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GRAFTING OF BUTYL ACRYLATE ONTO SODIUM SALT OF PARTIALLY CARBOXYMETHYLATED GUAR GUM USING CERIC IONS

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ABSTRACT

The graft copolymerization of butyl acrylate (BA) onto sodium salt of partially carboxymethylated guar gum (Na-PCMGG, $\overline{DS}$ = 0.497) has been carried out using ceric ammonium nitrate (CAN) as a redox initiator in an aqueous medium. The optimal reaction conditions have been evaluated by successively varying reaction conditions viz. amount of the backbone, concentrations of initiator, nitric acid and monomer as well as reaction time and temperature. The influence of various reaction conditions on the grafting yields have also been discussed. The experimental results have been analyzed according to the kinetics scheme of graft copolymerization proposed earlier and results are found to be in very good agreement. The reactivity of butyl acrylate toward graft copolymerization has been compared with that of literature data reported in the case of other vinyl monomers and plausible explanation has been furnished.TGA/DSC techniques have been used to study the thermal behaviour of Guar Gum, Na-PCMGG, $\overline{DS}$ = 0.497), Na-PCMGG-g-PBA and PBA samples and the results are discussed. The spectroscopic (IR) and Scanning Electron Microscopy (SEM) methods have been used to prove grafting.

Key words: *Sodium salt of Partially Carboxymethylated Guar Gum, Butyl Acrylate, Graft Copolymerization, Infrared Spectroscopy (IR), Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) and SEM*

INTRODUCTION

Grafting reactions provide a potential route for significantly altering the physical and the chemical properties of a substrate polymer to specific end uses. Modification of guar gum properties by graft copolymerization of vinyl monomers using different initiating systems have been the subject of research for the last decade [1-6]. However, the data on grafting of vinyl monomers onto sodium salt of partially carboxymethylated guar gum (Na-PCMGG) are scanty. As a part of our comprehensive research programme we have, therefore, successfully carried out the modification of Sodium salt of Partially Carboxymethylated Guar Gum (Na-PCMGG, $\overline{DS}$ = 0.497) by grafting of methyl acrylate (MA) [7], acrylonitrile (AN) [8], methyl methacrylate (MMA) [9] and ethyl methacrylate (EMA) [10] using ceric ammonium nitrate (CAN) as a redox initiator. We have also used CAN as a photoinitiator and successfully grafted MMA onto Na-PMGG ($\overline{DS}$= = 0.291) [11]. Recently, we have also compared the reactivity of different vinyl monomers towards grafting [12] and studied the effects of substrate structure and liquor ratio on percentage grafting [13] using the optimum reaction conditions established for affording maximum percentage of grafting of different vinyl monomers onto Na-PCMGG ($\overline{DS}$ = 0.497).

In the present investigation, we report the evaluation of the optimal reaction conditions for affording maximum percentage of grafting in the case of grafting of butyl acrylate (BA) onto Na-PCMGG ($\overline{DS}$ = 0.497) using CAN as a redox initiator and the results regarding characterization of the graft copolymer sample by IR, SEM and TGA/DSC techniques. This has been done not only to arrive at a good understanding of the kinetics and mechanism of grafting but also to obtain the basic information needed for the improvement of the products.

EXPERIMENTAL

Materials

Guar Gum (GG) was kindly supplied by H.B. Gum Industries Pvt. Ltd.; Kalol (Gujarat/India). The method of preparation and purification as well as the measurement of degree of substitution ($\overline{DS}$) of the Na-PCMGG were followed as described earlier [14-15]. The $\overline{DS}$ of Na-PCMGG sample was found to be 0.497. Butyl acrylate (BA) (Chiti-Chem. Corpn; Baroda, Guajarat State, India) was purified by extracting with aqueous sodium hydroxide solution and dried over sodium sulfate. The stabilizer free monomer was distilled and the middle fraction was used. Ceric Ammonium Nitrate and analar grade nitric acid (both Qualigens, Glaxo India Ltd.) were used without further 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. The low conductivity water was used for the preparation of solutions as well as for polymerization reactions.

Graft Copolymerization

A 500 mL three-necked flask equipped with mechanical stirrer, reflux condenser and a glass inlet-system was immersed in a constant temperature bath for grafting reactions. In a typical reaction, varying amount (0.5g to 3.0g, 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 1h at the desired temperature (15^0C to 50^0C). Freshly prepared 10 mL solution of CAN (1.0 X 10^{-2} M to 8.0 X 10^{-2} M) in nitric acid (nil to 0.8 M) was added and stirred for 20 min. Nitrogen gas was continuously passed through the reaction solution and freshly distilled BA (0.075 M to 0.70 M) was added. The grafting reactions were carried out for varying time intervals (0.5h to 10h). After the completion of the reaction, the mixture was immediately poured into 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 40^0C.

Extraction of Homopolymer

The coprecipitated ungrafted homopolymer, was extracted with acetone, in a soxhlet apparatus, for 48h to extract polybutylacrylate (PBA) from the crude graft copolymer. After complete removal of homopolymer, the pure graft copolymer was dried at 40^0C under vacuum to a constant weight.

Isolation of Grafted Chains

The graft copolymer of Na-PCMGG ($\overline{DS}$ = 0.497) containing PBA was hydrolyzed by refluxing it for 12h in 1N

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HCl as suggested by Brockway [16]. After all the Na-PCMGG went into the solution, resinous mass was obtained which was characterized by IR spectroscopy as PBA.

IR Spectroscopy

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

Thermogravimetric Analysis (TGA)

The thermal behavior of Guar Gum, Na-PCMGG ($\overline{DS}$ = 0.497), Na-PCMGG-g-PBA and BA has been examined in an inert atmosphere at a heating rate of 10^0C/min with the help of the Dupont 951 thermogravimetric analyzer.

Differential Scanning Calorimetry (DSC)

The DSC scans of Guar Gum, Na-PCMGG ($\overline{DS}$ = 0.497), Na-PCMGG-g-PBA and PBA have been recorded in nitrogen atmosphere at a scan rate of 10^0C/min on DSC 2920 TA instrument.

Scanning Electron Microscopy (SEM)

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

Grafting Yields and Kinetic Parameters

The grafting yields viz. percentage of grafting (%G) and percentage grafting efficiency (%GE) as well as the kinetic parameters viz. the rates of polymerization (R_p), graft copolymerization (R_g) and homopolymerization (R_h) were evaluated by using expressions as reported earlier [17].

RESULTS AND DISCUSSION

In the study of ceric ion-induced grafting of butyl acrylate (BA) onto Na-PCMGG ($\overline{DS}$ = 0.497), various reaction conditions were used to discover those optimum for grafting. The reaction conditions studied included amount of Na-PCMGG, concentrations of ceric ammonium nitrate (CAN), nitric acid (HNO_3) and monomer (BA) as well as reaction time and temperature.

Effect of Backbone concentration

The influence of backbone concentration on the grafting yields is represented in Fig. 1. It can be seen from this figure that %G consistently decreases with the increasing amount of Na-PCMGG but the value of %GE remains almost constant over the whole range of Na-PCMGG studied. The observed variation in % G could be attributed to the fact that even though with the increase in Na-PCMGG concentration the weight of the grafted side chains may increase but the decrease in the monomer-to-backbone ratio lowers %G. In addition to this, large number of Na-PCMGG macroradicals interact with each other to terminate the reaction as a result of which the termination rate of graft copolymerization becomes faster compared to that of initiation thereby also lowering %G. Similar results are also reported in the case of grafting of butyl acrylate onto gelatin [18], acrylonitrile onto sodium alginate [19] as well as onto sodium salt of partially carboxymethylated guar gum [8].

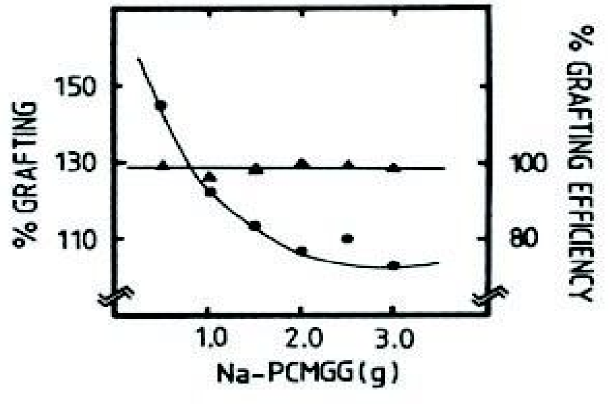

Figure 1: Effect of amount of Na PCMGG on : (●) - %G and (▲) - %GE

Effect of Initiator Concentration

Fig. 2 shows the influence of the initiator concentration on the grafting yields. The value of %G increases with increasing ceric-ion concentration and reaches a maximum value of 186.38 at $[Ce^{+4}]$ = 0.06 mol/L but with further increase in $[Ce^{+4}]$, % G decreases. However, the value of %GE remains almost constant over the whole range of initiator concentration studied. The observed increase in %G within the initiator concentration range of 0.01-0.06 mol/L may be due to the fact that within this concentration range the increasing concentration of ceric ions results in an increase in the total number of the complex Na-PCMGG-ceric ions which decompose to give more active sites on the backbone upon which grafting of BA takes place. Beyond $[Ce^{+4}]$ = 0.06 mol/L, the observed decrease in %G is attributed to the fact that 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 leading to the formation of homopolymer at the cost of grafting. Similar results are also observed in the literature [10, 19-21].

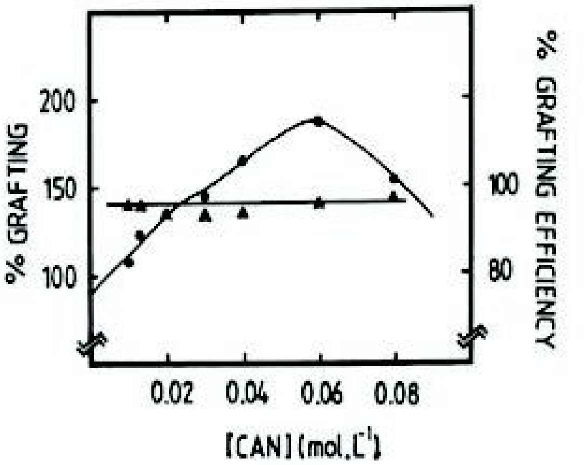

Figure 2: Effect if ceric ammonium nitrate concentration on : (●) - %G and (▲) - %GE

Effect of Nitric acid Concentration

The effect of nitric acid concentration on the grafting yields is shown in Fig. 3. Even at the zero concentration of nitric acid interestingly higher value of grafting is observed which is due to the fact that even in the absence of acid in an aqueous medium Na-PCMGG swells to a greater extent making the functional groups of Na-PCMGG more accessible towards grafting. As seen from this figure there exists an optimum concentration of $[HNO_3]$ = 0.2 M. Beyond this optimum value, the value of %G decreases and approaches the value which is even lower than in the absence of acid. The ceric-ion exists as Ce^{+4}, $[Ce(OH)_3]^{+3}$ and $[Ce\text{-}O\text{-}Ce]^{+6}$ in an aqueous solution and the concentrations of these species vary with the concentration of acid. The species like Ce^{+4} and $[Ce(OH)_3]^{+3}$ having smaller sizes facilitate the formation of a complex with Na-PCMGG resulting in an increase in %G as observed in Fig. 3. However, beyond the optimum concentration in addition to these species, an abundance of hydrogen protons which are generated at higher acid concentration accelerate the termination of growing grafted chains resulting in a decrease in %G as evidenced in Fig. 3. Moreover, ceric ion leads to the oxidative termination of the growing monomeric chains as per the following reaction [22-25]:

$$Ce^{+4} + Mn \longrightarrow Ce^{+3} + Mn + H^{+}$$

as a result of which also the decrease in %G is observed beyond the optimum concentration.

Effect of Monomer Concentration

The effect of butyl acrylate concentration on the grafting yields is shown in Fig. 4. It can be seen from this figure that with an increase in the monomer concentration the value of percentage grafting increases and reaches a maximum value of 128.44% at [BA] = 0.3 mol/L. However, further increase in monomer concentration leads to a decrease in %G. On the other hand the value of %GE decreases very slowly upto the optimum concentration of the monomer and remains almost constant with further increase in the monomer concentration. The observed decrease in %G with increasing monomer concentration could be ascribed to the greater availability of grafting sites to monomer. However, the decreasing trend of %G beyond [BA] = 0.3 mol/L is due to the competition between the homopolymerization and grafting where the former prevails over the latter at higher monomer concentration. In addition to this the excess monomer will also shield the graft copolymer radicals which are formed leading to inhibition of the rate of graft copolymerization. Similar results are also reported in the case of grafting of MMA onto silk fibers [26] as well as onto sodium salt of partially carboxymethylated guar gum [9].

Effect of Reaction Time

The results of Fig. 5 show the effect of the reaction time on the grafting yields. It can be observed from this figure that a value of 104.68% has been obtained for percentage grafting during first half an hour but thereafter the value increases up to a maximum of 125.36% within 2h. The increase in %G is due to the increase in the number of grafting sites on the Na-PCMGG backbone as reaction progresses. However, beyond the optimum value of reaction time i.e.2h, the value of %G decreases which is attributed to the depletion of monomer and initiator as well as shortage of the available grafting sites. When the reaction progresses, as observed from this figure the %G increases, even though the value of %GE decreases upto 2h because homopolymer is still forming. However, after 2h it is found to be increased up to 3h beyond which it almost levels off.

Fig. 6 represents the plot of log%G versus log(time) from which it can be seen that %G increases linearly for the first 2h, beyond which it decreases indicating that 2h is the optimum time for grafting.

Effect of Temperature

Fig. 7 represents the results regarding the influence of temperature on the grafting yields. As it can be seen from this

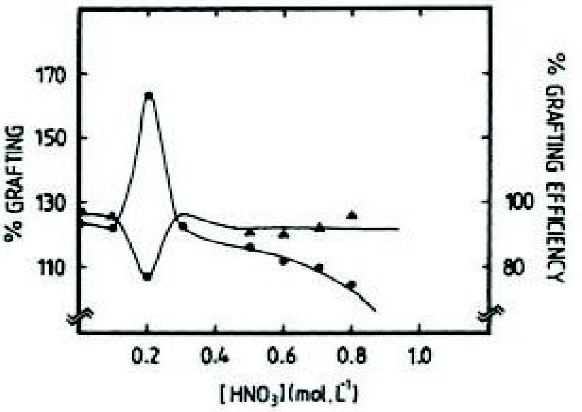

Figure 3: Effect of nitric acid concentration on : (●) - %G and (▲) - %GE

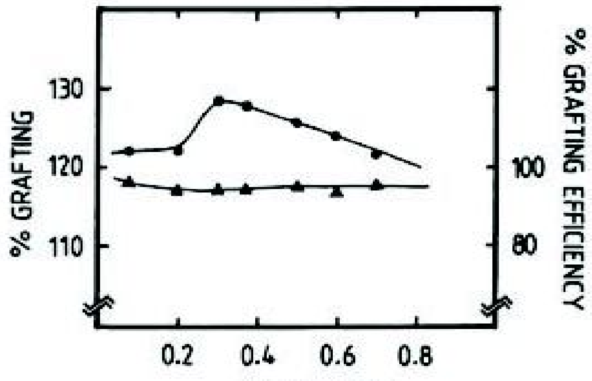

Figure 4: Effect of Butyl Acrylate (BA) concentration on: (●) - %G and (▲) - %GE

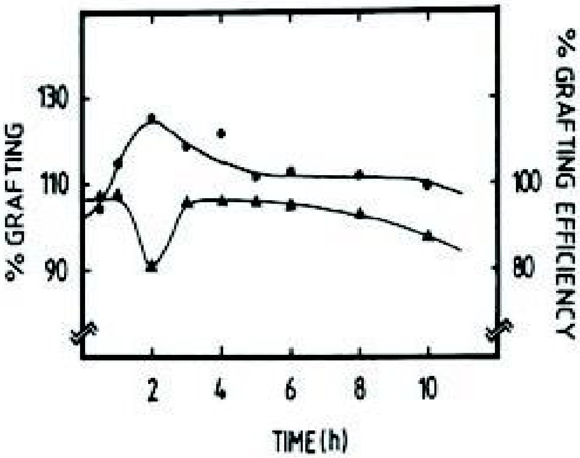

Figure 5: Influence of reaction time on : (●) - %G and (▲) - %GE

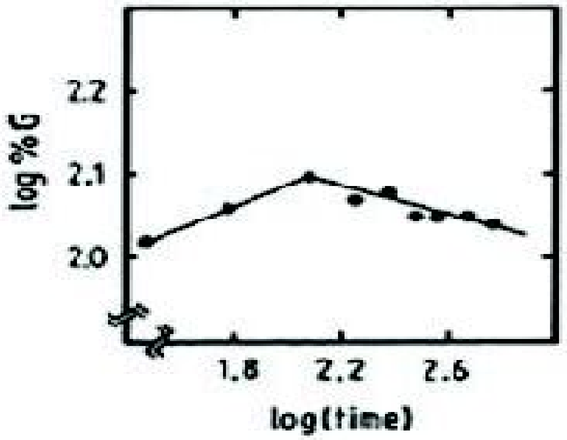

Figure 6: Plot of log %G versus log (time)

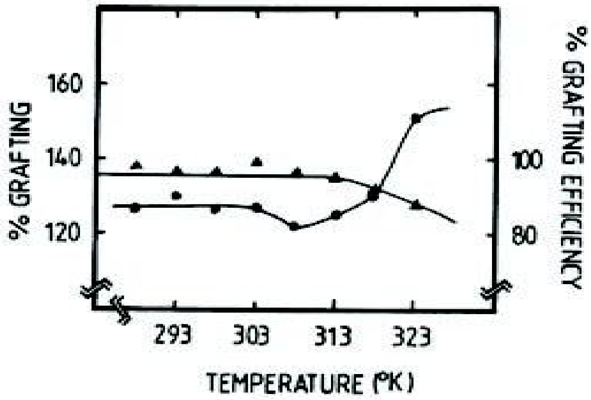

Figure 7: Influence of temperature on : (●) - %G and (▲) - %GE

figure that %G remains almost constant up to 30°C and then decreases slowly up to 35°C beyond which it increases continuously up to 50°C. On the other hand %GE remains almost constant from the very beginning up to 40°C and then decreases very slowly with further rise in temperature. The observed increase in percentage grafting beyond 35°C can be attributed to the faster decomposition of Na-PCMGG-Ceric complex so that more active sites are generated on the backbone leading to the increase in the rates of initiation and propagation of grafting. However, the observed decrease in %GE beyond 40°C could be ascribed to the fact that at higher temperature graft copolymerization occurs with poor selectivity.

Effect of Liquor Ratio

The results regarding the influence of liquor ratio on %G are tabulated in Table 1. It can be observed from this table that there is a continuous increase in %G from 102.50% to 144.68%, at a slower rate with the increase in the liquor ratio from 50 to 300 ml. soln./g. Na-PCMGG, except for the liquor ratio value 75. This observation can be explained on the basis of the fact that as the value of the liquor ratio decreases, the viscosity of medium increases which, in turn, hinders the movement of free radicals thereby decreasing %G. Thus, from the above discussion the optimized reaction conditions evaluated in the graft copolymerization of BA are : Na-PCMGG ($\overline{DS}$ = 0.497) = 2.0 g (dry basis); [CAN] = 0.06 mol/L; [HNO_3] = 0.20 mol/L; [BA] = 0.30 mol/L; Time = 2h; Temperature; = 40°C; Volume of Water = 133.55 ml; and Total Volume = 150 mL.

Table 1 : Effect of Liquor ratio on % grafting of butyl acrylate (BA) onto Sodium salt of Partially Carboxymethylated Guar Gum (Na-PCMGG,

Liquor ratio mL soln./g, Na - PCMGG	%Grafting (%G)
300 :1	144.68
150 : 1	121.99
100 : 1	113.07
75 : 1	106.52
60 : 1	109.84
50 : 1	102.50

[a] mL solution per g Na-PCMGG = Varied as shown; [CAN] = 0.013 mol/L; [HNO_3] = 0.10 mol/L; [BA] = 0.075 mol/L; Time = 4 h; Temperature = 35°C; Volume of Water = 138.40 mL; Total Volume = 150 mL.

KINETICS AND MECHANISM

The hydroxyl groups and carboxylate anions which are present in Na-PCMGG form a complex with ceric-ions and the complex may dissociate giving rise to free radicals onto Na-PCMGG. The mechanism of free radical graft copolymerization of BA onto Na-PCMGG ($\overline{DS}$ = 0.497) is expected to proceed according to the scheme, which has been proposed earlier by us [27]. The present experimental results, as tabulated in Tables 2 and 3, have been treated in light of the proposed kinetic scheme and accordingly the plot of R_g versus $[CAN]^{0.5}$ should be linear at lower [CAN]. Such type of typical plot obtained in the present case is shown in Fig. 8 which is found to be linear at lower [CAN], indicating that termination takes place by recombination of double radicals.

However, the plot deviates from linearity at higher initiator concentration further indicating that the termination occurs by single radical leading to the decrease in the rate of graft copolymerization. The influence of the concentration of the monomer (BA) as well as that of the initiator (CAN) on the overall rate of polymerization (R_p) as expected from the relationship derived earlier [27] is exemplified in Fig. 9. As evident, the plots of R_p versus $[M]^2$ and R_p versus $1/[Ce]^{+4}$ are found to be linear for the present case, supporting the proposed kinetic scheme [27].

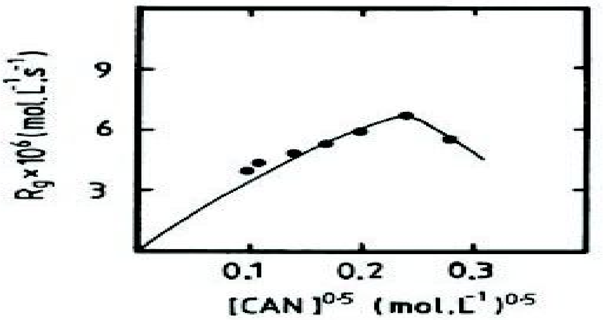

Figure 8: Plot of (●) R_g x 10^6 versus $[CN]^{0.5}$

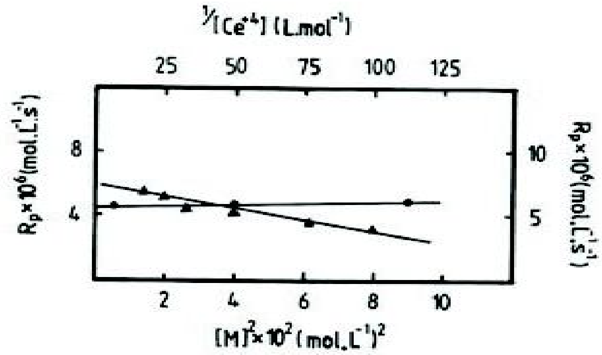

Figure 9: Plots of (●) R_p x 10^6 versus $[M]^2$ ad (▲) R_p x 10^6 versus $1/[Ce^{-4}]$

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

[CAN] X 10^3 ($mol.L^{-1}$)	R_p X 10^6 ($mol.L^{-1}.s^{-1}$)	R_g X 10^6 ($mol.L^{-1}.s^{-1}$)
10.0	4.06	3.90
13.0	4.57	4.41
20.0	5.19	4.88
30.0	5.56	5.26
40.0	6.31	5.96
60.0	7.00	6.73
80.0	5.71	5.54

[a] Na-PCMGG ($\overline{DS}$ = 0.497) = 1.0 g (dry basis), [CAN] = Varied as shown; [HNO_3] = 0.10 mol/L; [BA] = 0.075 mol/L; Time = 4h; Temperature = 35°C; Volume of water = 138.40 mL and Total volume = 150 mL.

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

[BA] ($mol.L^{-1}$)	R_p X 10^6 ($mol.L^{-1} s^{-1}$)
0.075	4.57
0.200	4.71
0.300	4.93

[a] Na-PCMGG ($\overline{DS}$ = 0.497) = 1.0 g (dry basis), [CAN] = 0.013 mol/L; [HNO_3] = 0.10 mol/L; [BA] = Varied as shown; Time = 4h; Temperature = 35°C; Volume of water = 138.40 mL and Total volume = 150 mL.

REACTIVITY OF VINYL MONOMERS

The maximum values of the grafting yields evaluated in the present case, under the evaluated optimum reaction conditions as discussed above, are tabulated in Table 4 along with those obtained in the case of grafting of MA and MMA onto Na-PCMGG ($\overline{DS}$= 0.497) earlier [7, 9] with a view to compare the reactivity of different vinyl monomers towards grafting. The perusal of the results of Table 4 shows the reactivity of different vinyl monomers varies towards grafting as per the following order :

MA > MMA > BA

With MMA, the extra $-CH_3$ at the vinylic position probably offers some more steric hindrance than MA and this is why MMA is found to be less reactive than MA. In the case of BA, the butyl group attached to the ester moiety offers greater steric hindrance making it less reactive than MMA towards grafting onto Na-PCMGG ($\overline{DS}$ = 0.497).

EVIDENCE OF GRAFTING

IR spectra of Na-PCMGG ($\overline{DS}$ = 0.497) and its graft copolymer, Na-PCMGG-g-PBA (not shown) have been compared to ascertain grafting. The IR spectrum of Na-PCMGG-g-PBA showed absorption bands of Na-PCMGG as well as an additional strong absorption band at ~1730 cm^{-1} assigned to C=O stretching of ester group ($-COOCH_3$), characteristic of the methacrylates. Moreover, the graft copolymer was hydrolyzed in order to isolate grafted PBA chains and the IR spectrum (not shown) of it showed the presence of C=O stretching at ~1730 cm^{-1} indicating that hydrolysis of the graft copolymer gives back butyl acrylate. This also provides a substantial evidence of grafting of BA onto Na-PCMGG ($\overline{DS}$ = 0.497).

Fig. 10 and 11 represent the scanning electron micrographs of Na-PCMGG ($\overline{DS}$ = 0.497) and Na-PCMGG-g-PBA respectively. Upon comparison of the scanning electron micrograph of Na-PCMGG-g-PBA (Fig. 11) with that of the ungrafted sample (Fig. 10) it is clearly evident that the grafted chains (PBA) have drastically changed the topology of the sample Na-PCMGG indicating that grafting has taken place.

Table 4 : Maximum values of the grafting yields obtained in the case of grafting of different vinyl monomers onto Sodium salt of Partially Carboxymethylated Guar Gum (Na-PCMGG, $\overline{DS}$ = 0.497) under the optimum reaction conditions^{a-c}.

Monomer	%Grafting (%G)	%Grafting Efficiency (%GE)	Reference
MA	206.00	85.99	7
MMA	172.38	97.15	9
BA	150.15	82.51	Present Work

Optimum Reaction Conditions for :

(a) MA :
Na-PCMGG ($\overline{DS}$ = 0.497) = 0.5 g (dry basis), [CAN] = 0.06 mol/L; [HNO_3] = 0.40 mol/L; [MA] = 0.147 mol/L; Time = 3h; Temperature = 30^{0}C; Volume of water = 138 mL and Total volume = 150 mL.

(b) 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 = 4h; Temperature = 25^{0}C; Volume of water = 136.45 mL and Total volume = 150 mL.

(c) BA:
Na-PCMGG ($\overline{DS}$ = 0.497) = 2.0 g (dry basis), [CAN] = 0.06 mol/L; [HNO_3] = 0.20 mol/L; [BA] = 0.30 mol/L; Time = 2h; Temperature = 40^{0}C; Volume of water = 133.55 mL and Total volume = 150 mL.

Thermogravimetric Analysis (TGA)

Fig. 12 represents the primary thermograms for Guar Gum and Na-PCMGG ($\overline{DS}$ = 0.497), obtained at a scan rate of 10^{0}C/min in an inert atmosphere. The overall degradation of Guar Gum (Fig. 12) involves only single step. The sample begins to decompose at 175^{0}C, rapidly loses 60% of its weight up to 285^{0}C. Beyond 285^{0}C, the weight loss is slow and gradual up to about 700^{0}C, leaving 16% residual weight. In the temperature range 285^{0}C-700^{0}C, the sample loses 24% of its original weight. The maximum rate of weight loss occurs at 275^{0}C. It can be further seen from this figure that the single step degradation of Na-PCMGG sample begins at 160^{0}C and proceeds at a faster rate up to 270^{0}C and the sample loses 45% of its original weight at this temperature. However, beyond this temperature degradation proceeds at a very slow rate up to 570^{0}C. This temperature range (i.e. 270-570^{0}C) involves about 18% weight loss. With further increase in temperature, the degradation is found to occur at a relatively fast rate up to 700^{0}C, compared to the degradation found to be proceeded in the earlier temperature range. The temperature at which the maximum rate of weight loss occurs is 265^{0}C. The overall degradation leaves about 14.5% residue. Figure 13 represents the primary thermograms obtained for Na-PCMGG (DS = 0.497), Na-PCMGG-g-PBA (%G = 150.15) and PBA at a scan rate of 10^{0}C/min in an inert atmosphere. It is evident from this figure that the overall degradation of Na-PCMGG-g-PBA exhibits two steps. The sample begins to

Fgure 10 : Scanning Electron Micrograph of Na-PCMGG ($\overline{DS}$ = 0.497) 400K)

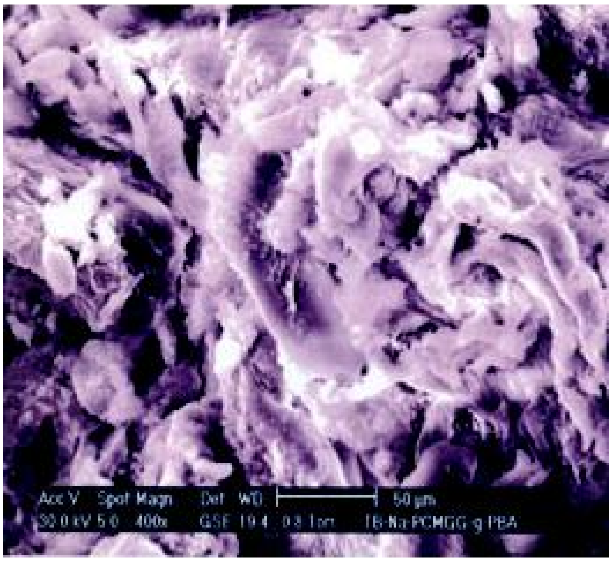

Figure 11 : Scanning Electron Micrograph of Na-PCMGG-g-PBA (%=150.15%) (400X)

decompose at about 130^{0}C and loses its weight very rapidly up to 310^{0}C during which the sample loses 45% of its weight. The second decomposition step is immediately followed and found to be proceeded with a slow rate up to 420^{0}C involving about 31% weight loss. The maximum rates of weight loss for the first and second decomposition steps are 245^{0}C and 350^{0}C respectively. The degradation is completed at about 420^{0}C leaving behind about 23% residual weight. On the other hand in the case of PBA, the overall degradation exhibits only single step which commences from 180^{0}C, followed by a very slow decrease in weight upto 315^{0}C. Beyond 315^{0}C, there is a steep weight loss involving about 69% upto 375^{0}C, with a maximum rate of weight loss at 345^{0}C. With further increase in temperature beyond 375^{0}C, the degradation proceeded slowly up to 490^{0}C. The sample leaves about 4.5% char yield.

The temperature characteristic values as well as the Integral Procedural Decomposition Temperature (IPDT) values of Guar Gum, Na-PCMGG ($\overline{DS}$ = 0.497), Na-PCMGG-g-PBA (%G = 150.15) and PBA are tabulated in Table 5. The examination of IPDT values indicates that the overall thermal stability of Guar Gum has been increased upon its carboxymethylation which may be due to the introduction of the polar groups into guar gum leading to the increased inter-molecular and intra-molecular interactions which ultimately imparts higher thermal stability to it. However, the observed decrease in the thermal stability of the graft copolymer i.e. Na-PCMGG-g-PBA compared to Na-PCMGG (DS = 0.497) is attributed to the tendency of the polyacrylates to undergo depolymerization upon pyrolysis [28].

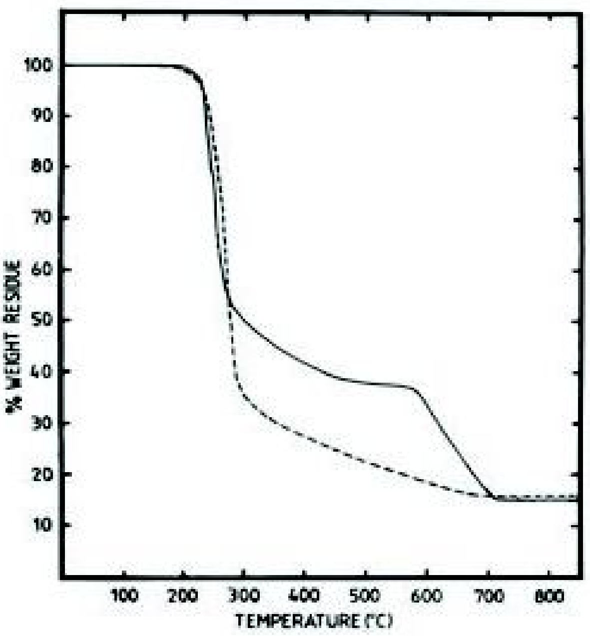

Figure 12 : TG thermograms for (- - -) Guar Gum and (-) Na-PCMGG ($\overline{DS}$ = 0.497)

Table 5 : Thermal Analysis of Guar Gum, Na-PCMGG ($\overline{DS}$ = 0.497), Na-PCMGG-g-PBA (%G = 150.15) and PBA samples.

Sample	Thermogravimetric Analysis Data							Transition Data from DSC	
	T_i ^{0}C (IDT)	T_f ^{0}C (FDT)	T_{max}		T_{10} (^{0}C)	T_{50} (^{0}C)	IPDT (^{0}C)	T_1 (^{0}C)	T_2 (^{0}C)
			Step 1	Step 2					
Guar Gum	175	700	275	-	240	275	401.33	145.15 (endo)	308.44 (exo)
Na-PCMGG	160	700	265	-	230	295	436.75	177.50 (endo)	282.18 (exo)
Na-PCMGG -g-PBA (%G = 150.15)	130	420	245	350	215	315	271.95	133.70 (endo)	269.44 (exo)
PBA	180	490	345	-	305	345	314.29	-	-

Differential Scanning Calorimetry

The transition temperature data of Guar Gum, Na-PCMGG ($\overline{DS}$ = 0.497), Na-PCMGG-g-PBA (%G = 150.15) and PBA samples obtained from their respective DSC thermograms (not shown) are also tabulated in Table 5. It can be observed from the results of this table that Guar Gum shows an endothermic peak at 145.15^{0}C and an exothermic peak at 308.44^{0}C. The observed endothermic peak may be due to the melting of guar gum and the exothermic peak is due to the decomposition of it. On the other hand for the case of Na-PCMGG sample the endothermic transition appeared at 177.50^{0}C and the exothermic transition observed at 282.18^{0}C are attributed respectively to the melting and the decomposition of the sample. The endothermic peak observed at 133.70^{0}C and the exothermic transition appeared at 269.44^{0}C in the case of the Na-PCMMGG-g-PBA sample is attributed to the gross melting and the decomposition of the sample. It is interesting to note that the DSC studies in comparison with TGA results also confirm the decrease in the thermal stability of Na-PCMGG due to grafting of BA onto it.

CONCLUSIONS

The optimized reaction conditions have been evaluated successfully in the case of grafting of butylacrylate onto Na-PCMGG ($\overline{DS}$ = 0.497) using CAN as a redox initiator. The effect of various reaction conditions on the grafting yields has been discussed. The experimental results are found to be in very good agreement with the kinetic scheme proposed earlier. The reactivity of BA towards grafting has been compared with other monomers and the plausible explanation has been furnished. TGA/DSC techniques have been used to characterize Guar Gum as well as Na-PCMMGG ($\overline{DS}$ = 0.497) and its graft copolymer (Na-PCMGG-g-PBA) and the results are discussed. The overall thermal stability of Guar Gum has been increased upon its carboxymethylation but it is decreased upon grafting of BA onto Na-PCMMG ($\overline{DS}$ = = 0.497). DSC studies also confirm about the decrease in the thermal stability of Na-PCMGG upon grafting of BA onto it. The evidence of grafting has been successfully ascertained by the spectroscopic (IR) and SEM techniques.

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References

[1] Bihari, K., Tripathi, M. and Taunk, K. (1999) Cu^{+2}/mandelic acid redox pair initiated graft copolymerization acrylamide onto guar gum. *Journal of Applied Polymer Science*, **71:** 739-745.

[2] Bihari, K., Tripathi, M., Taunk, K. and Kumar, R. (2000) Studies of graft copolymerization of acrylamide onto guar gum using peroxydiphosphate–metabisulphite redox pair. *Polymer International*, **49:** 153-157.

[3] Srivastava,A. and Bihari, K. (2007) Synthesis, Characterization and Study of Metal Ion Sorption Capacity and Water Swelling Behavior of Xanthan Gum-g-N,N'-Dimethylacrylamide. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, **44:** 453-462.

[4] Taunk,K. and Behari, K. (2000) Graft copolymerization of acrylic acid onto guar gum. *Journal of Applied Polymer Science*, **77:** 39-44.

[5] Bihari, K., Kumar, R., Tripathi, M. and Pandey, P. (2001) Graft Copolymerization of Methacrylamide onto Guar Gum using a Potassium Chormate/Malonic Acid Redox Pair *Macromolecular Chemistry and Physics*, **202:** 1873-1877.

[6] Chowdhury, P., Samui, S., Kundu, T. and Nandi, M. (2001) Graft polymerization of methyl methacrylate onto guar gum with ceric ammonium sulfate/dextrose redox pair. *Journal of Applied Polymer Science,* **82:** 3520-3525.

[7] Trivedi, J., Kalia, K., Patel, N. and Trivedi, H. (2005) Modification of Sodium salt of Partially Carboxymethylated Guar Gum by Graft Copolymerization with Methyl Acrylate. *Polymers and Polymer Composites***, 13:** 301-312.

[8] Trivedi, J., Kalia, K., Patel, N. and Trivedi, H. (2005) Ceric-Induced Grafting of Acrylonitrile onto Sodium salt of Partially Carboxymethylated Guar Gum. *Carbohydrate Polymers*, **60:** 117-125.

[9] Trivedi, J., Kalia, K., Patel, N. and Trivedi, H. (2005) Graft Copolymerization of Sodium Salt of Partially Carboxymethylated Guar Gum with Methyl Methacrylate: An examination of Reaction Variables. *Journal of Applied Polymer Science,* **96:**1855-1864.

[10] Trivedi, J., Kalia, K., Patel, N. and Trivedi, H. (2008) Grafting of Ethyl Methacrylate onto Sodium salt of Partially Carboxymethylated Guar Gum by Tetravalent Cerium Ion. *Journal of Polymer Materials,* **25:** 541-555.

[11] Thakar, M. and Trivedi, H. (2005) Ultraviolet-radiation-induced graft copolymerization of methyl acrylate onto the sodium salt of partially carboxymethylated guar gum. *Journal of Applied Polymer Science,* **97:**1977-1986.

[12] Trivedi, J., Kalia, K., Patel, N. and Trivedi, H. (2005) Grafting of Vinyl Monomers onto Sodium salt of Partially Carboxymethylated Guar Gum: Comparison of Their Reactivity. *Polymer- Plastics Technology & Engineering,* **44 :** 407-425.

[13] Trivedi, J., Kalia, K., Patel, N. and Trivedi, H. (2005) Ceric-Induced Grafting of Vinyl Monomers onto Sodium salt of Partially Carboxymethylated Guar Gum: Effects of Substrate Structure and Liquor Ratio. *Journal of Pure & Applied Sciences-"PRAJNA" (Sardar Patel University Journal),* **13:** 44-55.

[14] Joshi, K., Sinha, V., Patel, C. and Trivedi, H. (1995) Ceric-Induced Grafting of Acrylonitrile onto Sodium Salt of Partially Carboxymethylated Starch. *Journal of Macromolecular Science,Pure and Applied Chemistry,* **A32:** 133-146.

[15] Trivedi, H., Patel, C. and Patel, R. (1978) Polarographic studies of ion binding,I.Cadmium carboxymethylcellulose. *Die Angew Makromol Chemie,* **70:** 39-48.

[16] Brockway, C. and Seaberg, P. (1967) Grafting of polyacrylonitrile to granular corn starch. *Journal of Polymer Science Part A-1: Polymer Chemistry,* **5:** 1313-1326.

[17] Vijaykumar M., Reddy, C. and Joseph, K. (1985) Grafting of poly(glycidyl methacrylate) onto alginic acid. *European Polymer Journal,* **21:** 415-419.

[18] Chong, Li, Fong, Fu., Huang, M. and Lian, N. (1988) Graft Copolymerization of Butyl Acrylate onto Gelatin in the Presence of Ceric Ion. Journal of Macromolecular Science, Part A: Pure and Applied Chemistry, **25:** 1487-1513.

[19] Shah, S., Patel C. and Trivedi, H. (1992) Ceric-induced Grafting of Acrylonitrile onto Sodium Alginate. *High Performance Polymers.* **4:** 151-159.

[20] Egboh, S. and Jinadu, B. (1988) Modification of starch by graft copolymerization with methyl methacrylate. *Die Angew Makromol Chemie.* **163:** 93-99.

[21] Shah, S., Patel, C. and Trivedi, H. (1994) Ceric-induced grafting of ethyl-acrylate onto sodium alginate. Die Angew Makromol Chemie. **214:** 75-89.

[22] Collision, E. and Dainton, F. (1956) Termination of Chains in Vinyl Polymerization by Metal Salts. *Nature,* **177 :** 1224-1225.

[23] Collision, E., Dainton, F. and McNaughton, G. (1957) The effect of acrylamide on the X- and γ-ray yields of hydrogen peroxide from de-aerated water. *Transactions of the Faraday Society,* **53:** 357-362.

[24] Kantouch, A., Hebeish, A. and Bendak, A. (1971) Ce^{iv} initiated graft polymerization of methyl methacrylate on wool fibres. *European Polymer Journal,* **7:** 153-163.

[25] Saha, S. and Chaudhari, A. (1971) Effect of amines on the ceric ion-initiated polymerization of vinyl monomers I. Polymerization of acrylonitrile by ceric ion-triethylamine catalyst system. *Journal of Polymer Science Part A-1: Polymer Chemistry,* **9:** 1505-1516.

[26] Mohanty, N., Pradhan, B., Mohanta, M. and Das, H. (1983) Grafting vinyl monomers on silk fibres—I. Graft copolymerization of methyl methacrylate on silk by tetravalent cerium ion. *European Polymer Journal,* **19:** 415-418.

[27] Patel, B., Sinha, V. and Trivedi, H (1991) Graft copolymerization of sodium salt of partially carboxymethylated amylose with acrylonitrile. *Journal of Polymer Materials,* **8:** 321-328.

[28] Varma, D. and Sadhir, R. (1979) Radiation induced graft copolymerization of methyl methacrylate on natural and modified wool III. Thermal Behaviour. *Die Angew Makromol Chemie,* **81:** 179-191.