

## Photo-induced Synthesis and Characterization of Poly(methyl methacrylate) Grafted Sodium Salt of Partially Carboxymethylated Guar Gum

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**Abstract** Photo-induced graft copolymerization of methyl methacrylate (MMA) onto sodium salt of partially carboxymethylated guar gum (Na-PCMGG,  $\overline{DS} = 0.291$ ) was carried out in an aqueous medium using ceric ammonium nitrate (CAN) as photoinitiator to synthesize a novel graft copolymer, Na-PCMGG-g-PMMA, which may find its potential application as a metal adsorbent. The influences of synthesis variables such as concentrations of photoinitiator (CAN), nitric acid and monomer (MMA) as well as reaction time, temperature and amount of substrate on the grafting yields were studied and the reaction conditions for optimum photo-grafting were evaluated. At optimum concentration, the maximum values of the grafting yields achieved were  $G = 271.61\%$  and  $GE = 63.89\%$ . The experimental results were found to be in very good agreement with the proposed kinetic scheme. The photo-graft copolymerization of MMA onto Na-PCMGG ( $\overline{DS} = 0.291$ ) was also carried out in the presence and absence of ultraviolet radiation for studying the efficiency of the photoinitiator. The influence of carboxymethyl groups introduced onto the guar gum molecules with regard to its behavior towards ultra-violet radiation induced grafting with MMA was also investigated. Photo-grafting process was confirmed and the products were characterized with the help of the spectroscopic ( $^1\text{H-NMR}$  and FTIR) and SEM techniques.

**Keywords:** Photo-induced grafting; Methyl methacrylate; Sodium salt of partially carboxymethylated guar gum; Optimum reaction conditions; Characterization.

### INTRODUCTION

Graft copolymerization of vinyl monomers onto natural and synthetic polymers is a fascinating field of research and it has made paramount contribution towards better industrial and biomedical applications. Among grafting methods used, photo-grafting polymerization is widely known to be useful because of its significant advantages: less degradation of the backbone polymer, control over the grafting reaction in addition to attaining higher grafting efficiency, low cost of operation and selectivity to absorb UV light.

Guar gum (GG), an industrially important natural and renewable, non-ionic, rigid polymer<sup>[1]</sup> consists of a linear chain of  $\beta$ -D-mannopyranosyl units linked (1 $\rightarrow$ 4) with single member  $\alpha$ -D-galactopyranosyl units (1 $\rightarrow$ 6) as side branches. Due to the incomplete hydration of guar gum at ambient temperature and poor solution clarity as well as the desire for products with modified or special properties we have carried out carboxymethylation of guar gum to obtain sodium salt of partially carboxymethylated guar gum (Na-PCMGG). Guar gum and its derivatives find applications not only in petroleum, textile, paper, food and explosive industries but also in mining and minerals as well as in pharmaceuticals, medicines and drugs<sup>[2]</sup>. Thus, although guar gum and its derivatives find wide range of industrial applications, they also suffer from some drawbacks like

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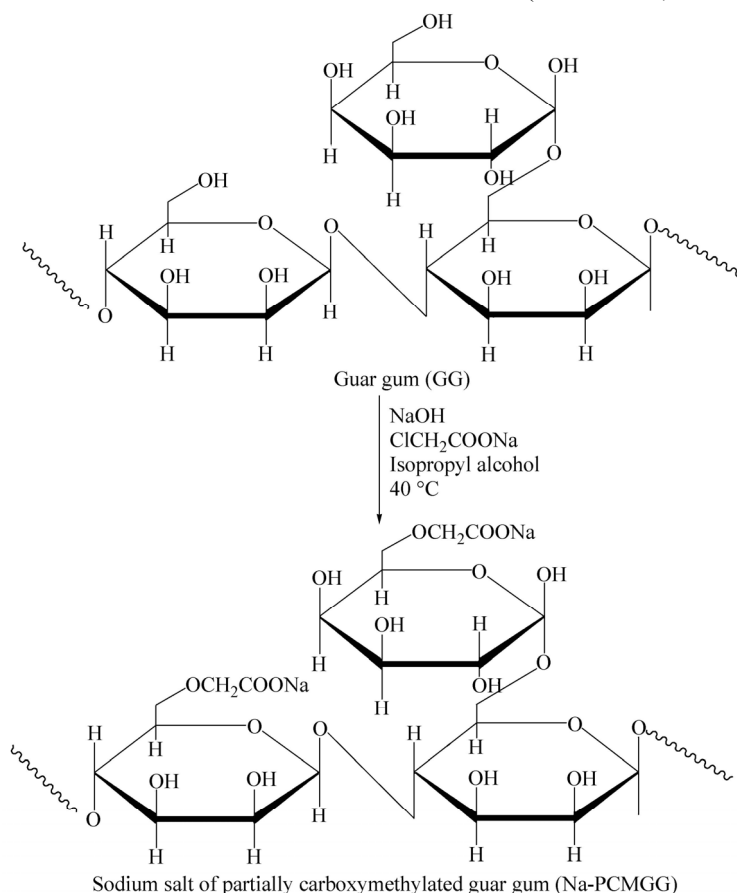
biodegradability<sup>[3]</sup>, which limits its uses considerably. These drawbacks can be improved through the grafting of vinyl monomers onto them thereby imparting new properties to the polymer backbone. To date many investigations have been carried out on grafting of vinyl monomers onto guar gum<sup>[4, 5]</sup> and partially carboxymethylated guar gum<sup>[6-9]</sup> using various redox initiating systems. However, reports on photo-grafting of vinyl monomers onto sodium salt of partially carboxymethylated guar gum are scanty available<sup>[10]</sup>. In the present work, we report the evaluation of the optimal reaction conditions for affording maximum percentage of photo-grafting of MMA onto Na-PCMGG ( $\overline{DS} = 0.291$ ) using ceric ammonium nitrate (CAN) as a photoinitiator and the characterization of the products using spectroscopic (<sup>1</sup>H-NMR and FTIR) and SEM techniques. This has been done not only to develop specialty polymeric materials but also to elucidate the photo-grafting mechanism over a range of values for reaction variables studied in the present work.

The work regarding the evaluation of the synthesized graft copolymer, Na-PCMGG-g-PMMA, for its potential application as a Pb(II) metal adsorbent by treating it with hydroxylamine in the presence of alkaline solution is in progress.

## EXPERIMENTAL

### Materials and Methods

Guar gum (GG) used in the present work was kindly supplied by H.B. Gum Industries Pvt. Ltd. (Kalol, India). The methods of preparation (Scheme 1) and purification as well as the measurement of degree of substitution ( $\overline{DS}$ ) of the sodium salt of partially carboxymethylated guar gum (Na-PCMGG) were followed as described earlier<sup>[11, 12]</sup>. The  $\overline{DS}$  of Na-PCMGG was found to be 0.291. MMA (Chiti Chem; Baroda, India) was washed



**Scheme 1** Preparation of sodium salt of partially carboxymethylated guar gum (Na-PCMGG)

with 2% sodium hydroxide solution to remove the stabilizer, washed with low conductivity water, till it was free from alkali and dried over anhydrous sodium sulphate. MMA was finally distilled at atmospheric pressure and the middle fraction was collected and used. CAN of reagent grade (Chiti Chem.; Baroda, India) was used as received. Analar grade nitric acid ( $\text{HNO}_3$ ) was used. Fresh solutions of the photoinitiator were used, prepared by dissolving the required amount of CAN in nitric acid. All other reagents and solvents used in the present work were of reagent grade. Nitrogen gas was purified by passing through a fresh pyragallol solution. Low conductivity water was used for the preparation of solutions as well as graft copolymer reactions.

### **Photo-graft Copolymerization**

#### *(i) Graft copolymer of Na-PCMGG (Na-PCMGG-g-PMMA)*

The photo-graft copolymerization reactions were carried out in a photochemical reactor supplied by Scientific Aids and Instruments Corp. (SAIC, Madras, India) as per the procedure described earlier<sup>[10]</sup>. A weighed amount of Na-PCMGG ( $\overline{\text{DS}} = 0.291$ , 0.25–3.0 g, dry basis) was dissolved in 100 mL of low conductivity water in the reaction flask, and the solution was stirred with continuous bubbling of a slow stream of nitrogen gas for half an hour. 2.5 mL of freshly prepared CAN solution ( $1.5 \times 10^{-3}$ – $20 \times 10^{-3}$  mol/L) in nitric acid (nil – 0.5 mol/L) was added to the reaction flask, and the contents were then flushed with purified nitrogen gas for half an hour followed by the addition of a known concentration of freshly distilled MMA (0.072–0.578 mol/L). The reaction flask was then assembled with an immersion well containing a 125-W medium pressure mercury lamp. The whole assembly (photochemical reactor) was placed in a dark cabinet after covering it completely with aluminum foil. The lamp was then illuminated. Water from a constant-temperature water circulation bath was circulated over the immersion well and the reaction flask. The solution then was irradiated with continuous stirring for different time intervals (0.5–10 h) in the temperature range of 20–50 °C. After the completion of the grafting reaction, the irradiated sample solution was removed carefully, and the crude graft copolymer was isolated by centrifugation. It was then purified by repeated washings with 95% methanol and finally with pure methanol. The crude copolymer sample of Na-PCMGG-g-PMMA thus obtained was dried in vacuum at 40 °C. The homopolymer (PMMA) was separated from the crude graft copolymer by carrying out exhaustive soxhlet extraction with benzene. After the complete removal of the homopolymer, the pure graft copolymer was dried at 40 °C in vacuum until a constant weight was obtained. The mechanistic pathway for the synthesis of the graft copolymer, Na-PCMGG-g-PMMA, is shown in Scheme 2.

#### *(ii) Graft copolymer of GG (GG-g-PMMA)*

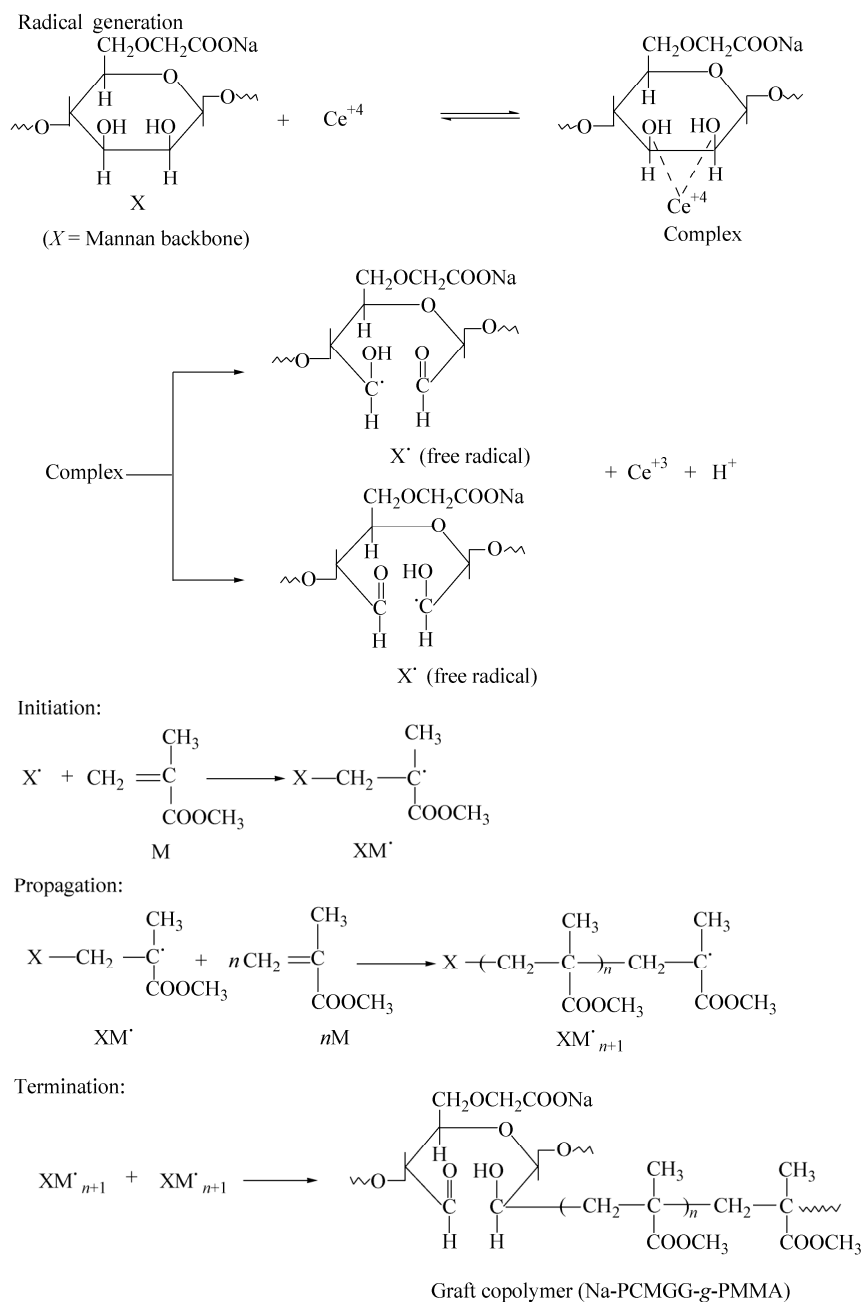
In order to understand the influence of introduction of the carboxymethyl groups (in GG molecule) on the grafting yields, we have also carried out the photo-grafting of MMA onto GG using the established optimal reaction conditions obtained in the case of photo-grafting of MMA onto Na-PCMGG ( $\overline{\text{DS}} = 0.291$ ) with CAN as a photoinitiator. The experimental procedure followed for the synthesis of the graft copolymer, GG-g-PMMA, is the same as discussed above.

### **Dark Method**

To compare the efficiency of CAN as a photoinitiator, the grafting of MMA onto Na-PCMGG ( $\overline{\text{DS}} = 0.291$ ) was carried out in the absence of the ultraviolet radiation (dark method) by following the above mentioned procedure using the following reaction conditions: Na-PCMGG (dry basis) = 2.0 g,  $[\text{HNO}_3] = 0.10$  mol/L,  $[\text{CAN}] = 4.0 \times 10^{-3}$  mol/L,  $[\text{MMA}] = 0.360$  mol/L, Time = 0.5–10 h, Temperature = 35 °C and Total volume = 105 mL.

### **Isolation of Grafted Chains**

The graft copolymer of Na-PCMGG ( $\overline{\text{DS}} = 0.291$ ) containing PMMA was hydrolyzed by refluxing for 12 h in 1N HCl as suggested by Brockway and Seaberg<sup>[13]</sup>. After all the Na-PCMGG went into the solution, a resinous mass was obtained which was characterized with IR spectroscopy.



Scheme 2 Mechanistic pathway for the synthesis of Na-PCMGG-g-PMMA

**FTIR Spectra**

The IR Spectra of guar gum, Na-PCMGG ( $\overline{DS} = 0.291$ ), Na-PCMGG-g-PMMA and PMMA were taken in KBr pellets using a Nicolet Impact 400D Fourier Transform Infra Red Spectrophotometer.

**<sup>1</sup>H-NMR Spectra**

<sup>1</sup>H-NMR spectrum of the grafted chain *i.e.* PMMA obtained after acid hydrolysis of the graft copolymer (Na-PCMGG-g-PMMA) was recorded on a Fourier Transform NMR Spectrometer (model R-1500) Hitachi, Japan with CDCl<sub>3</sub> as the solvent.

### Scanning Electron Microscopy (SEM)

Model ESEM TMP + EDAX, Philips make, was used to obtain the micrographs of guar gum, Na-PCMGG ( $\overline{DS} = 0.291$ ) and Na-PCMGG-g-PMMA ( $G = 271.61\%$ ).

### Grafting Yields and Kinetic Parameter

The percentage of grafting ( $G\%$ ), percentage of grafting efficiency ( $GE\%$ ) and rate of polymerization ( $R_p$ ) were evaluated by using the following expressions<sup>[14]</sup>:

$$G(\%) = \frac{\text{wt. of polymer grafted}}{\text{Initial wt of backbone}} \times 100 \quad (1)$$

$$GE(\%) = \frac{\text{wt. of polymer grafted}}{\text{wt. of polymer grafted} + \text{wt. of homopolymer}} \times 100 \quad (2)$$

$$R_p (\text{mol}/(\text{L} \cdot \text{s})) = \frac{\text{Weight of polymer grafted} + \text{Weight of homopolymer}}{\text{Mol. wt. of monmer} \times \text{Reaction time (s)} \times \text{Volume of the reaction mix. (mL)}} \times 10^3 \quad (3)$$

## RESULTS AND DISCUSSION

With a view to understanding the reaction mechanism of photo-grafting of poly(methyl methacrylate) onto Na-PCMGG, the effects of synthesis variables such as concentrations of photoinitiator (CAN), nitric acid, monomer (MMA) as well as reaction time, temperature and amount of substrate were studied and the reaction conditions for optimum photo-grafting have been evaluated.

### Effect of Backbone Concentration

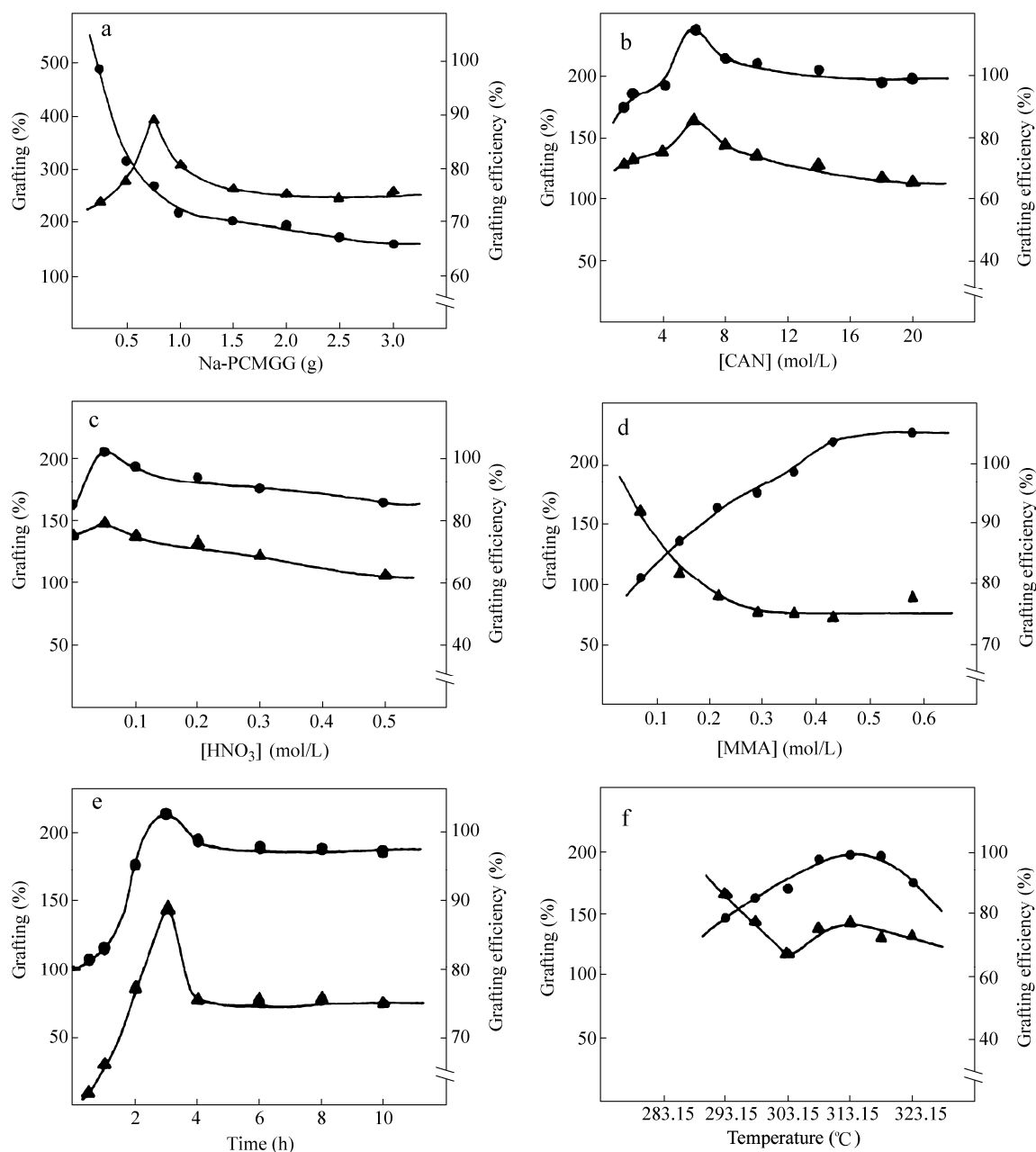
Figure 1(a) represents the influence of backbone concentration on the grafting yields. It is observed from this figure that the value of  $G$  decreases steadily in the whole range of backbone concentration studied. However, the value of  $GE$  increases in the beginning up to Na-PCMGG = 0.75 g and decreases further with increasing amount of Na-PCMGG. The results of this figure with regard to variation in  $G$  could be ascribed to the fact that although the weight of the grafted side chains increases with the amount of Na-PCMGG, the decrease in the monomer to backbone ratio lowers down the  $G$ . The observed decrease in  $GE$  beyond Na-PCMGG = 0.75 g is due to the simultaneous formation of homopolymer during the course of reaction. Similar results are also reported in the literature<sup>[7, 10, 14]</sup>.

### Effect of Photoinitiator Concentration

The influence of the photoinitiator (CAN) concentration on the grafting yields was studied by varying the concentration of CAN from  $1.50 \times 10^{-3}$  to  $20.0 \times 10^{-3}$  mol/L and the results are shown in Fig. 1(b). The values of  $G$  and  $GE$  are found to be increased with increase in ceric ion concentration up to  $[Ce^{+4}] = 6.0 \times 10^{-3}$  mol/L and reached maximum values of 237.70% and 85.27% respectively. Beyond the optimum value of the photoinitiator concentration, there is a decrease in the values of the grafting yields. The initial increasing trend in the grafting yield is due to the sufficient number of ceric(IV) ions in the reaction mixture at 0.1 mol/L concentration of nitric acid, which have been ultimately consumed in the formation of active sites onto Na-PCMGG, thereby facilitating the photo-graft copolymerization of MMA onto Na-PCMGG. The observed decrease in the grafting yields at higher photoinitiator concentration *i.e.* beyond  $[Ce^{+4}] = 6 \times 10^{-3}$  mol/L, may be attributed to the fast termination of the growing grafted chains. Further, homopolymer (PMMA) formation at higher photoinitiator concentrations, which competed with the photo-grafting reaction for the available monomer (MMA), could also lead to decrease in  $G$  and  $GE$ . Similar observations are reported in the literature<sup>[14, 15-18]</sup>.

### Effect of Acid Concentration

Figure 1(c) shows the effect of nitric acid concentration on the grafting yields. It is evident from this figure that there exists an optimum concentration of nitric acid (0.05 mol/L) which affords maximum  $G$  (205.63%) as well as  $GE$  (79.24%). Beyond the optimum concentration of nitric acid, both the values of  $G$  and  $GE$  are found to be



**Fig. 1** Influence of (a) amount of sodium salt of partially carboxymethylated guar gum (Na-PCMGG), (b) ceric ammonium nitrate (CAN) concentration, (c) nitric acid concentration, (d) methyl methacrylate (MMA) concentration, (e) reaction time and (f) reaction temperature on: *G* (●) and *GE* (▲)

decreased. Interestingly even at zero concentration of nitric acid a higher value of *G* is found which may be due to the possibility that, even in the absence of acid, in an aqueous medium Na-PCMGG ionizes fully to a greater extent which facilitates the diffusion of monomer as well as photoinitiator leading to a higher value of grafting. Below the optimum concentration, the observed increase in the values of *G* and *GE* with increase in nitric acid concentration may be attributed to an increase in the initiation rate of photo-grafting. On the other hand, the tendency of grafting yields to decrease with increase in nitric acid concentration, beyond the optimum value (0.05 mol/L), could be associated with a fast rate of termination because of the increased rate of generation of

free radical species as well as abundance of hydrogen proton. In addition, coagulation of colloidal homopolymer in solution at lower pH values would also retard diffusion of both monomer and photoinitiator thereby leading to the decreased grafting yields. Similar observations are reported in literature<sup>[14, 19, 20]</sup>.

#### ***Effect of Monomer Concentration***

The effect of monomer concentration on the grafting yields is shown in Fig. 1(d). It becomes evident that  $G$  increases continuously with the increase in the concentration of MMA up to 0.433 mol/L, beyond which it levels off. The possible explanation for this finding might be due to the following (i) with increasing monomer (MMA) concentration, the complexation between  $Ce^{+4}$  and monomer is enhanced (ii) at higher monomer concentration, a large number of the grafting polymeric chains that are formed are involved in generating additional active sites onto Na-PCMGG by the chain transfer reaction and (iii) the molecular weight of the grafts increases with increasing monomer concentration.

On the other hand, the observed decrease in GE in the whole range of the monomer concentration studied is attributed to the fact that the grafted chains acting as diffusion barriers, which may hinder the diffusion of monomer to the backbone leading to the poor availability of monomer for photo-grafting thereby resulting in the formation of homopolymer. Our observations are also in line with those reported elsewhere<sup>[9, 21–23]</sup>.

#### ***Effect of Reaction Time***

The influence of change in duration of photo-grafting reaction was studied by varying the time period from 0.5 h to 10 h and the results are shown in Fig. 1(e). It can be observed from this figure that initially the value of  $G$  increases with increase in reaction time and reaches a maximum value 213.66% within 3h; beyond which it decreases. The value of GE also varies in the similar way. Thus, the observed increase in the grafting yields up to 3 h can be explained on the basis of the fact that with increase in reaction time, the number of grafting sites on the Na-PCMGG backbone increases as a result of which the extent of initiation and propagation of photo-graft copolymerization also increases with reaction time leading to the increase in the grafting yields. On the other hand, the observed decrease in the grafting yields beyond the optimum reaction time may be presumably due to the detrimental effect of UV radiation onto the grafted side chains of PMMA at longer irradiation time intervals in the presence of the photoinitiator. Besides, beyond the optimum reaction time, the depletion of monomer and photoinitiator concentrations as well as shortage of the available grafting sites may lower the grafting yields. Similar time dependency of grafting yields is reported by other workers<sup>[15, 16, 19, 24, 25]</sup>.

#### ***Effect of Temperature***

In order to study the influence of temperature on the grafting yields, the photo-grafting reactions were carried out at seven different temperatures in the ranging of 20–50 °C. The results are presented in Fig. 1(f). It can be seen from this figure that the value of  $G$  increases with increase in temperature up to 40 °C, beyond this optimum temperature it decreases. However, the value of GE is found to be decreased from the very beginning up to 30 °C and increased further up to 40 °C, beyond which it further decreases. The favorable effect of temperature on  $G$  could be attributed to (a) enhanced diffusion of monomer molecules into the Na-PCMGG structure, (b) increase in mobility of monomer molecules and their collisions with Na-PCMGG macroradicals and (c) increase of propagation of the graft chains. However, the negative effect on grafting at and above 45 °C can be ascribed to the fact that at higher temperature photo-graft copolymerization occurs with poor selectivity. Similar results are also reported in the literature<sup>[26–29]</sup>.

#### ***Effect of Liquor Ratio***

The results regarding the influence of liquor ratio on  $G$  are tabulated in Table 1. It can be seen from this table that there is a continuous increase in  $G$  with increase in the liquor ratio. This observation can be explained on the basis of the fact that as the value of the liquor ratio decreases, the viscosity of the medium increases which, in turn, hinders the movement of free radicals, thereby decreasing  $G$ .

**Table 1.** Effect of liquor ratio (mL. soln/g, Na-PCMGG) on the photo-grafting of various vinyl monomers onto sodium salt of partially carboxymethylated guar gum (Na-PCMGG,  $\overline{DS} = 0.291$ )<sup>a</sup>

Liquor ratio (mL.soln/g, Na-PCMGG)	G (%)
420:1	488.60
210:1	314.65
140:1	267.25
105:1	214.76
70:1	201.30
52.5:1	194.41
42:1	171.68
35:1	155.24

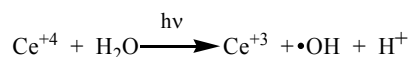
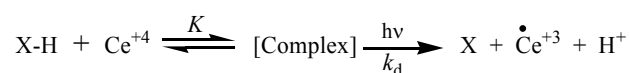
<sup>a</sup> Reaction conditions: Na-PCMGG : 0.25–3.0 g (dry basis); [CAN] :  $4.0 \times 10^{-3}$  mol/L; [HNO<sub>3</sub>] : 0.10 mol/L; [MMA] : 0.360 mol/L; time : 4 h; temperature : 35 °C and total volume : 105 mL

From the foregoing discussion, the optimized reaction conditions evaluated in the present study of photo-graft copolymerization of MMA onto Na-PCMGG ( $\overline{DS} = 0.291$ ) are: Na-PCMGG (dry basis) = 0.75 g, [CAN] =  $6.0 \times 10^{-3}$  mol/L, [HNO<sub>3</sub>] = 0.05 mol/L, [MMA] = 0.433 mol/L, time = 3 h, temperature = 40 °C and total volume = 105 mL. The maximum values of grafting yields achieved are  $G = 271.61$  and  $GE = 63.89$ .

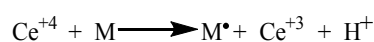
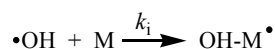
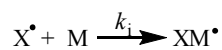
### KINETICS AND MECHANISM

The mechanism of the free radical photo-grafting of MMA onto Na-PCMGG ( $\overline{DS} = 0.291$ ) is expected to proceed according to the following proposed scheme<sup>[10]</sup>:

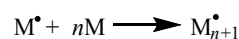
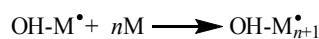
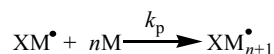
Radical generation:



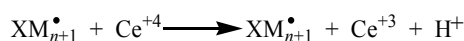
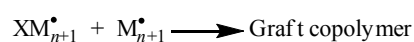
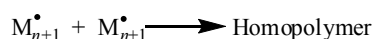
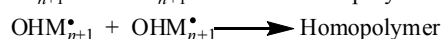
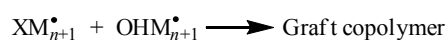
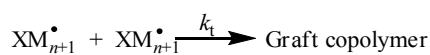
Initiation:



Propagation:



Termination:







Here, X–H denotes the reactive groups of Na-PCMGG and M is the monomer (MMA). With a steady state assumption, the following expressions [Eqs. (4) and (5)] were derived for the value of  $R_p$ :

$$R_p = k_p [XM_{n+1}^{\bullet}] [M] \quad (4)$$

$$R_p = k_p \left[ \frac{k_d \cdot k_i}{k_t} \right]^{1/2} [Ce^{+4}]^{1/2} [M] \quad (5)$$

$$R_p = R_g + R_h \quad (6)$$

The values of  $R_p$  evaluated for various monomer (MMA) and photoinitiator (CAN) concentrations, in the case of the photo-grafting of MMA onto Na-PCMGG ( $\overline{DS} = 0.291$ ) are presented in Tables 2 and 3 respectively.

**Table 2.** Rate of polymerization ( $R_p$ ) for photo-graft copolymerization of methyl methacrylate (MMA) onto sodium salt of partially carboxymethylated guar gum (Na-PCMGG,  $\overline{DS} = 0.291$ ) at various monomer concentrations<sup>a</sup>

[MMA] (mol/L)	$R_p \times 10^5$ (mol/L·s)	
	MMA	MA <sup>[10]</sup>
0.072	1.52	1.87
0.144	2.13	2.40
0.216	2.77	2.91
0.289	3.08	3.24
0.360	3.41	3.82
0.433	3.87	4.07

<sup>a</sup> Reaction conditions: Na-PCMGG : 2.0 g (dry basis); [CAN] :  $4.0 \times 10^{-3}$  mol/L; [HNO<sub>3</sub>] : 0.10 mol/L; [MMA] : varied as shown; time : 4 h; temperature : 35 °C and total volume : 105 mL

**Table 3.** Rate of polymerization ( $R_p$ ) for photo-graft copolymerization of methyl methacrylate (MMA) onto sodium salt of partially carboxymethylated guar gum (Na-PCMGG,  $\overline{DS} = 0.291$ ) at various ceric ammonium nitrate (CAN) concentrations<sup>a</sup>

[CAN] × 10 <sup>3</sup> (mol/L)	$R_p \times 10^5$ (mol/L·s)	
	MMA	MA <sup>[10]</sup>
1.50	3.24	2.94
2.00	3.41	3.25
4.00	3.41	3.82
6.00	3.68	3.86
8.00	3.68	3.87
10.00	3.70	3.85
14.00	3.83	3.93
18.00	3.86	4.07
20.00	4.02	4.13

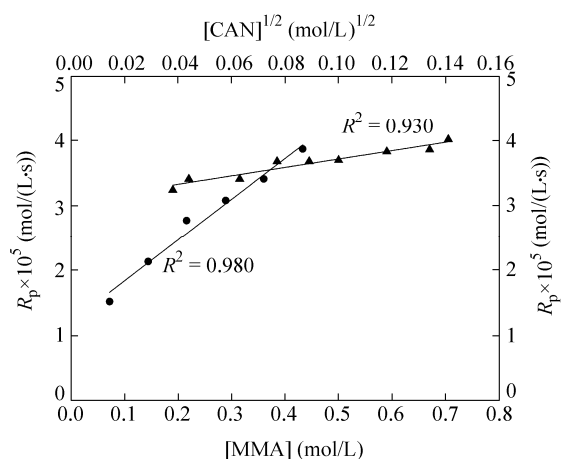
<sup>a</sup> Reaction conditions: Na-PCMGG : 2.0 g (dry basis); [CAN]: varied as shown; [HNO<sub>3</sub>] : 0.10 mol/L; [MMA] : 0.360 mol/L; time : 4 h; temperature : 35 °C and total volume : 105 mL

The effects of the concentration of the monomer (MMA) and photoinitiator (CAN) on  $R_p$ , as expected from the previous equations, are shown in Fig. 2. The plots of  $R_p$  versus the monomer concentration and  $R_p$  versus  $[Ce^{+4}]^{1/2}$  are found to be linear with good correlation coefficient, supporting the scheme.

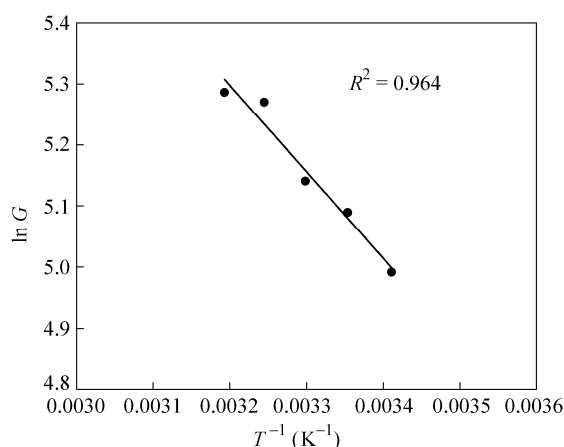
### Evaluation of Energy of Activation

As per the reaction mechanism which has been proposed in the present work the synthesis of the photo-induced free radical graft copolymer, Na-PCMGG-g-PMMA, involves mainly three steps. However, instead of calculating the activation energy ( $E_g$ ) for each of the steps involved we have also evaluated the value of the overall activation energy ( $E_g$ ) for the synthesis of the graft copolymer as evaluated by Leza *et al*<sup>[30]</sup>. The natural log of grafting ( $\ln G$ ) versus  $1/T$  was plotted for the initial portion of the curve, *i.e.* 20–40 °C [cf. Fig. 1(f)] as

shown in Fig. 3 and these values are found to fall on a straight line with good correlation coefficient value. The least square value of the overall activation energy of grafting ( $E_g$ ) was calculated and was found to be 11.78 kJ/mol (Table 4). However, we have reported earlier the overall activation energy ( $E_g$ ) in the case of photo-grafting of methyl acrylate (MA) onto Na-PCMGG ( $\overline{DS} = 0.291$ ) using CAN as a photo-initiator to be 9.88 kJ/mol<sup>[10]</sup>.



**Fig. 2** Plots of  $R_p$  (●) versus the monomer concentration and  $R_p$  (▲) versus  $[CAN]^{1/2}$



**Fig. 3** Plot of  $\ln G$  versus  $T^{-1}$ .

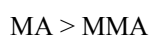
**Table 4.** Results of grafting yields ( $G$  and  $GE$ ) obtained in the case of photo-grafting of MA and MMA onto guar gum (GG) (under optimum reaction conditions derived for Na-PCMGG) and Na-PCMGG as well as the values of activation energy of grafting ( $E_g$ )

Structure	Monomer	Grafting Yields		$E_g$ (kJ/mol)	Reference
		$G$ (%)	$GE$ (%)		
GG	MA	184.67	83.42	–	10
	MMA	167.40	42.34	–	Present work
Na-PCMGG	MA	356.58	92.05	9.88	10
	MMA	271.61	63.89	11.58	Present work

Optimum Reaction Conditions for: MA: GG/Na-PCMGG (dry basis) = 1.0 g,  $[CAN] = 4.00 \times 10^{-3}$  mol/L,  $[HNO_3] = 0.20$  mol/L,  $[MA] = 0.433$  mol/L, time = 3.0 h, temperature = 35 °C and total volume = 105 mL  
 MMA: GG/Na-PCMGG (dry basis) = 0.75 g,  $[CAN] = 6.00 \times 10^{-3}$  mol/L,  $[HNO_3] = 0.05$  mol/L,  $[MMA] = 0.433$  mol/L, time = 3.0 h, temperature = 40 °C and total volume = 105 mL

### Reactivity of Methacrylates

With a view to comparing the reactivity of the methacrylates towards photo-grafting, the maximum values of the grafting yields obtained in the present case (under the evaluated optimum reaction conditions as discussed above) as well as the value of the overall activation energy ( $E_g$ ) are tabulated in Table 4 along with those reported earlier by us<sup>[10]</sup> in the case of photo-grafting of MA onto ( $\overline{DS} = 0.291$ ). It is seen (Table 4) that substantial amount of graft formation have been achieved regardless of the monomer used. However, the comparison of the results of Table 4 shows the following reactivity pattern:



With MMA, the extra  $-CH_3$  group at the vinylic position probably offers some more steric hindrance than MA. This is why MMA is less reactive than MA. Secondly, the lower value of  $E_g$  (9.88 kJ/mol) obtained in the case of MA, compared to that of MMA (11.78 kJ/mol) indicates the ease of occurrence of photo-grafting reaction as a result of which higher values of the grafting yields are observed in the case of MA compared to MMA (cf. Table 4).

The values of  $R_p$  evaluated for various monomer (MMA) concentrations, as per kinetic Eq. (4) and for various photoinitiator (CAN) concentrations, as per kinetic Eq. (5), are tabulated along with those obtained in the case of photo-grafting of methyl acrylate (MA)<sup>[10]</sup> onto Na-PCMGG (Tables 2 and 3). Upon inspection of the data (obtained within experimental limitations) tabulated in Tables 2 and 3, interestingly it becomes evident that the values of the overall rate of polymerization ( $R_p$ ) are higher in the case of photo-grafting of MA<sup>[10]</sup> compared to MMA indicating further that MA is more reactive than MMA.

#### Comparison of the Efficiency of CAN

The results of the grafting yields obtained with the photo and dark methods are depicted in Fig. 4. The grafting yields are found to be higher when the grafting of MMA was carried out onto Na-PCMGG ( $\overline{DS} = 0.291$ ) at various reaction time intervals using ultraviolet radiation, in comparison with the dark method. The observed higher grafting yields may be due to the fact that the complex, which is formed from the reaction between the functional groups of Na-PCMGG and ceric ions, may have dissociated to a greater extent in the presence of ultraviolet radiation (photo method) than in the absence of radiation (dark method), as a result of which a greater number of free radical sites may have been produced for grafting to occur with the photo method, leading to higher values of the grafting yields.

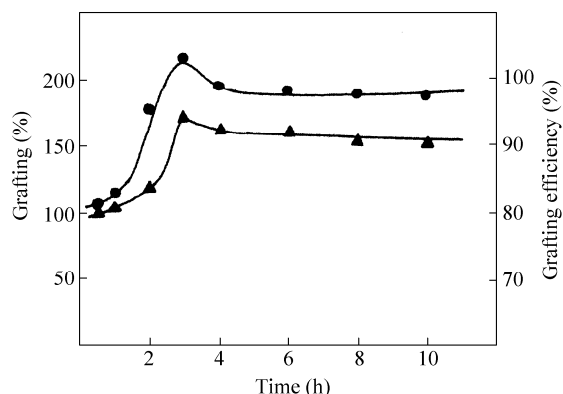


Fig. 4 <sup>1</sup>H-NMR spectrum of polymethyl methacrylate (PMMA) sample

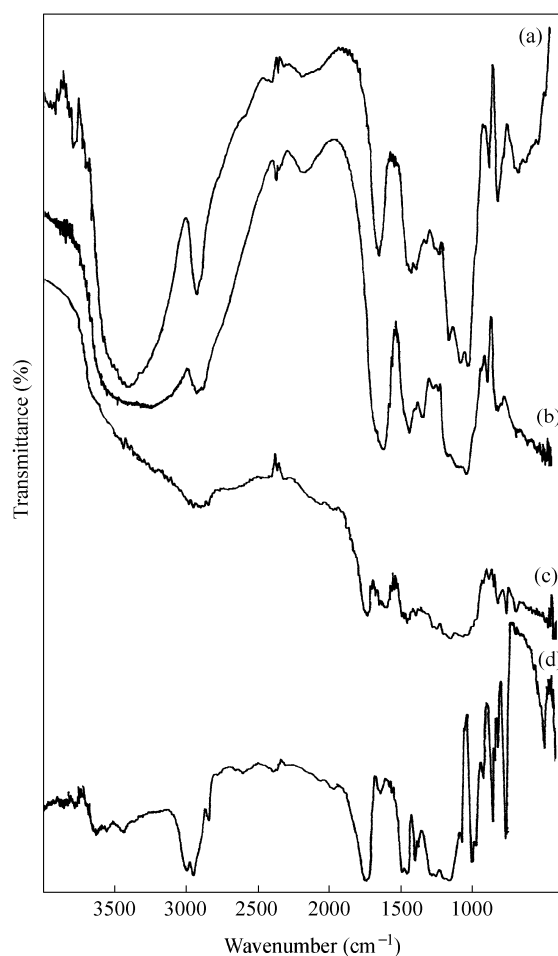
#### Effect of Substrate Structure

As shown in Table 4 the introduction of carboxymethyl groups in the GG molecule enhances the behaviour of GG towards photo-grafting of MMA. As a result of which the values of  $G$  and  $GE$  are found to be higher in the case of photo-grafting of MMA onto Na-PCMGG ( $\overline{DS} = 0.291$ ) compared to GG. This could be attributed to the combined influence of the following factors. First, the carboxymethyl groups increase the swellability of GG, thereby facilitating the diffusion of monomer (MMA) and photoinitiator (CAN); second the introduction of carboxyl groups along the GG chains introduces the negative charges which attract ceric ions to the GG molecules leading to the formation of more active sites on the GG backbone, available for the monomer (MMA), thus increasing the reactivity of GG. Similar results are also reported in the literature<sup>[10, 31, 32]</sup>.

#### Evidence of Photo-grafting

##### FTIR spectra

Figure 5 shows the IR spectrum of guar gum (spectrum a). The presence of a very strong and broad absorption band at  $\sim 3415\text{ cm}^{-1}$  is assigned to the OH stretching. Reasonably sharp absorption at  $\sim 2930\text{ cm}^{-1}$  may be attributed to the CH stretching. The absorption band appeared at  $\sim 1650\text{ cm}^{-1}$  is due to hydration of water. The  $-\text{CH}_2$  bending in GG is assigned to an absorption at  $\sim 1440\text{ cm}^{-1}$  and the band at  $\sim 1380\text{ cm}^{-1}$  is attributed to CH bending. The bending of OH is probably distributed at  $\sim 1300\text{ cm}^{-1}$  and  $\sim 1250\text{ cm}^{-1}$  frequencies.



**Fig. 5** FTIR spectra of (a) guar gum (GG), (b) Na-PCMGG, (c) Na-PCMGG-g-PMMA and (d) PMMA

The IR spectrum of Na-PCMGG ( $\overline{DS} = 0.291$ ) (Fig. 5, spectrum b) shows somewhat reduced intensity of the absorption, at  $\sim 3250 \text{ cm}^{-1}$  due to OH stretching, indicating that some of the OH groups present in GG sample were involved in carboxymethylation. The presence of a band at  $\sim 2930 \text{ cm}^{-1}$  is due to CH stretching. The band due to water (bending of water) appeared at  $\sim 1650 \text{ cm}^{-1}$  in GG sample is found to be absent in the Na-PCMGG sample. The asymmetric and symmetric vibrations due to  $-\text{COO}-$  moiety are assigned to  $1615 \text{ cm}^{-1}$  and  $1421 \text{ cm}^{-1}$  respectively. This could be attributed to the incorporation of carboxymethyl groups in guar gum.

The IR spectrum of Na-PCMGG-g-PMMA (Fig. 5, spectrum c) showed absorption bands of Na-PCMGG ( $\overline{DS} = 0.291$ ) [Fig. 5, Spectrum b] as well as an additional strong absorption band at about  $1750 \text{ cm}^{-1}$  assigned C=O stretching of the ester group ( $-\text{COOCH}_3$ ) characteristic of methacrylates. The IR spectrum of PMMA (Fig. 5, spectrum d) indicated the presence of C=O stretching at about  $1730\text{--}1750 \text{ cm}^{-1}$ . This result may be attributed to the fact that the hydrolysis of the graft copolymer gives back the grafted chains of PMMA. Thus, the results of the spectra (c) and (d) provide substantial evidence of the photo-grafting of MMA onto Na-PCMGG ( $\overline{DS} = 0.291$ ).

#### **<sup>1</sup>H-NMR Spectrum**

The <sup>1</sup>H-NMR spectrum of the hydrolyzed product (PMMA), obtained after hydrolysis of Na-PCMGG-g-PMMA is shown in Fig. 6 from which it may be inferred that the isolated product from the graft copolymer sample is PMMA. From Fig. 6, the NMR data and their assignment are shown below:

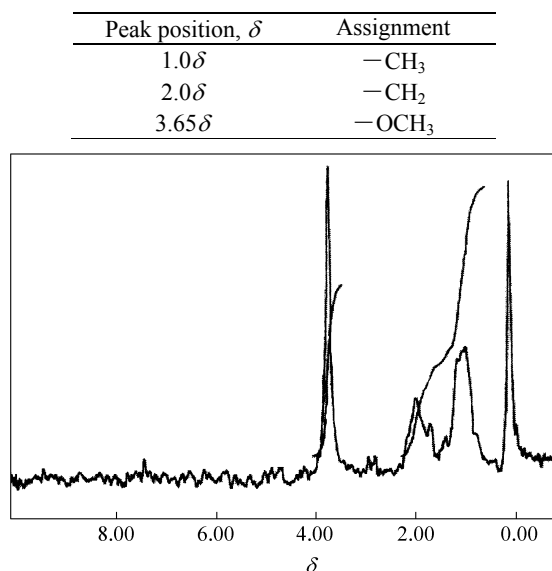


Fig. 6 Effect of reaction time on  $G$ : (●) – photo method and (▲) – dark method

Thus, the results of <sup>1</sup>H-NMR (Fig. 6) support the data obtained from IR studies thereby testifying to the existence of grafting of MMA onto Na-PCMGG ( $\overline{DS} = 0.291$ ).

#### Scanning Electron Microscopy (SEM)

The scanning electron micrograph of guar gum (Fig. 7a) shows discrete elongated granular structures separated from one another. Upon its carboxymethylation, the structure of guar gum got improved as shown in Fig. 7(b) wherein the topology of the granules was modified in such a way that some of the granules became attached by adhering themselves. However, the clustering of the granules appeared to be poor and the granules could be distinguished from one another. The surface topology of Na-PCMGG-g-PMMA ( $G = 271.61\%$ ) is shown in Fig. 7(c). Upon comparing the morphology of the grafted sample with that of the ungrafted material (Fig. 7b) it becomes evident that the lumpy morphology is observed in the case of the grafted sample, providing supportive evidence for grafting.

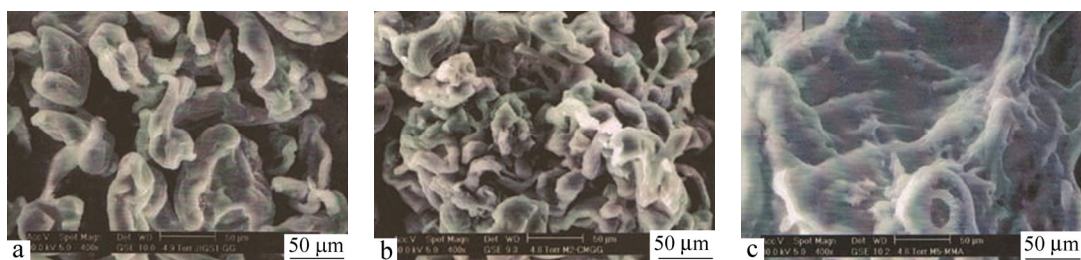


Fig. 7 Scanning electron micrographs of (a) Guar gum (400X); (b) Na-PCMGG (400X) and (c) Na-PCMGG-g-PMMA (400X).

#### CONCLUSIONS

In the present work, we have reported first time the establishment of the optimum reaction conditions in the case of photo-induced graft copolymerization of MMA onto Na-PCMGG ( $\overline{DS} = 0.291$ ) using CAN as a photo-initiator. The influence of various reaction conditions on the grafting yields has been discussed. Under the optimum reaction conditions the maximum percentage of grafting yields achieved are  $G = 271.61\%$  and  $GE = 63.89\%$ . The experimental results have been analyzed in terms of the earlier proposed kinetic scheme and are

found to be in very good agreement with it. The overall activation energy for photo-grafting is found to be 11.78 kJ/mol. The reactivity of MMA towards photo-graft copolymerization has been compared with that of MA and plausible explanation has been furnished for the observed differences in the reactivity. The evidence of photo-grafting has been ascertained by spectral ( $^1\text{H-NMR}$  and FTIR) and SEM techniques. A novel metal adsorbent can be synthesized after carrying out treatment of the optimally synthesized graft copolymer, Na-PCMGG-g-PMMA, with hydroxylamine in the presence of alkaline system. Further studies in this direction are in progress.

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