

Studies on Graft Copolymerization of 4-Vinylpyridine onto Guar Gum

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Received 25 May 2001; accepted 13 September 2001

ABSTRACT: Graft copolymerization of 4-vinylpyridine (4-VP) onto guar gum (GOH) using potassium monopersulfate (PMS)/thioacetamide (TAA) as a redox pair was studied in an aqueous medium under inert atmosphere. The concentration of potassium monopersulfate and thioacetamide should be 1.0×10^{-2} and 5.0×10^{-3} mol dm⁻³, respectively, for highest grafting ratio and efficiency. Efficient grafting was observed at 19.25×10^{-2} and 4.87×10^{-2} mol dm⁻³ concentration of 4-vinylpyridine and sulfuric acid, respectively. The optimum temperature for grafting is 30°C. As the time period of reaction is increased, the grafting ratio increases, whereas efficiency decreases. The plausible mechanism of grafting has been suggested. A sample of guar gum and guar-*g*-4-vinylpyridine were subjected to thermogravimetric analysis with the objective of studying the effect of grafting 4-vinylpyridine on the thermal stability of guar gum. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2380–2385, 2002

Key words: graft copolymer; guar gum; 4-vinylpyridine

INTRODUCTION

A novel polymer was prepared by grafting 4-vinylpyridine onto guar gum using potassium monopersulfate (PMS)/thioacetamide (TAA) redox pair. This polymer was prepared because poly(vinylpyridine) finds extensive applications as a reducing agent, oxidizing agent, classified ion exchanger, flocculent, antimicrobial resin, and so forth^{1–12} because of its reactive pyridyl nitrogen on the repeating units of vinylpyridine. Similarly, guar gum also enjoys a wide range of usage in industrial applications. Therefore, it was thought that guar gum-*g*-(4-vinylpyridine) would be more environmentally friendly and cost-effective than poly(4-vinylpyridine) and which would hold better properties of metal ion uptake, flocculent, and antimicrobial resin than those of guar gum.

EXPERIMENTAL

Material

Guar gum was received as a gift sample from Hindustan Gums and Chemicals (India) and 4-vinylpyridine, distilled under reduced pressure and sample boiling at 59°C and 14 mmHg, was collected and employed for experimental work. Potassium monopersulfate (Du Pont Co., Wilmington, DE) and thioacetamide (Aldrich, Milwaukee, WI) were used as received.

Graft Copolymerization

For each experiment the weighed amount of guar gum was added to rapidly stirred triple-distilled water in a reactor. Throughout the entire course of the reaction, the reaction mixture was purged with purified nitrogen and was kept at constant temperature. Definite amounts of PMS solution, 4-vinylpyridine, sulfuric acid, and thioacetamide were added to the reactor. The reaction mixture was poured into a water–methanol mixture,

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Contract grant sponsor: CSIR India; contract grant number: 01(1436)/97/EMR-II and RA.

Journal of Applied Polymer Science, Vol. 84, 2380–2385 (2002)
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where graft copolymer precipitates out and poly(4-vinylpyridine) remains in the solution. The precipitate was separated, dried, and weighed. The poly(4-vinylpyridine) was precipitated by the method given by Maria et al.¹³ The poly(4-vinylpyridine) thus obtained was separated, dried, and weighed.

Grafting parameters were calculated according to Fanta's definition¹⁴:

$$\text{Grafting ratio (\%G)} = \frac{\text{Polymer in graft}}{\text{Weight of substrate}} \times 100$$

Efficiency (%E)

$$= \frac{\text{Polymer in graft}}{\text{Total weight of polymer formed}} \times 100$$

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

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

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

RESULTS AND DISCUSSION

The effect of potassium monopersulfate, thioacetamide, 4-vinylpyridine, guar gum, hydrogen ion concentration, along with time and temperature, on grafting parameters was studied, to optimize the conditions for graft copolymerization.

Effect of Potassium Monopersulfate

The effect of potassium monopersulfate on graft copolymerization was studied by varying its concentration from 0.4×10^{-2} to 2.0×10^{-2} mol dm⁻³. It was observed that grafting ratio, efficiency, and add on increase on increasing the concentration of potassium monopersulfate from 0.4×10^{-2} to 1.0×10^{-2} mol dm⁻³ but beyond the above concentration range grafting ratio and add on decreased; however, grafting efficiency was maximum at 1.6×10^{-2} mol dm⁻³. The conversion of monomer to polymer decreases as the concentration was increased from 0.4×10^{-2} to 2.0×10^{-2} mol dm⁻³ (Table I). The enhancement of grafting within the cited range may be attributed to progressive reduction, producing sulfate ion and hydroxyl free radicals, which attack the guar gum molecule creating more free-radical sites to which monomer addition takes place. At higher concentration the decomposition of KHSO₅, to

Table I Effect of Potassium Monopersulfate (PMS) on Grafting Parameters

[PMS] ($\times 10^2$)	%G	%E	%A	%C	%H
0.4	294.27	41.39	74.63	33.06	58.61
1.0	374.24	71.23	78.91	24.43	28.77
1.6	253.37	73.53	71.70	16.02	26.47
2.0	220.65	69.70	68.81	14.72	30.30

[TAA] = 5.0×10^{-3} mol dm⁻³; [H⁺] = 4.87×10^{-2} mol dm⁻³; [VP] = 19.25×10^{-2} mol dm⁻³; [GOH] = 97.8×10^{-2} g dm⁻³; temperature = 35°C; time = 120 min.

HSO₄⁻, H₂O, O₂,¹⁵ takes place. Given that O₂ acts as a scavenger for free radicals, %G and %C decrease.

Effect of Thioacetamide

The variation of thioacetamide from 2.5×10^{-3} to 6×10^{-3} mol dm⁻³ reveals that grafting ratio, add on, and conversion all increase on increasing the concentration of thioacetamide. Whereas efficiency increases with an increase in thioacetamide concentration only up to 5.0×10^{-3} mol dm⁻³, thereafter it decreases (Fig. 1). The increase in grafting ratio, add on, and conversion on increasing the concentration of thioacetamide may result from the increase in the number of free radicals. The very high concentration of thioacetamide favors the formation of homopolymer, because of which grafting decreases.

Effect of Monomer

The effect of 4-vinylpyridine on graft copolymerization was studied by changing the concentration of 4-vinylpyridine from 10.06×10^{-2} to 39.50×10^{-2} mol dm⁻³. The grafting ratio and add on both increase with increase in the concentration of 4-vinylpyridine from 10.06×10^{-2} to 29.82×10^{-2} mol dm⁻³ but decrease on further increasing the concentration. However, maximum efficiency was observed when the concentration of 4-vinylpyridine was 19.25×10^{-2} mol dm⁻³ (Fig. 2). The conversion of monomer to polymer decreases as the concentration was increased from 10.06×10^{-2} to 39.50×10^{-2} mol dm⁻³. The increase of the grafting ratio with monomer concentration up to the cited range might be attributed to the greater availability of monomer molecules at the chain propagating site. The decrease in grafting efficiency and conversion at higher

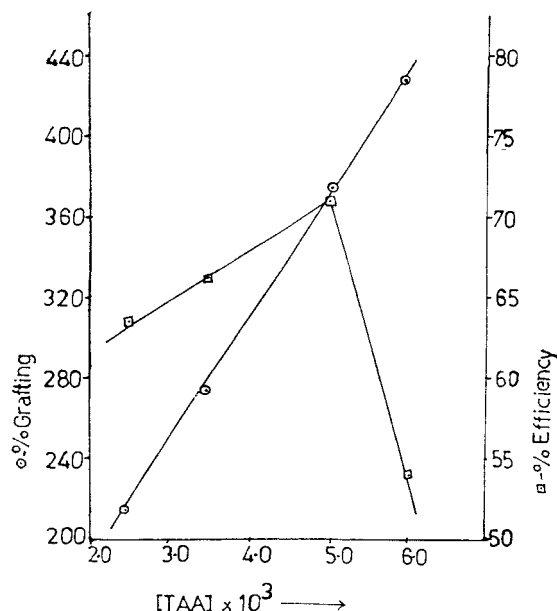


Figure 1 Effect of thioacetamide concentration. [PMS] = 1.0×10^{-2} mol dm⁻³; [4-VP] = 19.25×10^{-2} mol dm⁻³; [TAA] = 5.0×10^{-2} mol dm⁻³; [H⁺] = 4.875×10^{-2} mol dm⁻³; [GOH] = 97.8×10^{-2} g dm⁻³; [H⁺] = 4.875×10^{-2} mol dm⁻³; temperature = 35°C; time = 120 min.

monomer concentration is because of the increase in viscosity of the medium.

Effect of Guar Gum

The effect of guar gum was studied at varied concentrations ranging from 58.8×10^{-2} to 179.0×10^{-2}

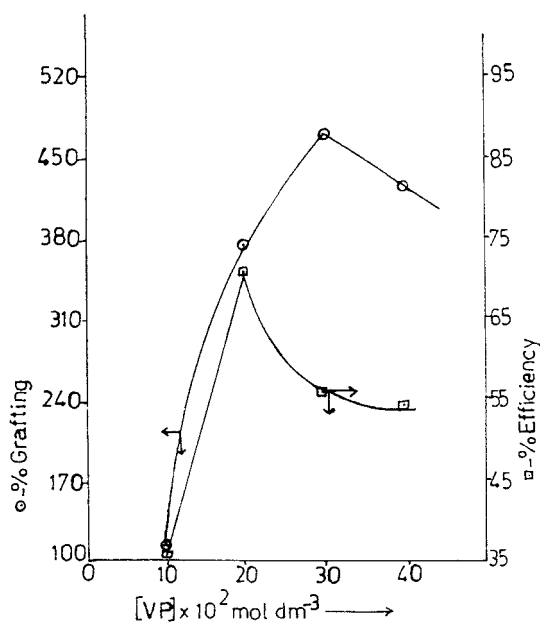


Figure 2 Effect of 4-vinylpyridine concentration. [PMS] = 1.0×10^{-2} mol dm⁻³; [TAA] = 5.0×10^{-2} mol dm⁻³; [GOH] = 97.8×10^{-2} g dm⁻³; [H⁺] = 4.875×10^{-2} mol dm⁻³; temperature = 35°C; time = 120 min.

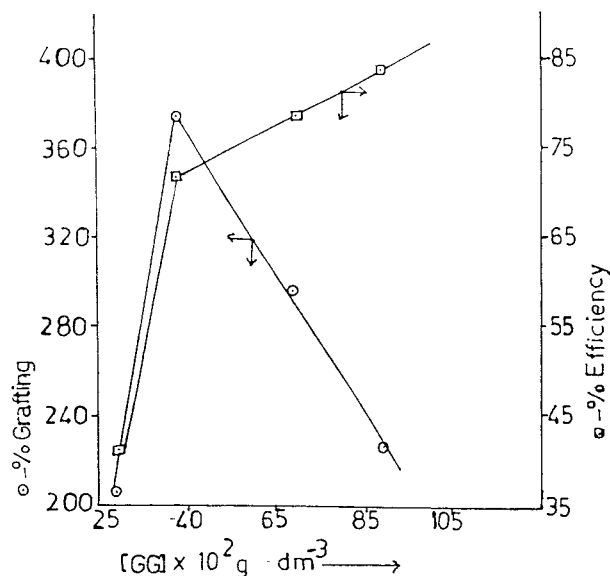


Figure 3 Effect of guar gum concentration. [PMS] = 1.0×10^{-2} mol dm⁻³; [4-VP] = 19.25×10^{-2} mol dm⁻³; [TAA] = 5.0×10^{-2} mol dm⁻³; [H⁺] = 4.875×10^{-2} mol dm⁻³; temperature = 35°C; time = 120 min.

$\times 10^{-2}$ g dm⁻³. As the concentration of guar gum was increased from 58.8×10^{-2} to 179.0×10^{-2} g dm⁻³, grafting efficiency increased (Fig. 3) but conversion and homopolymer decreased, whereas the grafting ratio was maximum at a guar gum concentration of 97.8×10^{-2} g dm⁻³. The above results can be explained by the fact that, as the concentration of guar gum increases, the viscosity of the medium increases, which hinders the movement of free radicals, thereby decreasing the grafting ratio, conversion, and homopolymer.

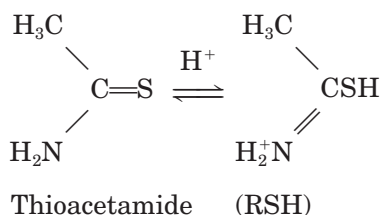
Effect of Hydrogen Ion

The variation of hydrogen ion concentration was affected by the addition of sulfuric acid to the reaction mixture. The variation of hydrogen ion from 3.25×10^{-2} to 8.125×10^{-2} mol dm⁻³ shows that grafting ratio and efficiency increase with an increase in hydrogen ion concentration up to 6.5×10^{-2} to 4.875×10^{-2} mol dm⁻³, respectively (Table II); however, conversion increases with increasing concentration of hydrogen ion. The grafting ratio, efficiency, and conversion all increase on increasing hydrogen ion concentration because thioacetamide is protonated, which in turn reacts with potassium monopersulfate to give free radicals.

Table II Effect of Hydrogen Ion Concentration ($[H^+]$) on Grafting Parameters

$[H^+]$ ($\times 10^3$)	%G	%E	%A	%C	%H
3.250	110.42	39.32	52.47	13.06	60.68
4.875	374.23	71.23	79.91	24.43	28.77
6.500	386.50	53.86	79.44	33.38	46.14
8.125	374.23	48.70	78.90	35.74	51.30

[PMS] = 1.0×10^{-2} mol dm $^{-3}$; [TAA] = 5.0×10^{-3} mol dm $^{-3}$; [VP] = 19.25×10^{-2} mol dm $^{-3}$; [GOH] = 97.8×10^{-2} g dm $^{-3}$; temperature = 35°C; time = 120 min.



Effect of Temperature

The grafting parameters were studied at different temperatures (Table III). It was observed that as the temperature was increased from 30 to 45°C, the grafting ratio and conversion decreased. With a rise in temperature potassium monopersulfate decomposes to give O $_2$, which reacts with primary free radicals, thereby lowering free-radical concentration. Therefore, higher temperature does not favor graft copolymerization.

Effect of Time

The time period of grafting was varied from 60 to 180 min (Table IV). As the time period is increased the grafting ratio, add on, and conversion increased but efficiency decreased. On increasing the time

Table III Effect of Temperature on Grafting Parameters

Temperature (°C)	%G	%E	%A	%C	%H
30	504.29	75.8	83.45	30.91	22.73
35	374.23	71.23	78.91	24.43	28.77
40	315.95	72.56	75.95	20.25	27.44
45	294.06	74.77	74.62	18.33	25.38

[PMS] = 1.0×10^{-2} mol dm $^{-3}$; [TAA] = 5.0×10^{-3} mol dm $^{-3}$; $[H^+] \times 4.875 \times 10^{-2}$ mol dm $^{-3}$; [4-VP] = 19.25×10^{-2} mol dm $^{-3}$; [GOH] = 97.8×10^{-2} g dm $^{-3}$; time = 120 min.

Table IV Effect of Time on Grafting Parameters

Time (min)	%G	%E	%A	%C	%H
60	218.20	75.51	68.57	13.44	24.49
90	253.37	72.96	71.70	16.15	27.04
120	374.23	71.23	78.91	24.43	28.77
180	406.95	58.11	80.27	32.57	41.89

[PMS] = 1.0×10^{-2} mol dm $^{-3}$; [TAA] = 5.0×10^{-3} mol dm $^{-3}$; $[H^+] = 4.875 \times 10^{-2}$ mol dm $^{-3}$; [4-VP] = 19.25×10^{-2} mol dm $^{-3}$; [GOH] = 97.8×10^{-2} g dm $^{-3}$; temperature = 35°C.

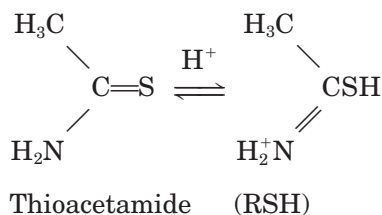
period, propagation of grafting chains and homopolymer takes place, which accounts for the higher grafting ratio and conversion and lower grafting efficiency.

Evidence of Grafting

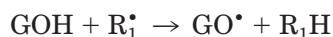
On comparing the IR spectra of guar gum and guar gum-*g*-(4-vinylpyridine), an additional broad band was observed at 1620–1440 cm $^{-1}$ and a widened band at 3400 cm $^{-1}$ in the grafted sample. The broad band at 1620–1440 cm $^{-1}$ is attributed to absorption, including stretching and contraction of all the bonds in the ring (C=C, C=N) and interaction between this stretching absorption.

Mechanism

Thioacetamide in the presence of acid forms an active species (RSH), which interacts with potassium monopersulfate, giving rise to R $_1^{\bullet}$.



Initiation



(where R $_1^{\bullet}$ = RS $^{\bullet}$ or SO $_4^{\bullet-}$)

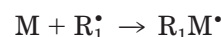
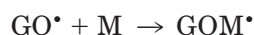
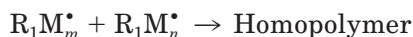
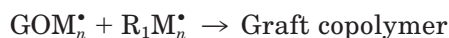
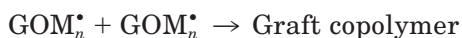


Table V Weight Loss at Different Temperatures

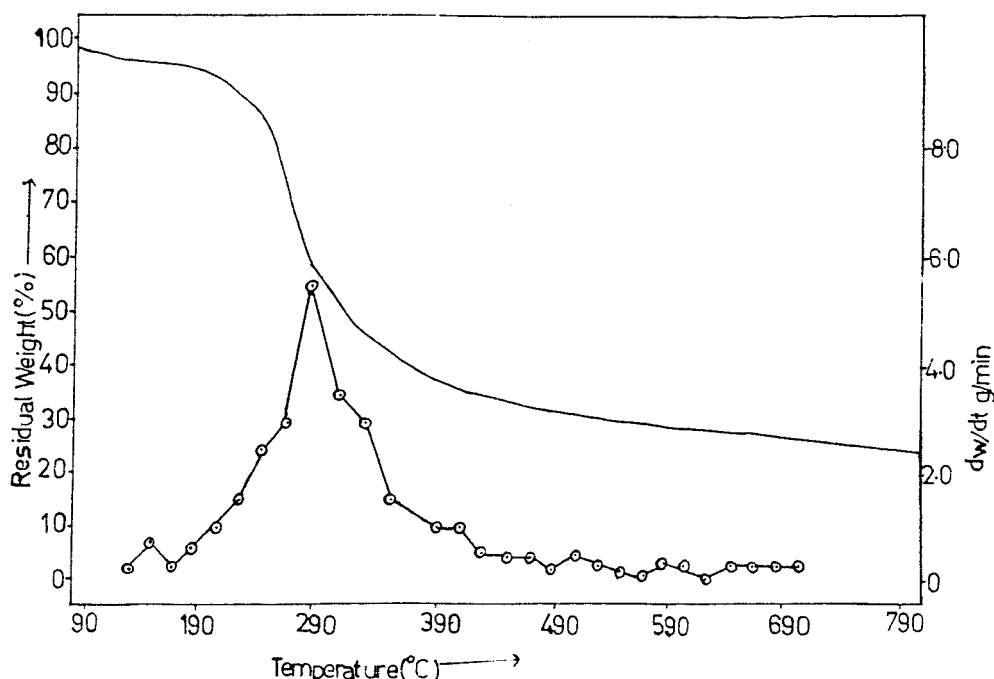
Temperature (°C)	Weight Loss (%)	
	Guar Gum	Guar Gum-g-(4-vinylpyridine)
100	3	3
200	7	7
300	35	45
400	75	63
500	81	68
600	88	70
700	92	73
800	95	75

Propogation**Termination****THERMOGRAVIMETRIC ANALYSES****Guar Gum**

Thermogravimetric analysis of guar gum (Table V) reveals that decomposition of guar gum started at 230°C; therefore, it is a single-step degradation process. The rate of weight loss increases on increasing the temperature up to 310°C, but thereafter, the rate of weight loss was found to decrease. About 68% weight loss occurred between 200 to 400°C, and at 800°C only 5% char yield was obtained. Nearly 75% of guar gum degraded at 400°C. Therefore, the final decomposition temperature (FDT) is low (i.e., 320°C). The polymer decomposition temperature (PDT), T_{\max} , and the integral procedural decomposition temperature (IPDT) of guar gum were found to be 280, 310, and 318.8°C, respectively.

Guar gum-g-(4-vinylpyridine)

One step reaction was observed in the degradation of guar gum-g-(4-vinylpyridine) (Fig. 4). The rate of weight loss increased on increasing the temperature from 190 to 300°C but gradually decreased thereafter. The PDT was 240°C and T_{\max} was 300°C, close to the T_{\max} of guar gum. About 56% weight loss was observed between 200 to 400°C (Table V). The IPDT was found to be 266.5°C, which is lower than the

**Figure 4** Thermogravimetric trace of guar-g-(4-vinylpyridine).

IPDT of guar gum, indicating that grafting of 4-vinylpyridine lowers the thermal stability of graft copolymer. The decomposition temperature (T_D°) below 40% weight loss of graft copolymer is lower than the T_D° of guar gum, but above 40% the weight loss T_D° of graft copolymer was higher than the T_D° of guar gum. At 800°C, 25% char yield was obtained.

The authors express their gratitude to CSIR India, for financial assistance to carry out this work in the form of research project no. 01(1436)/97/EMR-II and RA to K. Taunk.

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