Ultraviolet-Radiation-Induced Graft Copolymerization of Methyl Acrylate onto the Sodium Salt of Partially Carboxymethylated Guar Gum

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ABSTRACT: In an attempt to modify the sodium salt of partially carboxymethylated guar gum (Na-PCMGG; degree of substitution = 0.291), we studied the ultraviolet-radiation-induced graft copolymerization of methyl acrylate with ceric ammonium nitrate as a photoinitiator. The influence of the grafting yield was studied as a function of the different reaction parameters, and the optimum reaction conditions for photografting were determined. The various reaction parameters included the photoinitiator, nitric acid, and monomer (methyl acrylate) concentrations, the reaction time, the temperature, and the amount of the substrate. A kinetic scheme for photografting copolymerization was proposed, and the results were in good agreement with the kinetic scheme. The graft copolymerization of methyl acrylate onto Na-PCMGG (degree of substitution = 0291) in the presence and absence of ultraviolet radiation was also carried out for the study of the efficiency of the photoinitiator. The influence of carboxymethyl groups added to the guar gum molecule on its behavior toward ultraviolet-radiation-induced grafting with methyl acrylate was also investigated. The evidence of photografting was ascertained with IR spectroscopy and scanning electron microscopy techniques. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1977–1986, 2005

Key words: ultraviolet-radiation; carboxymethylated guar gum; methyl acrylate; kinetic scheme; characterization

INTRODUCTION

Grafting vinyl monomers to natural and synthetic polymers by means of chemical or radiation-initiated polymerization has been adopted as a potentially good means of altering the properties of the base polymers. In this work, we report the optimized reaction conditions for grafting methyl acrylate (MA) onto the sodium salt of partially carboxymethylated guar gum [Na-PCMGG; degree of substitution (DS) = 0.291] with ceric ammonium nitrate (CAN) as a photoinitiator. Our purpose is not only to develop specialty polymeric materials capable of functioning under hostile conditions but also to elucidate the grafting mechanism over a range of values for the reaction variables studied here. Earlier we carried out the saponification of polyacrylonitrile-containing graft copolymers of samples of sodium salt of partially carboxymethylated starch (Na-PCMS; DS = 0.317) as well as sodium salt of partially carboxymethylated amylose (Na-PCMA; DS = 0.313), and we measured their water retention values.[1,2] We also reported the synthesis, characterization, and evaluation of Na-PCMS-*g*-poly(methyl methacrylate) copolymers as new biodegradable plastics[3] as well as the evaluation of graft copolymers of agar of sustained release from Diclofenac sodium in a tablet form.[4]

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EXPERIMENTAL

Materials

Guar gum (GG) was kindly supplied by H. B. Gum Industries Pvt., Ltd. (Kalol, India). The preparation, purification, and DS measurement of Na-PCMGG were performed as described elsewhere.[5,6] The DS of Na-PCMGG was found to be 0.291. MA (Samir Tech Chem) was washed with a 2% sodium hydroxide solution to remove the stabilizer, was washed with distilled water until it was free of alkali, and was dried over anhydrous sodium sulfate. It was distilled under atmospheric pressure, and the middle fraction was collected and used. Reagent-grade CAN (Chiti Chem, Baroda, India) was used as received. Analar-grade nitric acid (HNO_3) was used. Fresh solutions of the initiator were used, made through the dissolution of the required amount of CAN in HNO_3. All the reagents and solvents used in this work were reagent-grade. N_2 gas was purified by passage through a fresh pyrogallol solution. Deionized water was used for the preparation of the solutions and for the polymerization reactions.

Photografting copolymerization

Graft copolymer of Na-PCMGG (DS = 0.291)

The grafting reactions were carried out in a photochemical reactor supplied by Scientific Aids and Instruments Corp. (Madras, India). A weighed amount of Na-PCMGG (DS = 0.291; 0.25–3.0 g) was dissolved in 100 mL of conductivity water in a reaction flask, and the solution was stirred for half an hour. A freshly prepared CAN solution (2.5 mL, 1.5×10^{-3}–20.0×10^{-3} mol/L) in HNO_3 (0–0.5 mol/L) was added to the reaction flask, and the contents were then flushed with purified nitrogen gas for half an hour; this was followed by the addition of a known concentration of freshly distilled MA (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. The lamp was then illuminated. Water from a constant-temperature water-circulation bath was circulated over the immersion 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 product was isolated by centrifugation. It was then purified via washing with dilute HNO_3 and repeated washings of deionized water. The crude copolymer sample of Na-PCMGG-*g*-poly(methyl acrylate) (PMA) thus obtained was dried *in vacuo* at 40°C. The homopolymer PMA was separated from the crude graft copolymer by extraction with acetone for 48 h. After the complete removal of the homopolymer, the pure graft copolymer was dried at 40°C *in vacuo* until a constant weight was obtained.

Graft copolymers of GG

To understand the influence of the addition of —CH_2COONa GG on the grafting yields, we carried out the grafting of MA onto GG under the optimized reaction conditions obtained for the grafting of MA onto Na-PCMGG (DS = 0.291), with CAN as a photoinitiator. The experimental procedure for the synthesis of the graft copolymer (GG-*g*-PMA) is the same as discussed previously.

Dark method

To compare the efficiency of CAN as a photoinitiator, we carried out the grafting of MA onto Na-PCMGG (DS = 0.291) as mentioned previously, in the absence of ultraviolet radiation (dark method), with the following reaction conditions : 2.0 g of Na-PCMGG (dry basis), 0.10 mol/L HNO_3 concentration, 0.360 mol/L monomer concentration, 4.00×10^{-3} mol/L CAN concentration, time of 0.5–10.0 h, temperature of 35°C, 100 mL of water, and a total volume of 105 mL.

The percentage of grafting (%G), percentage of grafting efficiency (%GE), and rate of polymerization (R_p) were evaluated as follows:[7]

$$\%G = \frac{\text{Weight of grafted polymer}}{\text{Initial weight of backbone}} \times 10^2$$

$$\%GE = \frac{\text{Weight of grafted polymer}}{\text{Weight of grafted polymer} + \text{Weight of homopolymer}} \times 10^2$$

$$R_p = \frac{\text{Weight of grafted polymer} + \text{Weight of homopolymer}}{\text{Molecular weight of monomer} \times \text{Reaction time (s)} \times \text{Volume of the reaction mixture (mL)}} \times 10^3$$

Isolation of grafted chains

The graft copolymer of Na-PCMGG (DS = 0.291) containing PMA was hydrolyzed via refluxing for 12 h in 1*N* HCL as suggested by Brockway and Seaberg.[8] After all the Na-PCMGG went into the solution, a resinous mass was obtained, which was characterized with IR spectroscopy.

IR spectra

IR Spectra of GG, Na-PCMGG (DS = 0.291), Na-PCMGG-*g*-PMA, and PMA (isolated by hydrolysis) were taken in KBr with a Nicolet Impact 400D Fourier transform infrared spectrophotometer (Madison, WI).

Scanning electron microscopy (SEM)

A Philips ESEM TMP/EDAX instrument (Eindhoven, The Netherlands) was used to obtain micrographs of GG, Na-PCMGG (DS = 0.291), and Na-PCMGG-*g*-PMA.

RESULTS AND DISCUSSION

Determination of the optimum reaction conditions

To evaluate the optimal conditions for the ultraviolet-radiation-induced graft copolymerization of MA onto Na-PCMGG (0.291) with CAN as a photoinitiator, we varied the various reaction parameters. The reaction parameters included the concentrations of the photoinitiator (CAN), HNO_3, and monomer (MA) as well as the reaction time, temperature, and amount of the substrate.

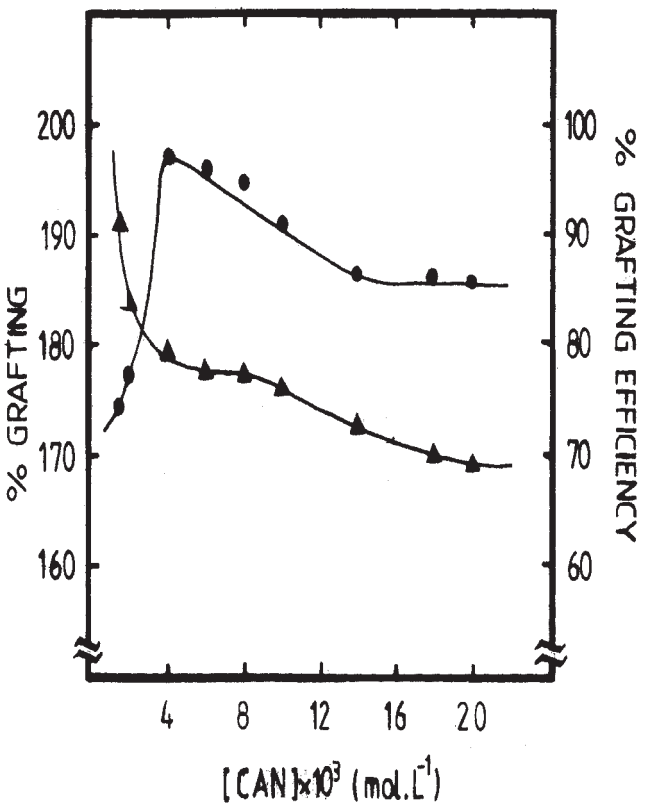

Figure 1 Effect of the CAN concentration (●) %G and (▲) %GE.

Effect of the photoinitiator concentration

Figure 1 shows the effect of the photoinitiator concentration on the grafting yield. %G increased initially up to $[Ce^{+4}] = 4.00 \times 10^{-3}$ mol/L and attained its maximum value at 197.29%. However, %GE decreased from the very beginning at a faster rate up to $[Ce^{+4}] = 4.00 \times 10^{-3}$ mol/L, and beyond this photoinitiator concentration, it decreased very slowly. Thus, the observed increase in %G within the photoinitiator concentration range of 1.50×10^{-3}–4.00×10^{-3} mol/L may be due to the fact that within this concentration range, the complex formation between the —OH groups and the carboxylate anion of Na-PCMGG and Ce^{+4} was facilitated, and the photodecomposition of the complex produced more active sites. Thus, this activation along the backbone was immediately followed by the graft copolymerization of MA onto the backbone. The observed decrease in the grafting yields (%G and %GE; cf. Fig. 1) at higher photoinitiator concentrations, that is, beyond $[Ce^{+4}] = 4.00 \times 10^{-3}$ mol/L, may be attributed to the fast termination of the growing grafted chains. Furthermore, homopolymer (PMA) formation at higher initiator concentrations, which competed with the grafting reaction for the available monomer (MA), could also lead to a decrease in %G and %GE.

Effect of the acid concentration

The effect of the HNO_3 concentration on the grafting yields is shown in Figure 2. The optimum concentration of HNO_3 was 0.20 mol/L, which afforded the maximum value of %G. An appreciable value of grafting was observed even at a zero concentration of HNO_3 (cf. Fig. 2); this may be due to the fact that, even in the absence of acid, in an aqueous medium Na-PCMGG ionizes fully to a greater extent, and this facilitates the diffusion of monomer as well as the photoinitiator, leading to an appreciable value of grafting. In the beginning, the observed increase in the values of the grafting yields with an increase in the HNO_3 concentrations was attributed to the increase in the concentrations of $[Ce(OH)]^{+3}$ and Ce^{+4} at the expense of $[Ce—O—Ce]^{+6}$. The ceric ions, Ce^{+4} and $[Ce(OH)]^{+3}$, being smaller in size, were more effective in their ability to form complexes with Na-PCMGG than $[Ce—O—Ce]^{+6}$. Beyond the optimum concentration of HNO_3, the grafting yields decreased (cf. Fig. 2); this could be explained by the fact that at higher concentrations of the acid, the species Ce^{+4} and $[Ce(OH)]^{+3}$ affected the termination steps, instead of propagating the chain, thus lowering %G.

Effect of the monomer concentration

The influence of the monomer (MA) concentration on %G and %GE is shown in Figure 3. %G increased

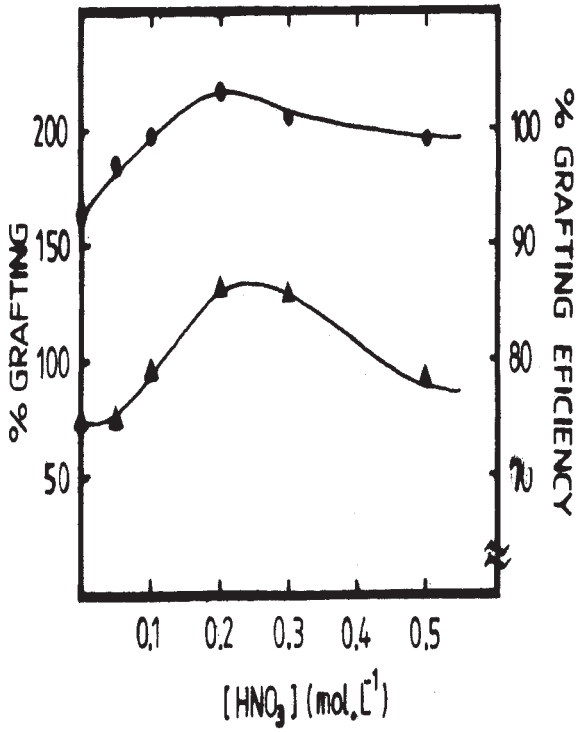

Figure 2 Effect of the HNO_3 concentration (●) %G and (▲) %GE.

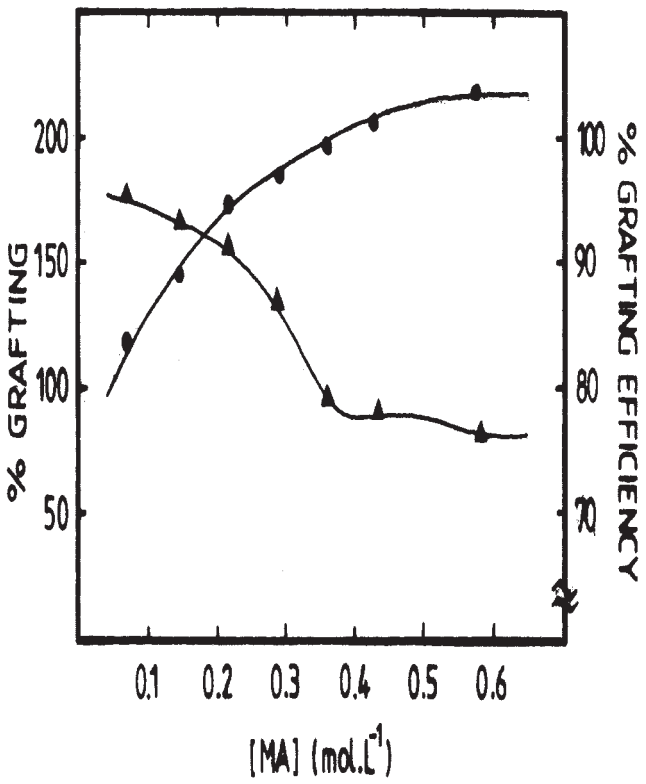

Figure 3 Effect of the MA concentration on (●) %G and (▲) %GE.

steadily up to 0.433 mol/L, and beyond this optimum concentration, %G leveled off. This result could be attributed to the gel effect,[9] that is, the increase in the viscosity of the medium due to the solubility of the homopolymer (PMA) in its own monomer (MA), which could be more pronounced with an increase in the monomer concentration. This caused hindrance in termination, particularly through the coupling of growing polymer chains. However, the other steps in the photografting copolymerization process, namely, initiation, propagation, and radical chain processes, were not affected to the same extent by increasing viscosity because the mobility of the polymer chains was restricted by the backbone structure. Besides this, the gel effect also caused swelling of Na-PCMGG, thus facilitating the diffusion of the monomer to the growing grafted chains and at the active sites on the backbone, thereby enhancing grafting. %GE decreased with increasing monomer concentration, and this showed that even when %G increased, it did not contribute to a progressive increase in the grafting efficiency. This may be due to the fact that the grafted chains acted as diffusion barriers, impeding the diffusion of the monomer (MA) into the backbone. As a result, less monomer was available for photografting, and most of it may have been used for homopolymerization.

Effect of the reaction time

The influence of the reaction time on the grafting yields are shown in Figure 4. %G and %GE increased with the reaction time up to 3 h. The maximum value of %G obtained at the optimum reaction time was 201.04%. This may be explained on by the fact that as the reaction time increased, the number of grafting sites on the backbone increased. As a result, the extent of initiation and propagation of photografting copolymerization also increased with the reaction time. However, beyond the optimum value of the reaction time (3 h), as the number of available sites for the photografting of the monomer on the Na-PCMGG backbone decreased, the reduction of %G and %GE was observed. The observed decrease in the values of the grafting yields was presumably due to the detrimental effect of UV radiation on the grafted side chains of PMA at longer irradiation times in the presence of the photoinitiator. In addition, the decrease in the value of the grafting yields beyond the optimum reaction time may be attributed to the depletion of the monomer and initiator concentrations as well as the shortage of available grafting sites.

Effect of the temperature

Figure 5 represents the results of %G and %GE for the photografting copolymerization of MA onto Na-PC-

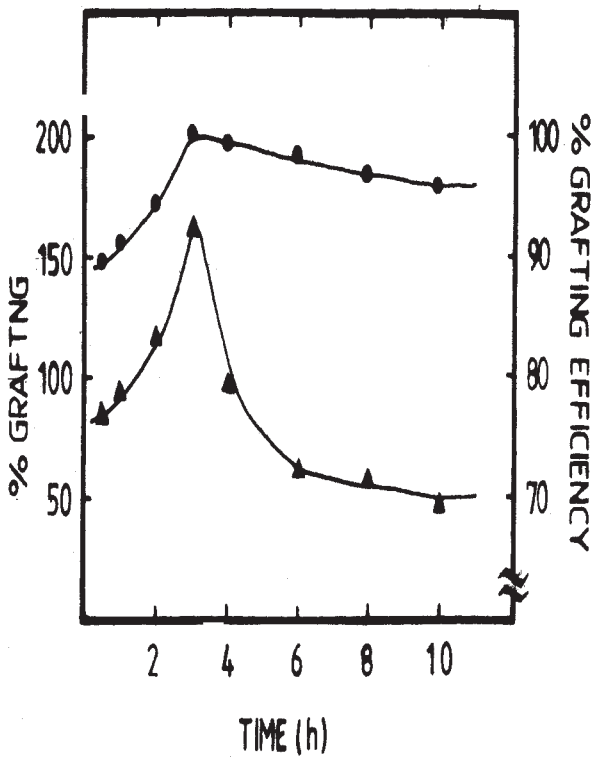

Figure 4 Influence of the reaction time on (●) %G and (▲) %GE.

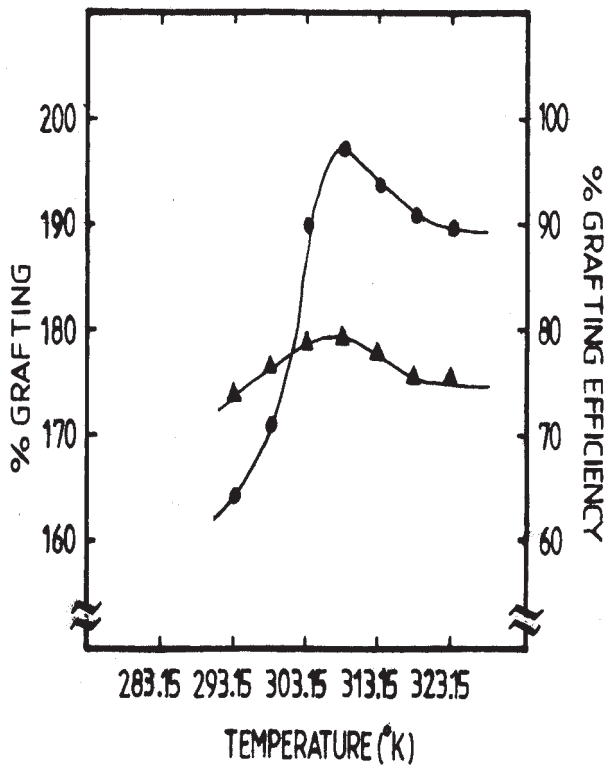

Figure 5 Influence of the temperature on (●) %G and (▲) %GE.

MGG (DS = 0.291) at various temperatures. %G increased with an increase in the temperature from 20 to 35°C but decreased with a further increase in the temperature. %GE behaved in the same way. The increase in %G and %GE with the temperature could be due to the faster photolysis of the Na-PCMGG/ceric complex, as well as the increased diffusion rate of the monomer from the aqueous phase of the backbone. The observed decrease in the grafting yields with rising temperature may also be attributed to the formation of the homopolymer (PMA). In addition, at higher temperatures, various hydrogen abstraction and chain-transfer reactions might have been accelerated and led to the decrease in %G and %GE.

Effect of the backbone concentration

The results of the grafting yields for the photografting copolymerization of MA onto Na-PCMGG (0.291) with various amounts of Na-PCMGG is shown in Figure 6. With increasing Na-PCMGG concentration, %G decreased steadily. However, %GE increased initially up to 1.0 g of Na-PCMGG and decreased further with increasing amounts of Na-PCMGG. These observed effects of increasing amounts of Na-PCMGG on %G and %GE for the photografting of MA (Fig. 6) may be explained by the fact that, although the weight of the grafted side chains could increase with the increase in the amount of Na-PCMGG and cause %GE to increase initially, the decrease in the monomer-to-backbone ratio lowered %G. When the concentration of Na-PCMGG was increased further, the rate of graft copolymerization may have been hindered by the high viscosity of the reaction system. Besides, high Na-PCMGG concentrations could produce more Na-PCMGG macroradicals, which could interact with one another to terminate the reaction, thus lowering %G. In addition, the more Na-PCMGG there was for a given amount of the monomer (MA), the more complex was formed during the course of photoirradiation and, consequently, the higher the number was of active sites generated on the polymeric substrate (Na-PCMGG) during the subsequent decomposition of the complex. As a result, %GE increased (cf. Fig. 6). The observed decrease in %GE with a further increase in the amount of Na-PCMGG indicated homopolymer formation.

Thus, on the basis of this discussion, the optimized reaction conditions obtained for the photoinitiated graft copolymerization of MA were as follows: 1.0 g of Na-PCMGG (dry basis), 0.20 mol/L HNO_3 concentration, 0.433 mol/L MA concentration, 4.00×10^{-3} mol/L CAN concentration, time of 3.0 h, temperature of 35°C, 98.40 mL of water, and a total volume of 105 mL.

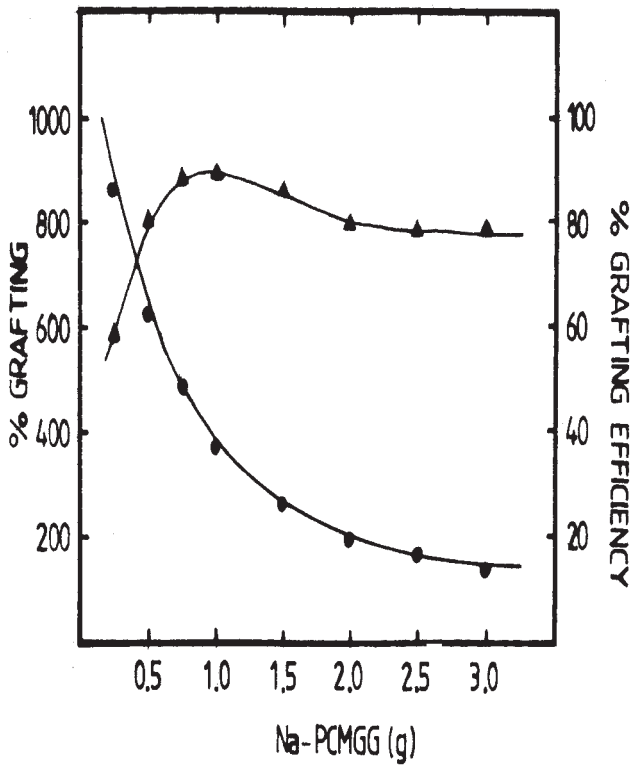

Figure 6 Influence of the amount of Na-PCMGG (DS = 0.291) on (●) %G and (▲) %GE.

TABLE I
R_p of the Photografting Copolymerization of MA onto Na-PCMGG (DS = 0.291) at Various Monomer Concentrations

[MA] (mol/L)	$R_p \times 10^5$ (mol L^{-1} sec^{-1})
0.072	1.87
0.144	2.40
0.216	2.91
0.289	3.24
0.360	3.82
0.433	4.07
0.578	4.35

Reaction conditions: Na-PCMGG = 2.0 g (dry basis), $[HNO_3]$ = 0.10 mol/L, [Monomer] = varied as shown, [CAN] = 4.00×10^{-3} mol/L, time = 4.0 h, temperature = 35°C, volume of water = 100 ± 4.0 mL, and total volume = 105 mL.

Kinetics and mechanism of photografting

The mechanism of the free-radical photografting of MA onto Na-PCMGG was expected to proceed according to the following proposed scheme.[10]

Radical generation

$$X\text{—}H + Ce^{+4} \overset{K}{\rightleftharpoons} [\text{Complex}] \underset{k_d}{\overset{h\nu}{\rightarrow}} X^{\bullet} + Ce^{+3} + H^{+}$$

$$Ce^{+4} + H_2O \overset{h\nu}{\longrightarrow} Ce^{+3} + {}^{\bullet}OH + H^{+}$$

Initiation

$$X^{\bullet} + M \overset{k_i}{\rightarrow} XM^{\bullet}$$

$${}^{\bullet}OH + M \overset{k_i'}{\rightarrow} OH\text{—}M^{\bullet}$$

TABLE II
R_p of the Photografting Copolymerization of MA onto Na-PCMGG (DS = 0.291) at Various Photoinitiator Concentrations

[CAN] × 10^3 (mol/L)	$R_p \times 10^5$ (mol L^{-1} s^{-1})
1.50	2.94
2.00	3.25
4.00	3.82
6.00	3.86
8.00	3.87
10.0	3.85
14.0	3.93
18.0	4.07
20.0	4.13

Reaction conditions: Na-PCMGG = 2.0 g (dry basis), $[HNO_3]$ = 0.10 mol/L, [Monomer] = 0.360 mol/L, [CAN] = varied as shown, time = 4.0 h, temperature = 35°C, volume of water = 100 mL, and total volume = 105 mL.

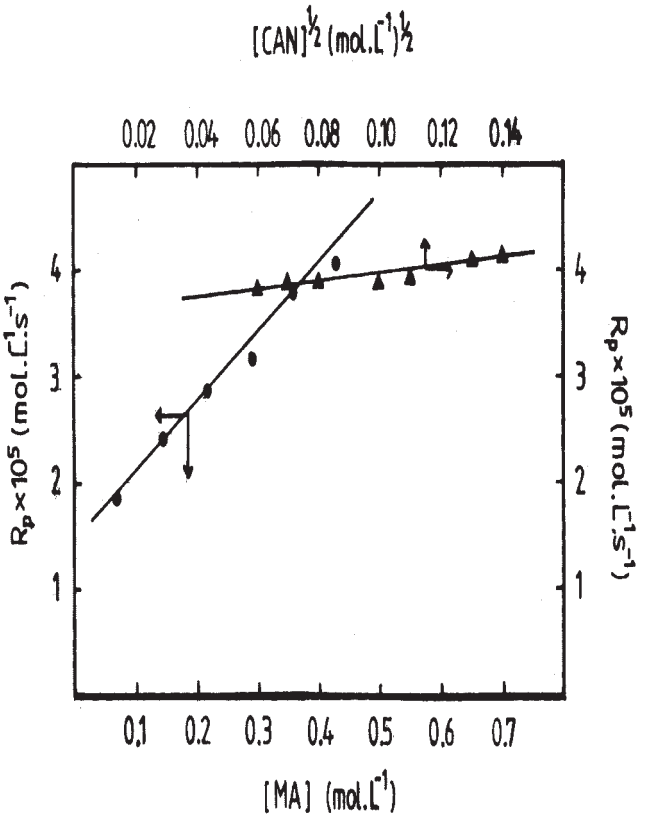

Figure 7 Plots of (●) $R_p \times 10^5$ versus the monomer concentration and (▲) $R_p \times 10^5$ versus $[CAN]^{0.5}$.

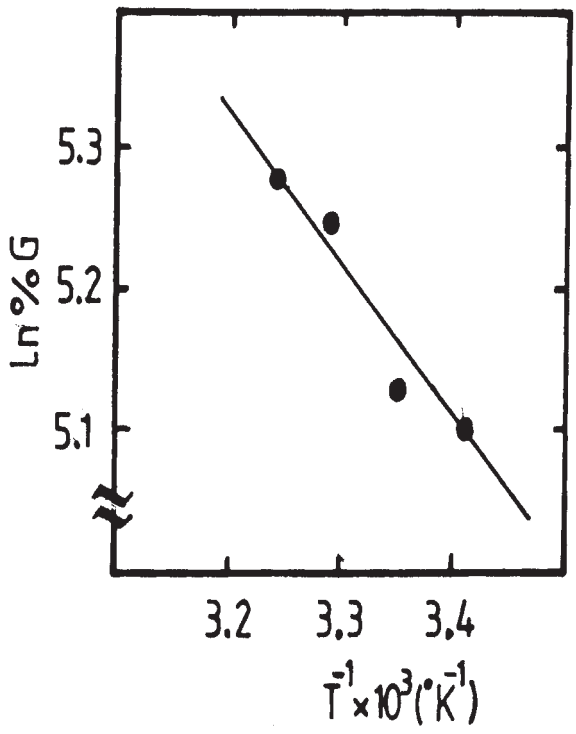

Figure 8 Plot of ln %G versus T^{-1}.

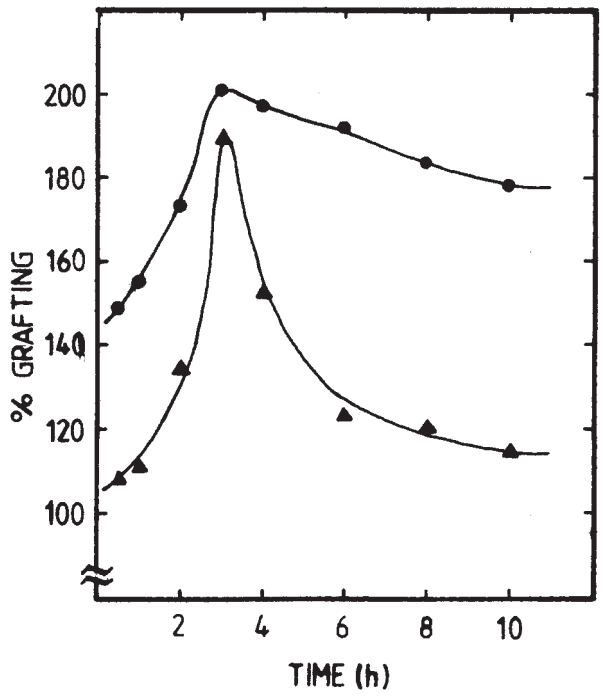

Figure 9 Effect of the reaction time on %G: (●) photo method and (▲) dark method.

$$Ce^{+4} + M \rightarrow M + Ce^{+3} + H^+$$

Propagation

$$XM^{\bullet} + nM \xrightarrow{k_p} XM^{\bullet}_{n+1}$$

$$OH\text{—}M^{\bullet} + nM \rightarrow OHM_{n+1}$$

$$M^{\bullet} + nM \rightarrow M^{\bullet}_{n+1}$$

Termination

$$XM^{\bullet}_{n+1} + XM^{\bullet}_{n+1} \xrightarrow{k_t} \text{Graft copolymer}$$

$$XM^{\bullet}_{n+1} + OHM^{\bullet}_{n+1} \rightarrow \text{Graft copolymer}$$

TABLE III
Results of Grafting Yields Obtained from the Photografting of MA onto GG and Na-PCMGG (DS = 0.291)

Structure	%G	%GE
Na-PCMGG[a] (DS = 0.291)	356.58	92.05
GG[a]	184.67	83.42

[a] Optimum reaction conditions for MA: GG/Na-PCMGG = 1.0 g (dry basis), $[HNO_3]$ = 0.20 mol/L, [MA] = 0.433 mol/L, [CAN] = 4.00×10^{-3} mol/L, time = 3.0 h, temperature = 35°C, volume of water = 98.40 mL, and total volume = 105 mL.

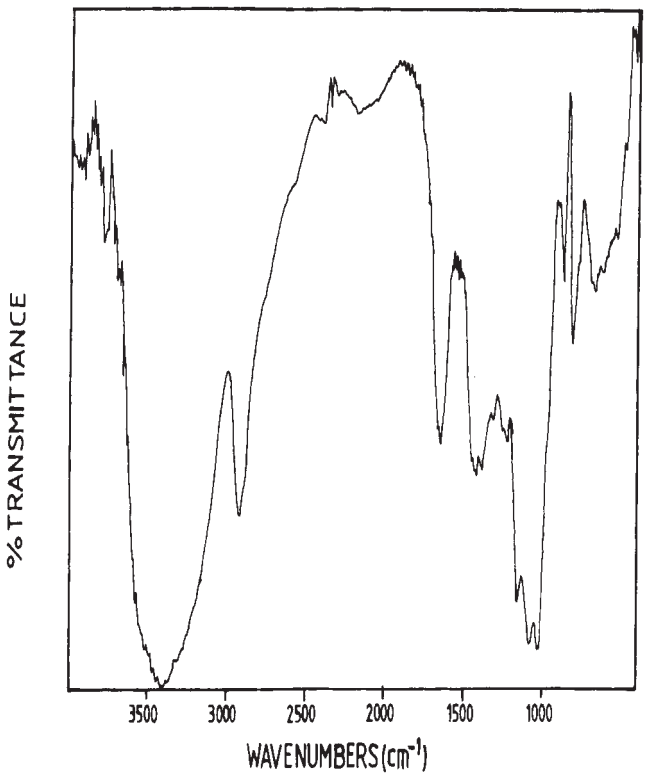

Figure 10 IR spectrum of a GG sample.

$$OHM^{\bullet}_{n+1} + OHM^{\bullet}_{n+1} \rightarrow \text{Homopolymer}$$

$$M^{\bullet}_{n+1} + M^{\bullet}_{n+1} \rightarrow \text{Homopolymer}$$

$$XM^{\bullet}_{n+1} + M^{\bullet}_{n+1} \rightarrow \text{Graft copolymer}$$

$$XM^{\bullet}_{n+1} + Ce^{+4} \rightarrow XM_{n+1} + Ce^{+3} + H^+$$

$$M^{\bullet}_{n+1} + Ce^{+4} \rightarrow M_{n+1} + Ce^{+3} + H^+$$

X—H denotes the reactive groups of Na-PCMGG, and M is the monomer (MA). With a steady-state assumption, the following expressions [eqs. (1) and (2)] were derived for R_p:[11]

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

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

$$R_p = R_g + R_h \quad (3)$$

The values of R_p evaluated for various monomer (MA) and photoinitiator (CAN) concentrations, for the photografting of MA onto Na-PCMGG (DS = 0.291), are given in Tables I and II, respectively.

The effects of the concentration of the monomer (MA) and photoinitiator (CAN) on R_p, as expected

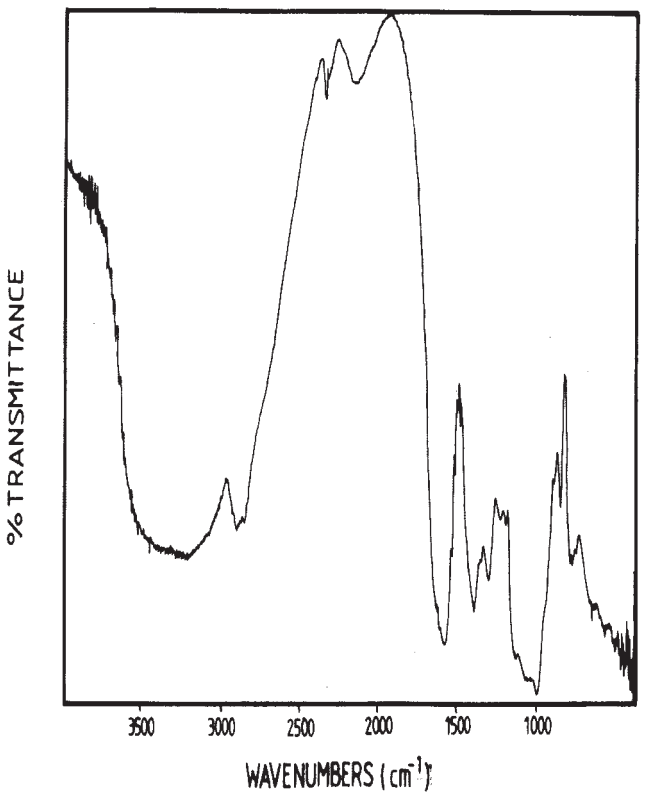

Figure 11 IR spectrum of an Na-PCMGG sample (DS = 0.291).

from the previous equations, are shown in Figure 7. The plots of R_p versus the monomer concentration and R_p versus $[Ce^{+4}]^{1/2}$ were linear in this case, supporting the previous scheme.

Evaluation of the energy of activation

Figure 8 shows ln %G versus the reciprocal of the temperature (T^{-1}) plotted for the initial portion of the curve, that is, 20–35°C (cf. Fig. 5). The values fell on a straight line. The least-square value of the overall activation energy of grafting was calculated from Figure 8 and was found to be 9.88 kJ/mol.

Comparison of the efficiency of CAN

The results of the grafting yields obtained with the photo and dark methods are depicted in Figure 9. The grafting yields were higher when the grafting of MA was carried out onto Na-PCMGG (DS = 0.291) at various reaction times with ultraviolet radiation, in comparison with the dark method. The observed higher grafting yields may be attributed to the fact that the complex, which 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, 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.

Effect of the substrate structure

In this work, the effect of adding functional groups such as carboxymethyl to the GG molecule on its susceptibility or behavior toward photografting with MA was investigated. For this purpose, the ceric-ion-initiated photografting of MA onto GG was carried out with the optimized reaction conditions obtained, as mentioned previously, for the photografting of MA onto Na-PCMGG (DS = 0.291), and the values of the grafting yields are given in Table III.

As shown in Table III, changing the chemical structure of GG by carboxymethylation enhanced the behavior of GG toward the grafting of MA. As a result, %G and %GE were higher for the grafting of MA onto Na-PCMGG (DS = 0.291), with respect to GG. This could be attributed to the combined influence of the following factors. First, the carboxymethyl groups increased the swellability of GG, thereby facilitating the diffusion of the monomer (MA) and initiator (CAN); second, the ionization of carboxyl groups along the GG chains added negative charges, which attracted ceric ions to the GG molecules, leading to the forma-

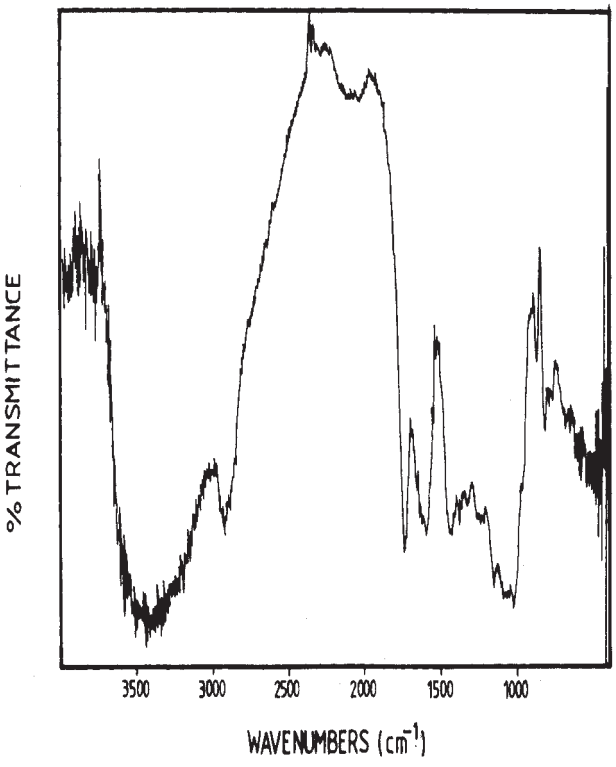

Figure 12 IR spectrum of an Na-PCMGG-*g*-PMA sample.

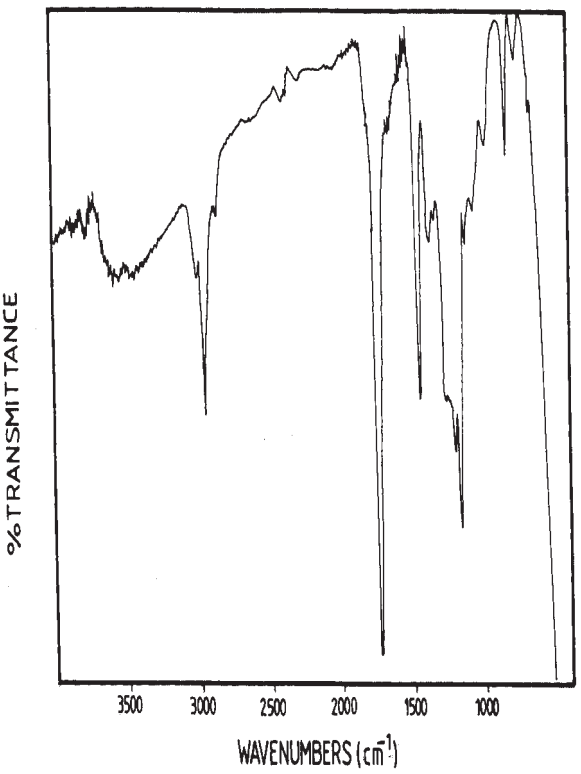

Figure 13 IR spectrum of a PMA sample.

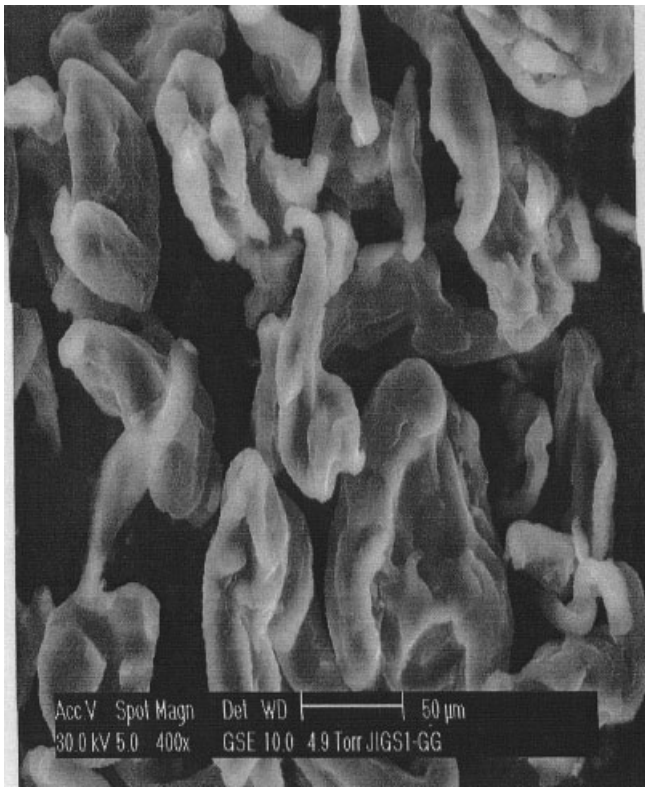

Figure 14 SEM micrograph (400×) of a GG sample.

tion of more active sites on the GG backbone available for the monomer (MA), thus increasing the reactivity of GG. Similar results were reported for the grafting of acrylonitrile (AN) onto Na-PCMA[12] and Na-PCMS[13] and the grafting of 4-vinyl pyridine[14] and vinyl monomers (AN, methyl methacrylate (MMA), and acrylamide (AAm)[15] onto partially carboxymethylated cotton.

Evidence of grafting

IR spectra

Figure 10 shows the IR spectrum of GG. The presence of a very strong and broad absorption band at approximately 3415 cm^{-1} was assigned to OH stretching. Reasonably sharp absorption at approximately 2930 cm^{-1} could be attributed to —CH stretching. The absorption band that appeared at 1650 cm^{-1} was due to the hydration of water. The —CH_2 bending in GG was assigned to an absorption at approximately 1440 cm^{-1}, and the frequency at approximately 1380 cm^{-1} was attributed to CH bending. The bending of OH was probably distributed at frequencies of 1300 and 1250 cm^{-1}. The IR spectrum of Na-PCMGG (DS = 0.291; Fig. 11) showed a somewhat reduced intensity of the absorption, at approximately 3250 cm^{-1} due to OH stretching, indicating that some of the OH groups present in the GG sample were involved in

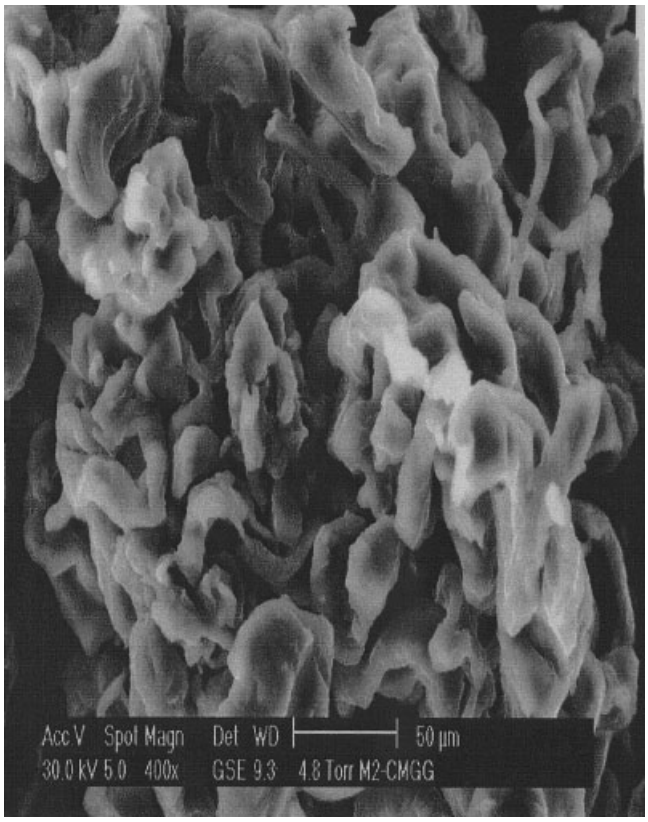

Figure 15 SEM micrograph (400×) of an Na-PCMGG sample (DS = 0.291).

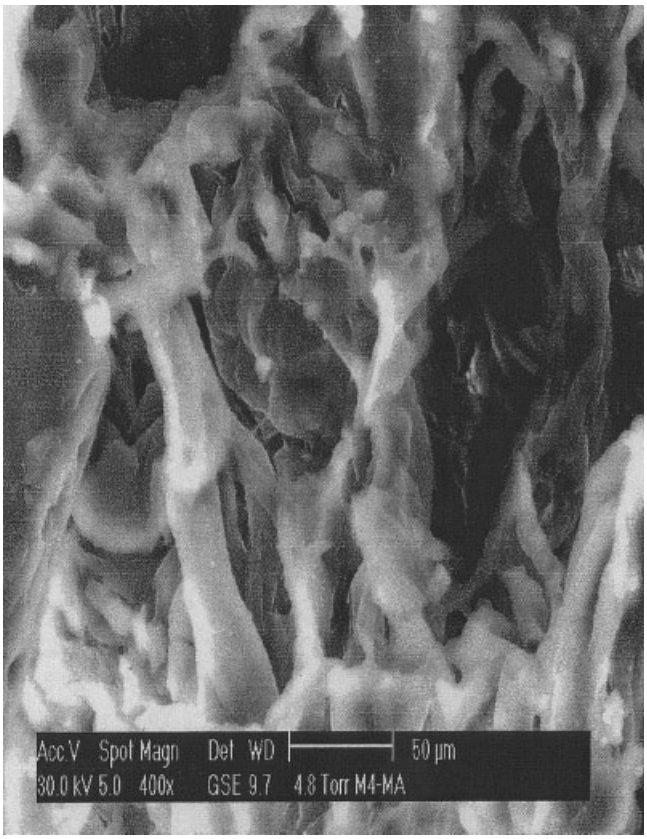

Figure 16 SEM micrograph (400×) of an Na-PCMGG-*g*-PMA sample (G = 197.29%).

carboxymethylation. The presence of a band at approximately 2930 cm^{-1} was due to —CH stretching. The band due to water (bending of water), which appeared at approximately 1650 cm^{-1} in the GG sample (cf. Fig. 10), was absent in the Na-PCMGG sample. The asymmetric and symmetric vibrations due to —C(=O)—O the moiety were assigned to 1615 and 1421 cm^{-1}, respectively. This could be attributed to the incorporation of carboxymethyl groups into GG. Figures 12 and 13 show the IR spectra of Na-PCMGG-*g*-PMA and PMA samples (isolated by hydrolysis), respectively. The IR spectra of the graft copolymer Na-PCMGG-*g*-PMA (Fig. 12) showed absorption bands of Na-PCMGG as well as an additional strong absorption band at about 1750 cm^{-1} assigned to the C═O stretching of the ester group (—$COOCH_3$), which was characteristic of MA. The IR spectrum of PMA (Fig. 13) indicated the presence of C═O stretching at about 1730 cm^{-1}. This result may be attributed to the fact that the hydrolysis of the graft copolymer gave back the grafted chain of PMA. Thus, the results of Figures 11 and 12 provide substantial evidence of the grafting of MA onto Na-PCMGG (DS = 0.291).

SEM

An SEM micrograph of GG (Fig. 14) showed discrete elongated granular structures separated from one another. Upon the carboxymethylation of GG, the structure of GG improved, as shown in Figure 15; the topology of the granules (Fig. 14) was modified in such a way that some of the granules became attached by adhering themselves. However, the clustering of the granules seemed to be poor, and the granules could be distinguished from one another. The surface topology of Na-PCMGG-*g*-PMA (%G = 197.29) is shown in Figure 16. Comparing the morphology of the grafted sample with that of the ungrafted material [GG (Fig. 14) and Na-PCMGG (Fig. 15)], we found that the grafted chains drastically changed the topology of the sample. As shown in Figure 16, a lumpy morphology was observed with MA. An SEM micrograph of Na-PCMGG-*g*-PMA (Fig. 16) revealed additional surface deposits, indicating that grafting took place.

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