Synthesis and Characterization of Xanthan Gum-*g*-*N*-Vinyl Formamide with a Potassium Monopersulfate/Ag(I) System

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ABSTRACT: A xanthan gum-*g*-*N*-vinyl formamide graft copolymer was synthesized through the graft copolymerization of *N*-vinyl formamide (NVF) onto xanthan gum with an efficient system, that is, potassium monopersulfate (PMS)/Ag(I) in an aqueous medium. The effects of the concentrations of Ag(I), PMS ($KHSO_5$), hydrogen ion, xanthan gum, and NVF along with the time and temperature on the graft copolymerization were studied by the determination of the grafting parameters (grafting ratio, add-on, conversion, grafting efficiency, and homopolymer) and the rate of grafting. The maximum grafting ratio was obtained at a 0.6 g/dm^3 concentration of xanthan gum. All the parameters showed an increasing trend with an increasing concentration of peroxymonosulfate, except the homopolymer percentage, which showed a decreasing trend. The grafting ratio, add-on conversion, grafting efficiency, and rate of grafting increased with the concentration of Ag(I) increasing from 0.8×10^{-2} to $1.2 \times 10^{-2} \text{ mol/dm}^3$. The optimum time and temperature for the maximum degree of grafting were 90 min and 35°C, respectively. The graft copolymer was characterized with IR spectral analysis, thermogravimetric analysis, and differential calorimetry analysis. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1637–1645, 2006

Key words: polysaccharide; synthesis; FTIR; thermal properties; graft copolymers

INTRODUCTION

Xanthan gum is an extracellular heteropolysaccharide of *Xanthomonas compestris*; it was the first biopolymer product of a fermentative based on corn sugar and has attained commercial status.[1,2] The molecule of xanthan gum is a rodlike, ordered secondary structure and is an anionic polyelectrolyte by virtue of the ionizable carboxyl group belonging to D-glucuronic acid residues and pyruvate acetal. It has been estimated that over half of microbial polysaccharide sales are used in the food industry,[3,4] and it also has wide industrial applications[5,6] because of its high thickening efficiency,[7] hydrogen-bonding properties,[8] good electrolytic compatibility, and low cost. Although it is used in various industrial applications, it suffers from drawbacks such as susceptibility to microbial attack, which limits its applications. This drawback can be improved through the graft copolymerization of vinyl monomers. Therefore, we have chosen a vinyl monomer, *N*-vinyl formamide (NVF), on the basis of increased applications in areas such as wastewater treatment,[9] sludge dewatering, and paper making.[10]

NVF is an isomer of acrylamide and is hydrophilic in nature, having low toxicity and high reactivity for polymerization. Furthermore, poly(*N*-vinyl formamide) and its derivatives comprise a novel class of water-soluble polymers.[11] The copolymer of NVF with poly(dimethylamino methyl methacrylate) show a good flocculation rate, final turbidity level, and floc strength.[12] NVF, once sufficiently purified, can be readily polymerized and subsequently hydrolyzed to give a high-molecular-weight polymer [poly(vinyl amine)] that cannot be prepared directly. Therefore, an attempt was made to graft NVF onto xanthan gum with potassium monopersulfate (PMS)/Ag$^+$ as a redox initiator, which would be more environmentally friendly and cost-effective than a pure one.

EXPERIMENTAL

Materials

Freshly distilled NVF (Aldrich, Milwaukee, WI) was used for grafting. Potassium monopersulfate was received as a gift sample from DuPont (Newton, CT), and xanthan gum was purchased from Sigma (St. Louis, MO) and used as received. Silver nitrate (Merck, Whitehouse Station, NJ) was used as received. For maintaining the hydrogen-ion concentration, sulfuric acid (E. Merck) was used.

Procedure for grafting

For each experiment, a xanthan gum solution was prepared by the slow addition of a calculated amount

[PMS] × 10² (mol/dm³)	G (%)	A (%)	C (%)	E (%)	H (%)	$R_g \times 10^6$ (mol L⁻¹ s⁻¹)
0.4	120	54.50	17.00	74.07	25.93	2.34
0.6	128	55.14	18.22	79.01	20.99	2.50
0.8	235	70.23	36.23	92.91	7.09	4.61
1.0	238	70.42	33.55	94.44	5.56	4.65
1.2	324	76.42	45.62	97.59	2.41	6.33

[a] $[AgNO_3] = 1.2 \times 10^{-3}$ mol/dm³; [NVF] = 10×10^{-2} mol/dm³; [H⁺] = 1.0×10^{-2} mol/dm³; [XOH] = 1.0 g/dm³; time = 120 min; temperature = 35°C; G = grafting ratio; A = add-on concentration; C = conversion; E = grafting efficiency; H = homopolymer concentration; R_g = rate of grafting.

of xanthan gum into a reactor containing triple-distilled water. Calculated amounts of NVF, sulfuric acid, and silver nitrate were added to the reactor, and a slow stream of nitrogen gas was passed for 30 min. A known amount of deoxygenated potassium monopersulfate was added to initiate the reaction. After the desired time, the reaction was stopped by air being allowed into the reactor. The graft copolymer was precipitated by the reaction mixture being poured into a water/methanol mixture. The precipitate was separated, dried, and weighed, whereas poly(N-vinyl formamide) remained in the solution.

Separation of the homopolymer

A pinch of hydroquinone was added to the remaining filtrate, which was concentrated under reduced pressure. The homopolymer content was precipitated by the concentrated filtrate being poured into pure methanol. The homopolymer was separated, dried, and weighed.

RESULTS AND DISCUSSION

The graft copolymer was characterized according to the following parameters:[13–15]

$$\text{Grafting ratio (\%)} = \frac{\text{Weight of grafted polymer}}{\text{Weight of substrate}} \times 100 \quad (1)$$

Add-on (%)

$$= \frac{\text{Weight of synthetic polymer}}{\text{Weight of graft copolymer}} \times 100 \quad (2)$$

Conversion (%)

$$= \frac{\text{Weight of polymer formed}}{\text{Weight of monomer charged}} \times 100 \quad (3)$$

Efficiency (%)

$$= \frac{\text{Weight of polymer in graft}}{\text{Weight of polymer formed}} \times 100 \quad (4)$$
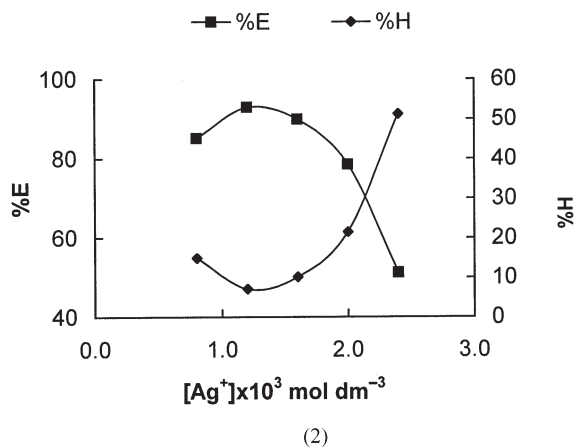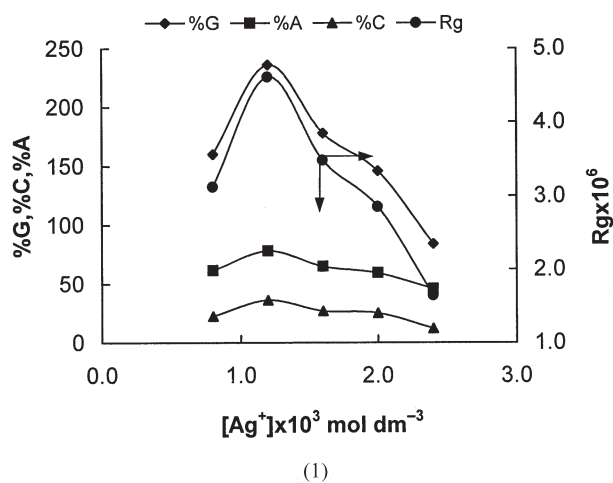

(1)

(2)

Figure 1 Effect of the silver-ion concentration ([PMS] = 0.8 × 10⁻² mol/dm³; [NVF] = 10.0 × 10⁻² mol/dm³; [H⁺] = 1.0 × 10⁻² mol/dm³; [XOH] = 1.0 g/dm³; time = 120 min; temperature = 35°C; G = grafting ratio; A = add-on concentration; C = conversion; R_g = rate of grafting; E = grafting efficiency; H = homopolymer concentration).

TABLE II
Effect of the Hydrogen-Ion Concentration[a]

$[H^+] \times 10^2$ (mol/dm^3)	G (%)	A (%)	C (%)	E (%)	H (%)	$R_g \times 10^6$ (mol L^{-1} s^{-1})
0.2	292.0	74.48	41.68	96.05	3.95	5.71
0.6	254.0	71.75	36.23	93.38	6.62	4.96
1.0	236.0	70.23	34.10	92.91	7.09	4.61
1.4	108.0	51.90	16.89	76.05	23.95	2.11
1.8	94.0	48.45	13.74	47.47	52.53	1.83

[a] $[AgNO_3] = 1.2 \times 10^{-3}$ mol/dm^3; [NVF] = 10×10^{-2} mol/dm^3; [PMS] = 0.8×10^{-2} mol/dm^3; [XOH] = 1.0 g/dm^3; time = 120 min; temperature = 35°C; G = grafting ratio; A = add-on concentration; C = conversion; E = grafting efficiency; H = homopolymer concentration; R_g = rate of grafting.

Homopolymer concentration (%)

$$= 100 - \text{Efficiency (\%)} \quad (5)$$

Rate of grafting

$$= \frac{\text{Weight of grafted polymer}}{\text{Volume} \times \text{Time} \times \text{Molecular weight of NVF}}$$
$$\times 1000 (\text{molL}^{-1} \text{s}^{-1}) \quad (6)$$

The effects of the concentrations of potassium monopersulfate, silver ion, sulfuric acid, NVF, and xanthan gum along with effects of time and temperature on the grafting parameters were studied in terms of the grafting ratio, add-on concentration, conversion, efficiency, homopolymer concentration, and rate of grafting.

Effect of the potassium monopersulfate concentration

The effect of the concentration of potassium monopersulfate on the grafting parameters was studied by the variation of the concentration of potassium monopersulfate (0.4×10^{-2} to 1.2×10^{-2} mol/dm^3), and the results are summarized in Table I. The grafting ratio, add-on concentration, efficiency, and rate of grafting increased with the concentration of potassium peroxymonosulfate increasing from 0.4×10^{-2} to 1.2×10^{-2} mol/dm^3, whereas the homopolymer percentage decreased. The enhancement of the grafting parameters might have been due to the progressive reduction of peroxymonosulfate by silver-ion, producing primary free radicals (SO_4^- and $\dot{O}H$), which attacked the xanthan gum molecules, creating free-radical sites, on which the addition of NVF molecules took place.

Effect of the silver-ion concentration

To study the effect of the silver-ion concentration on the grafting parameters, the silver-ion concentration was varied from 0.8×10^{-3} to 2.4×10^{-3} mol/dm^3, and the results are shown in Figure 1(1,2). With an increase in the silver-ion concentration up to 1.2×10^{-3} mol/dm^3, the values of the grafting ratio, add-on concentration, conversion, efficiency, and rate of grafting increased, but beyond this concentration, the values of the grafting parameters decreased, except for the percentage of the homopolymer, which increased. The increase in the values of the grafting parameters up to the cited concentration might have been due to the production of more primary free radicals resulting in the production of xanthan gum macroradicals at a faster rate. The decrease in the grafting parameters beyond 1.2×10^{-3} mol/dm^3 might have been due to the premature termination of growing grafted chains.

TABLE III
Effect of the NVF Concentration[a]

$[NVF] \times 10^2$ (mol/dm^3)	G (%)	A (%)	C (%)	E (%)	H (%)	$R_g \times 10^6$ (mol L^{-1} s^{-1})
5.0	190	65.51	55.46	82.60	17.40	3.71
10.0	236	70.23	36.23	92.61	7.09	4.61
15.0	258	72.06	24.65	94.85	5.15	5.04
20.0	170	62.96	15.25	72.03	27.97	3.32
25.0	164	62.12	12.82	69.49	30.51	3.20

[a] $[AgNO_3] = 1.2 \times 10^{-3}$ mol/dm^3; [PMS] = 0.8×10^{-2} mol/dm^3; $[H^+] = 1.0 \times 10^{-2}$ mol/dm^3; [XOH] = 1.0 g/dm^3; time = 120 min; temperature = 35°C; G = grafting ratio; A = add-on concentration; C = conversion; E = grafting efficiency; H = homopolymer concentration; R_g = rate of grafting.
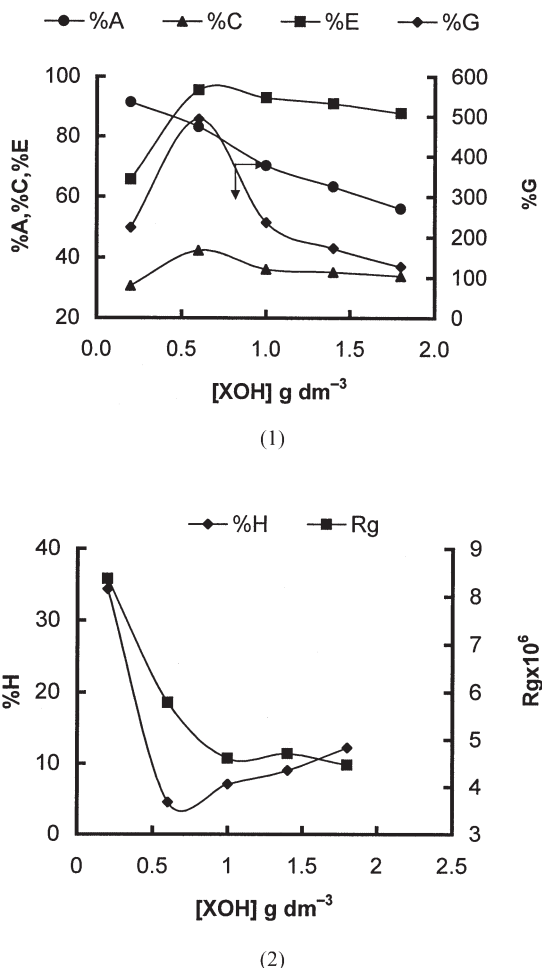
(1)

(2)

Figure 2 Effect of the xanthan gum concentration ([PMS] = 0.8×10^{-2} mol/dm³; [AgNO₃] = 1.2×10^{-3} mol/dm³; [NVF] = 10.0×10^{-2} mol/dm³; [H⁺] = 1.0×10^{-2} mol/dm³; time = 120 min; temperature = 35°C; E = grafting efficiency; A = add-on concentration; C = conversion; G = grafting ratio; H = homopolymer concentration; R_g = rate of grafting).

Effect of the hydrogen-ion concentration

The concentration of hydrogen ions played an important role during the reaction. The grafting ratio, add-on concentration, conversion, efficiency, and rate of grafting decreased with increasing hydrogen-ion concentration (Table II). With an increase in the hydrogen-ion concentration, the concentration of the H₂SO₅ species increased, and this resulted in a decrease in the concentration of HSO_5^-, thereby reducing the grafting parameters. This was also observed by other workers in our laboratory:[16]

$$HSO_5^- + H^+ \rightarrow H_2SO_5 \qquad (7)$$

Effect of NVF

The effect of the concentration of NVF on the grafting parameters was studied by the variation of the con-

(1)

(2)

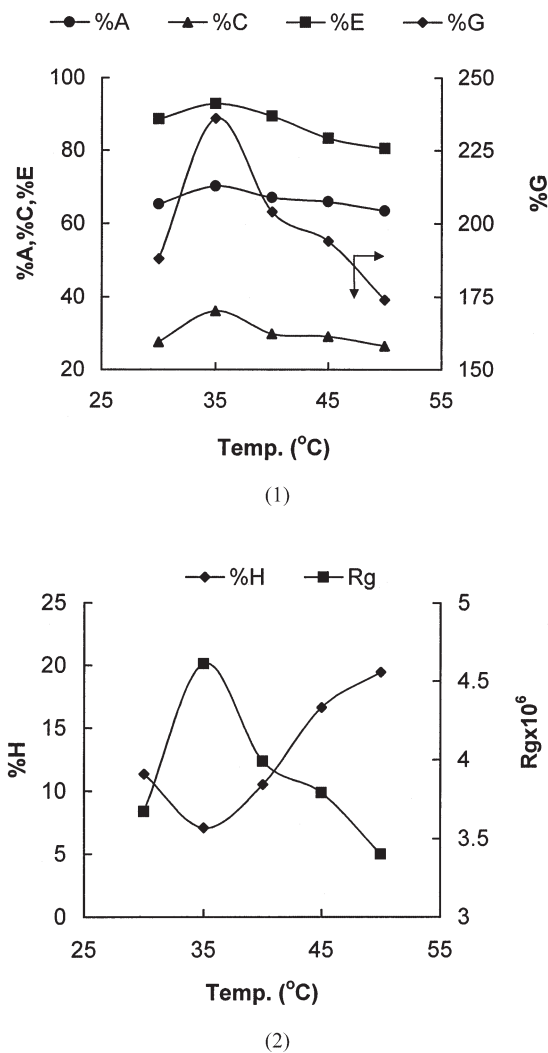**Figure 3** Effect of temperature ([PMS] = 0.8×10^{-2} mol/dm³; [AgNO₃] = 1.2×10^{-3} mol/dm³; [NVF] = 10.0×10^{-2} mol/dm³; [H⁺] = 1.0×10^{-2} mol/dm³; [XOH] = 1.0 g/dm³; time = 120 min; E = grafting efficiency; A = add-on concentration; C = conversion; G = grafting ratio; H = homopolymer concentration; R_g = rate of grafting).
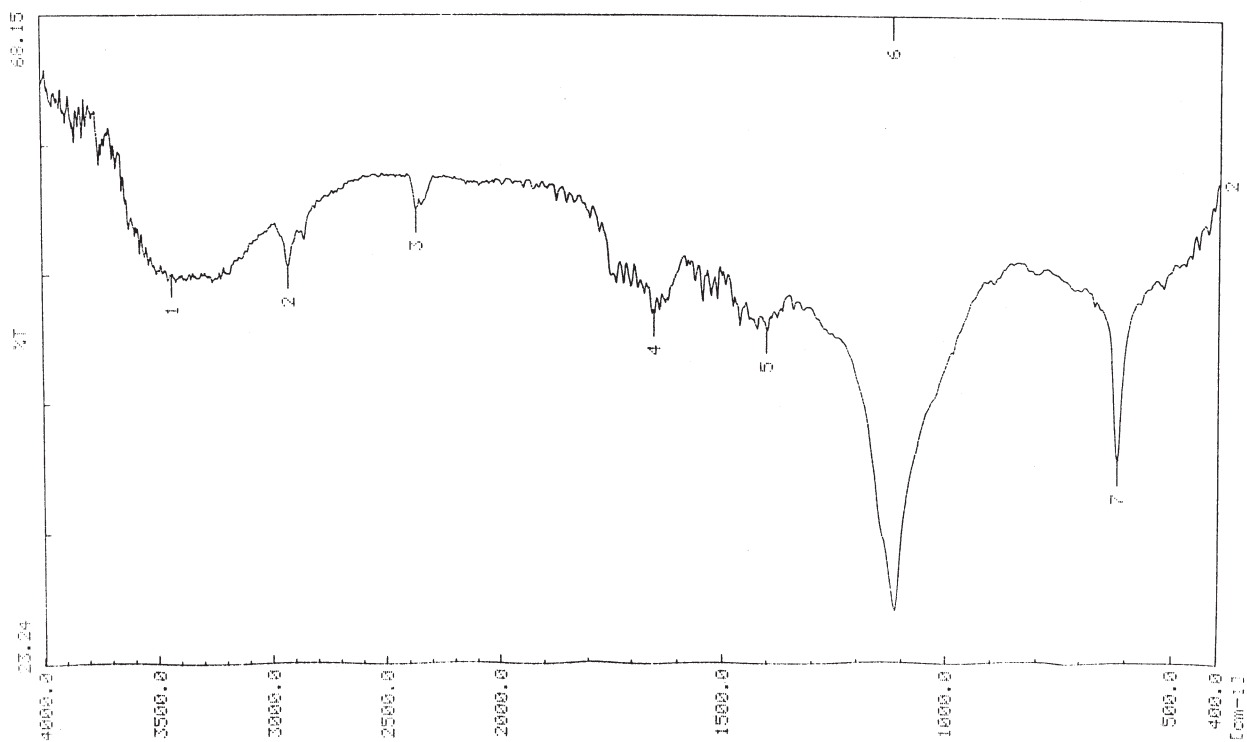
TABLE IV
Effect of the Time Period[a]

Time (min)	G (%)	A (%)	C (%)	E (%)	H (%)	$R_g \times 10^6$ (mol L⁻¹ s⁻¹)
60	158	61.83	25.29	76.41	23.59	6.18
90	264	70.93	37.54	97.05	2.96	6.88
120	236	70.23	36.23	92.91	7.09	4.61
150	176	63.76	27.16	78.57	21.43	2.75
180	160	62.68	26.63	73.68	26.32	2.08

[a] [AgNO₃] = 1.2×10^{-3} mol/dm³; [NVF] = 10×10^{-2} mol/dm³; [H⁺] = 1.0×10^{-2} mol/dm³; [XOH] = 1.0 g/dm³; [PMS] = 0.8×10^{-2} mol/dm³; temperature = 35°C; G = grafting ratio; A = add-on concentration; C = conversion; E = grafting efficiency; H = homopolymer concentration; R_g = rate of grafting.
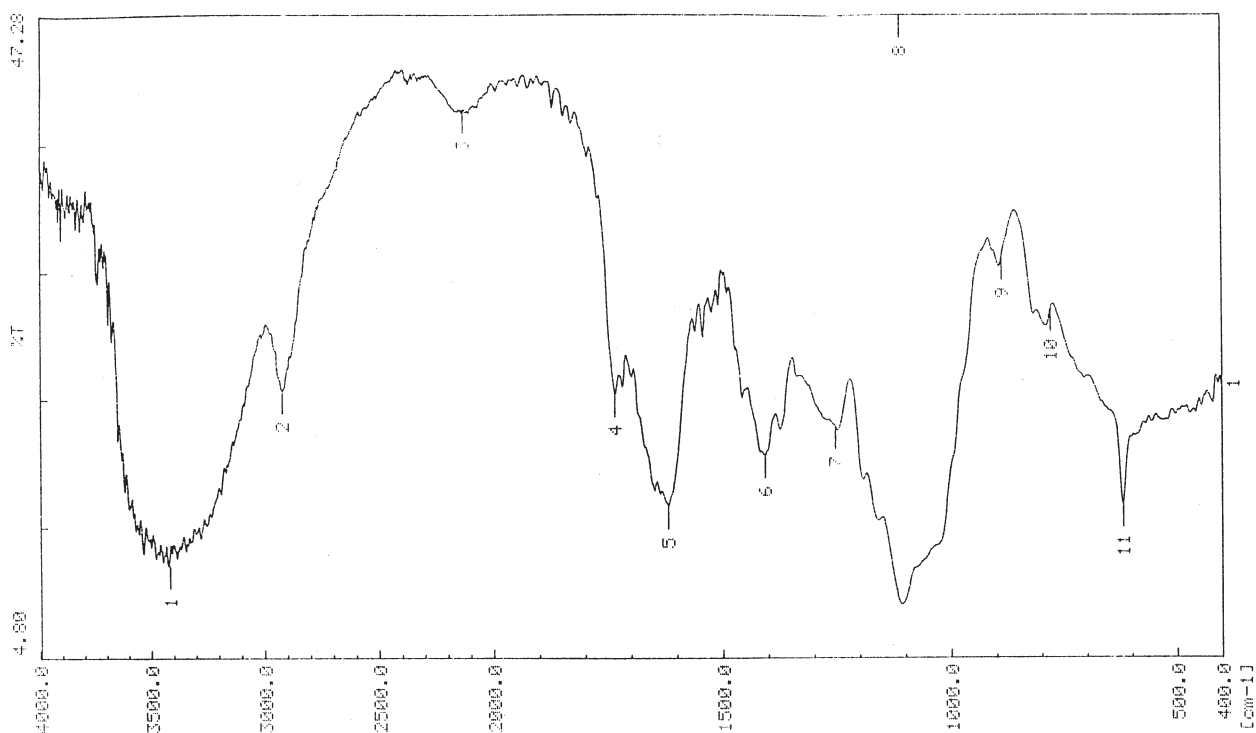
Figure 4 IR spectra of (1) xanthan gum and (2) xanthan gum-*g*-*N*-vinyl formamide.

centration of NVF from 5.0×10^{-2} to 25.0×10^{-2} mol/dm^3, and the results are summarized in Table III. When the concentration of NVF was increased up to 15.0×10^{-2} mol/dm^3, the grafting ratio, add-on concentration, efficiency, and rate of grafting increased, whereas the conversion decreased. An increase in the
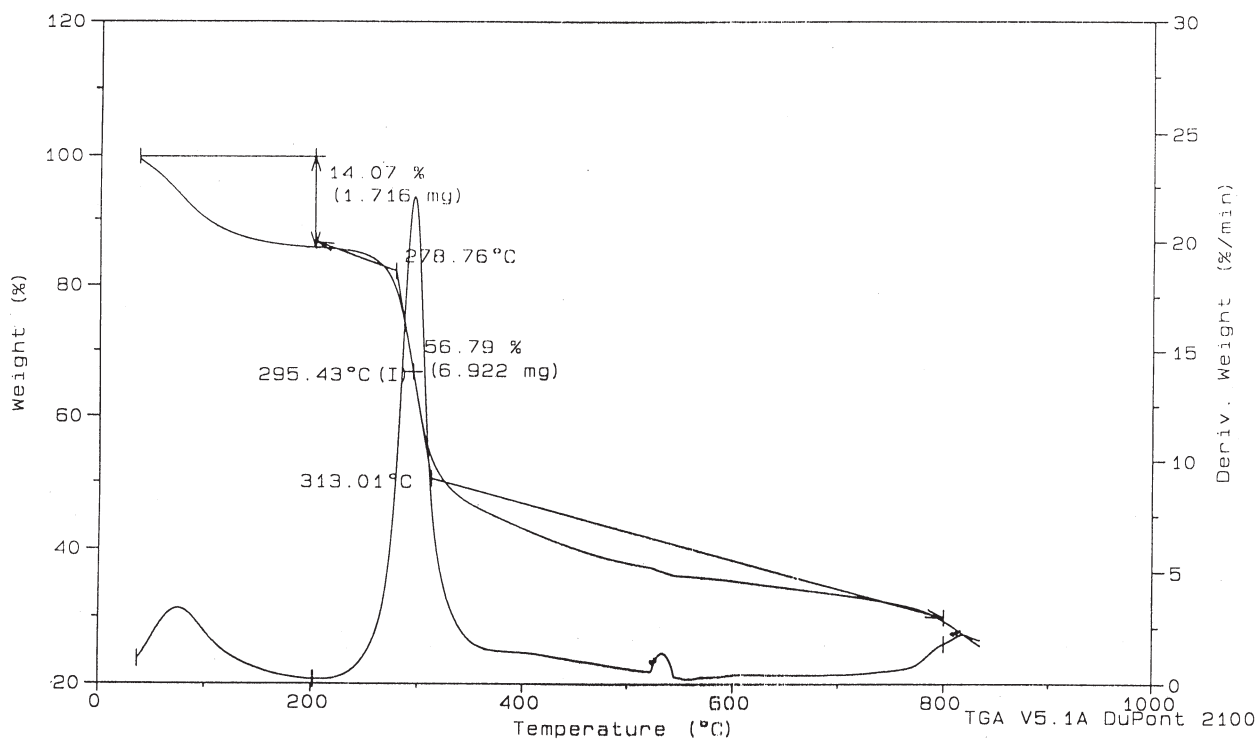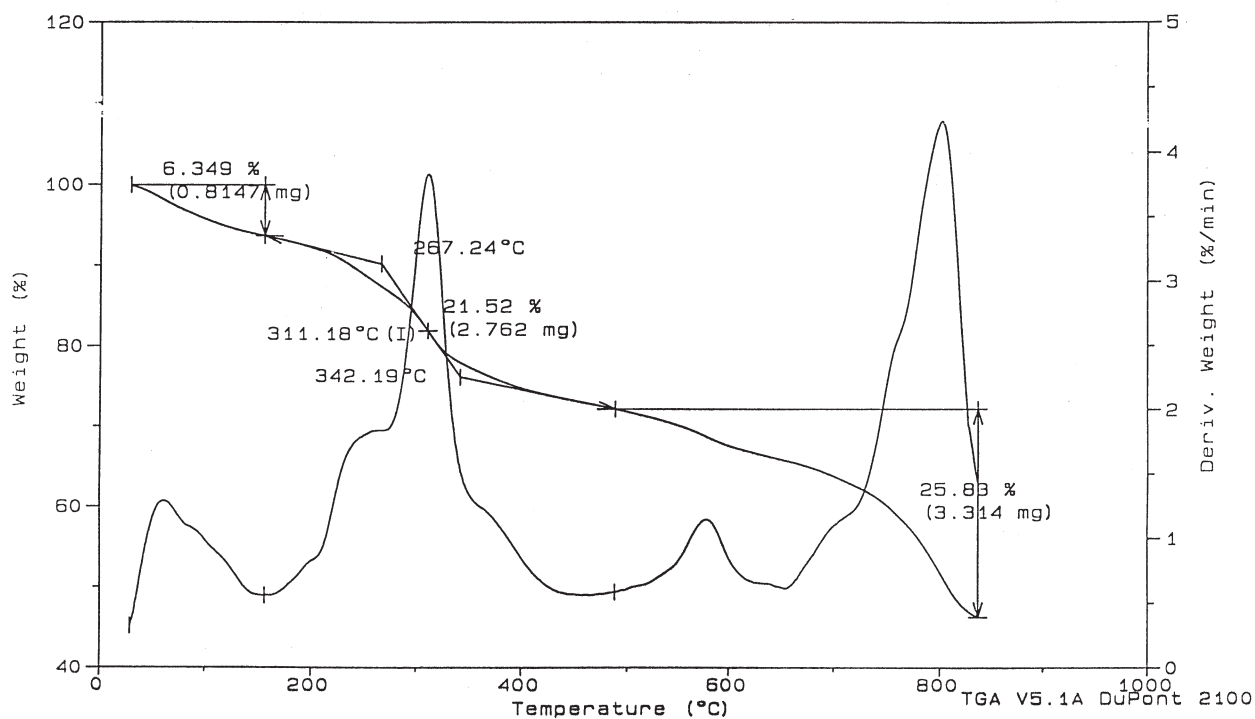
Figure 5 Thermogravimetric traces of (1) xanthan gum and (2) xanthan gum-*g-N*-vinyl formamide.

monomer concentration led to its accumulation at a close proximity to xanthan gum. The monomer molecules that were in the immediate vicinity of the reac-

tion sites became acceptors of xanthan gum macroradicals, and this resulted in chain initiation; thereafter, they themselves became free-radical donors to the

TABLE V
TGA

Sample[a]	PDT (°C)	FDT (°C)	T_{max} (°C)	IPDT (°C)	DSC Data			
					Exopeaks (°C)	Enthalpy (J/g)	Endopeaks (°C)	Enthalpy (J/g)
X_0	278.00	313.01	295.43	290.37	281.44	151.80	—	—
X_1	267.24	836.32	311.18	392.52	134.79	11.64	89.75	1.870
			800.00		294.11			

[a] X_0 = xanthan gum; X_1 = xanthan gum-*g*-*N*-vinyl formamide.

neighboring molecule, lowering the termination. When the concentration of NVF was increased beyond 15.0×10^{-2}, the grafting parameters decreased; this might be attributed to the increase in the viscosity of the reaction medium due to the preferential formation of the homopolymer at a higher concentration of the monomer.

Effect of the xanthan gum concentration

The effect of the concentration of xanthan gum was studied by the variation of the concentration of xanthan gum from 0.2 to 1.8 g/dm³ [Fig. 2(1,2)]. When the gum concentration was increased up to 0.6 g/dm³, the grafting parameters (grafting ratio, grafting efficiency, and conversion) increased, whereas beyond that, the grafting parameters decreased. The increment in the grafting parameters might be attributed to the greater availability of reaction sites, but with a further increase in the xanthan gum concentration, the viscosity of the reaction medium also increased, and this hindered the movement of free radicals; therefore, the grafting parameters decreased.

Effect of temperature

The effect of temperature on the grafting parameters was studied through changes in the temperature, and the results are shown in Figure 3(1,2). When the temperature was changed from 30 to 50°C, the grafting parameters increased up to 35°C and thereafter decreased. This could be explained as follows: with an

increase in temperature, the rate of production of primary free radicals increased, and because of this, more active sites were generated, and so an increase in the grafting parameters was observed. However, with a further increase in the temperature, the mobility of the macroradicals increased, and this led to termination, thereby reducing the grafting parameters.

Effect of time

To study the effect of time on the graft copolymerization, the reaction was carried out at different times, that is, from 60 to 180 min, and the results are summarized in Table IV. The grafting ratio, add-on concentration, conversion, efficiency, and rate of grafting increased from 60 to 90 min; beyond this, these parameters decreased, but the amount of the homopolymer increased. The increase in the grafting parameters might be attributed to the addition of more and more monomer molecules to the growing grafted chains, but with a further increase in the time interval, the mutual annihilation of growing grafted chains occurred, so the grafting ratio, add-on concentration, conversion, efficiency, and rate of grafting decreased.

Characterization

IR spectral analysis

The Fourier transform infrared spectra of the samples in KBr pellets were recorded with a Jasco FT/IR-5300. The IR spectra of xanthan gum and xanthan gum
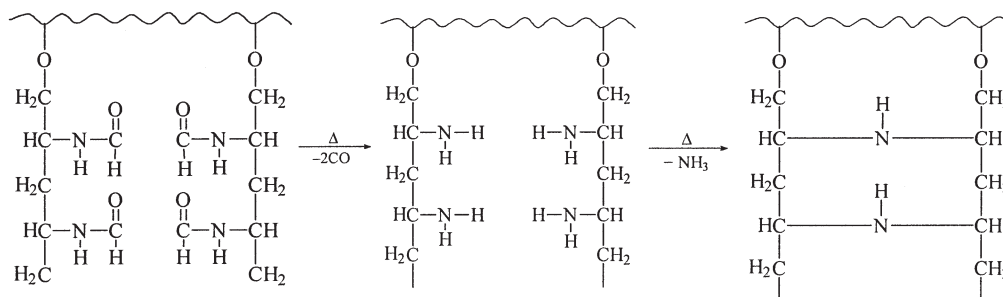
Scheme 1 Degradation of xanthan gum-*g*-*N*-vinyl formamide.

grafted NVF were taken in the range of 400–4000 cm^{-1}. The graft copolymer showed absorption bands of xanthan and also additional bands at 1649.2 and 1398.2 cm^{-1}, which were attributed to an amide I band due to C=O and C—N stretching vibrations, respectively, which are characteristic of poly(N-vinyl formamide). Thus, the presence of these additional bands indicated that grafting took place. The disappearance of O—H bending vibrations from the spectra of xanthan gum-g-N-vinyl formamide showed that the grafting might have taken place on the O—H site of the xanthan gum [Fig. 4(1,2)].
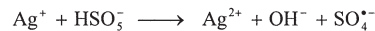
Thermogravimetric analysis (TGA)

The thermal behavior of xanthan gum and xanthan gum-g-N-vinyl formamide was examined with TGA and differential calorimetry (DSC) data, which were recorded on a General DuPont 2100 thermal analyzer (Delhi, India) within a temperature range of 0–1000°C at a heating rate of 10°C/min in an atmosphere of nitrogen [Fig. 5(1,2)].
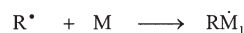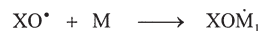
Xanthan gum

TGA of xanthan gum showed that the degradation of xanthan gum started at about 200°C. The rate of weight loss increased with an increase in the temperature. About 5–8% weight loss occurred below 100°C, and this was due to the desorption of water. About 50% weight loss occurred at 327.24°C; after that, the rate of weight loss decreased, and so it exhibited a single-step degradation process. The polymer decomposition temperature (PDT) and the temperature at which maximum degradation occurred (T_{max}) were 278.76 and 295.93°C, respectively (Table V). The DSC curve also supported this fact. A high enthalpy value of 151.8 J/g (Table V) indicated that within this temperature range, the maximum degradation of the polymer took place. About 70% xanthan gum degraded at 800°C. The final decomposition temperature (FDT) and integral procedural decomposition temperature (IPDT) were found at 313.01 and at 290.37°C, respectively. A char yield of 26.08% was obtained at 831.78°C.

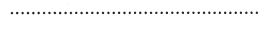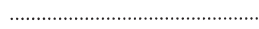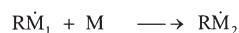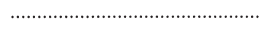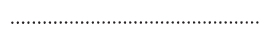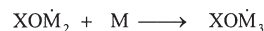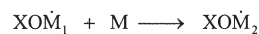### Xanthan gum-g-N-vinyl formamide

The degradation of xanthan gum-g-N-vinyl formamide started at 154.5°C. However, a 3.24% weight loss was observed at 95.9°C, which might have been due to the loss of absorbed water. PDT was 267.24°C. The graft copolymer showed a two-stage degradation process, that is, from 267 to 342.19°C and from 342 to 800°C. Therefore, two T_{max} values were obtained: 311 and 800°C (Table V). These two T_{max} values might have been due to the evolution of CO and NH_3 gases from pendent poly(N-vinyl formamide) chains at the
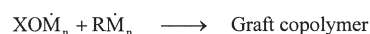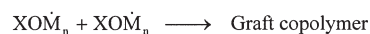
$$Ag^+ + HSO_5^- \longrightarrow Ag^{2+} + OH^- + SO_4^{\bullet-}$$

$$Ag^+ + HSO_5^- \longrightarrow Ag^{2+} + \dot{O}H + SO_4^{2-}$$

$$XOH + R^\bullet \longrightarrow XO^\bullet + RH \quad \left(R^\bullet = \dot{O}H, SO_4^{\bullet-} \right)$$

Initiation

$$XO^\bullet + M \longrightarrow XO\dot{M}_1$$

$$R^\bullet + M \longrightarrow R\dot{M}_1$$

Propagation

$$XO\dot{M}_1 + M \longrightarrow XO\dot{M}_2$$

$$XO\dot{M}_2 + M \longrightarrow XO\dot{M}_3$$

$$\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\cdots\cdots\cdots\cdots\cdots\cdots$$

$$XO\dot{M}_{(n-1)} + M \longrightarrow XO\dot{M}_n$$

$$R\dot{M}_1 + M \longrightarrow R\dot{M}_2$$

$$R\dot{M}_2 + M \longrightarrow R\dot{M}_3$$

$$\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\cdots\cdots\cdots\cdots\cdots\cdots$$

$$R\dot{M}_{n-1} + M \longrightarrow R\dot{M}_n$$

Termination

$$XO\dot{M}_n + XO\dot{M}_n \longrightarrow \text{Graft copolymer}$$

$$XO\dot{M}_n + R\dot{M}_n \longrightarrow \text{Graft copolymer}$$

$$R\dot{M}_n + R\dot{M}_n \longrightarrow \text{Homopolymer}$$
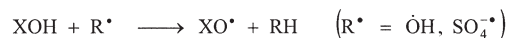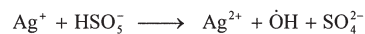
Scheme 2 Reaction mechanism. XOH, XO·, and M are the xanthan gum, xanthan gum macroradical, and monomer molecule, respectively.

respective temperatures. A weight loss of about 60% was observed at 813.63°C. Therefore, FDT was higher (836.32) in comparison with xanthan gum. IPDT of the graft copolymer was 392.52°C. A char yield of 45.58% was obtained at 836.32°C.

Thus, the thermal analysis data showed that the graft copolymer was more thermally stable than the backbone, with both IPDT and FDT considered. The maximum char yield also gave evidence for the enhanced thermal stability of the graft copolymer. Scheme 1 shows the degradation of xanthan gum-g-N-vinyl formamide.

Reaction mechanism

On the basis of experimental results, the reaction mechanism shown in Scheme 2 is suggested for the

graft copolymerization of NVF onto xanthan gum. Initially, the $\dot{O}H$ and SO_4^- radicals are generated by the interaction of Ag^+ and $KHSO_5$. The radicals abstract a hydrogen atom from the xanthan gum molecule, producing xanthan gum macroradicals. The monomer molecules, which are in the close vicinity of the reaction sites, become acceptors of xanthan gum macroradicals, and this results in chain initiation; thereafter, they themselves become free-radical donors to neighboring molecules. In this way, grafted chains grow. These chains are terminated by coupling to give the graft copolymer.

References

1. Rogovin, S. P.; Anderson, R. G.; Cadmus, M. C. J Biochem Microb Technol 1961, 3, 51.
2. Jeanes, A.; Piltsleg, J. E.; Senti, F. R. J Appl Polym Sci 1961, 519.
3. Arozarena, I.; Berthalo, H.; Empis, J.; Bunger, A.; Desonsa, I. Eur Food Res Technol 2001, 213, 312.
4. Uesugi, M.; Shizu, K. Jpn. Kokai Tokkyo Koho JP 144.071 (2003).
5. Stuchell, Y. M. U.S. Pat. Appl. 87,001 (2003).
6. Burdick, C. L.; Podlas, T. J. U.S. Pat. 6,576,048 (2003).
7. Goda, S. Jpn Kokai Tokkyo Koho JP 169.624 (2003).
8. Sakai, T.; Kojima, M.; Uzuhashi, Y. Jpn. Kokai Tokkyo Koho JP 192.703 (2003).
9. Burkert, H.; Brunnmueller, F.; Beyer, K. H.; Kroener, M.; Mueller, H. (to BASF A.G.). U.S. Pat. 4,444,667 (1984).
10. Monech, D.; Hartman, H.; Freudenberg, E.; Stange, A. (to BASF A.G.). U.S. Pat. 5,262,008 (1993).
11. Pinschmidt, R. J.; Renzhi, W.; Carroll, E.; Yacoub, K.; Drescher, J.; Nordquist, A.; Chen, N. J Macromol Sci Chem 1997, 34, 1885.
12. Hrymak, G. Z. N. Colloid Polym Sci 2002, 280, 167.
13. Fanta, G. F. In Block and Graft Copolymerization; Ceresa, R. J., Ed.; Wiley-Interscience: New York, 1973; Vol 1.
14. Nayak, N. C.; Das, H. K.; Singh, B. C. J Appl Polym Sci 1991, 42, 2391.
15. Mohanty, E.; Singh, B. C. J Appl Polym Sci 1998, 69, 2569.
16. Pandey, P. K.; Banerjee, J.; Taunk, K.; Behari, K. J Appl Polym Sci 2003, 89, 1341.