Graft Copolymerization of Sodium Salt of Partially Carboxymethylated Guar Gum with Methyl Methacrylate: An Examination of the Reaction Variables

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ABSTRACT: The graft copolymerization of methyl methacrylate (MMA) onto sodium salt of partially carboxymethylated guar gum (Na-PCMGG; degree of substitution = 0.497) with ceric ammonium nitrate as a redox initiator in an aqueous medium was studied. The optimized reaction conditions affording the maximum percentage of grafting of MMA onto Na-PCMGG were determined through the variation of the concentrations of nitric acid, ceric ammonium nitrate, MMA, and Na-PCMGG and of the temperature and time. The effects of these parameters on the grafting yields and the rates of polymerization, graft copolymerization, and homopolymerization were also studied, and the results were examined. The graft copolymer sample was characterized with IR spectroscopy, thermogravimetric analysis, differential scanning calorimetry, and scanning electron microscopy. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1855–1864, 2005

Key words: differential scanning calorimetry (DSC); graft copolymers; thermogravimetric analysis (TGA)

INTRODUCTION

Grafting is a fascinating field of research with unlimited prospects. Earlier, we reported the grafting of acrylonitrile onto sodium alginate (SA) with Fenton's reagent as an initiator[1,2] and investigated the biodegradable behavior of acrylonitrile grafted onto SA by studying its interactions with various microorganisms.[3] We also grafted acrylonitrile onto a styrene/maleic acid copolymer[4] as well as methyl acrylate and methyl methacrylate (MMA) onto SA[5] in the presence of Ce^{+4}, and we studied the thermal behavior of the graft copolymers.[6] Recently, we also reported the synthesis, characterization, and evaluation of graft copolymers of sodium salt of partially carboxymethylated starch and poly(methyl methacrylate) (PMMA) as new biodegradable plastics[7] as well as the evaluation of graft copolymers of agar for the sustained release of diclofenac sodium from tablets.[8]

In this investigation, we successfully carried out the grafting of MMA onto sodium salt of partially carboxymethylated guar gum [Na-PCMGG; degree of substitution (DS) = 0.497] with tetravalent cerium ions, and we evaluated the optimized reaction conditions of grafting. The graft copolymer thus synthesized was also characterized with different techniques.

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EXPERIMENTAL

Materials

Guar gum (GG) was kindly supplied by H. B. Gum Industries Pvt., Ltd. (Kalol, Gujarat, India). The methods of preparation and purification and the DS measurements of Na-PCMGG have been described elsewhere.[9,10] The DS value of Na-PCMGG was 0.497. MMA (Fluka Chemie AG CH-9471, Buchs, Switzerland) 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 finally distilled under atmospheric pressure, and the middle fraction was used. Analar-grade nitric acid was used. Fresh solutions of the initiator were used, which were made through the dissolution of the required amount of ceric ammonium nitrate (CAN) in nitric acid. All other reagents and solvents used in this work were reagent-grade. N_2 gas was purified by passage through fresh pyrogallol solutions. Deionized water was used for the preparation of the solutions and for the polymerization reactions.

Graft copolymerization

A 500-mL, three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a glass inlet

system was immersed in a constant-temperature bath for the grafting reactions. In a typical reaction, various amounts (0.5–3.0 g, dry basis) of Na-PCMGG (DS = 0.497) were dissolved in low-conductivity water (100 mL) with constant stirring and a slow, bubbling stream of nitrogen for 1 h at the desired temperature (15–45°C). A freshly prepared 10-mL solution of CAN (5.0×10^{-3} to $8.0 \times 10^{-2}M$) in nitric acid (0–1.0*M*) was added, and the mixture was stirred for 20 min. Nitrogen gas was continuously passed through the reaction solution, and freshly distilled MMA (0.037–0.295*M*) was added. The grafting reactions were carried out for different times (0.5–10 h). After the completion of the reaction, the mixture was immediately poured into an excess of methanol to precipitate out the polymer. The crude copolymer product was filtered, repeatedly washed with nitric acid and 90% methanol, and finally washed with pure methanol. The crude copolymer thus obtained was dried *in vacuo* at 40°C. The PMMA homopolymer was separated from the crude graft copolymer by extraction with benzene for 48 h. After the complete removal of the homopolymer, the pure graft copolymer was dried at 40°C *in vacuo* to a constant weight.

The grafting percentage, grafting efficiency, and rates of polymerization (R_p), graft copolymerization (R_g), and homopolymerization were evaluated as mentioned earlier.[11]

IR spectra

IR spectra of GG, Na-PCMGG (DS = 0.497), Na-PCMGG-*g*-PMMA, and PMMA were taken with KBr pellets with a Nicolet Impact 400 D Fourier transform infrared spectrophotometer.

Thermogravimetric analysis (TGA)

The thermal behavior of GG, Na-PCMGG (DS = 0.497), Na-PCMGG-*g*-PMMA, and PMMA was examined under an inert atmosphere at a heating rate of 10°C/min with the help of a DuPont 951 thermogravimetric analyzer.

Differential scanning calorimetry (DSC)

The DSC scans of GG, Na-PCMGG (DS = 0.497), Na-PCMGG-*g*-PMMA, and PMMA were recorded in a nitrogen atmosphere at a scanning rate of 10°C/min on a TA DSC 2920 instrument.

Scanning electron microscopy (SEM)

A Philips ESEM TMP/EDAX instrument was used to obtain micrographs of GG, Na-PCMGG (DS = 0.497), and Na-PCMGG-*g*-PMMA.

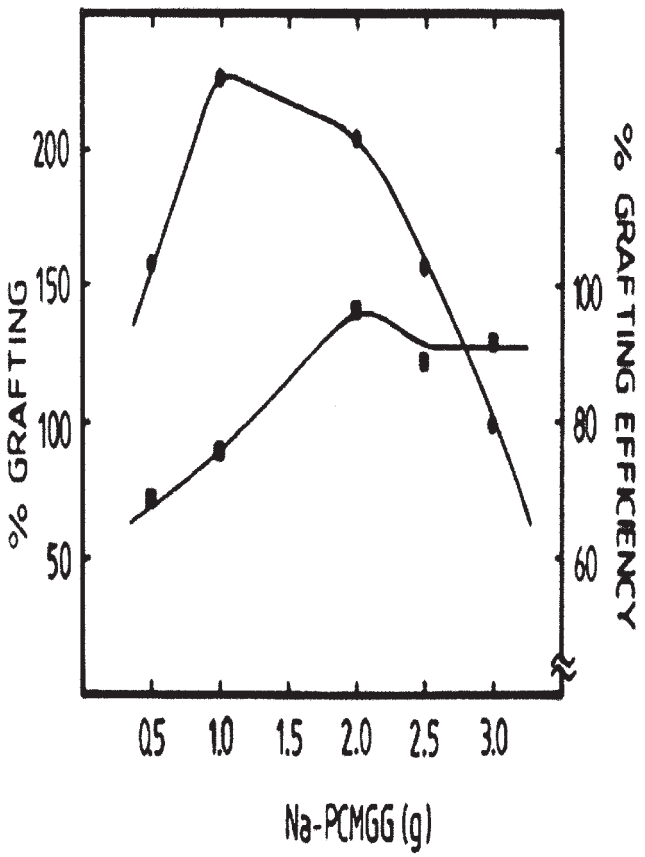

Figure 1 Influence of the sodium salt concentration of Na-PCMGG on (●) grafting and (■) grafting efficiency.

RESULTS AND DISCUSSION

Determination of the optimum reaction conditions

To optimize the conditions for grafting, we varied the amount of Na-PCMGG, the concentrations of the monomer (MMA), initiator (CAN), and nitric acid, and the time and temperature.

Effect of the amount of Na-PCMGG

The influence of different amounts of Na-PCMGG (DS = 0.497) on the grafting percentage and grafting efficiency is shown in Figure 1. The grafting percentage increased initially with an increasing amount of Na-PCMGG and reached a maximum value of grafting of 226.47%. Beyond the optimum amount of Na-PCMGG (i.e., 1.0 g), the grafting percentage decreased continuously. On the other hand, the grafting efficiency increased initially up to 2.0 g of Na-PCMGG and thereafter decreased and remained steady, as shown in Figure 1. Thus, the observed increases in both the grafting percentage and efficiency of grafting with Na-PCMGG may have been due to the formation of a higher number of Na-PCMGG macroradicals available for grafting. The subsequent reduction in the grafting percentage and grafting efficiency may be attributed

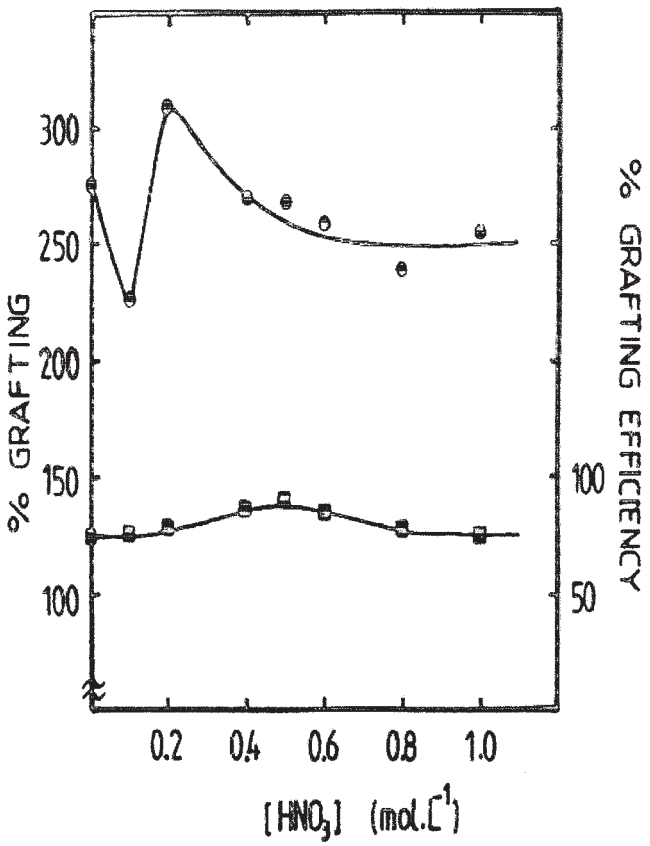

Figure 2 Effect of the nitric acid concentration on (●) grafting and (■) grafting efficiency.

to the increase in the viscosity of the medium, which hindered normal graft copolymerization. Similar results were reported for the grafting of acrylonitrile onto SA[12] and GG.[13]

Effect of the nitric acid concentration

Figure 2 shows the dependence of the grafting percentage and grafting efficiency on the nitric acid concentration. At a zero concentration of the acid, a very high value of the grafting percentage was observed and was attributed to the fact that, even in the absence of the acid, in an aqueous medium Na-PCMGG swelled to a greater extent; this made the functional groups of Na-PCMGG more accessible toward grafting. However, there existed an optimum concentration of acid (0.20 mol/L) that afforded the maximum grafting percentage. Beyond this optimum concentration of nitric acid, the grafting percentage decreased and reached a value even lower than that in the absence of the acid. The observed increase in the grafting percentage with an increase in the acid concentration may have been due to a decrease in the termination rate of the growing polymer chain or an increase in the initiation rate. However, beyond the optimum concentration of the acid, the decrease in the grafting percentage could be attributed to a corresponding reduction in ceric/Na-PCMGG complex formation as well as an increase in the termination rates. Rao and Kapur[14] and Shah et al.[12] made similar observations.

Effect of the initiator concentration

The effect of the Ce^{+4} ion concentration on the grafting yields is shown in Figure 3. With increasing ceric ion concentration, the grafting percentage increased and reached a maximum value of 258.74 at $[Ce^{+4}]$ = 0.03 mol/L, but with a further increase in the Ce^{+4} concentration, the grafting percentage decreased. However, the grafting efficiency decreased from the very beginning up to $[Ce^{+4}]$ = 0.03 mol/L and attained almost a constant value with a further increase in the initiator concentration. Thus, the observed increase in the grafting percentage within the CAN concentration range of 0.005–0.03 mol/L (Fig. 3) may be explained by the fact that in this concentration range, the increasing concentration of ceric ions resulted in an increase in the total number of the complex of Na-PCMGG and ceric ions, which decomposed to produce more active sites. Thus this, activation along the backbone was immediately followed by the graft copolymerization of MMA onto the Na-PCMGG backbone. The observed decrease in the grafting percentage at a higher concentration of the initiator was due

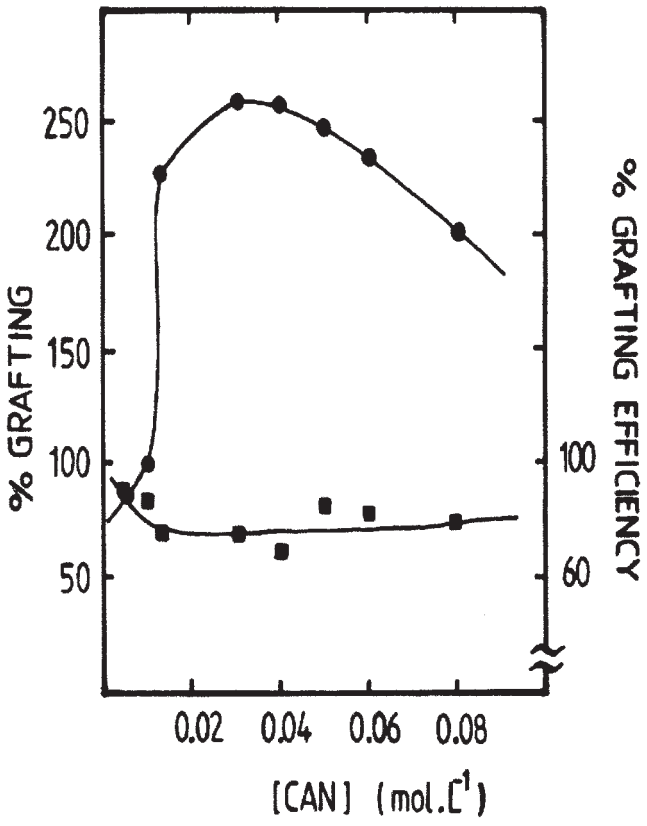

Figure 3 Effect of the CAN concentration on (●) grafting and (■) grafting efficiency.

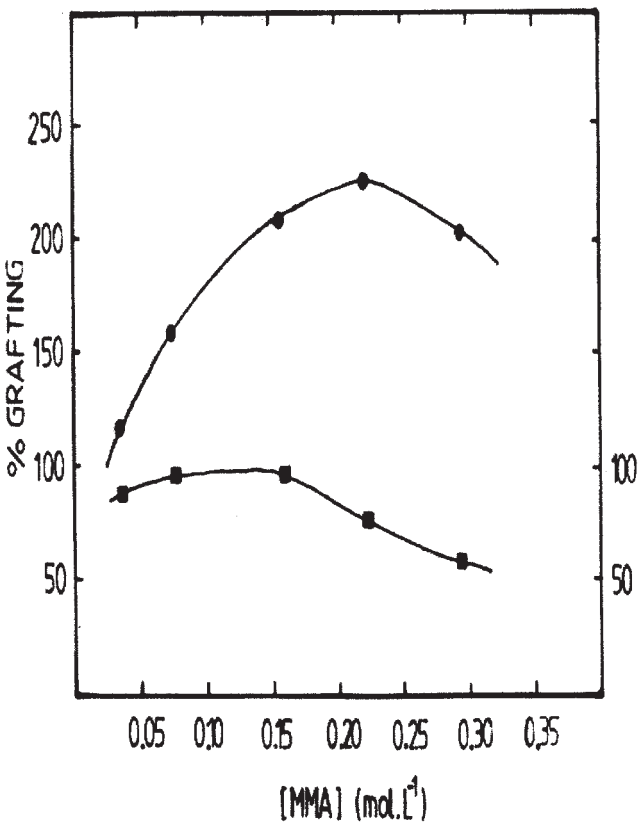

Figure 4 Effect of the MMA concentration on (●) grafting and (■) grafting efficiency.

to the efficiency of Ce^{+4} in taking part in the termination of growing grafted chains.[15,16] Moreover, at a higher ceric ion concentration, the complex formation between the monomer and ceric ions assumed predominance over that between Na-PCMGG and ceric ions. This favored the formation of the homopolymer at the cost of grafting. Also, because more and more of the monomer was used in the complex formation, the Na-PCMGG macroradicals did not find enough monomer in their vicinity to produce the graft.

Effect of the monomer concentration

Figure 4 presents the influence of the monomer concentration on the grafting yields. As the concentration increased from 0.037 to 0.295 mol/L, the grafting percentage increased with increase in the MMA concentration up to 0.222 mol/L, beyond which it decreased with a further increase in MMA. A lower concentration apparently favored graft copolymerization. With a higher monomer concentration, the concentration of PMMA macroradicals increased, and the rates of their combination and disproportionation were faster than the rate of their combination with Na-PCMGG molecules; therefore, the homopolymer and a lower percentage of grafting were produced. Moreover, once the graft copolymer radical formed, the excess monomer shielded the graft copolymer, and this may have inhibited R_g. In addition, the excess monomer was available for initiator radicals to initiate the homopolymerization reaction and thereby reduce the grafting efficiency (Fig. 4). Similar results have also been reported for the grafting of acrylonitrile onto SA[12] and sodium salt of partially carboxymethylated amylose.[17]

Effect of the reaction time

The influence of the reaction time on the grafting yields (grafting percentage and grafting efficiency) is presented in Figure 5. A value of about 114% was obtained for grafting in the first half-hour only. The increase in the value of the grafting percentage up to a maximum of 226.47% within 4 h was due to the increase in the number of grafting sites on the Na-PCMGG backbone as the reaction progressed. However, after 4 h, the grafting percentage decreased, and this was due to the depletion of the monomer and initiator concentrations and the shortage of available grafting sites. On the other hand, the grafting efficiency, as shown in Figure 5, decreased rapidly at the beginning of the reaction, perhaps because the monomer (MMA) molecules could not reach the radical sites easily and homopolymer (PMMA) formation was favored. When the reaction progressed, the amount of

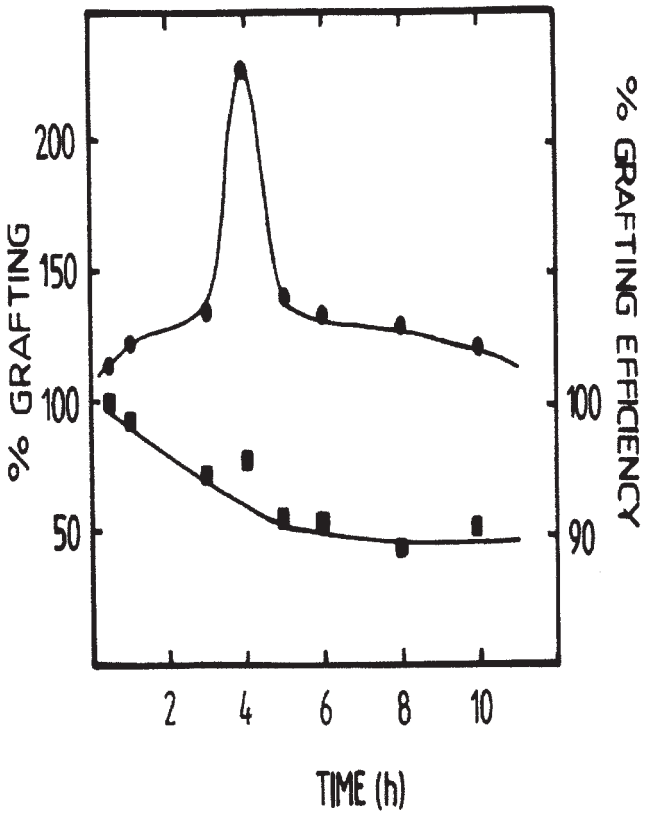

Figure 5 Influence of the reaction time on (●) grafting and (■) grafting efficiency.

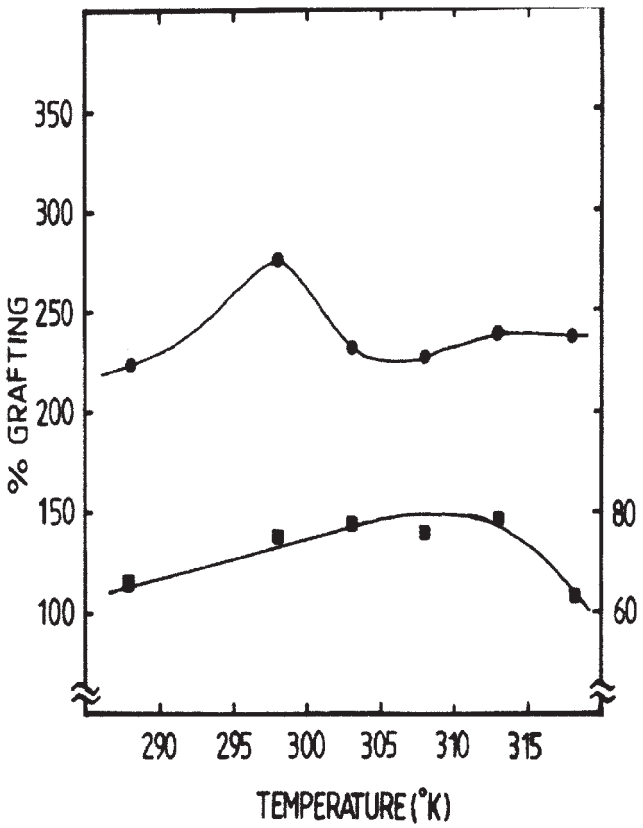

Figure 6 Influence of the reaction temperature on (●) grafting and (■) grafting efficiency.

the graft copolymer increased, even though the grafting efficiency still decreased and remained constant after 5 h because the homopolymer was still forming.

Effect of the temperature

Figure 6 shows the variation of the grafting percentage and grafting efficiency as a function of temperature. The grafting percentage increased with a rise in the temperature from 15 to 25°C but decreased thereafter with a further increase in the temperature. On the other hand, the grafting efficiency increased very slowly in the beginning and then decreased with a further increase in the temperature. Thus, the observed increase in the grafting percentage and grafting efficiency with the temperature could be interpreted in terms of the favorable influence of the temperature on (1) the faster decomposition of the Na-PCMGG/ceric complex (which led to more active sites being generated on the Na-PCMGG chains), (2) the swellability of Na-PCMGG, (3) the solubility of the monomer (MMA) molecules, (4) the diffusion and mobility of the monomer from the aqueous phase to the Na-PCMGG backbone, and (5) the rates of initiation and propagation of grafting. The observed decrease in the grafting yields could be ascribed to the fact that at higher temperatures, the graft copolymerization occurred with poor selectivity. In addition, various hydrogen-abstraction and chain-transfer reactions also might have been accelerated at higher temperatures, and this may have led to the reduction of the grafting percentage.

Thus, on the basis of this discussion, the optimized reaction conditions obtained for the graft copolymerization of MMA were as follows: 1.0 g of Na-PCMGG (DS = 0.497; dry basis), 0.20 mol/L HNO_3, 0.03 mol/L CAN, 0.222 mol/L MMA, 4 h, 25°C, 136.45 mL of water, and 150 mL of total volume.

TABLE I
R_g and R_p for the Grafting of MMA onto Na-PCMGG (DS = 0.497) at Various Initiator Concentrations

[CAN] $\times 10^{-3}$ (mol/L)	$R_g \times 10^5$ (mol L^{-1} s^{-1})	$R_p \times 10^5$ (mol L^{-1} s^{-1})
5.0	0.39	0.44
10.0	0.45	0.53
13.0	1.05	1.39
30.0	1.19	1.61
40.0	1.18	1.70
50.0	1.14	1.34
60.0	1.10	1.30
80.0	0.92	1.17

Na-PCMGG = 1.0 g (dry basis); [HNO_3] = 0.10 mol/L; [MMA] = 0.222 mol/L; time = 4 h; temperature = 35°C; volume of water = 136.45 mL; total volume = 150 mL.

Kinetics and mechanism

The kinetics and mechanism of the free-radical graft copolymerization of MMA onto Na-PCMGG (DS = 0.497) was expected to proceed according to the same scheme proposed earlier.[4] This can be represented by the data in Tables I and II. The plot of R_g versus $[CAN]^{0.5}$ was linear at a lower CAN concentration, as shown in Figure 7, indicating that termination occurred by the recombination of double radicals. On the other hand, at a higher CAN concentration, a deviation from the linearity was observed; this showed that termination took place because of single-radical termination, which resulted in a decrease in R_g.

TABLE II
R_p for Graft Copolymerization of MMA onto Na-PCMGG (DS = 0.497) at Various Monomer Concentrations

[MMA] (mol/L)	$R_p \times 10^5$ (mol L^{-1} s^{-1})
0.037	0.62
0.074	0.78
0.157	1.00
0.222	1.39

Na-PCMGG = 1.0 g (dry basis); [HNO_3] = 0.10 mol/L; [CAN] = 0.013 mol/L; time = 4 h; temperature = 35°C; volume of water = 136.45 ± 2.95 mL; total volume = 150 mL.

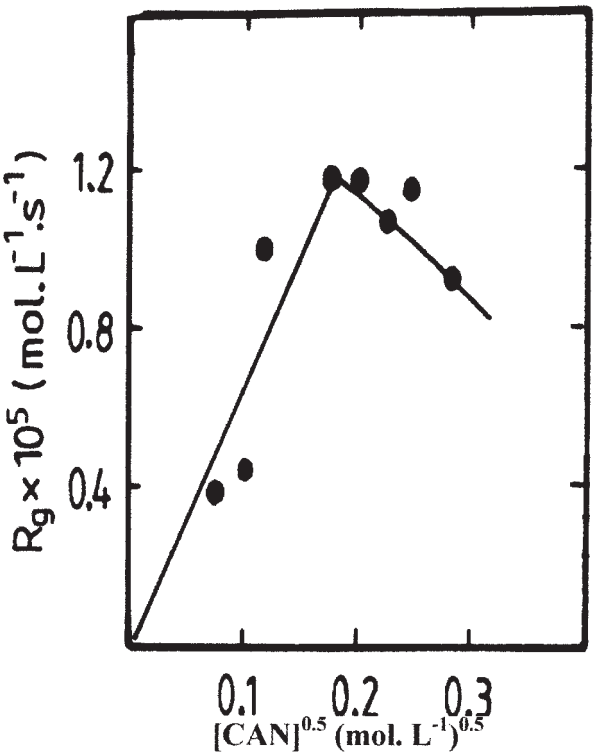

Figure 7 $R_g \times 10^5$ versus $[CAN]^{0.5}$.

The influence of the initiator concentration and the monomer concentration on the overall R_p value (Tables I and II) is shown in Figure 8. The plots of R_p

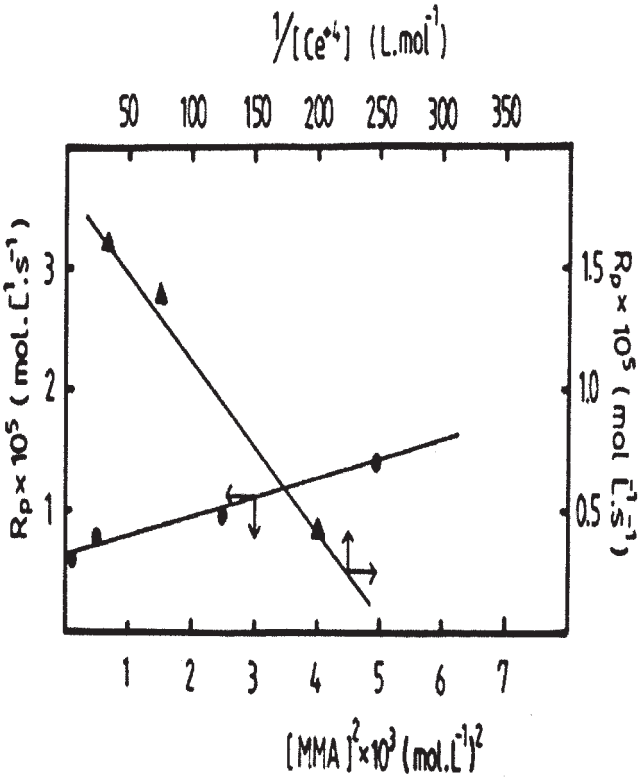

Figure 8 (●) $R_g \times 10^5$ versus $[M]^2$ and (▲) $R_g \times 10^5$ versus $1/[Ce^{+4}]$.

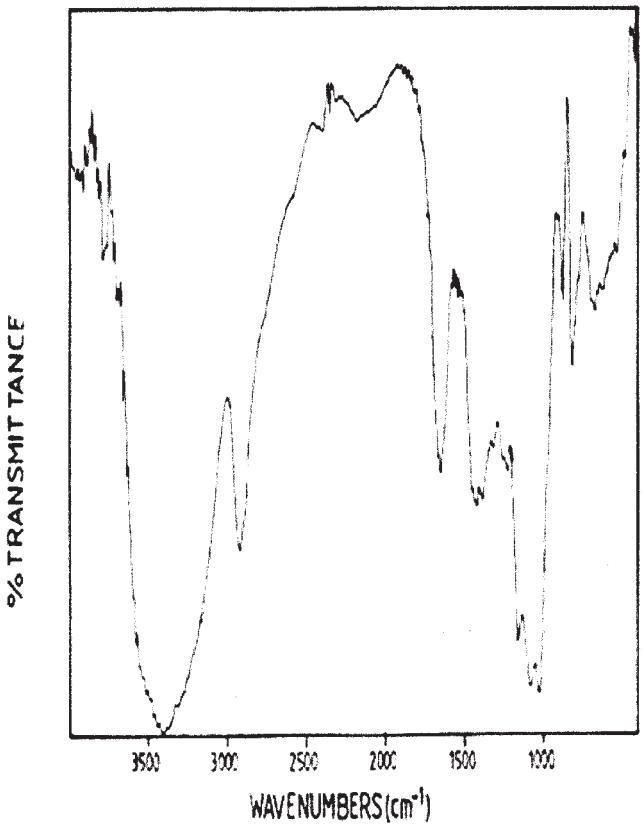

Figure 9 IR spectrum of a GG sample.

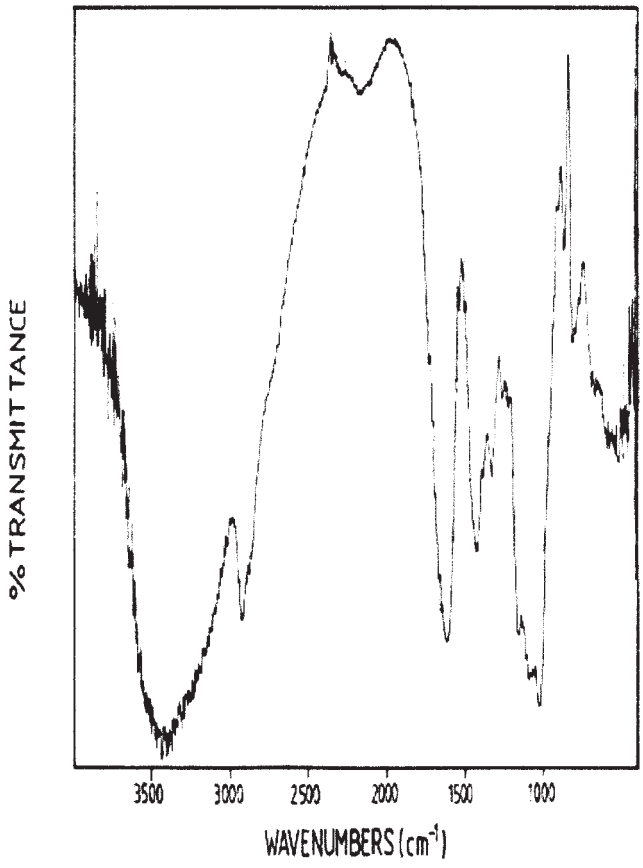

Figure 10 IR spectrum of an Na-PCMGG sample (DS = 0.497).

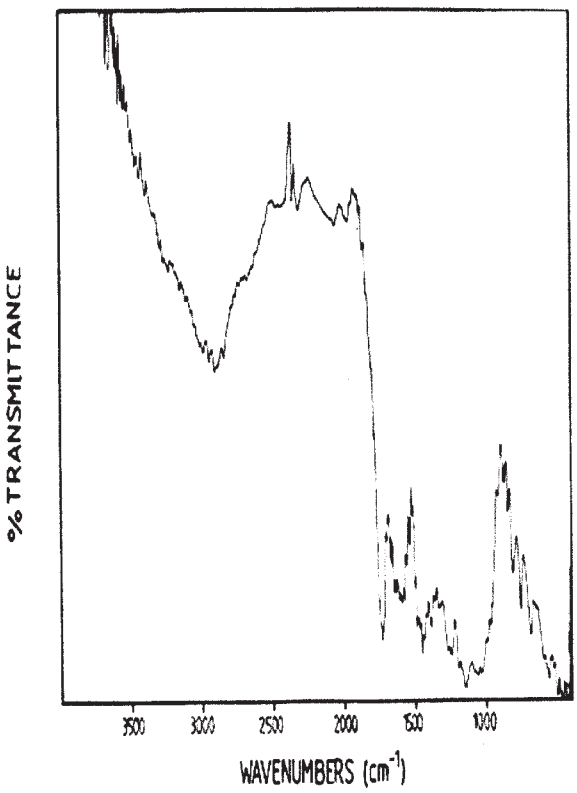

Figure 11 IR spectrum of an Na-PCMGG-*g*-PMMA sample (grafting percentage = 226.47).

versus $[M]^2$ and R_p versus $1/[Ce]^{+4}$ were linear and so supported the kinetic scheme proposed earlier.[4]

Evidence of grafting

IR spectra

Figure 9 shows the IR spectrum of GG. A very strong and broad absorption band at approximately 3415 cm^{-1} was assigned to OH stretching. A reasonably sharp absorption band at approximately 2930 cm^{-1} was attributed to —CH stretching. The absorption band at approximately 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 approximately 1300 and 1250 cm^{-1}.

The IR spectrum of Na-PCMGG (DS = 0.497; Fig. 10) showed a somewhat reduced intensity of the absorption at approximately 3408 cm^{-1} due to OH stretching, indicating that some of the OH groups present in the GG sample were involved in carboxymethylation. The band at approximately 2930 cm^{-1} was due to —CH stretching. The band due to water (bending of water) that appeared at approximately 1650 cm^{-1} for the GG sample (cf. Fig. 9) was absent for the Na-PCMGG sample. The asymmetric and symmetric vibrations due to thes Comp: $-C\lessgtr^{O}_{O}$ moiety were assigned to 1615 and 1427 cm^{-1}, respectively. This could be attributed to the incorporation of carboxymethyl groups into GG. In the GG sample, the —CH_2 bending was assigned to approximately 1440 cm^{-1} (cf. Fig. 9). On the other hand, for the Na-PCMGG sample (Fig. 10), the band at approximately 1427 cm^{-1} was a split band, and one part could be assigned to the bending of —CH_2.

Figures 11 and 12 show the IR spectra of Na-PCMGG-*g*-PMMA and PMMA samples, respectively (isolated by hydrolysis). The spectra of the graft copolymer (Fig. 11) showed absorption bands of Na-PCMGG (DS = 0.497; Fig. 10) as well as an additional band at approximately 1750 cm^{-1} assigned to —C≡O stretching of the ester group (—$COOCH_3$), which is characteristic of spectra of PMMA (Fig. 12). Thus, the presence of an additional band at approximately 1750 cm^{-1} in the graft copolymer, that is, Na-PCMGG-*g*-PMMA, indicated beyond a doubt that the grafting of MMA onto Na-PCMGG had taken place.

SEM

An SEM micrograph of GG (Fig. 13) showed discrete, elongated, granular structures separated from one another. Upon the carboxymethylation of GG, the struc-

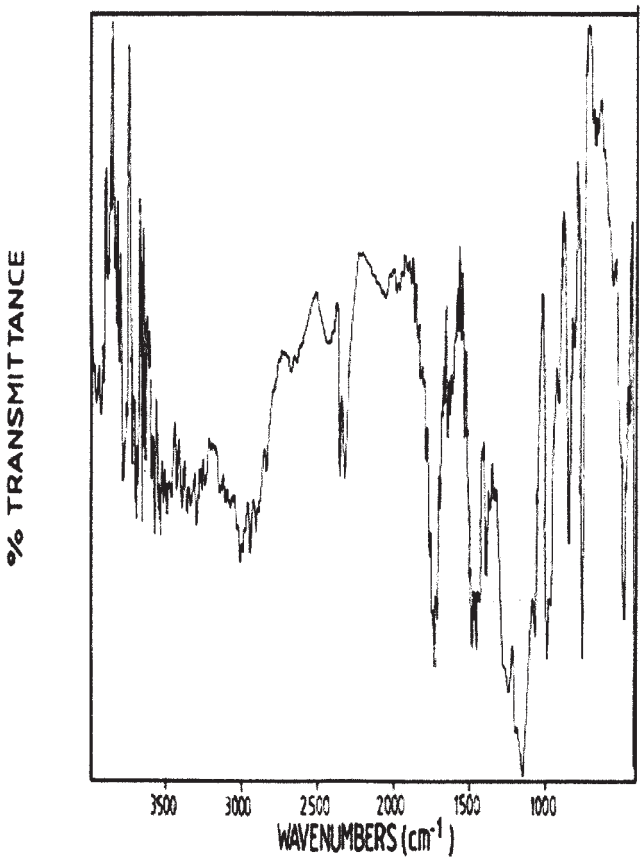

Figure 12 IR spectrum of a PMMA sample.

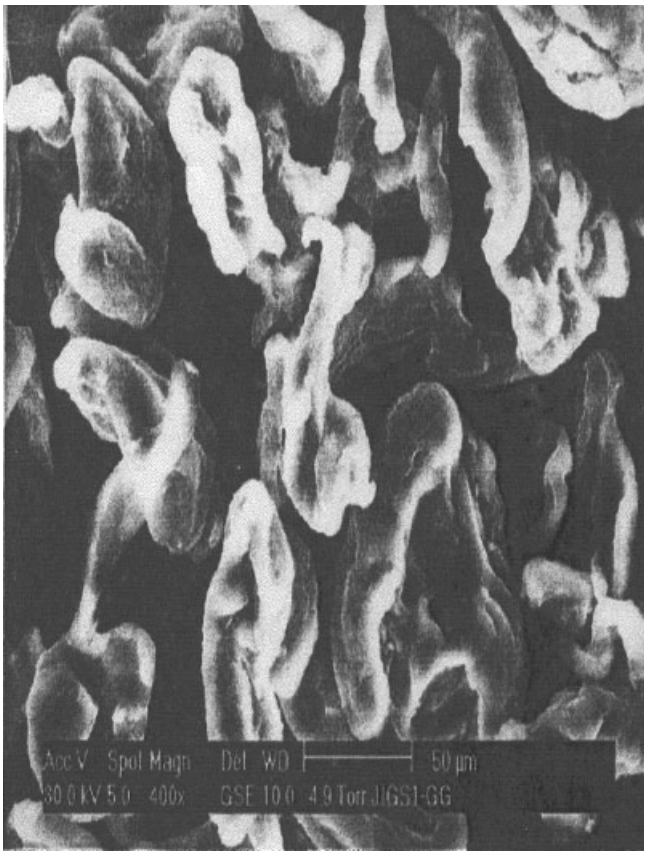

Figure 13 SEM micrograph of a GG sample (400×).

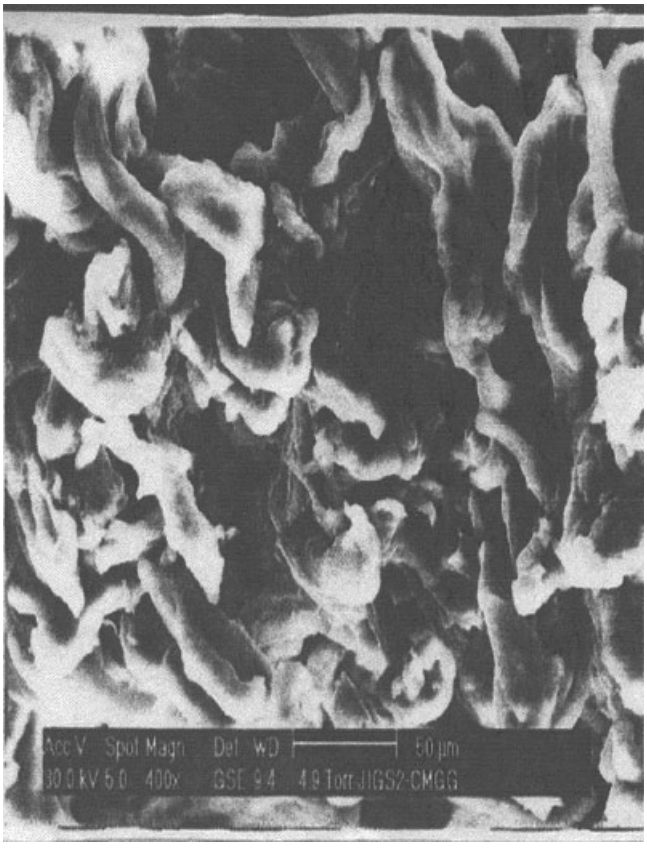

Figure 14 SEM micrograph of an Na-PCMGG sample (DS = 0.497; 400×).

Figure 15 SEM micrograph of an Na-PCMGG-*g*-PMMA sample (grafting percentage = 226.47; 400×).

ture of GG was improved, as shown in Figure 14; the topology of the granules (Fig. 13) was modified in such a way that some of the granules were attached by adhering to 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*-PMMA (grafting percentage = 226.47) can be seen in Figure 15. By comparing the morphology of the grafted sample (Fig. 15) with ungrafted material [GG (Fig. 13) and Na-PCMGG (Fig. 14)], we found that the grafted chains drastically changed the topology of the Na-PCMGG (DS = 0.497) sample. As shown in Figure 15, a lumpy morphology could be observed with MMA. An SEM micrograph of Na-PCMGG-*g*-PMMA (Fig. 15) revealed additional surface deposits indicating that grafting had taken place.

TGA

Figure 16 shows a primary thermogram of GG obtained at a scanning rate of 10°C/min in an inert atmosphere. The overall degradation of GG (Fig. 16) involved only a single step. The sample began to decompose at 225°C and rapidly lost 60% of its weight up to 325°C. Beyond 325°C, the weight loss was slow

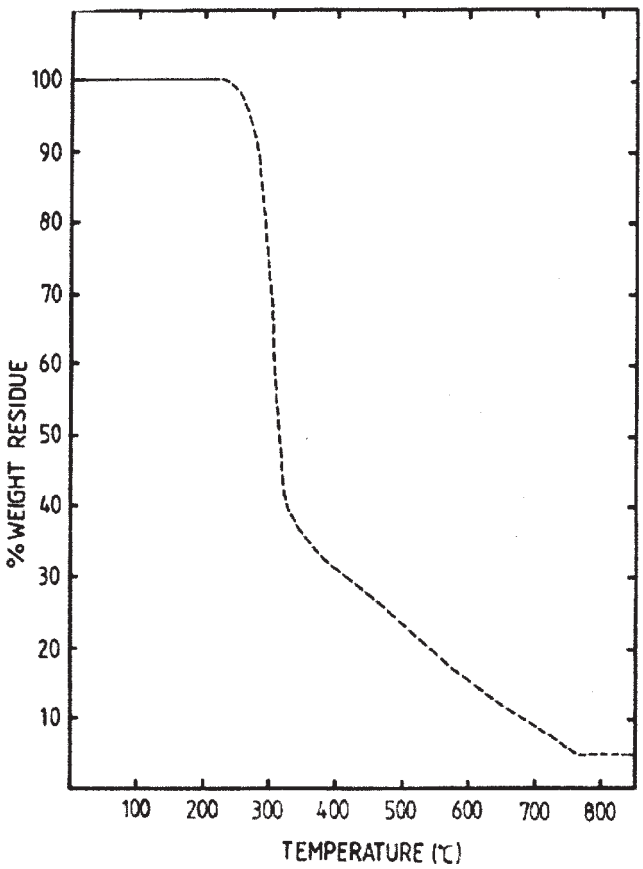

Figure 16 TGA thermogram of a GG sample.

and gradual up to about 765°C; 5% of the residual weight remained. In the temperature range of 325–765°C, the sample lost 35% of its original weight. The maximum rate of weight loss occurred at 315°C.

Figure 17 shows primary thermograms obtained at a scanning rate of 10°C/min for Na-PCMGG (DS = 0.497), Na-PCMGG-*g*-PMMA (grafting percentage = 226.47), and PMMA in an inert atmosphere. The Na-PCMGG sample showed a single step of degradation. The decomposition started at 215°C and proceeded at a faster rate up to 310°C; at this temperature, the sample lost 45% of its original weight. However, beyond this temperature, degradation proceeded at a very slow rate up to 625°C. This temperature range, that is, 310–625°C, involved about 17.5% weight loss. With a further increase in the temperature, the degradation occurred at a relatively fast rate up to 765°C, in comparison with the degradation in the earlier temperature range. The temperature at which the maximum rate of weight loss occurred was 300°C. The overall degradation left about 22% residue.

The overall thermal degradation of Na-PCMGG-*g*-PMMA had two steps. The first step, encompassing a temperature range of 160–305°C, involved about 20% weight loss, the rate of weight loss reaching a maximum at 275°C. This step was immediately followed by the second step, which involved about 67% weight loss over a temperature range of 305–780°C with a maximum rate of weight loss at 390°C. The sample left about 13% residue.

For PMMA (Fig. 17), the decomposition began at 200°C and proceeded very slowly up to 330°C, with about 10% weight loss. Beyond 330°C, the sample degraded very rapidly up to 455°C, with about 80.5% weight loss. The maximum weight loss occurred at 370°C. The degradation was complete at about 455°C; the residual weight was about 9.5%.

The characteristic temperature values and the integral procedural decomposition temperatures (IPDTs) of GG, Na-PCMGG (DS = 0.497), Na-PCMGG-*g*-PMMA (grafting percentage = 226.47), and PMMA are given in Table III. An examination of the IPDT values indicated that the overall thermal stability of GG increased upon its carboxymethylation, and this could be attributed to the addition of the polar groups to GG, which led to the increased intermolecular and intramolecular interactions, which ultimately imparted higher thermal stability to GG.

However, the observed decrease in the thermal stability of the graft copolymer of Na-PCMGG containing PMMA, in comparison with that of Na-PCMGG (DS = 0.497), was expected because polyacrylates are known to depolymerize upon pyrolysis.[18]

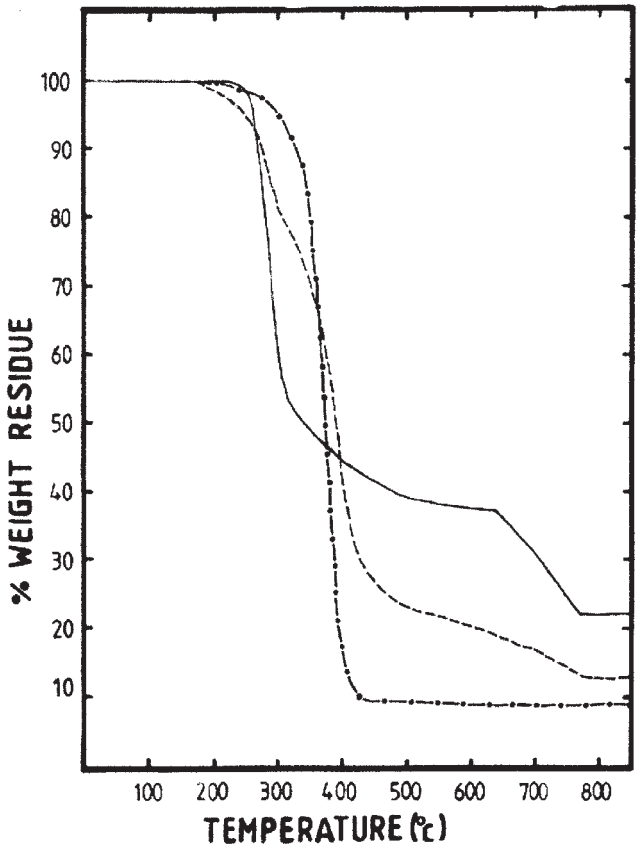

Figure 17 TGA thermograms of (—) Na-PCMGG (DS = 0.497), (- - -) Na-PCMGG-*g*-PMMA (grafting percentage = 226.47), and (- · -) PMMA.

TABLE III
Thermal Analysis of GG, Na-PCMGG (DS = 0.497), Na-PCMGG-*g*-PMMA (Grafting Percentage 226.47), and PMMA Samples

	TGA Data							Transition Data from DSC	
			T_{max} (°C)						
Sample	T_i (°C) (IDT)	T_f (°C) (FDT)	Step 1	Step 2	T_{10} (°C)	T_{50} (°C)	IPDT (°C)	T_1 (°C)	T_2 (°C)
GG	225	765	315	—	280	315	477.72	115.88 (endo)	313.53 (exo)
Na-PCMGG	215	765	300	—	270	340	531.80	177.50 (endo)	282.18 (exo)
Na-PCMGG-*g*-PMMA	160	780	275	390	275	385	484.88	188.69 (broad endo)	393.69 (broad endo)
PMMA	200	455	370	—	330	375	321.13	385.36 (endo)	—

IDT = initial decomposition temperature; FDT = final decomposition temperature; I_{max} = temperature for maximum rate of decomposition; I_{10} = temperature for 10% weight loss; I_{50} = half volatilization point temperature (i.e., the temperature at which half of the ultimate weight loss occurs); IPDT = integral procedural decomposition temperature.

DSC

The transition data of GG, Na-PCMGG (DS = 0.497), Na-PCMGG-*g*-PMMA (grafting percentage = 226.47), and PMMA samples obtained from their respective DSC thermograms (not shown) are given in Table III. GG had an endothermic peak at 115.88°C and an exothermic peak at 313.53°C. The endotherm may have been due to the loss of residual moisture, and the exotherm was attributed to the decomposition of the sample. On the other hand, for the Na-PCMGG sample, the endothermic transition at 177.50°C was due to the melting of Na-PCMGG, but the exothermic transition observed at 282.18°C was attributed to the decomposition of the sample.

The DSC scan of Na-PCMGG-*g*-PMMA (grafting percentage = 226.47) showed two broad endothermic transitions at 188.69 and 393.60°C. The transition at 188.69°C may have been due to the melting of the graft copolymer sample. In the temperature range of 278.69–430°C, this graft copolymer sample generally decomposed, and this was expected to yield an exotherm. However, during decomposition, the grafted chains of PMMA started unzipping, taking away the latent heat of evaporation of the monomer (MMA) and thereby overshadowing the exotherm by a huge endotherm at 393.60°C. The endothermic transition at 385.36°C was also due to the unzipping and evaporation of the monomer, which cooled the sample cell.

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