

Synthesis and Characterization of Polysaccharide Based Graft Copolymer by Using Potassium Peroxymonosulphate/Ascorbic Acid as an Efficient Redox Initiator in Inert Atmosphere

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ABSTRACT: Polysaccharide based graft copolymer (xanthan gum-g-4-vinyl pyridine) was synthesized using potassium peroxy monosulphate/ascorbic acid redox initiator in inert atmosphere at 40°C. By studying the effect of the concentration of monomer, peroxy monosulphate (PMS), ascorbic acid (AA), xanthan gum (XOH), hydrogen ion along with effect of time and temperature on grafting characteristics: grafting ratio (%G), add on (%A), conversion (%C), efficiency (%E), homopolymer (%H), and rate of grafting (Rg), the reaction conditions for optimum grafting were determined. The optimum concentration of AA, H⁺ ion, 4-VP for maximum grafting were found to be $10.0 \times 10^{-3} \text{ mol dm}^{-3}$, $2.5 \times 10^{-2} \text{ mol dm}^{-3}$, $10.0 \times 10^{-3} \text{ mol dm}^{-3}$, respectively. Maximum %G was obtained at mini-

mum concentration of xanthan gum i.e., at $40.0 \times 10^{-2} \text{ g dm}^{-3}$ and at maximum concentration of PMS i.e., at $10.0 \times 10^{-3} \text{ mol dm}^{-3}$. The optimum temperature and time duration of reaction for maximum % of grafting were found to be 45°C and 120 min respectively. The synthesized graft copolymer was characterized by FTIR analysis. Thermogravimetric analysis showed that the xanthan gum-g-4-vinyl pyridine is thermally more stable than pure gum. A probable mechanism was suggested for the graft copolymerization. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1407–1415, 2009

Key words: polysaccharide; synthesis; graft copolymer; thermal analysis; 4-vinyl pyridine

INTRODUCTION

Now-a-days more emphasis is given to biodegradable and natural polymers such as polysaccharides and proteins, which have been extensively used and investigated for industrial applications. One of them is xanthan gum, which is an extracellular heteropolysaccharide of *Xanthomonas campestris* and has important role in the development of industrially useful polymers. The structural unit of xanthan gum consist of β -(1→4)-D-glucopyranose glucan (as cellulose) backbone with side chains of -(3→1)- β -linked D-mannopyranose-(2→1)- β -D-glucuronic acid-(4→1)- β -D-mannopyranose on alternating residues. It is biodegradable renewable resource^{1,2} and because of this it is widely used in enhanced oil recovery,³ the high thickening efficiency,⁴ hydrogen bonding properties,⁵ good electrolytic compatibility, and low cost have resulted in xanthan gum being

extensively used in both food⁶ and industrial applications *viz.* in cosmetics,⁷ pharmaceuticals,⁸ additives.⁹ The graft copolymers of xanthan gum with acrylamide¹⁰ are used as turbulent drag reducers in sprinkler irrigation and as a flocculants in waste water treatment, ore treatment and as coatings for slow release urea fertilisers. Methyl methacrylate¹¹ grafted xanthan gum is applied to absorb metal ions, such as Hg²⁺ and Cu²⁺, whereas sulfonic acid and sulfomethyl¹² containing graft copolymer of xanthan gum are used in petroleum recovery because of its synergistic viscosity and as a thickener in textile and slurry explosives. On the other hand, poly (4-vinyl pyridine) or its derivatives has wide industrial applications because of the presence of pyridyl nitrogen on the repeating unit of poly (4-vinyl pyridine), which makes the polymer industrially important *viz.* to remove viruses from water,¹³ antimicrobial resins,¹⁴ to absorb heavy metal ion¹⁵ and amperometric biosensor with tyrosine¹⁶ *etc.* Several copolymers of 4-vinyl pyridine with different vinyl monomers are reported in literature,^{17–25} which have many industrial and biomedical applications like removal of Cr(VI) and Hg²⁺ from aqueous solution, as a binder in base coat for leather finishing,

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TABLE I
Effect of Potassium Peroxymonosulphate Concentration

[PMS] × 10 ³ (mol dm ⁻³)	%G	%E	%C	%A	%H	Rg × 10 ⁷ (mol L ⁻¹ s ⁻¹)
3.3	130.0	76.3	16.2	54.6	23.7	17.1
4.0	138.0	77.4	17.0	58.0	22.6	18.2
5.0	239.1	79.8	28.5	70.5	20.2	31.5
6.7	280.0	82.9	32.1	73.7	17.1	36.9
10.0	400.0	87.8	43.3	80.0	12.2	52.8

[AA] = 5.0 × 10⁻³ mol dm⁻³; [4-VP] = 10.0 × 10⁻² mol dm⁻³; [H⁺] = 2.5 × 10⁻² mol dm⁻³; [XOH] = 1.0 g dm⁻³; Time = 120 min.; Temp. = 40°C.

ion specific behavior with partially quaternized poly(4-vinyl pyridine) gel, effect of poly vinyl pyridine on the migration of monocytes through human cervical mucus, adsorption of Uranium and their fission products from HNO₃ medium and ion doping role in photo-induced process *etc.*

The potential uses and industrial applications of xanthan gum are reduced because of microbial attack and low surface area, poor workability, and bad mechanical properties limit the uses of 4-vinyl pyridine. On considering the potential uses of xanthan gum and 4-vinyl pyridine requires some modification. Modification of xanthan gum by graft copolymerization techniques allows one to chemically change the polysaccharide chain by introducing polymeric chain that confer different structural characteristics to the initial materials. Thus it was thought worthwhile to graft 4-vinyl pyridine onto xanthan gum to increase and improve the potential use of xanthan gum by employing potassium peroxy-monosulphate/ascorbic acid as a redox pair, and it was thought that the synthesized graft copolymer would be amphoteric in nature, more environmentally friendly and cost effective than poly (4-vinyl pyridine) and would hold better properties of metal ion uptake, flocculation and antimicrobial *etc.* than xanthan gum.

EXPERIMENTAL

Materials

The 4-vinyl pyridine (4-VP) (Aldrich, USA) was distilled under reduced pressure at 10 mmHg and

reduced temperature i.e., at 40°C and kept in deep freezer. The xanthan gum and potassium peroxy-monosulphate were also purchased from Aldrich (USA) and used as such. Other chemicals like, HCl, NH₄Cl and methanol from Merck, India were used as received. The solution of ascorbic acid (Aldrich, USA) was kept in nitrogen atmosphere to prevent aerial oxidation. For the hydrogen ion concentration sulfuric acid (Merck, India) of desired concentration was used.

Procedure for grafting

For each experiment xanthan gum solution was prepared by slow addition of calculated amount of xanthan gum into reactor containing triple distilled water. The calculated amount of 4-vinyl pyridine, sulfuric acid and ascorbic acid were added into the reactor and a slow stream of oxygen free nitrogen gas was passed for 30 min. A known amount of deoxygenated potassium peroxy-monosulphate solution was added to initiate the reaction. The reaction was carried out under a continuous flow of oxygen free nitrogen gas. After desired time period the reaction was stopped by letting air into reactor. The graft copolymer was precipitated by pouring the reaction mixture into the water-methanol mixture, where grafted xanthan gum precipitates out, after that the precipitate was separated, dried and weighed.

Separation of homopolymer

For the separation of poly (4-vinyl pyridine) the precipitate was filtered and took the filtrate in a flask.

TABLE II
Effect of Ascorbic Acid Concentration

[AA] × 10 ³ (mol dm ⁻³)	%G	%E	%C	%A	%H	Rg × 10 ⁷ (Mol L ⁻¹ s ⁻¹)
3.3	80.0	76.2	10.0	44.4	23.8	10.6
4.0	219.5	81.2	25.7	68.7	18.8	28.7
5.0	239.1	79.8	28.5	70.5	20.2	31.5
6.7	257.1	79.1	30.9	72.0	20.9	33.9
10.0	278.9	78.0	34.0	73.6	22.0	36.8

[PMS] = 5.0 × 10⁻³ mol dm⁻³; [4-VP] = 10.0 × 10⁻² mol dm⁻³; [H⁺] = 2.5 × 10⁻² mol dm⁻³; [XOH] = 1.0 g dm⁻³; Time = 120 min.; Temp. = 40°C.

TABLE III
Effect of Hydrogen Ion Concentration

$[H^+] \times 10^2$ (mol dm ⁻³)	%G	%E	%C	%A	%H	Rg $\times 10^7$ (mol L ⁻¹ s ⁻¹)
1.6	144.8	74.9	18.4	59.2	25.1	19.1
2.0	164.8	77.1	20.9	62.2	22.7	21.8
2.5	239.1	79.8	28.5	70.5	20.2	31.5
3.3	232.0	77.2	28.6	69.9	22.8	30.6
5.0	196.0	64.4	29.0	66.2	35.6	25.8

[PMS] = 5.0×10^{-3} mol dm⁻³; [4-VP] = 10.0×10^{-2} mol dm⁻³; [AA] = 5.0×10^{-3} mol dm⁻³; [XOH] = 1.0 g dm⁻³; Time = 120 min.; Temp. = 40°C.

To the filtrate a pinch of hydroquinone was added and concentrated under reduced pressure. This filtrate was treated with 10% volume aqueous HCl solution and then aqueous ammonia and NH₄Cl was added to precipitate out poly (4-vinyl pyridine) as reported by Mariya et al.²⁶ in 1997. The homopolymer was separated and dried in vacuum oven at room temperature then weighed.

RESULTS AND DISCUSSION

The grafting parameters were calculated according to Fanta definition²⁷ as follows.

Grafting ratio (G, %)

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

Grafting efficiency (E, %)

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

Add on (A, %)

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

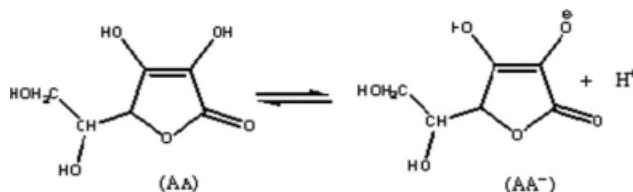
Conversion (C, %)

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

Homopolymer (H, %)

$$= 100 - \% \text{ grafting efficiency}$$

Besides above parameters rate of grafting was also calculated according to following formula.^{28,29}



Scheme 1 Effect of $[H^+]$ on production of free radical.

$$\text{Rate of grafting } R_g = \frac{1000 \times W}{V \times T \times M} \text{ mol l}^{-1}\text{s}^{-1}$$

Where W is the weight of grafted xanthan gum minus weight of pure gum; V, the volume of reaction mixture; T, the time of reaction in second; and M, the molecular weight of 4-vinyl pyridine.

To determine the optimal conditions for the grafting of 4-vinyl pyridine onto xanthan gum using PMS/Ascorbic acid as redox initiator, graft copolymerization was carried out under various conditions of reaction time, temperature and concentrations of potassium peroxymonosulphate, ascorbic acid, hydrogen ion, xanthan gum and 4-vinyl pyridine.

Influence of variables on grafting parameters

Effect of Peroxymonosulphate Concentration

The effect of peroxymonosulphate concentration on grafting reaction was studied at various concentration of potassium peroxymonosulphate (Table I). It was observed that grafting ratio, efficiency, conversion, add on and rate of grafting increased

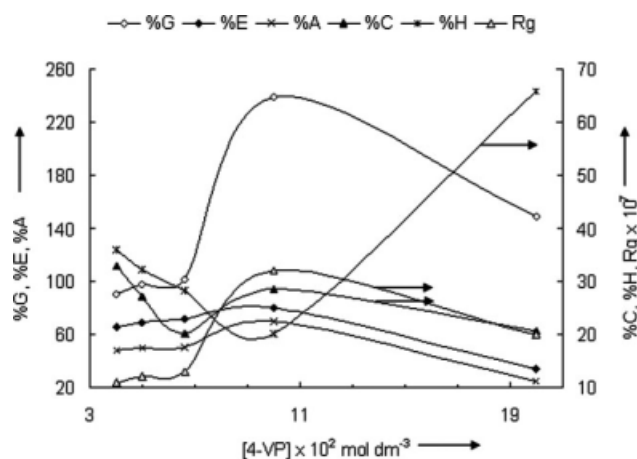


Figure 1 Effect of 4-vinyl pyridine concentration [PMS] = 5.0×10^{-3} mol dm⁻³; $[H^+] = 2.5 \times 10^{-2}$ mol dm⁻³; [AA] = 2.5×10^{-2} mol dm⁻³; [XOH] = 1.0 g dm⁻³; Time = 120 min.; Temp = 40°C; %G = Grafting ratio; %E = Efficiency; %C = Conversion; %A = Add on; %H = Homopolymer; Rg = Rate of grafting $\times 10^7$ mol L⁻¹ s⁻¹.

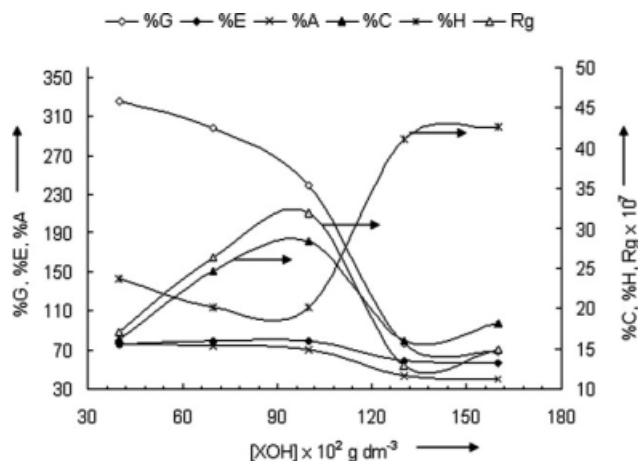


Figure 2 Effect of xanthan gum concentration [PMS] = 5.0×10^{-3} mol dm $^{-3}$; [H $^{+}$] = 2.5×10^{-2} mol dm $^{-3}$; [AA] = 2.5×10^{-2} mol dm $^{-3}$; [4-VP] = 10.0×10^{-2} mol dm $^{-3}$; Time = 120 min.; Temp. = 40°C; %G = Grafting ratio; %E = Efficiency; %C = Conversion; %A = Add on; %H = Homopolymer; Rg = Rate of grafting $\times 10^7$ mol L $^{-1}$ s $^{-1}$.

continuously on increasing the concentration of peroxymonosulphate from 3.3×10^{-3} to 10.0×10^{-3} mol dm $^{-3}$. The enhancement in grafting parameters within the cited range may be attributed because of the progressive reduction of peroxymonosulphate with ascorbic acid producing $\cdot\text{OH}$ and $\text{AA}\cdot$ as reactive species, which interact with 4-vinyl pyridine and xanthan gum molecules, to produce the 4-vinyl pyridine and xanthan gum free radicals. These xanthan gum macroradicals are attacking on 4-vinyl pyridine molecule to propagate the growing grafted chain.

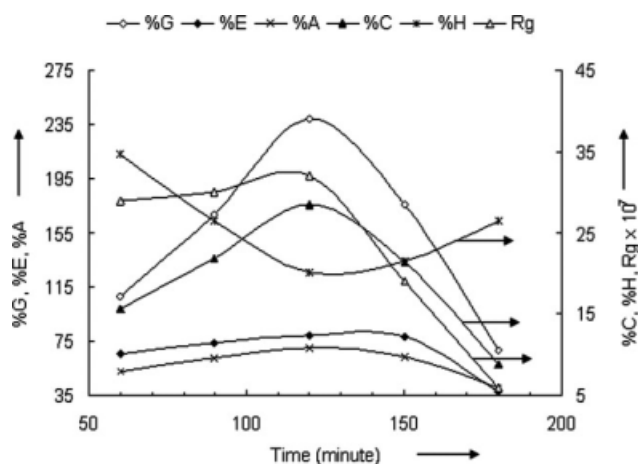


Figure 3 Effect of time [PMS] = 5.0×10^{-3} mol dm $^{-3}$; [H $^{+}$] = 2.5×10^{-2} mol dm $^{-3}$; [AA] = 5.0×10^{-3} mol dm $^{-3}$; [4-VP] = 10.0×10^{-2} mol dm $^{-3}$; [XOH] = 1.0 g dm $^{-3}$; Temp. = 40°C; %G = Grafting ratio; %E = Efficiency; %C = Conversion; %A = Add on; %H = Homopolymer; Rg = Rate of grafting $\times 10^7$ mol L $^{-1}$ s $^{-1}$.

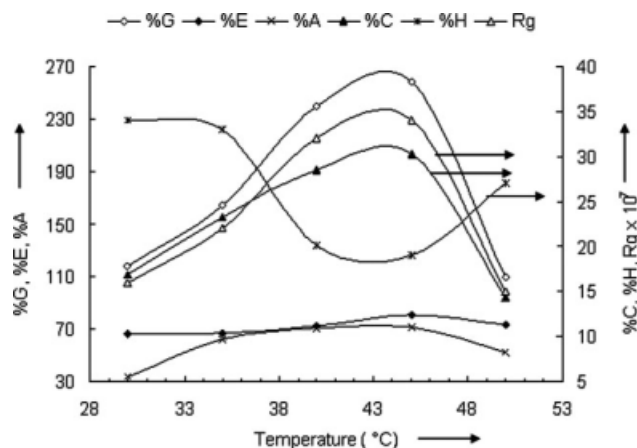


Figure 4 Effect of temperature [PMS] = 5.0×10^{-3} mol dm $^{-3}$; [H $^{+}$] = 2.5×10^{-2} mol dm $^{-3}$; [AA] = 5.0×10^{-3} mol dm $^{-3}$; [4-VP] = 10.0×10^{-2} mol dm $^{-3}$; [XOH] = 1.0 g dm $^{-3}$; Time = 120 min. %G = Grafting ratio; %E = Efficiency; %C = Conversion; %A = Add on; %H = Homopolymer; Rg = Rate of grafting $\times 10^7$ mol L $^{-1}$ s $^{-1}$.

Effect of Ascorbic acid Concentration

The results obtained by varying the concentration of ascorbic acid were summarized in Table II. The grafting ratio, conversion, add on, and rate of grafting increased on increasing the concentration of ascorbic acid from 3.3×10^{-3} to 10.0×10^{-3} mol dm $^{-3}$ while efficiency increased with increasing ascorbic acid concentration up to 4.0×10^{-3} mol dm $^{-3}$, but thereafter it decreased. The increase in grafting ratio, conversion, add on and rate of grafting with increase in the concentration of ascorbic acid might be attributed to increase in the formation of primary free radicals ($\cdot\text{OH}$ and $\text{AA}\cdot$).

Effect of Sulfuric acid Concentration

The effect of hydrogen ion concentration on grafting parameters was studied by varying the concentration of sulfuric acid from 1.6×10^{-2} to 5.0×10^{-2} mol dm $^{-3}$

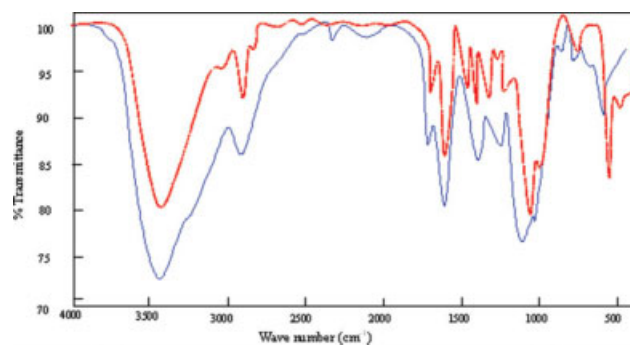
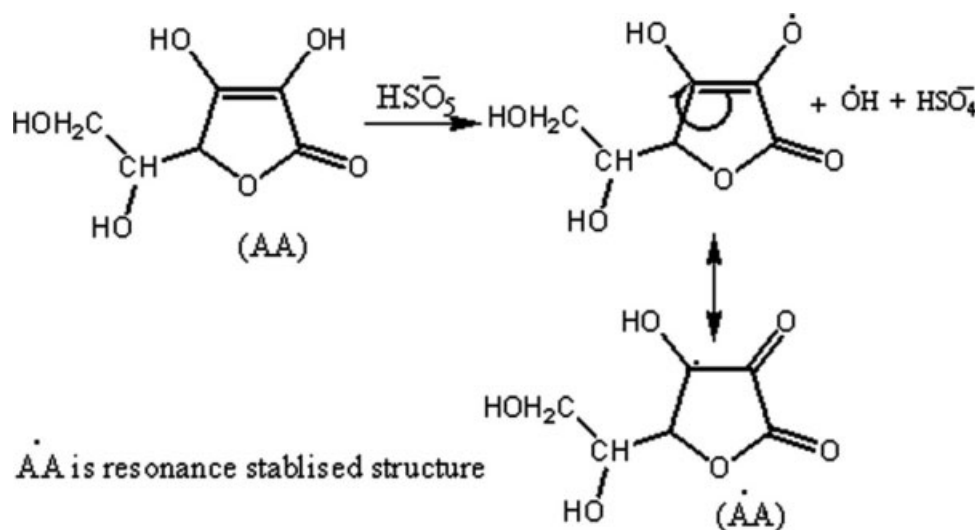


Figure 5 FTIR Spectra of xanthan gum (blue line) and xanthan gum-g-(4-vinyl pyridine) (red dotted line). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



Scheme 2 Generation of Primary free radicals.

and results were given in Table III. Grafting ratio, efficiency, add on and rate of grafting were found to increase on increasing the $[H^+]$ upto $2.5 \times 10^{-2} \text{ mol dm}^{-3}$, however, conversion increased continuously on increasing the concentration of hydrogen ion upto $5.0 \times 10^{-2} \text{ mol dm}^{-3}$. This behavior can be explained by Scheme 1.

On increasing the $[H^+]$, the concentration of AA species increased, which would react with peroxy-monosulphate to give primary free radicals. These primary free radicals react with 4-vinyl pyridine and xanthan gum molecules giving rise to xanthan gum and 4-vinyl pyridine radicals that are responsible for propagation of growing grafted chains, which results the increased value of grafting parameters (% G, % A, Rg, % E). But on further increasing the $[H^+]$ i.e., beyond $2.5 \times 10^{-2} \text{ mol dm}^{-3}$ the grafting ratio, efficiency, add on and rate of grafting were found to decrease and it might be due to the premature termination of xanthan gum radicals by AA^\bullet or $\bullet OH$ produced in excess at faster rate and to give more homopolymer.

Effect of 4-vinyl pyridine Concentration

The effect of monomer concentration on graft copolymerization was studied by changing the concentration of 4-vinyl pyridine from 4.0×10^{-2} to $20.0 \times 10^{-2} \text{ mol dm}^{-3}$ and graph is plotted between concentrations of 4-vinyl pyridine and grafting parameters (Fig. 1). The grafting ratio, efficiency, add on, conversion and rate of grafting were found to increase on increasing the 4-vinyl pyridine concentration from 4.0×10^{-2} to $10.0 \times 10^{-2} \text{ mol dm}^{-3}$ whereas homopolymer decreased considerably, but on further increasing the concentration of 4-vinyl pyridine the decrease in the values of grafting

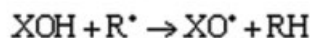
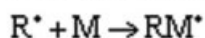
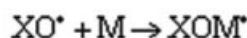
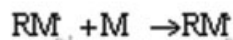
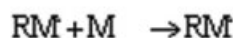
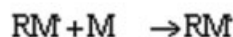
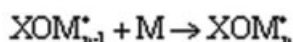
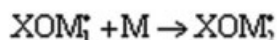
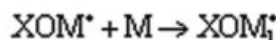
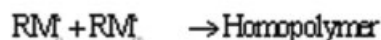
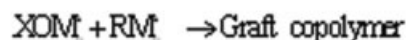
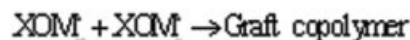
parameters were observed. The increase in grafting parameters with monomer concentration up to cited range might be due to greater availability of monomer molecule at chain propagating site. The decrease in the value of grafting parameters at higher concentration of monomer might be due to increase in viscosity of reaction medium and increase in viscosity is due to the solubility of poly (4-vinyl pyridine) in water.

Effect of Xanthan gum Concentration

The graft copolymerization of 4-vinyl pyridine onto xanthan gum was studied at different concentration of xanthan gum (Fig. 2). As the concentration of xanthan gum was increased from 40.0×10^{-2} to $100.0 \times 10^{-2} \text{ g dm}^{-3}$ conversion, efficiency and rate of grafting were found to increase. This might be due to the greater availability of more and more grafting sites (because of presence of sufficient amount of xanthan gum molecules), but on further increasing the concentration of xanthan gum, the value of conversion, efficiency, and rate of grafting was found to decreased while grafting ratio, add on and homopolymer decreased continuously i.e., from 40 to $160 \times 10^{-2} \text{ g dm}^{-3}$. This might be due to two factors: due to increased viscosity of reaction medium which hinders the movement of macro free radicals (xanthan gum) and 4-vinyl pyridine radicals or due to formation of more radicals which might interact to lead termination.

Effect of Time

The effect of change in duration of grafting reaction was studied by varying the time period from 60 to 180 min. and results are shown by plotting the

Formation of Free Radicals**Initiation****Propagation****Termination:**

Where $R^* = AA^*$ and OH

Scheme 3 Propagation and Graft copolymerization.

graph between times and grafting parameters (Fig. 3). There was an increase in grafting ratio, efficiency, add on and conversion with increasing time period of reaction from 60 to 120 min. but beyond this time period grafting ratio, efficiency, add on, conversion and rate of grafting decreased, where as homopolymer was found to increase. On increasing the time period from 60 to 120 min, propagation of grafting chains takes place due to availability of more active species, which accounts for higher grafting ratio. On further increase in time interval the mutual annihilation of growing grafted chains occurred, which resulted the decrease in grafting ratio, add on, efficiency, conversion and rate of grafting.

Effect of Temperature

The effect of temperature on grafting parameters was studied at various temperatures ranging from 30 to 50°C. Figure 4 indicates that, as the temperature increased from 30 to 45°C, increase in the values of grafting parameters was observed which might be explained on the basis of the fact that with increase in temperature, rate of production of more primary free radicals increased which generate more grafting sites at greater rate leads to increase the values of grafting parameters. However, beyond the optimum temperature further increase in temperature could result the decomposition of potassium peroxy-monosulphate into HSO_4^- , H_2O , O_2 as reported by Cotton and Wilkinson.³⁰ As O_2 acts as a scavenger for free radicals that would react with primary free radicals thereby lowering free radical concentration hence the decrease in grafting parameters was observed.

Evidence of Grafting: Infrared spectral analysis

The FTIR spectra of the samples in KBr pallets were recorded on Varian Excalibur 3000 series in the range 500–4000 cm^{-1} . On comparing the FTIR spectra of xanthan gum and xanthan gum-g-(4-vinyl pyridine) (Fig. 5), the following additional bands were appeared in the spectra of xanthan-gum-g-(4-vinyl pyridine). Following observation was also observed in previous publication³¹

- Poly (4-vinyl pyridine) ring stretching vibration occurred in the region at 1505.8 cm^{-1} and 1454.1 cm^{-1} . This absorption involves stretching and contraction of the entire bond in the pyridine ring (C=C, C=N) and interaction between these stretching modes.
- The band at 814.5 cm^{-1} was due to out of plane bending vibration of C-H of pyridine ring.

Thus the presence of these additional bands and disappearance of O-H bending vibration (1408 cm^{-1}) from the spectra of xanthan gum-g-(4-vinyl pyridine)

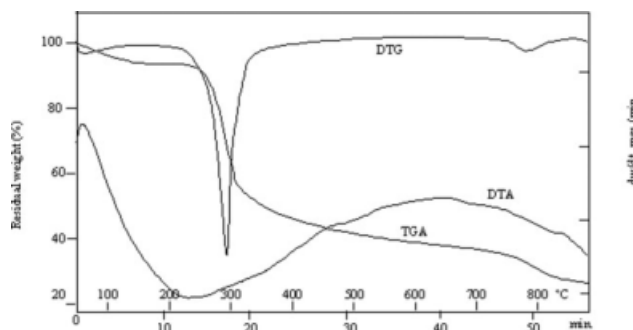


Figure 6 TGA/DTA, DTG trace of xanthan gum.

TABLE IV
Thermogravimetric Analyses of Ungrafted and Grafted Gum

Sample Code	PDT (°C)	FDT (°C)	T _{max} (°C)	IPDT (°C)	DTA peaks	
					Exopeaks (°C)	Endopeaks (°C)
C ₁	281.0	316.0	290.0	280.2	—	290.0
C ₂	200.0	348.4	284.4	335.9	—	815.0

TABLE V
Decomposition Temperature (DT)

Temp. (°C)	% Weight loss						
	10%	20%	30%	40%	50%	60%	70%
C ₁	270.0	282.0	297.0	310.0	343.0	600.0	850.0
C ₂	235.0	277.0	297.0	348.42	605.0	827.0	942.0

proves that the 4-vinyl pyridine has been grafted on OH site of the xanthan gum macromolecule.

Mechanism

The following mechanism was proposed for the graft copolymerization of 4-vinyl pyridine onto xanthan gum using peroxymonosulphate/ascorbic acid redox pair.

AA[•] and •OH free radicals were generated (Scheme 2) by the interaction of peroxymonosulphate and ascorbic acid, which abstracts hydrogen atom from xanthan gum molecules producing XO[•] macro radicals. The 4-vinyl pyridine molecules which were in close vicinity of the reaction sites become acceptor of xanthan gum macro radicals resulting in chain initiation of graft copolymer and thereafter themselves become free radical donor to neighboring molecules, in this way grafted chains grow, these chains were terminated by coupling to give graft copolymer (Scheme 3).

Thermal Analyses

The thermal analyses of xanthan gum and xanthan-gum-g-(4-vinyl pyridine) was carried out in an inert atmosphere with heating rate of 15°C/min and

which are recorded on a NETZSCH-Gerätebau GmbH thermal analyzer.

Xanthan gum

The degradation of xanthan gum started at about 232°C, and it shows a single step degradation process (Fig. 6). The rate of weight loss increased on increasing the temperature up to 296°C, but thereafter it decreased. Nearly 40% weight loss was occurred between 200 to 310°C, and 60% xanthan gum was degraded at about 600°C (Table V); therefore, final decomposition temperature (FDT) was very low i.e., 316°C. Polymer decomposition temperature (PDT), temperature at which maximum degradation (T_{max}) occurred and integral procedural decomposition temperature (IPDT) of xanthan gum were found to be 281°C, 290°C and 362°C, respectively, (Table IV). The differential thermal analysis (DTA) of xanthan gum also showed the gradual degradation of xanthan gum with endotherm peak at 290°C leads to maximum weight loss at this temperature and 24% char yield was obtained at 870°C.

Xanthan gum-g-(4-vinyl pyridine)

The graft copolymer began to degrade at about 110°C. However, 2% weight loss was observed

TABLE VI
Decomposition Temperature

Weight Loss (%)	Temp. (°C)								
	100	200	300	400	500	600	700	800	900
C ₁	3.3	6.0	33.0	55.0	57.0	60.0	65.0	73.0	—
C ₂	4.7	4.0	32.0	44.00	47.00	50.00	54.0	58.00	68.0

Where C₁ = Xanthan Gum, C₂ = Xanthan gum-g-(4-vinyl pyridine).

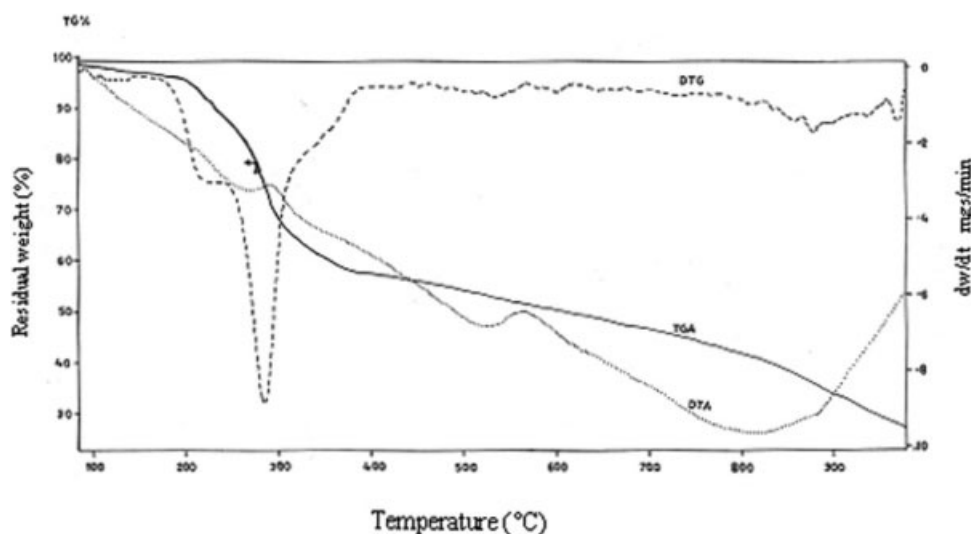
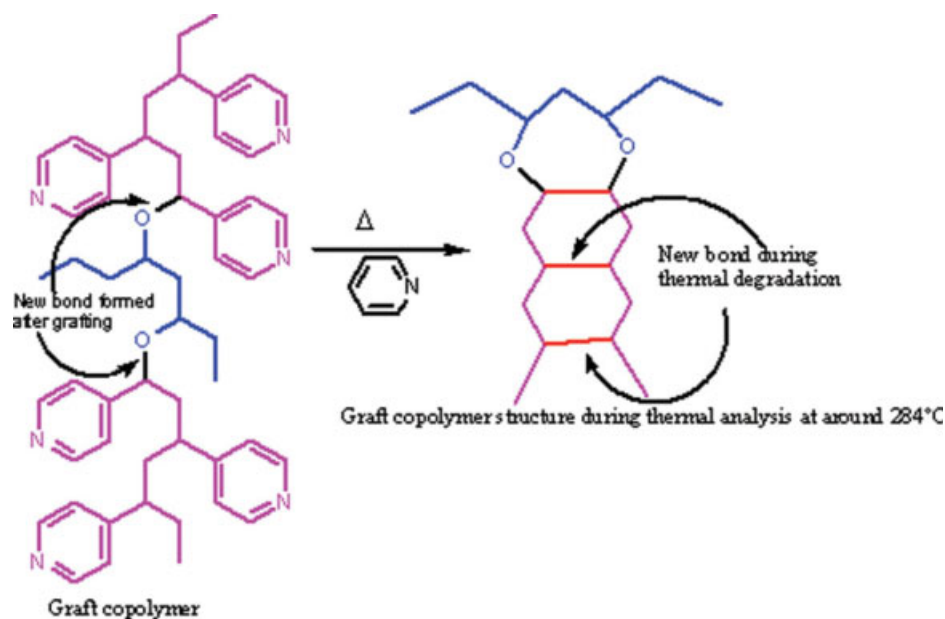


Figure 7 TGA/DTA, DTG trace of xanthan gum-g-(4-vinyl pyridine).

below 100°C, which was due to the absorbed water. Grafted xanthan gum also shows single step degradation process. The rate of weight loss increased on increasing the temperature from 180 to 350°C, but gradually decreased thereafter. The polymer decomposition temperature (PDT) and the temperature at which maximum degradation (T_{\max}) occurred were found to be 200°C and 284.4°C respectively, (Fig. 7). This T_{\max} was might be due to breaking of pyridine segment from xanthan gum-g-(4-vinyl pyridine) as shown in the Scheme 4, which was also confirmed by DTA of the graft copolymer, which showed maxi-

mum weight loss between 280.2°C to 525.4°C. About 42% weight loss was observed between 180 and 360°C. This weight loss was lower than the weight loss of xanthan gum in the same temperature range. The IPDT was found to be 280.2°C (Table IV) which is high than that of xanthan gum. The residual weight was obtained after 900°C, which is more than that of parent substrate. Thus above study shows that the grafted one is more thermally stable than the corresponding ungrafted polymer and similar observation was also found with acrylonitrile³² grafted xanthan gum.



Scheme 4 Schematic representation of thermal degradation of graft copolymer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

- The graft copolymerization was carried out in the presence of an efficient redox initiator i.e., PMS/Ascorbic acid; its efficiency has been determined by the continuous increased value of grafting parameters except homopolymer on increasing the concentration of redox initiator.
- Minimum concentration of xanthan gum was sufficient for achieving optimum value of %G.
- High temperature and long duration did not favor the graft copolymerization and rate of grafting is also decreased at optimum condition of time and temperature of reaction.
- Ftir spectral analysis was utilized to prove grafting of 4-vinyl pyridine on to xanthan gum.
- Thermal degradation of xanthan gum and xanthan gum-g-4-vinyl pyridine show that about 50% xanthan gum degraded at 343.0°C, whereas 50% grafted xanthan gum degraded at 605.0°C indicating more thermal stability of graft copolymer and high value of FDT, IPDT and Char yield are also support the high thermal stability of graft copolymer in comparison to backbone.
- The synthesized graft copolymer could be used as antibacterial or antimicrobial agent in water purification due to presence of pendent chain of poly (4-vinyl pyridine).

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