

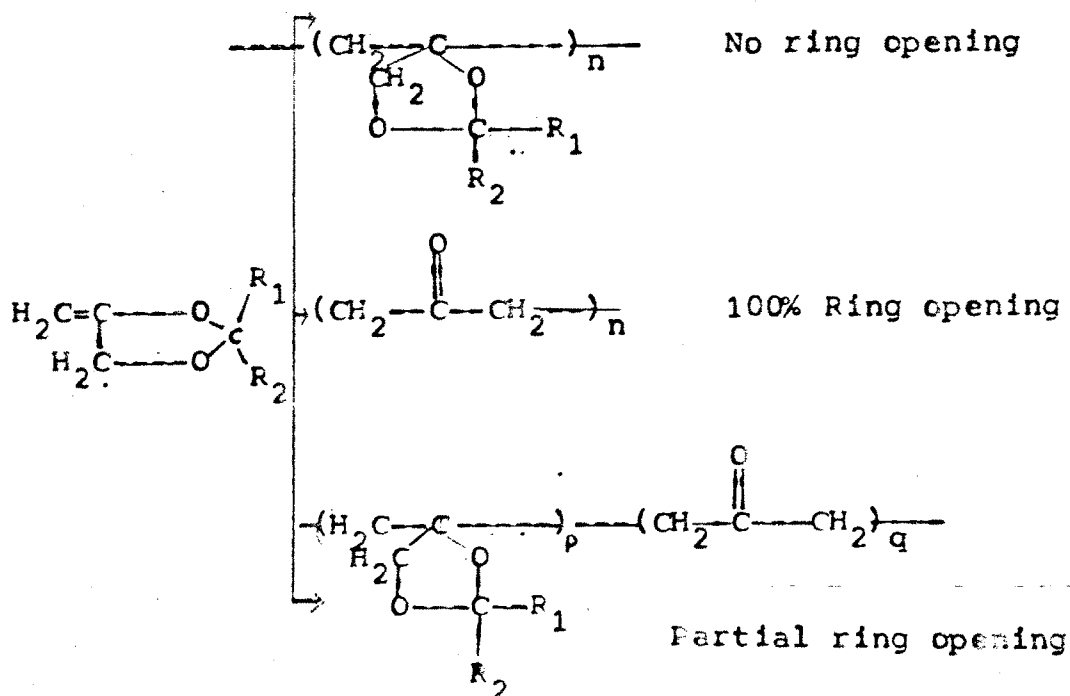
RESULTS AND DISCUSSION

CHAPTER II

RESULTS AND DISCUSSION

To study kinetics of polymerization, iodometry of the reaction mixture was carried out, as the monomers contained carbon carbon double bond. It is a customary technique for determination of monomer concentration, during polymerisation reaction, in which the monomer concentration decreases with time, consequently less bromine is consumed by the monomer and hence burette reading corresponding to liberated iodine increases with time. Preliminary experiments were carried out in a system comprising of electrodes dipped in a beaker. The reaction mixture was analysed periodically for change in concentration of monomer during polymerisation.

The present work was aimed at finding out whether polymerization process involved, ring opening and/or addition chain polymerization without ring opening. The possibilities were as following.



In any of the possibilities, concentration of monomer was expected to deplete and hence burette reading would increase.

However it was found that the burette reading decreased instead of increasing, when the reaction mixture was brominated and titrated against sodium thiosulphate solution. In this case the experimental set up consisted of a beaker in which two electrodes were immersed in the solution of monomer and supporting electrolyte. One of the possibilities for the decrease in the burette reading was that, the chloride anion could have been oxidised by the brominating mixture. Hence more consumption of brominating solution could have occurred. In order to confirm this possibility, an electrochemical setup was fabricated in which there were two compartments separated by a partition (represented in fig 1). The further experiments were performed using the modified setup, samples from anolyte and catholyte were removed periodically and were subjected to iodometry, when the anolyte showed a decrease in the burette reading while the catholyte showed an increase. The decrease in the burette reading with time can be explained on two counts.

- 1) As polymerization progressed temperature of the solution increased due to exothermicity of polymerization.
- 2) Passage of current increased with time.

2.1 ELECTROPOLYMERIZATION OF DMD

a) Choice of Electrodes : The observations of electrolysis of DMD using different electrodes in the polymerization setup, are indicated in Table 1

POLYMERIZATION OF DMD

Choice of Electrodes :-

TABLE - 1

2.1.1 ELECTROLYSIS OF DMD WITH DIFFERENT ELECTRODES

ANODE	CATHODE	OBSERVATION	
		POLYMERIZATION	ELECTRODE STABILITY
1. COPPER	COPPER	Not observed	Anode dissolves
2. STEEL	STEEL	Not observed	Anode dissolves
3. STEEL	COPPER	Not observed	Anode dissolves
4. SILVER	SILVER	Observed	Anode dissolves
5. GOLD	GOLD	Not observed	Anode dissolves
6. CARBON	CARBON	Observed	Anode swells
7. PLATINUM	PLATINUM	Observed	Highly stable

Concentration of DMD = 0.42 M

Supporting Electrolyte = Ammonium chloride

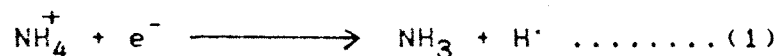
Current = 100 mA

Platinum electrodes showed not only an excellent stability but also offered, higher conductance of current during polymerization. Carbon electrodes (both as cathode and anode) were tried. These showed good results. However the anode was found to undergo swelling. When the carbon anode was replaced by platinum, the results obtained were quite satisfactory.

Copper and steel electrodes were entirely unsatisfactory as erosion in them was very severe and rapid.

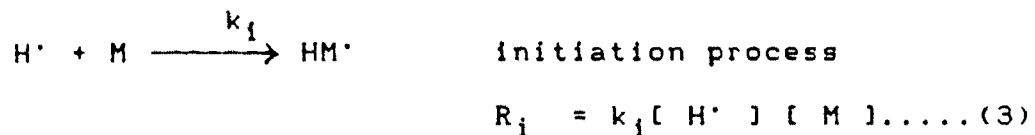
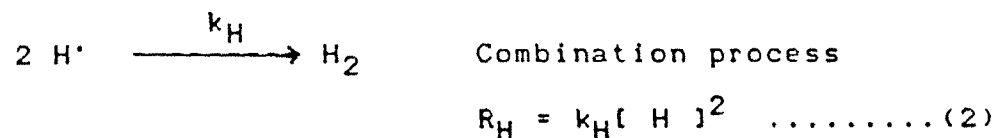
Silver and gold electrodes used in electropolymerization the electrodes remained shiny and bright. However, it was found that sol formation occurred. This was further confirmed by determining refractive indices of the anolytes. The anolyte formed by gold electrolyte could be visually noticed as the colour of the anolyte turned golden yellow, while silver electrodes caused a shiny anolyte.

At the cathode: The monomer was not electroactive therefore supporting electrolyte ammonium chloride was used in electrochemical polymerization. At the cathode ammonium ions get discharged as given below



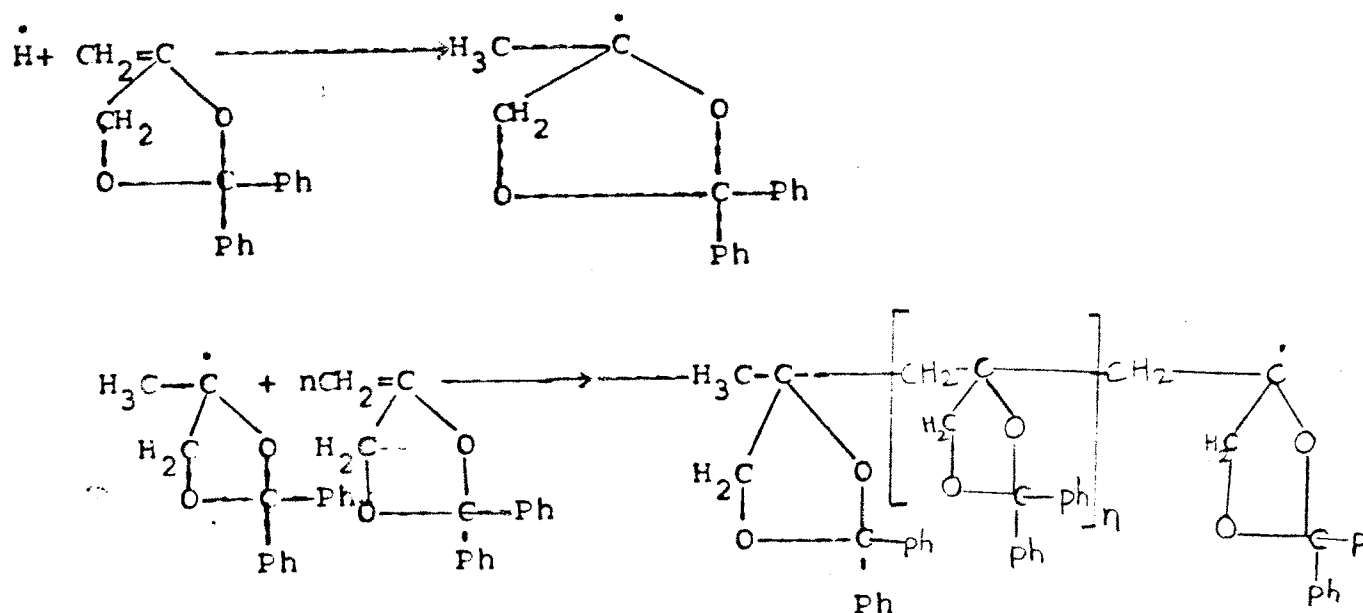
Ammonia gas generated was dissolved in water and only hydrogen gas was collected in the eudiometer. Hydrogen gas formed, during electrolysis is due to combination of hydrogen atoms (radicals). The hydrogen radicals formed can also be

consumed in initiating polymerization process as shown below



where R_H and R_i are the rates and k_H and k_i are the rate constants for combination and initiation processes respectively.

The mechanism of initiation and propagation by addition polymerization is given below



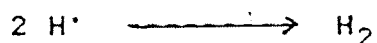
According to the scheme given above, the partitioning of hydrogen radicals into combination and initiation, should depend on the concentration of the monomer. Approach of steady state conditions to hydrogen radicals yields the relation,

$$\frac{[R_H]_{M=0} - [R_H]_{M=M}}{[R_H]_{M=0}} = f = \frac{k_i [M]}{k_H [H^\cdot] + k_i [M]} \quad \dots\dots(4)$$

where $[R_H]_{M=0}$ = Rate of hydrogen evolution in the absence of the monomer. (rate of evolution of hydrogen due to electrolyte only).

$[R_H]_{M=M}$ = Rate of hydrogen evolution at monomer concentration of M moles/Litre.

k_i in this treatment is the observed rate constant for initiation and is not corrected for inefficiencies arising due to other competing process that would involve H^\cdot , excepting the reaction.



The partition ratio, i.e. efficiency 'f' is the fraction of hydrogen radicals used up for initiation, [M] refers to monomer concentration and $[H^\cdot]$ is the steady state concentration of hydrogen radicals. As expected, the volume of hydrogen gas generated decreases with increase in the concentration of the monomer as illustrated in fig.2. The 'f' of the process at different magnitudes ,current are given in Table 2.

Equation (4) can be rearranged as

$$\frac{1}{f} = 1 + \frac{k_H [H^\cdot]}{k_i} \times \frac{1}{[M]} \quad \dots\dots\dots(5)$$

A plot of $1/f$ versus $1/[M]$ is shown in fig 8.

TABLE 2

2.2 CORRELATION OF 'f' WITH MONOMER CONCENTRATION
AND CURRENT STRENGTHS

Current (mA)	Conc. (Mole/L)	1/[M] (L/Mole)	f	Mean f	1/f
100	0.42		0.17		
200	0.42	2.3	0.15	0.156	6.41
300	0.42		0.14		
100	0.63		0.34		
200	0.63	1.59	0.31	0.310	3.22
300	0.63		0.28		
100	0.84		0.47		
200	0.84	1.19	0.43	0.44	2.27
300	0.84		0.42		

The steady state concentration of hydrogen radicals can be computed from equation (2) which can also be written as

$$[H\cdot] = \left[\frac{(1-f)I}{96500} \times \frac{10^3}{k_H \times V} \right]^{1/2} \dots\dots\dots(6)$$

where I is current in Amperes and V is volume of catholyte in mL. Since the energy of activation for combination of hydrogen atoms to form molecular hydrogen, is almost zero, the rate of combination of hydrogen radicals depends only on the number of collisions between hydrogen atoms. In other words the process is controlled by diffusion only. The rate constant for diffusion process can be given as

$$k_{diff.} = \frac{8 RT}{3000 \eta} \dots\dots\dots(7)$$

Viscosity (in terms of Poise) can be determined using following formula.

$$\eta = \frac{d \times t}{d_1 \times t_1} \times \eta_1 \dots\dots\dots(8)$$

where,

η = Viscosity of the solution of the monomer (Poise).

η_1 = Viscosity of DMF (Poise).

d & d_1 = Densities of the monomer solution and DMF.

t & t_1 = Time of flow in seconds for the monomer solution and DMF.

CLM
GIV

Table 3 gives the value of diffusion controlled rate constants ($k_{diff.}$) for electrolytic solution of different monomer concentrations [containing ammonium chloride] computed from viscosity measurements.

TABLE 3

2.3 DIFFUSION CONTROLLED RATE CONSTANTS FOR THE POLYMERIZATION MIXTURE PRIOR TO ELECTROLYSIS

$$\begin{aligned} \eta_1 &= 7.96 \times 10^{-3} \text{ Poise} \\ t_1 &= 170 \text{ seconds} \\ d_1 &= 0.9483 \text{ g/cc.} \end{aligned}$$

Conc. of DMQ	Flow time sec. (s)	Density d (g/cc.)	Viscosity (Poise)	Diffusion rate const. k_{diff} ($M^{-1} S^{-1}$)
0.42	184.0	1.043	0.9475×10^{-3}	7.06688×10^9
0.63	192.0	1.055	1.0016×10^{-3}	6.6851×10^9
0.64	199.2	1.061	1.0450×10^{-3}	6.4072×10^9

The steady state concentration of hydrogen radicals can be calculated by replacing k_H by k_{diff} in equation(6)

The equation becomes

$$[H^{\cdot}] = \left[\frac{(1-f)I}{96500} \times \frac{10^3}{k_{diff} \times V} \right]^{1/2} \dots\dots(9)$$

The steady state concentration of hydrogen radicals thus calculated are given in Table 4. It may be observed that with increase in monomer concentration, the steady state concentration of hydrogen radicals decreases only slightly. This may be attributed to very high value of k_H compared to that of k_i .

It may be also seen that the steady state concentration of hydrogen radicals varies linearly with the square root of current. Using these values of steady-state hydrogen radical concentrations $[H^{\cdot}]$ and the rate constant for hydrogen combination k_H , the values of initiation constant k_i are computed from the relation

$$k_i = \frac{f k_H [H^{\cdot}]}{(1-f) [M]} = \frac{f k_{diff} [H^{\cdot}]}{(1-f) [M]} \dots\dots\dots(10)$$

and are given in Table 5. The k_i values show good constancy for each range of concentration value and are proportional to the square root of current, consistent with the equation.

It can be easily shown that k_i is independent of $[M]$ eventhough $[M]$ appears in the expression due to the dependence of efficiency (f) on monomer concentration.

TABLE 4

2.4 STEADY STATE CONCENTRATION OF HYDROGEN RADICALS

Current (mA)	Conc. (Mole/L)	[H [•]]
100	0.42	4.9×10^{-8}
200	0.42	7.0×10^{-8}
300	0.42	8.6×10^{-8}
100	0.63	4.5×10^{-8}
200	0.63	6.5×10^{-8}
300	0.63	8.1×10^{-8}
100	0.84	4.1×10^{-8}
200	0.84	6.0×10^{-8}
300	0.84	7.5×10^{-8}

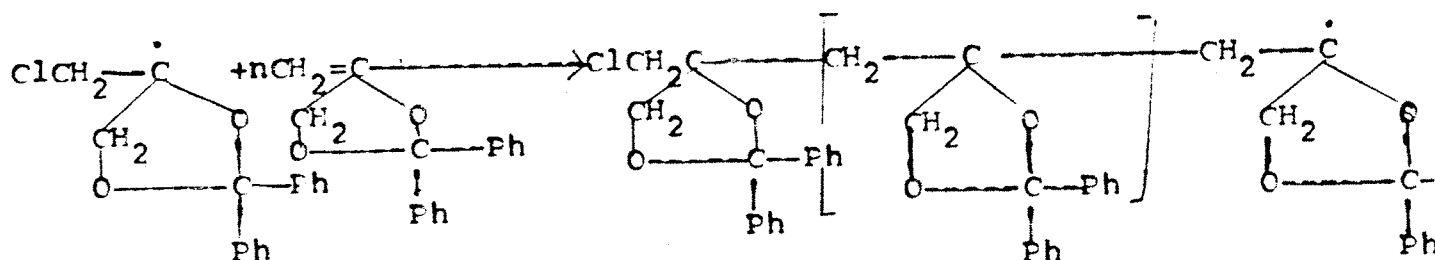
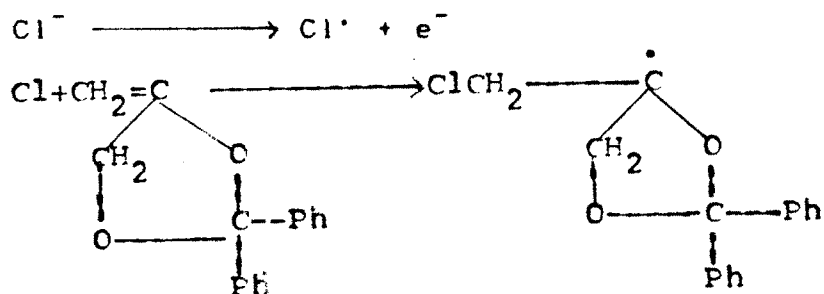
TABLE 5

2.5 INITIATION CONSTANT VALUES[IN $M^{-1} S^{-1}$]

Current (mA)	Conc. (Mole/L)	k_i	Mean k_i
100	0.42	168.0	
200	0.42	207.0	230.0
300	0.42	235.5	
100	0.63	245.9	
200	0.63	309.2	287.0
300	0.63	334.2	
100	0.84	277.3	
200	0.84	345.2	327.9
300	0.84	414.2	

At the Anode :

The anodic reaction that occurs in the electrolysis of ammonium chloride involves the oxidation of chloride ions to chloride radical. These radicals can initiate the polymerization process by addition to the double bond.



The chlorine radicals can also undergo combination forming molecular chlorine.

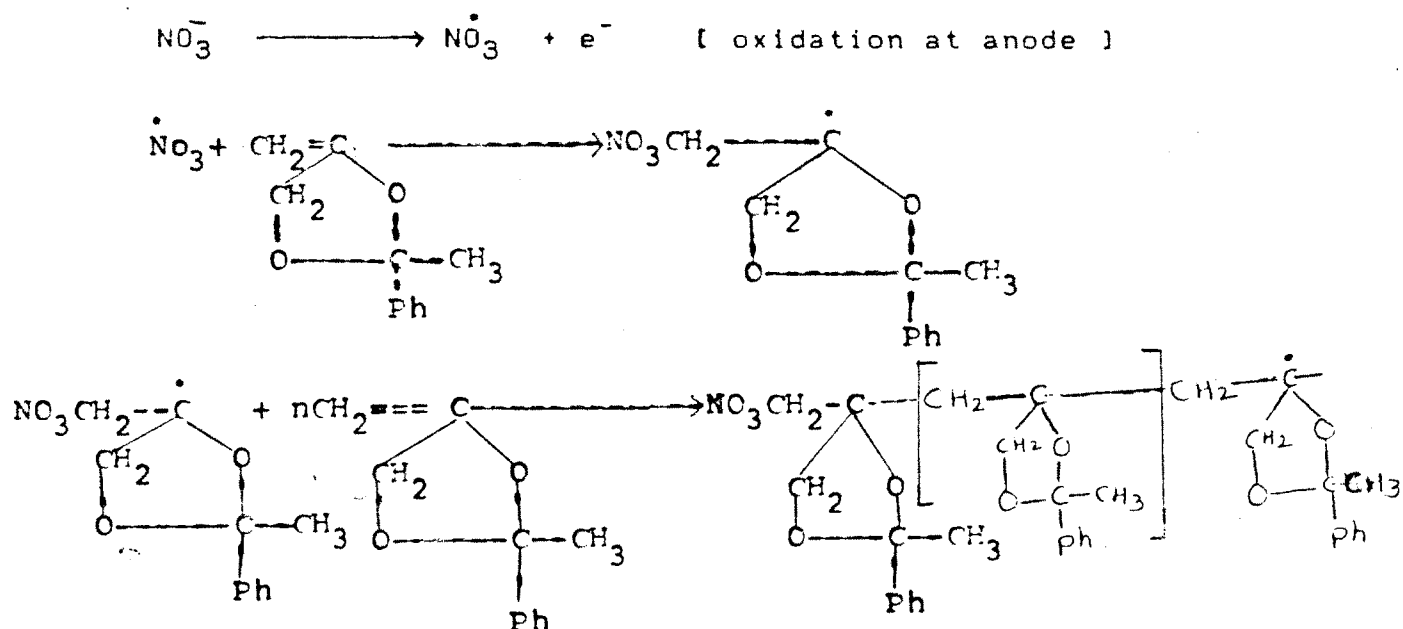


chlorine gas was collected from the anode compartment and identified, but quantitative correlation of this gas collection data was not tried as was done for hydrogen collection from the cathode compartment.

The initiated monomer radical undergoes propagation reactions leading to the formation of the polymer.

Polymerization of MPMD : The polymerization was carried out in presence of ammonium nitrate as supporting electrolyte. It was observed that no polymerization occurred in the cathode compartment.

Polymerization at Anode : Polymerization at anode using ammonium nitrate involves oxidation of nitrate anion to nitrate radical. The initiating ability of nitrate radicals in the electrochemical polymerization has been reported (46). The mechanism of polymerization is given as ..



polymerization studies indicated that higher current strength could be achieved with ammonium nitrate as supporting electrolyte, compared to that when ammonium chloride was used as supporting electrolyte. The reason for this was higher solubility of ammonium nitrate in DMF than ammonium chloride.

Viscosity : Since the Mark Houwink constants for the polymers were not known. Molecular weight could not be determined by intrinsic viscosity measurements. The value of inherent viscosity ($\ln \eta/c$) for PMPMD and PDMD was 0.14 dL/g and 0.19dL/g respectively.