

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