# Cu<sup>+2</sup>/Mandelic Acid Redox Pair Initiated Graft Copolymerization Acrylamide onto Guar Gum

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ABSTRACT: The effect of reaction conditions on the grafting parameters during the grafting of acrylamide (ACM) onto guar gum (GOH) by using a  $\text{Cu}^{+2}$ -mandelic acid (MA) redox couple was studied. On increasing the  $\text{Cu}^{+2}$  ion concentration  $(0.5 \times 10^{-2} \text{ to } 1.0 \times 10^{-2} \text{ mol dm}^{-3})$ , an increase in total conversion of monomer, grafting ratio, efficiency, and add on was observed. Grafting ratios increased with an increase in concentration of mandelic acid and reaches its maximum value at  $0.8 \times 10^{-2} \text{ mol dm}^{-3}$ . It was observed that grafting onto guar gum takes place efficiently when monomer and hydrogen ion concentrations are  $20.0 \times 10^{-2}$  and  $2.2 \times 10^{-2} \text{ mol dm}^{-3}$ , respectively. Optimum temperature and time for obtaining a maximum grafting ratio and efficiency was found to be  $35 \pm 0.2^{\circ}\text{C}$  and 2 h, respectively. The plausible mechanism of grafting was suggested. The graft copolymer was characterized by infrared spectroscopy and thermogravimetric analysis. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 739–745, 1999

Key words: redox pair; graft copolymerization; acrylamide; guar gum

# **INTRODUCTION**

The studies of the physical properties of acrylamide graft copolymer on different types of starches<sup>1-3</sup> cellulose,<sup>4</sup> and guar gum<sup>5</sup> revealed that various properties such as flocculation, solubility, thermal stability, binding strength, water retention, and drag-reducing effectiveness of the substrate increase on grafting the acrylamide onto each. However, grafting of acrylamide onto substrate is accompanied by the polymerization of acrylamide and consequently, the grafting ratio and efficiency decrease. These studies prompted us to search new redox pairs, which preferably give graft copolymer rather than homopolymer. The effect of redox components, monomer, reaction time, and temperature on grafting parame-

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ters were studied to obtain a graft copolymer of desirable grafting ratio.

### EXPERIMENTAL

#### **Graft Copolymerization**

For each experiment, the guar gum solution was prepared by slow addition of a known amount of guar gum to 100 ml of rapidly stirred deionized triple-distilled water in a reactor. Throughout the reaction period, the mixture was purged with the stream of purified nitrogen gas and kept at a constant temperature. A definite amount of  $CuSO_4$ ,  $H_2SO_4$ , and acrylamide was added to the reactor. The reaction was initiated by the addition of mandelic acid and was allowed to proceed for a desirable time period. The reaction products were then poured into a mixture of methanol and water.<sup>6</sup> The grafted guar gum precipitates out, whereas polyacrylamide remains in the solution.

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**Figure 1** Effect of  $[Cu^{+2}]$  on % grafting, % efficiency, % add on. [MA],  $2 \times 10^{-2}$  mol dm<sup>-3</sup>; [ACM],  $20 \times 10^{-2}$ mol dm<sup>-3</sup>; [H<sup>+</sup>],  $2.2 \times 10^{-2}$  mol dm<sup>-3</sup>; [GOH], 0.917 g dm<sup>-3</sup>; time, 120 min; and temperature, 35°C.

The precipitate thus obtained was separated, dried, and weighed.

#### **Homopolymer Content in Reaction**

A pinch of hydroquinone was added to the filtrate and then concentrated by distillation under reduced pressure. The polyacrylamide was precipitated by pouring the concentrated filtrate into excess of pure methanol. The homopolymer was separated, dried, and weighed.

# **RESULTS AND DISCUSSION**

The graft copolymers were characterized according to Fanta's definition.<sup>7</sup>

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

Grafting Efficiency (%*E*) =  $\frac{\text{Grafted Polymer}}{\text{Polymer Formed}} \times 100$ 

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

and

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

The amount of homopolymer formed is (100 – Grafting Efficiency).

The effects of the concentration of  $Cu^{+2}$ , mandelic acid, hydrogen ion, guar gum, and acrylamide, along with the effects of time and temperature on grafting ratio, grafting efficiency, add on, and total conversion of monomer were studied.

#### **Effect of Cupric Ion Concentration**

The effect of the  $[Cu^{+2}]$  on grafting parameters was studied by varying the concentration of  $Cu^{+2}$ from  $0.5 \times 10^{-2}$  to  $2.0 \times 10^{-2}$  mol dm<sup>-3</sup>. The grafting ratio, efficiency, and add on also increased when the concentration of cupric ion is



**Figure 2** Effect of  $[Cu^{+2}]$  on % homopolymer and % conversion. [MA],  $2 \times 10^{-2}$  mol dm<sup>-3</sup>; [ACM], 20  $\times 10^{-2}$  mol dm<sup>-3</sup>; [H<sup>+</sup>],  $2.2 \times 10^{-2}$  mol dm<sup>-3</sup>; [GOH], 0.917 g dm<sup>-3</sup>; time, 120 min; and temperature, 35°C.



Figure 3 Effect of [MA] on % grafting, % efficiency and % add on.  $[Cu^{+2}]$ ,  $1 \times 10^{-2}$  mol dm<sup>-3</sup>; [ACM], 20  $\times 10^{-2}$  mol dm<sup>-3</sup>; [H<sup>+</sup>],  $0.4 \times 10^{-2}$  mol dm<sup>-3</sup>; [GOH], 0.917 g dm<sup>-3</sup>; time, 120 min; and temperature, 35°C.

increased up to a peak of  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup> (Fig. 1); thereafter, the grafting reactions decreased; however, a reverse trend was observed for homopolymer (Fig. 2).

The enhancement in grafting may be attributed to the increase in the rate of production of primary free radicals that increased the number of grafting sites on the polymer backbone. The decrease in grafting ratio and total conversion may be attributed to the oxidative termination of primary free radicals.

## Effect of Mandelic Acid Concentration

The grafting reactions were conducted by varying the concentration of mandelic acid from  $0.4 \times 10^{-2}$  to  $4.0 \times 10^{-2}$  mol dm<sup>-3</sup>. Grafting ratio, efficiency, and add on all increase with increasing [MA] up to a peak amount of  $0.8 \times 10^{-2}$  mol dm<sup>-3</sup>; thereafter, the grafting reactions decrease (Fig. 3). As the concentration of MA is increased, a greater number of

primary free radicals are formed that enhance grafting; but at higher concentrations of MA, a greater amount of homopolymer is formed (Fig. 4).

## Effect of Acrylamide Concentration

The variation of acrylamide concentration from 10  $imes 10^{-2}$  to  $20 imes 10^{-2}$  mol dm<sup>-3</sup> during the reaction revealed that the grafting ratio, efficiency, and add on increased when also increasing the monomer concentration, but decreased as the monomer concentration exceeded 20  $\times$  10<sup>-2</sup> mol dm<sup>-3</sup> (Fig. 5). Increasing the monomer concentration resulted in it accumulating at closer proximity to the polymer backbone. The monomer molecules that are at the immediate vicinity of the reaction sites become acceptors of the guar gum radicals, which result in chain initiation; thereafter, they become free radical donors to the neighbouring molecules, lowering termination. The decrease in grafting ratio, efficiency, and add on could be interpreted in terms of an increase in viscosity of the medium due to the preferential formation of homopolymer at higher concentrations (Fig. 6).



Figure 4 Effect of [MA] on % homopolymer and % conversion.  $[Cu^{+2}]$ ,  $1 \times 10^{-2}$  mol dm<sup>-3</sup>; [ACM], 20  $\times 10^{-2}$  mol dm<sup>-3</sup>; [H<sup>+</sup>],  $0.4 \times 10^{-2}$  mol dm<sup>-3</sup>; [GOH], 0.917 g dm<sup>-3</sup>; time, 120 min; and temperature, 35°C.



Figure 5 Effect of [ACM] on % grafting, % efficiency and % add on.  $[Cu^{+2}]$ ,  $1 \times 10^{-2}$  mol dm<sup>-3</sup>; [MA],  $2 \times 10^{-2}$  mol dm<sup>-3</sup>; [H<sup>+</sup>],  $2.2 \times 10^{-2}$  mol dm<sup>-3</sup>; [GOH], 0.917 g dm<sup>-3</sup>; time, 120 min; and temperature, 35°C.

#### Effect of Guar Gum Concentration

The grafting parameters were studied by varying the concentration of guar gum from  $63.8 \times 10^{-2}$  to  $137.0 \times 10^{-2}$  g dm<sup>-3</sup> (Table I). As the concentration of guar gum increased from  $63.8 \times 10^{-2}$  to  $91.7 \times 10^{-2}$  g dm<sup>-3</sup>, the grafting ratio, efficiency, add on, and conversion also increased, but by further increasing the concentration of guar gum, a decrease in the grafting parameters was observed. The reason for the initial increase is that more grafting sites are available as the concentration of guar gum increased beyond the cited range, viscosity of reaction medium also increased, which hindered the movement of free radicals, thereby decreasing the %*C*.

# Effect of Hydrogen Ion Concentration

The extent of grafting the acrylamide onto guar gum with the Cu<sup>+2</sup>/MA redox system was found to be highly dependent on hydrogen ion concentration. The effect of hydrogen ion concentration on grafting parameters was studied by varying the concentration of sulfuric acid from  $0.4 \times 10^{-2}$  to  $4.0 \times 10^{-2}$  mol dm<sup>-3</sup>. Table II reveals that the grafting ratio, efficiency, and add on increased as the hydrogen ion concentration increased from  $0.4 \times 10^{-2}$  to  $2.2 \times 10^{-2}$  mol dm<sup>-3</sup>, but beyond this, the grafting parameters decreased. The initial increase may be explained on the basis that in the presence of H<sup>+</sup>, acrylamide changes to enolic form as follows:



$$\begin{array}{c} & \text{OH} \\ & | \\ \text{HO\dot{C}H}\text{--}\text{CH}\text{=-}\text{C}\text{--}\text{NH}_2 \\ \\ & \text{(A)} \end{array}$$

$$+ Cu^{+} + H^{+}$$



Figure 6 Effect of [ACM] on % homopolymer and % conversion.  $[Cu^{+2}], 1\times 10^{-2} \text{ mol } dm^{-3}; [MA], 2\times 10^{-2} \text{ mol } dm^{-3}; [H^+], 2.2\times 10^{-2} \text{ mol } dm^{-3}; [GOH], 0.917 \text{ g} dm^{-3}; time, 120 \text{ min; and temperature, } 35^{\circ}\text{C}.$ 

$[{\rm GOH}] \times 10^2 \\ ({\rm g~dm^{-3}})$	% Grafting	% Efficiency	% Add on	% Conversion	% Homopolymer
63.8	72.78	50.54	42.05	6.45	49.46
91.7	129.77	93.70	56.47	8.94	6.30
112.0	70.50	79.30	41.33	6.90	20.70
137.0	21.60	76.99	18.00	2.75	23.01

Table I Effect of [Guar gum] on Grafting Parameters

 $[Cu^{+2}] = 1 \times 10^{-2} \text{ mol dm}^{-3}; [MA] = 2 \times 10^{-2} \text{ mol dm}^{-3}; [H^+] = 2.2 \times 10^{-2} \text{ mol dm}^{-3}; [ACM] = 20 \times 10^{-2} \text{ mol dm}^{-3};$  Time = 120 min; Temp = 35°C.

The formation of the species (A) increases with an increase in  $[H^+]$ . The species (A) is capable of abstracting the hydrogen atom from the backbone of guar gum, resulting in the increase of guar gum radical; hence, the % G increases with an increase in  $[H^+]$ .

# **Effect of Time**

Table III shows that the grafting ratio and efficiency increase as the time period of the reaction is increased from 60 to 120 min, further increases in the time period decrease the grafting ratio and efficiency, whereas total conversion of monomer (%C) increases with an increase in time period, which means that the amount of homopolymer increases. This may be due to the degeneration of growing grafted chains with increases in the time period.

#### Effect of Temperature

Table IV reveals that the grafting ratio efficiency, add on, and conversion increased as the temperature increased from 25 to 35°C, but beyond this temperature, grafting decreased. The increase in grafting ratio, efficiency, and add on may be ascribed to (1) an increase in the rate of production of primary free radicals, which increases the number of grafting sites at polymer backbone or (2) an increase in temperature increases the rate of diffusion of acrylamide onto guar gum. The decrease in grafting ratio beyond 35°C may be attributed to premature termination of growing grafted chains.

## **Evidence of Grafting: IR Spectra**

On comparing the infrared (IR) spectra of guar gum-g-acrylamide and guar gum, the absorption bands corresponding to the amide group were observed in the spectra of guar gum-g-acrylamide, whereas these absorption bands were absent in the spectra of guar gum. A strong band at 1630 cm<sup>-1</sup> is due to the C=O band; the less intense band at 1590 cm<sup>-1</sup> is due to N—H bending. A broad band of medium intensity at 710–680 cm<sup>-1</sup> is due to out-of-plane NH wagging.

## Thermogravimetric Analysis (TGA)

*Guar Gum.* The decomposition of guar gum starts at 230°C and is a single-step degradation reaction (Fig. 7). The rate of weight loss increased upon increasing the temperature to 310°C, but decreased thereafter. Nearly 75% of guar gum degrades below 400°C; therefore, final decomposition temperature was very low, i.e., 320°C. Poly-

Table II Effect of $ H^+ $ on Grafting Param
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$\mathrm{[H^+]}  imes 10^2 \ \mathrm{(mol~dm^{-3})}$	% Grafting	% Efficiency	% Add on	% Conversion	% Homopolymer
0.4	68 70	72.58	40.72	6 11	27 42
1.3	100.00	85.94	50.00	7.51	14.06
2.2	129.77	93.70	56.47	8.94	6.30
2.6	29.00	58.59	22.48	3.19	41.41
4.0	19.62	48.91	10.40	2.59	51.09

 $[Cu^{+2}] = 1 \times 10^{-2} \text{ mol } dm^{-3}; \text{ [MA]} = 2 \times 10^{-2} \text{ mol } dm^{-3}; \text{ [GOH]} = 0.917 \text{ gm } dm^{-3}; \text{ Temp} = 35^{\circ}\text{C}; \text{ Time} = 120 \text{ min}.$ 

Time (min)	% Grafting	% Efficiency	% Add on	% Conversion	% Homopolymer
60	27.9	76.19	21.82	2.36	23.81
90	48.74	77.02	32.72	4.07	22.98
120	129.77	93.70	56.47	8.94	6.30
150	64.47	46.38	34.15	8.95	53.62
180	31.40	22.51	23.90	8.99	77.49

Table III Effect of Time on Grafting Parameters

 $[Cu^{+2}] = 1 \times 10^{-2} \text{ mol } dm^{-3}; [MA] = 2 \times 10^{-2} \text{ mol } dm^{-3}; H^+] = 2.2 \times 10^{-2} \text{ mol } dm^{-3}; [ACM] = 20 \times 10^{-2} \text{ mol } dm^{-3}; [GOH] = 0.917 \text{ g } dm^{-3}; Temp = 35^{\circ}C.$ 

mer decomposition temperature was found to be 280°C. Only 5% char yield was obtained at 800°C.

Guar Gum-g-acrylamide. The thermal degradation of guar gum-g-acrylamide with a 90% grafting ratio started at approximately 200°C. The degradation of three reaction stages appeared from 150 to 310°C, from 310 to 370°C, and from 370 to 430°C (Fig. 7). The polymer decomposition temperature was found to be 220°C. Beyond 40% weight loss, rate of weight loss decreased with increasing temperature; therefore, final decomposition temperature (i.e., 455°C) was higher than that of guar gum. The polymer decomposition temperature indicated that grafting of acrylamide lowers the initial decomposition temperature of graft copolymer because it was reported<sup>8</sup> that polyacrylamide degrades in the temperature range of 175–300°C by the formation of the imide group via cyclization of amide group and evolution of ammonia.

*Mechanism.* The following reaction mechanism is suggested for the graft copolymerization of acrylamide onto guar gum using  $Cu^{+2}$ -MA redox system.

The  $\dot{R}$  (primary radical) is formed by electron abstraction of MA as follows:

$$Cu^{+2} + Ph - CH - OH \longrightarrow$$

$$COOH$$

$$(MA)$$

$$Ph - \dot{C} - OH + Cu^{+} + H^{+}$$

$$COOH$$

$$(\dot{R})$$

where Ph is phenyl group.

Initiation

$$\dot{\mathbf{R}} + \mathbf{M} \longrightarrow \dot{\mathbf{R}}_1$$
$$\dot{\mathbf{R}}_1 + \mathbf{GOH} \longrightarrow \mathbf{R}_1 \mathbf{H} + \mathbf{GOH}$$

Propagation

$$\dot{\text{GO}} + \text{M} \longrightarrow \text{GOM}_1$$
  
 $\text{GOM}_1 + \text{M} \longrightarrow \text{GOM}_2$   
 $\dot{\text{GOM}}_{n-1} \longrightarrow \text{GOM}_n$ 

Temp (°C)	% Grafting	% Efficiency	% Add on	% Conversion	% Homopolymer
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25	70.11	78.50	41.21	5.76	21.50
30	119.19	91.38	54.37	8.42	8.62
35	129.77	93.70	56.47	8.94	6.30
40	84.9	68.09	45.93	8.05	31.91
45	58.99	56.29	37.10	6.76	43.71

 Table IV
 Effect of Temperature on Grafting Parameters

 $[Cu^{+2}] = 1 \times 10^{-2} \text{ mol dm}^{-3}; [MA] = 2 \times 10^{-2} \text{ mol dm}^{-3}; [H^+] = 2.2 \times 10^{-2} \text{ mol dm}^{-3}; [ACM] = 20 \times 10^{-2} \text{ mol dm}^{-3}; [GOH] = 0.917 \text{ g dm}^{-3}; Time = 120 \text{ min}.$ 



**Figure 7** Thermogravimetric trace of guar gum (——) and guar gum-g-acrylamide  $(-\cdot -)$ .

Termination

$$\operatorname{GO\dot{M}}_n + \operatorname{GO\dot{M}}_n \longrightarrow \operatorname{Graft} \operatorname{Copolymer}$$
  
 $\operatorname{GO\dot{M}}_n + \operatorname{G\dot{O}} \longrightarrow \operatorname{Graft} \operatorname{Copolymer}$   
 $\operatorname{GO\dot{M}}_n + \operatorname{\dot{R}} \longrightarrow \operatorname{Graft} \operatorname{Copolymer}$ 

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