Polymerization of Acrylamide Using Mandelic Acid / Permanganate Redox System in Acidic Medium

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Synopsis

A combined system of potassium permanganate and mandelic acid was found to initiate vinyl polymerization, specifically acrylamide. A study of the reaction kinetics of this system showed that free radicals are formed. The energy of activation was found to be 3.54 kcal/° mol in the temperature range 27–40°C, in nitrogen atmosphere.

INTRODUCTION

Water-soluble polymers of desired molecular weight can be synthesized by the use of a wide variety of chemicals called regulators or modifiers. The regulators not only control the molecular weight, but impart technically desirable properties such as plasticity, hardness, tensile strength, solubility, etc. Low molecular weight polymers find extensive use as dispersing and antiprecipitating agents in the petroleum and paper industry. As such they are used in mineral processing, to prevent scale formation in tanks and pipes and to prevent blinding of filter cloths due to the precipitation of calcium carbonate or calcium sulfate from the supersaturated process solutions. These polymers have also proved effective as flocculant modifiers[1] and as suspending agents in the leaching of high solid pulps (50–60% solids).[2]

Several acrylamide polymer flocculants have been tested as additives to improve percolation rates of old mill tailings to be used as mine back-fill materials.[3] The kinetics of oxidation of mandelic acid has been extensively studied by a number of workers[4,5a] and the formation of free radical has also been reported.[5b] Mandelic acid was found to initiate polymerization of acrylamide using $KMnO_4$ as an oxidant. The system was studied to examine whether this system followed the same kinetic features of vinyl polymerization by radicals of other hydroxy acids.[6a,b]

EXPERIMENTAL

Reagents

Acrylamide was recrystallized twice from methanol (G.R.) and dried in vacuum. Mandelic acid used was from BDH (U.K.). All other reagents were of AR or equivalent quality. The solvent, conductivity water, was prepared by

redistilling distilled water to which a small quantity of alkaline permanganate was added.
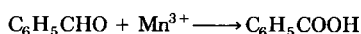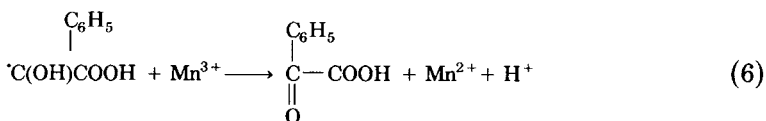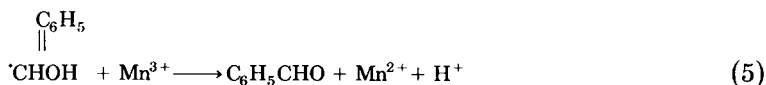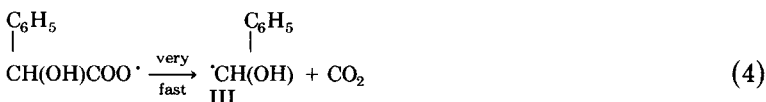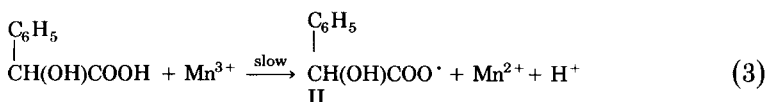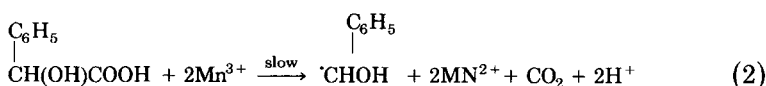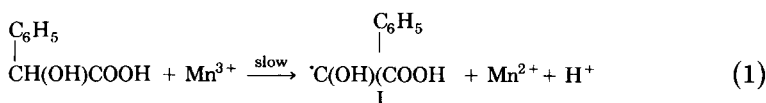
Polymerization Procedure

The polymerization was followed by a quantitative estimation of double bonds in acrylamide as described by Wallace and Young.[7] The experimental procedure was essentially the same as given by Misra et al.[8] The conversion was calculated by the formula given by Misra and Rebello.[9]

RESULTS AND DISCUSSION

Mechanism

It is well known that mandelic acid reacts with permanganate to form benzaldehyde, which is further oxidized to benzoic acid. In the polymerization of acrylamide by the $KMnO_4$–Mandelic acid redox pair, the manganese dioxide produced by the reaction between acrylamide and permanganate reacts with mandelic acid to yield Mn^{3+} ions. These Mn^{3+} ions then generate active free radicals with mandelic acid. Besides initiating polymerization, the primary radicals may undergo further reactions.

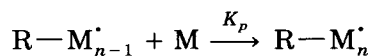The following reaction mechanism has been proposed:

$$\underset{\text{CH(OH)COOH}}{\overset{C_6H_5}{|}} + Mn^{3+} \xrightarrow{\text{slow}} \underset{\overset{\cdot C(OH)(COOH}{I}}{\overset{C_6H_5}{|}} + Mn^{2+} + H^+ \tag{1}$$

$$\underset{\text{CH(OH)COOH}}{\overset{C_6H_5}{|}} + 2Mn^{3+} \xrightarrow{\text{slow}} \underset{\cdot CHOH}{\overset{C_6H_5}{|}} + 2MN^{2+} + CO_2 + 2H^+ \tag{2}$$

$$\underset{\text{CH(OH)COOH}}{\overset{C_6H_5}{|}} + Mn^{3+} \xrightarrow{\text{slow}} \underset{\overset{CH(OH)COO\,\cdot}{II}}{\overset{C_6H_5}{|}} + Mn^{2+} + H^+ \tag{3}$$

$$\underset{\text{CH(OH)COO}\cdot}{\overset{C_6H_5}{|}} \xrightarrow[\text{fast}]{\text{very}} \underset{\overset{\cdot CH(OH)}{III}}{\overset{C_6H_5}{|}} + CO_2 \tag{4}$$

$$\underset{\cdot CHOH}{\overset{C_6H_5}{||}} + Mn^{3+} \longrightarrow C_6H_5CHO + Mn^{2+} + H^+ \tag{5}$$

$$\underset{\cdot C(OH)COOH}{\overset{C_6H_5}{|}} + Mn^{3+} \longrightarrow \underset{\underset{O}{\overset{||}{C}}{-}COOH}{\overset{C_6H_5}{|}} + Mn^{2+} + H^+ \tag{6}$$

$$C_6H_5CHO + Mn^{3+} \longrightarrow C_6H_5COOH$$

Free radicals I, II, or III (say $R\cdot$) may initiate polymerization or lead to formation of products in the reaction system. Kemp and Waters [10a,b] have

suggested formation of III in the cerium oxidation of mandelic acid. For 1 mol of mandelic acid 2 eq of Mn^{3+} are used.
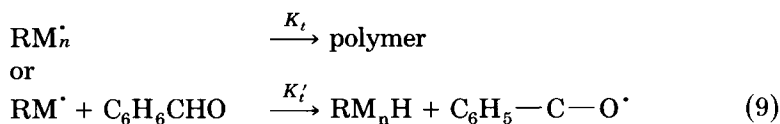
Initiation:

$$R^{\cdot} + M \xrightarrow{K_i} RM^{\cdot} \qquad (7)$$
$$\text{(monomer)}$$

Propagation:

$$RM^{\cdot} + M \xrightarrow{K_p} RMM^{\cdot} \qquad (8)$$

$$R{-}M_{n-1}^{\cdot} + M \xrightarrow{K_p} R{-}M_n^{\cdot}$$

Termination:

$$RM_n^{\cdot} \xrightarrow{K_t} \text{polymer}$$
or
$$RM^{\cdot} + C_6H_6CHO \xrightarrow{K_t'} RM_nH + C_6H_5{-}C{-}O^{\cdot} \qquad (9)$$

Benzaldehyde may bring about termination of the growing macroradical chain. The rate remains unaffected on increasing the concentration of mandelic acid. Independence of rate with respect to mandelic acid (MA) is observed at some concentrations.

Rate Expression

A rate expression may be derived by determining the concentration of free radicals by applying the steady state assumption [eq. (2)]. Now,

$$\frac{d}{dt}[R^{\cdot}] = k_1[MA][Mn^{3+}]^2 - K_i[R^{\cdot}][M] \qquad (10)$$

Applying steady state treatment, i.e.,

$$\frac{d}{dt}[R^{\cdot}] = 0$$

or, from eq. (10), we have

$$R^{\cdot} = \frac{k_1[MA][Mn^{3+}]^2}{K_i[M]} \qquad (11)$$

According to the kinetics of free-radical polymerization,

$$R_i = R_t$$

or

$$K_i[R^{\cdot}][M] = K_t[RM_n^{\cdot}] + K_t'[RM_n^{\cdot}][BA]$$

where [BA] stands for benzaldehyde concentration, or

$$\left[\mathrm{RM}_n^{\cdot}\right] = \frac{K_i[\mathrm{R}^{\cdot}][\mathrm{M}]}{K_t + K_t'[\mathrm{BA}]}$$

$$= \frac{K_i k_1[\mathrm{MA}][\mathrm{Mn}^{3+}]^2[\mathrm{M}]}{K_i K_t + K_t'[\mathrm{BA}][\mathrm{M}]}$$

$$= \frac{k_1[\mathrm{MA}][\mathrm{M}_n^{3+}]^2}{K_t + K_t'[\mathrm{BA}]} \tag{12}$$

Now

$$R_p = K_p\left[\mathrm{RM}_n^{\cdot}\right][\mathrm{M}]$$

or

$$R_p = \frac{K_p k_1[\mathrm{MA}][\mathrm{Mn}^{3+}]^2[\mathrm{M}]}{K_t + K_t'[\mathrm{BA}]} \tag{13}$$

Equation (13) is in agreement with our results which are discussed in detail in the next subsection.

Activator and Catalyst Dependence

The initial rate of polymerization and the limiting conversion were found to increase over a small range (8.19×10^{-2}–1.0×10^{-1} mol/dm^3) of activator, at fixed concentrations of catalyst (1.5×10^{-2} mol/dm^3 and monomer (10×10^{-2} mol/dm^3). In ideal redox systems, increase in initial rate as well as total conversion is due to formation of larger quantity of initiating free radicals. An enhancement in rate would therefore be expected at higher concentrations of mandelic acid. The same has been observed in the present system also in the above-mentioned concentration range. At a higher concentration of 2.47×10^{-1} mol/dm^3, decrease in initial rate as well as total conversion was observed, probably due to nonavailability of catalyst (Fig. 1).

The mechanism proposed predicts the formation of free radicals which are resonance-stabilized. The least stable radical initiates polymerization while others lead to formation of benzaldehyde, a known chain transfer agent. Chain transfer to benzaldehyde may also not be ruled out. The growing polymer chain may attack the benzaldehyde molecule, thus leading to termination [Eq. (9)].

The initial rates were found to be high in comparison to total conversion because as the reaction proceeds benzaldehyde is formed. Chain transfer to benzaldehyde brings about retardation in the rate, as radicals produced by chain transfer have lower activity. The primary radicals are able to initiate polymerization more efficiently than radicals formed by chain transfer.[11] In the presence of a chain transfer agent, whether retardation or complete
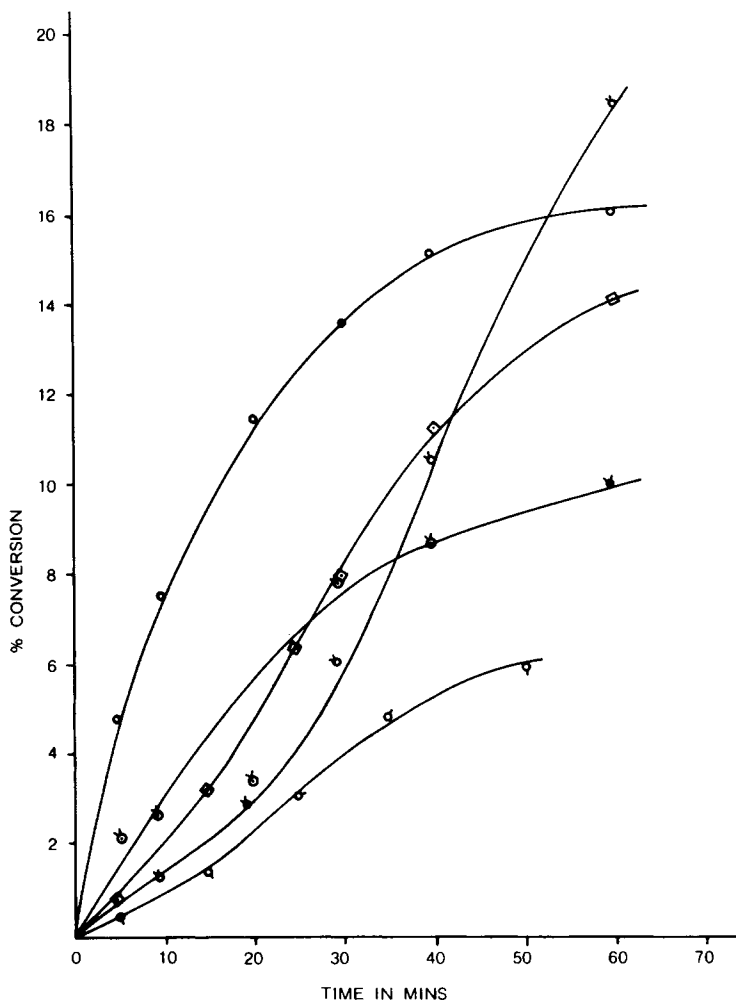
Fig. 1. Time versus % conversion curves for the polymerization of acrylamide with varying initial activator concentrations. Polymerization of acrylamide in aqueous homegenous solution with varying initial concentration of mandelic acid and fixed concentrations of:

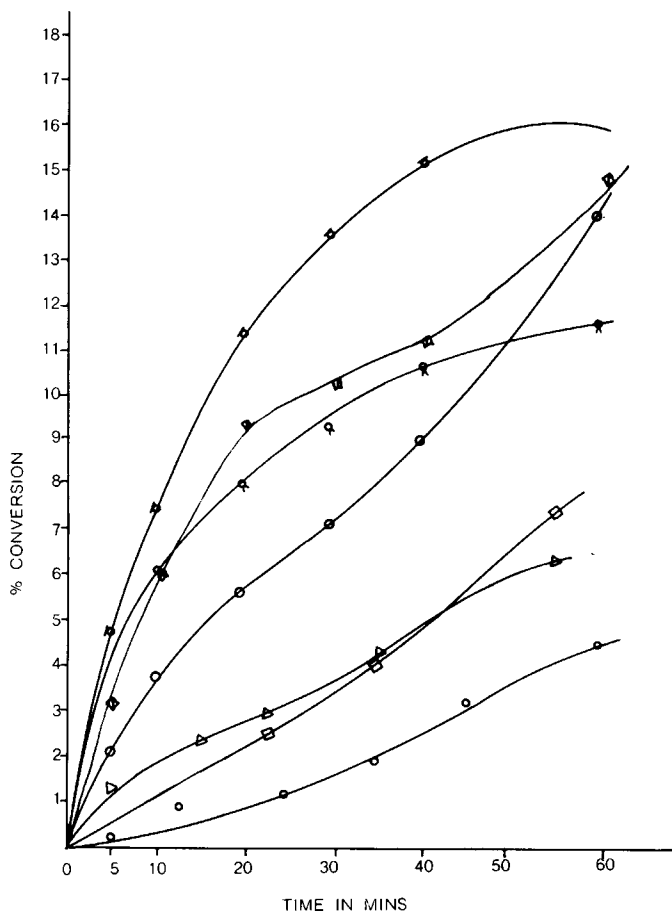| [Acrylamide]	$= 10.0 \times 10^{-2}$ mol/dm^3
[KMnO$_4$]	$= 1.5 \times 10^{-2}$ mol/dm^3
[H$_2$SO$_4$]	$= 1.5 \times 10^{-4}$ mol/dm^3
Temp	$= 35 \pm 0.2°$C
[Mandelic acid]⊙	$= 1.34 \times 10^{-1}$ mol/dm^3 control
⊙	$= 8.19 \times 10^{-2}$ mol/dm^3
⊡	$= 1.0 \times 10^{-1}$ mol/dm^3
⏅	$= 1.60 \times 10^{-1}$ mol/dm^3
⊙	$= 2.47 \times 10^{-1}$ mol/dm^3

Fig. 2. Time versus % conversion curves for the polymerization of acrylamide with varying initial concentrations of catalyst ($KMnO_4$). Polymerization of acrylamide in aqueous homeogenous solution with varying initial concentration of permanganate and fixed concentrations of:

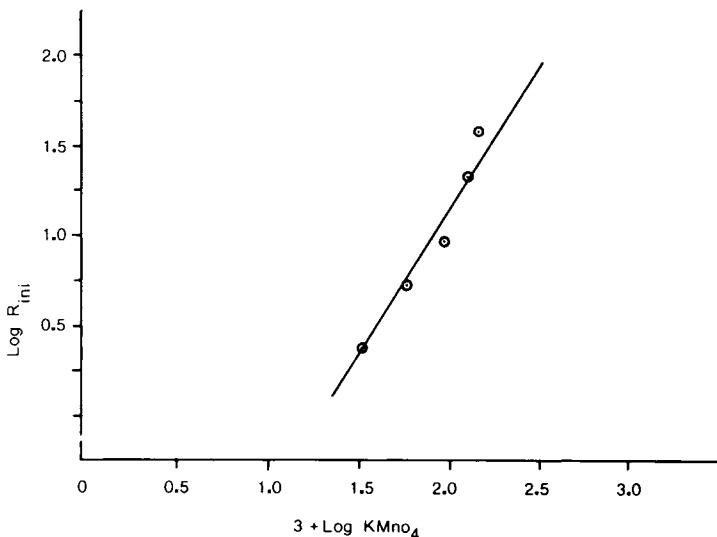| [Acrylamide]	$= 10.0 \times 10^{-2}$ mol/dm^3
[Mandelic acid]	$= 1.34 \times 10^{-2}$ mol/dm^3
[Sulfuric acid]	$= 1.5 \times 10^{-4}$ mol/dm^3
[$KMnO_4$] ⊙	$= 6.0 \times 10^{-3}$ mol/dm^3
⊡	$= 8.0 \times 10^{-3}$ mol/dm^3
▲	$= 1.0 \times 10^{-2}$ mol/dm^3
○	$= 1.2 \times 10^{-2}$ mol/dm^3
⊖	$= 1.5 \times 10^{-2}$ mol/dm^3 control
▨	$= 2.0 \times 10^{-2}$ mol/dm^3
⊙	$= 2.5 \times 10^{-2}$ mol/dm^3

Fig. 3. Double logarithmic plot of initial rate of polymerization (R_{ini}) in percent conversion per minute versus concentration of the catalyst ($KMnO_4$), in mol/dm^3.

inhibition takes place depends on the relative proportions and activities of these two types of radicals.

As mandelic acid alone is incapable of producing free radicals, it is unable to initiate polymerization. The generation of free radicals is governed by the amount of catalyst available in the system to participate in the redox reaction forming free radicals. The initial rates increase on increasing permanganate concentration in the range 6.0×10^{-3}–2.0×10^{-2} mol/dm^3 (Fig. 2). At a concentration of 2.5×10^{-2} mol/dm^3 both initial rate and limiting conversion decrease. The catalyst exponent, i.e., the slope of the double log plot between initial rate and $KMnO_4$ concentration (Fig. 3), is 2.2.

The oxidation of mandelic acid leads to the formation of various byproducts. Formation of both benzaldehyde and benzoic acid have been confirmed. Since these side reactions take place simultaneously with the formation of primary free radicals which initiate polymerization, permanganate is consumed in both these processes. The polymerization rate with respect to catalyst is therefore high as compared to other redox systems.[3a]

Rate Dependence on Monomer Concentration

The effect of varying the initial monomer concentration was an increase in the initial rate in the range 5.0–10.0×10^{-2} mol/dm^3 but, as higher concentration, 12.5–15.0×10^{-2} mol/dm^3 the percentage conversion decreased (Fig. 4). The order of the reaction with respect to the monomer concentration is 1.2 (Fig. 5).

Temperature Dependence

The effect of temperature was studied over the range 29–40°C. The initial rate and limiting conversion increase up to 35°C but further rise in tempera-
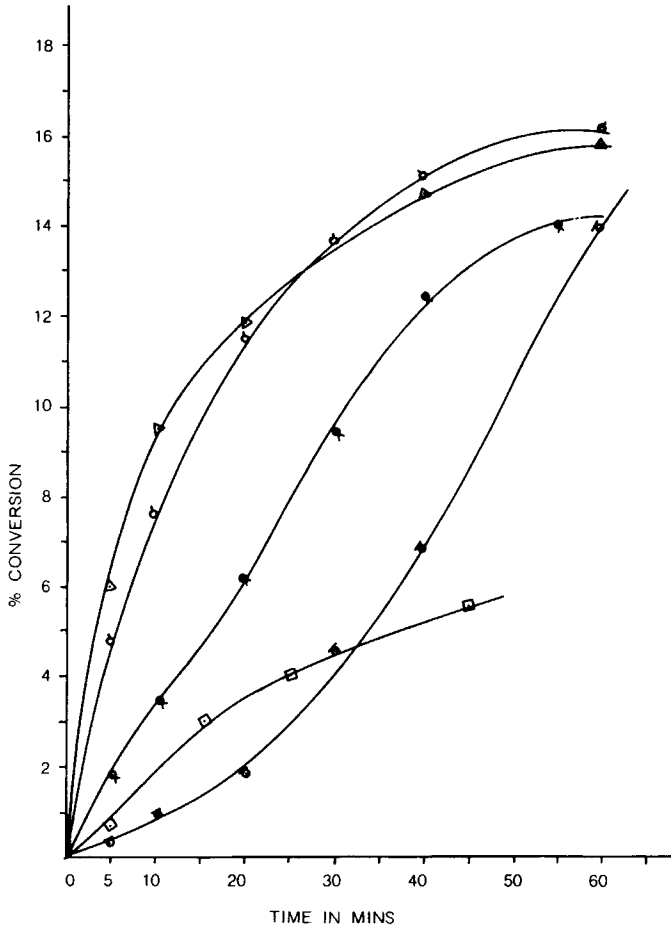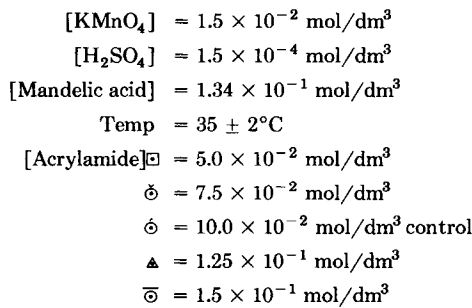
Fig. 4. Time versus percent conversion curves for the polymerization of acrylamide with varying initial monomer concentration. Polymerization of acrylamide in aqueous homogenous solution with varying initial concentrations of monomer (acrylamide) and fixed concentrations of:
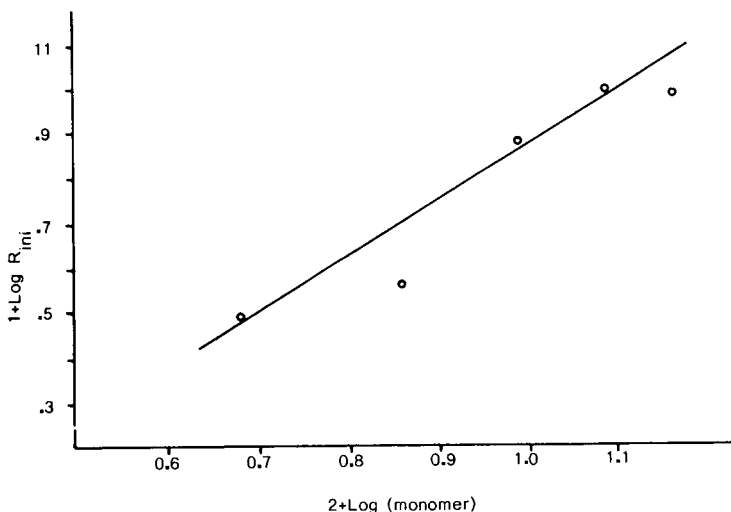
$$[KMnO_4] \quad = 1.5 \times 10^{-2} \text{ mol/dm}^3$$
$$[H_2SO_4] \quad = 1.5 \times 10^{-4} \text{ mol/dm}^3$$
$$[\text{Mandelic acid}] \quad = 1.34 \times 10^{-1} \text{ mol/dm}^3$$
$$\text{Temp} \quad = 35 \pm 2°C$$
$$[\text{Acrylamide}] \boxdot \quad = 5.0 \times 10^{-2} \text{ mol/dm}^3$$
$$\phantom{[\text{Acrylamide}]} \check{\odot} \quad = 7.5 \times 10^{-2} \text{ mol/dm}^3$$
$$\phantom{[\text{Acrylamide}]} \check{\odot} \quad = 10.0 \times 10^{-2} \text{ mol/dm}^3 \text{ control}$$
$$\phantom{[\text{Acrylamide}]} \blacktriangle \quad = 1.25 \times 10^{-1} \text{ mol/dm}^3$$
$$\phantom{[\text{Acrylamide}]} \overline{\odot} \quad = 1.5 \times 10^{-1} \text{ mol/dm}^3$$

Fig. 5. Double logarithmic plot of initial rate of polymerization (R_{ini}) in percent conversion per minute versus concentration of monomer acrylamide, in mol/dm^3.

ture showed a fall in limiting conversion. The overall energy of activation (E_{act}) as calculated from the Arrhenius plot (Fig. 6) was found to be 3.45 kcal/mol. Resonance stabilized free radicals are reported to have low E_{act}.[13]

Effect of Organic Solvents

Addition of aliphatic alcohols and DMF to the system in 5% v/v brought about an increase in induction period and a decrease in overall percentage polymerization. The effect observed was in the order.
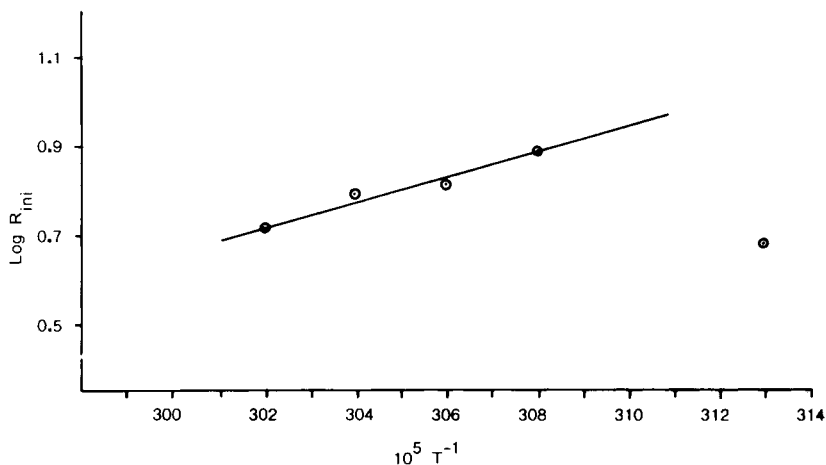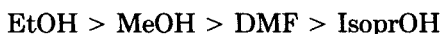
EtOH > MeOH > DMF > IsoprOH

Fig. 6. Arrhenius plot of the initial rate of polymerization (R_{ini}) vs reciprocal of absolute temperature (T) of polymerization.

The decrease may be due to:

(1) Addition of water-miscible organic solvents to the reaction medium decreases the area of shielding of a strong hydration layer in aqueous medium, resulting in the termination of radical end of the growing chain.
(2) In the presence of these solvents, some amount of catalyst is consumed in their oxidation, and thus the catalyst concentration in the reaction medium is reduced which obviously results in a fall in the overall rate of polymerization and limiting conversion.
(3) Due to transfer of macroradical chains to these solvents, a decrease in the rate of propagation and thereby that of polymerization is observed. The newly formed sluggish solvent radicals may not be capable of initiating polymerization. Similar effects have also been reported by earlier workers.[12a, b]

Effect of Retarders

Addition of retarders/chain transfer agents (methylamine) to the system brought about complete inhibition. Carbon tetrachloride and benzene brought about decrease in percentage polymerization due to increased chain transfer. The yield was very poor. Molecular weight of the polymer sample obtained was determined by viscosity measurements. It was calculated to be 58,336. The polymer obtained on adding 1 mL benzene to the reaction mixture has a low molecular weight of 583.0.

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