CHAPTER 5

ELECTROCHEMICALLY INITIATED POLYMERISATION OF ACRYLAMIDE USING SODIUM FORMATE AS ELECTROLYTE
5.1 Introduction

The use of carboxylate salts in Kolbe's electrosynthesis is well known. The application of electric current to the polymerisation of vinyl monomers particularly styrene and methylmethacrylate using carboxylate salts was pioneered by Wilson\textsuperscript{17,18}, Das and Palit\textsuperscript{41} and Goldschmidt and Stockel. Since then a number of workers have applied this process in the field of polymerisation but very few detailed kinetic analysis have since appeared in the literature.

Unfortunately the detailed mechanism of Kolbe electrosynthesis is not yet fully understood. Although the formation of radicals during Kolbe electrolysis has been proved unequivocally the very nature of these radicals is yet to be decided.

The important steps in the Kolbe reaction involving acetates in aqueous solution are the direct electrochemical oxidation of carboxylate ion and the subsequent decomposition of the radical formed:

\begin{align*}
\text{RCOO}^- \rightarrow & \text{RCOO}^+ + e^- \quad \text{... (25)} \\
\text{RCOO}^+ \rightarrow & \text{R}^* + \text{CO}_2 \quad \text{... (26)} \\
\text{R}^* + \text{R}^* \rightarrow & \text{R-R (main product)} \quad \text{... (27)}
\end{align*}

The role of metal electrode has been presumed to be the electrocatalyst for this reaction.

It has been established that the reaction proceeds in preference to oxygen evolution in aqueous acetate solution on platinum electrodes at higher potential ($\text{Ca} \geq 2.2\text{V}$)\textsuperscript{64}. At low potentials...
discharge of OH radicals in preference to acetate takes place and a transition occurs above 2.1V, after which the electrode process changes. Anodic oxidation of acetate ion is observed at about 2.3V. Normally in aqueous media high anode potential favours oxygen evolution in the absence of carboxylate salts.

Wynne-Iones and coworkers$^{65}$ have considered an initial oxide layer formation rather a film of adsorbed acetoxy radicals for the transition region. Discharge of acetate ions to form acetoxy radicals is considered to be the next step as also the rate and potential determining step. Subsequently decarboxylation of acetoxy radicals occur. Everson$^{15,66}$, however, advocated for a concerted process involving simultaneous one-electron transfer and decarboxylation

$$3\text{COO}^- \rightarrow R^* + \text{CO}_2 + e^- \quad \ldots \quad (28)$$

In the course of polymerisation experiments several attempts have been made by isotopic tracer technique to detect these radicals trapped as end groups. Unfortunately opinions vary to a large extent and no conclusive result has been achieved.

Some characteristic features of electroinitiated polymerisation system

Electroinitiated polymerisation systems are quite unique compared to chemical and photoinitiated polymerisation systems in that the generated free radicals are initially non-uniformly distributed and in fact, without any partition between the two electrodes there should be a gradient of radical concentration during their generation from one electrode to the other. Thus the various types of secondary
reactions which might affect the polymerisation kinetics make the system somewhat complicated. Further the process of electrolysis in presence of water itself evolves gases like oxygen at one electrode under certain potential which in turn might affect the polymerisation process. Moreover the various reaction products which are often more than one makes the process more complicated to understand. Finally, the effect of continuous passage of current during the growth cycle in the polymerisation reactions has not been thoroughly studied. Thus, the preliminary reports of various electroinitiated polymerisation systems in the literature are more or less speculative in nature and the results are confined only within a particular set of conditions.

The present investigation of constant current electrolysis of Acrylamide in water in presence of a salt, such as sodium formate offers a relatively simple system to study the polymerisation kinetics in solution which are less complicated by the fact that (i) the polymerisation system can be studied to a high conversion without any precipitation of the polymer or any of the electrolysis products, (ii) the amount of current can be adjusted within a wide range and does not pose any serious limitations as are normally encountered when using organic solvents and inorganic salts and (iii) the mechanism of Kolbe electrosynthesis reaction using carboxylate has been studied in much details compared to many other electrochemical systems.

5.2 Results and Discussion

It has been strikingly observed in the present polymerisation experiments (viz., Acrylamide-salt-water) that if the system is •
allowed to proceed without any control unit as soon as the current is set in, there is an immediate rise in the value of current and after this initial rise there is a gradual fall of current as polymerisation proceeds. Results of the control experiments of electrolysis of water in presence of salt under identical conditions without any monomer suggests that during electrolysis, a relatively stronger electrolyte the hydroxides are formed which lead to an initial increase in the value of current. Simultaneous polymerisation of the monomer increases the resistance in the system thereby making a gradual decrease in the value of current. However, all the experiments in the present work was carried out under controlled conditions and due consideration was given to the formation of sodium hydroxide during electrolysis when estimating the monomer conversion by bromatometric titration.

5.2a Effect of Nitrogen on the polymerisation rate

In an attempt to find out the effect of nitrogen on the rate of polymerisation, experiments were carried out in an inert atmosphere of purified nitrogen which was continuously bubbled through the reaction cell. It was expected that the rate of polymerisation would be higher, but unexpectedly the conversion was much less than when the experiments were carried out in presence of air. A slight increase in rate, however, occurred at the initial stages of reaction. The results are shown in Table 5.1 and Fig.1. Similar observations have been reported by Palit\(^{67}\) in the electroinitiated polymerisation of MMA in aqueous medium in presence of sodium acetate as electrolyte and also
FIG. 1 - EFFECT OF NITROGEN ON THE POLYMERISATION OF ACRYLAMIDE
AIR ------- NITROGEN

FIG. 2 - EFFECT OF HYDROQUINONE ON POLYMERISATION OF ACRYLAMIDE

1) WITHOUT HYDROQUINONE
2) 0.01% HYDROQUINONE (% OF MONOMER)
3) 0.15% HYDROQUINONE
4) 0.10% HYDROQUINONE
by Federova\textsuperscript{68} in MMA-H\textsubscript{2}SO\textsubscript{4} system. The latter worker observed no polymerisation in three hours at 1.3 volt in absence of air. However polymerisation started in presence of air within thirty minutes. Smith and Gilde\textsuperscript{69} on the other hand, have shown that there was no appreciable change in the polymerisation rate in presence of air or nitrogen in the system styrene-potassium acetate-water. While in the present study, no attempt has been made on the analysis of the evolved gases, it is known that only small amount of oxygen is formed under the present conditions employed. It is quite possible that small amount of oxygen accelerates the reaction through peroxide formation. The presence of large amount of nitrogen may, however, affect the peroxide formation resulting a relatively lower conversion.

<table>
<thead>
<tr>
<th>Acrylamide concentration moles/lit</th>
<th>Sodium formate concentration moles/lit</th>
<th>Current mA</th>
<th>Time hrs</th>
<th>% conversion With nitrogen</th>
<th>Without nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.5</td>
<td>100</td>
<td>0.5</td>
<td>5.6</td>
<td>4.1</td>
</tr>
<tr>
<td>1.0</td>
<td>0.5</td>
<td>100</td>
<td>1.0</td>
<td>7.3</td>
<td>5.8</td>
</tr>
<tr>
<td>1.0</td>
<td>0.5</td>
<td>100</td>
<td>1.5</td>
<td>8.1</td>
<td>8.6</td>
</tr>
<tr>
<td>1.0</td>
<td>0.5</td>
<td>100</td>
<td>2.0</td>
<td>9.5</td>
<td>14.5</td>
</tr>
</tbody>
</table>
5.2b **Inhibition period and effect of inhibitor**

One of the characteristic features of radical chain polymerisation is their susceptibility to inhibition. Various substances mainly impurities which consume free radicals generated for the polymerisation reactions is responsible for this process. Depending on the nature of the impurities, the process may show inhibition or a retardation phenomenon, the latter being a partial reduction in rate instead of complete inhibition. However, this phenomenon of inhibition by the conversion radical inhibitors can be employed as a diagnostic test for characterising a radical chain process and typical inhibitors employed for this purpose include quinones, diphenyl picryl hydrazyl (DPPH) etc. Although the effect of these inhibitions in thermal systems is well established, their role in electroinitiated polymerisation systems has not been extensively studied. One of the deviations in their behaviour in electroinitiated system has been reported by Tidwell and Doughty.\(^{49}\)

In the present system of Acrylamide-Sodium formate no significant inhibition period is observed during polymerisation as is evident from their time-conversion curves (fig.2). Various amounts of hydroquinone have been added and their effects have been studied through polymerisation experiments. The result of such experiments has been presented in Table 5.2. The inhibiting action of hydroquinone in the present system is quite apparent. However, the inhibiting effect of hydroquinone is less pronounced, in electroinitiated system as seen from their inhibition periods, compared to the conventional initiation
methods, using the same concentration of hydroquinone. At higher inhibitor concentration, the polymerisation rate gradually falls down, thus indicating a retarding effect on the system.

Table - 5.2

Effect of hydroquinone in electro-initiated polymerisation of Acrylamide

<table>
<thead>
<tr>
<th>Acrylamide concentration Moles/lit</th>
<th>Sodium formate concentration Moles/lit</th>
<th>Current mA</th>
<th>Hydroquinone % (w/w)</th>
<th>% conversion (in 2 hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.5</td>
<td>100</td>
<td>0</td>
<td>14.5</td>
</tr>
<tr>
<td>1.0</td>
<td>0.5</td>
<td>100</td>
<td>0.01</td>
<td>12.9</td>
</tr>
<tr>
<td>1.0</td>
<td>0.5</td>
<td>100</td>
<td>0.05</td>
<td>10.6</td>
</tr>
<tr>
<td>1.0</td>
<td>0.5</td>
<td>100</td>
<td>0.10</td>
<td>7.08</td>
</tr>
</tbody>
</table>

The reaction of hydroquinone at the applied voltage at anode of the electrolytic cell in alkaline medium may be written as under:

\[
\text{H}_0 \text{-} \text{O} \quad \xrightarrow{-2\text{H}^+} \quad 0 \quad \text{O} \quad \xrightarrow{+2\text{e}^-} \quad 0 \quad \text{O} \quad \xrightarrow{+2\text{H}^+} \quad \text{H}_0 \text{-} \text{O}
\]

It is well known that p-benzoquinone act as inhibitor in free radical polymerisation according to the following reactions producing relatively stable products 70 Ia, Ib, II, III.
5.2c Determination of activation energy

It has been generally observed that an increase in temperature tends to decrease the yield of coupling product in the Kolbe reaction following a radical pathway. The effect is less pronounced in non-aqueous systems. In the reactions following a carbonium ion intermediate, this effect seems to be not so sensitive although there are reports of several cases where a small change in temperature causes a very marked change. The yield of acrylamide polymer is found to increase with increasing temperature.
FIG. 3 - Arrhenius plot for the determination of activation energy.

FIG. 4 - Polymerisation of acrylamide with various salts as electrolyte.
Polymerisation experiments were carried out at different temperatures by placing the electrolytic cell in a constant temperature bath at 40°C, 45°C and 50°C using 1.0 molar acrylamide and 0.5 molar sodium formate at 150 mA current. The initial rate of polymerisation was calculated from the time conversion curve. From the slope of Arrhenius plot (Fig.3) the activation energy was calculated and found to be 10.3 k.cal/mole.

<table>
<thead>
<tr>
<th>Acrylamide concentration</th>
<th>Sodium formate concentration</th>
<th>Current (mA)</th>
<th>Temperature (°C)</th>
<th>Initial rate of polymerisation (moles/lit/sec x 10⁵)</th>
<th>Energy activation (K.cal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.5</td>
<td>150</td>
<td>40</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>0.5</td>
<td>150</td>
<td>45</td>
<td>10.6</td>
<td>10.3</td>
</tr>
<tr>
<td>1.0</td>
<td>0.5</td>
<td>150</td>
<td>50</td>
<td>12.0</td>
<td></td>
</tr>
</tbody>
</table>

The result is in tune with that obtained by Russian scientists for polymerisation of methacrylamide using sodium acetate as the electrolyte who obtained a value of 9.8 k.cal/mole. Some of the reported literature values using persulfate initiated system polymerisation of acrylamide is 16.9, 11.97 for KMnO₄-oxalic acid system and 7.3 for chlorate-sulfite system and 7.6 for hydroxylamine-H₂O₂ system.
5.2d **Effect of various salts as electrolyte**

A number of metal salts have been used to find out the effect of anions and cations on the rate of acrylamide polymerisation. These salts are the formates of K⁺, Na⁺, Ca⁺⁺, Ba⁺⁺, Zn⁺⁺, Mg⁺⁺ and the sodium salts of formic, acetic, propionic and butyric acids. The results are presented in Table 5.4 and Fig.4. The order of activity is found to be acetate > propionate > formate > butyrate in case of anions and Zn > K > Ca > Mg > Na > Ba in the formate series.

**Table 5.4**

Polymerisation of acrylamide with various salts as electrolyte

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Electrolyte concentration moles/lit</th>
<th>Monomer concentration moles/lit</th>
<th>Current mA</th>
<th>Initial rate of polymerisation moles/lit/sec x 10⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium formate</td>
<td>0.5</td>
<td>1.0</td>
<td>100</td>
<td>6.88</td>
</tr>
<tr>
<td>Barium formate</td>
<td>0.5</td>
<td>1.0</td>
<td>100</td>
<td>1.05</td>
</tr>
<tr>
<td>Calcium formate</td>
<td>0.5</td>
<td>1.0</td>
<td>100</td>
<td>4.00</td>
</tr>
<tr>
<td>Zinc formate</td>
<td>0.5</td>
<td>1.0</td>
<td>100</td>
<td>10.50</td>
</tr>
<tr>
<td>Magnesium formate</td>
<td>0.5</td>
<td>1.0</td>
<td>100</td>
<td>3.22</td>
</tr>
<tr>
<td>Sodium formate</td>
<td>0.5</td>
<td>1.0</td>
<td>100</td>
<td>2.44</td>
</tr>
<tr>
<td>Sodium acetate</td>
<td>0.5</td>
<td>1.0</td>
<td>75</td>
<td>6.77</td>
</tr>
<tr>
<td>Sodium propionate</td>
<td>0.5</td>
<td>1.0</td>
<td>75</td>
<td>3.88</td>
</tr>
<tr>
<td>Sodium butyrate</td>
<td>0.5</td>
<td>1.0</td>
<td>75</td>
<td>0.83</td>
</tr>
</tbody>
</table>

To explain the behaviour of various anions it is interesting to record the available data on the Kolbe electrosynthesis mechanism.
applied to polymerisation systems. In case of acetates the electrolytically generated species are acetoxy and methyl radicals. The lifetime of these acetoxy radicals is rather short and eventually decarboxylation occurs as the main reaction to yield methyl radicals. However that the initiation do not occur by the direct addition of methyl or acetoxy radical to the monomer is substantiated by the work of Funt et al who failed to detect any appreciable activity in the resulting polymer using acetates labelled with C-14 at C_1 and C_2 positions. Nevertheless the main reactions of methyl radicals are coupling and hydrogen abstraction. The methyl radicals do not however abstract hydrogen from the solvent to give methane as has been shown by Claudius and coworkers in their isotope trace study involving the Kolbe electrolysis products of acetates and deuteracetates in deuterium oxide and water respectively. Hence it seems that with the methyl radicals hydrogen abstraction from monomer occurs initially and the radicals thus produced are primarily responsible for the initiation process. In the case of acrylamide polymerisation Kunugi and coworkers have reported from the analysis of the evolved gases during electrolysis that the methyl radicals are predominantly active during the initiation process.

Propionates and Butyrates in their turn yield C_2H_5COO and C_3H_7COO respectively which subsequently give ethyl and propyl radicals for the initiation process. However, hydrogen abstraction reaction of ethyl radical to produce ethane is less favoured in the electrolyte reaction coupling seems to be the preferred reaction. Further, aqueous electrolysis of deuterium labelled propionates has indicated
the occurrence of disproportionation and hydrogen atom loss from \( \text{R}^* \) (reactions 29 and 30) only 5\% of ethane with respect to ethylene was formed under such conditions.

\[
2\text{CH}_3\cdot \text{CD}_2\text{COO}^* \rightarrow 2\text{CH}_3\cdot \text{CD}_2^* \rightarrow \text{CH}_2=\text{CD}_2 + \text{CH}_3\cdot \text{CD}_2\text{H} \quad \ldots (29)
\]

\[
2\text{CD}_3\cdot \text{CH}_2\text{COO}^* \rightarrow 2\text{CD}_3\cdot \text{CH}_2^* \rightarrow \text{CD}_2=\text{CH}_2 + \text{CD}_3\cdot \text{CH}_2\text{D} \quad \ldots (30)
\]

The greater loss of initiating species may in part account for a poor yield of polymer in using propionates in aqueous medium. Similar types of side reactions might also be responsible in case of butyrates from the lower rate of polymerisation. That the primary reaction product of electrolysis viz acetox, propionox and butyroxy radicals do not play a major role in the initiation mechanism is also evident from their stability considerations in which case the reverse order of polymerisation rate would have been shown by these electrolytes.

It is interesting to observe the position of formates in the particular series as they are known to decompose in a different manner than the other three members \(^{73,74}\). Although these reactions are superficially similar to Kolbe electrosynthesis reactions in that decarboxylation occurs, the overall process can be shown as

\[
\text{HC}00^{'-} \rightarrow \text{CO}_2 + \text{H}^+ + 2\text{e} \quad \ldots (31)
\]

\[
(\text{or} \quad \text{HC}00\text{H} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e} )
\]

No coupled Kolbe product like "\( \text{H}_2 \)" is formed in this case due to the oxidation of \( \text{H} \) to proton at noble metal anode. The oxidation may proceed either by direct electron-transfer or by some other route involving discharged free radicals e.g. adsorbed \( \text{O} \) or \( \text{OH} \) in aqueous
medium so that the actual substrate oxidation to some step in the process proceeds by a heterogeneous chemical step. The basic problem of formates is therefore, different from other types and also there is independent evidence of direct catalytic decomposition of HCOOH at platinum anode \(^75\). It is therefore, difficult to assess the relative reactivity of the derived species from the electrolytic reaction in the particular polymerisation system under the present experimental condition.

The effect of different cations on the rate of polymerisation has been studied using formates of Calcium, Barium, Magnesium, Sodium, Potassium and Zinc. No direct correlation has been found between the rate of polymerisation and the cation radius as has been observed in case of Aqueous polymerisation of Acrylamide using sodium acetate as electrolyte \(^32\) - the rate decreases as the radius increases. However, it has been reported that it is also associated with the formation of electrical double layer of the cations with the solvent molecules and on their subsequent discharge reactions at the electrode surface. A change in the nature of the solvent using these electrolytes would thus be neglected on the increase or decrease in the rate of polymerisation, and in fact by changing the solvent from water to ethylene glycol an enhanced rate of polymerisation was observed. In the present study also a two to threefold increases in rate has been observed when part of water (25-50\%) is replaced by ethylene glycol.

5.2e Effect of electrolyte concentration

A few experiments were carried out with varying concentration of sodium formate as the electrolyte. The results are presented in
Table 5.5 and shown in Fig.5. The rate of polymerisation increases markedly with the increase of electrolyte concentration and is due to

Table - 5.5

Effect of electrolyte concentration on polymerisation of acrylamide

<table>
<thead>
<tr>
<th>Acrylamide concentration moles/lit.</th>
<th>Electrolyte concentration moles/lit.</th>
<th>Current mA</th>
<th>Initial rate of polymerisation x 10^6 moles/lit/sec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.20</td>
<td>120</td>
<td>1.44</td>
</tr>
<tr>
<td>1.0</td>
<td>0.35</td>
<td>145</td>
<td>2.33</td>
</tr>
<tr>
<td>1.0</td>
<td>0.50</td>
<td>200</td>
<td>3.66</td>
</tr>
<tr>
<td>1.0</td>
<td>0.65</td>
<td>240</td>
<td>5.11</td>
</tr>
<tr>
<td>1.0</td>
<td>0.80</td>
<td>260</td>
<td>6.88</td>
</tr>
</tbody>
</table>

an enhanced rate of discharge of formate ions with higher current density. It is interesting to compare these results with that obtained by using sodium acetate as electrolyte. Although the latter polymerisation rate is much higher compared to that obtained by using sodium formate, the rate of increase with increasing electrolyte concentration is quite small particularly at high electrolyte concentration. It seems probable that the side reactions become quite prominent at higher electrolyte concentration with little increase in polymerisation rate. Thus acetates may engage themselves in the side reactions (eqns.32 to 35) as shown below:

\[
\text{CH}_3\text{COO}^- + \text{CH}_3\text{COO}^\cdot \rightarrow \text{C}_2\text{H}_6 + 2\text{CO}_2 + 2e^- \quad \cdots (32^*)
\]
**Figure 5.** Time curve for acrylamide polymerisation at different electrolyte concentration.

**Electrolyte - Sodium Formate**

1) 0.2 M/L
2) 0.35 M/L
3) 0.50 M/L
4) 0.65 M/L
5) 0.80 M/L

**Figure 6.** Effect of electrolyte concentration on the initial rate of polymerisation of acrylamide.

1) Sodium Acetate (taken from Ref. 32)
2) Sodium Formate
However, the chances of side reaction in case of formate is rather low and in fact the rate of polymerisation is directly proportional to the electrolyte concentration over a wide range (Fig. 6) whereas in case of sodium acetate the rate is directly proportional to the electrolyte concentration only in lower region (say, upto about 0.25 moles/lit).

5.2f Effect of variation of current on polymerisation rate

The rate of polymerisation in electroinitiated polymerisation systems carried out in presence of electrolytes would be expected to depend on the rate of generation of free radicals from the electrolytes during the passage of current. Although an increase in electrolyte concentration would lead to an increase in rate of polymerisation, this is simply due to an increase in conductance of the system resulting to a higher "free current" value as has been shown in Table 5.6 (Fig. 7). Another way of controlling the rate of discharge of ions and hence free radicals from the electrolyte is by altering the current density through the help of an external resistance system. By selecting suitable external resistance, it is possible to control the amount of current using a fixed electrolyte concentration. In the present experiments rate of polymerisation of acrylamide were measured over a range of 50 mA to 200 mA current using other conditions same. Below
50 mA current the rate of polymerisation was negligible. The rate increased with increasing current density and the molecular weight of the polymers decreased. When the initial rate of polymerisation is plotted against current a straight line is obtained indicating a direct dependence of rate of polymerisation on first power of current (Fig.8). The results are presented in Table 5.6. It can be seen from

<table>
<thead>
<tr>
<th>Acrylamide concentration mole/lit.</th>
<th>Sodium formate concentration mole/lit</th>
<th>Current mA</th>
<th>Initial rate x10^5 mole/lit/sec</th>
<th>F/L*</th>
<th>Degree of polymerisation (DP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.5</td>
<td>50</td>
<td>3.0</td>
<td>0.1862</td>
<td>90</td>
</tr>
<tr>
<td>1.0</td>
<td>0.5</td>
<td>75</td>
<td>6.75</td>
<td>0.2799</td>
<td>75</td>
</tr>
<tr>
<td>1.0</td>
<td>0.5</td>
<td>100</td>
<td>9.5</td>
<td>0.3724</td>
<td>63</td>
</tr>
<tr>
<td>1.0</td>
<td>0.5</td>
<td>150</td>
<td>15.0</td>
<td>0.5500</td>
<td>58</td>
</tr>
<tr>
<td>1.0</td>
<td>0.5</td>
<td>200</td>
<td>20.5</td>
<td>0.7448</td>
<td>44</td>
</tr>
</tbody>
</table>

* F/L = Faraday per litre.

(Fig.8) that if the rates of polymerisation is extrapolated to zero value (as shown by the dotted line) it does not pass through the origin. However, no such phenomenon has been observed when using sodium acetate as electrolyte. This marked deviation in polymerisation rate at lower currents and the absence of any significant polymerisation at even lower current probably indicates a different picture of radical generation from the electrolyte and their participation in initiating polymerisation reactions.
**FIG. 7** POLYMERISATION OF ACRYLAMIDE AT DIFFERENT CURRENTS
1) 50 mA
2) 75 mA
3) 100 mA
4) 150 mA
5) 200 mA

**FIG. 8** EFFECT OF CURRENT ON THE RATE OF POLYMERISATION OF ACRYLAMIDE.
1) SODIUM ACETATE (TAKEN FROM 52)
2) SODIUM FORMATE
Regarding the rate dependence of initiator in conventional radical polymerisation systems, it is proportional to the square root of initiator concentration. However, if the current density (or the electrolyte) is thought to be the initiator in electroinitiated polymerisation of acrylamide, its direct dependence with the rate of polymerisation is quite different from a conventional radical initiated thermal polymerisation systems.

5.2g Dependence of polymerisation rate on monomer concentration

In order to study the polymerisation kinetics and to understand the basic mechanism it is important to determine the order of free radical induced polymerisation reactions. Various authors agree, almost unanimously that the order of reaction with respect to the initiator concentration with respect to the intensity of light in photopolymerisation, is half in general case. As regards the order of reaction with respect to monomer concentration, however, opinions differ and various authors showed that the order of reaction varies generally between 1 and 2.

In the present study experiments were carried out over a range of monomer concentration (0.2 mole/lit to 2.0 moles/lit) at a constant current of 150 mA and a constant electrolyte concentration. The effect of monomer concentration on polymerisation rates and the degree of polymerisation has been summarised in Table 5.7. The initial rates of polymerisation have been calculated from the time conversion curves (Fig.10) for different monomer concentration. It
**FIG. 9.** PLOT OF INVERSE OF DEGREE OF POLYMERISATION VS. PARADAY PER LITRE.

**FIG. 10.** TIME-CONVERSION CURVES FOR ACRYLAMIDE POLYMERISATION AT DIFFERENT MONOMER CONCENTRATION.
1) 0.2%  
2) 0.5%  
3) 1.0%  
4) 1.5%  
5) 2.0%
Table 5.7

Effect of monomer concentration on acrylamide polymerisation

<table>
<thead>
<tr>
<th>Sodium formate concentration</th>
<th>Monomer concentration</th>
<th>Current mA</th>
<th>Initial rate of polymerisation</th>
<th>Degree of polymerisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>moles/lit</td>
<td>moles/lit</td>
<td></td>
<td>Moles/lit/sec x 10^5</td>
<td>D.P.</td>
</tr>
<tr>
<td>0.5</td>
<td>0.2</td>
<td>150</td>
<td>0.38</td>
<td>17</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
<td>150</td>
<td>1.55</td>
<td>23</td>
</tr>
<tr>
<td>0.5</td>
<td>1.0</td>
<td>150</td>
<td>3.33</td>
<td>29</td>
</tr>
<tr>
<td>0.5</td>
<td>1.5</td>
<td>150</td>
<td>6.11</td>
<td>43</td>
</tr>
<tr>
<td>0.5</td>
<td>2.0</td>
<td>150</td>
<td>9.17</td>
<td>52</td>
</tr>
</tbody>
</table>

can be seen from these curves that at lower monomer concentration the normal polymerisation behaviour is observed with a slight auto acceleration effect whereas with increasing monomer concentration a distinct retardation effect is operative in the system. When a plot of initial rate of polymerisation vs. monomer concentration is made, no linear relationship is obtained. Instead a dependence of three-half power of the monomer to the initial rate of polymerisation is observed as shown in fig.11. This result is in agreement with the previous results obtained in this laboratory by using sodium acetate as electrolyte in aqueous medium.

It has been pointed out that in a steady state condition if the initiator efficiency 'f' is much lower, than the rate of polymerisation varies with three-half power of the monomer concentration.
FIG. 11. DEPENDENCE OF INITIAL RATE OF POLYMERISATION ON MONOMER CONCENTRATION
Russian Scientists however reported that in electroinitiated polymerisation system the instantaneous monomer concentration varies to
the rate of reaction to first order for both Acrylamide and Methacrylamide in ethylene glycol-water mixture using sodium acetate as
electrolyte. According to Riggs and Rodriguez, the rate of polymerisation varies 1.25 times the initial monomer concentration when
Acrylamide is thermally polymerised by using persulfates as initiator. Dainton used dilatometry and rotating sector experiments in
non-electrolyte systems to find out rate dependence on monomer concentration and in general his results followed the classical pattern of
free radical polymerisation. Rodriguez and Givey carried out kinetic study of Acrylamide polymerisation with persulfate-metabi-
sulfite initiator systems and according to these authors the rate depends on three-half power of the initial monomer concentration and
five-half fold on the instant monomer concentration. However, with chlorate-sulfite redox system Suen found that although initial rates
of acrylamide polymerisation depended on three-half power of monomer concentration, the conversion-time data best filled by a five-halves
power on the monomer concentration.

When the rate of polymerisation $R_p$ is plotted against inverse of degree of polymerisation at constant current, no straight line is
obtained and a curved line results (Fig.12). From this figure it is apparent that a polymer forming process is present in the system
which is firstly independent of rate and secondly $1/DP$ increases at a higher rate more rapidly than in direct proportion to $R_p$. Thus the
conversion is evidently due to some transfer reactions involved in
FIG. 12 PLOT OF RECIProCAL DEGREE OF POLYMERISATION vs. INITIAL RATE OF POLYMERISATION

FIG. 13: VARIATION IN CURRENT EFFICIENCY AND CONVERSION WITH MONOMER CONCENTRATION.

1) CS. FOR 100% MONOMER CONVERSION.
2) PLOT FOR % CONVERSION vs. ACRYLAMIDE CONCENTRATION.
3) PLOT OF CS. VS. ACRYLAMIDE CONCENTRATION.
Table - 5.8
Variation in current efficiency and percentage conversion with initial monomer concentration

<table>
<thead>
<tr>
<th>Monomer concentration (mole/lit.)</th>
<th>Current (mA)</th>
<th>% Conversion in 2 hours</th>
<th>Current efficiency</th>
<th>100% current efficiency</th>
<th>Molecules of polymer per electrical event</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>150</td>
<td>6.80</td>
<td>6.2</td>
<td>18.18</td>
<td>0.359</td>
</tr>
<tr>
<td>0.5</td>
<td>150</td>
<td>10.08</td>
<td>10.04</td>
<td>45.45</td>
<td>0.434</td>
</tr>
<tr>
<td>1.0</td>
<td>150</td>
<td>12.50</td>
<td>11.1</td>
<td>90.90</td>
<td>0.377</td>
</tr>
<tr>
<td>1.5</td>
<td>150</td>
<td>17.08</td>
<td>13.7</td>
<td>136.36</td>
<td>0.315</td>
</tr>
<tr>
<td>2.0</td>
<td>150</td>
<td>20.82</td>
<td>17.2</td>
<td>181.80</td>
<td>0.326</td>
</tr>
</tbody>
</table>

The process. From this experiment it has also been observed that the molecular weight of the resulting polymers are very low even over a tenfold increase in monomer concentration. It would appear, therefore, that considerable chain transfer to monomer is taking place. Also this low value might suggest that some important termination mechanism may be operative other than transfer to monomer.

The termination in the present electroinitiated polymerisation system may be of three types, firstly spontaneous or normal bimolecular termination, between two growing radicals, secondly electrolyte type and thirdly between a growing polymer chain and a primary radical of monomer responsible for initiation from which hydrogen has been abstracted by the radical derived from the electrolyte. The degree of polymerisation may then expressed as

\[
DP = \frac{R_p}{R_t} = \frac{R_p}{R_m + R_t + R_c} \quad \ldots (36)
\]
when \( R_p \) = rate of propagation,
\( R_m \) = rate of termination with monomer radical,
\( R_t \) = rate of spontaneous termination,
\( R_c \) = rate of electrolytic termination.

Again,

\[
R_p = k_p \sqrt{M} \frac{J}{M} \quad \ldots (37)
\]

\[
R_m = k_m \sqrt{M} \frac{J}{M} \quad \ldots (38)
\]

\[
R_t = k_t \sqrt{M} \quad \ldots (39)
\]

\[
R_c = k_c \sqrt{M} \frac{J}{M} \quad \ldots (40)
\]

where \( \sqrt{M} \) = concentration of monomer
and \( \sqrt{I} \) = current expressed as Faraday/litre.

Eqn. (36) can be rearranged after substitution to give

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

i.e., \[
\frac{1}{DP} - \frac{k_t}{k_p^2} \frac{R_p}{\sqrt{M}^2} = \frac{k_m}{k_p} + \frac{k_e}{k_p} \frac{\sqrt{I}}{\sqrt{M}} \quad \ldots (41)
\]

The validity of this equation can be tested by plotting the right hand of this equation against \( \sqrt{I} \) at constant monomer concentration provided the value of \( k_t/k_p^2 \) is known. In the present set up no experiment has been performed to determine the value of \( k_p \) and \( k_t \). However precise values of \( k_p \) and \( k_t \) for aqueous polymerisation of acrylamide have been determined by Dainton\(^78,79\) who have suggested
that the unusual high value of \( k_p/k_t \) is due to a higher propagation rate compared to a lower termination rate. If this value of \( k_p \) and \( k_t \) (viz. (1.80±0.15) \( \times 10^4 \) l.mole\(^{-1}\) sec\(^{-1}\) and (1.45±0.2) \( \times 10^7 \) l.mole\(^{-1}\) sec\(^{-1}\)) is used, it can be observed that the second term in the right hand side becomes very very small compared to the present 1/DP values. Thus whereas 1/DP values are in the range of \( 10^{-3} \) order, the second term is of the order of \( 10^{-7} \). Hence the second term can be neglected for practical purposes and a plot of 1/DP against \( \sqrt{I} \) at constant monomer concentration would be linear. The slope and intercept of which will give the value of \( \frac{k_e}{k_p} \) and \( \frac{k_m}{k_p} \) respectively. Fig.9 shows such a plot and the values of \( \frac{k_e}{k_p} \) and \( \frac{k_m}{k_p} \) are 1.9\( \times 10^{-2} \) and 7\( \times 10^{-3} \) respectively. These values are rather small compared to the value of \( \frac{k_t}{k_p} \) as obtained by Dainton indicating the two other termination are not of much significance. It is interesting to compare these results with that obtained by Tidwell and Doughty for electroinitiated polymerisation of styrene using NaBF\(_4\) as electrolyte in a solvent such as sulpholane when the system proceeds via an ionic mechanism. Electrolytic termination has been shown to occur to a considerable extent in that system. However, in our present system the low value of \( \frac{k_e}{k_p} \) and \( \frac{k_m}{k_p} \) indicates neither any significant electrolytic termination or termination with the monomer derived radical.

From a knowledge of the yield of polymer and the number of faradays passed the current efficiency (CE) the number of moles of monomer polymerised per faraday can be calculated. It can be observed
from Fig.13 that the polymer formed per faraday is quite low against current efficiency for 100% conversion and as the initial monomer concentration increases this difference also increases, indicating the wastage of current at a higher rate as the polymerisation process proceeds.

By dividing the current efficiency by the average DP of the polymer the number of molecules of polymer produced per electrical event is obtained. As can be seen in Table over the whole range the initiation is apparently efficient, between 30 and 45% and there appears to be no transfer. This is in agreement with the values obtained for transfer reactions.

5.2h Dependence of rate of polymerisation on pH of the medium

Polymerisation of acrylamide was carried out at three different pH of the medium of electrolysis. The pH was maintained by using suitable amount of formic acid in the system. The time-conversion curve for this is shown in Fig.14 and from these the initial rates of polymerisation were calculated. The results are presented in Table.

<table>
<thead>
<tr>
<th>pH of the medium of electrolysis</th>
<th>Acrylamide concentration moles/lit.</th>
<th>Current mA</th>
<th>Initial rate of polymerisation moles/lit/sec x10^5</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.6</td>
<td>1.0</td>
<td>150</td>
<td>2.8</td>
</tr>
<tr>
<td>4.75</td>
<td>1.0</td>
<td>150</td>
<td>3.6</td>
</tr>
<tr>
<td>5.5</td>
<td>1.0</td>
<td>150</td>
<td>4.7</td>
</tr>
</tbody>
</table>
FIG 14. CONVERSION-TIME CURVES FOR ACRYLAMIDE POLYMERISATION AT DIFFERENT PH OF THE MEDIUM OF ELECTROLYSIS
1) PH-3.6  2) PH-4.75  3) PH-5.5
It can be seen from the table that the rates of polymerisation increases with increasing pH of the medium. This is probably due to the presence of acrylamide in its protonated form which has a lower activity than acrylamide itself.

\[
\text{CH}_2 = \text{CH} - \text{C} = \text{NH}_2
\]

This is in agreement with the results obtained during electroinitiated copolymerisation experiments using acrylamide-acrylic acid system.

5.3 Kinetic scheme

The simple kinetic scheme shown in eqns. (42)-(45) is proposed.

Initiation:

\[
q + R^- \xrightarrow{k_e} R^* \quad \ldots \quad (42)
\]

\[
R^* + M \xrightarrow{k_m} RH + I^* \quad \ldots \quad (43)
\]

\[
I^* + M \xrightarrow{k_i} M^* \quad \ldots \quad (44)
\]

Propagation:

\[
M^* + M \xrightarrow{k_p} \sim M^* \quad \ldots \quad (45)
\]

Termination:

\[
M^* + \sim M^* \xrightarrow{k_t} P \quad \ldots \quad (46)
\]

\[
\sim M^* + e \xrightarrow{k_{te}} P \quad \ldots \quad (47)
\]

\[
\sim M^* + I^* \xrightarrow{k_{tm}} P \quad \ldots \quad (48)
\]
Here q is electronic charge and R\textsuperscript{−}, R\textsuperscript{•}, M, I\textsuperscript{•} and P are salt, ion radical, monomer, monomer derived radical and polymer respectively.

Equation (42) signifies the formation of primary radicals from the ions of the electrolyte. The next step equation (43) is the abstraction of hydrogen from the monomer (in this acrylamide) by the primary radicals to give monomer derived radicals I\textsuperscript{•} which subsequently initiate polymerisation of the monomers (eqn.44). Eqn.(45) represents propagation steps and the termination steps are written in eqns. (46) to (48) where three types of termination have been considered viz. bimolecular termination involving two growing chains, electrolytic termination and termination of the growing polymer radical with monomer derived radicals. Corresponding rate constants are written as k with the respective subscripts.

The rate of reaction is \( k_p \frac{\sum M\cap M\cap}{M\cap} \) \hfill \ldots (49)

The rate of initiation Ri is proportional to R. Hence we can write

\[
R_i = \int k_e \sum R\cap q = \int k_e \sum R\cap i
\]

when i is the current used.

Assuming three types of termination, the rate of termination would be given by

\[
R_t = k_t \sum M\cap + k_{te} \sum M\cap + k_{tm} \sum M\cap
\]

Under steady state conditions,

\[
k_t \sum M\cap + k_{te} \sum M\cap + k_{tm} \sum M\cap = \int k_e \sum R\cap i
\]

... (52)