Grafting of Acrylamide onto Guar Gum Using KMnO₄ / Oxalic Acid Redox System

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Synopsis

The grafting of acrylamide onto guar gum in aqueous medium initiated by KMnO₄/oxalic acid redox system has been studied gravimetrically at the temperature $35 \pm 0.2°C$. The effect of redox components, acrylamide concentration and quantity of guar gum has been studied in terms of percentage and efficiency of grafting. A plausible mechanism of grafting and a suitable rate expression has been suggested. The rate of grafting was found to increase with increase in temperature and concentrations of redox components and acrylamide, but, at high concentration of guar gum, the rate was found to decrease.

INTRODUCTION

Guar gum is a naturally occurring nonionic polysaccharide consisting of straight chain mannan with single membered galactose branches joined to two units of mannose by β-D-(1 → 4) linkages. Guar gum is galactomannan. It is derived from the seeds of guar plant "cyanaposis tetragonolobus," family Leguminosae. Guar gum can give very high viscosity even at 1% concentration in water. It is being used as a viscosity builder and water binders in many industries like mining, textile, explosive, paper, and petroleum, etc. Although advantageous, this viscosity is very difficult to control, and that is why guar gum is rarely used in its natural form. Solutions of guar gum are stable for a shorter time. It is fermented and enzymatically hydrolyzed by microorganisms. In order to remove these drawbacks, guar gum is modified in two ways: (1) derivatization of functional groups and (2) grafting of vinyl monomers.

Modification of guar gum by derivatization include carboxymethylation,[1,2] ethylation,[3] oxidation,[4] Phosphation,[5] and sulfation,[6] and it is shown that these modified guar gums will have better properties and applicability than unmodified or natural guar gum. Sufficient literature is available on the derivatization of guar gum, but available information about modification of guar gum by grafting of vinyl monomers onto it is rare.[7-10] By graft copolymerization the desirable properties of the original polymer are retained, and additional properties are provided by the addition.

Vinyl graft copolymerization through chemical initiation is an easier process than thermal, photochemical, and other methods of initiation because activation energy for the redox initiation is quite low in comparison to other initiation methods; therefore, graft copolymerization can be carried out at relatively low temperature producing high yield of grafted polymer. The

possibility of side reactions at low temperature is also negligible. Grafting of vinyl monomers onto wool, nylon fibers through redox initiators, has been investigated by several workers,[11] but the grafting of water-soluble vinyl monomers onto water-soluble natural polymer is quite rare.

Here we report the results of the grafting of acrylamide onto guar gum in aqueous medium using $KMnO_4$–oxalic acid redox system at $35 \pm 0.2°C$ in a nitrogen atmosphere.

EXPERIMENTAL

Acrylamide (E. Merck) was recrystallized twice from methanol (G. R.) and dried in vacuum. Oxalic acid and Potassium permanganate (B. D. H. Analar Grade) were used without further purification. Commercial guar gum was purified by dissolving in water and reprecipitating in methanol. All solutions were prepared in doubly distilled water.

Graft Copolymerization

Weighed amounts of purified guar gum and acrylamide were dissolved in 25 mL water in a two-necked flask. A definite amount of oxalic acid is added to the reaction flask, which was purged with purified nitrogen for about 30 min. A known amount of $KMnO_4$ was added. The time of addition of $KMnO_4$ was taken as zero time, and the graft copolymerization was carried out for the desired time. Polyacrylamide (homopolymer) formed during the graft copolymerization was separated using a methanol and water mixture. The guar gum-g-acrylamide along with some quantity of polyacrylamide formed in the system was poured in a mixture of methanol and water (35 : 15 v/v) whereby the homopolymer completely dissolves. Grafted material was dried and weighed. The percentage and efficiency of grafting were calculated according to Kojima et al.[2]:

$$\% \text{ grafting} = \frac{W_1 - W_0}{W_0} \times 100$$

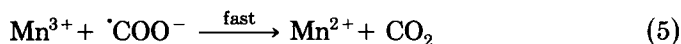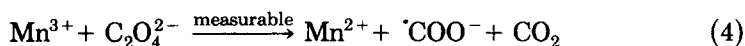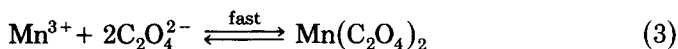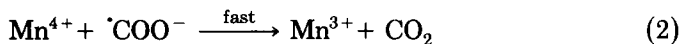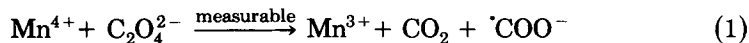$$\% \text{ efficiency} = \frac{W_1 - W_0}{W_2} \times 100$$

where W_1, W_0, and W_2 denote, respectively, the weight of grafted guar gum, the weight of original guar gum, and the weight of monomer used.

RESULTS AND DISCUSSION

Mechanism

In permanganate-containing redox systems, generally oxidant reacts first with monomer and generates active manganese dioxide, which then reacts with oxalic acid to give primary free radicals. Launer and Yost[13] for the first

time suggested a mechanism involving the following steps:

$$Mn^{4+} + C_2O_4^{2-} \xrightarrow{\text{measurable}} Mn^{3+} + CO_2 + {}^{\cdot}COO^- \tag{1}$$

$$Mn^{4+} + {}^{\cdot}COO^- \xrightarrow{\text{fast}} Mn^{3+} + CO_2 \tag{2}$$

$$Mn^{3+} + 2C_2O_4^{2-} \xrightleftharpoons{\text{fast}} Mn(C_2O_4)_2 \tag{3}$$

$$Mn^{3+} + C_2O_4^{2-} \xrightarrow{\text{measurable}} Mn^{2+} + {}^{\cdot}COO^- + CO_2 \tag{4}$$

$$Mn^{3+} + {}^{\cdot}COO^- \xrightarrow{\text{fast}} Mn^{2+} + CO_2 \tag{5}$$

Weiss[14] suggested that the continuous production of active ${}^{\cdot}C_2O_4^{2-}$ in this system is governed by the reaction

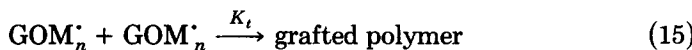$$Mn^{3+} + C_2O_4^{2-} \rightarrow Mn^{2+} + {}^{\cdot}C_2O_4^- \tag{5'}$$
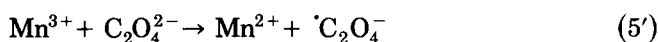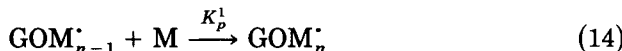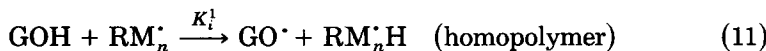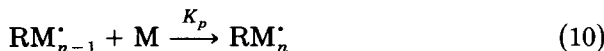
The formation of free radicals (${}^{\cdot}COO^-$ and ${}^{\cdot}C_2O_4^-$) has also been confirmed by end group technique[15]

Graft copolymerization may be represented as:

$$Mn^{4+} + Red \xrightarrow{K_1} Mn^{3+} + R^{\cdot} \tag{6}$$

$$Mn^{3+} + Red \xrightarrow{K_2} Mn^{2+} + R^{\cdot} \tag{7}$$
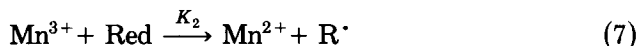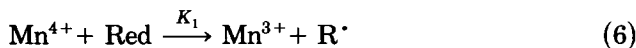
(where $R^{\cdot}$ stands for ${}^{\cdot}COO^-$ or ${}^{\cdot}C_2O_4^{2-}$ radicals)

$$R^{\cdot} + M \xrightarrow{K_i} RM^{\cdot} \tag{8}$$

$$RM^{\cdot} + M \xrightarrow{K_p} RMM^{\cdot} \tag{9}$$

$$RM_{n-1}^{\cdot} + M \xrightarrow{K_p} RM_n^{\cdot} \tag{10}$$

$$GOH + RM_n^{\cdot} \xrightarrow{K_i^1} GO^{\cdot} + RM_nH \quad \text{(homopolymer)} \tag{11}$$

$$GO^{\cdot} + M \xrightarrow{K_p^1} GOM^{\cdot} \tag{12}$$

$$GOM^{\cdot} + M \xrightarrow{K_p^1} GOMM^{\cdot} \tag{13}$$

$$GOM_{n-1}^{\cdot} + M \xrightarrow{K_p^1} GOM_n^{\cdot} \tag{14}$$

$$GOM_n^{\cdot} + GOM_n^{\cdot} \xrightarrow{K_t} \text{grafted polymer} \tag{15}$$

It is apparent from the above mechanism that ${}^{\cdot}C_2O_4^-$ or ${}^{\cdot}COO^-$ can initiate the graft polymerization by abstracting H^- atom from the backbone polymer guar gum to generate the macroradical (GO${}^{\cdot}$). However, the generation of

macroradical by eq. (11) is more likely, since initiation of vinyl polymerization is a faster reaction than H^- abstraction by primary radicals because primary radicals ($R^{\cdot}$) will be more reactive towards monomer to form macroradical in comparison to the abstraction of hydrogen atom from guar gum. It may be due to the following:

1. In reaction medium the monomer molecule will diffuse more readily to radical ($R^{\cdot}$) in priority to long backbone chain of guar gum. The smaller size of monomer molecules will make them more diffusable,[16] and thus they will preferably react with primary radical ($R^{\cdot}$).

2. The addition of primary radicals to monomer molecules simply involves the rearrangement of π electrons to form a single covalent bond while the process of abstraction of hydrogen atom from the backbone chain of guar gum involves addition of hydrogen atom to radical ($R^{\cdot}$) preceeded by the breaking of the O—H bond also. Obviously the energy requirements for later reaction should be higher than the former one favoring the formation of homomacroradical.
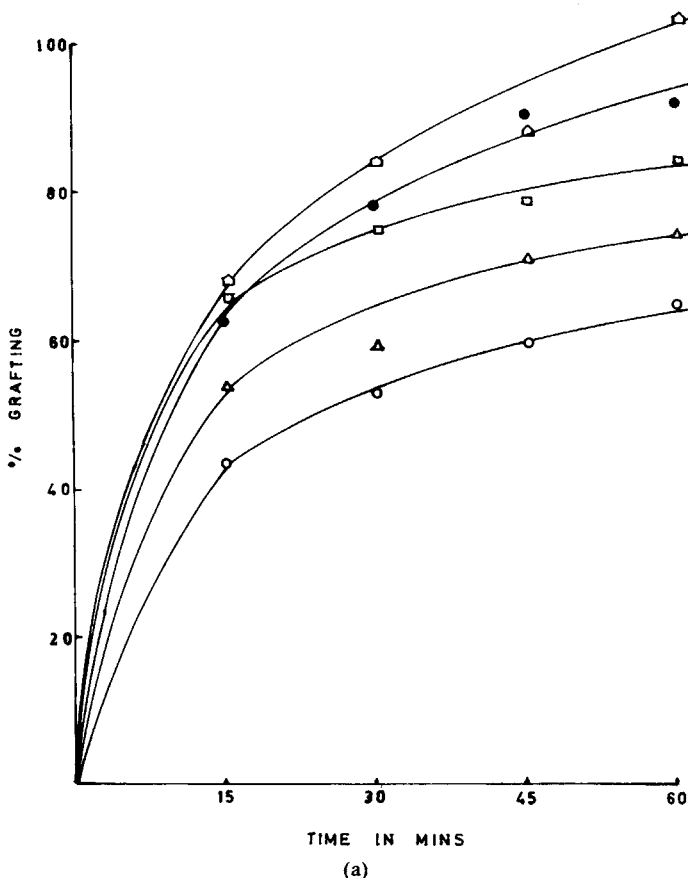

(a)

Fig. 1.   Effect of oxalic acid concentration on (a) % grafting and (b) % efficiency at [acrylamide] = 20×10^{-2} mol/L, [KMnO$_4$] = 20×10^{-4} mol/L, [guar gum] = 0.10 g, temperature = $35 \pm 0.2°C$. [oxalic acid] (mol/L): (○) 20×10^{-3}; (△) 30×10^{-3}; (□) 40×10^{-3}; (⬦) 50×10^{-3}; (●) 70×10^{-3}. (c) Double logarithmic plot of rate of grafting vs. oxalic acid concentration.

3. The primary radicals $(R^{\cdot})$ are more stable and therefore less reactive than macroradical $(RM_n^{\cdot})$. Their less reactivity or more stability is due to the greater number of resonating structures of primary radicals $({}^{\cdot}COO^{-}$ and $C_2^{\cdot}O_4^{2-})$ than macroradical $(RM_n^{\cdot})$.

4. The primary radicals $(R^{\cdot})$ prefer to add on monomer molecule because the newly formed radical $(RM^{\cdot})$ becomes more stable than the parent $(R^{\cdot})$ due to resonance while the guar gum radical $(GO^{\cdot})$ will not be as stable.

Rate Expression

Rate of grafting

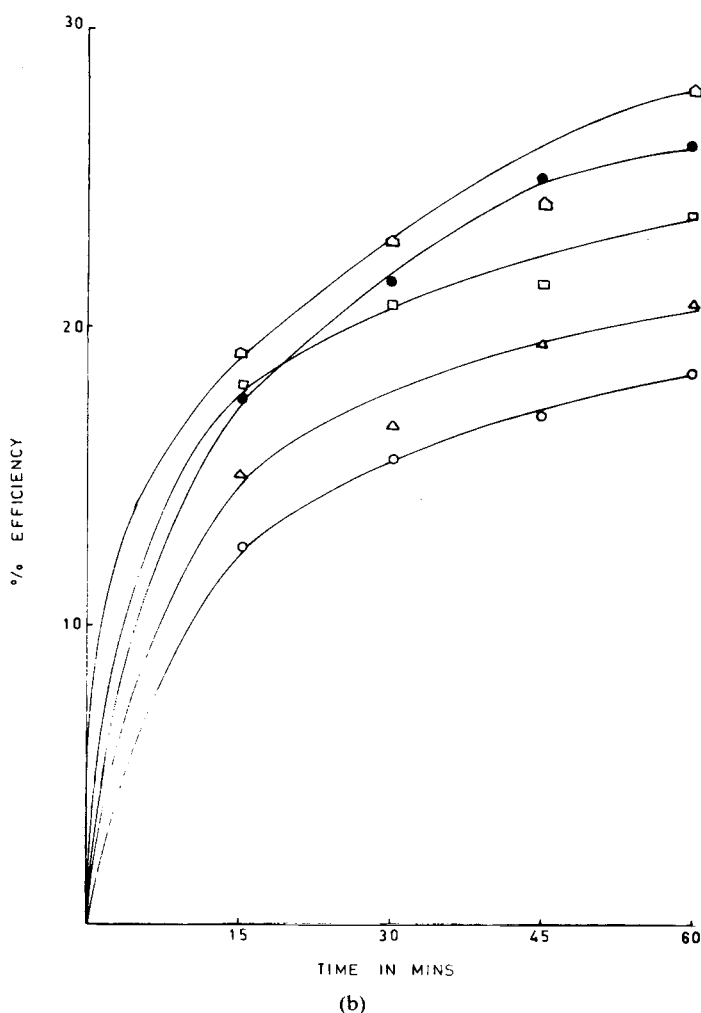$$R_g = K_p[\text{GOM}^{\cdot}][\text{M}]$$

Fig. 1. (Continued from the previous page.)

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

$$R_g = K_p \left(\frac{K_d K_i^1}{K_t} \right)^{1/2} [M][Red]^{1/2} \{ K_1 [Mn^{4+}] + K_2 [Mn^{3+}] \}^{1/2}$$

$$\times \left\{ \frac{[GOH]}{K_p[M] + K_i^1[GOH]} \right\}^{1/2}$$

The numerical value of the factor $\{ K_1[Mn^{4+}] + K_2[Mn^{3+}] \}^{1/2}$ will depend on the value of $[Mn^{3+}]$ ions as, besides, the eq. (7) $[Mn^{3+}]$ ions are being consumed in other reactions [also eqs. (3) and (5)].

This is true also as $[Mn^{4+}]$ ions are derived by reaction between monomer and oxidant only. Here the value of the term $K_p[M] + K_i^1[GOH]$ will be greater than $[GOH]$.

The above rate equation may also be written as

$$R_g = K_p \left(\frac{K_d K_i^1}{K_t} \right)^{1/2} [M][Red]^{1/2}[OX]^x[GOH]^y$$

Here value of x will be decided by the concentrations of $[Mn^{3+}]$ ions and will have a value greater than 0.5, which has also been found to be true as the
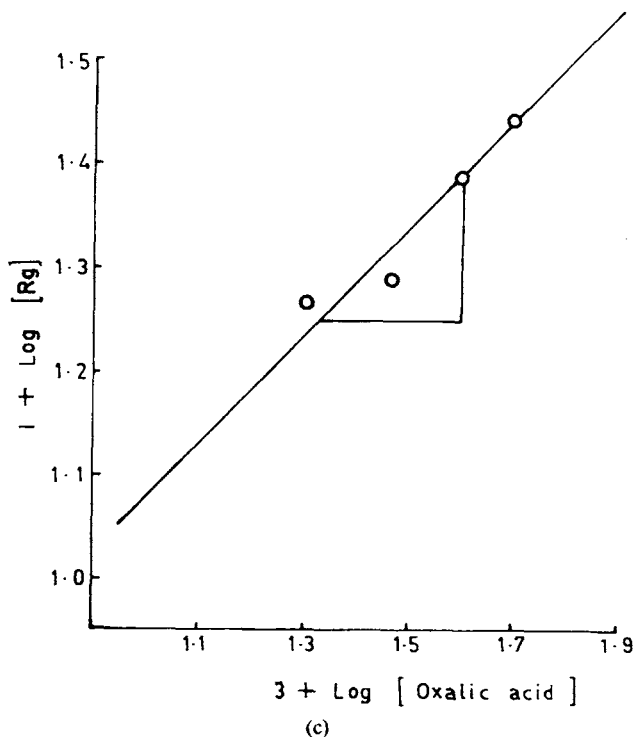

(c)

Fig. 1. *(Continued from the previous page.)*

exponent over oxidant has been calculated to be 0.83.

Our experimental results agree with this kinetics scheme little deviations have also been explained in the text. Therefore,

$$\text{rate of grafting} = K\,[\text{M}][\text{Red}]^{1/2}[\text{OX}]^{x}[\text{GOH}]^{y}$$

where y may vary depending upon its concentrations.

Effect of Redox Components

Oxalic Acid Effect

The effect of oxalic acid was studied in the range $(20–70 \times 10^{-3}$ mol/L$)$ at fixed concentrations of acrylamide $(20 \times 10^{-2}$ mol/L$)$ and $KMnO_4$ $(20 \times 10^{-4}$ mol/L$)$.

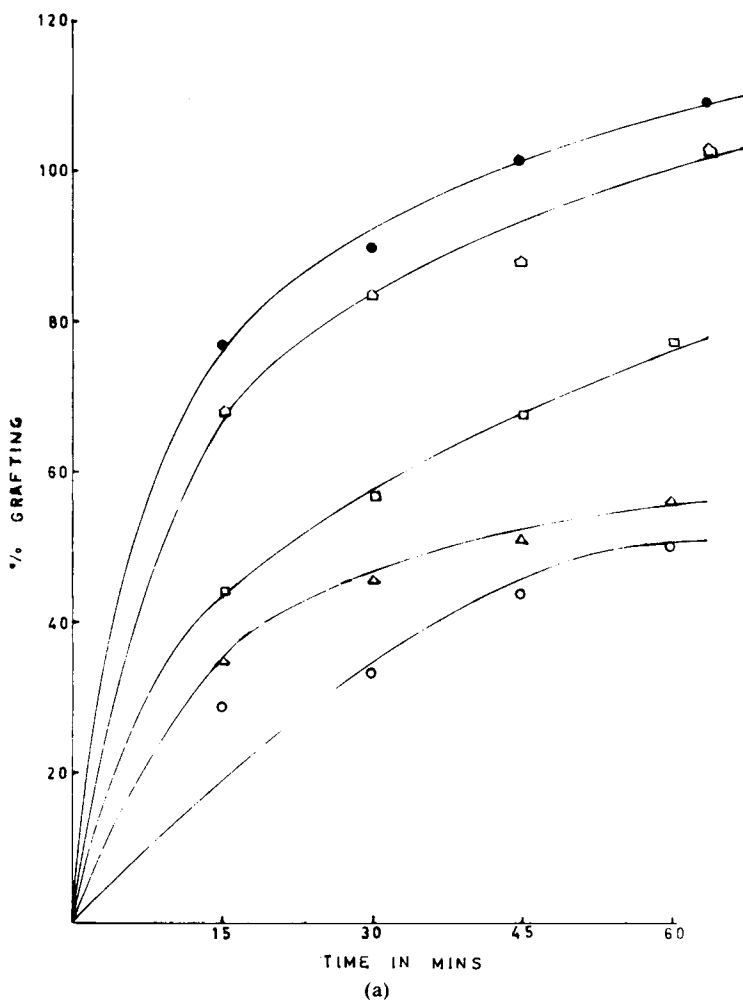Fig. 2.   Effect of $KMnO_4$ concentration on (a) % grafting and (b) % efficiency at [acrylamide] = 20×10^{-2} mol/L, [guar gum] = 0.10 g, [oxalic acid] = 50×10^{-2} mol/L, temperature = $35 \pm 0.2°C$. [$KMnO_4$] (mol/L): ($\bigcirc$) 8.0×10^{-4}; ($\triangle$) 12×10^{-4}; ($\square$) 16×10^{-4}; ($\ominus$) 20×10^{-4}; ($\bullet$) 28×10^{-4}. (c) Double logarithmic plot of rate of grafting vs. $KMnO_4$ concentration.

As shown in the Figures 1(a) and 1(b) that both percent grafting and efficiency increases with oxalic acid concentration up to certain range. Increase in the amount of oxalic acid brings about an increase in the numbers of free radicals ($\cdot C_2O_4^{2-}$ or $\cdot COO^-$) according to eqs. (1), (3), and (5'), thereby increasing both percent and efficiency of grafting.

But further increase (50×10^{-3} mol/L) causes a decrease in percent and efficiency of grafting. It may be due to the reason that, at higher concentration of oxalic acid, the rate of generation as well as the concentration of reactive species (Mn^{3+}) is suppressed because of the increased rate of side reactions like

$$MnO_2 + 2H^+ \rightarrow Mn^{2+} + H_2O + [O]$$
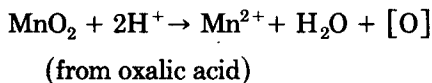
(from oxalic acid)

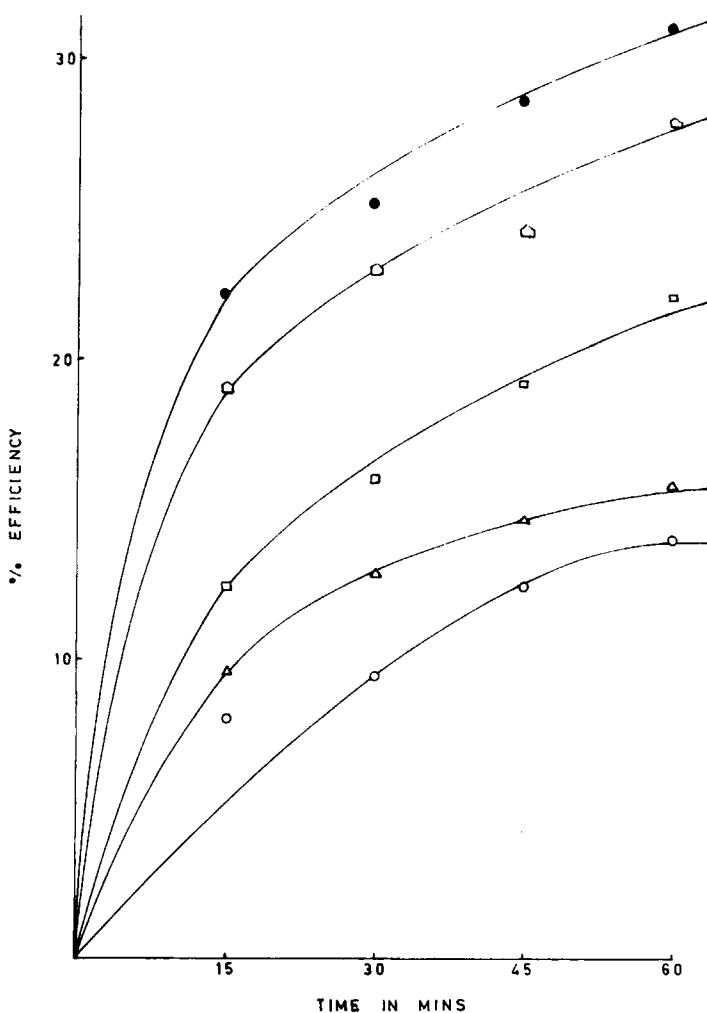which continually produce inhibiting oxygen. This idea finds support from the

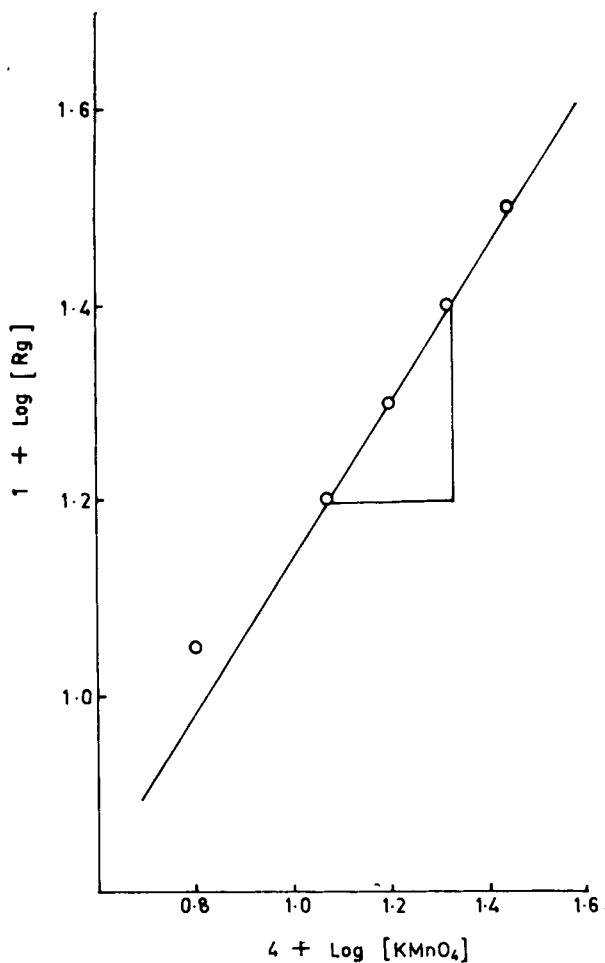Fig. 2. (*Continued from the previous page.*)

observation of Launer and Yost[13] that at higher ratio of oxalic acid to permanganate the production of carboxyl radical intermediates is suppressed.

The order of reaction with respect to oxalic acid was determined from the double log plot between rate of grafting (% grafting/time) and oxalic acid concentration in mol/L. It was found to be 0.48, indicating a bimolecular termination process [Fig. 1(c)].

KMnO$_4$ Effect

Figures 2(a) and 2(b) represent the change in percent and efficiency of grafting at varying concentrations of the KMnO$_4$ (8.0–28 × 10^{-4} mol/L) and fixed concentrations of the oxalic acid (50 × 10^{-3} mol/L) and guar gum.

It is obvious from the figures that the increase in catalyst concentration results in an increase in the percentage and efficiency of grafting. Since oxalic acid remains always in excess, this behaviour is quite expected only because of increased rate of generation of primary radicals [eqs. (1)–(5)] the number of
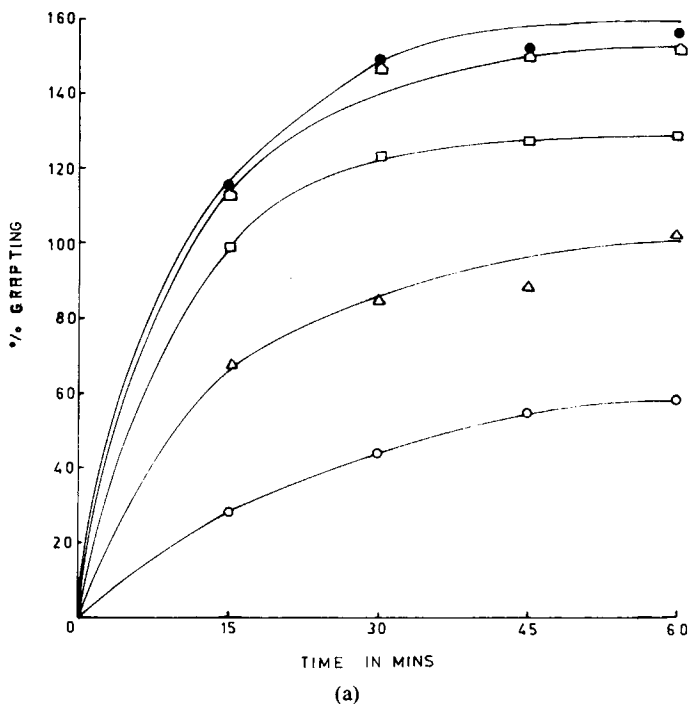

Fig. 2.   (*Continued from the previous page.*)

Fig. 3. (a) Effect of acrylamide concentration on % grafting. [Guar gum] = 10 g, [oxalic acid] = 50 × 10⁻³ mol/L, [KMnO₄] = 20 × 10⁻⁴ mol/L, temperature = 35 ± 0.2°C. [Acrylamide] (mol/L): (O) 10 × 10⁻²; (△) 20 × 10⁻²; (□) 30 × 10⁻²; (◇) 40 × 10⁻²; (●) 50 × 10⁻². (b) Double logarithmic plot of rate of grafting vs. acrylamide concentration.

propagating radicals and also the number of grafting species on the backbone of guar gum. Order of reaction with respect to $KMnO_4$ concentration was found to be 0.83 as shown in Figure 2(c), which is a little higher than half normally observed in bimolecular termination process. It may be due to some dissolved metal ions or other species in the system taking part in the termination step, shifting bimolecular termination to unimolecular.

The deviation from normal half-order dependence to a slightly higher value indicates that, while quadratic termination is predominant, linear termination also occurs to a small extent. The nature of the species which take part in the first order termination of polymer radicals is not evident. The mixing of the two modes of termination is basically responsible for the slightly higher value in the catalyst exponent.[17]

Monomer Dependence

The initial rate of grafting was found to increase with an increase in initial concentration of monomer [Fig 3(a)] in the range $10–50 × 10^{-2}$ mol/L, keeping other ingredients constant.

There is a marked increase in graft yield with increasing monomer concentration. Since the copolymerization reaction was carried out at the same
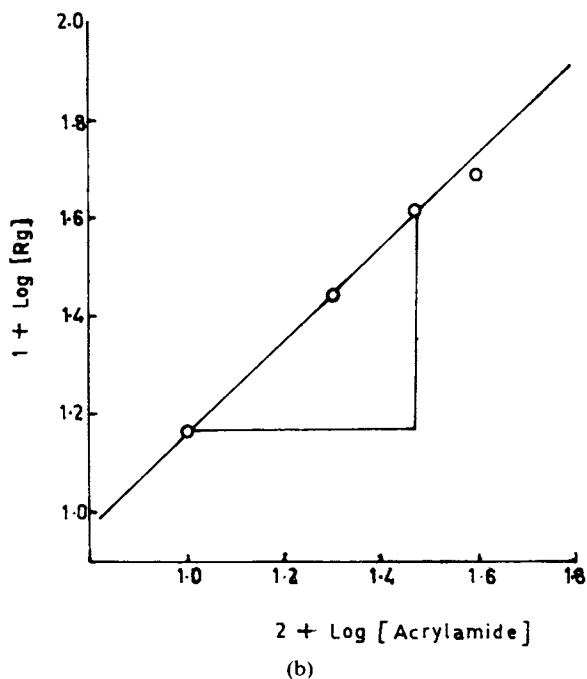
Fig. 3.   (*Continued from the previous page.*)

temperature and at the same reaction conditions, it is possible that the concentration, nature, and efficiency of the free radicals and other species generated during the process of grafting would be the same. The higher rate of grafting observed upon increasing the monomer concentration in this system could be attributed to the reason that the increase in monomer concentration of availability of monomer molecules for grafting increases; thereby grafting increases.

Order of reaction with respect to acrylamide concentration was found to be 0.93 [Fig. 3(b)].

Guar Gum Effect

The effect of guar gum concentration on grafting was studied in the range 0.05–0.25 g at fixed concentrations of acrylamide (20×10^{-2} mol/L), $KMnO_4$ (20×10^{-4} mol/L), and oxalic acid (50×10^{-3} mol/L).

As shown in Tables Ia and Ib, both percent and efficiency of grafting increases (up to 0.10 g) with guar gum concentration.

Increase in percent grafting and efficiency at a little higher concentration may be due to availability of more grafting sites. It is also possible that some of the guar gum molecules react with primary radicals to generate backbone macroradicals such as
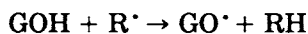
$$GOH + R^{\cdot} \rightarrow GO^{\cdot} + RH$$

TABLE Ia
Effect of Guar Gum Concentration on Percent Grafting[a]

Wt of guar gum (g)	% Grafting after			
	15 min	30 min	45 min	60 min
0.05	46.8	78.8	81.6	99.6
0.10	67.8	84.2	88.2	102.8
0.15	38.5	54.8	66.4	70.4
0.20	25.2	38.8	49.9	56.4
0.25	28.2	40.2	48.2	56.6

[a] Oxalic acid = 50×10^{-3} mol/L $KMnO_4 = 20 \times 10^{-4}$ mol/L. Acrylamide = 20×10^{-2} mol/L, temperature = $35 \pm 0.2°C$.

TABLE Ib
Effect of Guar Gum Concentration on Percent Efficiency[a]

Wt of guar gum (g)	% Efficiency			
	15 min	30 min	45 min	60 min
0.05	13.1	22.1	23.0	28.0
0.10	19.0	23.6	24.8	29.0
0.15	11.0	15.4	18.6	19.8
0.20	7.0	11.0	14.0	15.8
0.25	8.2	11.3	13.5	15.9

[a] See footnote to Table Ia.

But after a certain quantity of guar gum (0.10 g), there is a decrease in grafting. The decrease in grafting rate at a higher concentration of guar gum may be due to gel effect,[18] i.e., increase in viscosity of the medium causes hinderance in normal graft copolymerization.

Temperature Dependence

The effect of temperature on graft copolymerization was studied in the range 25–50°C at fixed concentrations of acrylamide (20×10^{-2} mol/L, oxalic acid (50×10^{-3} mol/L) $KMnO_4$ (20×10^{-4} mol/L), and guar gum.

The overall activation energy as calculated from the slope of the Arrhenius plot (Fig. 4) is 9.17 kcal/mol within the temperature range 25–50°C.

As expected, increasing the polymerization temperature results in an increase in % grafting. The increase in grafting percentage at higher temperature may be due to the following:

1. When the temperature of the reaction medium increases, viscosity of the medium decreases, which in turn increases the mobility of the backbone chain of the guar gum polymer; thus in reduced viscous medium the backbone coil is little extended due to which the sites for grafting of vinyl monomer increase.

2. With increase in temperature the rate of generation of primary radicals increases, which consequently brings about an increase in the grafting rates.

3. Grafting onto polymer involves the abstraction of the H atom by macroradical. For the vinyl chain it has been found that, on increasing the
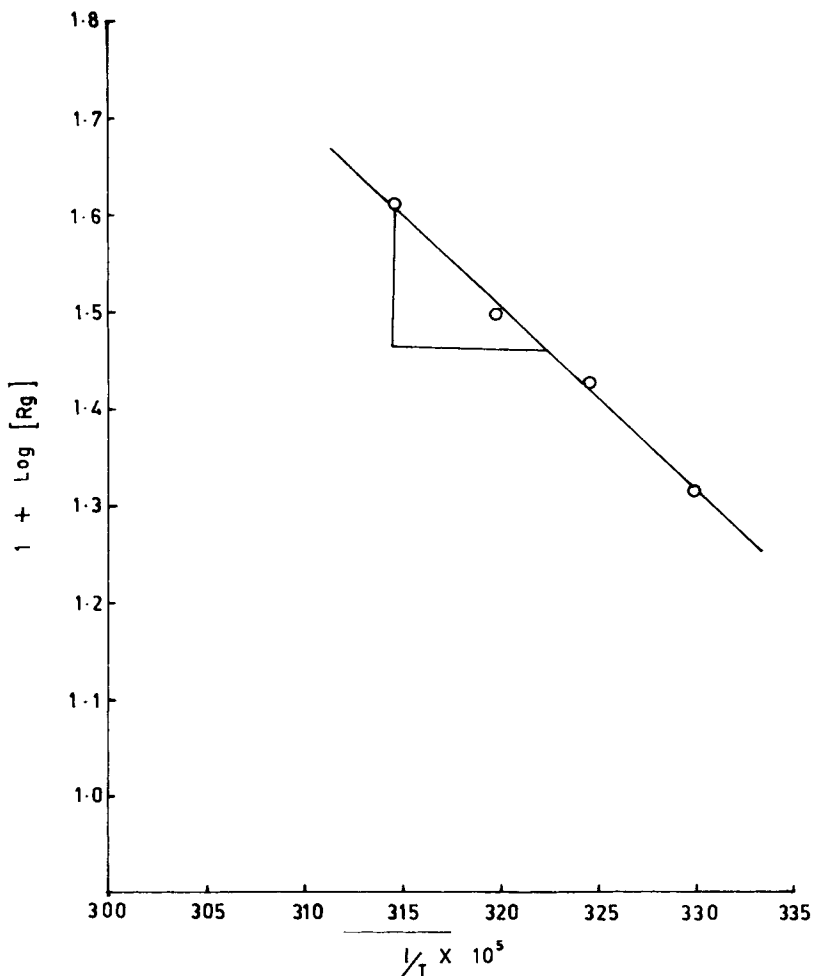
Fig. 4. Arrhenius plot of the rate of grafting (R_g) vs. reciprocal of absolute temperature (T) of polymerization.

temperature, the rate of hydrogen abstraction also increases,[19] which results in an enhanced rate.

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