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Electroinitiated Polymerization of Acrylamide Using Tartaric Acid as Electrolyte

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ABSTRACT

Acrylamide has been polymerized electrochemically in aqueous medium in the presence of tartaric acid, and the effects of such reaction variables as monomer concentration, electrolyte concentration, and current on the rates of polymerization have been studied. The mechanisms of initiation and termination have been discussed in the light of the observed kinetic data. Initiation is believed to occur through the generation of radical ions during electrolysis, and electrolytic termination is found to be negligible during the polymerization process.

INTRODUCTION

Electroinitiated polymerization of vinyl monomers using the Kolbe electrosynthesis technique is now well established. Alkali metal salts alone or in combination with acid have been used as electrolyte for this purpose [1, 2]. These reactions are known to proceed via a radical pathway although the detailed mechanism is less clear in most

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cases. The use of dibasic acid in particular is quite interesting from the mechanistic point of view as these systems might involve the formation of diradical or radical ions. To clarify this point we have chosen tartaric acid as the electrolyte for polymerization experiments. In this paper we report the results of electroinitiated polymerization of acrylamide (AM) monomer in aqueous medium in the presence of tartaric acid.

EXPERIMENTAL

Materials

Acrylamide (BDH, England) was recrystallized twice from chloroform solution. The purity of the monomer was checked by bromatometric titration and was found to be over 99.9%.

Tartaric acid (AnalaR grade) was used without further purification.

Water was doubly distilled in an all-glass Pyrex apparatus and was purged with nitrogen after collection.

Polymerization Procedure

Polymerization experiments were carried out in an electrolytic cell of the conventional cylindrical type made from Pyrex glass tubing of 2.5 cm diameter and 7.5 cm length. Two platinum electrodes of 1 cm diameter were placed parallel to each other at a distance of 2 cm. The cell was placed in a thermostatic bath maintained at a constant temperature, and a constant current was employed from a fixed dc supply by means of a suitable resistance system.

The monomer was dissolved in water along with the electrolyte and placed in the cell. A constant current was passed through the reaction mixture for the desired time period. At the end of the specified time period the polymers were precipitated by the addition of a minimum of 20 volumes of acetone with constant stirring. The polymers were filtered, washed thoroughly with dry acetone, and dried at 40°C under vacuum to constant weight. The course of reaction was followed by bromatometric assay using a $KBrO_3$-KBr mixture and after withdrawing samples at regular intervals.

Molecular Weight

The molecular weights of the polymers were determined from viscosity measurements in water solution at 30 ± 0.05°C using an Ubbelohde-type viscometer. The following relationship was used [3]:

$$[\eta] = 6.3 \times 10^{-5} (M)^{0.80}$$

where $[\eta]$ is the intrinsic viscosity and M is the molecular weight.

RESULTS AND DISCUSSION

The conversion-time curves for AM polymerization at various monomer concentrations are shown in Fig. 1. A pronounced autoacceleration effect is observed at higher conversions and is presumably due to an increase in the viscosity of the medium. The rates of polymerization (R_p) were calculated from the slope of the initial linear zone of the plots. The molecular weights of the resulting polymers were found to be quite high (Table 1). A first-order dependence of R_p on monomer concentration is observed (Fig. 2). The plot of R_p versus 1/DP at constant current is also linear (Fig. 3), where DP is the degree of polymerization.

The effect of addition of hydroquinone (HQ) in the AM polymeriza-

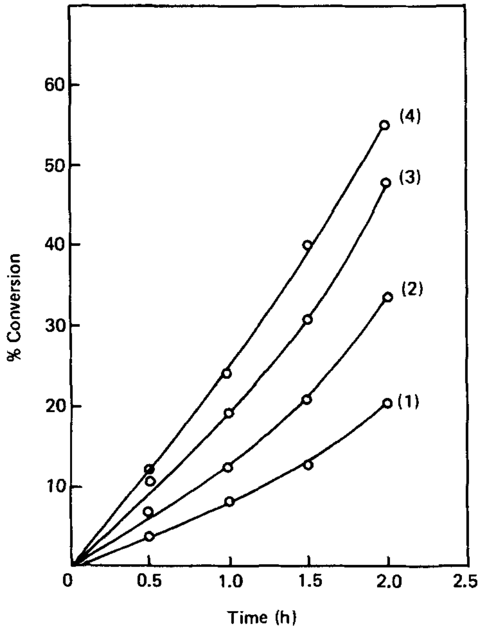


FIG. 1. Conversion-time curves for acrylamide polymerization at various monomer concentrations in moles/liter: (1) 0.3, (2) 0.5, (3) 0.8, (4) 1.0.

TABLE 1. Effect of Monomer Concentration on the Polymerization of Acrylamide

[AM] (mol/L)	[Tartaric acid] (mol/L)	Current (mA)	Initial rate of polymerization (mol/L/s) × 10^5	Average degree of polymerization (DP)
0.3	0.75	80	2.2	1320
0.5	0.75	80	4.0	1530
0.8	0.75	80	6.1	1880
1.0	0.75	80	7.1	2080

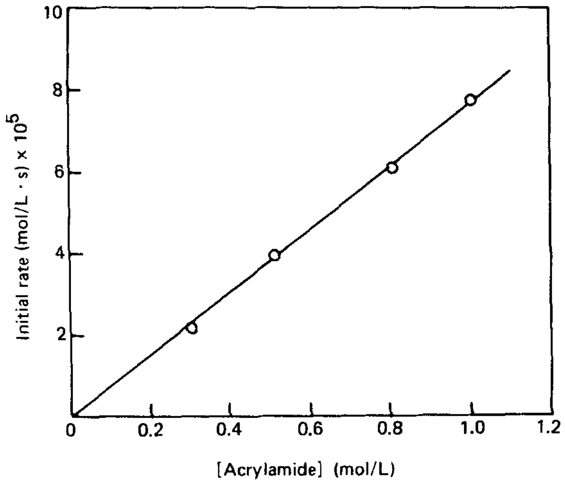


FIG. 2. Dependence of initial rates of polymerization on monomer concentration.

tion using tartaric acid as the electrolyte is shown in Fig. 4. It can be seen that HQ in the present system does not function as an efficient inhibitor.

Figure 5 shows the results of variation of electrolyte concentration on the rate of AM polymerization (Table 2). A linear relationship is obtained when R_p is plotted against electrolyte concentration. It is to be noted that the electrolyte concentrations used in these cases were quite high. These high concentrations are necessary in order to attain

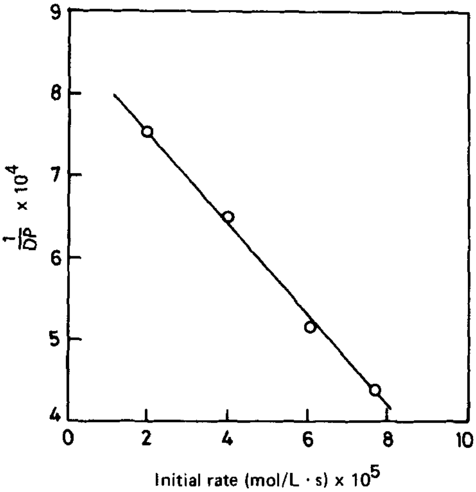


FIG. 3. Plot of reciprocal degree of polymerization vs initial rates of polymerization at constant current.

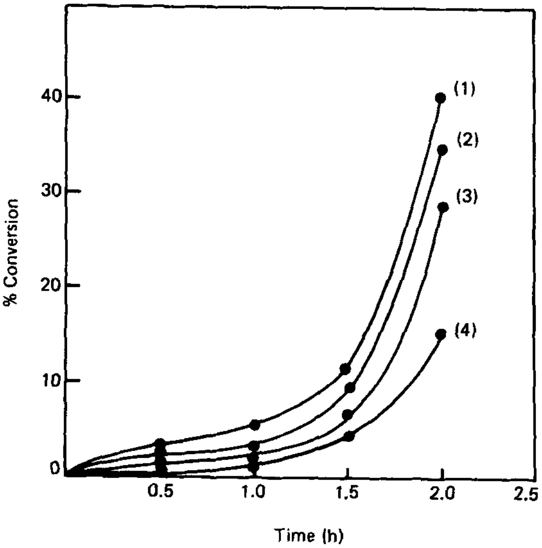


FIG. 4. Effect of hydroquinone (HQ) concentration on acrylamide polymerization: (1) without HQ, (2) 0.1% HQ (w/v of monomer), (3) 0.5% HQ, (4) 1.0% HQ.

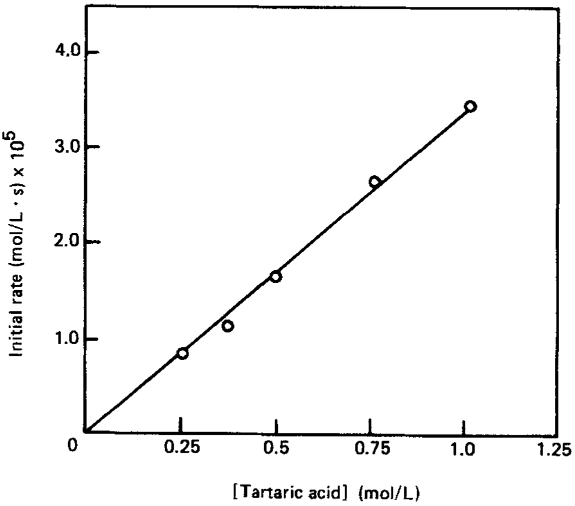


FIG. 5. Dependence of initial rates of polymerization on the electrolyte concentration for acrylamide.

TABLE 2. Effect of Electrolyte Concentration on the Polymerization of Acrylamide

[AM] (mol/L)	[Tartaric acid] (mol/L)	Current (mA)	Initial rate of polymerization (mol/L/s)$\times 10^5$
1.0	0.25	50	0.83
1.0	0.37	50	1.11
1.0	0.50	50	1.67
1.0	0.75	50	2.77
1.0	1.00	50	3.88

sufficient conductance in the system, and they are obviously a limitation for electroinitiated polymerization in general.

The overall energy of activation for the polymerization system as obtained from the measurement of rates of polymerization at different temperatures and calculated from Arrhenius plots of log R_p vs 1/T (Fig. 6) is found out to be 11.5 kcal/mol (Table 3).

It is reasonable to assume that the rates of polymerization would generally be influenced by a change in current density because of the

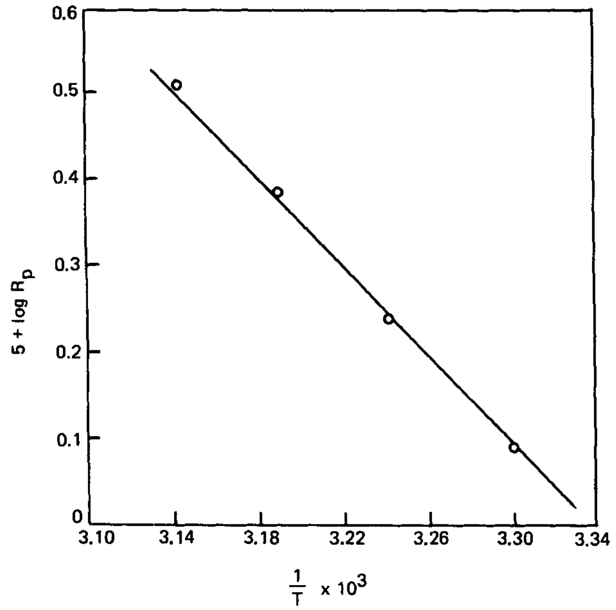


FIG. 6. Effect of temperature on the electroinitiated polymerization of acrylamide using tartaric acid as the electrolyte.

TABLE 3. Effect of Temperature on the Polymerization of Acrylamide

[AM] (mol/L)	[TA] (mol/L)	Current (mA]	Temperature (°C)	Initial rate of polymerization (mol/L/s) $\times 10^5$	Overall energy of activation (kcal/mol)
0.5	0.37	50	30	0.83	11.5
0.5	0.37	50	35	1.73	
0.5	0.37	50	40	2.50	
0.5	0.37	50	45	3.33	

change in the rate of generation of primary radicals. This effect of variation of current on the polymerization rate has been studied and the results are shown in Table 4 (Fig. 7). It can be seen that R_p values increase with increasing current, and there exists a linear relationship between R_p and current, at least within the range of 40 to

TABLE 4. Dependence of the Rate of Polymerization of Acrylamide on Current

[AM] (mol/L)	[TA] (mol/L)	Current (mA)	Farad per liter	Initial rate of polymerization (mol/L/s) × 10^5	Average degree of polymerization
1.0	0.75	50	0.1865	2.77	1380
1.0	0.75	60	0.2239	3.33	1250
1.0	0,75	80	0.2980	6.66	1170
1.0	0.75	90	0.3350	13.85	1010

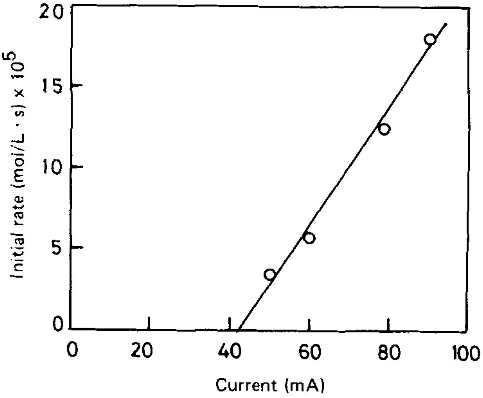


FIG. 7. Dependence of initial rates of polymerization on the current for the electroinitiated polymerization of acrylamide.

100 mA. The molecular weight of the resulting polymers decreased with an increase in current density (I). The plot of 1/DP versus I (in farad/liter) is linear (Fig. 8).

The current efficiency, i.e., the number of monomer molecules polymerized per farad, calculated from the yield of polymer and number of farads passed is found to be quite high for the polymerization system (Fig. 9) and approaches the theoretical limit, especially at high monomer concentrations.

By dividing the current efficiency by the average DP of the polymer, the number of molecules of polymer produced per electrical event is obtained. These values, shown in Table 5, are rather small, indicating little transfer during the electrolytic process.

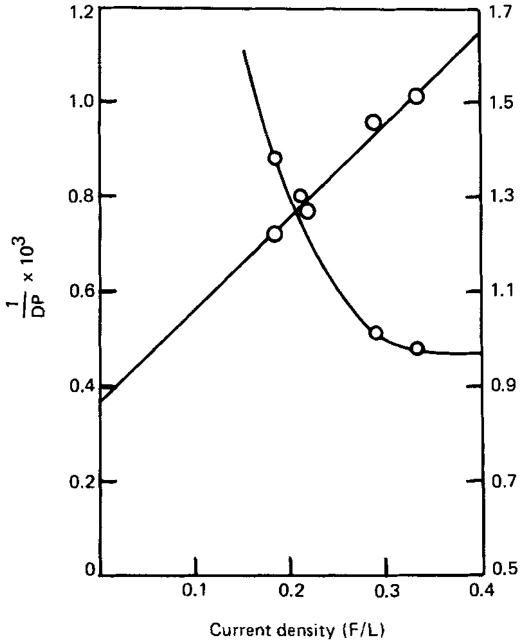


FIG. 8. Effect of current on the molecular weight of polyacrylamide formed during electropolymerization.

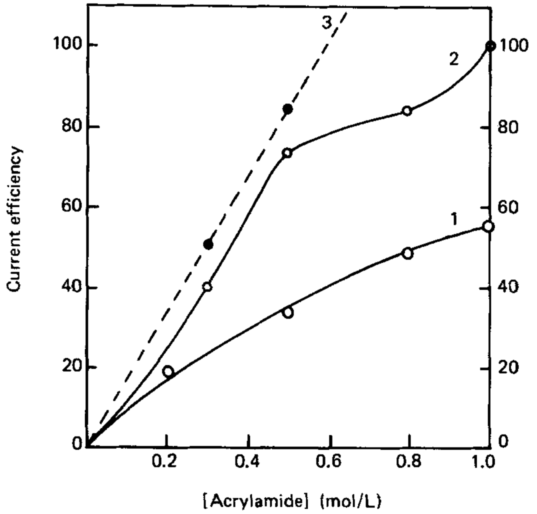


FIG. 9. Variation in current efficiency and percentage conversion with initial monomer concentration for acrylamide polymerization.

TABLE 5. Variation in Current Efficiency and Percentage Conversion with Initial Monomer Concentration

[AM] (mol/L)	[TA] (mol/L)	Current (mA)	Time (h)	Conversion (%)	Current efficiency (mol/F)	100% Current efficiency (mol/F)	Molecules polymer/ electrical event
0.3	0.37	50	2	20.0	40.0	50.0	0.019
0.5	0.37	50	2	33.5	73.9	83.3	0.039
0.8	0.37	50	2	48.1	83.9	134.2	0.044
1.0	0.37	50	2	54.8	100.7	167.3	0.053

Termination Reactions

A rough estimate of k_p^2/k_t value may be obtained from a plot of $1/DP$ against $R_p/[M]^2$ according to

$$\frac{1}{DP} = \frac{k_t}{k_p^2}\frac{R_p}{[M]^2} + \sum \frac{R_{tr}}{R_p}$$

assuming that only bimolecular termination, mainly by combination, occurs between two growing polymer chains. The second term in the right-hand side of the equation is included to cover chain transfer effects, if any, and is assumed not to affect the value of k_p^2/k_t at low rates of polymerization. Thus the value of k_p^2/k_t is found to be 0.59, and such a high value is not unusual, particularly for acrylamide polymerization, due to the fact that k_t values are often quite low [4]. The true value of k_p^2/k_t, however, would obviously depend upon the exact mode of termination during the polymerization process.

Assuming that in electroinitiated polymerization involving a radical mechanism two types of termination may occur, viz., bimolecular termination between two growing polymer radicals and electrolytic termination, DP may be expressed (in the absence of any transfer reaction) as

$$\frac{1}{DP} = \frac{R_t + R_e}{R_p} \tag{1}$$

where R_p, R_t, and R_e refer to the corresponding rates of propagation, bimolecular termination, and electrolytic termination, respectively.

Substituting the corresponding rate equation, Eq. (1) may be written as

$$\frac{1}{DP} = \frac{R_p}{[M]^2}\frac{k_t}{k_p^2} + \frac{k_e}{k_p}\frac{[I]}{[M]} \tag{2}$$

where $[M]$ = concentration of monomer and $[I]$ = current expressed as farad/liter.

Rearranging Eq. (2):

$$\frac{1}{DP} - \frac{R_p}{[M]^2}\frac{k_t}{k_p^2} = \frac{k_e}{k_p}\frac{[I]}{[M]} \tag{3}$$

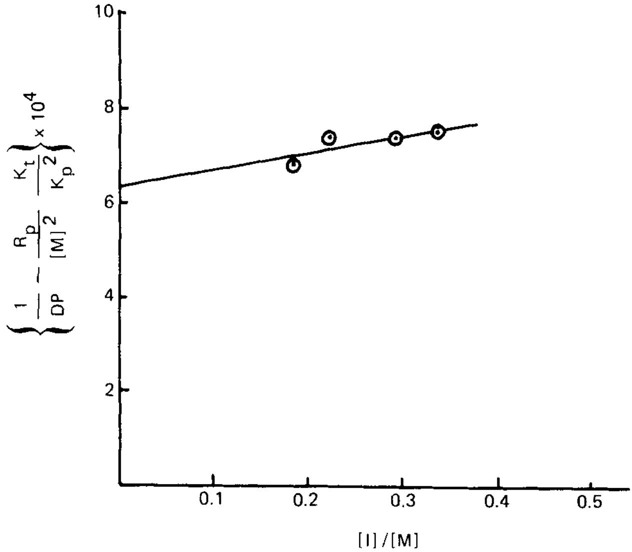
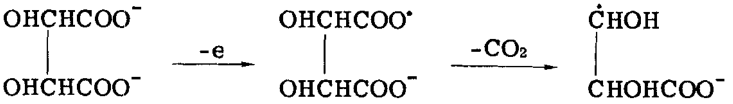


FIG. 10. Plot of $\left\{\frac{1}{DP} - \frac{R_p}{[M]^2}\frac{K_t}{K_p^2}\right\}$ vs $\frac{[I]}{[M]}$ for the electroinitiated polymerization of acrylamide in the presence of tartaric acid.

Thus the value of k_e/k_p obtained from the slope of the plot of the left-hand side of Eq. (3) against [I]/[M] is 4×10^{-4} (Fig. 10) which is quite low and shows that there is no appreciable electrolytic termination in the present system.

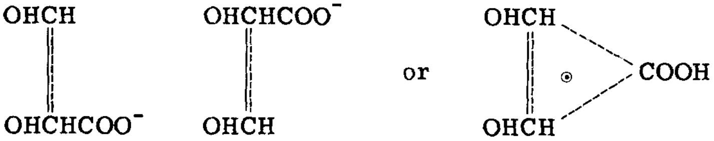
Mechanism of Initiation

Electrolysis in the presence of tartaric acid may produce diradicals, i.e., it is known that a number of orthodicarboxylic acids generate the corresponding hydrocarbons on Kolbe electrosynthesis through the formation of diradicals. On the other hand, it is quite probable that monoradicals are formed when tartaric acid is electrolyzed according to the following scheme:



$$\begin{array}{c} OHCHCOO^- \\ | \\ OHCHCOO^- \end{array} \xrightarrow{-e} \begin{array}{c} OHCHCOO^{\bullet} \\ | \\ OHCHCOO^- \end{array} \xrightarrow{-CO_2} \begin{array}{c} \dot{C}HOH \\ | \\ CHOHCOO^- \end{array}$$

Polymerization experiments carried out under controlled conditions and using a very short period of electrolysis followed by prolonged standing shows that continuous polymerization takes place through the whole period, even in the absence of any current. This "postpolymerization" behavior is probably due to the presence of radical ions which are fairly active even in the presence of air and to some extent in the presence of hydrogen peroxide. The monoradical which is thus formed might be stabilized by the neighboring hydroxyl group or by resonance between two almost similar structures:



It is interesting to note that no postpolymerization behavior is observed in electroinitiated polymerization systems unless current is passed initially, even for a very short period. This initial passage of current probably helps in the formation of the radical ions. Although some of the radical ions are much more stable compared to ordinary free radicals having a very short lifetime, their exact nature is yet to be established. It might be possible that the structure and reactivity of these radical ions are prime considerations in the postpolymerization effect.

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