

# Graft Polymerization of Methyl Methacrylate onto Guar Gum with Ceric Ammonium Sulfate/Dextrose Redox Pair

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**ABSTRACT:** The effect of different reaction conditions on the grafting of methyl methacrylate (MMA) onto guar gum (GG) has been studied in detail. The grafting efficiency was optimal under the following conditions: MMA at 1.13 mol/L; ceric ammonium sulfate at  $6.32 \times 10^{-3}$  mol/L; dextrose monohydrate at  $2.428 \times 10^{-3}$  mol/L; GG at 4 g/L; temperature at 50°C; and time at 210 min. Fourier transform infrared spectroscopy was used for the confirmation of copolymer formation. Thermogravimetric analysis of GG and a representative graft copolymer were studied. A probable mechanism of grafting has been suggested. The biodegradability of the resulted copolymer was evaluated. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 3520–3525, 2001

**Key words:** guar gum; grafting; biodegradation; methyl methacrylate; kinetics of mechanism

## INTRODUCTION

Graft polymerization is one of the techniques employed by polymer chemists for modifying the properties of a polymer. Guar gum (GG), a seed galactomannan,<sup>1,2</sup> is known to be susceptible to easy biodegradation.<sup>3,4</sup> Polymethyl methacrylate (PMMA) is a nonbiodegradable<sup>5</sup> and effective drug reducer polymer.<sup>3</sup> PMMA was selected for grafting to obtain PMMA-g-GG, which has well-balanced physicochemical properties.

To date, a large volume of work has been reported on grafting vinyl monomers<sup>3,4,6,7</sup> from GG using different redox pairs as initiators. But the grafting efficiency (GE) of this redox pair is considerably low. Ceric ion is a widely used initiator for grafting natural polymers.<sup>8–10</sup> However, this initiator alone has the limitation of producing

large quantities of homopolymers. Hence, ceric ammonium sulfate (CAS) coupled with dextrose monohydrate (DM) has been chosen. The beauty of this redox pair is that it generates negligible amount of homopolymers with high GE.

The present investigation is a detailed study of (a) some major factors that affect graft polymerization of MMA onto GG using the CAS–DM redox pair in aqueous medium and (b) the physicochemical properties of the synthesized graft copolymer.

## EXPERIMENTAL

### Materials

Guar gum (GG)<sup>11</sup> was procured from S.K. Chemical (Calcutta, India) and was subjected to Soxhlet extraction with 95% ethanol for 5 days to remove protein and fat impurities. Methyl methacrylate (MMA; Merck, Schuchardt, Germany) was purified before use.<sup>8</sup> Ceric ammonium sulfate (CAS;

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Himedia Laboratories Pvt. Ltd., India) and dextrose monohydrate (DM; Sisco Chemical Industries, India) were dried before use.

### Graft Copolymerization

Graft copolymerization<sup>8,9</sup> was carried out in a two-necked round-bottomed flask that was kept in a constant temperature bath maintained at the required temperature. A definite amount of GG was soaked with a requisite quantity of MMA monomer for ~ 15 min before graft copolymerization was started. Water and DM were then added to the reaction mixture followed by ceric salt. Nitrogen atmosphere was maintained throughout the entire reaction period. After the specific time interval, the reaction was arrested by quenching with hydroquinone. To remove homopolymer, the sample was precipitated with acetone. Finally, the sample was extracted with acetone in a Soxhlet apparatus for 4 h to dissolve all the homopolymers. The colorless product was dried under vacuum at 50°C for > 24 h to a constant weight.

### Characterization

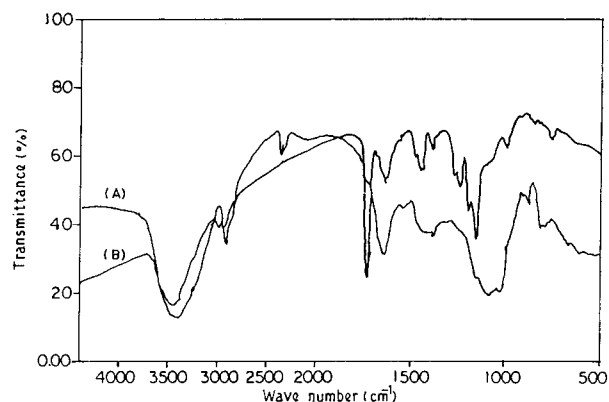
Percentage of grafting (PG), grafting efficiency (GE), and rate of grafting ( $R_g$ ) were used to evaluate the graft copolymerization according to the following relations:<sup>8</sup>

$$\text{GE (\%)} = (\text{weight of PMMA grafted} \times 100) / \text{weight of MMA charged} \quad (1)$$

$$\text{PG (\%)} = (\text{weight of PMMA grafted} \times 100) / \text{weight of graft copolymer} \quad (2)$$

$$R_g = (\text{weight of PMMA grafted}) / (\text{Mol Wt of MMA} \times \text{reaction time (s)} \times \text{reaction volume (m}^3)) \quad (3)$$

Fourier transform infrared (FT-IR) spectra of the samples (KBr pellets at a concentration of 1:100) were recorded on a Perkin Elmer Spectrum RX FT-IR system in the range 4000–400  $\text{cm}^{-1}$ . Thermogravimetric analysis (TGA) was conducted using a Stanton Redcraft thermal analyzer (STA 780) in air at a rate of 10°C/min. A Toshniwal digital conductivity meter (COLI 10A), a Systronics digital pH meter (model 335), and a Systronics spectrometer (model 105) were used for specific



**Figure 1** FT-IR spectra of (A) pure guar gum and (B) grafted guar gum.

conductivity, transmittance, and pH measurements, respectively, as in our earlier publications.<sup>12,13</sup> Physical properties were measured on graft copolymer sheets that were prepared with a hydraulic press. A universal testing machine and durometer were used to measure tensile strength and hardness, respectively. Swelling coefficient ( $q$ ) was determined by swelling the sample in acetone at room temperature for 72 h and calculating  $q$  according to the following relation:<sup>14</sup>

$$q = (m - m_0) / m_0 \quad (4)$$

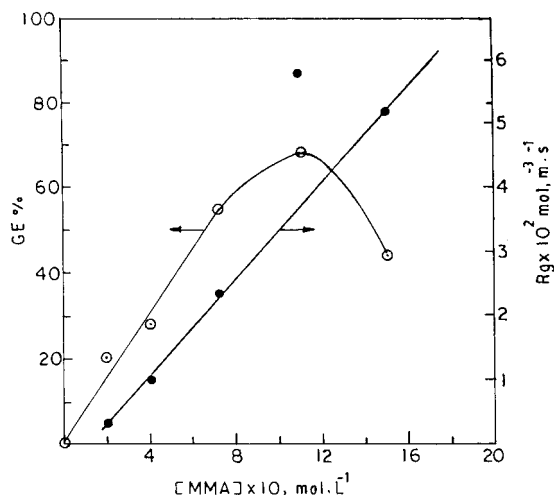
where  $m$ ,  $m_0$ , and  $d$  are the weight of the swelled sample, weight of the original sample, and density of the solvent, respectively.

### Evidence of Grafting

The FT-IR spectra of GG and a representative GG-g-PMMA are shown in Figure 1. The spectrum of the grafted GG indicates a strong absorption band at 1731  $\text{cm}^{-1}$  that is absent in the FT-IR spectrum of GG. The absorption peak at 1731  $\text{cm}^{-1}$  is due to the presence of an ester group.<sup>15,16</sup> This result provides substantial evidence of grafting onto GG. To separate the grafted side chain polymer from the GG backbone, the grafted copolymer was subjected to acid hydrolysis according to the procedure reported earlier.<sup>9</sup> The FT-IR spectrum of the dried product was identical to that reported<sup>16,17</sup> for PMMA, which unambiguously indicated the formation of GG-g-PMMA.

### Effect of Monomer Concentration

The GE of MMA on to GG as a function of monomer concentration is shown in Figure 2. GE in-

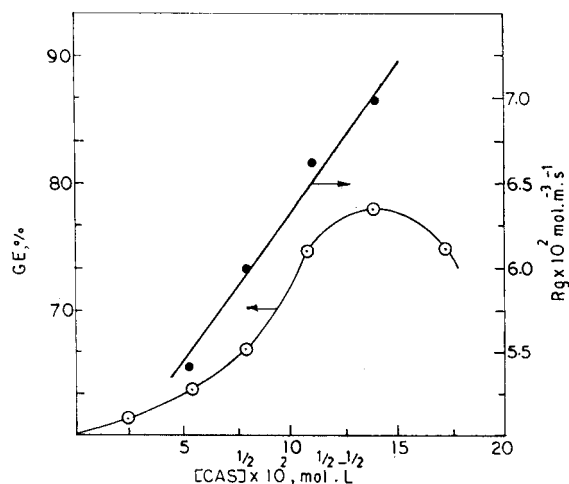


**Figure 2** Effect of monomer concentration on grafting parameters ([PVA] = 4 g/L, [CAS] =  $6.32 \times 10^{-3}$  mol/L, [DM] =  $2.42 \times 10^{-3}$  mol/L, time = 3.5 h, temperature = 50°C).

creases with increasing concentration of MMA initially up to 1.13 mol/L and then decreases with further increase in MMA. The initial increase in GE could be associated with the greater availability of monomer molecules in the proximity of GG. As a result, the chance of molecular collision of the reactants will be greater. Under these conditions, grafting of MMA onto GG would be favored because of the immobility of GG macroradicals (sites for grafting; see eq. 7). The decrease in GE after a certain level of MMA (1.13 mol/L) is probably due to homopolymerization. PG and  $R_g$  follow the same order as GE.

#### Effect of Initiator Concentration

The results obtained by changing the initiator concentration on the graft polymerization are presented in Figure 3. The GE increases rapidly with the CAS concentration up to  $12.64 \times 10^{-3}$  mol/L, then slowly up to  $18.96 \times 10^{-3}$  mol/L and then decreases gradually. This result can be reasonably explained as follows: as the initiator level increases, the number of free radicals on the GG backbone increases (see eq. 6). This explanation accounts for the substantial increment in GE up to a certain CAS content, beyond which the decrease in GE may be ascribed to hindrance of the diffusion of monomer molecules to the active sites on GG due to the presence of excess  $Ce^{4+}$  ion, which results in preferential homopolymerization.<sup>18,19</sup> PG follows the same trend as GE.  $R_g$

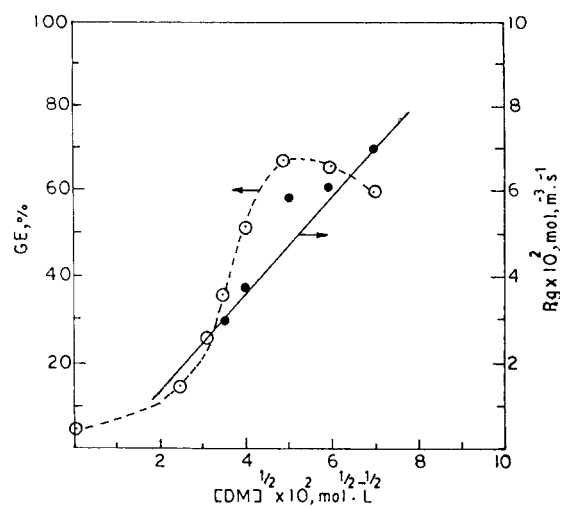


**Figure 3** Effect of initiator concentration on grafting parameters ([PVA] = 4 g/L, [MMA] = 1.13 mol/L, [DM] =  $2.42 \times 10^{-3}$  mol/L, time = 3.5 h, temperature = 50°C).

increases continuously with the increase of CAS level.

#### Effect of Dextrose Concentration

The variation of GE with DM concentration is shown in Figure 4. The GE increases significantly with increase of DM level up to  $2.428 \times 10^{-3}$  mol/L and then decreases gradually with the further increase of DM concentration. In the presence of  $Ce^{4+}$  ions, DM forms free radicals that act



**Figure 4** Effect of dextrose concentration on grafting parameters ([PVA] = 4 g/L, [MMA] = 1.13 mol/L, [CAS] =  $6.32 \times 10^{-3}$  mol/L, time = 3.5 h, temperature = 50°C).

**Table I Effect of Temperature on Grafting Parameters<sup>a</sup>**

Temperature, °C	GE, %	$R_g \times 10^2$ , mol m <sup>-3</sup> s <sup>-1</sup>
35	1.49	0.113
45	10.28	0.920
50	67.03	5.990
55	55.32	4.950

<sup>a</sup> [GG] = 4 g/L, [MMA] = 1.13 mol/L, [CAS] =  $6.32 \times 10^{-3}$  mol/L, time = 210 min.

as an initiator (see eq. 6), which is probably the reason for the initial rise in GE. Excess DM may reduce all the ceric ions to cerus ions. Hence, GE is diminished beyond a particular concentration of DM ( $2.428 \times 10^{-3}$  mol/L). However,  $R_g$  increases continuously with the increase of DM level.

#### Effect of Acid Concentration

The preliminary experimental results (data not shown) revealed that the system in the absence of acid gives rise to a good extent of grafting. The presence of acids decreases the GE (because the system itself produces H<sup>+</sup> ions via the reaction shown in eq. 6). However, addition of a small amount of acid resists the hydrolysis of ceric salt. Hence, graft copolymerization was carried out in presence of sulfuric acid.

#### Effect of Temperature

The data given in Table I show the effect of temperature on graft polymerization of MMA onto GG. It is evident that with the increase in temperature, the GE increases, reaches a maximum at 50°C, and then decreases. The favorable effect of temperature could be ascribed to (a) enhanced

diffusion of the initiator onto the GG and (b) increase in mobility of monomer molecules and their collision with GG macroradicals. The decrease in GE after a certain temperature (50°C) can be attributed to higher rate of termination of the growing chain and volatilization of monomer.  $R_g$  follows the same order as GE.

#### Effect of Time

The GE of MMA onto GG following different reaction periods is shown in Table II. The GE increases with the increase in reaction period. However, it should be noted that after 120 min, the increase in GE is marginal. The effect of time on grafting can be explained as follows: it is obvious that the longer the contact time of monomer molecules with GG macroradical sites, the greater is the grafting. The leveling off of GE after a certain time can only be attributed to the depletion of initiator and monomer concentration with the progress of reaction.

#### Thermogravimetric Analysis (TGA)

Comparative TGA data for pure GG, pure PMMA, and *g*-PMMA are shown in Figure 5. The TG curves indicate the better thermal stability of the graft copolymer with respect to GG.

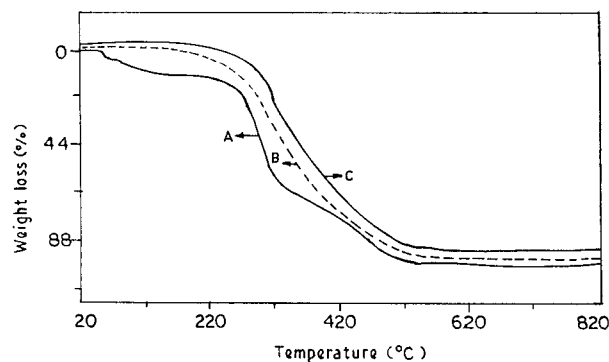
#### Kinetics and Mechanism

The rate of graft copolymerization is largely dependent on the concentration of monomer and initiator at a fixed level of GG. The effect of monomer concentration on  $R_g$  is shown in Figure 2. The plot of  $R_g$  versus [MMA] is linear, indicating the grafting reaction is first order with respect to the monomer. The relationships between (a)  $R_g$  and [CAS]<sup>1/2</sup> and (b)  $R_g$  and [DM]<sup>1/2</sup> (Figures 3 and 4,

**Table II Effect of Time on Grafting Parameters<sup>a</sup>**

Time (min)	GE (%)	H (%)	Specific Conductivity (m · mhos/cm)	pH	Transmission (%)
0	00.00	00.00	52.6	3.8	15.1
60	38.83	61.17	54.1	3.7	19.3
120	61.44	38.56	65.3	3.6	31.4
180	62.68	37.32	67.2	3.5	66.2
240	63.83	36.17	70.4	3.4	70.1
300	65.34	34.66	74.9	3.4	86.7

<sup>a</sup> [GG] = 4 g/L, [MMA] = 1.13 mol/L, [CAS] =  $6.32 \times 10^{-3}$  mol/L, temperature = 50°C, [DM] =  $2.42 \times 10^{-3}$  mol/L.

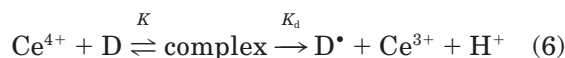


**Figure 5** Thermogravimetric analysis of (A) GG, (B) *g*-GG, and (C) PMMA.

respectively) are also linear. Therefore, the following rate equation is established:

$$R_g = K[\text{MMA}][\text{CAS}]^{1/2}[\text{DM}]^{1/2} \quad (5)$$

The mechanism of grafting is suggested as follows:



The following rate expressions are derived on the basis of the reactions shown in eqs.6–11 and an assumption of steady state for the free radicals (D, G, and GM):

$$d[\text{D}^\bullet]/dt = K_d K [\text{Ce}^{4+}][\text{D}] - k_i[\text{D}^\bullet][\text{GH}] = 0 \quad (12)$$

$$[\text{D}^\bullet] = K_d K [\text{Ce}^{4+}][\text{D}]/k_i[\text{GH}] \quad (13)$$

$$d[\text{G}^\bullet]/dt = k_i[\text{D}^\bullet][\text{GH}] - k'_i[\text{G}^\bullet][\text{M}] = 0 \quad (14)$$

$$[\text{G}^\bullet] = \{K_d K/k'_i\}[\text{Ce}^{4+}][\text{D}]/[\text{M}] \quad (15)$$

$$d[\text{GM}_n^\bullet]/dt = k'_i[\text{G}^\bullet][\text{M}] - k_t[\text{GM}_n^\bullet]^2 = 0 \quad (16)$$

$$[\text{GM}_n^\bullet] = \{k_d K/k_t\}^{1/2}[\text{Ce}^{4+}]^{1/2}[\text{D}]^{1/2} \quad (17)$$

$$R_g = k_p[\text{GM}_n^\bullet][\text{M}]$$

$$= k_p \{K_d K/k_t\}^{1/2}[\text{Ce}^{4+}]^{1/2}[\text{D}]^{1/2}[\text{M}] \quad (18)$$

where M, D, GH, and Ce represent monomer (MMA), DM, GG, and CAS, respectively.

Equation 18 is identical with eq.5, which was established from the experiment. This similarity indicates that the reaction mechanism just suggested is acceptable. Furthermore, the formation of a metastable complex<sup>20</sup> and its subsequent decomposition to cerus and hydrogen ions (eq. 6) has been confirmed by spectrophotometric and pH measurements. CAS has a characteristic absorption band<sup>8</sup> at 380 nm. The increase in transmission (Table II) of the system at 380 nm indicates the conversion of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$ . The formation of  $\text{H}^+$  via the reaction shown in eq. 6 is revealed by the fall of pH and the gradual rise of specific conductivity of the systems (Table II). The carbon-based GG macroradical<sup>21</sup> that is formed via the reaction shown in eq. 7, actually initiates the graft copolymerization.

## CONCLUSION

MMA can be easily graft copolymerized onto GG using a CAS/DM redox pair as an initiator in aqueous medium. The reaction variables, such as monomer, initiator, pH, time, and temperature, affect considerably the efficiency of MMA towards grafting. The GG-*g*-PMMA has better thermal stability than GG.

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