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A NEW REDOX INITIATING SYSTEM FOR THE POLYMERIZATION OF VINYL MONOMERS

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ABSTRACT

A new redox system, dioxane-ascorbic acid, has been investigated for the homopolymerization of vinyl monomers. Detailed kinetic studies on the aqueous polymerization of acrylamide by this initiating system have been done iodometrically at 35 ± 0.2°C. The effect of various additives, such as organic solvents, inorganic salts, surfactants, etc., on the rate of polymerization has been studied. The retardation constants for organic solvents have been evaluated by the "intercept method." The overall energy of activation has been found to be 8.75 kcal/deg/mol, within the temperature range 25–45°C. A suitable mechanism has been suggested. The following rate expression: $R_p \alpha$ [acrylamide]$^{1.0}$ [dioxane]$^{1.0}$ [ascorbic acid]^0, has been observed.

INTRODUCTION

Ascorbic acid coupled with suitable oxidant has been found to be an effective redox system for polymerization of vinyl monomers in aqueous medium. The use of organic solvents as chain modifiers and diluents in polymerization reactions is well known, but not much attempt has been made to use them as polymerization initiators. Recently, while studying the effect of organic solvents in ascorbic acid containing redox polymerization, it was observed that by addition of small amounts of dioxane to the system, both the initial rate of polymerization and the maximum

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conversion were enhanced dramatically. Since redox initiation by organic solvents is rather infrequent, this study was undertaken to examine the potentiality of the dioxane–ascorbic acid system as a polymerization initiator. The superiority of the present system lies in the fact that no modifier needs to be added from outside to regulate the molecular weight of the polymer, because dioxane itself is acting as a modifier as well as initiator. The present paper deals with the detailed study of kinetics of aqueous polymerization of acrylamide in air atmosphere at 35 ± 0.2°C using the dioxane–ascorbic acid system.

EXPERIMENTAL

Preparation of Materials

Acrylamide (E. Merck, India) was recrystallized twice from methanol (Merck, Germany) and dried in vacuum. Methyl methacrylate (B.D.H., A.R.) and acrylonitrile (B.D.H., A.R.) were also purified by known procedure before use. Ascorbic acid was a Sarabhai Merck, India Guaranteed Reagent. The solution of dioxane (Sarabhai Merck, A.R) was prepared in conductivity water. Fresh solutions were prepared for each run in conductivity water.

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Technique

The polymerization was followed by a quantitative estimation of double bonds in acrylamide iodometrically, as described by Wallace et al. [1]. The apparatus, the polymerization technique, and the formula for calculating the percentage conversion were identical to those used by Misra et al. [2, 3].

Molecular Weight Determination

For molecular weight determination, the samples of polymers, viz., polyacrylamide, poly(methyl methacrylate), and poly(acrylonitrile), were prepared and purified by two reprecipitations. The samples were then dried at 40°C. The viscosity of very dilute aqueous solution of the polymer was determined at room temperature. Finally, the molecular weights were calculated by using the following relationships [4]:

(a) For poly(acrylamide) in water:

$$[\eta]\ 30° \pm 0.5°C = 6.8 \times 10^{-4} \cdot M^{0.66} \quad (1)$$

(b) For poly(methyl methacrylate) in acetone:

$$[\eta]\ 20° \pm 0.5°C = 3.90 \times 10^{-5} \cdot M^{0.76} \quad (2)$$

(c) For poly(acrylonitrile) in DMF:

$$[\eta]\ 20° \pm 0.5°C = 17.7 \times 10^{-5} \cdot M^{0.78} \quad (3)$$

where $[\eta]$ is the intrinsic viscosity of the polymer solution and M is viscosity average molecular weight of the polymer.

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TABLE 1. Efficiency of Dioxane–Ascorbic Acid Initiating System

S. no.	Monomer	[Monomer]	[Dioxane] (mol/L)	[Ascorbic acid] (mol/L)	Solvent used	Polymer	M.wt of polymer	% conversion
1	Acrylamide	0.05 *M*	11×10^{-2}	11×10^{-3}	Water	Polyacrylamide	10,000	74
2	Methyl-methacrylate	0.1 *M*	11×10^{-2}	11×10^{-3}	Acetone	Polymethylmethacrylate	2,100	65
3	Acrylonitrile	0.1 *M*	11×10^{-2}	11×10^{-3}	DMF	Polyacrylonitrile	5,000	30

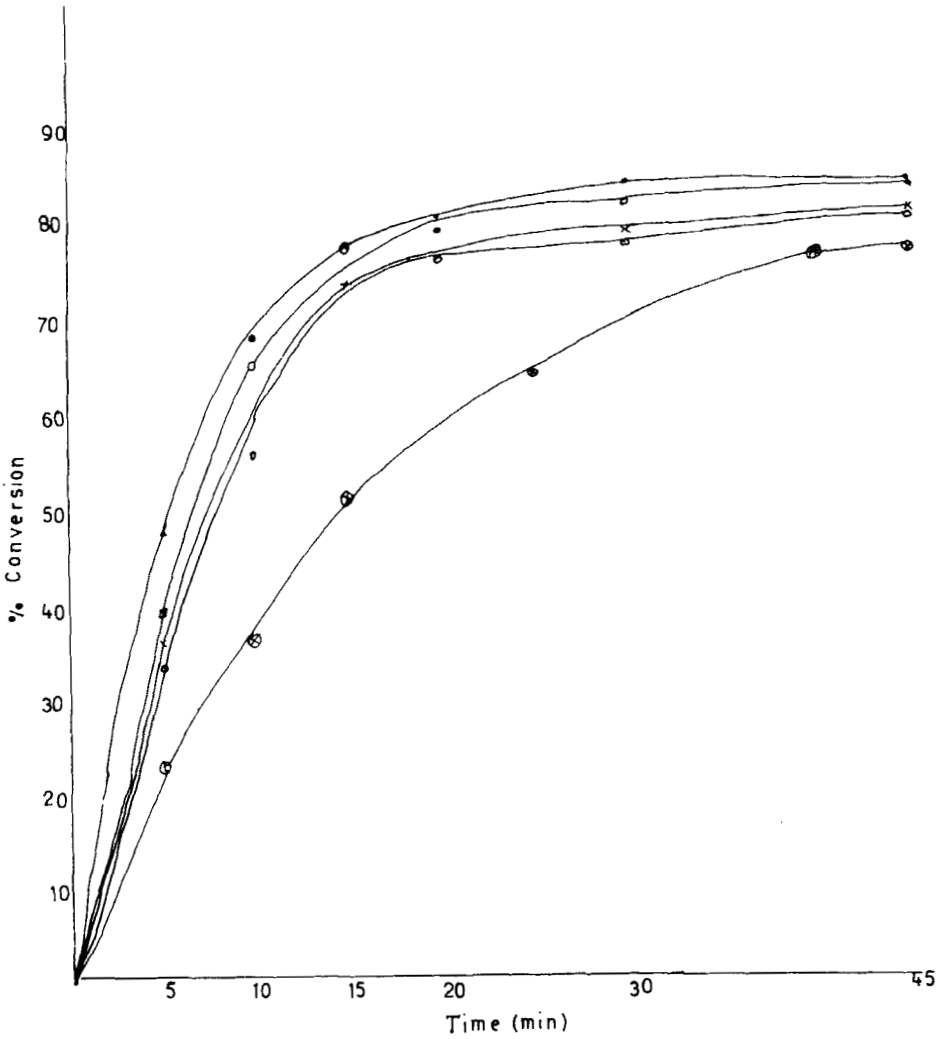

FIG. 1. Time-versus-conversion curve for the polymerization of acrylamide, with varying concentration of dioxane, at fixed concentration of [acrylamide] = 5×10^{-2}mol/L, [ascorbic acid] = 11×10^{-3}mol/L, temp. 35 ± 0.2°C. (⊕) 7.0×10^{-2}, (○) 9.3×10^{-2}, (×) 11.7×10^{-2}, (□) 14.0×10^{-2}, (●) 17.6×10^{-2}mol/L.

RESULTS AND DISCUSSION

Efficiency of the System

The redox polymerization of various vinyl monomers, viz., acrylamide, methyl methacrylate, and acrylonitrile, has been studied using the same dioxane–ascorbic acid system. The efficiency of the present dioxane–ascorbic acid system in the polymerization of vinyl monomers is tabulated in Table 1.

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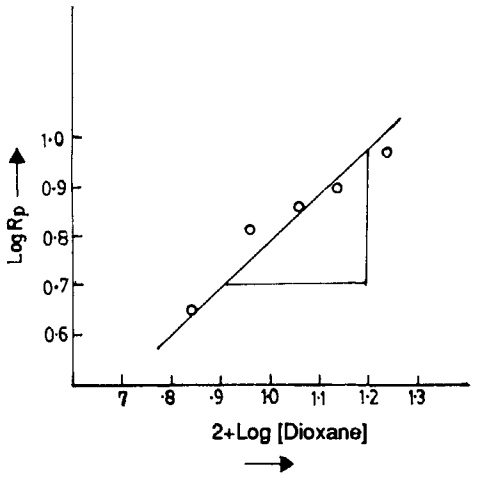

FIG. 2. Double log plot of initial rate of polymerization (R_p in % conversion per minute) versus the inital concentration of dioxane, slope = 0.95.

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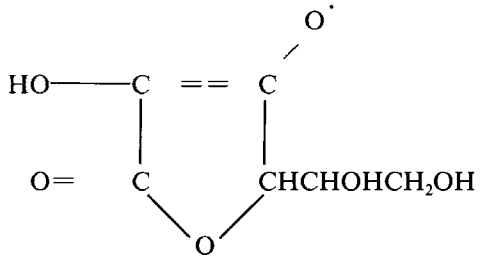
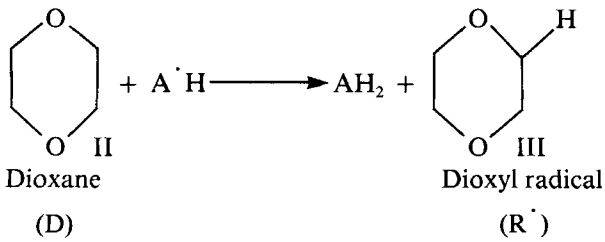
Mechanism

For the first time, we studied the dioxane-ascorbic acid initiating system for vinyl polymerization. The process is of free radical nature. Cocatalytic activity of oxygen in ascorbic acid-containing systems has been demonstrated by serveral workers [5]. Ascorbic acid is oxidized with atmospheric oxygen to dehydroascorbic acid via free radical intermediate (I); this has been studied by Piette et al. [6] and Weissberger et al. [7].



(I)

Dioxane(II), which is a cyclical ether, forms stable dioxyl radical(III) by loss of hydrogen by reacting with ·AH radical [8]. Since all the hydrogen atoms in dioxane are equivalent, any of the hydrogens may be lost to give the dioxyl radicals ($R^{\cdot}$):



(3′)

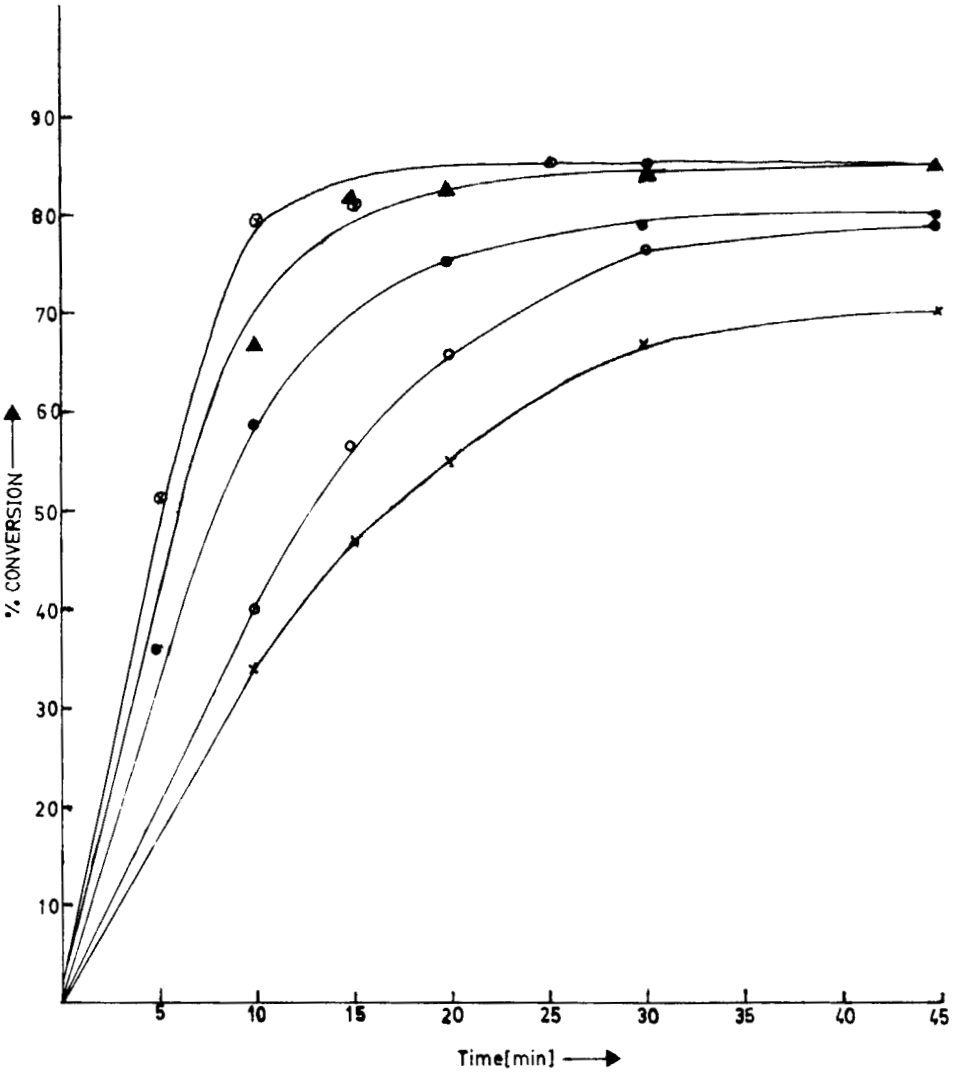


FIG. 3. Time-versus-conversion curve for the polymerization of acrylamide with varying concentration of acrylamide at fixed concentration of [ascorbic acid] = 11×10^{-3}mol/L, [dioxane] = 11×10^{-2}mol/L, temp. 35 ± 0.2°C. (×) 2.5×10^{-2}, (○) 4.0×10^{-2}, (●) 5×10^{-2}, (▲) 6.0×10^{-2}mol/L. (⊗) 7.5×10^{-2}mol/L.

The overall mechanism for the polymerization of acrylamide initiated with dioxane-ascorbic acid may be represented as follows:

$$2AH_2 + O_2 \xrightarrow{k_1} 2A^{\cdot}H + H_2O_2 \quad (4)$$

$$A^{\cdot}H + \text{dioxane} \xrightarrow{k_2} AH_2 + \text{dioxyl radicals} \quad (5)$$

(D) ($R^{\cdot}$)

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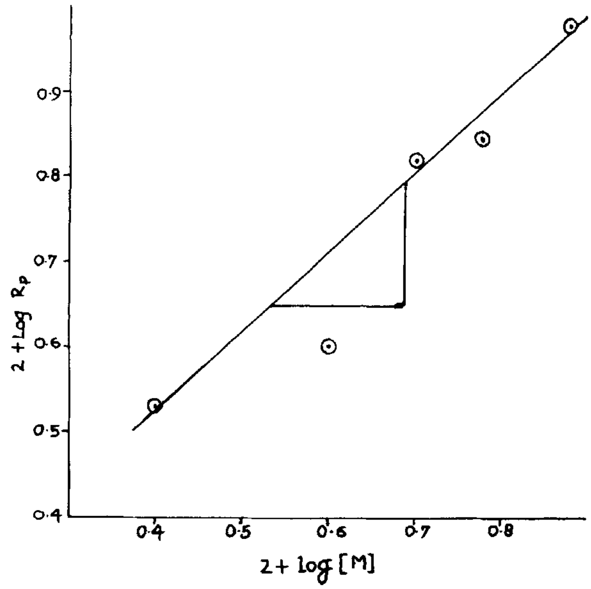

FIG. 4. Double logarithmic plot of the initial rate of polymerization (R_p in % conversion/minute) versus the initial concentration of monomer acrylamide, slope = 0.95.

$$\mathrm{R^{\cdot} + CH_2{=}CH(CONH_2)} \xrightarrow{k_i} \underset{(\mathrm{M^{\cdot}})}{\mathrm{R{-}CH_2{-}C^{\cdot}HCONH_2}} \tag{6}$$

$$M^{\cdot} + M \xrightarrow{k_p} M^{\cdot}_1 \tag{7}$$

$$\vdots \qquad\qquad \vdots$$

$$M^{\cdot}_{n-1} + M \longrightarrow M^{\cdot}_n$$

$$M^{\cdot}_n + \mathrm{A^{\cdot}H} \xrightarrow{k_t} \text{polymer} \tag{8}$$

$$M^{\cdot}_n \xrightarrow{k'_t} \text{polymer} \tag{9}$$

$$M^{\cdot}_n + (\mathrm{D}) \xrightarrow{k_3} \text{polymer} + \underset{(\mathrm{R^{\cdot}})}{\text{dioxyl radical}} \tag{10}$$

Rate Expression

A suitable rate expression may be derived by determining the concentrations of free radicals by applying steady-state assumptions.

As an approximation, the rate of polymerization may be taken as that of propagation. Therefore, we may write rate of polymerization:

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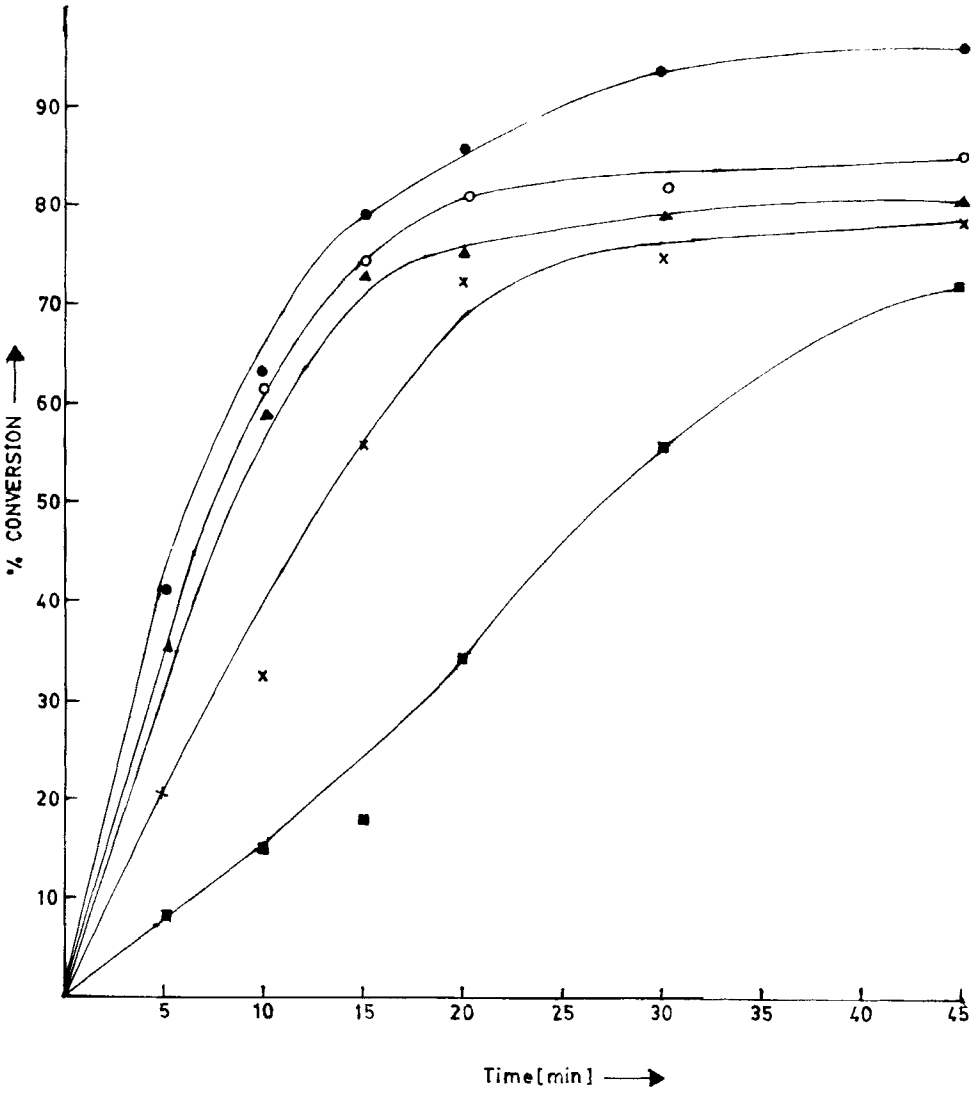

FIG. 5. Time-versus-conversion curve for the polymerization of acrylamide, with varying temperature at fixed concentration of [dioxane] = 11 × 10^{-2}mol/L, [acrylamide] = 5 × 10^{-2}mol/L, [ascorbic acid] = 11 × 10^{-3}mol/L. (■) 25°, (×) 30°, (○) = 40°C, (▲) 35°, (●) 45°C.

$$R_p = k_p[M]\,[M_n^{\cdot}] \tag{11}$$

The concentration of $M_n^{\cdot}$ radicals may indirectly be determined by applying steady-state assumptions. For determination of $[M_n^{\cdot}]$, we assume that the rate of initiation (R_i) becomes equal to that of termination (R_t), i.e.:

$$R_i = R_t$$

or

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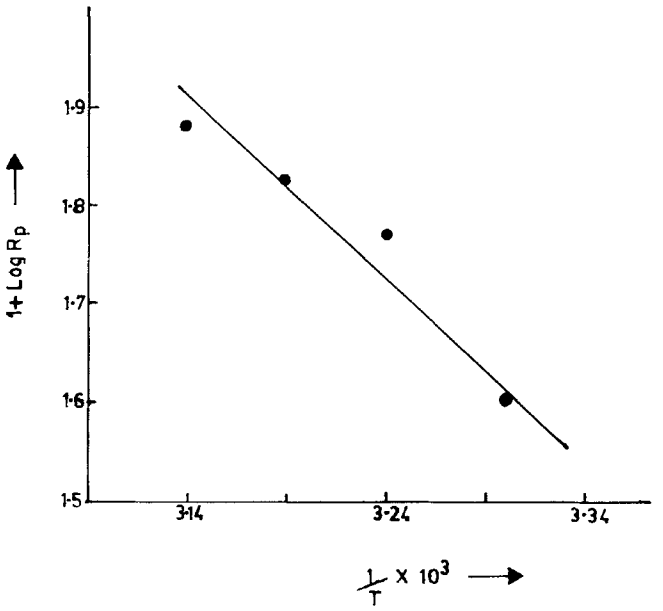

FIG. 6. Arrhenius plot of the initial rate of polymerization R_p versus $1/T$. Energy of activation E_0 = 8.75 kcal/mol/deg.

$$k_i[R^{\cdot}]\,[M] = k_t[M_n^{\cdot}]\,[A^{\cdot}H] + k_3[M_n^{\cdot}]\,[D] + k'_t[M_n^{\cdot}] \tag{12}$$

or

$$[M_n^{\cdot}] = \frac{k_i[R^{\cdot}]\,[M]}{(k_t[A^{\cdot}H] + k_3[D] + k'_t)} \tag{13}$$

To determine the value of $[R^{\cdot}]$, we apply the steady-state assumptions to dioxyl radicals $R^{\cdot}$, i.e.:

$$\frac{d}{dt}[R^{\cdot}] = k_2[A^{\cdot}H]\,[D] + k_3[M_n^{\cdot}]\,[D] - k_i[R]\,[M] = 0 \tag{14}$$

or

$$[R^{\cdot}] = \frac{k_2[A^{\cdot}H]\,[D] = k_3[M_n^{\cdot}]\,[D]}{k_i[M]} \tag{15}$$

Since the dioxane is predominantly consumed in the free radical generation step [Eq. (5)], we may assume that the concentration of dioxane participating in the chain transfer reaction [Eq. (10)] will be negligible, and therefore it may be assumed that $k_2[A^{\cdot}H]\,[D] \gg k_3[M_n^{\cdot}]\,[D]$.

Now Eq. (15) becomes

$$[R^{\cdot}] = \frac{k_2[A^{\cdot}H]\,[D]}{k_i[M]} \tag{16}$$

On substituting the value of $[R^{\cdot}]$ from Eq. (16) to Eq. (13), we have

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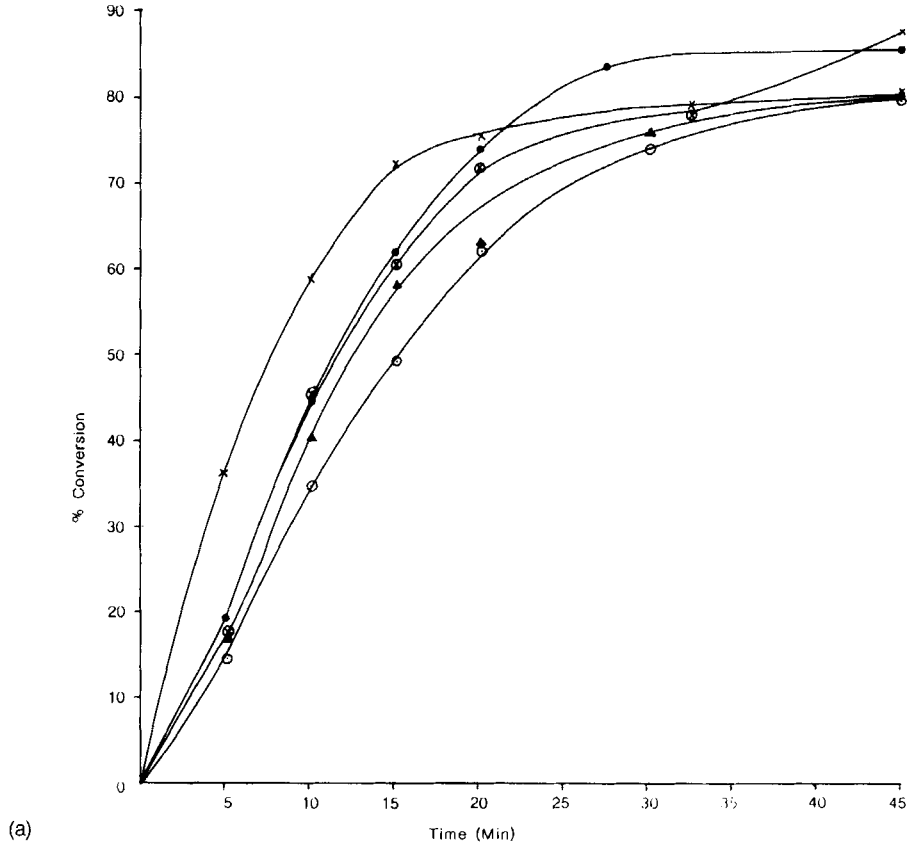
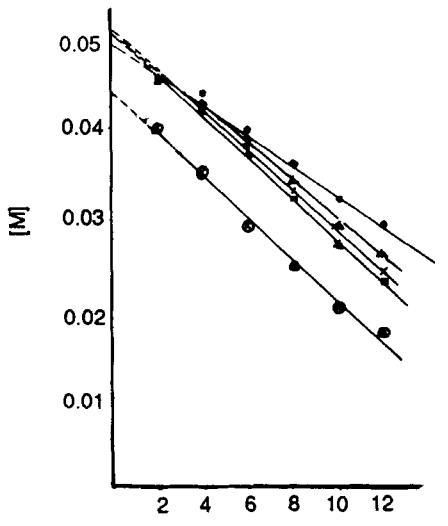


(a)



(b)

FIG. 7. (a) Time-versus-conversion curve for the polymerization of acrylamide showing the effect of added organic solvents (by volume) at fixed concentration of [acrylamide] = 5×10^{-2}mol/L, [ascorbic acid] = 11×10^{-3}mol/L, [dioxane] = 11×10^{-2}mol/L, temp. 35°C ± 0.2°C. (×) Control, (⊙) methanol, (▲) ethanol, (⊕) butanol, (●) DMF. (b) [M]-versus-time curve for calculation of retardation constant of various retarders. (●) Methanol, (△) ethanol, (■) DMF, (×) butanol, (⊕) control.

TABLE 2. Retardation Constants of Various Organic Solvents Used as Retarders in Polymerization of Acrylamide at Fixed [Monomer] = 5 × 10^{-2}mol/L, [Dioxane] = 11 × 10^{-2}mol/L, [Ascorbic Acid] = 11 × 10^{-3}mol/L, Temp. = 35 ± 0.2°C

S. no.	Solvent	Amount added	I retardation constant
1	Methanol	5% (v/v)	0.027
2	Ethanol	5% (v/v)	0.026
3	DMF	5% (v/v)	0.025
4	Butanol	5% (v/v)	0.028

$$[M_n^{\cdot}] = \frac{k_2 k_i[A^{\cdot}H]\,[D]\,[M]}{k_i[M]}\left[\frac{1}{k_t[A^{\cdot}H] + k_3[D] + k'_t}\right]$$

$$= \frac{k_2[A^{\cdot}H]\,[D]}{(k_t[A^{\cdot}H] + k_3[D] + k'_t} \tag{17}$$

From Eq. (11) and Eq. (17), we have

$$R_p = \frac{k_2 k_p[M]\,[D]\,[A^{\cdot}H]}{(k_t[A^{\cdot}H] + k'_t)} \tag{18}$$

Now, in the studied range of ascorbic acid concentration (4.5–8 × 10^{-3}mol/L), the rate was found to be independent of the activator concentration; therefore, we may suppose that the termination of macroradicals ($M_n^{\cdot}$) by $A^{\cdot}H$ radicals must have been a prominent reaction. Therefore, we can assume that $k_t[A^{\cdot}H] > k'_t$.

$$\text{Now Eq. (18) becomes } R_p = \frac{k_p k_2[M]\,[D]}{k_t} \tag{19}$$

Equation (19) clearly shows an independence relationship between R_p and ascorbic acid concentration.

In addition, when the concentration of activator (ascorbic acid) exceeds 8 × 10^{-3}mol/L, primary radical termination (of $A^{\cdot}H$) starts taking place so that the concentration of $A^{\cdot}H$ radicals reacting with dioxan [Eq. (5)] becomes less than the concentration taking part in the termination [Eq. (8)] and primary radical termination step. Therefore, we may assume that

$$k_2[A^{\cdot}H] < k_t[A^{\cdot}H]$$

and therefore Eq. (18) reduces to

$$R_p = \frac{k_p k_2[M]\,[D]}{k_t[A^{\cdot}H]^x} \tag{20}$$

also neglecting k'_t in comparison to the $k_t[A^{\cdot}H]$ value. Equation (20) clearly shows that the rate of polymerization will vary inversely with $[A^{\cdot}H]^x$ concentration above 8 × 10^{-3}mol/L, showing a decrease in rate of polymerization with increasing ascorbic acid concentration. Here x may have any positive value.

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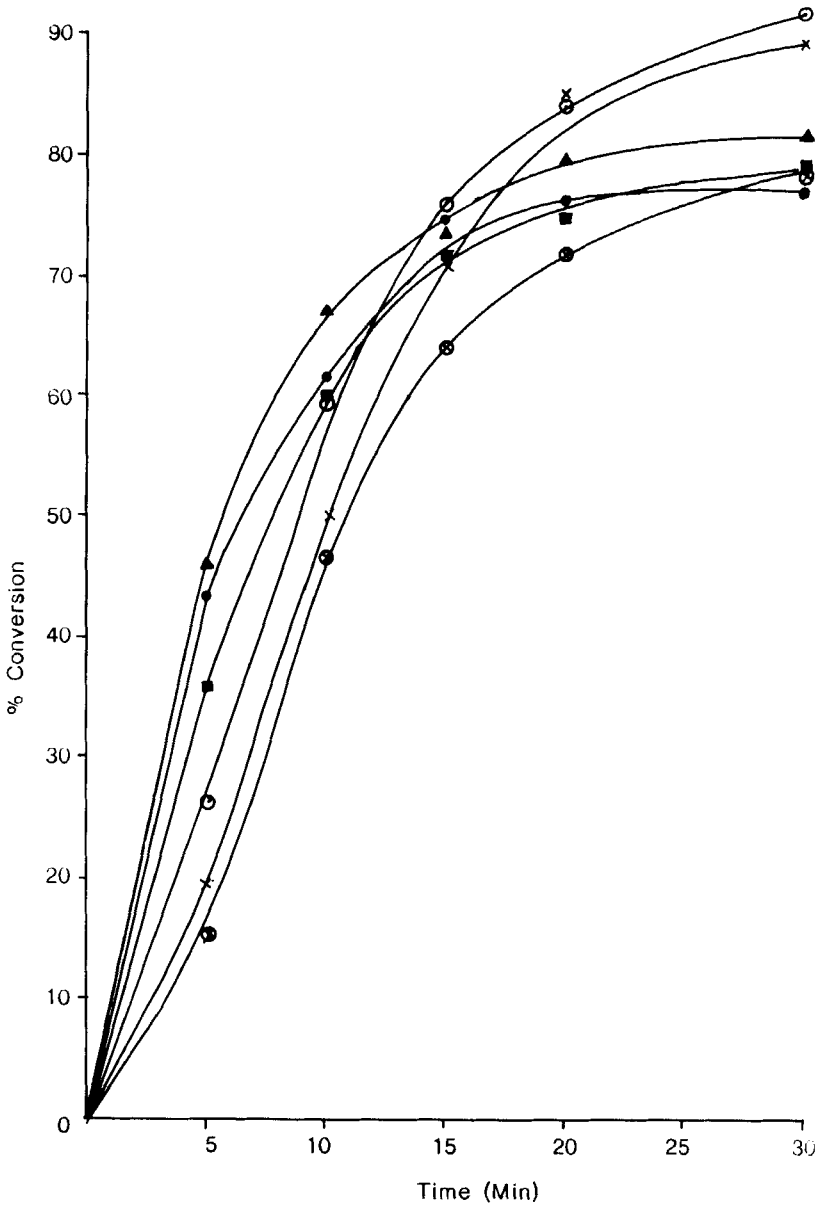

FIG. 8. Time-versus-conversion curve for the polymerization of acrylamide showing the effect of added neutral salts (in equal amount) at fixed concentration of [acrylamide] = 5×10^{-2}mol/L, [ascorbic acid] = 11×10^{-3}mol/L, [dioxane] = 11×10^{-2}mol/L, Temp. 35° ± 0.2°C. (■) Control, (⊙) KBr, (×) KCl, (●) Na_2SO_4, (⊕) Li_2SO_4, (▲) K_2SO_4.

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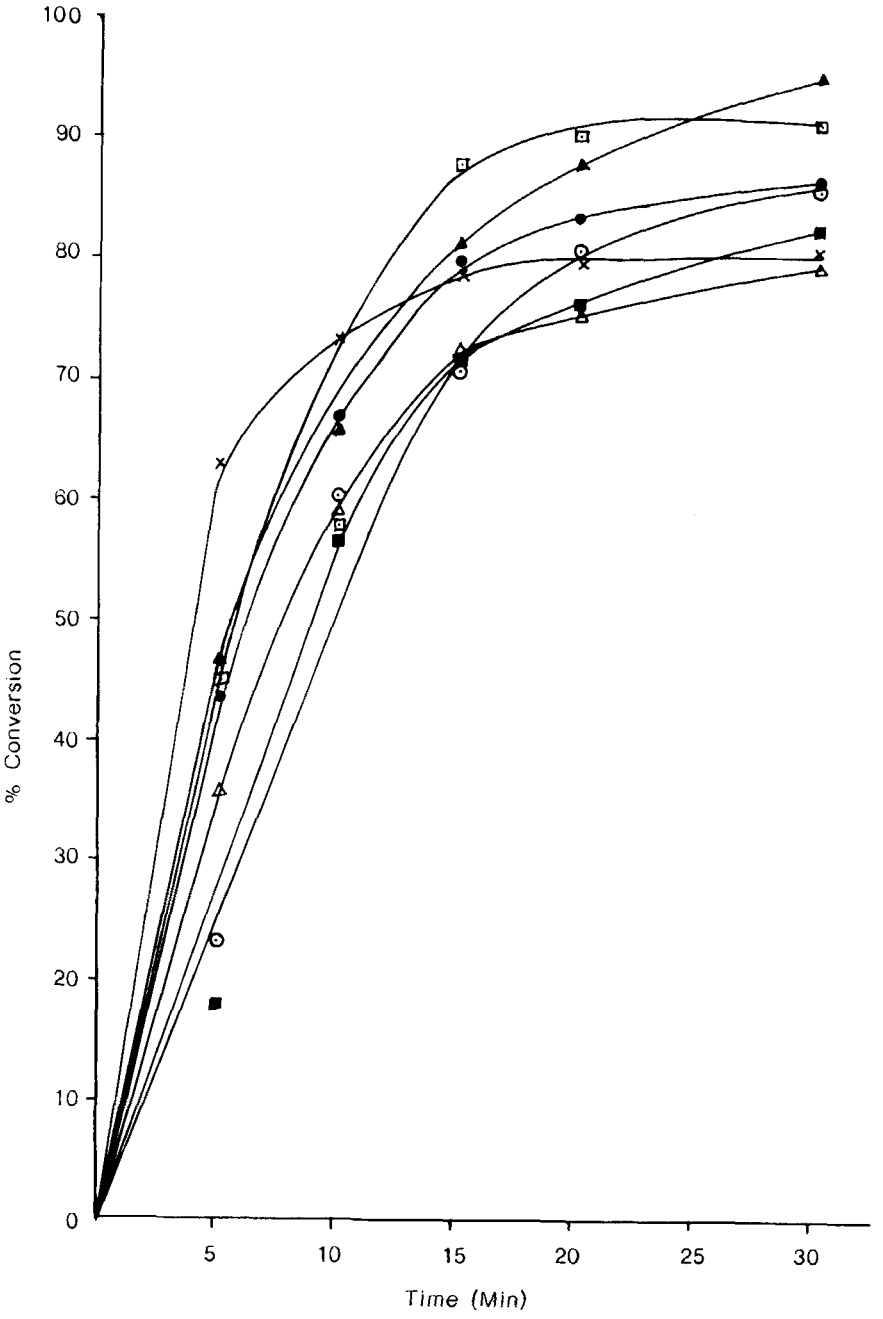

FIG. 9. Time-versus-conversion curve for the polymerization of acrylamide showing the effect of surfactants at fixed concentration of [acrylamide] = 5×10^{-2}mol/L, [ascorbic acid] = 11×10^{-3}mol/L, [dioxane] = 11×10^{-2}mol/L, temp. 35 ± 0.2°C. (△) Control, sod. oleate, (▲) 0.0005 *M*, (○) 0.001 *M*, CTAB, (●) 0.002 *M*, (■) 0.005 *M*, (×) 0.01 *M*.

Effect of Dioxane

The initial rate of polymerization as well as the limiting conversion tends to increase with increasing dioxane concentration in the range 5.8–17.6 $\times$ 10^{-2}mol/L at fixed concentration of ascorbic acid and acrylamide (Fig. 1). Increase in dioxane concentration also increases the rate of generation of initiating free radicals [Eqs. (4–6)] and hence the initial rate and maximum conversion. The order of rate of polymerization with respect to dioxane had been found to be 0.96 from the double logarithmic plot between the concentration of dioxane and rate of polymerization (Fig. 2). The first-order dependence of rate on dioxane may be attributed to the linear chain termination of macroradical by metal ion, or with some impurity present in the system.

Effect of Ascorbic Acid

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The initial rate was found to be unaffected with increasing concentration of ascorbic acid in the range 4.5–8.0 $\times$ 10^{-3}mol/L, thus indicating a zero-order dependence on ascorbic acid concentration. The rate was found to decrease at higher concentrations of ascorbic acid (above 8.0 $\times$ 10^{-3}mol/L). In the absence of ascorbic acid, no polymerization occurs. In the presence of ascorbic acid, free radicals ($A^{\cdot}H$, dioxyl($R^{\cdot}$) radicals) are generated by Reactions (4–6). However, concentration of ascorbic acid in the range 4.5–8.0 $\times$ 10^{-3}mol/L had no effect on the initial rate or on maximum conversion, which may be due to the balance existing between the generation and termination of radicals. At higher concentrations of ascorbic acid $A^{\cdot}H$ radical significantly undergoes primary radical termination, and therefore, the concentration of primary free radicals decreases.

Effect of Acrylamide

Dependence of the polymerization rate on the concentration of the monomer was studied by varying the concentration of monomer over the range 2.5–7.5 $\times$ 10^{-2}mol/L. The rate of polymerization increases linearly with increasing monomer concentration (Fig. 3) owing to the increased availability of monomer molecules in the propagating step. The monomer exponent as calculated from double logarithmic plot (Fig. 4) has been found to be 1.0, which is of the same order as reported earlier [9–11].

Effect of Temperature

When the temperature of the reaction medium increases from 25 to 45°C, the rate of free radical generation is facilitated, which, in turn, will increase the initial rate and maximum conversion (Fig. 5). The overall energy of activation, as calculated from the Arrhenius plot (Fig. 6), was found to be 8.75 kcal/mol/deg, which is of the same order as found in similar systems [9–11].

Effect of Organic Solvents

Organic solvents are among the mild retarders in addition polymerization. In the present work, the effect of various water-miscible organic solvents (methanol, ethanol, butanol, DMF, etc.) on the course of polymerization was studied both qualitatively and quantitatively in view of their polymerization-retarding efficiency.

Addition of 5% v/v of these solvents to the reaction mixture was found to depress the initial as well as maximum conversion (Fig. 7a). The increasing order of depression of the initial rate of polymerization was as follows:

BuOH < DMF < ethanol < methanol

The decrease may be due to the following:

1. The added organic solvent penetrates the hydration layer of macroradicals and reduces the shielded area, resulting in exposure of the macroradical chain to various primary and growing macroradicals for premature termination, which cause a decrease in the initial rate and maximum conversion.
2. The retarding effect of the solvents may also be due to the transfer of the growing macroradical chain to the added solvents. Such a chain transfer occurs by abstraction of hydrogen atom of solvent molecule producing new radical, which may or may not be capable of initiating polymerization.

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The retardation constants were calculated by using the "intercept method" proposed by Bajpai and Bajpai [12]. According to the intercept method, for a single retarder added to the reaction medium,

$$[\mathrm{M}] = \frac{I[W_0]}{\dfrac{X - X'}{X'}} - \frac{I\,kt}{\dfrac{X - X'}{X'}} \tag{21}$$

where I is the retardation constant, W_0 is the initial concentration of the solvent, X and X' are the rate of disappearance of monomer under normal and retarded conditions, respectively, and k is the constant. For the linear portion of percentage conversion versus t curve, X and X' will also be constant. It is evident from Eq. (21) that a plot drawn between [M] versus t would be a straight line; from the intercept, I can easily be calculated.

On the basis of the above-mentioned method, the retardation constants for organic solvents have been evaluated from the plot drawn between [M] versus time (Fig. 7b) and are summarized in Table 2.

The order of retardation by the organic solvents, on the basis of the numerical values of retardation constants, is as follows:

BuOH > MeOH > EtOH > DMF

while on the basis of % conversion versus time curve, the following increasing order of retarding beahvior of the solvents has been observed:

BuOH < DMF < EtOH < MeOH

The difference between the two orders observed is quite obvious, as the solvents added to the reaction medium were equivolume (not equimolar) in amount.

Effect of Neutral Salts

Addition of various inorganic salts to the reaction medium depresses the initial rate of polymerization, but the maximum conversion was found to increase (Fig. 8). In the case of K_2SO_4, the initial rate and the maximum conversion were both found to increase. The depression in the initial rate of polymerization may be due to ionic dissociation of the added electrolyte, which interferes with the normal polymerization process, leading to premature termination of the growing polymer chain. The increase in the maximum conversion may be due to the cocatalytic activity of added metal ion. In the case of K_2SO_4, cocatalytic activity might have set in from the very beginning of the polymerization, whereas in the case of other neutral salts, such a situation arose after some time.

Effect of Surfactants

Both cationic and anionic surface-active agents behave in a similar fashion in the present system (Fig. 9). The initial rate as well as the maximum conversion was found to increase with the addition of sodium oleate and CTAB to the system in the concentration below, above, and at their CMC value. The emulsifying action of surfactants increases the solubility and availability of monomer molecules. In addition, the peptizing action of surfactants prevents the macroradicals from coalescing. Both the above-mentioned factors result in an increase in the initial rate and maximum conversion.

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CONCLUSIONS

The dioxane-ascorbic acid system was found to be an efficient redox initiating system for the polymerization of vinyl monomers. In the case of polymerization of acrylamide, the reaction rate was first order with respect to the acrylamide and dioxane and independent of the concentration of ascorbic acid.

The usefulness of the system lies in the fact that dioxane behaves simultaneously as initiator and modifier. This system may find applications in the preparation of low-molecular-weight polymers.

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