SYNTHESIS AND CHARACTERIZATION OF POLY(BUTYL METHACRYLATE) GRAFTED SODIUM SALT OF PARTIALLY CARBOXYMETHYLATED GUAR GUM

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An unreported graft copolymer of polybutyl methacrylate (PBMA) with sodium salt of partially carboxymethylated guar gum (Na-PCMGG, $\overline{DS}$ = 0.497) was synthesized using ceric ammonium nitrate (CAN) as a redox initiator. The reaction variables including concentrations of initiator, nitric acid, monomer and amount of the backbone, as well as time and temperature, were varied to establish the optimal reaction conditions. The influence of these reaction variables on the grafting yields was discussed. The kinetic scheme of free radical graft copolymerization was also proposed and the experimental results were found to agree very well with it. The reactivity of butyl methacrylate towards graft copolymerization has been compared with that reported in literature and a plausible explanation has been furnished. The graft copolymer sample was characterized by the FT-IR, SEM and TGA techniques. The synthesized graft copolymer, Na-PCMGG-g-PBMA, may find application as a tablet matrix for the release of a model drug.

Keywords: sodium salt of partially carboxymethylated guar gum, graft copolymerization, butyl methacrylate, optimum reaction conditions, characterization

INTRODUCTION

Grafting provides a significant route to alter the physical and chemical properties of the polysaccharide substrate for specific end uses. Due to the simple mechanism of electron transfer and low activation energy,[1] the Ce (IV)-induced graft copolymerization of vinyl monomers onto polysaccharide substrate is a widely used method for property modification of natural and renewable polymers.[2-3] Guar gum (GG), an industrially important natural and renewable, nonionic, rigid polymer[4] consists of a linear chain of β-D-mannopyranosyl units linked $(1\rightarrow 4)$ with single membered α-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 pharmaceutics, medicines and drugs.[5] Thus, although guar gum and its derivatives find wide range of industrial applications, they also suffer from some drawbacks, like biodegradability,[6] which considerably limit its uses. These drawbacks can be overcome by grafting vinyl monomers onto guar gum, thereby imparting new properties to the polymeric backbone. However, in the graft copolymerization reaction, the choice of the monomer, the grafting method and the carbohydrate backbone are key factors that control the properties of the final product. In this investigation, we have introduced the carboxymethyl groups in the GG molecule to increase the swellability of GG and thereby facilitate the diffusion of monomer and initiator (CAN). Besides, the ionization of carboxymethyl groups along the GG chains will introduce negative charges, which will attract ceric ions to the GG molecule, leading to the formation of more active sites on the GG backbone, thus increasing the reactivity of GG towards grafting.

Many investigations have been carried out on grafting of vinyl monomers onto guar gum using various redox pairs.[7-9] However, to the best of our knowledge, there are no reports on the modification of sodium salt of partially carboxymethylated guar gum (Na-PCMGG) via grafting. We have already reported the grafting of methyl acrylate (MA),[10] acrylonitrile (AN),[11] methyl methacrylate (MMA),[12] ethyl methacrylate (EMA)[13] and butyl acrylate (BA)[14] onto Na-PCMGG ($\overline{DS}$ = 0.497) using ceric ammonium nitrate (CAN) as a redox initiator. We have also used CAN as a photoinitiator and successfully grafted MMA onto Na-PCMGG ($\overline{DS}$ = 0.291).[15] However, a comprehensive literature survey reveals that recently three different grades of graft copolymers of carboxymethyl guar gum containing poly(acrylamide) have been synthesized by varying the concentration of ceric ammonium nitrate and have been tested for flocculation performance.[16] The synthesis and solution properties of graft copolymers based on carboxymethyl guar backbone, bearing poly(N-isopropylacrylamide) have also been reported.[17] The grafting of 4-vinyl pyridine,[18] N-N'-dimethylacrylamide,[19] 2-acrylamidoglycolic acid,[20] N-vinyl-2-pyrrolidone[21] and methacrylic acid[22] onto partially carboxymethylated guar gum have also been studied, using different initiating systems, viz. potassium bromate/thiourea, potassium peroxymonosulphate/thiourea, potassium peroxymonosulphate/glycolic acid and potassium peroxymonosulphate/silver nitrate. However, the use of these different initiating systems provided an appreciable amount of the corresponding homopolymer (generally in the range of 29%-55%) during graft copolymerization of the respective monomers onto partially carboxymethylated guar gum. On the contrary, as seen in the present work, the use of ceric ion for graft copolymerization, leads to the minimum formation of homopolymer because the grafting is generally considered to result from propagation of radical sites generated on the polymeric substrate. Recently, the optimization of the reaction conditions for the carboxymethylation of guar gum and the characterization of the resulting products have been reported.[23]

In the present study, the optimal reaction conditions, for grafting of butyl methacrylate (BMA) onto Na-PCMGG ($\overline{DS}$ = 0.497) using a ceric-ion-induced solution polymerization technique, have been evaluated. The influence of various reaction parameters on the grafting yields has been discussed. Poly(butyl methacrylate) is an important class of hydrophobic polymers, which exhibit a low glass-transition temperature, allowing deformation and compaction of the grafted particles, which can be used in the formation of a tablet matrix for the release of a model drug;[24] this has encouraged us to graft it onto Na-PCMGG. The spectroscopic (IR), SEM and thermal (TGA) methods have been used to characterize the samples. This investigation has been carried out not only to get a good understanding of the kinetics and mechanism of grafting, but also to develop specialty polymeric materials.

EXPERIMENTAL

Materials and methods

Guar gum (GG) was kindly supplied by H. B. Gum Industries Pvt. Ltd, Kalol (Gujarat/India). The methods of preparation and purification, as well as the measurement of the degree of substitution ($\overline{DS}$) of the sodium salt of partially carboxymethylated guar gum (Na-PCMGG) were carried out as described earlier.[11] The $\overline{DS}$ of Na-PCMGG was found to be 0.497. Butyl methacrylate (BMA) (Aldrich) was purified by vacuum distillation and the middle fraction was used. Ceric ammonium nitrate and analar grade nitric acid (both Qualigens, Glaxo India Ltd.) were used without purification. All other reagents and solvents used in the present work were of reagent grade. The nitrogen gas was purified by passing through fresh pyrogallol solution. Low conductivity water was used for preparing the solutions, as well as for polymerization reactions.

Graft copolymerization

A 500 mL three-necked flask equipped with a stirrer, a reflux condenser and a gas inlet system was immersed in a constant temperature bath for grafting reactions. In a typical reaction, a varying amount (0.5-3.0 g, dry basis) of Na-PCMGG ($\overline{DS}$ = 0.497) was dissolved in low conductivity water (100 mL) with constant stirring and bubbling a slow stream of nitrogen gas for 1 h at the desired temperature (15 °C to 55 °C). A freshly prepared 10 mL solution of CAN (5×10^{-3} M to 8×10^{-2} M) in nitric acid (nil to 1.0 M) was added and stirred for 20 min. Nitrogen gas was continuously passed through the reaction solution and freshly distilled BMA (0.05 M to 0.70 M) was added. The grafting reactions were carried out at different time intervals (0.5 h to 10 h). After completion of the reaction, the mixture was immediately poured into the excess of methanol. The crude copolymer product was filtered, repeatedly washed with nitric acid, as well as 95% methanol, and finally washed with pure methanol. The crude copolymer thus obtained was dried to

constant weight in a vacuum oven at 40 °C. The coprecipitated ungrafted homopolymer was extracted with acetone in a soxhlet apparatus for 48 h to extract the polybutyl methacrylate (PBMA) from the crude graft copolymer. After the complete removal of the homopolymer, the pure graft copolymer was also dried at 40 °C under vacuum to a constant weight.

Isolation of grafted chains

The graft copolymer of Na-PCMGG ($\overline{DS}$ = 0.497) containing PBMA was hydrolyzed by refluxing it for 12 h in 1 N HCl, as suggested by Brockway[25] for the isolation of the grafted PBMA chains.

IR Spectroscopy

IR spectra of Na-PCMGG ($\overline{DS}$ = 0.497), Na-PCMGG-g-PBMA and PBMA were taken in KBr pellets, using a Nicolet impact 400D Fourier Transform Infra Red Spectrophotometer.

Thermogravimetric Analysis (TGA)

The thermal behaviour of Na-PCMGG ($\overline{DS}$ = 0.497), Na-PCMGG-g-PBMA (%G = 156.96) and PBMA has been examined in an inert atmosphere at a heating rate of 10 °C/min with the help of the Dupont 951 thermogravimetric analyzer.

Scanning Electron Microscopy (SEM)

Model ESM TMP + EDAX, Philips, has been used to obtain the micrographs of Na-PCMGG ($\overline{DS}$ = 0.497) and Na-PCMGG-g-PBMA.

Grafting yields and kinetic parameters

The grafting yields viz. percentage of grafting (%G), percentage grafting efficiency (%GE) and percentage of homopolymer (%H_p), as well as the kinetic parameters, viz. the rates of polymerization (R_p) and graft copolymerization (R_g), were evaluated using the following expressions:[26]

$$\%\ G = \frac{\text{Wt. of Polymer Grafted}}{\text{Initial Wt. of backbone}} \times 100 \quad (1)$$

$$\%\ GE = \frac{\text{Wt. of Polymer Grafted}}{\text{Wt. of Polymer Grafted + Wt. of Homopolymer}} \times 100 \quad (2)$$

$$\%\ H_p = 100 - \%\ GE \quad (3)$$

$$R_p\ (\text{mol.L}^{-1}.\text{s}^{-1}) = \frac{\text{Weight of Polymer Grafted + Weight of Homopolymer}}{\text{Mol.wt.of monomer x Reaction time (sec) x Vol. of the reaction mix.(ml)}} \times 10^3 \quad (4)$$

$$R_g\ (\text{mol.L}^{-1}.\text{s}^{-1}) = \frac{\text{Weight of Polymer Grafted}}{\text{Mol.wt.of monomer x Reaction time (sec) x Vol. of the reaction mix.(ml)}} \times 10^3 \quad (5)$$

RESULTS AND DISCUSSION

Determination of optimal reaction conditions

The optimal reaction conditions for maximum percentage of grafting of BMA onto Na-PCMGG ($\overline{DS}$ = 0.497) have been evaluated by varying various reaction parameters.

Effect of backbone concentration

Fig. 1 shows the effect of backbone concentration on the grafting yields. It is observed from this figure that the value of %G decreases very rapidly in the beginning up to Na-PCMGG = 1.5 g, but thereafter it decreases very slowly and almost levels off. However, the value of %GE increases slowly up to Na-PCMGG = 1.5 g, beyond which it decreases and also levels off at Na-PCMGG = 2.5 g. The results depicted in 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 monomer to backbone ratio lowers down the %G rapidly up to Na-PCMGG = 1.5 g, but beyond this value the extent of decrease in %G is observed to be at a slow rate, due to the slower addition of grafted PBMA side chains, compared to the amount of Na-PCMGG increased. However, the observed decrease in %GE beyond Na-PCMGG = 1.5 g is due to the simultaneous formation of homopolymer during the course of reaction. Similar results are also reported in the literature.[10, 11, 20, 27, 28]

Effect of initiator concentration

The influence of initiator concentration on the grafting yields is represented in Fig. 2. It becomes evident from this figure that %G increases within the CAN concentration range of 0.005-0.06 mol/L and reaches a maximum value of % G = 198.71% at Ce^{+4} = 0.06 mol/L and thereafter it decreases with further increase in initiator concentration. On the other hand, %GE remains almost constant initially, but decreases beyond [Ce^{+4}] = 0.05 mol/L. Upon increasing the concentration of the

initiator up to 0.06 mol/L, the value of %G increases, which is due to an increase in the active sites formed on the polysaccharide chains. The observed decrease in %G and %GE at higher CAN concentration is a well-known phenomenon and is attributed to the increasing participation of the ceric ions in the termination of the growing grafted chains.[29] Secondly, at higher concentration of the initiator, the complex formation between the monomer and ceric ion assumes predominance over that between Na-PCMGG and ceric ion. This would favour the homopolymer formation at the cost of grafting. Also, since more and more of the monomer is utilized in the complex formation, the Na-PCMGG macroradicals do not find enough monomer in its vicinity to produce graft. Similar observations are also reported in the literature.[10, 30-36]

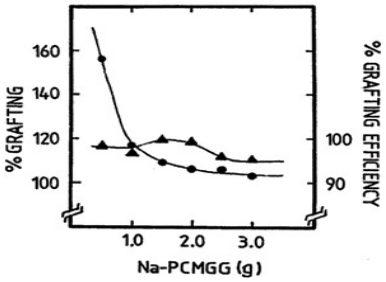


Figure 1: Effect of Na-PCMGG amount on: (●) - %G; or (▲) - %GE

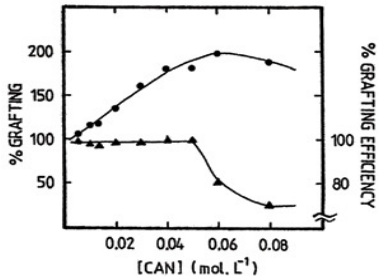


Figure 2: Effect of ceric ammonium nitrate concentration on: (●) - %G; or (▲) - %GE

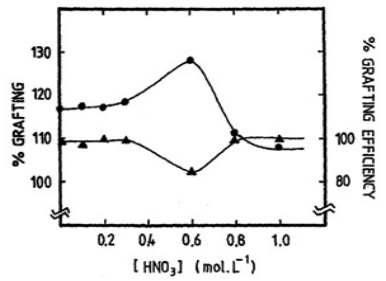


Figure 3: Effect of nitric acid concentration on: (●) - %G; or (▲) - %GE

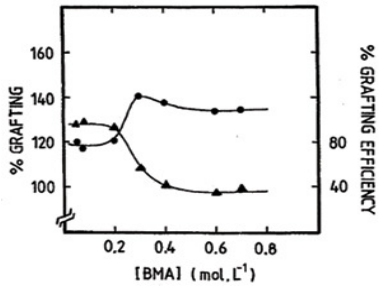


Figure 4: Effect of butyl methacrylate (BMA) concentration on: (●) - %G; or (▲) - %GE

Effect of nitric acid concentration

Fig. 3 represents the effect of nitric acid concentration on the grafting yields. As reported earlier, [10-13] in the present case, at zero concentration of acid a high value of %G is observed. With the increase in acid concentration, the value of %G increases and reaches a maximum value at $[HNO_3]$ = 0.60 mol/L, beyond which it decreases. On the other hand, %GE initially remains constant up to $[HNO_3]$ = 0.30 mol/L, beyond which it decreases up to the optimum concentration of the acid and then increases with further increase in acid concentration, followed by leveling off its value. The observed increase in %G is attributed to the formation of a complex between ceric-ion species, i.e. Ce^{+4} and $[Ce(OH_3)]^{+3}$, and Na-PCMGG. The observed decrease in %G is due to the reduction of the complex formation, as well as increase in the polymer termination rates. Similar results are also reported in the literature.[27,37-39]

Effect of monomer concentration

The dependence of the grafting yields on the monomer concentration is reflected in Fig. 4. It can be seen from this figure that %G initially remains constant up to [BMA] = 0.20 mol/L, but thereafter, it increases and reaches a maximum value of 140.79% at [BMA] = 0.30 mol/L. The enhancement of grafting by increasing the monomer concentration could be attributed to the greater availability of grafting sites on Na-PCMGG macroradicals to monomer molecules. However, with further increase in monomer concentration, %G decreases. On the other hand, %GE also remains constant up to [BMA] = 0.20 mol/L, but beyond that concentration it decreases. The observed decrease in %G and %GE, beyond

the optimum monomer concentration, is attributed to the formation of homopolymer by the combination and disproportionation reactions of the PBMA macroradicals. Further, the formation of more homopolymer results in an increase in the viscosity of the reaction medium, thereby restricting the mobility of the growing polymeric chains to the active sites and hence a decrease in grafting is observed. Similar results are also reported in the literature.[33]

Effect of reaction time

The effect of reaction time on the grafting yields is demonstrated in Fig. 5. It is evident from this figure that %G increases with the increase in reaction time and reaches a maximum value of 128% within 3 h, which is due to the increase in the number of active sites on the polysaccharide backbone. After the optimum value, i.e. 3 h, %G decreases because of the depletion in monomer and initiator concentrations, as well as shortage of the available grafting sites. However, the value of %GE does not change appreciably over the reaction time studied. Similar results are also reported in the literature.[35]

Effect of temperature

One of the important reaction parameters is temperature, which plays a key role in every graft copolymerization reaction. In the present study, graft copolymerization reaction has been investigated in the temperature range from 15 °C to 55 °C, while keeping other parameters constant. The influence of temperature on the grafting yields is shown in Fig. 6. It is evident from this figure that the percentage of grafting remains almost constant with the rise in temperature from 15 °C to 35 °C, but beyond 35 °C, it increases and attains the optimum value at 45 °C, and then decreases with a further rise in temperature. The value of %GE also remains almost constant up to 35 °C and then decreases up to 45 °C and increases with further increase in temperature. Variation of %G with temperature, in the temperature range of 15 °C to 45 °C, is due to the fact that with the initial rise in temperature, the kinetic energy of the molecules increases, more and more radicals move with faster rate to the Na-PCMGG backbone, resulting in the increase in %G. However, after reaching the optimum temperature, with further increase in temperature, a considerable amount of homopolymer is formed, which results in an increase in the viscosity of the reaction mixture and it provides a hindrance for the radicals to move toward the actives sites of the Na-PCMGG backbone, resulting in the decrease in percent grafting. Secondly, at higher temperature, the substantial increase in the rate of chain transfer and chain termination reactions between grafted chains and monomer molecules would also lead to the observed decrease in grafting. Similar results are also reported in the literature.[10,11,18,40]

Effect of liquor ratio

The effect of liquor ratio on %G is tabulated in Table 1. It can be seen from this table that there is a continuous increase in %G from 102.95% to 156.33%, at a slower rate with the increase in the liquor ratio from 50 to 300 mL soln per g Na-PCMGG, except for the liquor ratio value of 75. This observation can be attributed to 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.

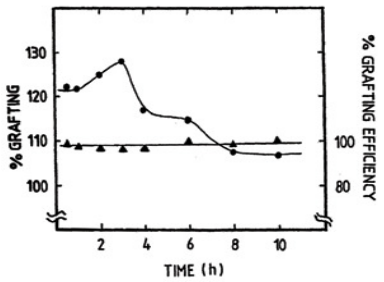


Figure 5: Influence of reaction time on: (●) - %G; or (▲) - %GE

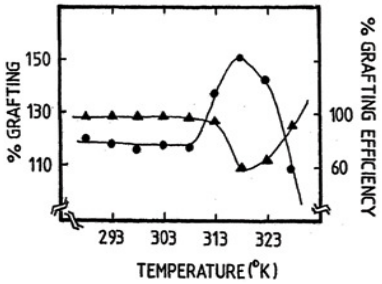


Figure 6: Influence of temperature on: (●) - %G; or (▲) - %GE

Table 1
Effect of liquor ratio on % grafting of butyl methacrylate onto sodium salt of partially carboxymethylated guar gum (Na-PCMGG, $\overline{DS}$ = 0.497)[a]

Liquor ratio mL soln/g Na-PCMGG	% Grafting (% G)
300:1	156.33
150:1	117.20
100:1	109.03
75:1	106.19
60:1	106.67
50:1	102.95

[a]mL soln per g Na-PCMGG = varied as shown; [CAN] = 0.013 mol/L; [HNO_3] = 0.10 mol/L; [BMA] = 0.075 mol/L; Time = 4 h; Temperature = 35 °C; Volume of water = 138.20 mL; Total volume = 150 mL

The optimized reaction conditions thus evaluated in the present case of graft copolymerization of BMA are: Na-PCMGG ($\overline{DS}$ = 0.497) = 1.5 g (dry basis), [CAN] = 0.06 mol/L, [HNO_3] = 0.60 mol/L, [BMA] = 0.30 mol/L, Time = 3 h, Temperature = 45 °C, Total volume = 150 mL.

Kinetics and mechanism

There are reactive groups like hydroxyl and carboxylate anion in Na-PCMGG. These groups form a complex with ceric-ion and the complex may dissociate giving rise to free radical sites onto Na-PCMGG.

The mechanism of free radical graft copolymerization of BMA onto Na-PCMGG ($\overline{DS}$ = 0.497) is expected to proceed according to the following proposed scheme:[10]

(i) Radical generation:

$$X\text{-}H + Ce^{+4} \underset{}{\overset{K}{\rightleftharpoons}} [Complex] \xrightarrow{k_d} X^{\bullet} + Ce^{+3} + H^{+} \quad (6)$$

(ii) Initiation:

$$X^{\bullet} + M \xrightarrow{k_i} XM^{\bullet} \quad (7)$$

$$Ce^{+4} + M \xrightarrow{k_i'} M^{\bullet} + Ce^{+3} + H^{+} \quad (8)$$

(iii) Propagation:

$$XM^{\bullet} + nM \xrightarrow{k_p} XM^{\bullet}_{n+1} \quad (9)$$

$$M^{\bullet} + nM \xrightarrow{k_p'} M^{\bullet}_{n+1} \quad (10)$$

(iv) Termination: two types of termination may take place:

(a) At lower Ce^{+4} concentrations, the growing chain is terminated by the recombination of double radicals:

$$XM^{\bullet}_n + XM^{\bullet}_n \xrightarrow{k_{t_1}} \text{dead polymer} \quad (11)$$

$$M^{\bullet}_m + M^{\bullet}_m \xrightarrow{k'_{t_1}} \text{dead polymer} \quad (12)$$

$$XM^{\bullet}_n + M^{\bullet}_m \xrightarrow{k''_{t_1}} \text{dead polymer} \quad (13)$$

(b) At higher Ce^{+4} concentration, the growing chain is terminated by a single radical:

$$XM^{\bullet}_n + Ce^{+4} \xrightarrow{k_{t_2}} XM_n + Ce^{+3} + H^{+} \quad (14)$$

$$M^{\bullet}_m + Ce^{+4} \xrightarrow{k'_{t_2}} M_m + Ce^{+3} + H^{+} \quad (15)$$

(v) Oxidation:

$$X^{\bullet} + Ce^{+4} \xrightarrow{k_0} \text{oxidation products} + Ce^{+3} + H^{+} \quad (16)$$

where X – H denotes the reactive groups of Na-PCMGG, M is the monomer, K is the equilibrium constant, and k_d, k_i, k_i', k_p, k_p', k_{t_1}, k'_{t_1}, k''_{t_1}, k_{t_2}, k'_{t_2} and k_o are the rate constants of the respective reactions. It is assumed that $k_p = k_p'$, $k_{t_1} = k'_{t_1} = k''_{t_1}$ and $k_{t_2} = k'_{t_2}$.

For the case of double radical termination, assuming a steady state, the rate of graft copolymerization, R_g:

$$R_g = \frac{k_p k_d^{0.5} K}{k_{t_1}^{0.5}} \times \frac{[X-H][M][Ce(IV)]^{0.5}}{k_d K[X-H] + k_i[M]^{0.5}} \quad (17)$$

The rate of homopolymerization R_h is:

$$R_h = \frac{k_p k_i'}{k_{t_1}^{0.5}} \times \frac{[M]^2\,[Ce(IV)]^{0.5}}{\left(k_d K[X-H] + k_i[M]\right)^{0.5}} \quad (18)$$

and the total rate of polymerization, R_p would be:

$$R_p = R_g + R_h \quad (19)$$

Similarly, for the case of single radical termination:

$$R_g = \frac{k_p k_d K}{k_{t_2}} \times \frac{[M]^2 [X - H]}{[M] + (k_o / k_i)[Ce(IV)]} \quad (20)$$

$$R_h = \frac{k_p k_i'}{k_{t_2}} \times [M]^2 \quad (21)$$

$$R_p = R_g + R_h = \frac{k_p}{k_{t_2}} [M]^2 \left\{ \frac{k_d K [X - H]}{[M] + (k_o/k_i)[Ce(IV)]} + k_i' \right\} \quad (22)$$

The data given in Tables 2 and 3 satisfy the equations discussed above. The effect of the concentration of CAN on R_g can be understood from the data presented in Table 2. The plot of R_g versus $[CAN]^{0.5}$ should be linear at lower [CAN], according to Eq. 17. Such a type of typical plot is shown in Fig. 7; it is seen that the plot is linear at lower [CAN], which agrees with termination by recombination of double radicals (Eq. 17), but at higher [CAN], the plot deviates from linearity. This may be due to single radical termination (Eq. 20), which decreases the rate of graft copolymerization.

Katai *et al.*[41] reported that $k_o/k_i = 50$ for the study of the ethylene glycol acrylonitrile system and further stated that k_o is in general considerably larger than k_i. Accordingly, one can write:

$$(k_o/k_i)[Ce^{+4}] >> [M] \quad (23)$$

and hence Eqs. (20) and (22) are reduced to:

$$R_g = \frac{k_p k_d K}{k_{t_2}} \times \frac{[M]^2 [X - H]}{(k_o/k_i)[Ce(IV)]} \quad (24)$$

and, respectively,

$$R_p = \frac{k_p}{k_{t_2}} [M]^2 \left\{ \frac{k_d K[X - H]}{(k_o/k_i)[Ce(IV)]} + k'_i \right\} \quad (25)$$

The effect of the concentration of BMA as well as that of initiator [CAN], on the overall rate of polymerization (R_p) is shown in Fig. 8 and the plots of R_p versus $[M]^2$ (keeping [Ce(IV)] constant) and R_p versus $1/[Ce^{+4}]$ (keeping [M] constant) are found to be linear, supporting the above scheme.

Reactivity of methacrylates

With a view to compare the reactivity of the methacrylates towards grafting, the maximum values of the grafting yields obtained in the present case (under the optimum reaction conditions discussed above) are tabulated in Table 4, along with those reported earlier by us[12,13] in the case of grafting MMA and EMA onto Na-PCMGG ($\overline{DS}$ = 0.497). The results (Table 4) show that, under the optimal conditions, the reactivity of methacrylates towards grafting follows the order: MMA > EMA > BMA.

Thus, the relative reactivity of the methacrylates towards grafting decreases with the increase in the alkyl group length starting from MMA to EMA and BMA. The increase in the alkyl group length increases the steric hindrance, leading to the reduced accessibility of the larger methacrylates to the macroradical centers (active sites) on the polysaccharide backbone. Thus, being a highly crowded monomer, compared to EMA and MMA, BMA forms a complex with Ce^{+4} less readily, and accordingly affords the least %G (cf. Table 4).

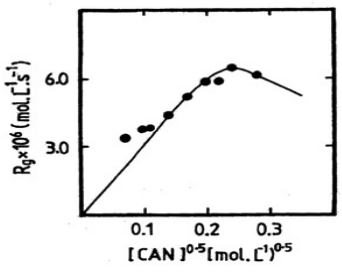


Figure 7: Plot of (●) R_g x10^6 versus $[CAN]^{0.5}$

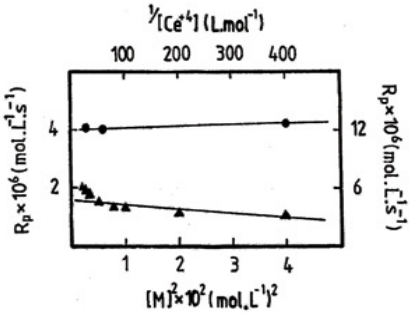


Figure 8: Plots of (●) R_p x 10^6 versus $[M]^2$ and (▲) R_p x 10^6 versus $1/[Ce^{+4}]$

Table 2
Rates of graft copolymerization (R_g) and polymerization (R_p) for grafting of BMA onto Na-PCMGG ($\overline{DS}$ = 0.497) at various initiator concentrations[a]

[CAN] X 10^3	R_p X 10^6 (mol. $L^{-1}.s^{-1}$)	R_g X 10^6 (mol. $L^{-1}.s^{-1}$)
5.0	3.44	3.40
10.0	3.87	3.78
13.0	3.95	3.82
20.0	4.45	4.40
30.0	5.32	5.23
40.0	5.86	5.85
50.0	5.93	5.88
60.0	8.07	6.47
80.0	8.69	6.12

Na-PCMGG ($\overline{DS}$ = 0.497) = 1.0 g (dry basis); [CAN] = varied as shown; [HNO_3] = 0.10 mol/L; [BMA] = 0.075 mol/L; Time = 4 h; Temperature = 35 °C; Volume of water = 138.20 mL; Total volume = 150 mL

Table 3
Rate of polymerization (R_p) for grafting of BMA onto Na-PCMGG ($\overline{DS}$ = 0.497) at various monomer concentrations[a]

[BMA] (mol. L^{-1})	R_p X 10^6 (mol. $L^{-1}.s^{-1}$)
0.050	4.08
0.075	4.03
0.200	4.21

[a]Na-PCMGG ($\overline{DS}$ = 0.497) = 1.0 g (dry basis); [CAN] = 0.013 mol/L; [HNO_3] = 0.10 mol/L; [BMA] = varied as shown; Time = 4 h; Temperature = 35 °C; Volume of water = 138.20 mL; Total volume = 150 mL

Table 4
Maximum values of grafting yields obtained for grafting methacrylates onto sodium salt of partially carboxymethylated guar gum (Na-PCMGG, $\overline{DS}$ = 0.497) under optimum reaction conditions[a-c]

Monomer	% Grafting (%G)	%Grafting efficiency (%GE)	%Homopolymer (%H_p)	Reference
MMA	172.38	97.15	2.85	12
EMA	164.75	98.19	1.81	13
BMA	156.96	83.85	16.15	Present work

Optimum reaction conditions for: (a) MMA:Na-PCMGG ($\overline{DS}$ = 0.497) = 1.0 g (dry basis), [CAN] = 0.03 mol/L; [HNO_3] = 0.20 mol/L; [MMA] = 0.222 mol/L; Time = 4 h; Temperature = 25 °C and Total volume = 150 mL; (b) EMA:Na-PCMGG ($\overline{DS}$ = 0.497) = 1.0 g (dry basis), [CAN] = 0.02 mol/L; [HNO_3] = 0.30 mol/L; [EMA] = 0.074 mol/L; Time = 4 h; Temperature = 25 °C and Total volume = 150 mL; (c) BMA:Na-PCMGG ($\overline{DS}$ = 0.497) = 1.5 g (dry basis), [CAN] = 0.06 mol/L; [HNO_3] = 0.60 mol/L; [BMA] = 0.30 mol/L; Time = 3 h; Temperature = 45 °C and Total volume = 150 mL

Characterization

Infrared (IR) spectra

IR spectra of Na-PCMGG ($\overline{DS}$ = 0.497) [Fig. 9 (a)] and its graft copolymer, Na-PCMGG-g-PBMA [Fig. 9 (b)] are compared to confirm grafting. The IR spectrum of Na-PCMGG-g-PBMA showed absorption bands of Na-PCMGG and an additional strong band at ~1730 cm^{-1} due to C=O stretching of the ester group (-$COOCH_3$), characteristic of the methacrylates. Moreover, this graft copolymer was also hydrolyzed in order to isolate the PBMA grafted chains. The IR spectrum of PBMA [Fig. 9 (c)] also showed the presence of C=O stretching at ~1730 cm^{-1}. This is

due to the fact that hydrolysis of the graft copolymer gives back polybutyl methacrylate (PBMA). The IR spectrum of PBMA also provided substantial evidence of grafting of BMA onto Na-PCMGG ($\overline{DS}$ = 0.497).

Scanning Electron Microscopy (SEM)

The SEM technique is considered to be an effective tool to study the surface topology of different kinds of polymers. A comparative study of the scanning electron micrographs of Na-PCMGG ($\overline{DS}$ = 0.497) [Fig. 10 (a)] and Na-PCMGG-g-PBMA (%G = 156.96) [Fig. 10 (b)] have been used as supportive evidence of grafting. The comparison of the micrographs showed distinct morphological differences in their surface topology, indicating that grafting had taken place.

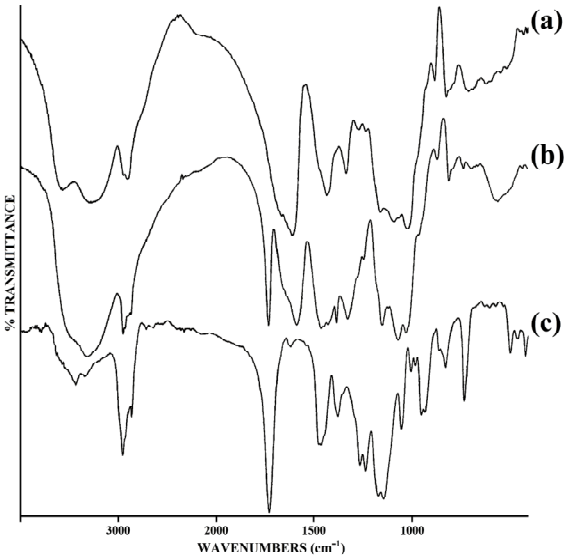
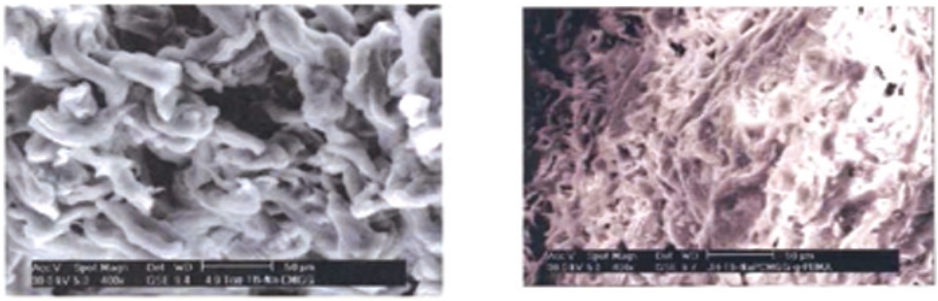


Figure 9: IR spectra of (a) Na-PCMGG ($\overline{DS}$ = 0.497), (b) Na-PCMGG-g-PBMA (%G = 156.96) and (c) polybutyl methacrylate (PBMA) samples

Thermogravimetric Analysis (TGA)

Fig. 11 shows the primary thermograms obtained at a scan rate of 10 °C/min for Na-PCMGG ($\overline{DS}$ = 0.497), Na-PCMTGG-g-PBMA (%G = 156.96) and PBMA in an inert atmosphere. It is seen from this figure that the single step degradation of Na-PCMGG begins at 160 °C and proceeds at a faster rate up to 270 °C with 45% loss in its original weight. However, beyond this temperature, degradation proceeds at a very slow rate up to 570 °C. This temperature range (i.e. 270-570 °C) involves about 18% weight loss. With further increase in temperature, the degradation is found to occur at a relatively faster rate up to 700 °C, compared to the degradation proceeded in the earlier temperature range. The temperature at which the maximum rate of weight loss occurs is 265 °C. The overall degradation leaves about 14.5% residue. The overall thermal degradation of Na-PCMGG-g-PBMA (%G = 156.96) involves only a single step of degradation. The degradation begins at 190 °C and proceeds slowly up to 405 °C, when the degradation is complete, leaving about 28% residual weight. In the case of PBMA (Fig. 11), the overall degradation involves two steps. The first step, encompassing the temperature range 210-290 °C, involves about 67.5% weight loss, the rate of weight loss reaching a maximum at 265 °C. This step is immediately followed by the second step, involving about 30% weight loss over the temperature range 210-480 °C with a maximum rate of weight loss at 345 °C. The sample leaves only about 2 wt% residue.



(a) (b)

Figure 10: Scanning electron micrographs of (a) Na-PCMGG ($\overline{DS}$ = 0.497) (400X) and (b) Na-PCMGG-g-PBMA (%G = 156.96) (400X) samples

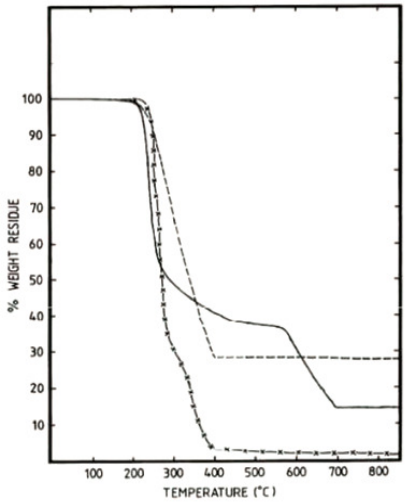


Figure 11: TG thermograms for (—) Na-PCMGG ($\overline{DS}$ = 0.497); (—x—) Na-PCMGG-g- PBMA (%G = 156.96) and (- --) PBMA at 10 ^{o}C/min

Table 5
Thermogravimetric analysis of Na-PCMGG ($\overline{DS}$ = 0.497), Na-PCMGG-g-PBMA (% G = 156.96) and PBMA samples

Sample	T_i ^{o}C (IDT)	T_f ^{o}C (FDT)	T_{max} (^{o}C)		T_{10}	T_{50}	IPDT[a] (°C)
			Step-1	Step-2	(°C)	(°C)	
Na-PCMGG	160	700	265	–	230	295	436.75
Na-PCMGG-g-PBMA	190	405	305	–	250	340	513.08
PBMA	210	480	265	345	245	270	304.26

[a]IPDT = A^{*} (T_f - T_i) + T_i, where A^{*} is the fractional area under the thermogravimetric curve normalized with respect to residual weight, T_f and T_i are the temperatures of completion of weight loss and initiation of weight loss, respectively.

The values of the temperature characteristics, as well as the integral procedural decomposition temperature (IPDT) of Na-PCMGG ($\overline{DS}$ = 0.497), Na-PCMGG-g-PBMA (%G = 156.96) and PBMA, are tabulated in Table 5. The values of IPDT indicate that the overall thermal stability of Na-PCMGG ($\overline{DS}$ = 0.497) has been increased upon grafting of BMA onto it. The results of TGA

(Fig. 11 and Table 5) thus also provide additional evidence of grafting.

CONCLUSION

Grafting of BMA has been successfully carried out onto Na-PCMGG ($\overline{DS}$ = 0.497), using CAN as a redox initiator, and the optimum reaction conditions have been evaluated by successively varying various reaction parameters. The influence of these parameters on the grafting yields has been discussed. Under the optimum reaction conditions, the maximum percentages of the grafting yields achieved are %G = 156.96 and %GE = 83.85. The reactivity of BMA towards graft copolymerization has been compared with that reported for grafting of other methacrylates (MMA and EMA) and the results are found to be consistent. A plausible explanation has been provided for the observed differences in the reactivity of methacrylates towards grafting. The results of the effect of liquor ratio on percent grafting indicated that the value of %G decreases with the decrease in the liquor ratio. The experimental results are found to be in good agreement with the earlier proposed kinetic scheme. Various analytical techniques, such as FTIR, SEM and TGA confirmed the grafting of poly(butyl metacrylate) on the Na-PCMGG chains.

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