

Grafting of Poly(Acrylonitrile) onto Guar Gum Using Potassium Persulfate/Ascorbic Acid Redox Initiating System

U. D. N. BAJPAI,* VEENA MISHRA, and SANDEEP RAI

Polymer Research Laboratory, Department of Post Graduate Studies and Research in Chemistry, R. D. University, Jabalpur 482001, India

SYNOPSIS

The grafting of poly(acrylonitrile) onto guar gum in aqueous medium initiated by the potassium persulfate/ascorbic acid redox system has been studied gravimetrically at the temperature of $35 \pm 0.2^\circ\text{C}$ in the presence of atmospheric oxygen. A plausible mechanism of graft copolymerization has been suggested on the basis of experimental results. The effect of grafting on the water and saline retention capacities has been studied and compared with the values obtained for ungrafted guar gum. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Guar gum is a nonionic branched chain natural polymer. It consists of straight mannose units joined by β -D (1-4) linkage having β -D galactopyranose units to this linear chain by (1-6) linkages. Guar gum forms viscous, colloidal, dispersion when hydrated in cold water. It is being used as a viscosity builder and water binder in such industries as mining, textiles, explosives, paper, petroleum, etc. Although advantageous, this viscosity is difficult to control. Grafting of vinyl monomers onto wool, nylon fiber through redox initiators has been studied by several workers,¹⁻⁴ but the grafting of vinyl monomers onto water-soluble natural polymers like guar gum is very rare. With a view that grafted guar gum may find better applications in comparison to ungrafted material, this work of graft copolymerization of vinyl monomers onto guar gum has been undertaken in our laboratory.^{5a-d}

In the present communication we report the results of the grafting of poly(acrylonitrile) onto guar gum in aqueous medium using persulfate/ascorbic acid redox initiating system at $35 \pm 0.2^\circ\text{C}$ in the presence of atmospheric oxygen.

EXPERIMENTAL

Ascorbic acid and potassium persulfate (BDH, AnalaR) were used without further purification. Acrylonitrile was distilled in a stream of nitrogen before use. Guar gum was purified by dissolving it in water and reprecipitating with methanol. All solutions were prepared in double-distilled water.

Graft Copolymerization

A calculated amount of purified guar gum, acrylonitrile, and ascorbic acid were taken in water in a 150 mL flask and thermostated at $35 \pm 0.2^\circ\text{C}$ temperature. After 30 minutes a definite amount of persulfate was added to it and this time was taken as zero time. Total volume of reaction mixture was kept constant at 25 mL. The separation of guar gum-*g*-polyacrylonitrile from polyacrylonitrile (homopolymer) was done by pouring the reaction mixture, after desired intervals of time, into large quantity of distilled dimethylformamide. The method of calculating percentage grafting and the efficiency of grafting has been described earlier^{5a} by using the expressions

$$\% \text{ Grafting} = (W_1 - W_0)/W_0 \times 100$$

$$\% \text{ Efficiency} = (W_1 - W_0)/W_2 \times 100$$

* Present Address: Visiting Professor, Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimotocho, Osaka 558, Japan.

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Table I Percentage Grafting and Efficiency for Grafting of Polyacrylonitrile onto Guar Gum in Aqueous Medium^a

Expt.	Concentration of (K ₂ S ₂ O ₈)M/L	Percentage Grafting and Efficiency (given in parens)			
		Time (min)			
		15	30	45	60
1	10 × 10 ⁻³	33 (20.47)	48 (29.77)	54 (33.49)	60 (38.46)
2	20 × 10 ⁻³	33 (20.47)	49 (30.39)	56 (34.73)	72 (44.66)
3	30 × 10 ⁻³	47 (29.15)	84 (52.10)	98 (60.79)	111 (68.85)
4	40 × 10 ⁻³	50 (31.01)	88 (54.59)	99 (61.41)	115 (71.33)
5	50 × 10 ⁻³	54 (33.49)	98 (60.79)	116 (71.96)	121 (75.68)

^a Conducted at varying concentrations of potassium persulfate and at fixed concentrations of [Acrylonitrile]-8.8 × 10⁻² M/L [Ascorbic acid]-2.3 × 10⁻² M/L, [Guar gum]-0.1 g, Temperature-35 ± 0.2°C.

where W_0 is weight of guar gum, W_1 is the weight of grafted guar gum, and W_2 is the weight of monomer used.

Determination of Water and Saline Retention Capacity

The water retention capacity of the ungrafted as well as grafted guar gum was determined by a suction technique. A weighed amount of dried polymer was taken in a previously dried and weighed sintered glass crucible (G-4) which then was filled with 50 mL of water and after 30 minutes suction from a vacuum pump was applied. The glass crucible was then weighed to determine the amount of water retained per gram of the dried material and this was taken as water retention capacity. Similarly, saline retention capacity was determined by using 1% aqueous sodium chloride solution.

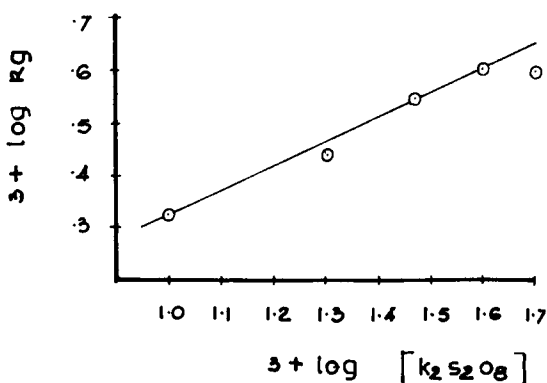


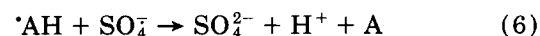
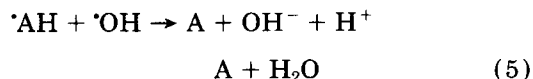
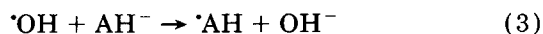
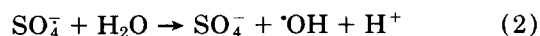
Figure 1 Double logarithmic plot of the rate of grafting (R_g , % grafting per minute) vs. concentration of potassium persulfate.

RESULTS AND DISCUSSION

Mechanism

Free radicals are being generated by the reaction between ascorbic acid and persulfate. Reaction between persulfate and ascorbic acid involves a chain mechanism⁶ due to the formation of sulfate ion radicals which are well-known chain carriers. The overall mechanism may be represented as:

Formation of free radicals:



Mechanism for graft copolymerization:

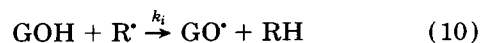
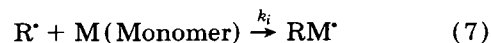


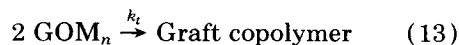
Table II Percentage Grafting and Efficiency for Grafting of Polyacrylonitrile onto Guar Gum in Aqueous Medium^a

Expt No.	Concentration of Ascorbic Acid M/L	Percentage Grafting and Efficiency (given in parens)			
		Time (min)			
		15	30	45	60
1	2.3×10^{-2}	33 (20.47)	49 (29.77)	54 (33.49)	61 (38.46)
2	2.7×10^{-2}	54 (33.49)	57 (35.35)	68 (42.18)	86 (53.34)
3	3.1×10^{-2}	65 (40.32)	68 (42.18)	84 (52.10)	92 (57.07)
4	3.4×10^{-2}	78 (48.38)	89 (55.21)	99 (61.41)	116 (71.96)
5	4.1×10^{-2}	75 (46.52)	96 (59.55)	112 (69.47)	123 (76.30)

^a Conducted at varying concentration of ascorbic acid and at a fixed concentration of [Acrylonitrile]– 8.8×10^{-2} M/L, [Persulfate]– 10×10^{-3} M/L, [Guar gum]–0.1 g, Temperature $35 \pm 0.2^\circ\text{C}$.



(Guar gum radical)



It is apparent from the above reactions that SO_4^- and/or A^{\cdot}H radicals may initiate the graft copolymerization by H abstraction from the guar gum backbone. However, we have proposed the generation of guar gum macroradical (GO^{\cdot}) by eq. (10) since initiation of vinyl polymerization is a faster reaction than H abstraction by primary radicals.

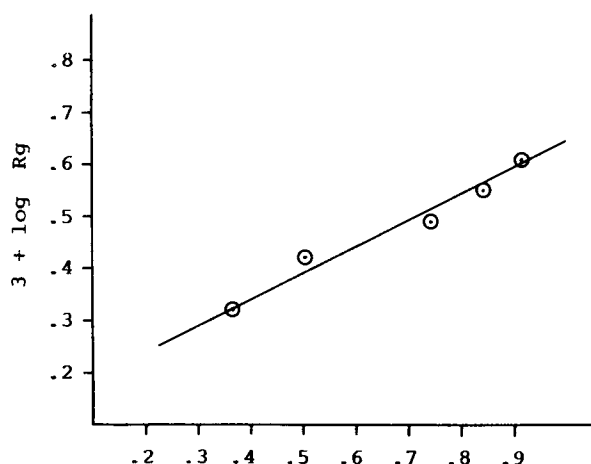


Figure 2 Double logarithmic plot of the rate of grafting vs. concentration of ascorbic acid.

The rate of grafting,

$$R_g = K [\text{GOM}_n^*] [\text{M}] \quad (14)$$

On applying steady-state conditions, the rate expression may be derived as,

$$R_g = K [\text{M}] [\text{S}_2\text{O}_8^{2-}]^{0.5} [\text{AA}]^{0.5} [\text{GOH}]^x \quad (15)$$

where AA stands for ascorbic acid and is equivalent to AH^{\cdot} . The value of x depends upon the concentration of the guar gum.

Potassium Persulfate Effect

The change in the percentage and efficiency of grafting at varying concentrations of persulfate (10.0 – 50.0×10^{-3} M/L) at fixed concentration of acrylonitrile (8.8×10^{-2} M/L), ascorbic acid (2.3×10^{-2} M/L) and guar gum (0.1 g) has been studied and the results are depicted in Table I.

The observed increase in percent grafting and efficiency of grafting with the increase in the concentration of persulfate is due to the generation of more primary free radicals [eq. (4)]. The number of propagating radicals increases, which in turn increases the number of grafting sites on the backbone of the guar gum. The observed order with respect to persulfate concentration as obtained from the slope of a curve in double log plot between rate of grafting and concentration of persulfate was found to be 0.5 (Fig. 1).

Ascorbic Acid Effect

The effect of ascorbic acid has been studied in the range (2.3 – 4.1×10^{-2} M/L) at fixed concentration

Table III Percentage Grafting and Efficiency for Grafting of Polyacrylonitrile onto Guar Gum in Aqueous Medium^a

Expt.	Concentration of Acrylonitrile M/L	Percentage Grafting and Efficiency (given in parens)			
		Time (min)			
		15	30	45	60
1	8.8×10^{-2}	33 (20.47)	48 (29.77)	54 (33.49)	62 (38.46)
2	13×10^{-2}	47 (19.43)	53 (21.91)	78 (32.25)	95 (39.28)
3	17×10^{-2}	54 (16.74)	65 (20.16)	106 (32.87)	123 (38.15)
4	22×10^{-2}	83 (20.59)	109 (27.04)	129 (32.009)	160 (39.70)
5	26×10^{-2}	109 (22.53)	122 (25.22)	142 (29.36)	177 (36.10)

^a Conducted at varying concentration of acrylonitrile and at fixed concentration of [Persulfate]- 10×10^{-3} M/L, [Ascorbic acid]- 2.3×10^{-2} M/L, [Guar gum]-0.1 g, Temperature $35 \pm 0.2^\circ\text{C}$.

of acrylonitrile (8.8×10^{-2} M/L), potassium persulfate (10.0×10^{-2} M/L), guar gum (0.1 g) and at temperature $35 \pm 0.2^\circ\text{C}$. It is observed that both percentage grafting and efficiency of grafting increase (Table II) with the increase in the concentration of ascorbic acid which may be due to the generation of more primary free radicals [(eqs.) 3 and 4]. These primary radicals in turn will generate more grafting sites by the mechanism discussed above.

The order with respect to ascorbic acid concentration, obtained from the double log plot (Fig. 2), has been found to be 0.5 matching with the value obtained in our rate expression.

Monomer Effect

The initial rate of grafting was found to increase with an increase in the concentration of the mono-

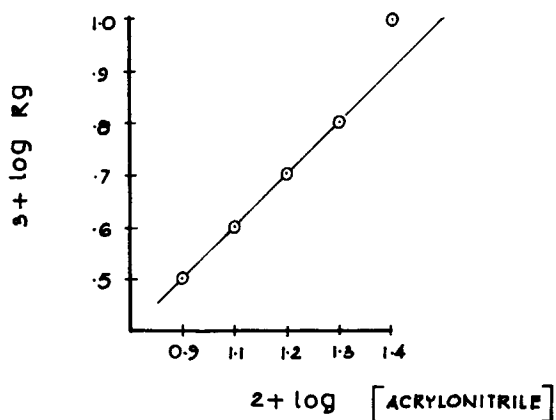


Figure 3 Double logarithmic plot of the rate of grafting vs. concentration of monomer.

mer, acrylonitrile, in the range 8.8 to 26.0×10^{-2} M/L when other parameters were kept constant (Table III). The increase in the rate of grafting as well as efficiency with the increase in acrylonitrile concentration may be due to two reasons viz., the formation of more M_n^* radicals generating more grafting sites and the availability of extra monomer molecules for grafting.

The order with respect to monomer concentration was found to be unity (Fig. 3).

Guar Gum Effect

The effect of the concentration of guar gum was studied in the range (0.1–0.4 g) with other ingredients at constant concentrations (Table IV). It was found that both percentage grafting as well as grafting efficiency decrease with the increase in guar gum concentration in the studied range which may be due to the increase in the viscosity of the medium causing hinderance in normal graft copolymerization.

Temperature Effect

The rate of grafting as well as the efficiency of grafting have been found to increase with the increase in temperature of the reaction medium from 25 to 50°C (Table V). This observed increase at higher temperature may be due to the:

1. Increased number of collisions between the monomer and guar gum molecules that results due to the viscosity of the medium,

Table IV Percentage Grafting and Efficiency for Grafting of Polyacrylonitrile onto Guar Gum in Aqueous Medium^a

Expt. No.	Concentration of Guar Gum in Mg	Percentage Grafting and Efficiency (given in parens)			
		Time (min)			
		15	30	45	60
1	100	33 (20.47)	48 (29.77)	54 (33.49)	62 (38.46)
2	120	29.16 (21.71)	35.83 (26.67)	43.33 (32.25)	54.16 (42.32)
3	140	25 (21.71)	32.85 (28.53)	37.85 (32.87)	46.42 (40)
4	160	13.75 (13.64)	18.125 (17.99)	36.875 (36.60)	30.625 (30.39)

^a At varying concentration of Guar gum and at fixed concentration of [Acrylonitrile]- 8.8×10^{-2} M/L, [Persulfate]- 10×10^{-3} M/L, [Ascorbic acid]- 2.3×10^{-2} M/L, Temperature- $35 \pm 0.2^\circ\text{C}$.

Table V Percentage Grafting and Efficiency for Grafting of Polyacrylonitrile onto Guar Gum in Aqueous Medium^a

Expt.	Temperature ($^\circ\text{C}$)	Percentage Grafting and Efficiency (given in parens)			
		Time (min)			
		15	30	45	60
1	25	30 (18.61)	40 (24.81)	50 (31.01)	60 (37.22)
2	30	32 (19.85)	44 (27.29)	52 (32.25)	60 (37.22)
3	35	33 (20.47)	48 (29.77)	54 (33.49)	62 (38.46)
4	40	36 (22.332)	52 (32.25)	57 (35.35)	67 (41.56)
5	45	40 (24.813)	54 (33.49)	59 (36.60)	72 (44.66)
6	50	47 (29.156)	57 (35.359)	67 (41.563)	73 (45.285)

^a Conducted at varying temperatures and at fixed concentration of [Acrylonitrile]- 8.8×10^{-2} M/L, [Persulfate]- 10×10^{-3} M/L, [Ascorbic acid]- 2.3×10^{-2} M/L, [Guar gum]-0.1 g.

2. Formation of more active sites on the guar gum backbone due to the enhanced rate of generation of primary free radicals,
3. Enhancement in the activity of monomer.

The overall energy of activation was calculated from the Arrhenius plot (Fig. 4) and the value was obtained to be 4.03 Kcal/mol within the temperature range $25\text{--}50^\circ\text{C}$. Such value has been obtained in several other redox systems.⁷

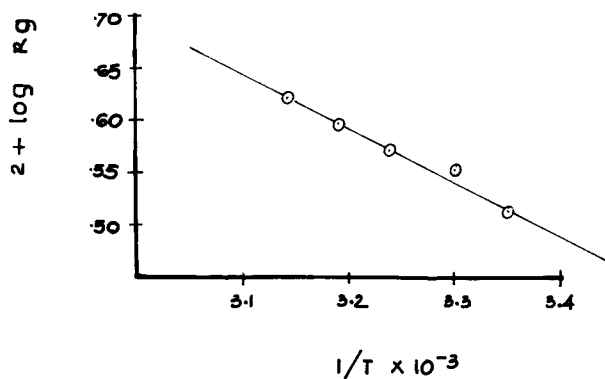


Figure 4 Arrhenius plot of the rate of grafting (R_g) vs. reciprocal of absolute temperature ($1/T$) of grafting; energy of activation (E_a) = 4.03 Kcal/mol.

Solvent Effect

The effect of such organic solvents as DMSO, MeOH, EtOH, and BuOH has been studied by the addition of 5% v/v of the solvent to the reaction medium. The rate of grafting as well as grafting efficiency were found to decrease in the presence of all the added solvents (Table VI). Such decrease in percentage grafting and in efficiency may be due to the consumption of persulfate (oxidant) in the oxidation of the added solvents, thereby decreasing the concentration available for the reaction with ascorbic acid to generate primary free radicals. The slug-

Table VI Percentage Grafting and Efficiency for Grafting of Polyacrylonitrile onto Guar Gum in Aqueous Medium^a

Expt. No.	Solvent	Percentage Grafting and Efficiency (given in parens)			
		Time (min)			
		15	30	45	60
1	Control	33 (20.47)	48 (29.77)	54 (33.49)	62 (38.46)
2	Butanol	30 (18.61)	27 (16.74)	47 (29.15)	57 (35.35)
3	Ethanol	24 (14.88)	31 (19.23)	44 (27.29)	55 (33.00)
4	Methanol	19 (11.78)	33 (20.47)	44 (27.29)	53 (32.87)
5	DMSO	11 (6.82)	27 (16.74)	37 (22.95)	50 (31.01)

^a At fixed concentration of [Acrylonitrile]- 8.8×10^{-2} M/L, [Persulfate]- 10×10^{-3} M/L, [Ascorbic acid]- 2.3×10^{-2} M/L, [Guar gum]-0.1 g, Temperature- $35 \pm 0.2^\circ\text{C}$ on addition of different water miscible organic solvents in 5% v/v.

Table VII Water Retention Value (WRV) and Saline Retention Value (SRV) of the Grafted Guar Gum with Varying Percentage Grafting

Sample No.		% Grafting	WRV	SRV
1	Guar gum	0.0	29.15	26.35
2	Guar gum-g-polyacrylonitrile	62.0	13.47	10.00
3	Guar gum-g-polyacrylonitrile	72.0	9.97	8.04
4	Guar gum-g-polyacrylonitrile	95.0	6.26	5.60

gish radicals obtained by the oxidation of added solvents are not capable of initiating a new chain.

Water and Saline Retention Properties of the Grafted Guar Gum

The water retention property of the guar gum is due to the interaction between hydroxyl groups of guar gum and water molecules through hydrogen bonding. The grafting of the vinyl monomers onto guar gum also occurs through the hydroxyl group present in its backbone, thereby decreasing the number of hydroxyl groups. Obviously, the water retention capacity of the grafted material should be less if the monomer grafted onto it has no extra hydrophilic groups in it. In the present case, both water retention as well as saline retention capacity of the guar gum have been decreased on the grafting of acrylonitrile onto guar gum. The decrease has been found to be dependent on percent grafting. The results are depicted in Table VII.

REFERENCES

1. I. William, E. R. Allen, and J. S. Racciato, Ger. Pat., 2,756,870 (1978).
2. R. Nordgren, U.S. Pat., 3,225,028 (1966).
3. D. H. Wheeler and J. L. Keen, U.S. Pat., 2,321,596 (1966).
4. Jpn. Pat., 80,165,009 (1981).
5. (a) U. D. N. Bajpai and S. Rai, *J. Appl. Polym. Sci.*, **35**, 1169 (1988); (b) U. D. N. Bajpai, A. Jain, and A. K. Bajpai, *Acta Polimerica*, **41**(11), 577 (1990); (c) U. D. N. Bajpai, Alka Jain, and Sandeep Rai, *J. Appl. Polym. Sci.*, **39**, 2187 (1990); (d) U. D. N. Bajpai and Alka Jain, *Acta Polimerica* (to appear).
6. U. S. Mehrotra and S. P. Mushran, *J. Ind. Chem. Soc.*, **47**, 41 (1970).
7. G. S. Misra and U. D. N. Bajpai, *Prog. Polym. Sci.*, **8**, 61-131 (1982).

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