Synthesis and Characterization of Graft Copolymer (Guar Gum–*g*–*N*-vinyl-2-pyrrolidone) and Investigation of Metal Ion Sorption and Swelling Behavior

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ABSTRACT: Graft copolymer of *N*-vinyl-2-pyrrolidone with guar gum was synthesized and its reaction conditions were optimized for better yield using potassium peroxymonosulfate (PMS) and glycolic acid (GA) as a redox initiator. The effect of PMS, GA, hydrogen ions, guar gum, and *N*-vinyl-2-pyrrolidone (NVP) along with reaction time and temperature were studied by determining the grafting parameters: grafting ratio, efficiency, conversion, add-on, homopolymer, and rate of grafting. It was observed that the maximum yield occurred at with a time of 120 min at a temperature of 45°C and a guar gum concentration of 0.4 g/L concentration. The graft copolymer was characterized by infrared spectroscopy and thermal analysis. The activation energy for the grafted and ungrafted gum was calculated. It was observed that the graft copolymer was thermally more stable than the pure gum. The swelling and metal ion sorption behavior of guar gum and guar gum-*g*-*N*-vinyl-2-pyrrolidone also were studied. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2480–2489, 2006

Key words: graft copolymer; biodegradable; swelling; FTIR; thermal properties

INTRODUCTION

The chemical modification of natural polymers by grafting has received considerable attention in recent years. Guar gum, which is a naturally occurring high-molecular-weight carbohydrate polymer, has the characteristics of being rigid and nonionic.[1,2] It consists of (1→4)-β-D-manno-pyranosyl units with α-D-galacto-pyranosyl units attached by 1→6 linkages. It enjoys a wide range of uses in industry[3–6] and is widely used in the food industry.[7] Although guar gum has wide industrial applications, it suffers from some drawbacks like biodegradability,[8] which limits its uses considerably. These drawbacks can be improved through the grafting of vinyl monomer, which imparts new properties to the polymeric backbone.

Similarly, *N*-vinyl-2-pyrrolidone, a hydrophilic and nontoxic monomer, has various industrial applications.[9,10] Poly(*N*-vinyl-2-pyrrolidone) has had commercial success because of its biological compatibility, low toxicity, adhesive characteristics, and unusual complexing ability. The grafting of *N*-vinyl-2-pyrrolidone onto guar gum has not been reported in the literature. Recently, the synthesis of a graft copolymer of *N*-vinyl-2-pyrrolidone with silica, polytetrafluro-ethylene, and poly(vinylidine fluoride) through a different process was reported, but the yield was very low,[11] and no details were given about the grafting parameters.[12] These properties and applications of *N*-vinyl-2-pyrrolidone and guar gum prompted us to synthesize a graft copolymer of *N*-vinyl-2-pyrrolidone and guar gum by using an efficient redox pair like potassium peroxymonosulfate and glycolic acid. The aim of the work reported in this article was to synthesize the graft copolymer and to study its swelling, thermal, and metal ion sorption behaviors.

EXPERIMENTAL

Materials

Freshly distilled *N*-vinyl-2-pyrrolidone (Merck) has been used. Potassium peroxymonosulfate (PMS; Sigma) and glycolic acid (Merck) were used as such without further purification. Guar gum, a gift from Hindustan Gums and Chemicals Ltd. (India), was used as received. Sulfuric acid (E. Merck) was used to maintain the hydrogen ion concentration. Methanol (BDH) and acetone (BDH) were used for precipitation. The other chemical reagent was of analytical pure grade and used without further purification.

Procedure for graft copolymerization

For each experiment guar gum solution was prepared by adding the desired amount of guar gum to 50 mL
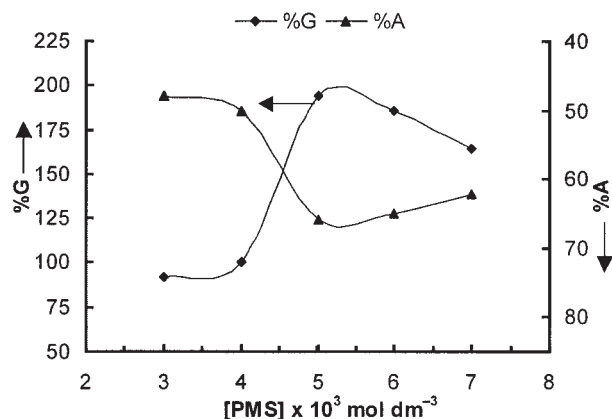
Figure 1 Effect of potassium peroxymonosulfate concentration ([GOH] = 1.0 g/dm^3, [NVP] = 12.0 × 10^{-2} mol/dm^3, [H$^+$] = 6.0 × 10^{-3} mol/dm^3, [GA] = 4.0 × 10^{-3} mol/dm^3, time = 120 min, temperature = 40°C; %G, grafting ratio; %A, add on).

of triple-distilled water in a reactor kept in a thermostat at the desired temperature. A calculated amount of N-vinyl-2-pyrrolidone, glycolic acid, and sulfuric acid solutions were added to the guar gum solution. A known amount of deoxygenated potassium peroxymonosulfate solution was added to initiate the reaction. The reaction was performed under a continuous flow of oxygen-free nitrogen gas. After a desired interval, the reaction was stopped by letting air into the reactor. The grafted sample was precipitated by pouring the reaction mixture into a water–methanol mixture. The precipitate was filtered, dried, and weighed. The filtrate was concentrated by distillation under reduced pressure in the presence of hydroquinone. The poly(N-vinyl-2-pyrrolidone) was precipitated by pouring the concentrated filtrate into acetone. The poly(N-vinyl-2-pyrrolidone) thus obtained was separated, dried, and weighed.

RESULTS AND DISCUSSION

The graft copolymers were characterized according to Fanta's definition,[13] and the rate of grafting[14] were as follows:

Grafting ratio (%G)

$$= \frac{\text{weight of grafted polymer}}{\text{weight of substrate}} \times 100$$

Grafting efficiency (%E)

$$= \frac{\text{weight of grafted polymer}}{\text{weight of polymer formed}} \times 100$$

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

Conversion (%C)

$$= \frac{\text{weight of polymer formed}}{\text{weight of monomer charged}} \times 100$$

Homopolymer (%H) = 100 − % grafting efficiency

Rate of grafting (Rg)

$$= \frac{1000 \times \text{weight of grafted polymer}}{\text{volume} \times \text{time} \times \text{mol. wt. of NVP}} \text{ moll}^{-1}\text{ S}^{-1}$$

Determination of optimum reaction conditions

The effect of variables on the grafting parameters and the rate of grafting was studied to determine the optimum conditions for grafting. The variables included the concentrations of potassium peroxymonosulfate, glycolic acid, sulfuric acid, N-vinyl-2-pyrrolidone, and guar gum and the reaction time and temperature.

Effect of peroxymonosulfate concentration

The effect of peroxymonosulfate concentration on the grafting parameters was studied at various concentration of peroxymonosulfate, and the results are shown in Figures 1 and 2. It was observed that the grafting ratio, add-on, conversion, efficiency, and rate of grafting increased with an increasing concentration of peroxymonosulfate from 3.0 × 10^{-3} to 5.0 × 10^{-3} mol/dm^3, but with further increases in the concentration of peroxymonosulfate beyond 5.0 × 10^{-3} mol/dm^3, it was observed that the grafting parameters and rate of grafting decreased and that homopolymer increased. The increase in the grafting parameters might be attributed to the progressive reduction of peroxymonosulfate by glycolic acid, producing primary free radicals, which attacked the xanthan gum, creating more active sites, at which monomer addition took place.
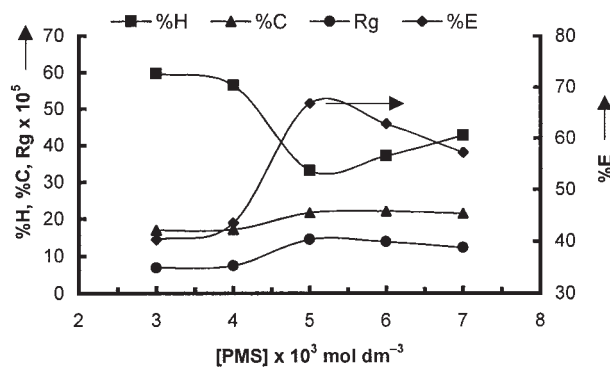

Figure 2 Effect of potassium peroxymonosulfate concentration ([GOH] = 1.0 g/dm^3, [NVP] = 12.0 × 10^{-2} mol/dm^3, [H$^+$] = 6.0 × 10^{-3} mol/dm^3, [GA] = 4.0 × 10^{-3} mol/dm^3, time = 120 min, temperature = 40°C; %C, conversion; %E, efficiency; %H, homopolymer; R_g, rate of grafting).
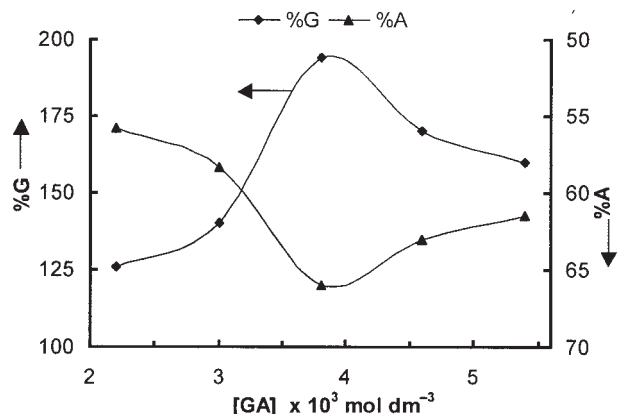
Figure 3 Effect of glycolic acid concentration ([GOH] = 1.0 g/dm^3, [NVP] = 12.0 × 10^{-2} mol/dm^3, [H$^+$] = 6.0 × 10^{-3} mol/dm^3, [PMS] = 5.0 × 10^{-3} mol/dm^3, time = 120 min, temperature = 40°C; %G, grafting ratio; %A, add on).

The decrease in the grafting parameters at higher concentrations might have been a result of the premature termination of the growing grafted chain.

Effect of glycolic acid concentration

The results obtained by varying the concentration of glycolic acid from 2.4 × 10^{-3} to 5.6 × 10^{-3} mol/dm^3 are shown in Figures 3 and 4. It was observed that the grafting ratio, add-on, conversion, efficiency, and rate of grafting increased with increasing concentrations of glycolic acid from 2.4 × 10^{-3} to 4.0 × 10^{-3} mol/dm^3; but beyond this concentration the grafting parameters and rate of grafting decreased. The increase in grafting parameters might be attributed to the increase in the number of primary free radicals, but a high concentration of glycolic acid, that is, beyond 4.0 × 10^{-3} mol/dm^3, favored the formation of poly(N-vinyl-2-pyrrolidone) over grafting, thereby decreasing the grafting parameters and rate of grafting.

Effect of sulfuric acid concentration

To examine the effect of the concentration of hydrogen ions on graft copolymerization, the process was carried out at various concentrations of hydrogen ions (from 2.0 × 10^{-3} to 10.0 × 10^{-3} mol/dm^3), and the results are summarized in Table I. The grafting parameters and rate of grafting were found to decrease continuously with increasing concentrations of hydrogen ions. This behavior might have occurred because of the formation of H$_2$SO$_5$ species; thus, the concentration of HSO$_5^-$ decreased This resulted in less production of primary free radicals, which governed the graft copolymerization, thereby decreasing the grafting parameters. This also was observed by other workers in our laboratory.[15]

$$HSO_5^- + H^+ \rightarrow H_2SO_5$$
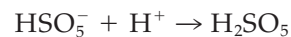
Effect of guar gum concentration

The effect of the concentration of guar gum on the grafting parameters was studied by varying the concentration of guar gum from 0.4 to 1.8 g/dm^3, and the results are shown in Figures 5 and 6. It was observed that the grafting ratio and add-on decreased continuously with an increasing concentration of guar gum. This behavior could be explained by the concentration of guar gum as well as the viscosity of the reaction medium increasing, which hindered the diffusion of primary free radicals and thereby decreased the grafting parameters and rate of grafting.

Effect of N-vinyl-2-pyrrolidone concentration

The effect of the concentration of N-vinyl-2-pyrrolidone on graft copolymerization was studied by varying the concentration of N-vinyl-2-pyrrolidone (N-VP) from 4.0 × 10^{-2} to 20.0 × 10^{-2} mol/dm^3 (Table II). It was observed that grafting ratio (%G), add-on (%A), grating efficiency (%E), and rate of grafting (R$_g$) increased with the concentration of N-vinyl-2-pyrrolidone increasing from 4.0 × 10^{-2} to 12.0 × 10^{-2} mol/dm^3, which might have been a result of the greater availability of monomer molecules in close proximity to the polymer backbone. The monomer molecules in the immediate vicinity of the reaction sites became acceptors of guar gum radicals (GO$^\bullet$), resulting in chain initiation, and thereafter they became free-radical donors to the neighboring molecules (monomer), leading to lowering the termination and increasing the grafting parameters. But beyond 12.0 × 10^{-2} mol/dm^3, the grafting parameters and rate of grafting decreased, which could be attributed to the increased
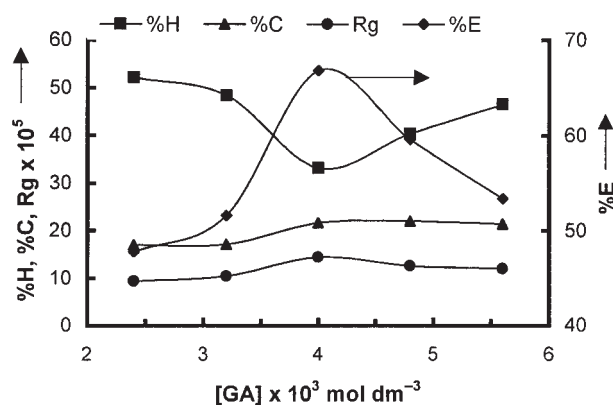
Figure 4 Effect of glycolic acid concentration ([GOH] = 1.0 g/dm^3, [NVP] = 12.0 × 10^{-2} mol/dm^3, [H$^+$] = 6.0 × 10^{-3} mol/dm^3, [PMS] = 5.0 × 10^{-3} mol/dm^3, time = 120 min, temperature = 40°C; %C, conversion; %E, efficiency; %H, homopolymer; R$_g$, rate of grafting).

TABLE I
Effect of H$^+$ Ion Concentration

S.N.	[H$^+$] ($\times 10^3$ mol/dm^3)	%G	Rg $\times 10^5$ mol L^{-1}s^{-1}	%A	%C	%E	%H
1	2.0	225	40.10	69.20	24.60	69.00	31.00
2	4.0	210	26.20	67.70	23.10	68.10	31.90
3	6.0	194	14.56	65.98	21.74	66.89	33.11
4	8.0	154	11.56	60.62	21.20	54.46	45.53
5	10.0	134	10.06	57.26	20.84	48.20	51.79

[GOH] = 1.0 g/dm^3; [NVP] = 12.0 $\times 10^{-2}$ mol/dm^3; [PMS] = 5.0 $\times 10^{-3}$ mol/dm^3; [GA] = 4.0 $\times 10^{-3}$ mol/dm^3; time = 120 min; temperature = 40°C.

viscosity of the reaction medium because of the preferential formation of homopolymer at higher concentrations of monomer.

Effect of time

The effect of change in duration of grafting reaction has been studied by varying the time period from 60 to 180 min, and the results are given in Table III. It has been observed that the %G, %A, %E, conversion (%C), and R_g increased with increases in time from 60 to 120 min; but beyond this, the grafting parameters and rate of grafting decreased, whereas homopolymer was found to increase. With increasing time, the propagation of grafting chains occurred because of the availability of more active species, which accounted for the higher grafting. With further increases in the interval, mutual annihilation of growing grafted chains occurred, which resulted in the grafting parameters and rate of grafting decreasing but homopolymer formation increasing.

Effect of temperature

The effect of temperature on the grafting parameters and rate of grafting was studied by varying the temperature from 30°C to 50°C (Table IV). It was observed that as the temperature was increased from 30°C to 45°C, %G, %A, %E, %C, and R_g also increased. The values of these parameters might have increased because with the increase in temperature, the rate of primary free radicals produced and the diffusion of N-vinyl–2–pyrrolidone to guar gum free radicals both increased. However, beyond the optimum value, a further increase in temperature could result in the decomposition of potassium peroxymonosulfate into HSO$_4^-$, H$_2$O, and O$_2$.[16] Because O$_2$ is a scavenger of free radicals, it lowers the free-radical concentration, resulting in decreased values of the grafting parameters.

Mechanism

On the basis of the experimental results, the following tentative mechanism is proposed for the graft copolymerization of N-vinyl-2-pyrrolidone onto guar gum using a potassium peroxymonosulfate and glycolic acid redox pair. Initially, peroxymonosulfate reacted with glycolic acid to form a complex. Subsequently, the complex dissociated to generate free radicals, R$^\bullet$, as follows:

Figure 5 Effect of guar gum concentration ([H$^+$] = 6.0 $\times 10^{-3}$ mol/dm^3, [NVP] = 12.0 $\times 10^{-2}$ mol/dm^3, [GA] = 4.0 $\times 10^{-3}$ mol/dm^3, [PMS] = 5.0 $\times 10^{-3}$ mol/dm^3, time = 120 min, temperature = 40°C; %G, grafting ratio; %A, add on).
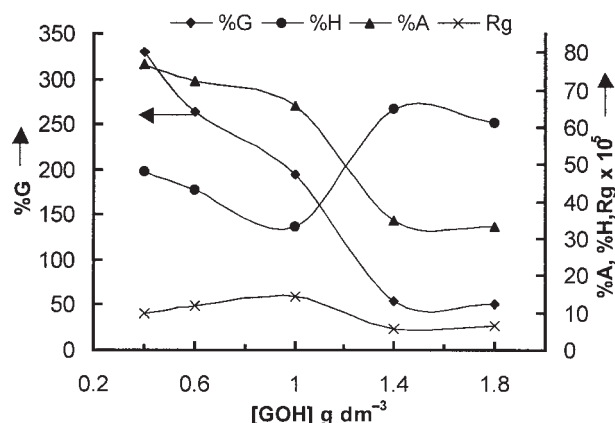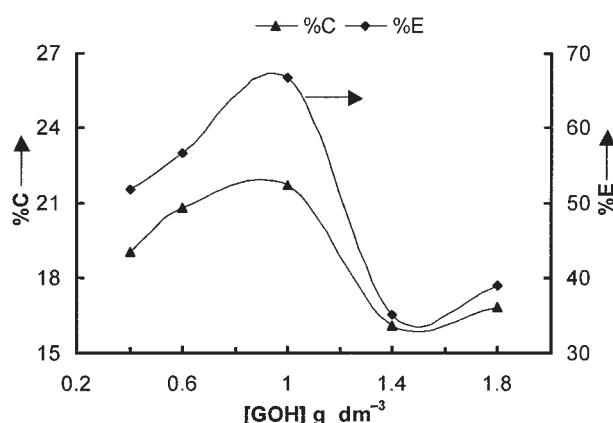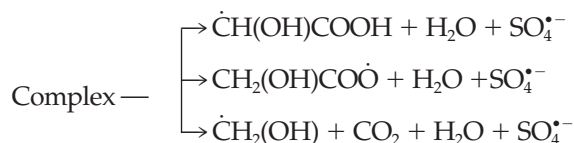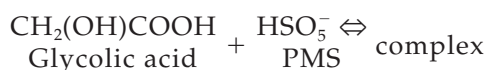
Figure 6 Effect of guar gum concentration ([H$^+$] = 6.0 $\times 10^{-3}$ mol/dm^3, [NVP] = 12.0 $\times 10^{-2}$ mol/dm^3, [GA] = 4.0 $\times 10^{-3}$ mol/dm^3, [PMS] = 5.0 $\times 10^{-3}$ mol/dm^3, time = 120 min, temperature = 40°C; %C, conversion; %E, efficiency; %H, homopolymer; R_g, rate of grafting).

TABLE II
Effect of NVP Concentration

S.N.	[NVP] ($\times 10^2$ mol/dm^3)	%G	Rg ($\times 10^5$ mol L^{-1}s^{-1})	%A	%C	%E	%H
1	4.0	142	10.66	58.67	58.93	54.19	45.80
2	8.0	170	12.76	62.96	31.49	60.71	39.28
3	12.0	194	14.56	65.98	21.74	66.89	33.11
4	16.0	166	12.46	62.40	15.63	59.71	40.28
5	20.0	90	6.75	47.36	10.90	37.13	62.86

[GOH] = 1.0 g/dm^3; [PMS] = 5.0×10^{-3} mol/dm^3; [H$^+$] = 6.0×10^{-3} mol/dm^3; [GA] = 4.0×10^{-3} mol/dm^3; Time = 120 min; temperature = 40°C.

R$^\bullet$ = CH$_2$(OH)CO$\dot{O}$, $\dot{C}$H(OH)COOH, $\dot{C}$H$_2$(OH)

or SO$_4^{\bullet -}$

$$\underset{\text{Glycolic acid}}{CH_2(OH)COOH} + \underset{\text{PMS}}{HSO_5^-} \Leftrightarrow complex$$

$$Complex \longrightarrow \begin{cases} \rightarrow \dot{C}H(OH)COOH + H_2O + SO_4^{\bullet -} \\ \rightarrow CH_2(OH)CO\dot{O} + H_2O + SO_4^{\bullet -} \\ \rightarrow \dot{C}H_2(OH) + CO_2 + H_2O + SO_4^{\bullet -} \end{cases}$$
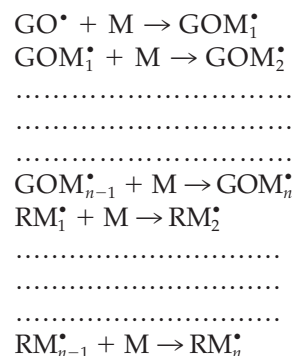
The R$^\bullet$ radicals extracted hydrogen atoms from the guar gum molecules, producing guar gum macroradicals (GO$^\bullet$), which were secondary free radicals. The monomer molecules, which were in close proximity to the reaction sites, became acceptors of guar gum macroradicals, resulting in chain initiation. Thereafter they themselves became free-radical donors to the neighboring molecules, leading to propagation. These grafted chains were terminated by coupling to produce graft copolymer.
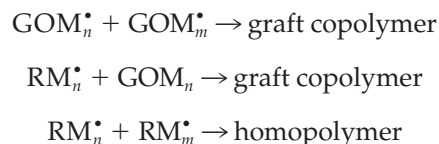
Initiation

$$GOH + R^\bullet \rightarrow \underset{\text{Guar gum macroradical}}{GO^\bullet + RH}$$

$$M + R^\bullet \rightarrow RM^\bullet$$
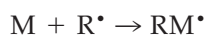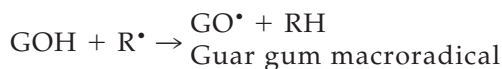
Where GOH → guar gum and M → monomer

Propagation

$$GO^\bullet + M \rightarrow GOM_1^\bullet$$
$$GOM_1^\bullet + M \rightarrow GOM_2^\bullet$$
$$\dots\dots\dots\dots\dots\dots\dots$$
$$\dots\dots\dots\dots\dots\dots\dots$$
$$\dots\dots\dots\dots\dots\dots\dots$$
$$GOM_{n-1}^\bullet + M \rightarrow GOM_n^\bullet$$
$$RM_1^\bullet + M \rightarrow RM_2^\bullet$$
$$\dots\dots\dots\dots\dots\dots$$
$$\dots\dots\dots\dots\dots\dots$$
$$\dots\dots\dots\dots\dots\dots$$
$$RM_{n-1}^\bullet + M \rightarrow RM_n^\bullet$$

Termination

$$GOM_n^\bullet + GOM_m^\bullet \rightarrow graft\ copolymer$$

$$RM_n^\bullet + GOM_n \rightarrow graft\ copolymer$$

$$RM_n^\bullet + RM_m^\bullet \rightarrow homopolymer$$

Infrared spectral analyses

The IR spectra of samples in KBr pellets were recorded using a Perkin Elmer FTIR spectrophotometer (PARAGON 1000) in the range 500–4000 cm^{-1}. Many bands appeared in the spectra of guar gum (Fig. 7), corresponding to the polysaccharide backbone. In addition to these bands, additional bands appeared in the spectra of guar gum-g-N-vinyl-2-pyrrolidone (Fig. 8), such as a C=O stretching band at 1661 cm^{-1}, and a C—N stretching band at 1430.2 cm^{-1}, corresponding

TABLE III
Effect of Time

S.N.	Time (min)	%G	Rg ($\times 10^5$ mol L^{-1}s^{-1})	%A	%C	%E	%H
1	60	134	10.06	57.26	18.47	54.38	45.61
2	90	164	12.31	62.12	20.27	60.74	39.25
3	120	194	14.56	65.98	21.74	66.89	33.11
4	150	160	12.01	61.53	21.00	57.14	42.85
5	180	120	9.45	55.75	20.84	45.32	54.67

[GOH] = 1.0 g dm^{-3}; [NVP] = 12.0×10^{-2} mol dm^{-3} [H$^+$] = 6.0×10^{-3} mol dm^{-3}; [GA] = 4.0×10^{-3} mol dm^{-3} [PMS] = 5.0×10^{-3} mol dm^{-3}; Temp. = 40°C

TABLE IV
Effect of Temperature

Sample No.	Temperature (°C)	%G	Rg ($\times 10^5$ mol L^{-1}s^{-1})	%A	%C	%E	%H
1	30	102	7.65	50.49	17.09	44.73	55.26
2	35	118	8.85	54.12	17.54	50.42	49.57
3	40	194	14.56	65.98	21.74	66.89	33.11
4	45	200	15.01	66.66	22.49	76.92	22.07
5	50	100	7.50	50.00	17.69	42.37	57.62

[GOH] = 1.0 g/dm^3; [NVP] = 12.0 × 10^{-2} mol/dm^3; [H$^+$] = 6.0 × 10^{-3} mol/dm^3; [GA] = 4.0 × 10^{-3} mol/dm^3; time = 120 min; [PMS] = 5.0 × 10^{-3} mol/dm^3

to a carbonyl group and C—N bond of poly(N-vinyl-2-pyrrolidone). In a comparison of the spectra of guar gum and guar gum–g–N-vinyl-2-pyrrolidone, it also was observed that some bands disappeared with changes in the spectra of guar gum-g-N-vinyl-2-pyrrolidone like O—H bending vibration, indicating that grafting might have occurred at the —OH site of the backbone.

Thermogravimetric analysis

The thermal behavior of guar gum and guar gum-g-N-vinyl-2-pyrrolidone was recorded on a NETZSCH-Geratebau GmbH thermal analyzer up to 1500°C at a heating rate of 20°C/min in an N$_2$ atmosphere.

Guar gum

Figure 9 shows that the degradation of guar gum started at about 200°C. A weight loss of about 5.94% occurred at 100°C, a result of absorbed of water. The rate of weight loss increased with increasing temperature, attaining its maximum at 304.5°C and decreasing thereafter. Therefore, this was a single-step degradation process. The polymer decomposition temperature (PDT) and temperature at which maximum weight loss occurred (T_{max}) were found to be 287.5°C and 304.5°C, respectively. This T_{max} was confirmed by the differential thermal analysis curve, which showed a broad endothermic peak at 313.0°C. About 70% of guar gum degraded at 378.2°C. Therefore, the final
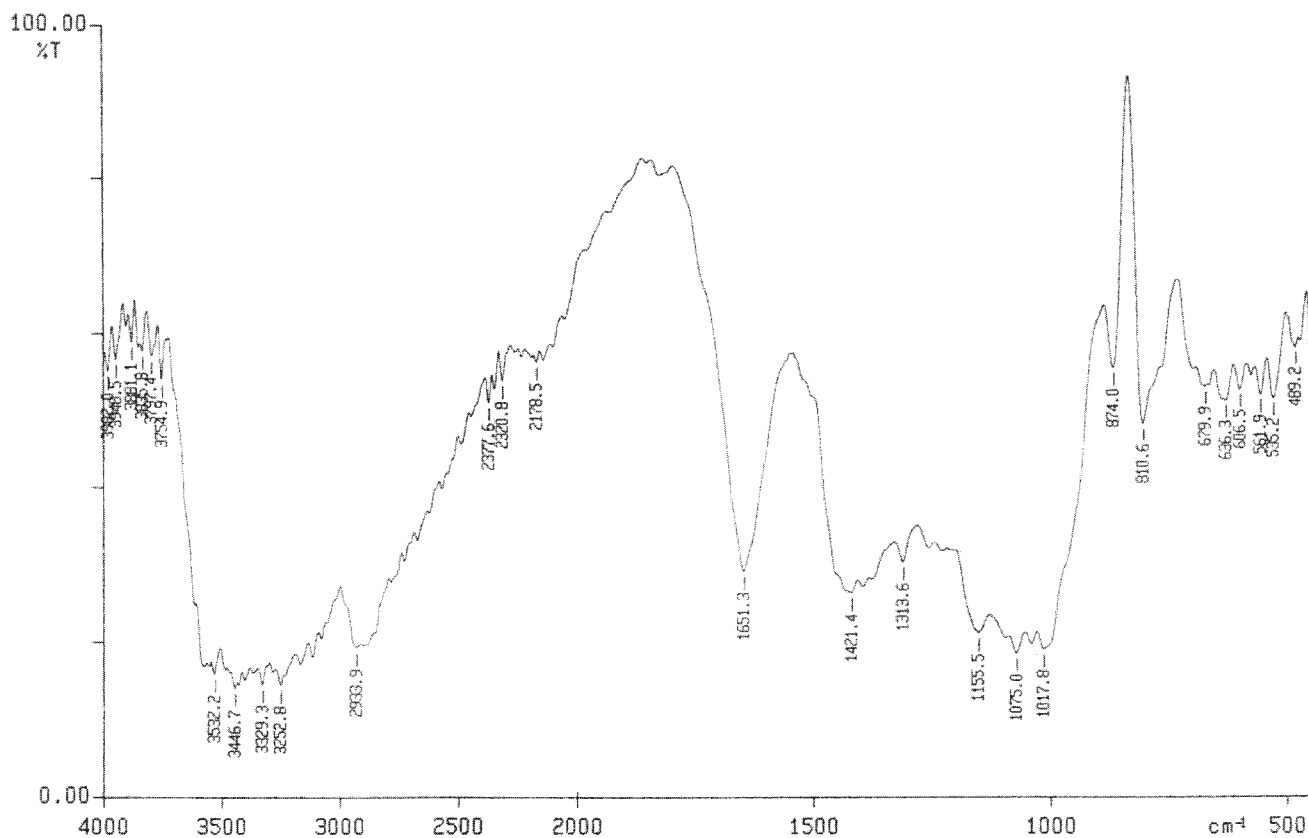

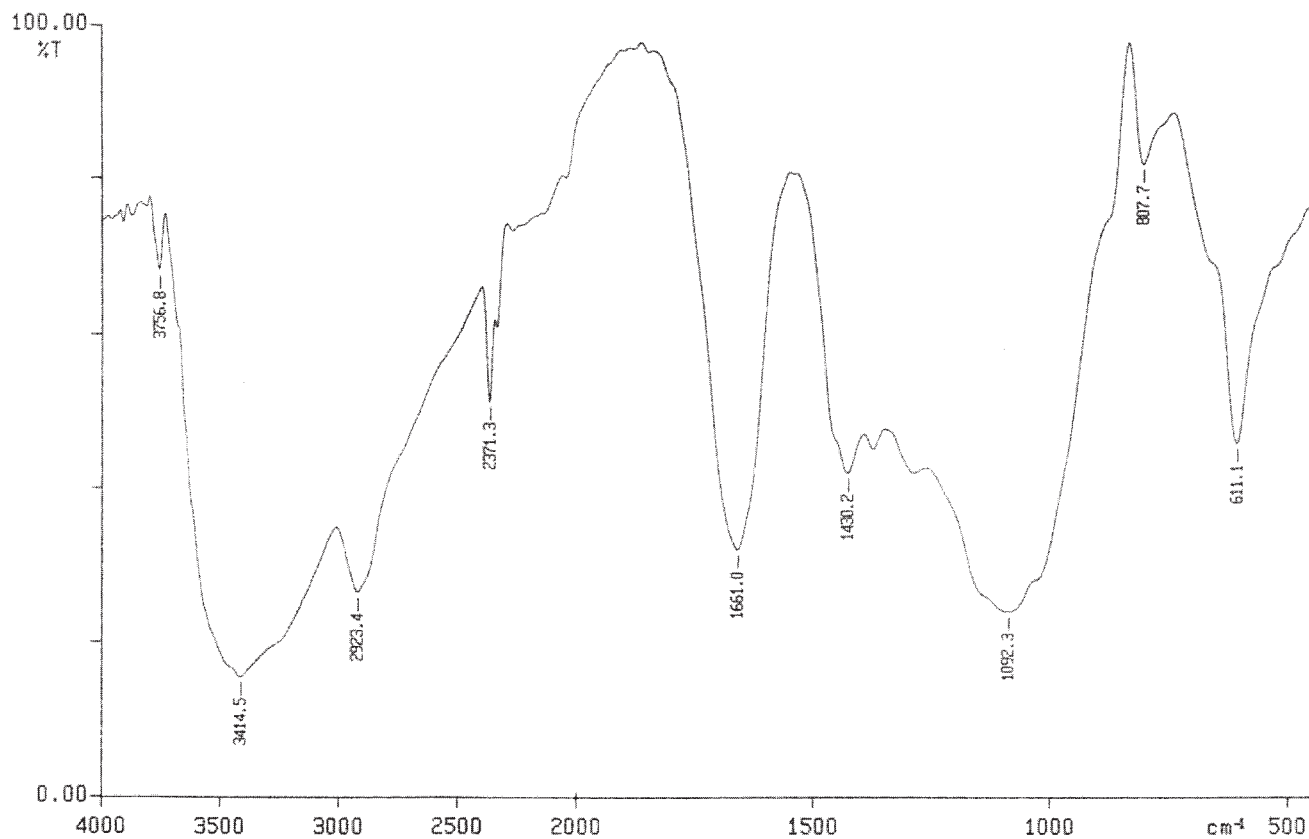**Figure 7** IR spectra of guar gum.

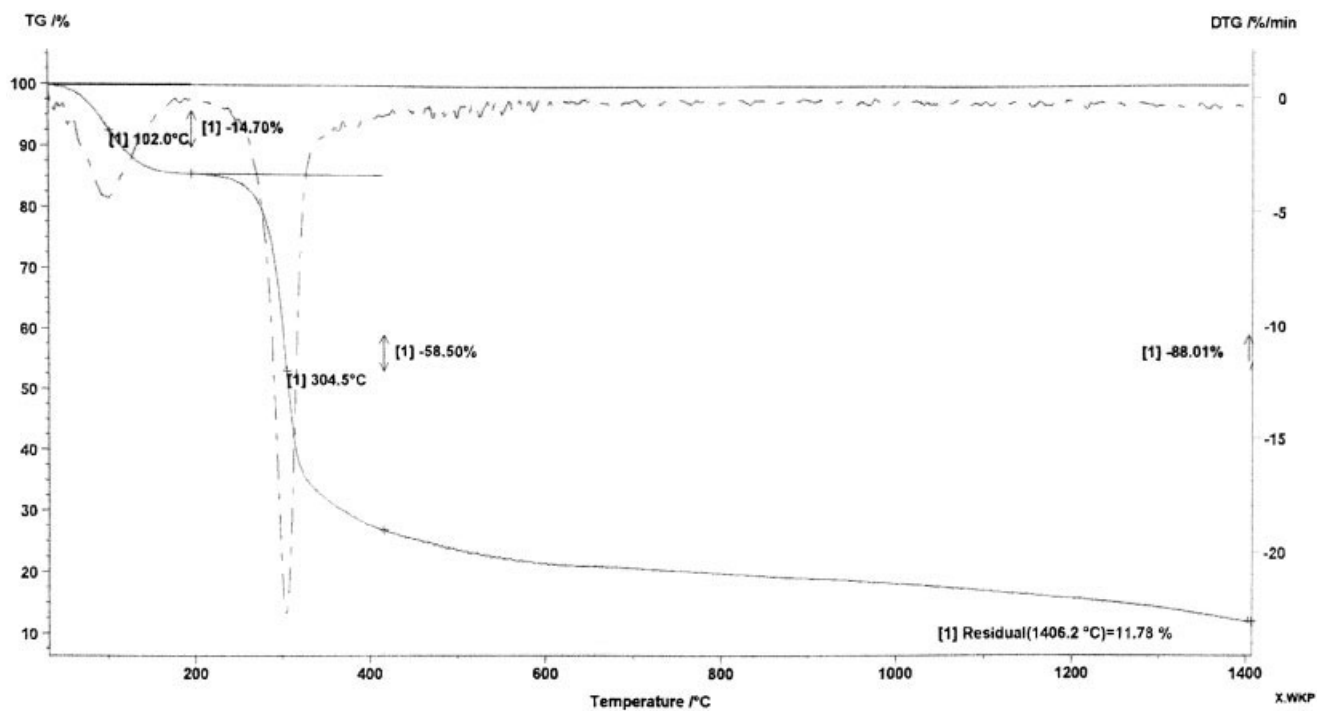**Figure 8** IR spectra of guar gum–*g*–*N*-vinyl–2–pyrrolidone.

Figure 9 Thermogravimetric curve of guar gum.

TABLE V
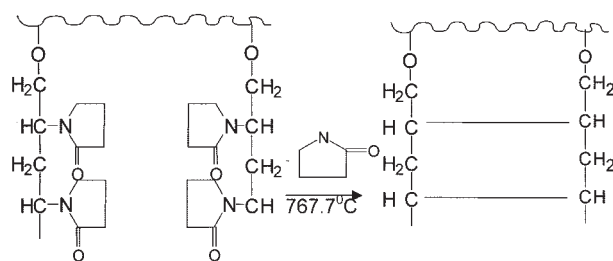**Thermogravimetric Analyses of Guar Gum and Guar Gum–g– (N-vinyl-2-pyrrolidone)**

Sample Code	PDT (°C)	IPDT (°C)	FDT (°C)	T_{max} (°C)	DTA peaks	
					Exopeaks (°C)	Endopeaks (°C)
G	287.50	266.65	380.25	304.5	—	313.0
						824.0
G_P	206.25	345.42	800.00	244.6	—	786.1
				767.6		903.0

decomposition temperature (FDT) was low and was found to be 380.2°C. The integral procedural decomposition temperature (IPDT) and char yield of 11.78% were 266.6°C and 1406.2°C, respectively (Table V). There was a linear relationship between $\Delta\log dw/dt$ and $\Delta\log w$, where dw/dt is the rate of weight loss and w is the residual weight, which could not be obtained.

Guar gum-g-N-vinyl-2-pyrrolidone

The graft copolymer began to degrade at 200°C. A weight loss of 2.22% at 100°C is the result of desorption of water. Thermal degradation of graft copolymer was completed in two steps, from 180°C to 614.0°C and from 767.6°C to 956.0°C (Fig. 10). Therefore, there were two T_{max} values, one at 244.6°C and a second at 767.7°C. A weight loss of about 17.5% occurred in the second step of the degradation process, which might have been the result of the elimination of the pyrrolidone ring from the

pendant chain of poly(N-vinyl-2-pyrrolidone) on guar gum. This was also confirmed by the differential thermal analysis (DTA) curve, which showed a broad endothermic peak at 786.1°C. The PDT, IPDT, FDT, and 27.02% char yield temperature were 206.25°C, 345.42°C, 800°C, and 1406.7°C, respectively (Table V). A representation of the thermal degradation of guar gum-g-N-vinyl-2-pyrrolidone follows.
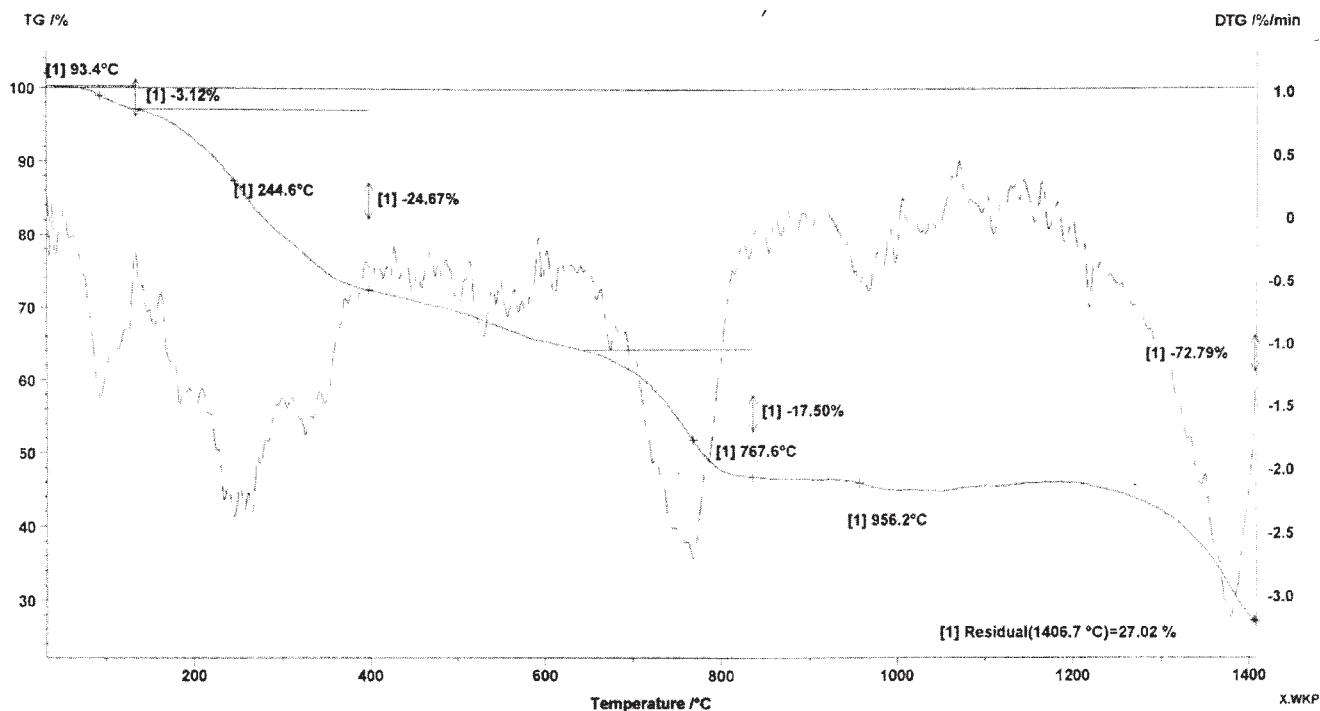

Scheme1

Figure 10 Thermogravimetric curve of guar gum–g–N–vinyl–2–pyrrolidone.

With the help of thermogravimetric analysis curves, the kinetics of degradation were evaluated by Broido's method.[17] According to this method, the weight of a material, W, at any time, t, that is, W_t, is related to the proportion of initial molecules not yet decomposed by eq. (1)

$$Y = \frac{W_t - W_0}{W_0 - W_\infty} \qquad (1)$$

where W_0 is the initial weight of the material and W_∞ is the weight of the residue at the end of degradation.

$$\ln \ln 1/Y = -(E_a/R)(1/T) + \text{constant} \qquad (2)$$

where E_a is the energy of activation, R is the gas constant, and T is the temperature (K). Eq. (2) was used to estimate E_a. The energy of activation was evaluated from eq. (2) by plotting $\ln \ln 1/Y$ versus $1/T$, the slope of straight line of which gave the energy of activation. For guar gum and guar gum–g–N-vinyl-2-pyrrolidone, the E_a was 9.8 and 15.0 kcal/mol, respectively.

Thus, the thermal analysis data showed that the graft copolymer was thermally more stable than the backbone when both decomposition temperatures (IPDT, FDT) and the energy of activation were considered. A high char yield also supports the enhanced thermal stability of the graft copolymer.

Sorption studies

To study the swelling behavior of the graft copolymer, 0.05 g of a sample was placed in 20 mL of triple-distilled water and kept undisturbed for 24 h. The water on the surface of the swollen graft copolymer (guar gum–g–N-vinyl-2-pyrrolidone) was removed by gently pressing between the folds of filter paper, and the increase in weight was recorded. Percent swelling (Ps) and swelling ratio (Sr) were calculated with the following expressions[18]:

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

$$Sr = \frac{\text{Wt. of swollen polymer} - \text{Wt. of dry polymer}}{\text{Weight of dry polymer}}$$

The results (Table VI) showed that the percent swelling and swelling ratio of graft copolymer increased with an increasing percentage of the grafting ratio. This was because N-vinyl-2-pyrrolidone is a hydrophilic monomer. Thus, with an increased grafting ratio, the proportion of the graft copolymer that was

TABLE VI
Swelling Behavior of Guar Gum–g–N-vinyl-2-pyrrolidone

Sample No.	Polymer	$[NVP] \times 10^2$ mol dm^{-3}	%G	P_S	S_R
1	G_{P_1}	4.0	142.0	155.0	1.55
2	G_{P_2}	8.0	170.0	170.0	1.70
3	G_{P_3}	12.0	194.0	230.0	2.30
4	G_{P_4}	16.0	166.0	125.0	1.25
5	G_{P_5}	20.0	90.0	100.0	1.00

$[GOH] = 1.0 \text{ g/dm}^3$; $[GA] = 4.0 \times 10^{-3} \text{ mol/dm}^3$; $[H^+] = 6.0 \times 10^{-3} \text{ mol/dm}^3$; $[PMS] = 5.0 \times 10^{-3} \text{ mol/dm}^3$; time = 120 min; temperature = 40°C.

hydrophilic increased because the number of chains of pendant poly(N-VP) on guar gum increased, thereby increasing the swelling of the graft copolymer.

Metal ion sorption studies

Metal ion sorption was studied in graft copolymers of different concentrations of N-vinyl-2-pyrrolidone ranging from 4.0×10^{-2} to 20×10^{-2} mol/dm^3. To synthesize these graft copolymers, 0.020 g of graft copolymer was placed in 10 mL of a metal ion solution of known concentration and kept for 24 h. The strength of unabsorbed metal ions was determined by standard methods. The sorption of five metals—Cu, Ni, Zn, Pb, and Hg—was analyzed. The sorption behavior of the polymeric backbone and the graft copolymer for these five metal ions was investigated using the following parameters[19]:

Percent uptake (Pu)

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

Partition coefficient (Kd)

$$= \frac{\text{Amount of metal ion in polymer}}{\text{Amount of metal ion left in solution}}$$

$$\times \frac{\text{Vol. of solution (ml)}}{\text{Wt. of dry polymer (gm)}}$$

Retention Capacity (Qr)

$$= \frac{\text{Amount of metal ion in polymer } (mEq)}{\text{Wt. of dry polymer } (gm)}$$

The sorption behavior results, determined as percentage of ion uptake (P_u), partition coefficient (K_d), and retention capacity (Q_r), are given in Table VII. It was observed that the P_u, K_d, and Q_r increased directly as the percentage of the grafting ratio increased, which may have been a result of the increased number of

TABLE VII
Sorption of Metal Ions in Guar Gum and Guar Gum–*g*–*N*-vinyl-2-pyrrolidone

Sample code	$[NVP] \times 10^2$ mol dm^{-3}	% G	Percent uptake (Pu)					Partition coefficient (Kd)					Retention Capacity (Qr)				
			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+}
G	—	—	3.4	1.72	1.27	0.64	0.24	17.68	8.75	6.44	3.24	1.24	0.36	0.03	0.16	0.37	0.15
GP$_1$	4.0	142	6.47	3.98	2.25	1.72	0.54	34.60	20.72	11.36	8.79	2.76	0.68	0.76	0.29	1.01	0.35
GP$_2$	8.0	170	10.63	4.78	2.42	2.77	0.73	59.47	25.14	12.26	14.21	3.60	1.12	0.99	0.31	1.62	0.46
GP$_3$	12.0	194	12.90	5.86	3.90	2.99	1.28	74.10	31.14	20.34	15.42	6.49	1.36	1.12	0.57	1.75	0.83
GP$_4$	16.0	166	10.25	5.21	2.94	1.17	1.28	57.10	27.52	15.13	5.95	6.49	1.08	1.0	0.38	0.68	0.83
GP$_5$	20.0	90	6.22	4.17	2.06	0.96	0.91	33.19	21.80	10.41	4.84	4.62	0.65	0.80	0.27	0.50	0.15

$[GOH] = 1.0$ g/dm^3; $[PMS] = 5.0 \times 10^{-3}$ mol/dm^3; $[GA] = 4.0 \times 10^{-3}$ mol/dm^3; $[H^+] = 6.0 \times 10^{-3}$ mol/dm^3; time = 120 min; temperature = 40°C.

G, guar gum; G$_P$, guar gum–*g*–*N*-vinyl-2-pyrrolidone.

pendant chains of poly(*N*-vinyl-2-pyrrolidone) on guar gum. The results also showed that of the five metal ions, the graft copolymer took up the least Hg^{++}.

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