Photo-Induced Graft Copolymerization of Acrylonitrile onto Sodium Salt of Partially Carboxymethylated Guar Gum

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ABSTRACT: Photo-induced graft copolymerization of acrylonitrile (AN) onto sodium salt of partially carboxymethylated guar gum (Na-PCMGG, $\overline{DS} = 0.291$) was carried out in an aqueous medium using ceric ammonium nitrate (CAN) as photo-initiator to synthesize a novel graft copolymer, Na-PCMGG-g-PAN, which may find potential application as a superabsorbent hydrogel. Studying the influence of concentrations of photo-initiator (CAN), nitric acid, monomer (AN) as well as reaction time, temperature, and amount of substrate on the grafting yields, the reaction conditions for optimum grafting were evaluated. Maximum values of the grafting yields achieved were %G = 285.77 and %GE = 70.76 at optimized conditions. The proposed kinetic scheme could explain very well the experimental results. The influence of different kind of acids on the grafting yields was also studied. Grafting process was confirmed with the help of FTIR, thermal (TGA/DSC), and SEM techniques. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41371.

INTRODUCTION

Chemical modification of polymers can provide a potential route for altering the physical and mechanical properties significantly. The modification of polymers via grafting has been the subject of much interest and has made paramount contribution towards better industrial and biomedical applications. Amongst the grafting methods used, photo-induced grafting is widely recognized to be useful because of its significant advantages: less degradation of the backbone polymer, control over the grafting reaction in addition to attaining higher grafting efficiency, low cost of operation, and selectivity to absorb UV light.

Guar gum (GG), an industrially important natural and renewable, non-ionic, rigid polymer[1] consists of a linear chain of β-D-mannopyranosyl units linked $(1 \rightarrow 4)$ with single member α-D-galactopyranosyl units $(1 \rightarrow 6)$ as side branches. Incomplete hydration of guar gum at ambient temperature, its poor solution clarity and the desire for products with modified or special properties have prompted us to carry out carboxymethylation of guar gum to obtain sodium salt of partially carboxymethylated guar gum (Na-PCMGG). Guar Gum and its derivatives find applications not only in petroleum, textile, paper, food, and explosive industries but also in mining, minerals, pharmaceuticals, medicines, and drugs.[2] Guar gum and its derivatives, although find wide range of industrial applications, they also suffer from some draw backs like biodegradability,[3] which limits its uses considerably. These draw backs can be improved

through the grafting of vinyl monomers onto them, thereby imparting new properties to the polymer backbone. In this investigation, we have introduced the carboxymethyl groups in the GG molecule to increase the swellability of GG and thereby facilitating the diffusion of monomer and photo-initiator (CAN). Ionization of carboxymethyl groups along the GG chains will introduce negative charges which will attract ceric ions to the GG molecules, leading to the formation of more active sites on GG backbone, thus increasing the reactivity of GG towards grafting.

Many investigations have been carried out on grafting of vinyl monomers onto guar gum[4,5] and partially carboxymethyled guar gum[6–9] using various redox pairs. However, reports on photo-grafting of vinyl monomers onto sodium salt of partially carboxymethylated guar gum are scanty.[10,11] The present work, aims to evaluate the optimized reaction conditions for photo-grafting of AN onto Na-PCMGG ($\overline{DS} = 0.291$) using CAN as a photo-initiator. The photo-graft copolymer, Na-PCMGG-g-PAN has been duly characterized. This has been done not only to develop specialty polymeric materials but also to elucidate the photo-grafting mechanism over a range of values for the reaction variables studied in the present work. The nitrile groups of the optimally synthesized graft copolymer, Na-PCMGG-g-PAN, may be completely converted into a mixture of hydrophilic carboxamide and carboxylate groups during alkaline hydrolysis, followed by *in situ* crosslinking of the grafted PAN chains, as per the procedure described earlier,[12] leading to the formation
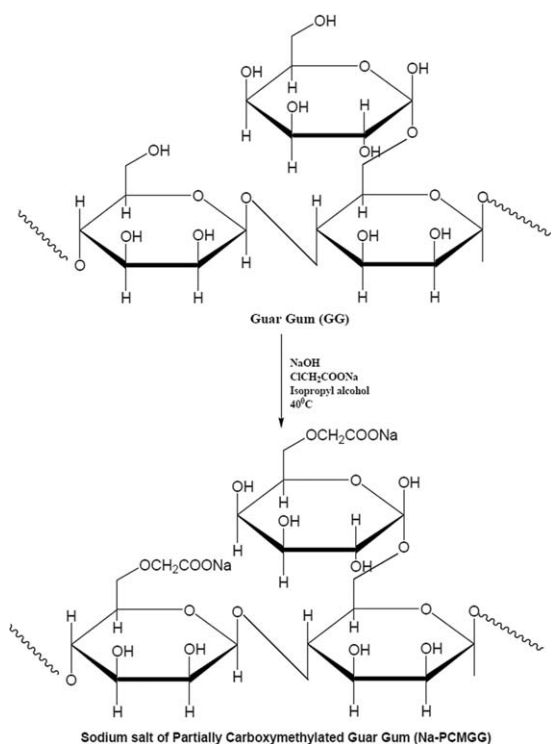
Scheme 1. Preparation of sodium salt of partially carboxymethylated guar gum (Na-PCMGG).

Figure 1. Photo-chemical reactor.

of the superabsorbent hydrogel, H-Na-PCMGG-g-PAN, which may find potential use in the personal health care products.

EXPERIMENTAL

Materials and Methods

Guar gum (GG) used in the present work was kindly supplied by H. B. Gum Industries (Kalol, India). Preparation (Scheme 1) and purification as well as the measurement of degree of substitution ($\overline{DS}$) of the sodium salt of partially carboxymethylated guar gum (Na-PCMGG) were carried out as described earlier.[13,14] The $\overline{DS}$ of Na-PCMGG was found to be 0.291. AN (Samir Tech. Chem., Baroda, India) was distilled out at an atmospheric pressure and the middle fraction was collected and used. CAN of reagent grade (Chiti Chem.; Baroda, India) was used as received. Analar grade nitric acid (HNO_3) was used. Fresh solutions of the photo-initiator were used, prepared by dissolving the required amount of CAN in nitric acid. All other reagents and solvents used in the present work were of reagent grade. Nitrogen gas was purified by passing through a fresh pyragallol solution. Low conductivity water was used for the preparation of solutions as well as graft copolymer reactions.

Photo-Graft Copolymerization

The photo-graft copolymerization reactions were carried out in a photo-chemical reactor (Figure 1) supplied by Scientific Aids and Instruments (SAIC, Madras, India) as per the procedure described earlier.[10] A weighed amount of Na-PCMGG ($\overline{DS}$ = 0.291, 0.25–3.0 g, dry basis) was dissolved in 100 mL of low conductivity water in the reaction flask, and the solution was
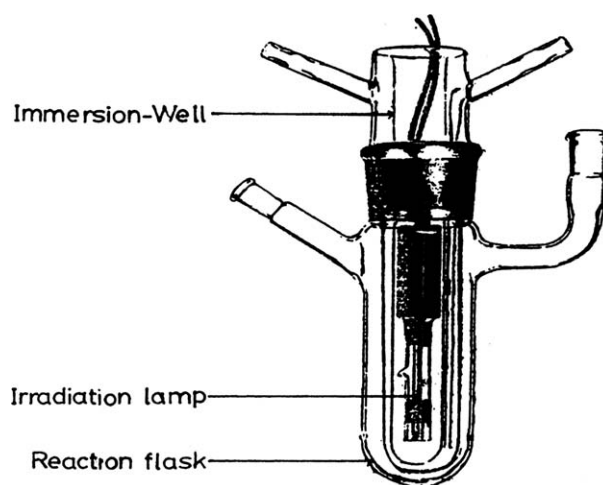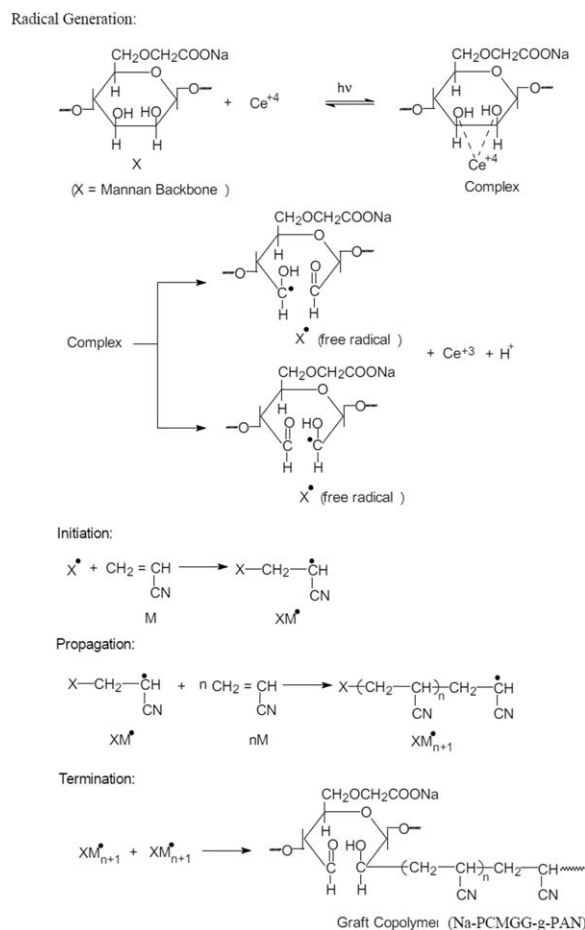
stirred with continuous bubbling of a slow stream of nitrogen gas for half an hour. About 2.5 mL of freshly prepared CAN solution ($1.5 \times 10^{-3}-20 \times 10^{-3}$ mol L^{-1}) in nitric acid (nil–0.5 mol L^{-1}) was added to the reaction flask, and the contents were then flushed with purified nitrogen gas for half an hour, followed by the addition of a known concentration of freshly distilled AN (0.072–0.578 mol L^{-1}). The reaction flask was then assembled with an immersion well containing a 125-W medium pressure mercury lamp. The whole assembly (photo-chemical reactor) was placed in a dark cabinet after covering it completely with aluminum foil. The lamp was then illuminated. Water from a constant-temperature water circulation bath was circulated over the immersion well and the reaction flask. The solution then was irradiated with continuous stirring for different time intervals (0.5–10 h) in the temperature range of 20–50°C. After the completion of the grafting reaction, the irradiated sample solution was removed carefully, and the crude graft copolymer was isolated by centrifugation. It was then purified by repeated washings with 95% methanol and finally with pure methanol. The crude copolymer sample of Na-PCMGG-g-PAN thus obtained was dried in vacuum at 40°C. The homopolymer (PAN) was separated from the crude graft copolymer by carrying out exhaustive soxhlet extraction with DMF. After the complete removal of the homopolymer, the pure graft copolymer was dried at 40°C in vacuum until a constant weight was obtained. The mechanistic pathway for the synthesis of the graft copolymer, Na-PCMGG-g-PAN, is shown in Scheme 2.

Influence of Different Kind of Acids on Photo-Grafting

To study the influence of different kind of acids (viz. HCl and H_2SO_4) on photo-grafting, we carried out the photo-graft copolymerization reactions exactly in the similar manner as described above, using the following reaction conditions : Na-PCMGG = 2.0g (dry basis); [CAN] = 4×10^{-3} mol L^{-1}; [HCl] or [H_2SO_4] = nil to 0.50 mol L^{-1}; [AN] = 0.360 mol L^{-1}; time = 4 h; temperature = 35°C; volume of water = 100 mL, and total volume = 105 mL. After completion of reaction the crude graft copolymer samples were also isolated and purified as described above.

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

Figure 2. Effect of amount of Na-PCMGG ($\overline{DS}$ = 0.291) on: (•) %G and (▲) %GE.

Grafting Yields and Kinetic Parameter

The percentage of grafting (%G), percentage of grafting efficiency (%GE) and rate of polymerization (R_p) were evaluated as follows[10]:

$$\% \, G = \frac{\text{Weight of polymer grafted}}{\text{Initial weight of backbone}} \times 100$$

$$\% \, GE = \frac{\text{Weight of polymer grafted}}{\text{Weight of polymer grafted} + \text{Weight of homopolymer}} \times 100$$

$$R_p (\text{molL}^{-1}\text{s}^{-1}) = \frac{\text{weight of polymer grafted} + \text{weight of homopolymer}}{\text{Mol. wt. of monomer} \times \text{reaction time (s)} \times \text{vol. of the reaction mix. (mL)}} \times 10^3$$

Isolation of Grafted Chains

The graft copolymer of Na-PCMGG ($\overline{DS}$ = 0.291) containing PAN was hydrolyzed by refluxing for 12 h in 1N HCl as suggested by Brockway and Seaberg.[15] After all the Na-PCMGG went into the solution, a resinous mass was obtained which was characterized with IR spectroscopy.

FTIR Spectra

The IR Spectra of Guar Gum, Na-PCMGG ($\overline{DS}$ = 0.291), Na-PCMGG-g-PAN and PAN were taken in KBR pellets using Nicolet Impact 400D Fourier Transform Infrared Spectrophotometer.

Thermogravimetric Analysis (TGA)

The thermal behavior of Na-PCMGG ($\overline{DS}$ = 0.291), Na-PCMGG-g-PAN and PAN were examined in an inert atmosphere at a heating rate of 10°C min^{-1} with the help of Dupont 951 thermogravimetric analyzer.

Differential Scanning Calorimetry (DSC)

The DSC scans of Na-PCMGG ($\overline{DS}$ = 0.291), Na-PCMGG-g-PAN and PAN were recorded in nitrogen atmosphere at a scan rate of 5°C min^{-1} on DSC 2920 TA instrument.

Scanning Electron Microscopy (SEM)

Model ESEM TMP + EDAX, Philips make was used to obtain the micrographs of Guar Gum, Na-PCMGG ($\overline{DS}$ = 0.291) and Na-PCMGG-g-PAN (%G = 285.77).
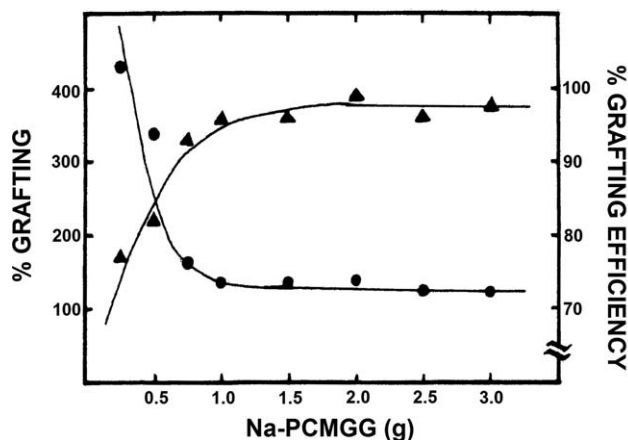
RESULTS AND DISCUSSION

To gain an insight into the mechanism of the photo-grafting reaction, the effect of variables in the synthesis such as amount of substrate, concentrations of photo-initiator, nitric acid and monomer as well as time and temperature were studied.

Effect of Backbone Concentration

Figure 2 shows the influence of varying amount of Na-PCMGG on the grafting yields. It can be seen from this figure that in the beginning up to 1 g of Na-PCMGG, %G decreased very rapidly beyond which it remains almost constant. However, on the other hand %GE increased initially up to Na-PCMGG = 1.0 g and then remains practically constant with further increase in the amount of Na-PCMGG. The observed increase in %GE with an increase in the amount of Na-PCMGG is due to the increase in the weight of the grafted side chains. The descending trend in %G was due to the high viscosity of Na-PCMGG solution. With increase in concentration of Na-PCMGG, the viscous reaction medium made the diffusion of both monomer and the photo-initiator near to Na-PCMGG more difficult, thereby greatly hindering the rate of photo-graft copolymerization. In addition, the decrease in the monomer-to-backbone ratio also accounted for the observed decrease in %G. Similar observations have also been reported earlier.[16–21]
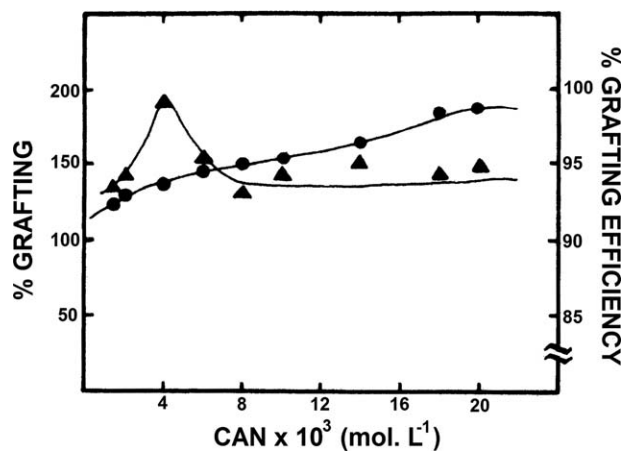
Figure 3. Effect of ceric ammonium nitrate concentration on: (•) %*G* and (▲) %GE.

Figure 4. Effect of nitric acid concentration on: (•) %*G* and (▲) %GE.

Effect of Photo-Initiator Concentration

The effect of the photo-initiator (CAN) concentration on photo-graft copolymerization was studied by varying the concentration of CAN from 1.5×10^{-3} to 20×10^{-3} mol L^{-1}. The results are presented in Figure 3; it is seen that %*G* increased steadily in the whole range of photo-initiator concentration studied. However, the value of %GE increased initially and reached maximum value of 99.35% at $[Ce^{+4}] = 4.00 \times 10^{-3}$ mol L^{-1}, beyond which it decreased with further increase in the photo-initiator concentration. The increasing trend in the grafting yields is attributed to the formation of more and more grafting sites onto the backbone, due to the photo-decomposition of the complex formed between Na-PCMGG and Ce^{+4}. Thus, once the activation along the backbone took place it was immediately followed by the graft copolymerization. Decrease in %GE at higher concentration of the photo-initiator is attributed to the termination of growing grafted chains by excess ceric ions. Similar results are also reported in the literature.[22–24]

Effect of Acid Concentration

The influence of the HNO$_3$ concentration on the grafting yields was studied by varying the acid concentration in the range nil–0.5 mol L^{-1} and the results are depicted in Figure 4. It is evident from the figure that there exists an optimum concentration of nitric acid (0.10 mol L^{-1}) to provide maximum %*G* (136.30%) and %GE (99.35%). Beyond the optimum concentration of nitric acid, both the values, %*G* and %GE were found to decrease. Interestingly, even at zero concentration of nitric acid the value of %*G* was found to be 116.35% (cf., Figure 4); this is due to the possibility that, even in the absence of acid, Na-PCMGG ionizes to a greater extent in an aqueous medium, thus facilitating the diffusion of monomer as well as photo-initiator leading to a higher value of grafting yields. Below the optimum concentration the observed increase in the values of the grafting yields with increase in the nitric acid concentration is attributed to an increase in the initiation rate of photo-grafting. However, at higher acid concentrations, the observed decrease in the percentage of grafting could be due to a corresponding reduction in ceric-Na-PCMGG complex formation as well as an increase in polymer termination rates.[25–29]
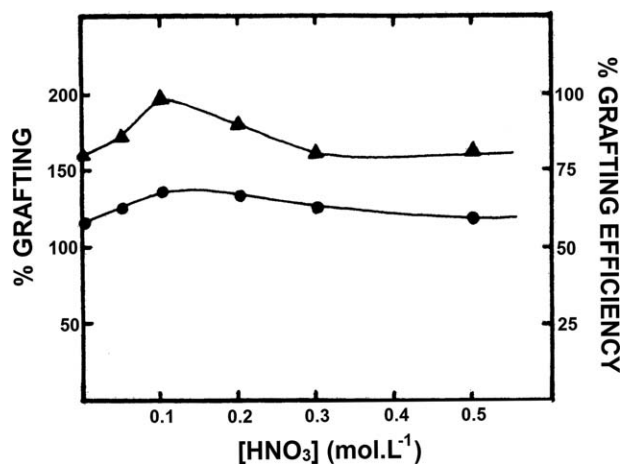
Effect of Monomer Concentration

Figure 5 shows the influence of the monomer (AN) concentration on %*G* and %GE. The value of %*G* increased very slowly in the beginning up to 0.216 mol L^{-1} and achieved the maximum value of %*G* = 136.30 at [AN] = 0.360 mol L^{-1}. The value of %GE also varied in the similar manner. The enhancement of the grafting yields with increasing monomer concentration could be traced to the greater availability of grafting sites to monomer. However, at higher monomer concentrations, the concentration of monomer macroradicals increases and the rates of their combination and disproportionation are faster than the rate of their combination with Na-PCMGG molecules. Therefore, the homopolymerization becomes the preferred process and decrease in %*G* and %GE is observed. Similar results are also reported in the literature.[7,21,29–36]

Effect of Reaction Time

Grafting reaction was also studied by varying the time period from 0.5 to 10 h and the results are depicted in Figure 6. It can be seen from this figure that the value of %*G* increased with increase in reaction time up to 6 h and thereafter it remains unchanged with further increase in time. The value of %GE
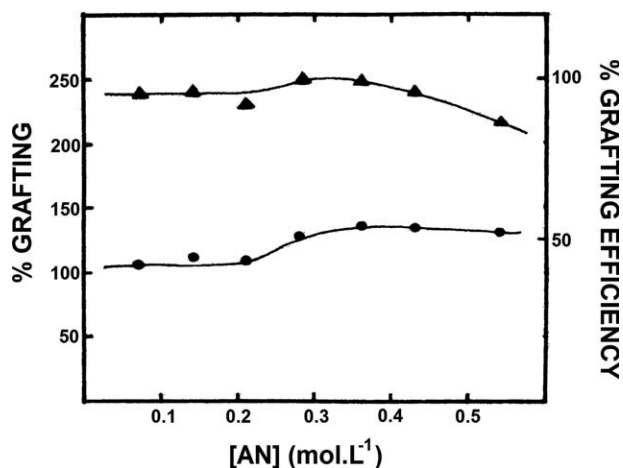

Figure 5. Effect of acrylonitrile (AN) concentration on: (•) %*G* and (▲) %GE.
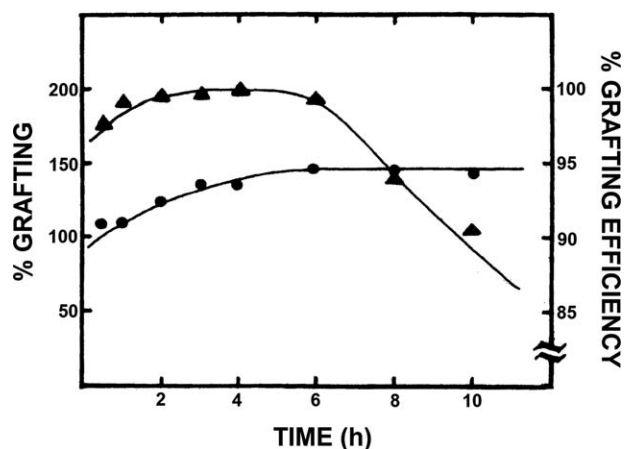
Figure 6. Influence of reaction time on: (•) %G and (▲) %GE.

Figure 7. Plots of (•) %G and (▲) %GE versus temperature.

also increased in the beginning with reaction time and decreased steadily beyond 6 h. The increase in the values of the grafting yield is due to the fact that the number of grafting sites on the backbone increased with reaction time as a result of which the extent of initiation and propagation of photo-graft copolymerization also increased with reaction time. The observed decrease in the grafting yield beyond the optimum reaction time may be presumably due to the detrimental effect of UV radiation onto the grafted side chains of PAN at larger irradiation time intervals in the presence of the photo-initiator. Besides, the observed leveling off of the values of %G beyond 6h could be attributed to a decrease in concentration for both photo-initiator and monomer, thereby causing a reduction in the number of sites on the backbone available for photo-grafting as the reaction proceeded. Similar time dependency of grafting yields was reported by other workers.[32,37–42]

Effect of Temperature

To study the influence of temperature on the grafting yields, photo-grafting reactions were carried out at seven different temperatures, ranging from 20 to 50°C. The results are presented in Figure 7. It can be seen from the figure that the values of the grafting yields (%G and %GE) increased slowly with increase in temperature and reached maximum values of the grafting yields at 35°C. Beyond the optimum temperature, the value of %G essentially remained constant, while the value of %GE decreased slowly. The favorable influence of temperature on grafting yields could be ascribed to enhanced diffusion of AN and CAN molecules onto the Na-PCMGG backbone and thereby increasing the rate of photo-decomposition of the complex formed between Ce^{+4} and Na-PCMGG. However, at higher temperature, the photo-graft copolymerization occurred with poor selectivity. In addition, various hydrogen and chain transfer reactions also might be accelerated at higher temperature, causing the decreased grafting yields. Similar results are also reported by earlier researchers.[39,42,43]

The optimum reaction conditions thus obtained for photo-initiated graft copolymerization of AN onto Na-PCMGG ($\overline{DS}$ = 0.291) were: Na-PCMGG = 0.25 g (dry basis); [CAN] = 4 × 10^{-3} mol L^{-1}; [HNO$_3$] = 0.10 mol L^{-1}; [AN] = 0.289 mol L^{-1}; time = 6 h; temperature = 40°C and Total Volume = 105 mL.
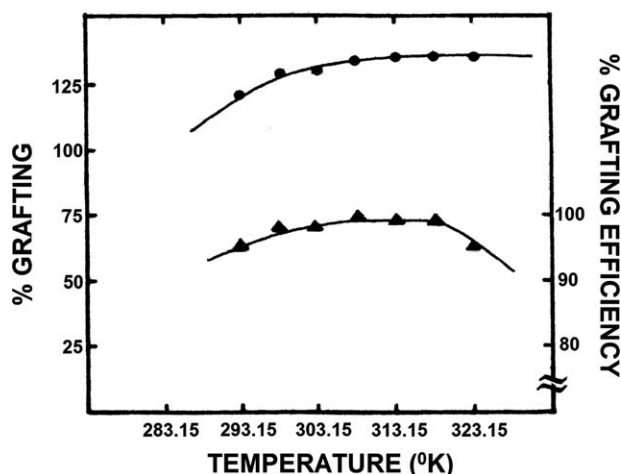
The maximum values of the grafting yields achieved were %G = 285.77 and %GE = 70.76.
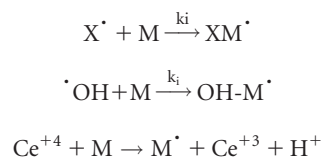
KINETICS AND MECHANISM

The mechanism of the free radical photo-grafting of AN onto Na-PCMGG ($\overline{DS}$ = 0.291) is expected to proceed according to the following scheme which we have proposed earlier[10]:
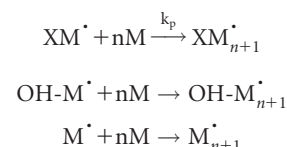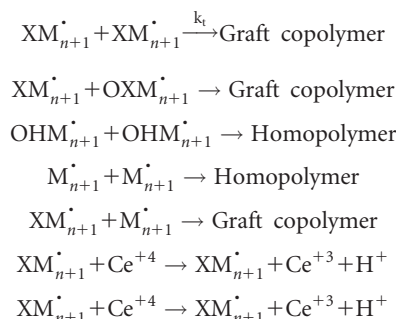
Radical Generation:

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

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

Initiation:

$$X^{\bullet} + M \xrightarrow{k_i} XM^{\bullet}$$

$${}^{\bullet}OH + M \xrightarrow{k_i} OH\text{-}M^{\bullet}$$

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

Propagation:

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

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

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

Termination:

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

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

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

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

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

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

$$XM^{\bullet}_{n+1} + Ce^{+4} \rightarrow XM^{\bullet}_{n+1} + Ce^{+3} + H^{+}$$
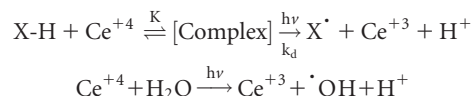
Here, X–H denotes the reactive groups of Na-PCMGG and M is the monomer (AN). With a steady state assumption, the

Table I. Rate of Polymerization (R_p) for Photo-Graft Copolymerization of Acrylonitrile (AN) onto Sodium Salt of Partially Carboxymethylated Guar Gum (Na-PCMGG, $\overline{DS}$=0.291) at Various Monomer Concentrations[a]

AN (mol L^{-1})	$R_p \times 10^5$ (mol L^{-1} s^{-1})
0.072	2.66
0.144	2.86
0.216	2.94
0.289	3.19
0.360	3.42
0.433	3.44
0.578	3.73

[a] Reaction conditions: Na-PCMGG : 2.0 g (dry basis); [CAN] : 4.0 × 10^{-3} mol L^{-1}; [HNO$_3$] : 0.10 mol L^{-1}; [AN] : Varied as shown; Time : 4 h; Temperature : 35°C and Total Volume : 105 mL.

following expressions [eqs. (4) and (5)] were derived for the value of R_p:

$$R = k_p \left[XM_{n+1}^{\bullet} \right] [M]$$

$$R = k_p \left[\frac{k_d^{\bullet} k_i}{k_t} \right]^{1/2} \left[Ce^{+4} \right]^{1/2} [M]$$

$$R_p = R_g + R_h$$

The values of R_p evaluated for various monomer (AN) and photo-initiator (CAN) concentrations, for the photo-grafting of AN onto Na-PCMGG ($\overline{DS}$ = 0.291) are presented in Tables I and II, respectively.

The effects of the concentration of the monomer (AN) and photo-initiator (CAN) on R_p, as expected from the previous equations, are shown in Figure 8. The plots of R_p versus the monomer concentration and R_p versus $[Ce^{+4}]^{1/2}$ were found to be linear with good correlation coefficient, supporting the previous scheme.

Table II. Rate of Polymerization (R_p) for Photo-Graft Copolymerization of Acrylonitrile (AN) onto Sodium Salt of Partially Carboxymethylated Guar Gum (Na-PCMGG, $\overline{DS}$=0.291) at Various Ceric Ammonium Nitrate (CAN), Photoinitiator Concentrations[a]

CAN × 10^3 (mol L^{-1})	$R_p \times 10^5$ (mol L^{-1} s^{-1})
1.50	3.27
2.00	3.41
4.00	3.42
6.00	3.82
8.00	3.96
10.00	4.17
14.00	4.39
18.00	4.90
20.00	4.90

[a] Reaction conditions: Na-PCMGG : 2.0 g (dry basis); [CAN] : Varied as shown; [HNO$_3$] : 0.10 mol L^{-1}; [AN] : 0.360 mol L^{-1}; time : 4 h; temperature : 35°C, and total volume : 105 mL.
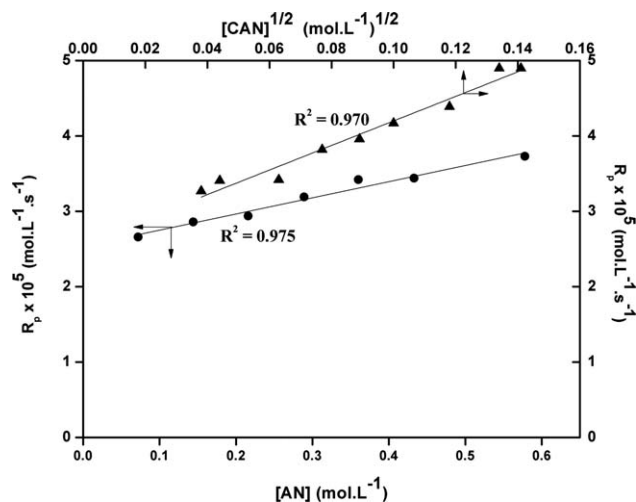

Figure 8. Plots of (•) $R_p \times 10^5$ versus the monomer concentration and (▲) $R_p \times 10^5$ versus [CAN]$^{1/2}$.

Evaluation of Energy of Activation

The natural log of % grafting (ln %G) versus $1/T$ was plotted for the initial portion of the curve, i.e. 20–35°C (cf., Figure 7) as shown in Figure 9 and these values are found to fall on a straight line with good correlation coefficient value. The least square value of the overall activation energy of grafting (E_g) was calculated and was found to be 5.38 kJ mol^{-1}.

Effect of Different Kind of Acids

The influence of the different kind of acid concentrations on the photo-grafting of AN onto Na-PCMGG is shown in Figure 10. It can be seen from this figure that %G increased with increase in nitric acid as well hydrochloric acid concentrations up to 0.10 mol L^{-1} but thereafter it decreased. On the other hand %G decreased continuously with increasing sulfuric acid concentration.

The observed decrease in %G at higher concentration of acid (cf., Figure 10) could be associated with a fast rate of termination because of increase rate of generation of free radical species as well as abundance of hydrogen protons. In addition,
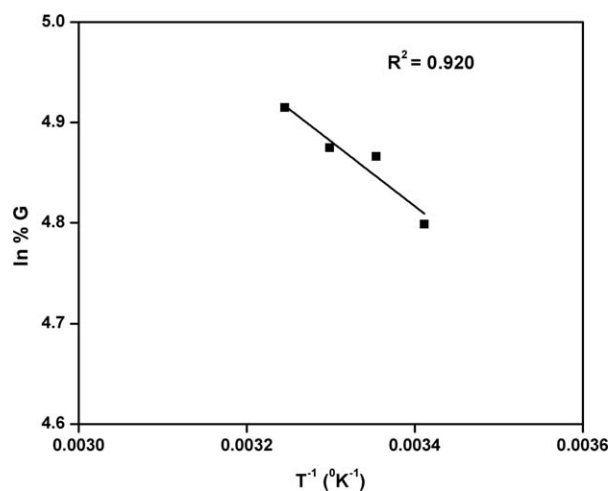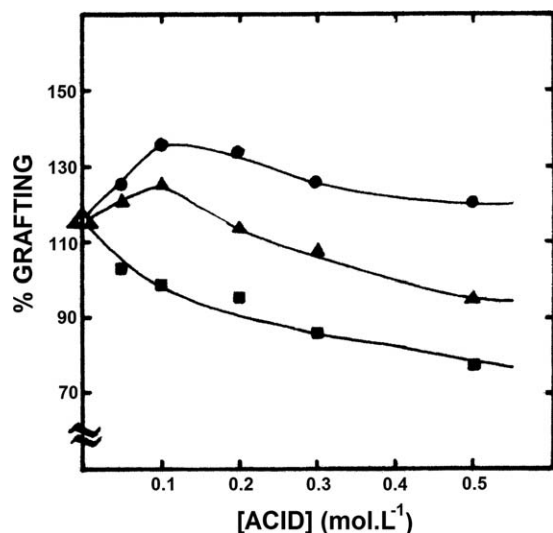

Figure 9. Plot of ln %G versus T^{-1}.

Figure 10. Effect of different kinds of acid concentrations on %*G*: (•)—HNO₃; (▲)—HCl; and (■)—H₂SO₄.

coagulation of colloidal homopolymer (PAN) which possibly could not dissolve in aqueous mixture of the AN would retard diffusion of both monomer and initiator into Na-PCMGG, thereby leading to decreased grafting. Further larger particles of the PAN homopolymer, may block UV light to an extent thus decreasing grafting.

The results of Figure 10 indicate that the effectiveness of the acid towards photo-grafting followed the order: nitric acid > hydrochloric acid > sulfuric acid. These observed differences in graft yields, when different acids were used could be explained in terms of differences in (a) ability to favor formation of ceric-Na-PCMGG complex, (b) affinity of the acid free radical species for Na-PCMGG, (c) efficiency of the initiating species, (d) the half-life of the free radicals formed and (e) capability of the acid free radical species to combine and/or participate in Na-PCMGG macroradical formation and growing grafted chain. Similar results are also reported in the literature.[44,45]

Evidence of Grafting

FTIR Spectroscopy. Figure 11(a) shows the IR spectrum of guar gum (GG). The presence of a very strong and broad absorption band at ∼3415 cm^{-1} was assigned to the OH stretching. Reasonably sharp absorption at ∼2930 cm^{-1} may be attributed to the CH stretching. The absorption band at ∼1650 cm^{-1} was due to water. The —CH₂ bending in GG was assigned to an absorption at ∼1440 cm^{-1} and the frequency at ∼1380 cm^{-1} was attributed to CH bending. The OH bending was probably distributed at ∼1300 cm^{-1} and ∼1250 cm^{-1} frequencies.

The IR spectrum of Na-PCMGG ($\overline{DS}$ = 0.291) [Figure 11(b)] shows somewhat reduced intensity of the absorption, at ∼3250 cm^{-1} due to OH stretching, indicating that some of the OH groups present in GG sample were involved in carboxymethylation. The presence of a band at ∼2930 cm^{-1} was due to CH stretching. The band due to bending of water molecule at ∼1650 cm^{-1} in GG sample [Figure 11(a)] was found to be absent in the Na-PCMGG sample. The asymmetric and

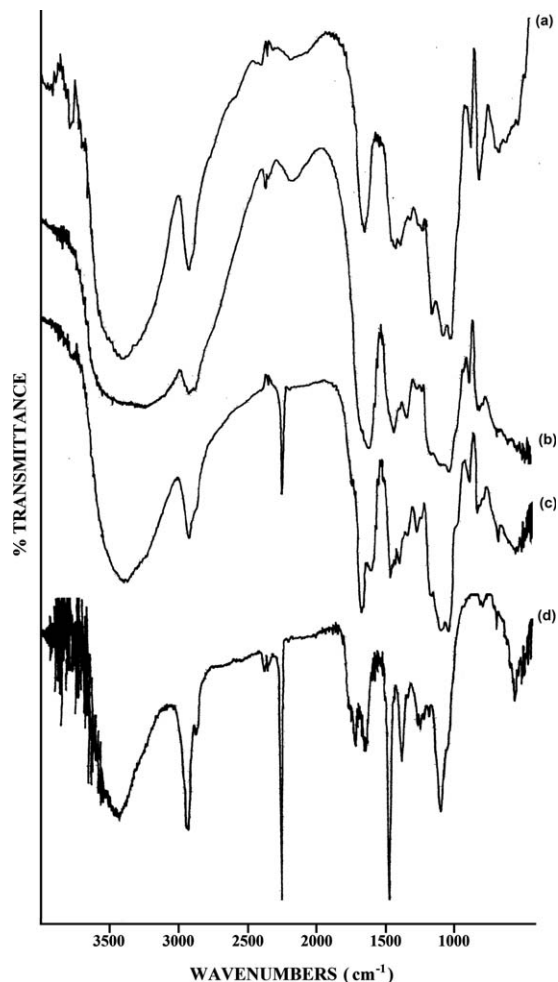**Figure 11.** FT-IR spectra of (a) Guar Gum (GG); (b) Na-PCMGG; (c) Na-PCMGG-*g*-PAN; and (d) PAN.

symmetric vibrations due to —COO— moiety were assigned to 1615 and 1421 cm^{-1}, respectively. This is attributed to the incorporation of carboxymethyl groups in Guar gum.

The IR spectra of Na-PCMGG-*g*-PAN [Figure 11(c)] showed absorption bands of Na-PCMGG ($\overline{DS}$ = 0.291) [Figure 11(b)]; in addition to a peak at ∼2253 cm^{-1} indicating the presence of C≡N moiety which is characteristic of PAN [Figure 11(d)].

Thermogravimetric Analysis (TGA). Figure 12 shows the primary thermograms obtained at a scan rate of 10°C min^{-1} for Na-PCMGG ($\overline{DS}$ = 0.291), Na-PCMGG-*g*-PAN and PAN in an inert atmosphere. It can be observed from this figure that Na-PCMGG sample shows a single step of degradation. The decomposition starts at 225°C and proceeds at a faster rate up to 305°C and at this temperature the sample loses 43% of its original weight. Beyond this temperature the degradation proceeds at a very slow rate up to 600°C and this temperature range i.e., 305–600°C involves about 20% weight loss. With further increase in temperature the degradation is found to occur at a relatively fast rate up to 785°C, compared to the degradation proceeded in the earlier temperature range. The temperature at
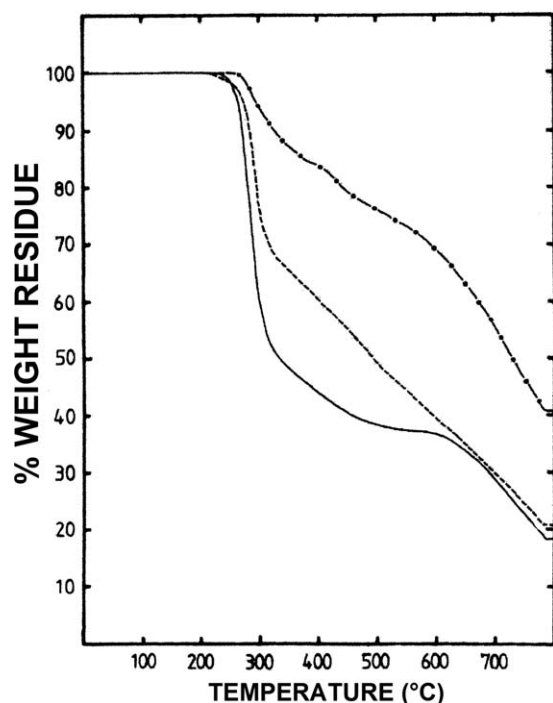
Figure 12. TG thermograms for (—)Na-PCMGG ($\overline{DS}$ = 0.291); (----)Na-PCMGG-*g*-PAN and (-•-•-•) PAN at 10°C min^{-1}.

Figure 13. Differential scanning calorimetric (DSC) scans for (a) Na-PCMGG ($\overline{DS}$ = 0.291), (b) Na-PCMGG-*g*-PAN and (c) PAN at a heating rate of 5°C min^{-1} in nitrogen atmosphere.

which the maximum rate of weight loss occurs is 300°C. The overall degradation leaves about 18.5% residue.

From this figure, it can be seen further that in the case of Na-PCMGG-*g*-PAN the overall degradation involves a single step. The sample begins to decompose at about 210°C and proceeds at a fast rate up to 300°C involving about 25% weight loss. Beyond which the degradation follows at a slow rate. The degradation is complete at about 785°C leaving about 20.5% residual weight. The maximum rate of weight loss occurs at 400°C. In the case of PAN it is observed from the figure that the sample involves single step of degradation. The degradation occurs in the temperature range 265–785°C involving about 59.5% weight loss with a maximum weight loss at 585°C. The final residue at 785°C amounts to about 40.5%.

The temperature characteristic values as well as the value of the integral procedural decomposition temperature (IPDT) of Na-PCMGG ($\overline{DS}$ = 0.291), Na-PCMGG-*g*-PAN (%G = 285.77) and PAN are tabulated in Table III. The examination of IPDT values indicates the overall thermal stability of Na-PCMGG ($\overline{DS}$ = 0.291) has been increased to a greater extent upon grafting of
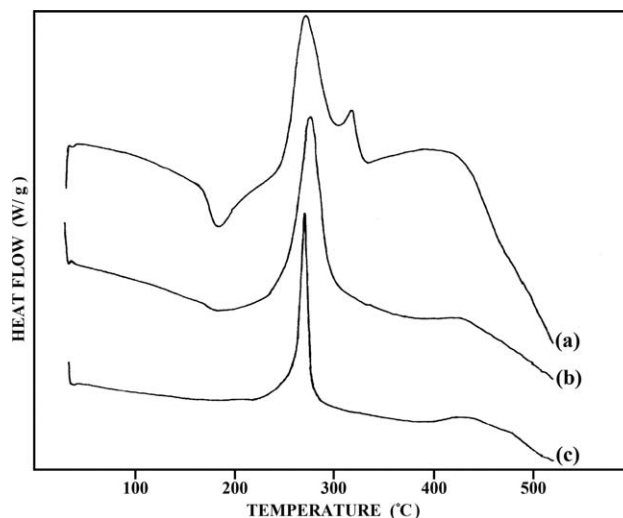
AN onto it. The increased ring formation at higher temperatures may be responsible for the observed higher value of IPDT for the graft copolymer sample compared to that of Na-PCMGG ($\overline{DS}$ = 0.291).[26] However, the value of IPDT for PAN sample is found to be higher than that of the graft copolymer (Na-PCMGG-*g*-PAN) as well as Na-PCMGG ($\overline{DS}$ = 0.291) samples. Thus, the results of TGA (Figure 12 and Table III) also provide an additional evidence of grafting.

Differential Scanning Calorimetry (DSC). The DSC scans of Na-PCMGG ($\overline{DS}$ = 0.291), Na-PCMGG-*g*-PAN (%G = 285.77) and PAN are shown in Figure 13(a–c) and their transition data are represented in Table III. It can be seen from the Figure 13(a) that Na-PCMGG ($\overline{DS}$ = 0.291) sample shows the endothermic transition at 183.41°C which may be due to the melting of Na-PCMGG but the exothermic transition observed at 269.94°C is attributed to the decomposition of the sample.

The endothermic transition appeared at 208.02°C and an exothermic peak appeared at 275.85°C in the case of the graft copolymer, Na-PCMGG-*g*-PAN [Figure 13(b)] may be attributed respectively to the gross melting and gross decomposition of the graft copolymer sample. The DSC scan of PAN [Figure 13(c)] shows the sharp exothermic transition at 270.60°C which may be due to pyrolytic decomposition of the sample. Further, the DSC scans of Na-PCMGG ($\overline{DS}$ = 0.291) and Na-PCMGG-

Table III. Thermal Analysis of Na-PCMGG ($\overline{DS}$ = 0.291), Na-PCMGG-*g*-PAN, and PAN Samples

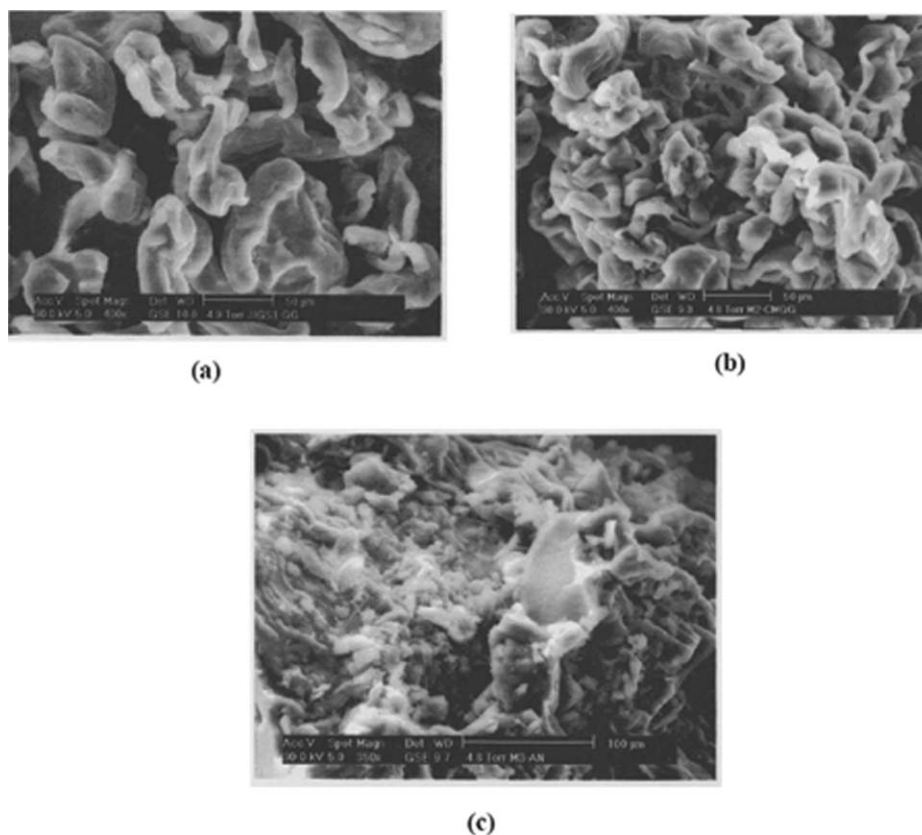| Sample	Thermogravimetric analysis date						Transition data from DSC	
	T_i (°C) (IDT)	T_f (°C) (FDT)	T_{max} (°C)	T_{10} (°C)	T_{50} (°C)	IPDT (°C)	T_1 (°C)	T_2 (°C)
Na-PCMGG	225	785	300	270	335	545.56	183.41 (endo)	269.94 (exo)
Na-PCMGG-*g*-PAN	210	785	400	282	485	580.87	208.02 (endo)	275.85 (exo)
PAN	265	785	585	325	730	684.79	270.60(exo)	–

Figure 14. Scanning electron micrographs of (a) Guar Gum (×400); (b) Na-PCMGG (×400); and (c) Na-PCMGG-*g*-PAN (×400).

g-PAN show different exothermic patterns, which also provides that grafting has indeed taken place.

Scanning Electron Microscopy (SEM). The scanning electron micrograph of Guar Gum [Figure 14(a)] showed discrete elongated granular structures separated from one another. Upon its carboxymethylation, the structure of Guar Gum just changed as shown in Figure 14(b), wherein the topology of the granules [Figure 14(a)] was modified in such a way that some of the granules became attached to each other. However, the clustering of the granules appeared to be poor and the granules could be distinguished from one another. The surface topology Na-PCMGG-g-PAN (%G = 285.77) is shown in Figure 14(c). Upon comparing the morphology of the grafted sample with that of the ungrafted material [Figure 14(b)], it became evident that the stiff morphology with lower adhering characteristics was observed in the case of the grafted sample, providing supportive evidence for further grafting.

CONCLUSIONS

We have reported for the first time the optimum reaction conditions for photo-induced graft copolymerization of AN onto Na-PCMGG ($\overline{DS} = 0.291$) using CAN as a photo-initiator. The influence of various reaction conditions on the grafting yields was discussed. Under the optimized reaction conditions the maximum percentage of grafting yields achieved were %G = 285.77 and %GE = 70.76. The experimental results were analyzed in terms of the earlier proposed kinetic scheme and

found to be in good agreement with it. The overall activation energy for photo-grafting was 5.38 kJ mol^{-1}. The influence of different kind of acids on the grafting yields was investigated and the results indicated that the effectiveness of the acid towards photo-grafting followed the order: nitric acid > hydrochloric acid > sulfuric acid. Various analytical techniques such as FT-IR, TGA, DSC, and SEM confirmed the grafting of poly(acrylonitrile) on the Na-PCMGG chains. Preliminary studies suggest that a novel superabsorbent hydrogel can be synthesized by saponification of the optimally synthesized graft copolymer, Na-PCMGG-*g*-PAN using 0.7N NaOH at 90–95°C. The superabsorbent hydrogel may find application for personal health care products. Further studies in this direction are currently in progress.

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