Synthesis and Characterization of Chitosan-*g*-Methacrylic Acid and Studies of Its Additional Physicochemical Properties, Such as Swelling, Metal-Ion Sorption, and Flocculation Behavior

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ABSTRACT: The aim of this study was to examine the synthesis of a graft copolymer of chitosan and methacrylic acid (MAA) by free-radical polymerization with a potassium peroxymonosulfate/cyclohexanone (CY) redox system in an inert atmosphere. The optimum reaction conditions affording maximum grafting ratio (%G), grafting efficiency (%E), add on (%A), and conversion (%C) were determined. The grafting parameters were found to increase with increasing concentration of MAA up to 24×10^{-2} mol/dm^3, but thereafter, these parameters decreased. With increasing concentration of peroxymonosulfate from 0.6×10^{-2} to 1.2×10^{-2} mol/dm^3, %G, %A, and %E increased continuously. All of these grafting parameters increased with increasing concentration of CY up to 1.2×10^{-2} mol/dm^3, but beyond this concentration, the grafting parameters decreased. With various concentrations of chitosan from 0.6 to 1.4 g/dm^3, the maximum %G, %A, and %E were obtained at 1.4 g/dm^3. %G, %A, and %C decreased continuously with various concentrations of hydrogen ions from 2×10^{-3} to 6×10^{-3} mol/dm^3. The grafting parameters increased with increasing temperature up to 35°C, but thereafter, these parameters decreased. With increasing time period of reaction from 60 to 180 min, %G, %A, and %E increased up to 120 min, but thereafter, these parameters decreased. The graft copolymer was characterized by Fourier transform infrared spectroscopy and thermogravimetric analysis. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 2429–2439, 2009

Key words: addition polymerization; graft copolymers; monomer

INTRODUCTION

The synthesis of new hybrid polymer materials[1] has become a rapidly expanding field in the area of polymer science. So an attempt was made to synthesize a graft copolymer of chitosan and methacrylic acid (MAA), and some of the properties were studied to make it more useful and also increase its applications. Chitosan is currently at the focus of increasing scientific and economic interest[2] among all polysaccharides because of its significance in nature and technology. It is a unique basic polysaccharide in nature because of the presence of an amino group (—NH$_2$) in its backbone. It is a polymer of β-(1,4) linked-2-amino-2-deoxy-D-glucopyranose derived by the *N*-deacetylation of chitin, an abundant and naturally occurring polysaccharide with annual production very near the levels of cellulose and which consists mainly of β-(1-4)-2-deoxy-D-glucose units[3] in aqueous alkaline medium.[4] It occurs in marine invertebrates and the shells of marine crustaceans, that is, shrimps and crabs.[5,6] Because of its wide availability and unique chemical and biological properties, such as biocompatibility, nontoxicity, and antimicrobial properties,[7–9] it has found wide applications in a variety of areas, such as biomedicine[10–13] and the pharmaceutical industry.[14] Despite its wide ranging applications, it suffers from its drawbacks such as biodegradability,[15] which limits its uses. The drawback i.e., biodegradability can be improved by modification through the grafting[16–18] of vinyl monomers onto it; thus, the graft copolymer will enhance its properties, such as swelling, metal-ion uptake, and flocculation. By this method, not only can its biodegradability be improved but also its physicochemical properties can be increased because the additional properties of the monomer are superimposed onto the polymeric backbone of chitosan. In our studies, chitosan was chosen as a backbone in which both hydroxyl and amino groups were possible sites for the reaction to incorporate new desired functional groups of the monomer. In this article, the

grafting of MAA onto chitosan is reported with the objective of not only modifying the properties but also increasing the applications of chitosan. For this purpose, MAA, which is hydrophilic in nature, was chosen as a monomer. One of the interesting fields of application of poly(methacrylic acid) (PMAA) is in thickening. Thickening action in water might be used as the secondary recovery of petroleum in oil fields, hydraulic fluids, and even liquid rocket fuels.[19] It also shows adhesive properties that make it useful for applications such as skin protection in the medical field.[20] This article describes the synthesis of a graft copolymer (chitosan-g-MAA), as a new hybrid material, which may be used as superabsorbents, coating materials, and flocculants to remove impurities from coal-mine wastewater.

EXPERIMENTAL

Materials

MAA (Sigma-Aldrich Co. Ltd, Gillingham, Dorset, SP8 4XT, UK) was distilled in the presence of copper turnings under reduced pressure (14 mm and 55°C), and only the middle fraction was used. Cyclohexanone (CY; E. Merck, India) was also fractionally distilled at room temperature (35°C) and was used as a reductant. Chitosan, purchased from Sigma, and peroxymonosulfate (PMS; Sigma) were used as received. To maintain the hydrogen ion concentration, sulfuric acid (E. Merck) was used. The other chemical reagents were of analytical grade. All of the solutions were prepared in triple-distilled water. For flocculation studies, coking and noncoking coals were used as received from Steel Plant (Bokaro, India).

Procedure for the graft copolymerization

All reactions were carried out under an oxygen-free nitrogen atmosphere. For each experiment, a chitosan solution was prepared by the addition of the desired amount of chitosan to a mixture of acetic acid and triple-distilled water in a reactor kept by a thermostat at the desired temperature. The calculated amounts of MAA, CY, and sulfuric acid solutions were added to a reactor containing the chitosan solution. A known amount of deoxygenated PMS was added to initiate the reaction. The reaction was performed under a continuous flow of oxygen-free nitrogen gas. After a desired interval of time, we stopped the reaction by letting air into the reactor. We precipitated the grafted sample by pouring the reaction mixture into methanol mixture. The precipitate was filtered, dried, and weighed. The filtrate was concentrated by distillation under reduced pressure in the presence of a small amount of hydroqui-

none. We precipitated the PMAA by pouring the concentrated filtrate into a $5N$ H_2SO_4 solution. PMAA, thus obtained, was separated, dried, and weighed.

RESULTS AND DISCUSSION

The graft copolymer was characterized by the following grafting parameters:[21]

$$\text{Grafting ratio} \, (\%G) = \frac{\text{Grafted polymer}}{\text{Weight of substrate}} \times 100$$

$$\text{Grafting efficiency} \, (\%E) = \frac{\text{Grafted polymer}}{\text{Polymer formed}} \times 100$$

$$\text{Add on} \, (\%A) = \frac{\text{Synthetic polymer}}{\text{Graft copolymer}} \times 100$$

$$\text{Conversion} \, (\%C) \frac{\text{Polymer formed}}{\text{Monomer charged}} \times 100$$

$$\text{Homopolymer} \, (\% H) = 100 - \% E$$

The effects of the variation of the PMS, MAA, CY, sulfuric acid, and chitosan concentrations, along with the time and temperature, on the grafting parameters were studied.

Effect of the PMS concentration

The effect of the concentration of PMS on the grafting parameters was studied from 0.6×10^{-2} to 2.2×10^{-2} mol/dm^3. %G, %A, and %C increased continuously, and the results are shown in Figure 1. This behavior might be explained on the basis of the progressive reduction of PMS by CY, which produced a free-radicals.[22,23] The radicals attacks on the chitosan molecule create more sites to which monomer addition could take place (see Scheme 1).

Effect of the MAA concentration

The effect of the monomer concentration on the grafting parameters was studied by the variation of the concentration of MAA from 12×10^{-2} to 36×10^{-2} mol/dm^3, and the results are summarized in Table I. %G, %A, and %E increased with increasing concentration of MAA up to 24×10^{-2} mol/dm^3 because of the greater availability of monomer molecules that were in close proximity to the polymer backbone. The monomer molecules that were in the immediate vicinity of the reaction sites became acceptors of the chitosan macroradical (ChX$\surd$); this
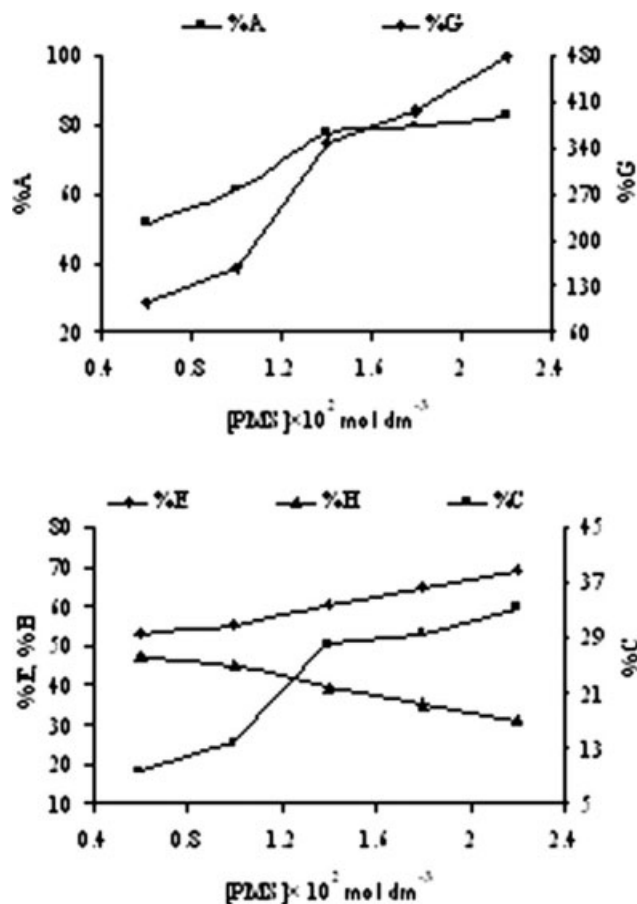
Figure 1 Effect of the PMS concentration ($[H^+] = 4 \times 10^{-3}$ mol/dm^3; $[CY] = 1.2 \times 10^{-2}$ mol/dm^3; time = 120 min; $[MAA] = 24 \times 10^{-2}$ mol/dm^3; [Chitosan] = 1.0 g/dm^3; temperature = 35°C).

resulted in chain initiation, and thereafter, these molecules themselves became free-radical donors to neighboring monomer molecules, which caused the lowering of the termination. The decrement in %G, %A, and %E was due to an increase in the viscosity of the reaction medium.

Effect of the CY concentration

The effect of the concentration of CY on the grafting parameters was studied by the variation of the concentration of CY from 0.8×10^{-2} to 1.6×10^{-2} mol/dm^3, and the results are shown in Figure 2. %G, %A, and %E increased with increasing concentration of CY from 0.8×10^{-2} to 1.2×10^{-2}, but beyond this cited range, the value of these parameters decreased. The increase in the grafting parameters might have been due to an increase in the number of primary free radicals. However, a higher concentration of CY beyond this cited range, that is, 0.8×10^{-2} to 1.2×10^{-2} mol/dm^3, favored the formation of PMAA over grafting, which thereby decreased these grafting parameters.

Effect of the chitosan concentration

The effect of the concentration of chitosan gum on the grafting parameters was studied by the variation of the concentration of chitosan from 0.6 to 1.4 g/dm^3, and the results are summarized in Table II. %G, %A, and %E increased continuously with increasing concentration of chitosan from 0.6 to 1.4 g/dm^{-3}. The increment might have been due to the availability of more and more grafting active sites on the chitosan, where PMAA could be grafted.

Effect of the hydrogen ion concentration

To examine the effect of the hydrogen ion concentration on the grafting parameters, the reaction was carried out at various concentration of sulfuric acid, and the results are shown in Figure 3. %G, %A, and %E decreased continuously with increasing concentration of sulfuric acid from 2×10^{-3} to 6×10^{-3} mol/dm^3. This behavior might have occurred due to the formation of inactive $H_2SO_5^-$ species; thus, the concentration of HSO_5^- decreased, which resulted in the production of fewer primary free radicals.
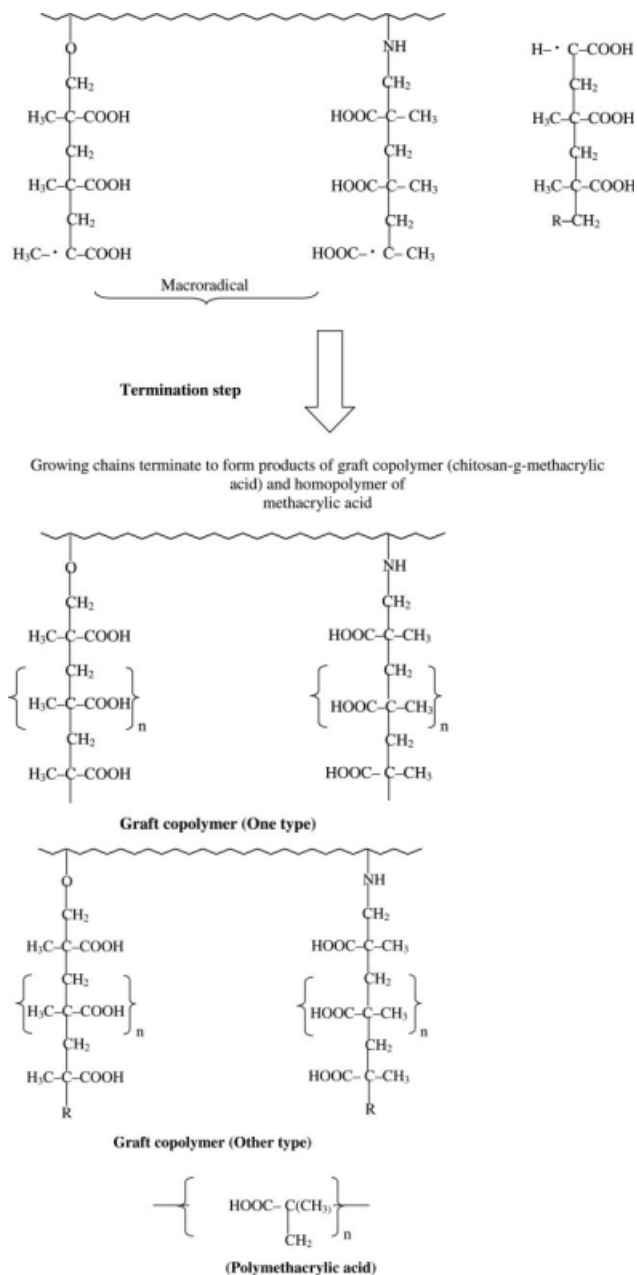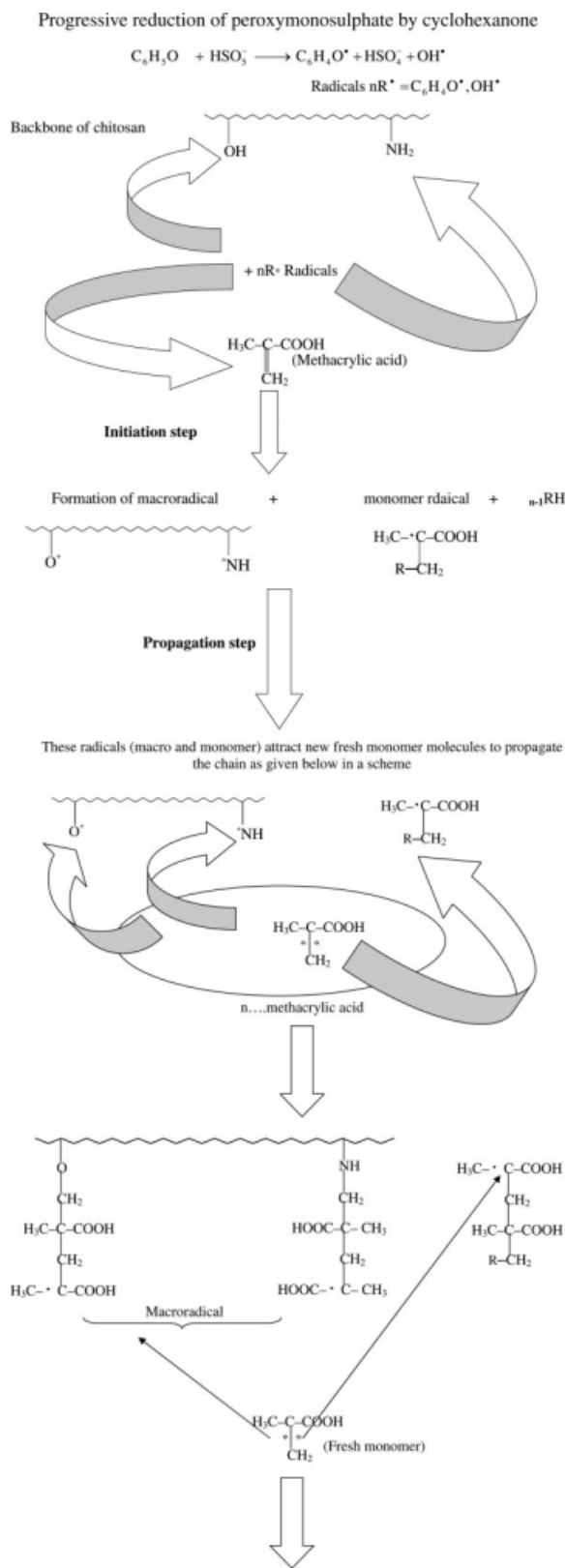
Effect of the temperature

The results obtained for the grafting parameters at different temperatures from 25 to 45°C are summarized in Table III. %G, %A, and %E increased with increasing temperature of the reaction medium from 25 to 35°C. The increment in grafting parameters was attributed to an increase in the production of primary free radicals with a consequent increase in the number of grafting sites on the polymer backbone and an increase in the rate of diffusion of PMAA onto the polymer backbone. These parameters decreased because of the premature termination of growing grafted chains at a higher temperature.
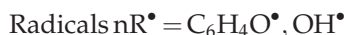
Effect of the time

The effect of the time duration on the grafting reaction was studied by the variation of the time period from 60 to 180 min, and the results are shown in Figure 4. With increasing time period from 60 to 120 min, the availability of more active species resulted in an increase in the grafting parameters. However, with a further increase in the time period, a decrement in these parameters was observed, which might have been due to the termination of growing grafted chains.
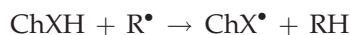
MECHANISM

On the basis of the experimental results, the following tentative mechanism is proposed for the graft

Progressive reduction of peroxymonosulphate by cyclohexanone

$$C_6H_5O + HSO_5^- \longrightarrow C_6H_4O^{\bullet} + HSO_4^- + OH^{\bullet}$$

$$\text{Radicals } nR^{\bullet} = C_6H_4O^{\bullet}, OH^{\bullet}$$

Backbone of chitosan

+ nR· Radicals

H₃C—C—COOH (Methacrylic acid)

Initiation step

Formation of macroradical   +   monomer rdaical   +   n-1RH

Propagation step

These radicals (macro and monomer) attract new fresh monomer molecules to propagate the chain as given below in a scheme

n....methacrylic acid

Macroradical

(Fresh monomer)

Scheme 1 Reactions involved in the formation of graft copolymer through redox polymersation.

Macroradical

Termination step

Growing chains terminate to form products of graft copolymer (chitosan-g-methacrylic acid) and homopolymer of methacrylic acid

Graft copolymer (One type)

Graft copolymer (Other type)

(Polymethacrylic acid)

Scheme 1 (Continued)

$$C_6H_5O + HSO_5^- \rightarrow C_6H_4O^{\bullet} + HSO_4^- + OH^{\bullet}$$

$$\text{Radicals } nR^{\bullet} = C_6H_4O^{\bullet}, OH^{\bullet}$$

Initiation

$$M + R^{\bullet} \rightarrow RM^{\bullet}$$

$$ChXH + R^{\bullet} \rightarrow ChX^{\bullet} + RH$$

copolymerization of MAA onto chitosan with a PMS and CY redox pair. The mechanism can be represented as

where ChXH represents chitosan, ChX$\sqrt{}$ represents the macroradicals, X is O or NH, and M is the monomer.

TABLE I
Effect of MAA

[MAA] $\times 10^2$ mol/dm³	%G	%E	%A	%C	%H
12	285.6	54.9	74.1	50.4	45.2
18	303.9	57.7	75.2	33.9	42.3
24	349.7	60.6	77.8	27.9	39.5
30	261.7	56.4	72.4	17.9	43.7
36	205.2	53.7	67.2	12.3	46.3

[Chitosan] = 1.0 g/dm³; [PMS] = 1.4 $\times 10^{-2}$ mol/dm³; [H⁺] = 4 $\times 10^{-3}$ mol/dm³; [CY] = 1.2 $\times 10^{-2}$ mol/dm³; time = 120 min; temperature = 35°C.

$$ChX^\bullet = ChO^\bullet \text{ or } Ch\overset{\bullet}{N}H \text{ (macroradical)}$$

Propagation

$$ChX^\bullet + M \rightarrow ChXM^\bullet$$

$$ChXM^\bullet + M \rightarrow ChXM_1^\bullet$$

$$ChXM_1^\bullet + M \rightarrow ChXM_2^\bullet$$

$$ChXM_{n-1}^\bullet + M \rightarrow ChXM_n^\bullet$$

$$RM^\bullet + M \rightarrow RM_1^\bullet$$

$$RM_1^\bullet + M \rightarrow RM_2^\bullet$$

$$RM_{n-1}^\bullet + M \rightarrow RM_n^\bullet$$

Termination

$$ChXM_n^\bullet + ChXM_m^\bullet \rightarrow Graft\,copolymer$$

$$ChXM_n^\bullet + RM_n^\bullet \rightarrow Graft\,copolymer$$

$$RM_m^\bullet + RM_n^\bullet \rightarrow Homopolymer$$
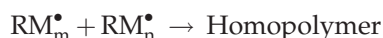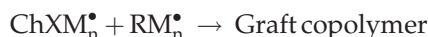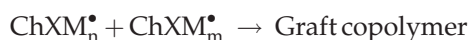
EVIDENCE OF GRAFTING

IR spectroscopy

The IR spectra of the ungrafted and grafted samples were recorded with Jasco FTIR-5300 model instrument (Chennai, India) in the range 500 to 4000 cm⁻¹ to provide proof of the grafting. The infrared spectrum of chitosan showed strong peaks at 3388.3 and 1593.4 cm⁻¹ due to OH stretching and NH bending vibrations, respectively. When the IR spectra of chitosan and chitosan-*g*-MAA were compared (the graphs are shown in Figures 5 and 6), the graft copolymer (chitosan-*g*-MAA) showed variations in the intensity of the OH stretching and NH bending
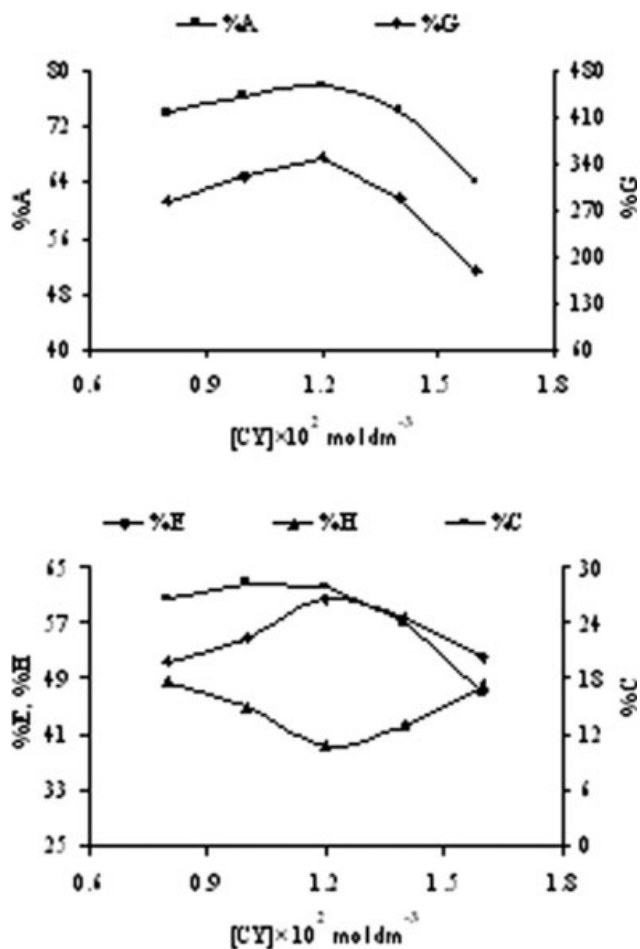

Figure 2 Effect of the CY concentration ([H⁺] = 4 $\times 10^{-3}$ mol/dm³; [PMS] = 1.4 $\times 10^{-2}$ mol/dm³; time = 120 min; [MAA] = 24 $\times 10^{-2}$ mol/dm³; [Chitosan] = 1.0 g/dm³; temperature = 35°C).

vibrations, and a shift of the peak appeared because of OH stretching from 3388.3 to 3401.8 cm⁻¹ along with a shift of the peak appearing because of NH bending vibrations from 1593.4 to 1562.1 cm⁻¹, which indicated the participation of hydroxyl groups and amino groups in the chemical reaction. In addition to this, the grafting of the monomer was confirmed by characteristic absorption bands at 1632.1 and 1400.5 cm⁻¹ due to the —C=O stretching and OH

TABLE II
Effect of the Chitosan Concentration

[Chitosan] (g/dm³)	%G	%E	%A	%C	%H
0.6	299.2	53.1	74.9	27.3	46.9
0.8	301.5	56.5	75.1	25.9	43.6
1.0	349.7	60.5	77.8	27.9	39.5
1.2	372.3	64.6	78.8	27.9	35.5
1.4	447.4	67.8	81.7	31.9	32.3

[PMS] = 1.4 $\times 10^{-2}$ mol/dm³; [MAA] = 24 $\times 10^{-2}$ mol/dm³; [H⁺] = 4 $\times 10^{-3}$ mol/dm³; [CY] = 1.2 $\times 10^{-2}$ mol/dm³; temperature = 35°C; time = 120 min.

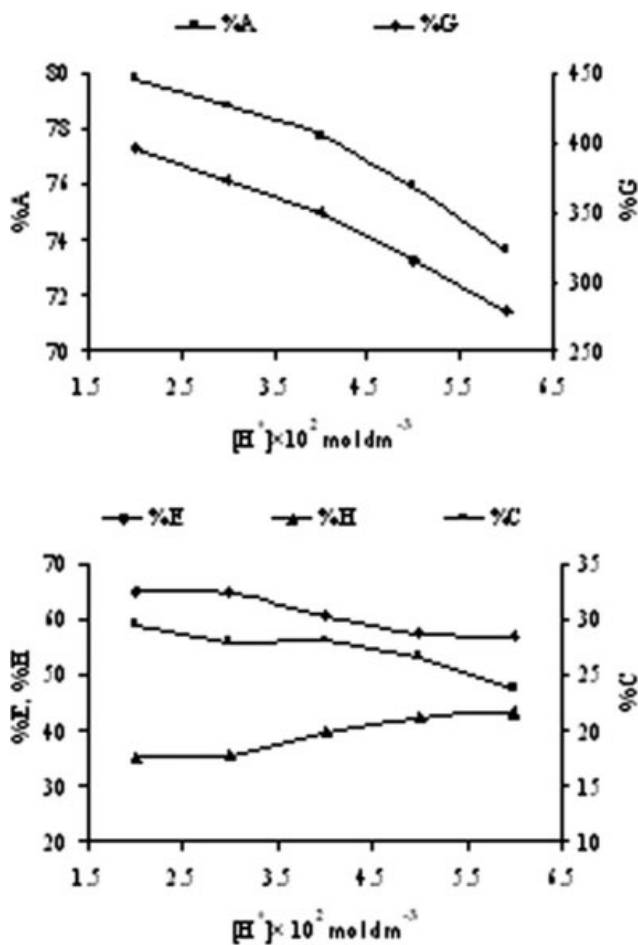**Figure 3** Effect of the hydrogen ion concentration ([CY] = 1.2 × 10^{-2} mol/dm^3; [PMS] = 1.4 × 10^{-2} mol/dm^3; time = 120 min; [MAA] = 24 × 10^{-2} mol/dm^3; [Chitosan] = 1.0 g/dm^3; temperature = 35°C).

bending vibrations of the carboxylic group of MAA, respectively. The appearance of additional bands due the attachment of the pendant chain of MAA in the graft copolymer and the disappearance of OH bending vibrations appeared at 669.0 cm^{-1}, and also, C—N stretching vibrations appeared at 1027.8 cm^{-1} in chitosan from the spectrum of chitosan-g-MAA, which showed that grafting had taken place on the OH and NH$_2$ sites of the chitosan backbone.

Thermal analysis

The thermograms were recorded on a Netzsch-STA 409C/CD thermal analyzer (Chennai, India) from 0 to 1400°C and with a heating rate of 15°C/min in an atmosphere of nitrogen. The results are summarized in Table IV.

Chitosan

The thermogravimetric analysis curve of chitosan showed a single-step degradation. The 16.3% weight

TABLE III
Effect of the Temperature

Temperature (°C)	%G	%E	%A	%C	%H
25	220.5	53.1	68.8	20.1	46.9
30	277.2	56.8	73.5	23.6	43.3
35	349.7	60.5	77.8	27.9	39.5
40	239.7	57.7	70.6	20.1	42.4
45	164.5	54.1	62.2	14.7	45.9

[Chitosan] = 1.0 g/dm^3; [MAA] = 24 × 10^{-2} mol/dm^3; [PMS] = 1.4 × 10^{-2} mol/dm^3; [H$^+$] = 4 × 10^{-3} mol/dm^3; [CY] = 1.2 × 10^{-2} mol/dm^3; time = 120 min.

loss at a temperature 93.8°C might have been due to a loss of absorbed water. It started to degrade at 114°C. The polymer decomposition temperature (PDT) was found at 157°C. The rate of weight loss increased with increasing temperature from 186.3 to 218.3°C and, thereafter, decreased and attained a maximum value at about 512.5°C. The temperature at which maximum degradation occurred (T_{max}) was 300°C (Fig. 7), which was also confirmed by a sharp endothermic peak present in the differential thermal
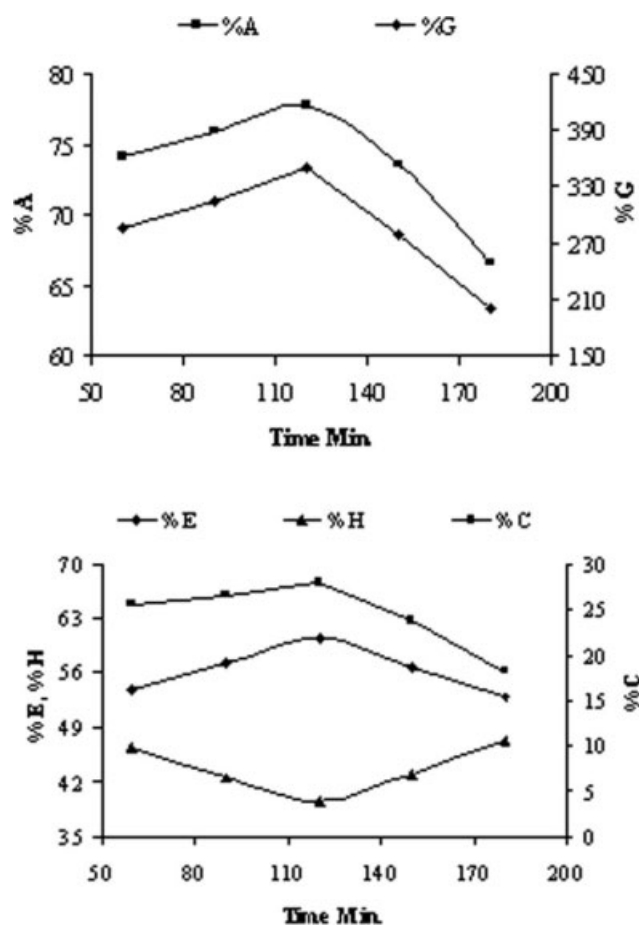

Figure 4 Effect of the time ([H$^+$] = 4 × 10^{-3} mol/dm^3; [PMS] = 1.4 × 10^{-2} mol/dm^3; temperature = 35°C; [CY] = 1.2 × 10^{-2} mol/dm^3; [MAA] = 24 × 10^{-2} mol/dm^3; [Chitosan] = 1.0 g/dm^3).
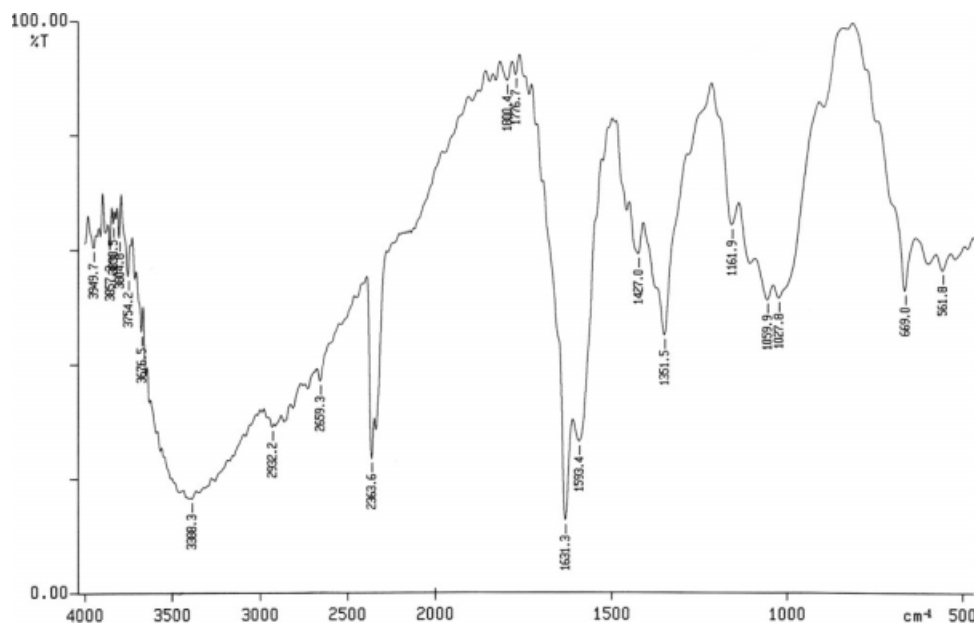
Figure 5 IR spectrum of chitosan.

analysis (DTA) curve of chitosan at 310°C (Fig. 8). The final decomposition temperature (FDT) and integral procedural decomposition temperature (IPDT) were found at 700 and 248.4°C, respectively.

Chitosan-*g*-MAA

The 19.2% weight loss at 100°C might have been due to a loss of absorbed water. The degradation of chitosan-*g*-MAA started to degrade at about 157.3°C. PDT was found at 160°C. The degradation of the graft copolymer occurred in two steps (see Scheme 2), that is, between 200–300 and 800–900°C temperature ranges (Fig. 9). Therefore, two T_{max} values were found at 237.5 and 831°C, respectively. First, T_{max} might have been due to the elimination of H_2O from
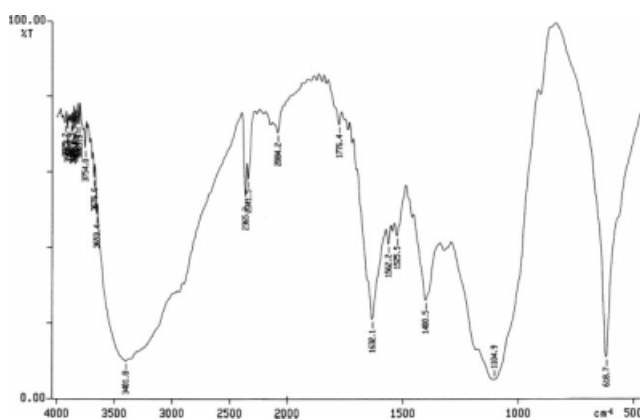

Figure 6 IR spectrum of chitosan-*g*-MAA.

the pendant chain of MAA, which was also confirmed by the endothermic peak present in the DTA curve of the graft copolymer of chitosan with MAA at 260.2°C. Second T_{max} might have been due to the elimination of CO_2 from the pendant chain of MAA attached to the polymeric backbone of chitosan (Fig. 10). A maximum weight loss of 27.5% was found at 700°C; therefore, FDT was found at 875°C. IPDT was found to be at 330.54°C. The two steps degradation and the high value of final decomposition favored the idea that the graft copolymer was thermally more stable than the polymeric backbone.

PHYSICOCHEMICAL PROPERTIES

Swelling behavior

The swelling behavior of different samples of the graft copolymer was studied, and the results are given in Table V. The different samples of the graft copolymer were synthesized at different concentrations of monomer. The preweighed samples (0.02 g each) were immersed in 20 mL of triple-distilled

TABLE IV
Thermogravimetric Analysis

Sample code	PDT (°C)	IPDT (°C)	FDT (°C)	T_{max} (°C)	DTA peaks Exopeaks (°C)	Endopeaks (°C)
C	157	248.4	700	300.0	—	310.6
Cp	169	330.5	875	237.5, 831.0	—	235.2
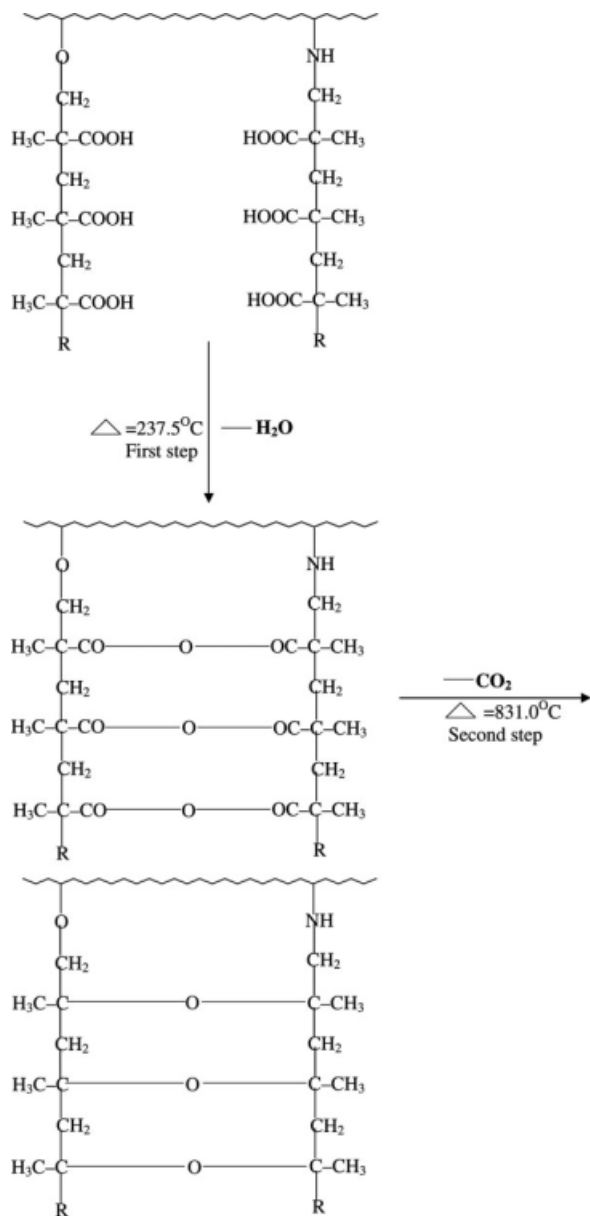
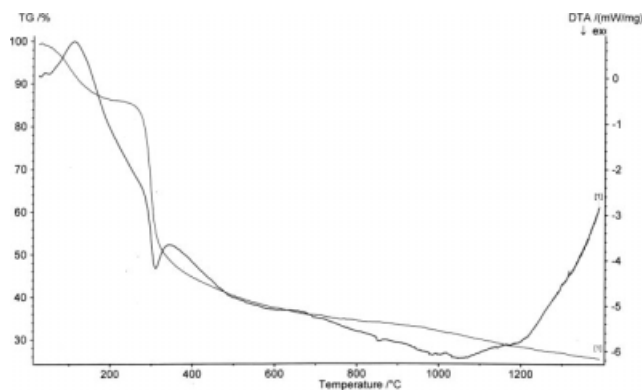**Scheme 2** Degradation steps of the graft copolymer chitosan-*g*-MAA.

Figure 8 Differentia thermal analysis (DTA) trace of chitosan.

water and kept undisturbed for 10 h at room temperature until equilibrium was reached. The swollen samples were then removed from triple-distilled water, quickly wiped with filter paper to remove droplets on the surface, and weighed.

The percentage swelling (P_s) and swelling ratio (S_r) were calculated with the following expressions:[24]

$$Ps = \frac{\text{wt. of the swollen polymer} - \text{wt. of the dry polymer}}{\text{wt. of dry polymer}}$$
$$\times 100$$

$$Sr = \frac{\text{wt. of the swollen polymer} - \text{wt. of the dry polymer}}{\text{wt. of the dry polymer}}$$

As observed from the results (given in Table IV), P_s and S_r of the graft copolymer increased with increasing percentage grafting, which depended on monomer concentration. The percentage hydrophilic character in the graft copolymer increased with
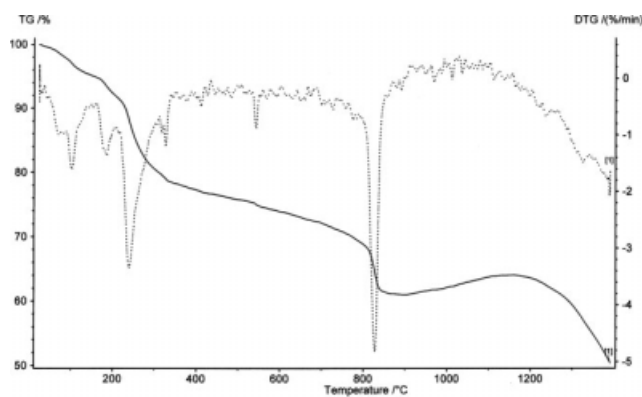

Figure 7 Thermogravimetric trace of chitosan.

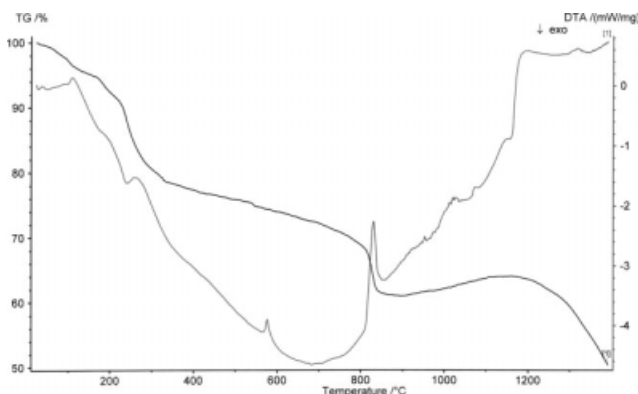**Figure 9** Thermogravimetric trace of chitosan-*g*-MAA.

Figure 10 Differentia thermal analysis (DTA) trace of chitosan-*g*-MAA.

increasing chain of pendent PMAA onto chitosan, which thereby increased the swelling capabilities of the graft copolymer.

Metal-ion sorption

Metal-ion sorption studies were carried out on graft copolymers of different compositions, which were synthesized with various concentrations of MAA from 12×10^{-2} to 36×10^{-2} mol/dm^3. For this, 0.02 g of the graft copolymer was placed in 10 mL of a metal-ion solution of known concentration and kept for 24 h. The strength of unabsorbed metals solution was determined by a standard method.[25] For the metal-ion sorption studies, we chose five metals ions, Cu^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, and Hg^{2+}. The sorption behavior of the polymeric backbone and graft copolymer for five metals ions was investigated with the following parameters:[26]

Percent ion uptake (P_u)

$$= \frac{\text{Amount of metal ion in the polymer}}{\text{amount of the metal ion in the feed}} \times 100$$

TABLE V
Swelling Behavior

Sample	[MAA] $\times 10^2$ mol/dm^3	%G	P_s	S_r
A	12	285.6	176	1.76
B	18	303.9	198	1.98
C	24	349.7	284	2.84
D	30	261.7	145	1.45
E	36	205.2	130	1.30

[Chitosan] = 1.0 g/dm^3; [PMS] = 1.4×10^{-2} mol/dm^3; [CY] = 1.2×10^{-2} mol/dm^3; [H$^+$] = 4×10^{-3} mol/dm^3; temperature = 35°C; time = 120 min.

Partition coefficient (K_d)

$$= \frac{\text{Amount of metal ion in the polymer}}{\text{amount of metal ion in the solution}}$$
$$\times \frac{\text{Volume of solution (ml)}}{\text{weight of dry polymer}}$$

Retention capacity (Q_r)

$$= \frac{\text{Amount of the metal ion in the Polymer (mol equiv)}}{\text{Weight of the dry Polymer (g)}}$$

The results of the sorption behavior of chitosan and its grafted polymer with MAA were studied in terms of P_u, K_d, and Q_r. The results are shown in Table VI. The values of P_u, K_d, and Q_r increased directly as %G increased, which might have been due to increased pendent chains of PMAA. The results also show that Hg^{2+} was least able to be taken up in comparison to the other four metal ions.

Flocculation performance

In a 1.0-L beaker, 200 cc of a 1 wt % coal suspension was placed. The beaker was placed on a flocculator with a stirrer blade dipped in the suspension. Under

TABLE VI
Sorption Studies of Metal Ions on Chitosan and Chitosan-*g*-MAA

Sample code	[MAA] $\times 10^2$ mol/dm^3	%G	P_u					K_d					Q_r				
			Cu^{2+}	Ni^{2+}	Zn^{2+}	Pb^{2+}	Hg^{2+}	Cu^{2+}	Ni^{2+}	Zn^{2+}	Pb^{2+}	Hg^{2+}	Cu^{2+}	Ni^{2+}	Zn^{2+}	Pb^{2+}	Hg^{2+}
C	—	—	4.4	3.3	2.5	2.8	1.8	22.8	17.0	12.7	14.3	9.4	2.1	1.6	1.3	1.4	0.9
C$_{P1}$	12	285.6	5.2	4.7	3.8	4.2	3.3	27.4	24.8	19.8	21.7	16.9	2.5	2.3	2.0	2.1	1.6
C$_{P2}$	18	303.9	7.9	6.8	5.3	6.2	4.5	42.8	36.4	28.1	32.8	23.6	3.8	3.3	2.8	3.1	2.2
C$_{P3}$	24	349.7	9.5	8.4	7.6	8.1	6.3	52.8	46.1	41.2	44.3	33.8	4.6	4.1	4.0	4.1	3.1
C$_{P4}$	30	261.7	8.1	7.4	5.1	6.9	4.9	44.0	40.0	27.1	37.3	25.8	3.9	3.6	2.7	3.5	2.4
C$_{P5}$	36	205.2	4.9	4.1	2.7	3.6	2.5	26.2	21.5	13.7	18.5	12.6	2.4	2.0	1.4	1.8	1.2

[Chitosan] = 1.0 g/dm^3; [PMS] = 1.4×10^{-2} mol/dm^3; [CY] = 1.2×10^{-2} mol/dm^3; [H$^+$] = 4.0×10^{-3} mol/dm^3; time = 120 min; temperature = 35°C.
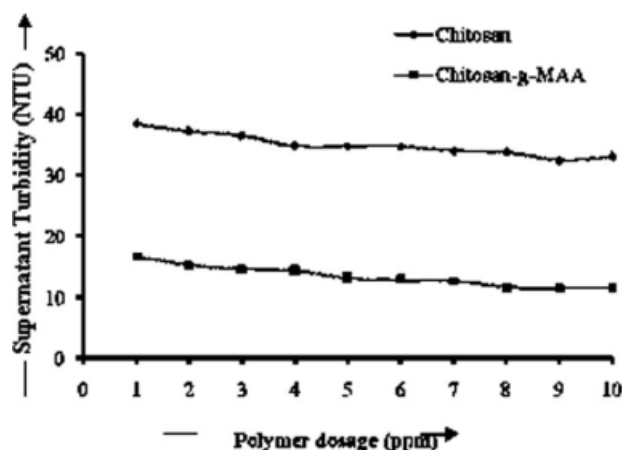
Figure 11 Effect of the polymer dosage on the turbidity of coking coal.

low stirring conditions, the required quantity of polymer solution was added to the beaker to make a predetermined dose with respect to suspension volume. After the addition of polymer solution, the suspension was stirred at a constant speed for 15 min. The flocs were allowed to settle down for 0.5 h. Clean supernatant liquid was drawn from a depth of 1.0 cm, and its turbidity was measured with a digital nephelometer (supplied by Iso-Tech System, Varanasi) to express the turbidity in nephelometric units (NTU). At the time of mixing, the concentration of flocculants should have been very low so that the polymer solution was uniformly dispersed. The turbidity values of the supernatant liquids were taken as a measurement of the flocculation efficiency of the backbone chitosan and graft copolymer of MAA with chitosan. Plots of the supernatant turbidity versus polymer dosage for coking and noncoking
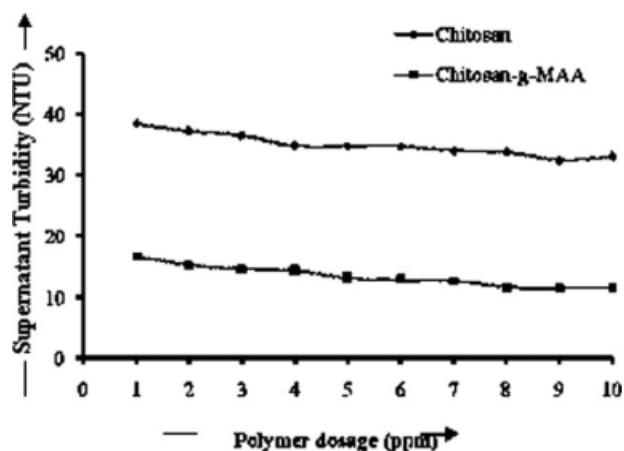
coals are presented in Figures 11 and 12. It is obvious that the grafted copolymer (chitosan-*g*-MAA) showed better performance with low turbidity than did the chitosan itself. This phenomenon could be explained by consideration of the bridging mechanism.[27] In grafted copolymer, the dangling of PMAA chains had better approachability as acrylamide[28] to the contaminant coal particles, hence, increasing its flocculation capability. By the grafting of PMAA onto chitosan, an efficient flocculant was obtained, which may be used for the treatment of coal mine wastewater.

CONCLUSIONS

The spectroscopic data confirm that the grafting of MAA might have taken place at the hydroxyl and amino groups, which was supported by a tentative mechanism suggested for grafting. The thermal analysis data showed that the grafted polymer was thermally more stable than pure chitosan. The synthesized graft copolymer, that is, chitosan-*g*-MAA, showed better results for swelling, metal-ion sorption, and flocculation in comparison to chitosan; thus, the graft copolymer showed an enhancement in these properties due to grafting and could be exploited very well industrially.

Figure 12 Effect of the polymer dosage on the turbidity of noncoking coal.

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