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Synthesis of partially carboxymethylated guar gum-*g*-4-vinyl pyridine and study of its water swelling, metal ion sorption and flocculation behaviour

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Abstract

Unreported graft copolymer of 4-vinyl pyridine (4VP) with partially carboxymethylated guar gum (Cmg) was synthesized and reaction conditions were optimised using a bromate/thiourea redox pair under an inert atmosphere at 40 °C. Studies have been done to observe the effect of reactants on grafting parameters by varying the reactant concentration. Grafting ratio, add on and conversion show a decrement on increasing the concentration of partially carboxymethylated guar gum beyond 1.0 g dm^{-3}. The grafting parameters increase on increasing the concentration of 4-vinyl pyridine from 13×10^{-2} to 25×10^{-2} mol dm^{-3}, $\mathrm{BrO_3}^-$ from 4×10^{-3} to 10×10^{-3} mol dm^{-3} and thiourea from 1.6×10^{-3} to 4.8×10^{-3} mol dm^{-3}. Optimum temperature and time for grafting of 4-vinyl pyridine on partially carboxymethylated guar gum are found to be 40 °C and 120 min, respectively. Metal ion uptake and flocculation behaviour have been also studied and found that graft copolymer shows enhancement in these properties than substrate. Swelling behaviour of graft copolymer has been investigated. The graft copolymer is characterized by FTIR and thermal analysis.

Keywords: Graft copolymer; Metal ion sorption; Water swelling behaviour; Flocculating properties; Partially carboxymethylated guar gum; 4-Vinyl pyridine

1. Introduction

Modification of natural polymers by graft copolymerisation is anticipated to be quite promising technique as it functionalises these biopolymer to their potential, imparting desirable properties onto them. Thus, in recent years, much attention has been paid on chemical modification of these natural macromolecules through grafting (Behari, Pandey, Taunk, & Kumar, 2001; Pandey, Srivastava, Tripathy, & Behari, 2006; Srivastava, Banerjee, Mishra, & Behari, 2005).

Partially carboxymethylated guar gum is a derivative of guar gum, which is a naturally occurring galactomannan polysaccharide isolated from the seed endosperm and having linear chain of β-D mannopyranose joined by (1–4) linking with α-D-galactopyranosyl units attached by 1,6 links in the ratio of 1:2 (Sinha & Kumria, 2001). Due to immense potential and low price, this versatile polymer is used as a vehicle for oral controlled release purpose (Skinner, Harcum, Barnum, & Guo, 1998). Guar gum and its derivatives find numerous other applications such as in oil industry they act as major ingredients in drilling muds and fingering fluids whereas in textile industry, help to improve printing quality (Turk & Schneider, 2000). Even though guar gum and its derivatives enjoy wide number of applications, however like other polysaccharides they are susceptible to easy biodegradation (Srivastava, Tripathy, Mishra, & Behari, 2007) which could be improved by grafting vinyl monomers onto them.

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Poly(4-vinyl pyridine) is an important class of polymer, which exhibit interesting properties due to presence of nitrogen atom in the pyridine ring. 4-Vinyl pyridine grafted poly(ethylene-terephthalate) fibers are found to adsorb hexavalent chromium from aqueous solution (Yigitoglu & Arslan, 2005). In addition, these speciality polymers find many attractive applications in polyelectrolytes, polymeric reagents etc. 4-Vinyl pyridine also show antibacterial property (Gao, He, Guo, & Wang, 2006).

To date many investigations have been carried on grafting of vinyl monomers onto guar gum using various redox pairs (Bajpai & Rai, 1988) however, reports on grafting of partially carboxymethylated guar gum is in scanty (Trivedi, Kalia, Patel, & Trivedi, 2005). Therefore, present work aimed to prepare graft copolymer of partially carboxymethylated guar gum and 4-vinyl pyridine so that to develop a product with high water swelling capacity and could be exploited industrially for metal ion sorption and flocculation. Synthesis of carboxymethylated guar gum-*g*-4-vinyl pyridine has been done using bromate/thiourea redox pair under N_2 atmosphere.

2. Experimental

2.1. Materials

4-vinyl pyridine (4VP) (Aldrich Co. USA) was distilled under reduced pressure at 14 mm Hg and 59 °C; and drop of mercury was added to avoid yellowness and kept in deep freezer. Potassium bromate (E. Merck) and thiourea (E. Merck) was used as such. Partially carboxymethylated guar gum was received as gift sample from Hindustan Gums and Ltd, India. For maintaining hydrogen ion concentration, sulphuric acid (E. Merck) has been used. All solutions were prepared in triple distilled water.

2.2. Procedure for grafting

For each experiment partially carboxymethylated guar gum solution was prepared by slow addition of weighed amount of partially carboxymethylated guar gum into the reactor containing triple distilled water with rapid stirring in reactor. A calculated amount of 4-vinyl pyridine, thiourea, and sulphuric acid solutions were added into the reactor and then a stream of purified nitrogen gas has been passed for at least 30 min to remove the oxygen from the reaction. A known amount of deoxygenated potassium bromate solution was added to initiate the reaction. Throughout the reaction period, the mixture was purged with the stream of purified nitrogen gas and kept at constant temperature. After desired time period the reaction was stopped by letting air into the reactor. The grafted sample was precipitated by pouring the reaction mixture into pure methanol, where grafted carboxymethylated guar gum precipitated out. The precipitate has been separated, dried and weighed.

2.3. Separation of homopolymer

To the filtrate a pinch of hydroquinone has been added and concentrated by distillation under reduced pressure. The poly(4-vinyl pyridine) was precipitated with aqueous ammonia and NH_4Cl. The polymer was separated dried and weighed in vacuum oven at room temperature.

3. Characterizations

3.1. FTIR analysis

The infrared spectra analysis has been done to prove grafting. For this the IR spectra of ungrafted and grafted samples in KBr pellets have been recorded with JASCO FT/IR-5300 model in the range 500–4000 cm^{-1}.

3.2. TGA/DTA analysis

The thermal analysis of partially carboxymethylated guar gum and 4-vinyl pyridine grafted partially carboxymethylated guar gum has been carried in inert atmosphere at heating rate of 15 °C/min within temperature range of 0–1400 °C on NETZSCH-STA 409 C/CD thermal analyzer.

3.3. Swelling test

For the swelling studies, 0.02 g of each grafted sample synthesized by varying the concentration of 4-vinyl pyridine, has been taken and immersed in 20 ml of distilled water (triple) and kept undisturbed for 24 h. The surface water on the swollen graft copolymer has been removed by softly pressing it between the folds of filter paper. An increase in weight of graft copolymer has been recorded. Calculation of the percent swelling (P_S) and swelling ratio (S_R) is done by the following expression (Abd EL-Rehim, Hegazy EL-Sayed, & Ali, 2000) and results are summarized in Table 5.

$$\text{Swelling ratio } (S_R) = \frac{\text{Weight of swollen sample} - \text{weight of dry sample}}{\text{Weight of dry sample}}$$

$$\text{Percent swelling } (P_S) = \text{Swelling ratio } (S_R) \times 100$$

3.4. Metal ion sorption test

The metal ion sorption study has been carried out by using samples of graft copolymers, which have been synthesized by varying the concentration of 4-vinyl pyridine from 12×10^{-2} to 28×10^{-2} mol dm^{-3}. For carrying out this study 0.02 g of graft copolymer has been taken in 10 ml of metal ion solution of known concentration, and kept for 24 h. The strength of sorbed metal ion has been determined by titrating the remaining metal ions. The results of sorption behaviour of partially carboxymethylated guar gum and its grafted polymer with 4-vinyl pyridine has been determined in terms of different parameters (Rivas, Maturana, Molina, Gomez-Anton, & Pierola, 1998) i.e. percent ion uptake (P_u), partition coefficient (K_d), retention capacity (Q_r).

$$\text{Percent uptake } (P_u) = \frac{\text{Amount of metal ion in the polymer}}{\text{Amount of metal ion in feed}} \times 100$$

$$\text{Partition coefficient } (K_d) = \frac{\text{Amount of metal ion in the polymer}}{\text{Amount of metal ion left in the solution}} \times \frac{\text{Volume of solution (ml)}}{\text{Weight of dry polymer}}$$

$$\text{Retention capacity } (Q_r) = \frac{\text{Amount of metal ion in the polymer (m Eq.)}}{\text{Weight of dry polymer (g)}}$$

3.5. *Viscosity of polymer solutions*

Viscosity was measured by using Ubbelhode capillary viscometer. During the measurement, temperature was maintained at 30 °C in thermostat. From efflux time of polymer solution (t) and that of solvent 1.0 M NaCl (t_o), relative viscosity $\eta_{rel} = \eta/\eta_o$ was obtained. Specific viscosity was calculated from the relationship $\eta_{sp} = \eta_{rel} - 1$. Knowing the concentration of polymer solution (C) in (g/dl), reduced viscosity was calculated for a set of 5 polymer concentrations.

3.6. *Flocculating properties*

At the time of mixing, concentration of flocculants was very low so that polymer solution could be uniformly dispersed. Turbidity values of supernatant liquids have been taken as the measurement of flocculation efficiency of backbone partially carboxymethylated guar gum and graft copolymer. In 1.0 L beaker, 200 ml of 1.0 wt% coal suspension was taken. The beaker was placed on flocculator dipping the stirrer blade in the suspension. Under a low stirring condition, required quantity of polymer solution was added to beaker to make predetermined dose with respect of 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 half an hour. Clear supernatant liquid was drawn from a depth of 1.0 cm and its turbidity was measured using a digital nephelometer (Model 341 EI).

4. Results and discussion

4.1. *Grafting parameters*

The graft copolymer has been characterized by following grafting parameters (Fanta, 1973)

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

$$\text{Grafting efficiency } (\%E) = \frac{\text{Weight of grafted polymer}}{\text{Weight of polymer formed}} \times 100$$

$$\text{Add on } (\%A) = \frac{\text{Weight of synthetic polymer}}{\text{Weight of graft copolymer}} \times 100$$

$$\text{Conversion } (\%C) = \frac{\text{Weight of polymer formed}}{\text{Weight of monomer charged}} \times 100$$

$$\text{Homopolymer } (\%H) = 100 - \%\text{ grafting efficiency}$$

4.2. *Determination of optimum grafting conditions*

The effects of variations in concentrations of potassium bromate, thiourea (TU), hydrogen ion (H^+), partially carboxymethylated guar gum (Cmg), 4-vinyl pyridine (4VP) along with the effect of time and temperature on grafting parameters have been studied.

4.2.1. *Effect of bromate ion concentration*

The bromate-thiourea system is a novel initiator for the aqueous polymerization of vinyl monomers. The effect of bromate ion concentration on grafting reaction has been studied and the results are presented in Fig. 1a and b. It was observed that grafting ratio, conversion and add on increases on increasing the bromate ion concentration from 4.0×10^{-3} to 8×10^{-3} mol dm^{-3}, but beyond this concentration range, grafting parameters decrease. The enhancement of grafting parameters within the cited range of bromate ion concentration is due to the progressive reduction of potassium bromate with thiourea producing bromide ion and isothiocarbamide free radicals which attack on the partially carboxymethylated guar gum molecule creating more free radicals site on to which monomer addition takes place. Beyond 8×10^{-3} mol dm^{-3} the decrease of grafting parameters can be explained due to following reasons:

1. At higher bromate ion concentration it might react with the partially carboxymethylated guar gum macro radical or with the growing radical, thus reducing the extent of grafting.
2. Oxidation of the active groups on the backbone, thereby preventing the formation of free radicals.
3. Due to the liberation of appreciable amount of oxygen, the radical may die, causing decrement in concentration of radicals.

4.2.2. *Effect of thiourea concentration*

Increment in the concentration of thiourea from 1.6×10^{-3} to 4.8×10^{-3} mol dm^{-3} (Table 1) shows the increment in grafting parameters and decrease in homopolymer formation. The increment in grafting parameters

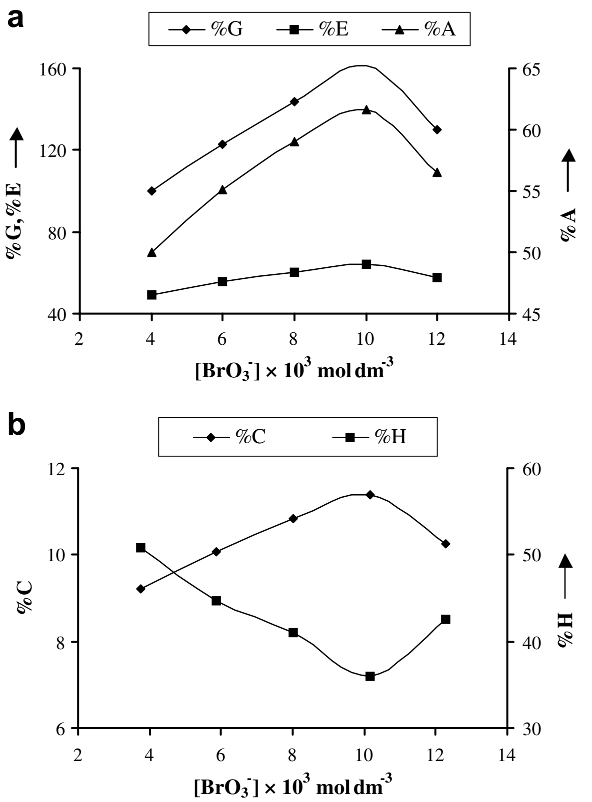


Fig. 1. (a) and (b) Effect of bromate. [Cmg] = 1.0 g dm^{-3}, [Thiourea] = 3.2 × 10^{-3} mol dm^{-3}, [4VP] = 21 × 10^{-2} mol dm^{-3}, [H$^+$] = 5 × 10^{-3} mol dm^{-3}, temp. = 40 °C, time = 120 min, %G = grafting ratio, %A = add on, %C = conversion, %E = efficiency, %H = homopolymer.

Table 1
Effect of thiourea concentration

[TU] × 10^3 mol dm^{-3}	%G	%E	%A	%C	%H
1.6	96.0	48.2	48.9	9.0	51.8
2.4	121.0	54.8	54.7	9.9	45.2
3.2	144.0	60.1	59.0	10.8	39.8
4.0	160.0	64.3	61.5	11.9	35.7
4.8	171.0	65.5	63.1	11.9	34.5

[4VP] = 21 × 10^{-2} mol dm^{-3}, [BrO$_3^-$] = 8 × 10^{-3} mol dm^{-3}, [Cmg] = 1.0 g dm^{-3}, [H$^+$] = 5 × 10^{-3} mol dm^{-3}, temp. = 40 °C, time = 120 min.

within cited range of thiourea concentration is due to the availability of primary free radicals that are produced from the reaction of protonated species of thiourea with bromate.

4.2.3. Effect of 4-vinyl pyridine (4VP) concentration

The effect of 4-vinyl pyridine on graft copolymerization has been studied by changing the concentration of 4-vinyl pyridine from 13 × 10^{-2} to 29 × 10^{-2} mol dm^{-3}. The grafting ratio efficiency, add on and conversion increase on increasing the concentration of 4VP from 13 × 10^{-2} to 25 × 10^{-2} mol dm^{-3}, whereas homopolymer decreases considerably (Fig. 2a and b), but on further increasing the 4VP concentration, the values of these grafting parameters decrease. The increase in grafting parameters could be explained due to greater availability of monomer at chain propagating site. The monomer molecule, which is at the immediate vicinity of the reaction sites, become acceptor of partially carboxymethyl guar gum radicals resulting in chain initiation and thereafter, it becomes free radical donor to the neighbouring molecule leading to lowering of termination. The decrease in grafting ratio, add on could be interpreted in terms of increase in viscosity of the medium due to solubility of poly(4-vinyl pyridine).

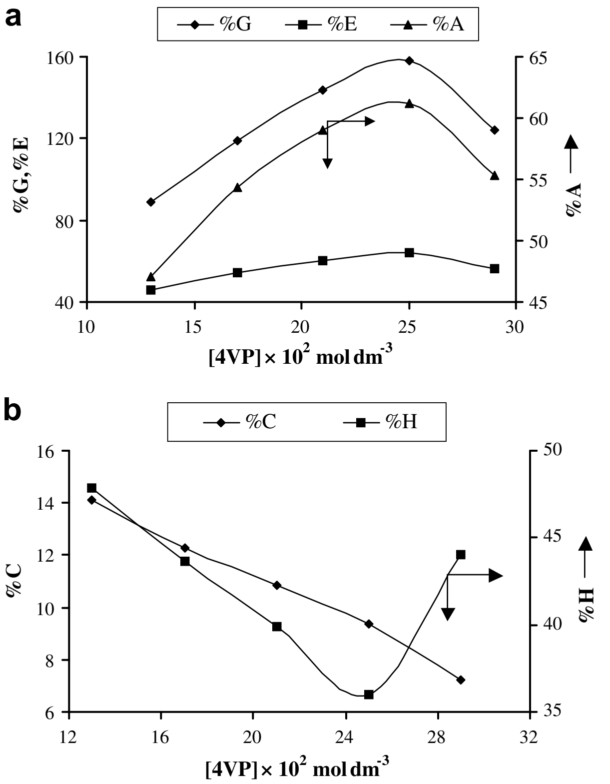


Fig. 2. (a) and (b) Effect of monomer. [Cmg] = 1.0 g dm^{-3}, [Thiourea] = 3.2 × 10^{-3} mol dm^{-3}, [BrO$_3^-$] = 8 × 10^{-3} mol dm^{-3}, [H$^+$] = 5 × 10^{-3} mol dm^{-3}, temp. = 40 °C, time = 120 min; %G = grafting ratio; %A = add on; %C = conversion; %E = efficiency; %H = homopolymer.

4.2.4. Effect of partially carboxymethylated guar gum

The graft copolymerization of 4-vinyl pyridine onto partially carboxymethylated guar gum has been studied at different concentrations of carboxymethylated guar gum. As the concentration of partially carboxymethylated guar gum is increased from 0.6 to 1.0 g dm^{-3} (Fig. 3a and b). Grafting ratio, efficiency, add on and conversion increase. This may be due to greater availability of grafting site at carboxymethylated guar gum. As the concentration is further increased beyond 1.0 g dm^{-3}, viscosity of reaction increases, which hinders the movement of free radicals thereby, decreasing the grafting parameters.

4.2.5. Effect of hydrogen ion concentration

The effect of hydrogen ion concentration on grafting parameters has been shown in Table 2. It has been

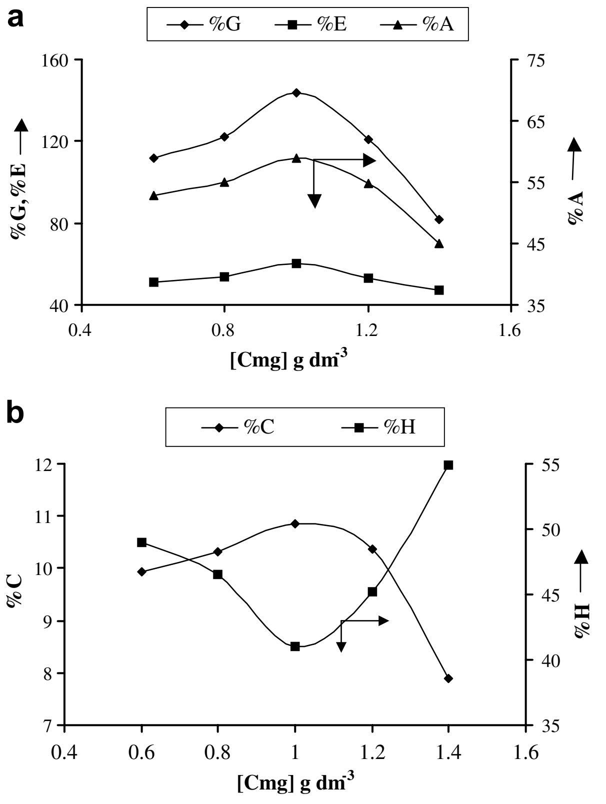


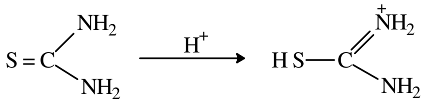
Fig. 3. (a) and (b) Effect of Cmg. $[BrO_3^-] = 8 \times 10^{-3}$ mol dm^{-3}, [4VP] $= 21 \times 10^{-2}$ mol dm^{-3}, $[H^+] = 5 \times 10^{-3}$ mol dm^{-3}, [Thiourea] = 3.2×10^{-3} mol dm^{-3}, temp. = 40 °C, time = 120 min, %G = grafting ratio; %A = add on; %C = conversion, %E = efficiency; %H = homopolymer.

Table 2
Effect of $[H^+]$ concentration

$[H]^+ \times 10^3$ mol dm^{-3}	%G	%E	%A	%C	%H
3	85.0	45.0	45.9	8.5	55.0
4	105.0	51.3	51.2	9.3	48.7
5	144.0	60.1	59.0	10.8	39.9
6	163.0	66.0	57.6	11.2	34.0
7	135.0	58.0	57.4	10.5	42.0

$[4VP] = 21 \times 10^{-2}$ mol dm^{-3}, $[BrO_3^-] = 8 \times 10^{-3}$ mol dm^{-3}, [TU] = 3.2×10^{-3} mol dm^{-3}, [Cmg] = 1.0 g dm^{-3}, temp. = 40 °C, time = 120 min.

observed that grafting ratio, add on, efficiency and conversion increase up to 6×10^{-3} mol dm^{-3} and beyond that homopolymer formation increases. This behaviour could be explained by the fact that on increasing H^+ concentration the rate of formation of protonated thiourea species also increases which reacts with bromate giving rise to primary free radicals and these primary free radicals react with partially carboxymethylated guar gum and 4-vinyl pyridine, giving rise to free radicals which were responsible for increasing the grafting parameter.



$$S{=}C(NH_2)_2 \xrightarrow{H^+} HS{-}C({=}\overset{+}{N}H_2)NH_2$$

But on further increase in the H^+ ion i.e. beyond 6×10^{-3} mol dm^{-3} the grafting ratio, add on and conversion are found to decrease, which might be due to excess hydrogen ion react with bromate to form $HBrO_3$. This species further decomposes to give oxygen in excess quantity, which acts as scavenger and grafting parameters show decreasing trend.

$$2KBrO_3 + H_2SO_4 \rightarrow 2HBrO_3 + KSO_4$$

$$2HBrO_3 \rightarrow Br_2 + H_2O + O_2$$

4.2.6. Effect of time period

On varying the time period from 60 to 180 min it was found that there is an increase in grafting ratio, efficiency, add on and conversion. On increasing the time period, propagation of grafting chain takes place due to availability of more active species, which accounts for higher grafting, resulting into increase in grafting parameters (Fig. 4a and b).

4.2.7. Effect of temperature

The results obtained for grafting parameters at different temperatures have been summarized in Table 3. It has been observed that, as the temperature is increased 30–40 °C, grafting ratio, add on, efficiency and conversion show increment. This may be attributed to the fact that with increase in temperature rate of production of more primary

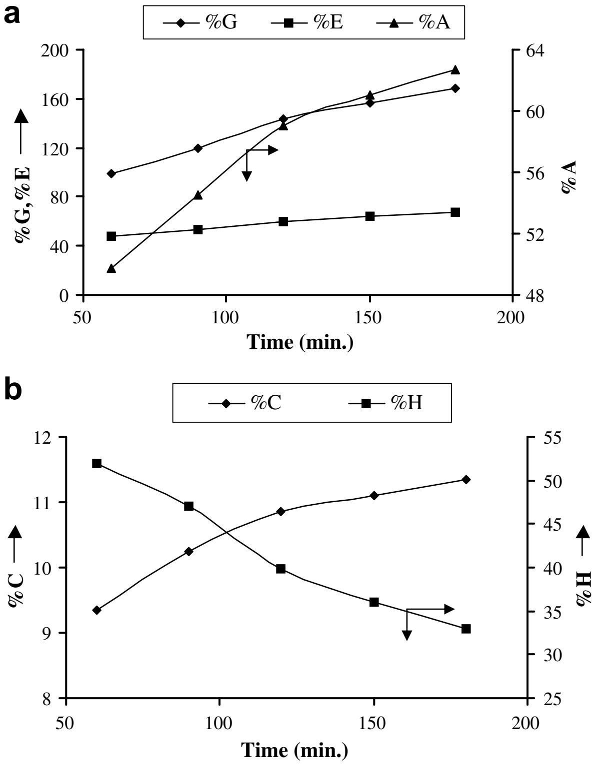


Fig. 4. (a) and (b) Effect of time. [Cmg] = 1.0 g dm^{-3}, [Thiourea] = 3.2×10^{-3} mol dm^{-3}, $[BrO_3^-] = 8 \times 10^{-3}$ mol dm^{-3}, [4VP] = 21×10^{-2} mol dm^{-3}, $[H^+] = 5 \times 10^{-3}$ mol dm^{-3}, temp. = 40 °C, %G = grafting ratio; %A = add on; %C = conversion, %E = efficiency %H = homopolymer.

Table 3
Effect of temperature

Temp. (°C)	%*G*	%*E*	%*A*	%*C*	%*H*
30	96.5	49.5	49.1	8.8	50.5
35	119.0	55.1	54.3	9.8	44.9
40	144.0	60.1	59.0	10.8	39.8
45	124.0	57.0	55.3	9.0	43.0
50	102.0	53.8	50.5	6.9	46.1

$[4VP] = 21 \times 10^{-2}$ mol dm^{-3}, $[BrO_3^-] = 8 \times 10^{-3}$ mol dm^{-3}, $[TU] = 3.2 \times 10^{-3}$ mol dm^{-3}, $[Cmg] = 1.0$ g dm^{-3}, $[H^+] = 5 \times 10^{-3}$ mol dm^{-3}, time = 120 min.

free radicals increase causing an increase in these parameter and also incorporation of 4VP molecule into the domain of partially carboxymethylated guar gum free radicals. However, further increase in temperature i.e. beyond 40 °C, results in the decrement of grafting parameter, which might be due to destruction of the free radicals at higher temperature.

5. Evidence of grafting

5.1. IR spectroscopy

On comparing the IR spectra of partially carboxymethylated guar gum and and 4VP grafted partially carboxymethylated guar gum (Figs. 5 and 6) following additional peaks appeared in the spectra of partially carboxymethylated guar gum-*g*-4VP. At 3066 cm^{-1} band appeared due to C–H stretching of aromatic ring and band for C═N stretching in ring appeared at 1519 cm^{-1}. These additional bands are characteristics of 4-vinyl pyridine. The decrement in intensity of OH bending vibrations and appearances of additional bands which are characteristic of 4VP in the spectrum of partially carboxymethylated guar gum-*g*-4VP indicate that grafting might have taken place on OH site.

5.2. Thermal analysis

5.2.1. Partially carboxymethylated guar gum

The degradation of partially carboxymethylated guar gum started at about 230 °C. It was a single step process and the rate of weight loss increased with increasing the temperature up to 405 °C but thereafter it decreased. Nearly 50% weight loss occurred between 337.5 °C and 350 °C (Fig. 7). Therefore final decomposition temperature (FDT) was low i.e. 425 °C. The polymer decomposition temperature (PDT) has been found at 235 °C. The integral procedural decomposition temperature (IPDT), and temperature at which maximum degradation occurs (T_{max}) have been found at 229 °C and 282 °C, respectively (Table 4). Degradation of partially carboxymethylated guar gum started with depolymerization through random chain scission associated with degradation followed by molecular arrangements. A char yield of about 25% was obtained at 900 °C.

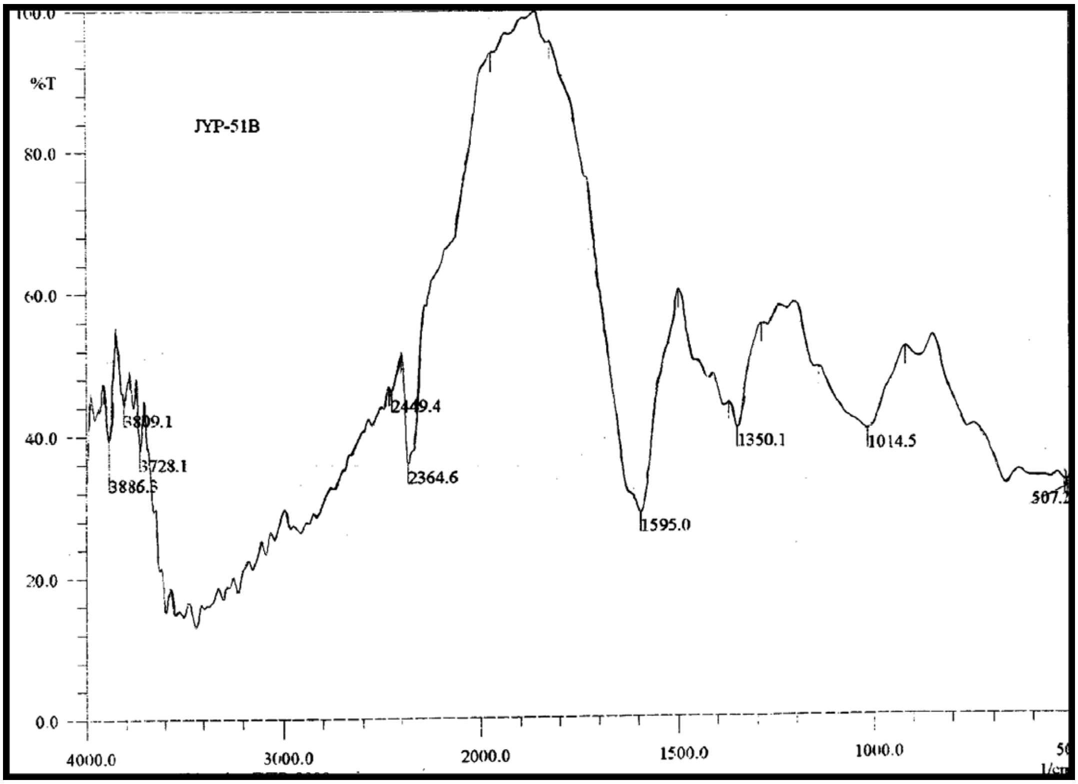


Fig. 5. IR spectrum of partially carboxymethylated guar gum.

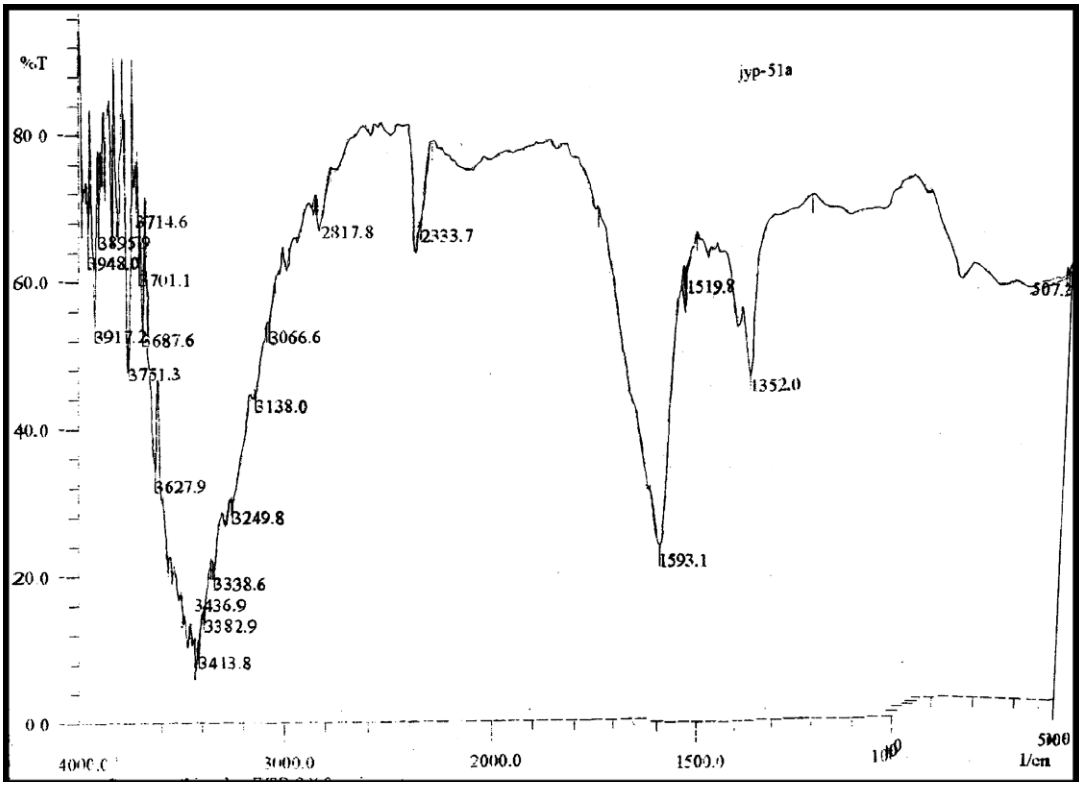


Fig. 6. IR spectrum of partially carboxymethylated guar gum-*g*-4-vinyl pyridine.

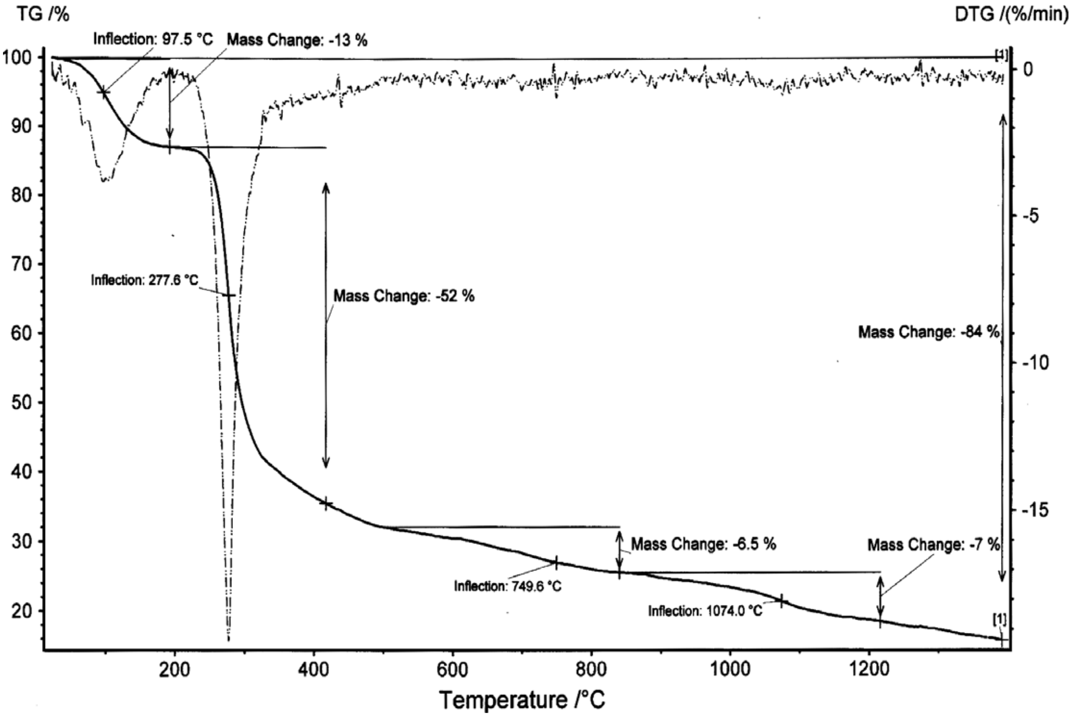


Fig. 7. Thermogravimetric trace of partially carboxymethylated guar gum.

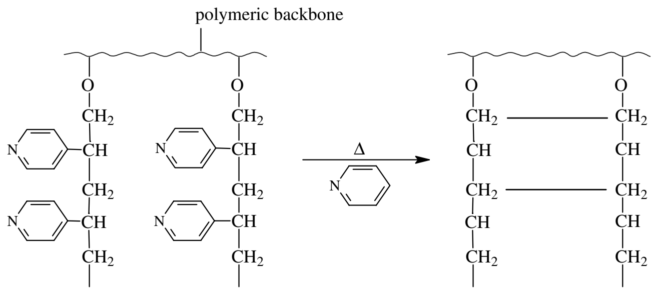
5.2.2. *Partially carboxymethylated guar gum-g-4-vinyl pyridine (4VP)*

The graft polymer started degrading about 185 °C. The weight loss of 10% at 131 °C was due to loss of absorbed water. The degradation has taken place in single step only (Fig. 8).

The rate of weight loss increased rapidly with increase in temperature from 200 °C to 410 °C and after that it

Table 4
Thermogravimetric analysis

Sample	PDT (°C)	FDT (°C)	T_{max} (°C)	IPDT (°C)
Cmg	235	425	282	229
Cmg-g-4VP	200	950	263	262

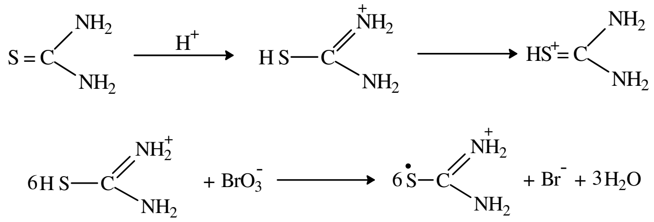


Scheme 1. Proposed schematical presentation of degradation pathway of graft copolymer.

decreased gradually (Table 4). Nearly 70% of weight loss of graft copolymer occurred at 819 °C. The polymer decomposition temperature has been found at 200 °C and the maximum degradation of grafted copolymer i.e. T_{max} was obtained at 263 °C, which is higher than ungrafted partially carboxymethylated guar gum. The integral procedural decomposition temperature (IPDT) has been found at 262 °C. The final decomposition temperature (FDT) was at 950 °C, which is very high as compared to the ungrafted polymer suggesting that grafting of 4VP has introduced thermal stability in the backbone. A char yield of about 29% was obtained at 900 °C. The high value of FDT, IPDT and char yield of grafted sample indicates that the graft copolymer is more stable than parent polymer (Table 4 and Fig. 8) (Scheme 1).

6. Mechanism

On the basis of experiments, following tentative mechanism has proposed for the system. It is assumed that in presence of hydrogen ion, thiourea sgets protonated, which reacts with bromate ion to give isothiocarbamide radicals. These radicals abstract hydrogen atom from the backbone (Cmg) molecule producing partially carboxymethylated guar gum free radicals. The monomer molecules which were near vicinity of the reaction sites, become acceptor of partially carboxymethylated guar gum radicals resulting in chain initiation and thereafter themselves become free radicals donor to neighboring molecules thus grafted chain grows. Termination of chain occurs by coupling to yield graft copolymer.



$$S{=}C(NH_2)_2 \xrightarrow{H^+} HS{-}C({=}\overset{+}{N}H_2)NH_2 \longrightarrow HS^+{=}C(NH_2)_2$$

$$6\,HS{-}C({=}NH_2^+)NH_2 + BrO_3^- \longrightarrow 6\,\dot{S}{-}C({=}\overset{+}{N}H_2)NH_2 + Br^- + 3H_2O$$

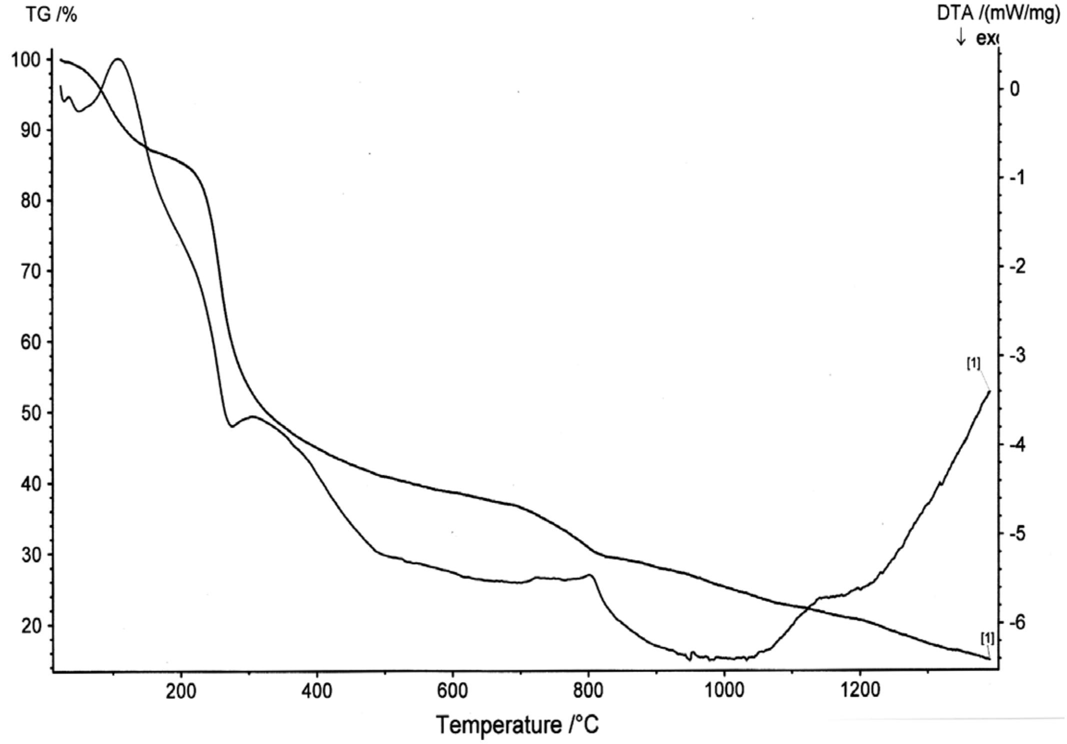
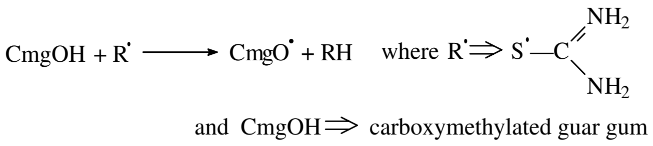


Fig. 8. Thermogravimetric trace of partially carboxymethylated guar gum-g-4-vinyl pyridine.

Initiation



$$\mathrm{CmgOH} + \mathrm{R}^{\bullet} \longrightarrow \mathrm{CmgO}^{\bullet} + \mathrm{RH} \quad \text{where } \mathrm{R}^{\bullet} \Rightarrow \mathrm{S}^{\bullet}\!-\!\mathrm{C}(=\mathrm{NH}_2)\mathrm{NH}_2$$

$$\text{and CmgOH} \Rightarrow \text{carboxymethylated guar gum}$$

Propagation

$$\mathrm{CmgO}^{\bullet} + \mathrm{M} \rightarrow \mathrm{CmgOM}_1^{\bullet}$$
$$\mathrm{CmgOM}_1^{\bullet} + \mathrm{M} \rightarrow \mathrm{CmgOM}_2^{\bullet}$$
$$\mathrm{CmgOM}_2^{\bullet} + \mathrm{M} \rightarrow \mathrm{CmgXOM}_3^{\bullet}$$

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$$\mathrm{CmgOM}_{n-1}^{\bullet} + \mathrm{M} \rightarrow \mathrm{CmgOM}_n^{\bullet}$$

Termination

$$\mathrm{CmgOM}_m^{\bullet} + \mathrm{CmgOM}_n^{\bullet} \rightarrow \text{graft copolymer}$$
$$\mathrm{CmgOM}_m^{\bullet} + \mathrm{RM}_n^{\bullet} \rightarrow \text{graft copolymer}$$
$$\mathrm{RM}_n^{\bullet} + \mathrm{RM}_m^{\bullet} \rightarrow \text{Homopolymer}$$

7. Swelling test

The results of water swelling behaviour of grafted carboxymethylated guar gum has been summarised in Table 5, which depicts that swelling ratio and swelling percent increase with increase in percent grafting ratio which is dependent upon monomer concentration. Since 4-vinyl pyridine is a hydrophilic monomer, it increases the water retention character of graft copolymer. Increased swelling capacity with increased grafting is further supported by the fact that as grafting is increased, it may result into coiling network of poly(4VP) pendant chain, which imbibes more water. Carboxymethyl group also increases the swellability of polysaccharides (Patel, Patel, & Trivedi, 1999). The presence of carboxymethyl group of substrate and a hydrophilic monomer, both factors are responsible for good swelling capacity of graft copolymer.

Table 5
Swelling behaviour

Sample	$[4VP] \times 10^2$ mol dm^{-3}	%G	Swelling ratio (Sr)	Percent swelling (Ps)
A	13	89	6.1	610
B	17	119	7.2	720
C	21	144	8.9	890
D	25	158	9.7	970
E	29	124	7.5	750

$[4VP] = 21 \times 10^{-2}$ mol dm^{-3}, $[BrO_3^-] = 8 \times 10^{-3}$ mol dm^{-3}, $[TU] = 3.2 \times 10^{-3}$ mol dm^{-3}, $[Cmg] = 1.0$ g dm^{-3}, $[H^+] = 5 \times 10^{-3}$ mol dm^{-3}, time = 120 min, temp. = 40 °C where A, B, C, D and E = graft copolymer.

8. Metal ion sorption behaviour of carboxymethylated guar gum and its graft copolymer

The amount of sorbed metal ion has been determined by titrating the remaining metal ions at a constant P^H and results have been obtained by calculating different parameters i.e. percent ion uptake (P_u), partition coefficient (K_d), retention capacity (Q_r) which has been shown in Table 6. For this study five metal ions have been chosen, that are Cu^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+} and Hg^{2+}. Results also show that Hg^{2+} was least uptakable and Cu^{2+} was most uptakable in comparison to other four metal ions of them, which have been used. The value of percent ion uptake (P_u), partition coefficient (K_d) and retention capacity (Q_r) first increase as the percent grafting ratio of grafted polymer is increased, which reaches maximum when grafting ratio is 144% however for all metal ions, these parameters decrease with decrement in grafting ratio, which might be due to the fact that as grafting increases, the density of sorption sites for metal ions are increased due to availability of additional functional groups of poly-pendent chain of monomer, which further increases with increased grafting. Morever, functional group incorporated by grafting and its ability to interact with metal ion play important role in the determination of selectivity and quantum of metal ion uptake (Srivastava & Behari, 2007).

9. Intrinsic viscosity of polymer solutions

Intrinsic viscosity $[\eta]$ was obtained from common ordinate intercept on extrapolation of plots of reduced viscosity versus concentration. Intrinsic viscosity results been

Table 6
Metal ion sorption

Sample	$[4VP] \times 10^2$ mol dm^{-3}	%G	Percent uptake (P_u)					Partition coefficient (K_d)					Retention capacity (Q_r)				
			Cu^{2+}	Pb^{2+}	Ni^{2+}	Zn^{2+}	Hg^{2+}	Cu^{2+}	Pb^{2+}	Ni^{2+}	Zn^{2+}	Hg^{2+}	Cu^{2+}	Pb^{2+}	Ni^{2+}	Zn^{2+}	Hg^{2+}
Cmg	—	—	5.4	2.8	4.6	3.7	1.2	28.8	14.7	24.5	19	6.4	2.6	1.4	2.2	1.9	0.6
A	13	89	9.0	3.7	5.7	4.3	2.1	53.0	19.5	30.2	22.6	11	4.3	1.9	2.7	2.2	1.0
B	17	119	12.9	5.0	7.5	6.0	2.9	74.7	26.5	41.0	32	15	6.2	2.5	3.6	3.0	1.4
C	21	144	14.8	6.1	9.8	7.1	4.2	87.4	32.6	54.7	39	22.1	7.0	3.1	4.7	3.6	2
D	25	158	20.5	7.9	11.9	8.5	5.3	129.3	42.9	67.8	46.2	27.9	9.8	4	5.7	4.3	2.5
E	29	124	14.3	5.8	8.1	6.5	3.1	84.5	29.2	52.2	35.8	18.7	6.9	2.8	4.5	3.4	1.7

$[4VP] = 21 \times 10^{-2}$ mol dm^{-3}, $[BrO_3^-] = 8 \times 10^{-3}$ mol dm^{-3}, $[TU] = 3.2 \times 10^{-3}$ mol dm^{-3}, $[Cmg] = 1.0$ g dm^{-3}, $[H^+] = 5 \times 10^{-3}$ mol dm^{-3}, time = 120 min, temp. = 40 °C where A, B, C, D and E = graft copolymer.

shown in (Figs. 9 and 10). Intrinsic viscosity of partially carboxymethylated guar gum and partially carboxymethylated guar gum-g-4-vinyl pyridine is found to be 6.4 and 4.3, respectively. The graft copolymer of 4-vinyl pyridine shows lower intrinsic viscosity than partially carboxymethylated guar gum because longer grafted chains are available. Sufficiently longer graft chains make the molecules very flexible and thus reduce the viscosity drastically (Ungeheur, Bewersdorff, & Singh, 1989).

10. Flocculating performance

Plots of supernatant turbidity versus polymer dosage for coking and non-coking coals are given in (Figs. 11 and 12). It has been found that grafted copolymer (Cmg-g-4VP) gives better performance by showing lower turbidity than partially carboxymethylated guar gum itself. This phenomenon could be explained by considering bridging mechanism (Deshmukh, Singh, & Chaturvedi, 1985). In grafted copolymer, the dangling of poly(4VP) chains have better approachability to the contaminant coal particles hence increases its flocculation capability. The difference in turbidity value in coking coal and noncoking coal in coal suspension is due to difference in negative charge density, which is higher in non-coking coal in aqueous solution (Gregory, 1982). Thus, by grafting of poly-4-vinyl pyridine onto partially carboxymethylated guar gum, efficient flocculants have been obtained and it could be used for the treatment of coal wastewater.

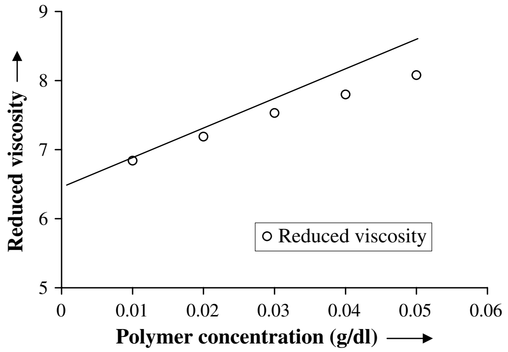

Fig. 9. Viscosity of partially carboxymethylated guar gum.

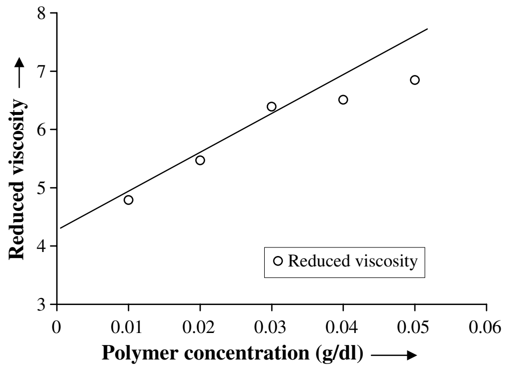

Fig. 10. Viscosity partially carboxymethylated guar gum-*g*-4-vinyl pyridine.

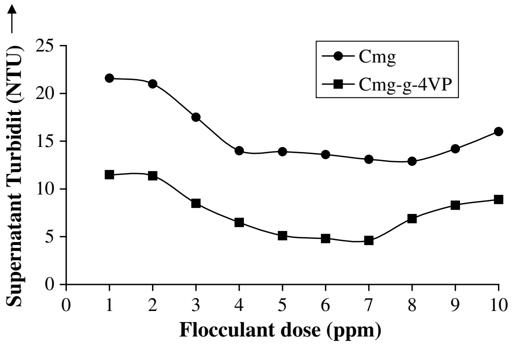

Fig. 11. Flocculation behaviour of grafted and ungrafted Cmg in coking coal.

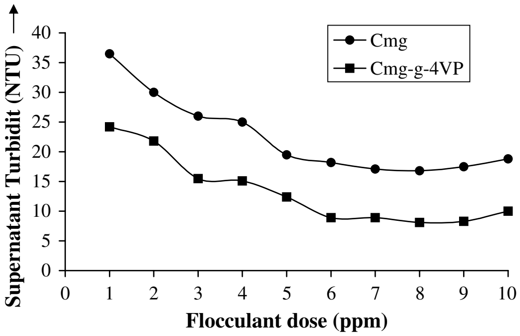

Fig. 12. Flocculation behaviour of grafted and ungrafted Cmg in noncoking coal.

11. Conclusions

Partially carboxymethylated guar gum grafted with 4-vinyl pyridine has been synthesized by employing efficient redox pair i.e. bromate/thiourea. The spectroscopic data confirm that the grafting of 4-vinyl pyridine has occurred at hydroxyl group of Partially carboxymethylated guar gum. The thermal analysis data show that the grafted partially carboxymethylated guar gum is thermally more stable than the ungrafted partially carboxymethylated guar gum considering the higher values of IPDT, FDT. The synthesized graft copolymer shows very good water swelling capacity, metal ion sorption and flocculating properties, which thereby reveals enhancement in these properties due to grafting.

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