ELECTROLYTICALLY INITIATED POLYMERIZATIONS

presented by

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ABSTRACT

Methyl methacrylate was polymerized in a homogenous organic medium composed of a solvent of high dielectric constant, an ionizable salt and the monomer. Application of a direct current provided a controlled initiation of the polymerization process by the discharged ionic species. The influence of the type of solvent, electrode material, electrode spacing, salt, pre-electrolysis and stirring on the yield and molecular weight of the polymer was assessed in preliminary experiments. Polymers of high molecular weight were obtained. The yield of polymer was linearly dependent on the time and kinetic analysis showed that the rate of reaction was directly proportional to both the current and monomer concentration. The molecular weight showed an inverse dependence on the current. The type of reaction mechanism was proved to be free radical and the initiating species was predominantly methyl radical CH_3. A rate scheme is proposed.

The behaviour of the same monomer, methyl methacrylate in a homogenous aqueous system of dioxane and concentrated nitric acid was also examined. The rate, molecular weight and current relationship followed a similar trend as in the former system. However, the molecular weight of the polymer was much lower and the rate of reaction was proportional to the square root of current. The reaction mechanism was found to be free radical at the anode and a super-imposed process of free radical and anionic at the cathode.

In copolymerization experiments, the reactivities of different cations for initiating a polymerization and the reaction mechanisms were investigated.

The effect of reducible organic compounds on the yield of the polymer was also studied.

INTRODUCTION

GENERAL CONSIDERATION

It is well known that a polymer is simply a large molecule, built up from a repetition of small chemical units, which may be either linearly linked or branched to form a three dimensional network. Usually, polymers can be differentiated into two broad classes namely, condensation polymers, in which certain atoms present in the monomers are absent in the structural units and addition polymers, where the structural units and monomers are identical (1). Since only the latter concerns our work, it will be discussed extensively.

KINETICS OF FREE RADICAL POLYMERIZATION

Addition polymerization is classified into two main categories; radical polymerization and ionic or co-ordination polymerization depending whether the initiating species are radicals, positive or negative ions or co-ordination complexes. The overall polymerization involves three basic steps; initiation, propagation, and termination (2). Initiation of the chain is accomplished by adding certain compounds which decompose to form free radicals or by thermal or photochemical means. The free radical generated is added to a monomer molecule and thus propagates the chain.

$$\text{initiator} \xrightarrow{k_d} 2\,R\cdot \qquad \text{initiation}$$

$$R\cdot + M \xrightarrow{k_i} RM_1\cdot$$

$$R_{n-1}^{\cdot} + M \xrightarrow{k_p} RM_n\cdot \qquad \text{propagation}$$

The cessation of growth of polymer chain generally occurs by interaction of two radicals either by combination to give a polymer molecule

$$RM_n\cdot + RM_m\cdot \xrightarrow{k_{tc}} RM_nM_mR$$

or by disproportionation to provide two polymer molecules

$$RM_n\cdot + RM_m\cdot \xrightarrow{k_{td}} RM_n + RM_m$$

The symbols k_d, k_i, k_p, k_{tc} and k_{td} represent the rate constant of reactions for decomposition of initiator, initiation, propagation, termination by combination or disproportionation respectively.

Another important mechanism by which a polymer can be formed without destruction of the radical is by the process of chain transfer, to either the monomer, initiator, solvent or polymer (3)

$$RM_n\cdot + M \xrightarrow{k_{trM}} RM_n + M\cdot$$

where M = transfer agent and k_{trM} = rate constant of chain-transfer reaction.

In the derivation of the kinetic scheme above, the assumption is made that all the radicals have the same reactivity regardless of the kinetic chain length and that the rate of formation of radicals is equal to the rate of their disappearance.

IONIC POLYMERIZATION

Although ionic polymerizations have received less attention due to the difficulties of measuring polymerization rates, the knowledge in this field is rapidly expanding. Most of the early work in anionic polymerization was confined to qualitative studies on the effect of the metal gegen ion and solvent on polymer micro structures and copolymer compositions. It has been shown that carbanion polymerization is easily initiated by metallic sodium (5)(6), alkali metal alkyls, (4,5,6) and amide ions (7,8) with monomers which facilitate nucleophilic attack. However, most of the base-catalysed polymerizations were carried out in liquid ammonia and the reactions were complicated by chain transfer to the solvent. Recent studies tend to concentrate on polymerizations conducted in hydrocarbons and ethers where chain termination is absent or negligible if the system is rigorously purified and the reactions are carried out in absence of moisture and air. Marked differences in rate and kinetics of polymerization and in the micro structure of the resultant polymer are observed between polymerizations carried out in hydrocarbon or ether solvents. It has been considered by some authors (9, 10) that polymerizations conducted in ethers of relatively high dielectric constant are true anionic whereas those in hydrocarbon solvents have intermediates of a predominantly covalent character.

Cationic polymerization research reported in the literature, is chiefly concerned with initiation by Friedel-Crafts initiators such as BF_3, $AlCl_3$, etc. using specific monomers which contain groups that promote the release of electrons at the double bond (11,12). Further treatment of this topic has been discussed thoroughly by Plesch (13) and will not be presented here.

MOLECULAR WEIGHT AVERAGE

Recognition of the average molecular weight of a polymer as a rigorously defined and precisely measurable structural feature was accomplished by Carothers (14), Flory (15) Kraemer and Lansing (16), Dostal, and Mark (17) who, on sound theoretical grounds have shown the dependence of the average molecular weight on the different methods of measurements employed. In general, two types of molecular weight averages are of importance; the number average molecular weight and the weight average molecular weight. The former is defined as the total weight of polymer divided by the number of moles which it contains. Actually it is a measurement of the number of solute molecules present rather than an indication of their sizes and thus is very sensitive to changes in the weight fractions of low molecular species. By contrast, the weight averages emphasize the significance of large molecules and are found by measurement of any property whose amplitude is not only proportional to the amount of polymer present but also to the mass of the particles. The ratio of these two averages is a measure of the polydisperity of the system.

A third average molecular weight, the so called Z average, is simply a higher statistical moment of the aforementioned averages which gives higher weighting to the molecular size of the particle. Other molecular weight averages can be defined but their experimental usefulness is doubtful (18).

Defined mathematically, these averages can be expressed as follows:

$$\text{Number average} \quad \overline{M_n} = \frac{\Sigma N_i M_i}{\Sigma N_i}$$

$$\text{Weight average} \quad \overline{M_w} = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i}$$

$$\text{Z average} \quad \overline{M_z} = \frac{\Sigma N_i M_i^3}{\Sigma N_i M_i^2}$$

Since the rate of growth and termination are random processes, it has been generally accepted that the distribution of molecular weight follows the most probable pattern with number averages at the peak succeeded the weight averages and Z averages respectively.

VISCOMETRY

In the early work of Staudinger (19), the molecular weight [M] of a linear polymer was found to be directly proportional to its intrinsic viscosity [n] in dilute solution.

$$[n] = KM$$

Although this relationship is not strictly true, it provided the bases for further theoretical work by Huggin (20) who established the expression

$$[n] = KM^{\alpha}.$$

where K is a constant whose value is independent of the molecular weight but depends on the polymer, solvent, and temperature. The second constant α is dependent on the shape of the solute molecule and ranges in value from zero for a perfect sphere to two for rigid rods. However, absolute molecular weights cannot be determined viscometrically unless the dependence of intrinsic viscosity on molecular weight has been established empirically by an absolute method such as osmotic pressure or light scattering. Flory (21,22) has shown the viscosity average of a heterogenous polymer lies between the number average and the weight average but the exact relationship depends on the conditions of propagation.

In evaluation of intrinsic viscosity, the scientific symbols and equations generally encountered are summarized in Table 1 (77).

Expressed mathematically in terms of concentration $[c]$, and extrapolated to infinite dilution by means of Huggins equation (25,26), the intrinsic viscosity $[n]$ can be defined as

$$n_{sp/c} = [n] + k' [n^2] c$$

or alternately

$$\ln n_{r/c} = [n] - k'' [n^2] c$$

where k', k" are constants for a series of polymers of different molecular weights.

In spite of inherent difficulties, viscosity measurements constitute a rapid and convenient means for determining the molecular weight of a polymer and are expecially useful for comparative purposes and for assessing molecular weight trends.

TABLE 1

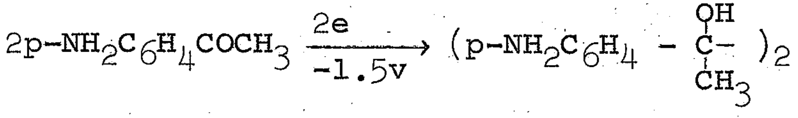
Nomenclature of solution viscosity

Common name (23)	Precise name (24)	Symbol and defining equation
Relative viscosity	Viscosity ratio	$n_r = n/n_o = t/t_o$
Specific viscosity	-	$n_{sp} = n_{r-1} = (n-n_o)/n_o$ $= (t-t_o)/t_o$
Reduced viscosity	Viscosity number	$n_{red} = n_{sp}/c$
Inherent viscosity	Logarithmic viscosity number	$n_{int} = \ln n_r/c$
Intrinsic viscosity	Limiting viscosity number	$n = (n_{sp}/c)_{c=o} = (\ln n_r/c)_{c=o}$

ELECTRO-ORGANIC PROCESSES

Electrode processes are well established in inorganic chemistry but their applications to organic chemistry, especially to the nature of the reaction mechanisms are still obscure. It has been shown that the products or intermediate species obtained during anodic or cathodic electrolysis may depend to some extent upon variables such as electrode potential (27), the medium (28, 29), catalytic effect of the electrodes (30) and added substances (31), agitation, and temperature (32). Allen (33) has attempted to correlate some of those factors with respect to electrode potential and has presented a considerable amount of experimental evidence for specific cases of both aqueous and non-aqueous systems. However, no conclusive results or definite rules have been drawn concerning the efficiency of an electrode for anodic oxidation or cathodic reduction. He indicates that sometimes metals such as zinc, lead, mercury etc., with high hydrogen overpotentials will facilitate reduction while the reverse is true for oxidation. Often by utilizing the same electrode, the same medium, and the same temperature, it is possible to obtain different products from the same starting material by merely changing the electrode potential. This has been demonstrated by Allen and Fearn (34) in the reduction of p-amino acetophenone at a mercury cathode. The formation of either the hydrol or the pinacol depends upon the potential at the mercury cathode

$$p\text{-}NH_2C_6H_4COCH_3 \xrightarrow[-1.1v]{2e} p\text{-}NH_2C_6H_4CH(OH)CH_3$$



$$2p\text{-}NH_2C_6H_4COCH_3 \xrightarrow[-1.5v]{2e} (p\text{-}NH_2C_6H_4 - \overset{OH}{\underset{CH_3}{C}}-)_2$$

The same phenomenon may be applied to electro-initated polymerization.

During cathodic reduction or anodic oxidation, the active intermediate species may be a free radical (35,36), anion or cation depending upon the electrode potential and experimental conditions employed. They are capable of initiating polymerization of vinyl compounds.

LITERATURE REVIEW

(a) FREE RADICAL POLYMERIZATION

Cathodic

The possibility of initiating the polymerization of vinyl compounds by means of electrolytic processes has not received very much attention. The first report of this kind of initiation came from Wilson and his coworkers (37). They demonstrated that methyl methacrylate,acrylic acid and its methyl ester were polymerized by cathodic hydrogen in an aqueous methanol medium using dilute sulphuric acid as electrolyte and attempted to correlate the yield with hydrogen over-voltage. It was found that only certain metals such as Pb, Sn, Pt, Bi, Fe, possessing a high hydrogen voltage were able to initiate polymerization, and that the efficiency of the system tended to increase with increasing hydrogen over-voltage. The proposed mechanism was the formation of a hydrogen atom at the cathode and its addition to a monomeric molecule, followed by the growth of the resulting free radical until termination. Little, if any, reduction of the monomer was observed.

This work was supported by Palit and Das (38) in 1950. Originally they attempted to polymerize methyl methacrylate and styrene in propane-1,2-diol solution with acetate or methyl radicals generated by Kolbe electrolysis of sodium acetate but the result did not prove to be as successful as expected. Instead, insoluble polymer was obtained at the smooth platinum cathode which was attributed to an initiation by hydrogen or sodium atom. A similar approach was undertaken by Parravano (39) in 1951 who polymerized methyl methacrylate in 0.1 N sulphuric acid using different electrode materials, and electrodes loaded with different amounts of hydrogen. He established a correlation between yield and hydrogen over-voltage of the cathode in full agreement with Wilson's work. Parravano also found that the efficiency of initiation was low compared with the total hydrogen released by electrolysis. In 1953, Kern and Quast (40) performed similar types of experiments using aqueous hydrogen chloride as electrolyte instead of dilute sulphuric acid. They reported the polymerization of 270 moles of monomer per mole of hydrogen discharge. The polymerization was assessed to be a radical mechanism since molecular oxygen was shown to be an inhibitor. The rates of polymerization were not reproducible due to the coating of the cathode surface. Initiation by H_2 absorbed on a Pd catalyst was unsuccessful and hydrogenation was the only reaction observed. This was contrary to Parravanos results.

The difference was accounted by the fact that Parravano did not shake the mixture. Activated hydrogen in Pd was also tried as part of the oxidation and reduction initiation system. Among these, those using a potassium persulphate, benzyl peroxide, and ferric ions system were successful while those using a hydrogen peroxide, benzyl peroxide, and potassium chlorate system were not. Under certain conditions, catalytic hydrogenation and polymerization were competing reactions.

Indirect Method

An indirect method was attempted by Kolthoff and Ferstandig (41) who polymerized acrylonitrile by forming an activator electrolytically in a redox system.

$$Fe^{+3} + e \longrightarrow Fe^{+2}$$

$$Fe^{+2} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH\cdot$$

The initial ferric ions were reduced cathodically to ferrous ions and then reoxidized by hydrogen peroxide. The active intermediate species, hydroxyl free radicals, were released and then used to initiate the polymerization. Other oxidizing agents such as potassium persulphate were also employed. Electrolysis was not confined to the electrode region and very good yields were reported. With a current of 20 ma, polymerization of acrylonitrile had reached 100% conversion after 15 hours in the potassium persulphate-sulphuric acid system.

Anodic

The first successful anodic polymerization was described by Goldschmidt and Stöckel (42). They showed that styrene and acrylonitrile could be polymerized by free radicals generated by means of Kolbe electrolysis in a fatty acid medium.

$$RCO_2^- \xrightarrow{-e} RCO_2\cdot \longrightarrow R\cdot + CO_2$$

With a current density of 1-4 ma/cm^2, styrene was mainly converted into dimer and trimer at the anode in a sodium acetate and acetic acid medium but some polymer of a low molecular weight, 3,200, was also isolated. Similarly, dimers of acrylonitrile were obtained.

Further work was conducted by Smith and Gilde (43) who dimerized both butadiene and isoprene anodically in methanolic solution of potassium acetate. They also reported high molecular weight polymers of methyl methacrylate, vinyl chloride and vinyl acetate with an intrinsic viscosity of approximately 0.80 - 0.99 at a current density of 1.11 ampere/sq. in. to .22 amp/sq. in. in the heterogenous system of potassium acetate and water (44). The polymer isolated in each case was neither stereospecific nor cross-linked. An attempt to study some aspects of stereo-chemistry of electrode processes was also achieved by the same authors (45) who found that electrolysis of methanolic solution of potassium propionate in presence of butadiene formed only trans isomer of 4-octene. Lindsey and Peterson (46) on the other hand, were only able to obtain dimers of butadiene.

Recently, polymerization of styrene, acrylonitrile and methyl methacrylate in a non-aqueous medium of acetic acid and acetic anhydride saturated with lithium acetate was reported by Breitenbach (48). The reaction mechanism was assumed to be free radical.

(b) IONIC POLYMERIZATION

Cationic

Cationic polymerization of vinyl compounds by electrode processes was first claimed by Breitenbach and coworkers (48) (47) who polymerized styrene, N-vinyl carbazole and isobutyl vinyl ether by anionic discharge of suitable anions ClO_4^-, BF_4^- etc., in a nitro benzene medium. The proposed mechanism was

$$(ClO_4)^- \longrightarrow (ClO_4)\cdot + e$$

$$(ClO_4)\cdot + M \longrightarrow (ClO_4)^- + M^+$$

The yields of polymer were comparatively high but the molecular weights obtained were very low with an intrinsic viscosity ranging from 7.5 - 9.1 ml/g. However it is believed that the reaction proceeds without the passage of current since BF_4^-, ClO_4^- are very strong cationic catalysts (49)(50)(51).

Anionic

Another type of polymerization was observed by Yang, McEwen and Kleinberg (52) who assumed a direct initiation of styrene by electrons supplied by the cathode during the electrolysis of sodium iodide in anhydrous pyridine with magnesium electrodes. Further experiments were reported by Breitenbach (53) who polymerized acrylonitrile by cathodic discharge of tetra-alkyl ammonium ions. At that time, the reaction mechanism was believed to be free radical as indicated by

$$(C_2H_5)_4N^+ + e^- \longrightarrow (C_2H_5)_4N\cdot$$

$$(C_2H_5)_4N\cdot \longrightarrow (C_2H_5)_3N + C_2H_5\cdot$$

but later it was proved to be anionic by copolymerization studies (47)(48). However, most of the work reported by Breitenbach in the literature is incomplete and the results are confusing and sometimes even misleading. Experiments conducted were exploratory and no detailed studies in any system were performed.

In summary, most of the early work in electro-induced cathodic polymerization was conducted in an aqueous medium with mineral acids as initiators. The polymer obtained was always insoluble in the system and sometimes even coated the electrodes. A partial attempt to relate the yield of polymer with hydrogen over-voltage was achieved but the molecular weight of the polymer was not noted. In anodic polymerization, Kolbe electrolysis was used as a source of free radicals and the reaction was carried out in a heterogenous system. The polymer isolated was always of low molecular weight and sometimes only dimers or trimers were obtained. The dependence of the viscosity of the polymer on current was slightly mentioned.

Cationic and anionic polymerizations by electrode processes were examined recently. The authors seemed to accentuate interest in the formation of the polymer but not the mechanism of the reaction.

NATURE AND PURPOSE OF OUR INVESTIGATION

A brief review of the previous papers in electro-initiated polymerization strongly indicates that most of the work done has been exploratory in nature and the scope of the field is not properly developed. Electron transfer processes which occur at the electrodes of the electrolytic cells provide excellent means of the controlled initiation of polymerization reactions. The ease with which the electrical processes can be programmed, varied and measured, and the inherent simplicity of the elementary electrode reactions contribute to the attractiveness of this method of polymerization.

For free radical reactions, the conventional initiation processes based on the thermal decomposition of a labile compound impose severe restrictions on the effective temperature range in which polymerization can be conducted at a convenient rate. Once the reaction is under way, its further control is limited by sluggish character of thermal transfer and, in general, the reaction can be stopped only by contamination with a foreign chemical compound or inhibitor. Electrical processes can, however, be started and stopped with ease. Similar considerations apply to ionically initiated reactions.

The difficulties often encountered in electro-induced polymerizations are the coating of electrodes, insoluble polymer, low yield, low molecular weight and dimerization. All these factors tend to render kinetic studies impossible in our early work. However, if a proper system is employed, some of these complications may be removed.

Since most of the early studies were confined to qualitative aspects of the reactions, it was our intention to place more emphasis on the reaction mechanism, initiating species, the effects of current, electrode material, solvent, initiating salt on the yields and molecular weights of the resultant polymer of a particular system to develop a general understanding in electro-induced polymerization.

EXPERIMENTAL PROCEDURE

SALT AND SOLVENT SYSTEM

Monomer and Solvent Purification

Monomeric methyl methacrylate was obtained from Rohm and Haas, Philadelphia, U.S.A. It was stabilized by approximately 60 parts per million of hydroquinone to prevent polymerization during shipping and storage. The monomer was freed of inhibitor by repeated washing with 10% NaOH, distilled water, then dried over $CaSO_4$ and fractionally distilled under reduced pressure.

Other monomers used, such as styrene, vinyl acetate, acrylonitrile, methacrylic acid and esters of acrylic acid were purified by adding a small amount of initiator followed by distillation under atmospheric pressure or reduced pressure depending upon the conditions.

Dimethyl sulfoxide and dimethyl formamide were dried, the former over calcium hydride, and used without further purification.

Unless otherwise indicated, the other reagents employed were of reagent grade purity and were used for subsidiary experiments without further purification.

Apparatus

In these first studies, a variety of cells and voltage supplies were employed. For most measurements, a high stability constant current supply especially designed by W. G. Hoyle of the National Research Council of Canada was employed. This furnished a controlled current in the range 1.5 ma to 15 ma with a constancy of ± 0.04%. For the higher current range, an Ambitrol 4005 was used. In general, the applied voltage ranged between 2 and 4 volts. Due to the low resistance of the system employed, a constant current supply, stabilized by high resistances to deliver different current strengths at the same time was chosen for the kinetic studies.

Cells were of simple glass design with provision for bubbling with an inert gas. For some measurements, a cell with divided compartments separated by a fritted glass disc was employed. The electrodes generally used were either platinum or carbon. The use of a carbon to carbon joint to avoid corrosion of the metal contact proved to be advantageous. For the majority of the experiments, the cell was of cylindrical test-tube shape and contained two plane graphite electrodes of 23.9 cm^2 area separated by teflon spacers to 1/8 inch spacing. Platinum electrodes having an area of one square inch and a spacing of approximately half an inch in a slightly different designed cell with a side tube opening for removal of sample were employed for all the work in the concentrated nitric acid and dioxane system. The apparatus and instruments used are shown in Figure I.

Kinetic Studies

It was found that in the non-aqueous system with dimethyl sulfoxide as the medium and zinc acetate as initiator, an efficient purification of the solvent and salt components , predominantly to remove electrolytic impurities and water could be achieved by pre-electrolysing the solution before the addition of monomer.

In typical experiments, samples containing 37.5 ml of monomer, an equal volume of solvent and 3 gms of a salt were placed in the electrolytic cells and polymerization was

FIGURE I(a). Divided polymerization cell.

(a) Mercury contact.

(b) Medium porosity sintered glass disc.

(c) Platinum electrode.

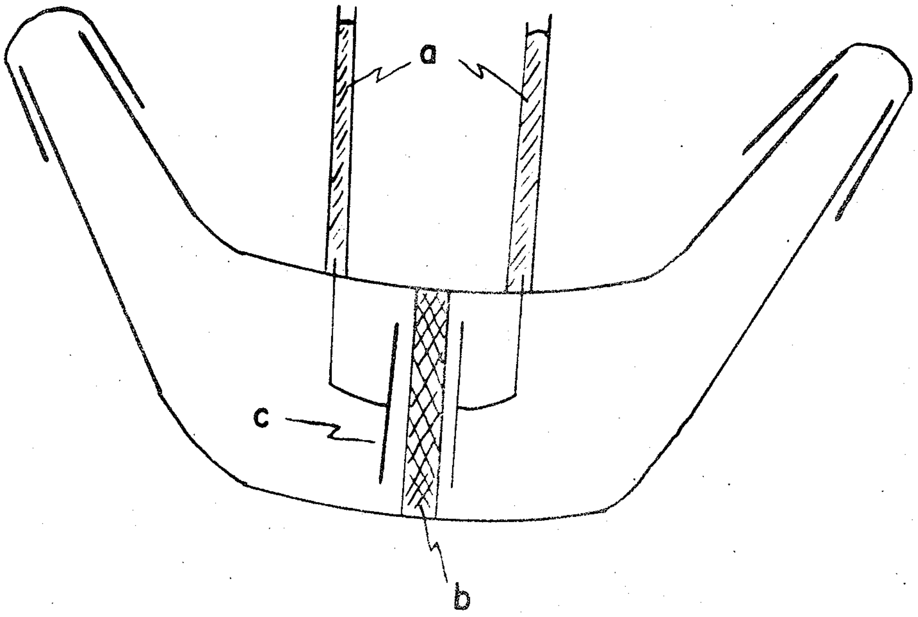

a
c
b

FIGURE I(b). Polymerization cell used for rate determination.

(a) Carbon electrodes.

(b) N_2 inlet.

(c) N_2 outlet.

(d) Teflon spacing.

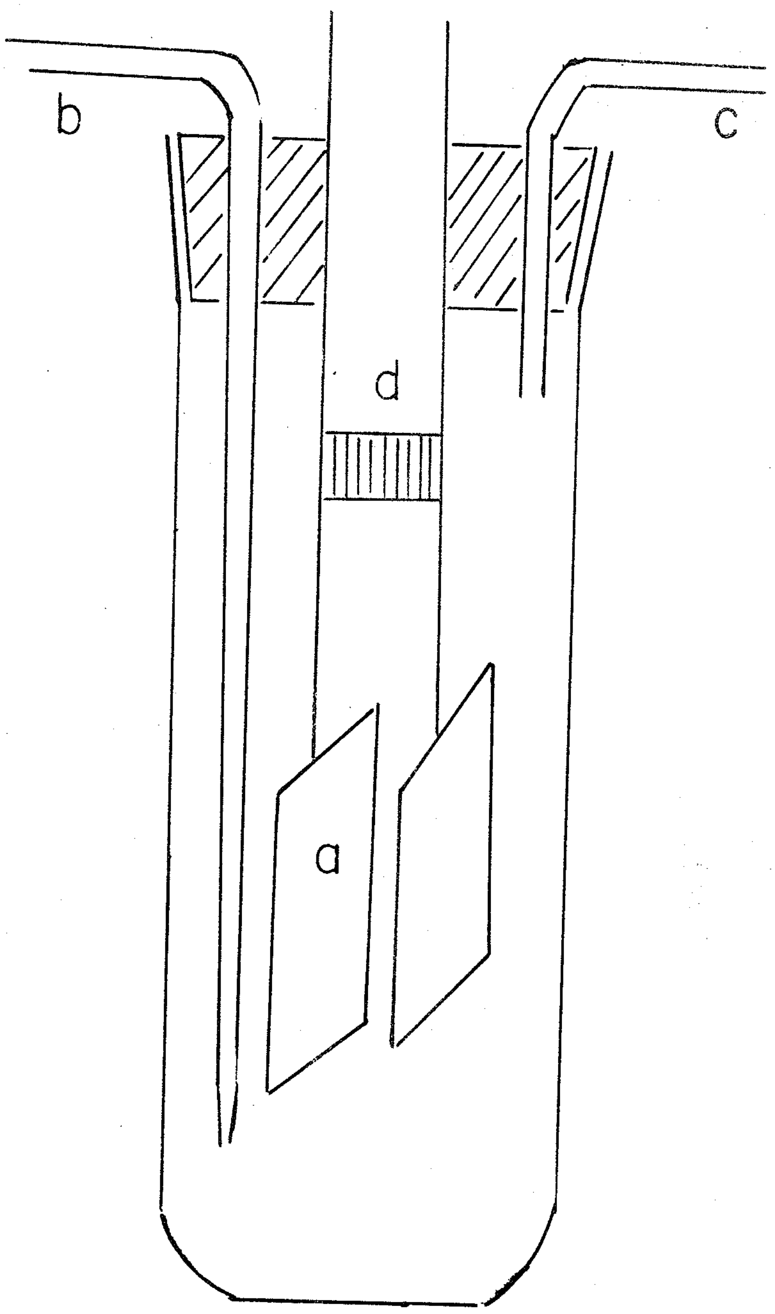
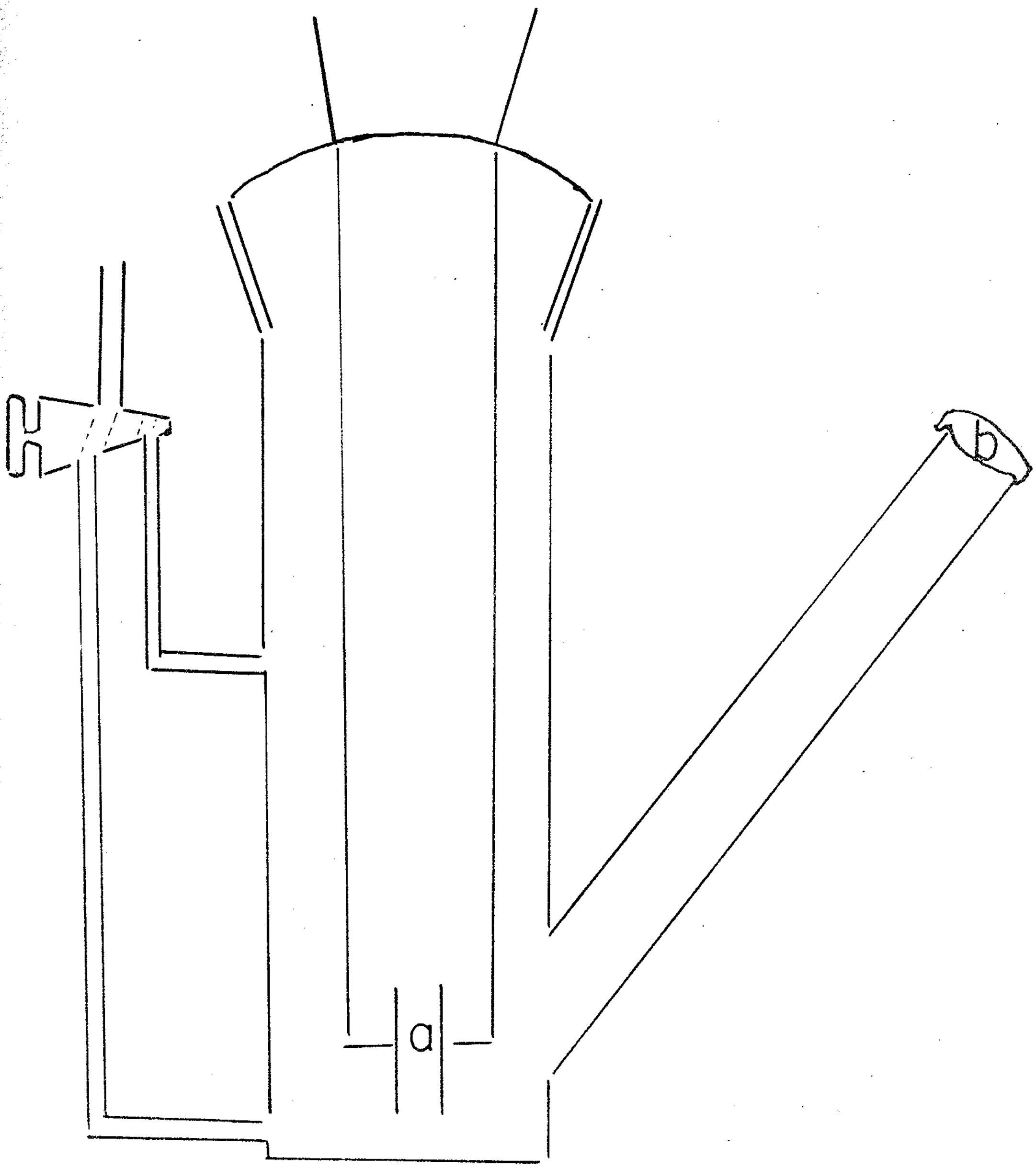

b
c
d
a

FIGURE I(c). Modified polymerization cell.

(a) Platinum electrodes.

(b) Self-sealing gasket.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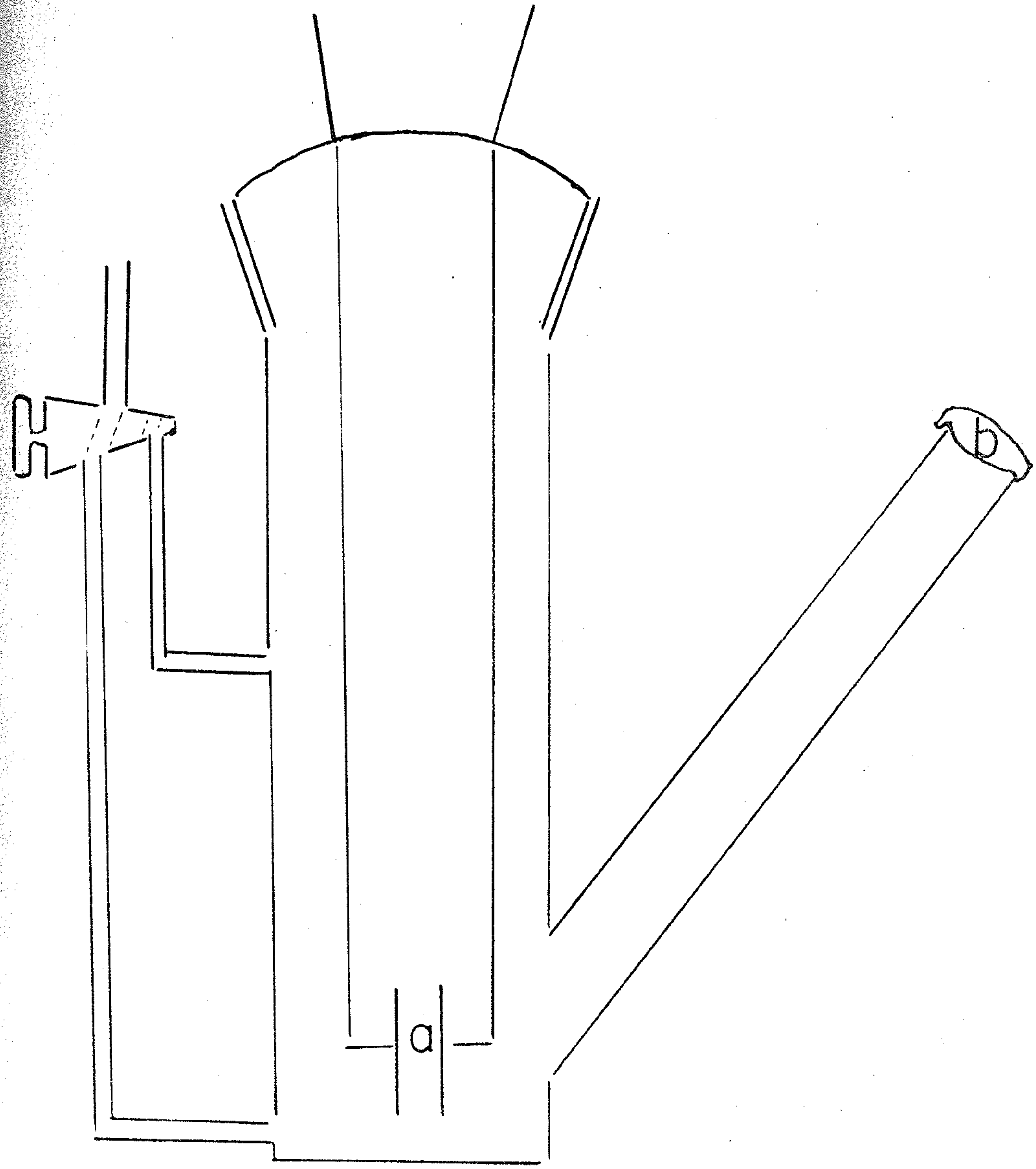
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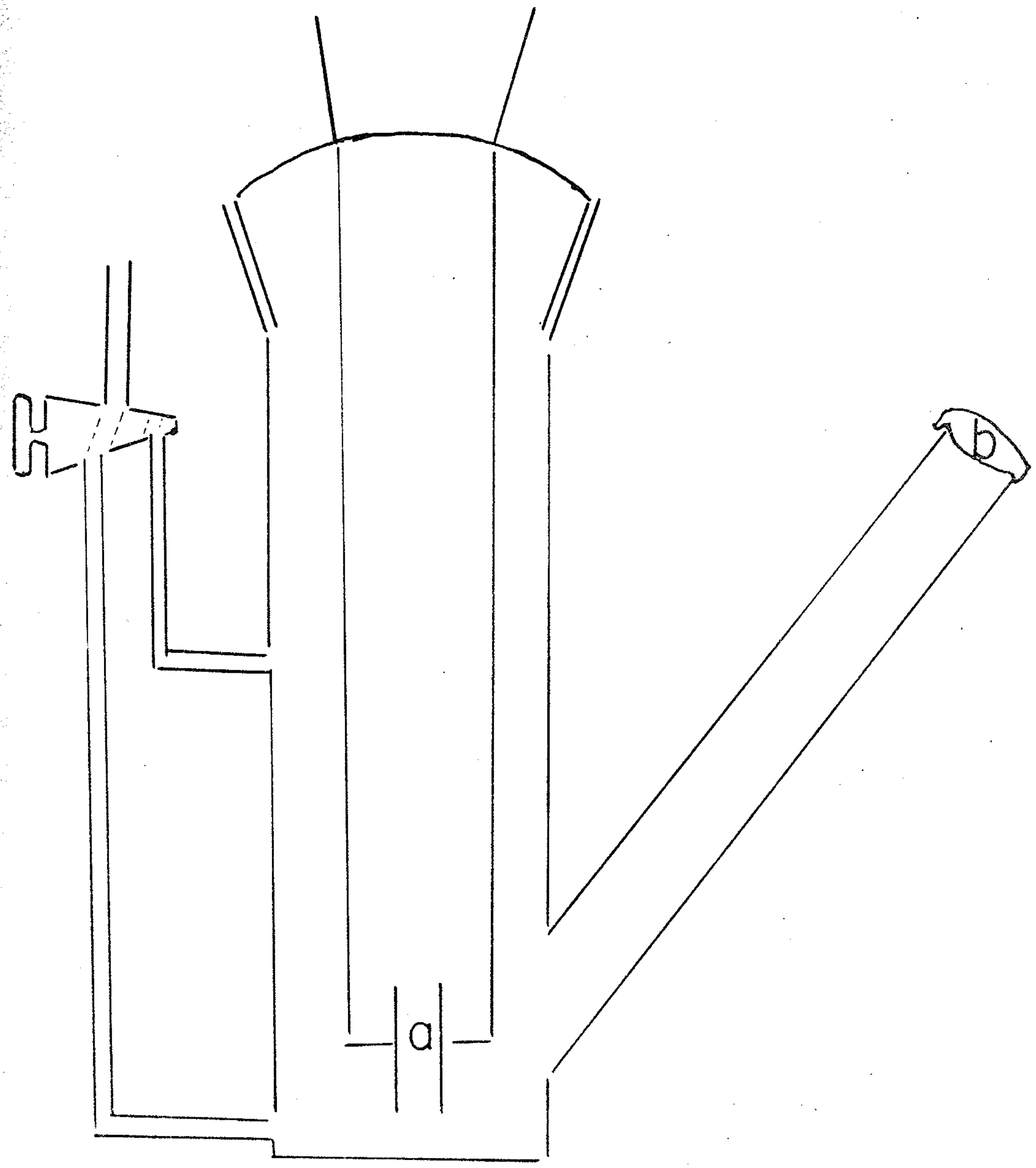

a
b

FIGURE I(d). Constant current supply.

(1-15 ma)

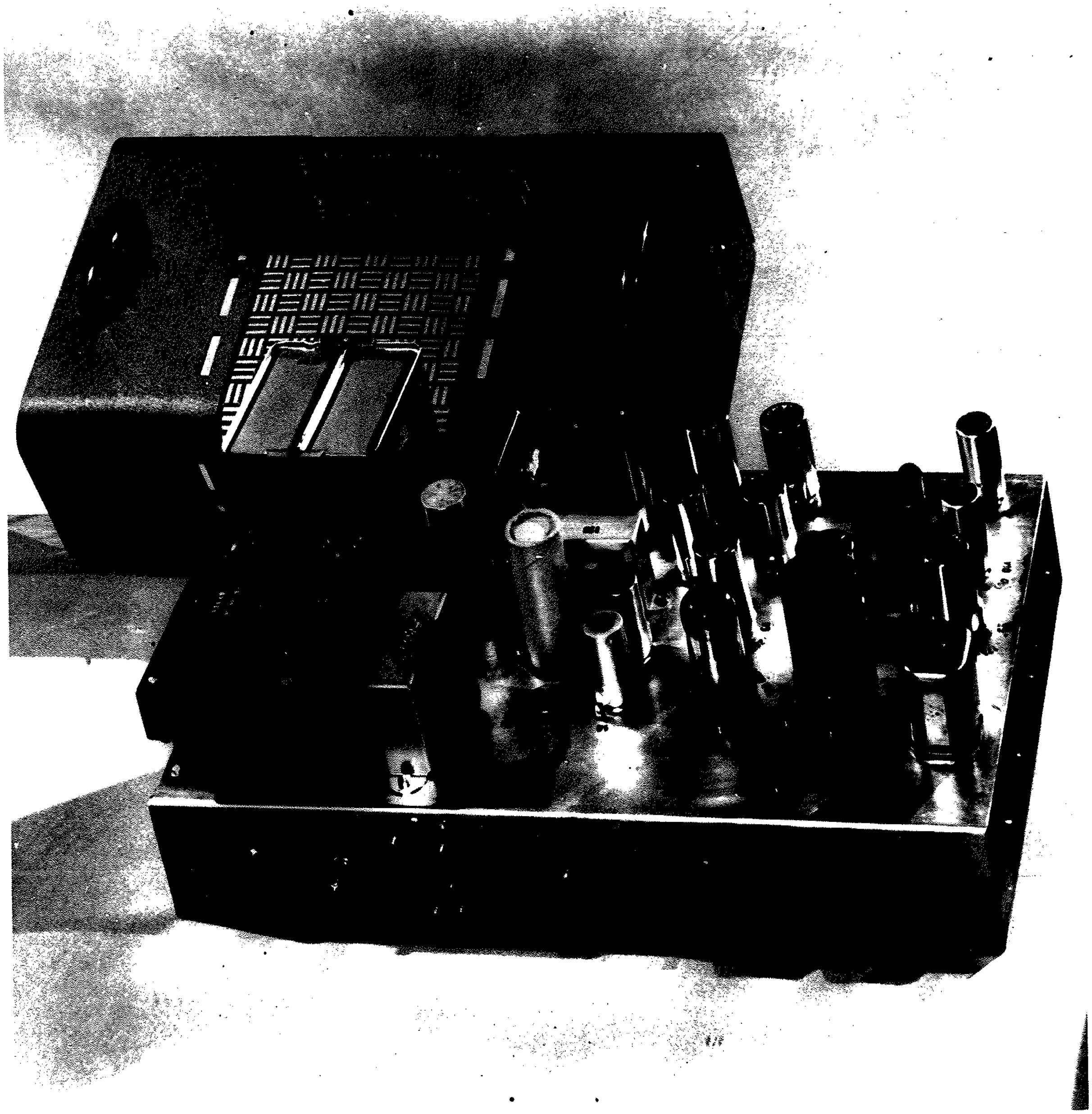
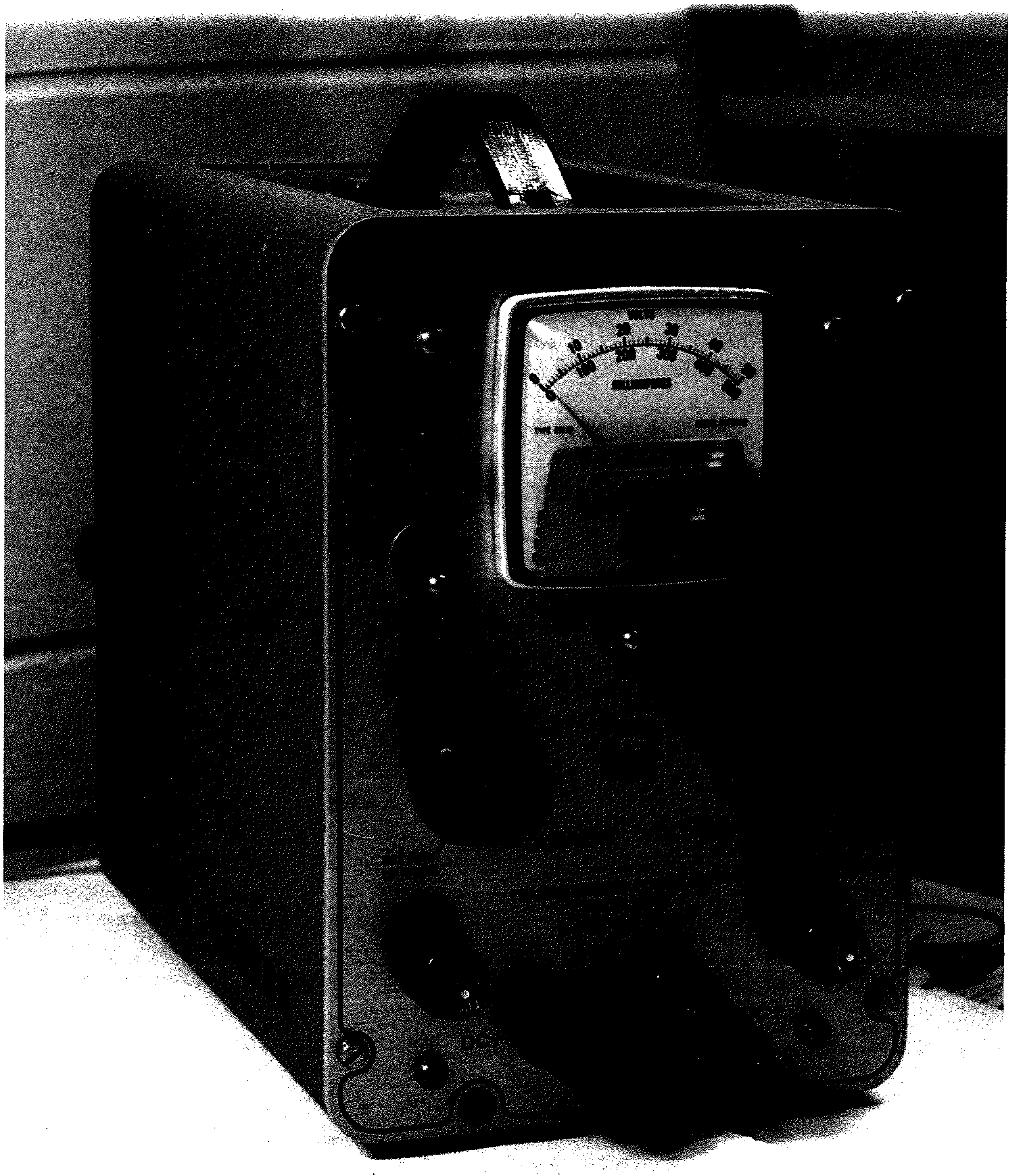


FIGURE I(e). Constant current supply.

(25-500 ma)


VOLTS
0
10
20
30
40
50
0
100
200
300
400
500
MILLIAMPERES
DC

conducted at different but constant current values in each cell at room temperature. Samples of 5 ml volume were withdrawn consecutively at 6 hr periods by means of a surgical syringe and the yield of the polymer was determined accurately by precipitation with cold methanol, redissolution, reprecipitation, drying and weighing. Usually it is desirable to use a methanol and water mixture for complete precipitation, but in our case, cold methanol at -30° C was preferred to obtain polymer in powder form. Further details are treated in the results and the discussion.

Molecular Weight Determination

Of the several methods available for the determination of average molecular weight of large molecules or polymers, the viscosity method constitutes the simplest and most rapid means. From the molecular weight distribution curve, the viscosity average lies between the number average and weight average. Since we are only interested in the effect of current changes on the molecular weight of the polymer, the viscosity method is most suitable for our purpose.

Intrinsic viscosities were measured in methyl ethyl ketone at 25° C in Ubbelohde Viscometers (Figure II) and the molecular weights were determined from the Staudinger equation

$$[n] = KM^{\alpha}$$

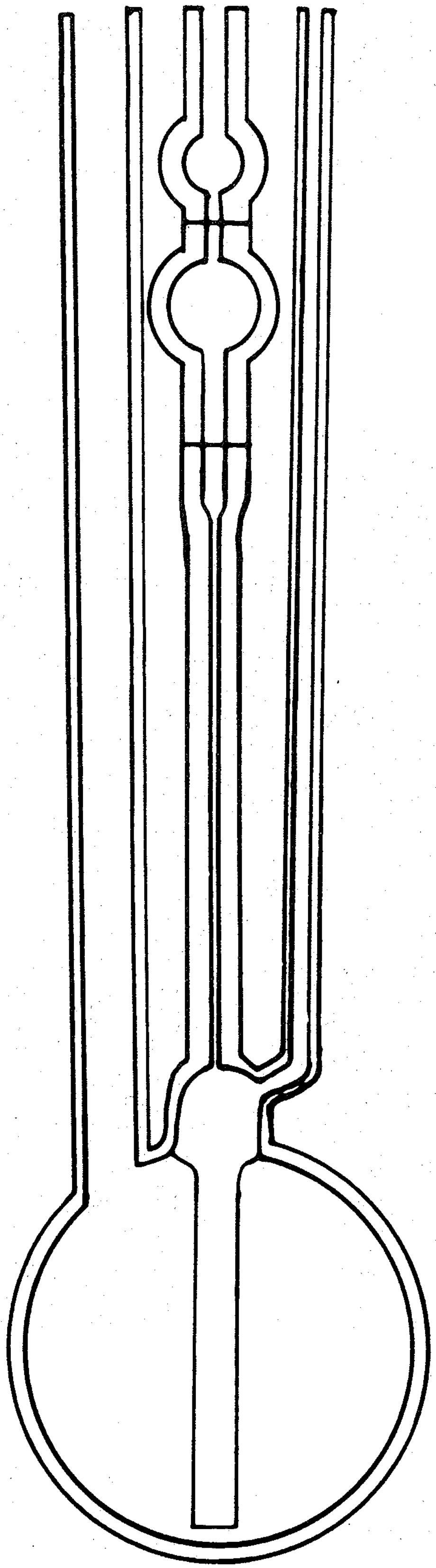
using $K = 6.8 \times 10^{-5}$ and $\alpha = 0.72$ (55)(56)(63).

The constants K and α are different for different molecular weight ranges and change with solvent. The literature was consulted to choose the best values which fit the experimental results for the estimation of molecular weights. The molecular weight range employed was from 35,000 - 10,000,000.

Tracer Studies on Initiating Species and Reaction Mechanism

Labelled zinc acetate with C^{14} in C_1 position was prepared by dissolving tagged sodium acetate-1-C^{14} of known radioactivity concentration in a certain amount of water and adding a known quantity of zinc acetate solution to allow exchange of acetate ions. The resulting solution was heated to 100° C and the water vapour was removed by suction. Part of the acetate ion was decomposed in this process and final concentration of labelled zinc acetate was estimated by

FIGURE II. Ubbelohde Viscometer.



liquid scintillation counting. A similar method was used to prepare zinc acetate-2-C^{14}. The techniques and principles involved in scintillation counting will be treated under copolymerization.

Experiments with tagged zinc acetate in $_1C^{14}$ and $_2C^{14}$ positions respectively as initiators in the polymerization of methyl methacrylate in dimethyl sulfoxide medium were conducted in divided cells at a fixed current for the same period of time. Since the original activity of tagged zinc acetate, the time, the current, and the final activity of the polymer are known, the initiating species can be determined.

Analysis of the copolymer composition to determine whether the reaction mechanism was anionic, free radical, or cationic was first suggested by Walling (57)(58). In our present study, a copolymerization of equal volume mixture of methyl methacrylate and C^{14} labelled styrene was conducted in a divided cell. The mole fraction of styrene in the copolymer was calculated from the activity of a known quantity of copolymer and the standard.

DIOXANE SYSTEM

Kinetic Studies

In the system of dioxane and nitric acid, the experimental procedure employed was similar to that discussed in salt and solvent system. Polymerization of the monomer, methyl methacrylate was conducted in a cylindrical cell equipped with a side arm for removal of the sample. Platinum electrodes having an area of one square inch and a spacing of 1/2" were used instead of carbon electrodes and the initial volume was changed to 100 ml. The reaction mixture contained 50% of monomer, 37.5% solvent, and 12.5% of initiator by volume. Samples of 5 ml volume were withdrawn at 2 hr intervals or less. A cold methanol and water mixture in the ratio of 3:1 was employed for complete precipitation since using a very high current, the molecular weight of the polymer was low and occasionally formed a colloidal solution with cold methanol.

The reaction mechanism was established by copolymerization as before. The monomer, styrene by itself was only partially miscible with dioxane and nitric acid but a homogenous solution was formed when an equal volume mixture of styrene and methyl methacrylate was used.

Molecular Weight Determination

Intrinsic viscosities of the polymer were measured exactly the same as in the dimethyl sulfoxide and zinc acetate system using the Staudinger equation:

$$[n] = KM^{\alpha}$$

where K is 6.8×10^{-5} and

α is 0.72

The molecular weight of the polymer was obtained directly from the viscosity and molecular weight curve. The average molecular weight obtained is only a rough estimation and lies between weight average and number average as discussed previously.

COPOLYMERIZATION

Preparation of Reaction Mixture

Two hundred and twenty-six micro curies of C^{14} labelled styrene from Tracer Laboratories in California, stabilized by picric acid was diluted to a volume of 25 ml with distilled styrene. One ml of the dilutent was mixed with approximately 400 ml of purified styrene and the resultant solution was distilled under reduced pressure to remove the inhibitor. The actual activity of styrene was estimated by comparing with a standard. The solvent was saturated with different inorganic salts and then an equal volume mixture of C^{14} tagged styrene and methyl methacrylate was added.

Polymerization

The majority of experiments on copolymerization of styrene and methyl methacrylate were conducted in dimethyl formamide. Approximately 60 ml of the reaction mixture prepared above was pipetted into both compartments of the electrolytic cell and a constant current was passed for a certain period of time. The copolymers formed from both electrodes were precipitated and the yields were compared. Some of the inorganic salts used were only slightly soluble or partially ionized in the solvent. The resistance of the solution was comparatively higher than usual and the voltage required during polymerization sometimes reached to 400 or

500 volts.

C^{14} Counting

Of the methods available for the determination of C^{14}, liquid scintillation counting is most suitable for our purposes. It provides the advantages of high sensitivity, energy discrimination, 4π geometry and low background for a given sample size which are not present in the alternative techniques of gas and end window counting.

In the application of the internal scintillation counting method, the technical problems encountered are sample insolubility and quenching effects. The former can be partially compensated by use of mixed solvents (60) and aluminium stearate gel scintillators (61) while the latter can be estimated by the use of the Tri-Carb Spectrometers. The two channels provided by the Spectrometer can examine different portions of the energy spectrum in an unquenched sample yielding a fixed ratio of the two scaler counts. With quenching, the ratio changes markedly and this can be related to counting efficiency. In the following discussion, this ratio of counts from each channel is reported as the A and B ratio

In our present work, Model 314EX of Tri-Carb Spectrometer series was used. The polymer was dissolved directly in a scintillator solution containing five grams of 2,5 diphenyl oxazole (PPO), 70 gms of naphthalene and 0.1 gm of 1,4(2-(5-(phenyl oxazolyl)-benzene)POPOP per litre of xylene (62). The weight of polymer generally used was 0.1 gm and all the counts were performed on 1% solution of active polymer in liquid scintillator. The sample bottles employed were of cylindrical shape with a white plastic screw cap and have a volume of 20 ml.

Samples to be counted were put on an aluminium turnable which was controlled by automatic loading device into the counting chamber and the counts per min or per 10 min are typed out by the digital printer. The degree of quenching was indicated by the A and B ratio and efficiency of the counting system was read from the standardized curve.

Standardization was achieved by using samples of known activity and comparing with the actual counts obtained. The efficiency of the system was calculated at different activities and plotted against the A and B ratio. The block diagram of the electronic device in the Tri-Carb liquid scintillation spectrometer is shown in Figure III.

Radioactive decay events occuring in a sample cause scintillations which are seen simultaneously by both photo multiplier tubes giving rise to pulses at the photo tube output. Relatively high operating voltage is required for low energy events while the opposite is true for energic events.

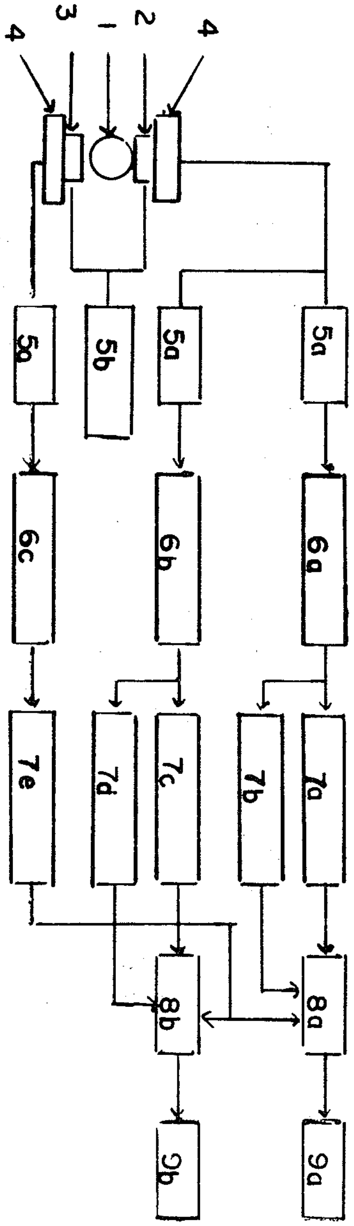
Pulses from the photomultiplier pass through preamplifiers and into the three separate amplifiers. Pulses from the "Analyzer" photo tube then go to discriminator pairs A-B and C-D for pulse height analyses. The "Monitor" photo tube functions to distinguish whether a pulse comes from a decay event or photomultiplier tube noise. Pulses falling between A and B are fed to the red scaler and those between C and D are fed to the green scaler. Output pulses from all discriminators pass through the logic circuitry and only simultaneous occured pulses from both photomultiplier are counted.

Lower level discriminators A, C and A' are devised to reject low energy "shot noise" arising from preamplifiers and a separate gain control is provided for each channel.

FIGURE III. Block diagram of liquid scintillation counting system.

1. Sample compartment.
2. Analyzer phototube.
3. Monitor phototube.
4. Pre-amplifier.

5a. Gain control.
5b. High voltage.
6a. Channel I amplifier.
6b. Channel II amplifier.
6c. Monitor amplifier.
7a. Discriminator A.
7b. Discriminator B.
7c. Discriminator C.
7d. Discriminator C.
7e. Discriminator A'.
8a. Red logic.
8b. Green logic.
9a. Red scaler.
9b. Green scaler.


4
3
1
2
4
5a
5b
5a
5a
6c
6b
6a
7e
7d
7c
7b
7a
8b
8a
9b
9a

When the voltage is raised to count low energy isotopes, pulses from higher energy events may become very high and the gain control permits discrimination of these energic pulses within selected discrimination levels.

Reducible Organic Compounds

Most of the experiments that concerned with initiation of polymerization by reducing organic material at the cathode, were conducted in divided cells separated by a fritted glass disc with round platinum electrodes of a surface area of .785 sq. in. very close to it. A constant current was passed for a period of time depending upon other experimental conditions. A small amount of cupric chloride was added to increase the efficiency of reduction and to act as an electrolyte since most reducible organic compounds give a low conductance. Generally, equal volumes of solvent and reducible organic materials mixed with the same volume of monomer were used.

DATA CALCULATION AND RESULTS

SALT AND SOLVENT SYSTEM

PRELIMINARY INVESTIGATION ON YIELD AND MOLECULAR WEIGHT OF POLYMER

Solvent

For the study of the kinetics of polymerization, a suitable solvent with a high dielectric constant was sought. The solvent had to fulfill the conditions of the solubility of monomer and polymer and yet provide for a sufficient ionization of the salt to furnish a medium of high conductivity.

It was found that dimethyl sulfoxide was an excellent solvent which met these requirements. Further studies later indicated that dimethyl formamide was also suitable. In addition, several other solvents were found to be of limited usefulness producing either a low yield or a polymer of low molecular weight. The results of these investigations are summarized in Table 2.

Salt

The choice of a suitable inorganic salt to provide an efficient conducting medium was restricted by the low solubilities of many salts in the suitable solvents selected. We originally intended to employ acetoxy radicals as initiators (or methyl radicals) and accordingly sought the suitable acetate. Although zinc acetate was used for most of the study reported here, the results with other salt systems are presented in Table 3.

Electrode Material

Several types of electrode materials were investigated. Graphite, platinum, lead and mercury were employed. It was found the yields were similar in graphite and platinum but a lower molecular weight was found with the latter. Lead was unsatisfactory despite its high electrode potential because it gave a reduced yield of polymer. Mercury was also unsuitable for the anode. The results obtained are presented in Table 4.

TABLE 2

Effect of solvent on yield and molecular weight of polymer.

Solvent	Zn Acetate (gms)	Current (ma)	Time (hrs)	Total wt. of polymer (gms)	Mol. Wt.
aniline	1	4	21	.01	-
pyridine	2	9	21	.53	-
diethylamine	2	10	20	1.50	5.00×10^4
hydroxypropionitrile	1	10	20	2.50	-
triethylenetetraamine	1	10	20	2.30	1.42×10^5
dimethyl sulfoxide	3	9	24	2.42	4.50×10^5
dimethyl formamide	3	10	21	3.96	4.20×10^5

TABLE 3

Relative yields of polymer in 24 hours in dimethyl sulfoxide with different salt systems.

Salt	Yield (gms)
Ammonium acetate	1.30
Sodium nitrate	.72
Sodium chloride	.75
Zinc chloride	1.09
Aluminum chloride	1.56
Potassium thiocyanide	0.00

TABLE 4

Effect of electrode material on yield of polymer in 24 hours.

Electrode		Current (ma)	Wt. of polymer (gms)	Molecular weight
Anode	Cathode			
Carbon	Carbon	9	2.43	4.5×10^5
Platinum	Platinum	9	2.20	2.8×10^5
Lead	Lead	15	0.17	-
Mercury	Carbon	10	0.00	-
Carbon	Mercury	10	2.15	-

Monomer

Attempts to polymerize other monomers such as styrene and vinyl acetate by the dimethyl sulfoxide system with zinc chloride and zinc acetate as initiators proved unsuccessful. A very low yield of polystyrene was obtained with a molecular weight of only 12,000. No polymer was formed with vinyl acetate. Other systems such as acetic acid, acetic anhydride, with potassium acetate and lithium acetate as initiators, were used to polymerize vinyl acetate. Insoluble gelatinous polymer was formed around the electrodes which was suspected to be of a highly cross-linked nature. The yield was comparatively high. The results are summarized in Table 5.

TABLE 5

Relative yields of polymer in 24 hours with different monomers.

Monomers	Systems	Current (ma)	Time (hrs)	Yield (gms)	Molecular Weight
Methyl methacrylate	Dimethyl sulfoxide zinc acetate	15	24	4.3	4.6×10^5
Styrene	(1) Dimethyl sulfoxide zinc acetate	15	48	0.1	-
	(2) Dimethyl sulfoxide zinc chloride		66	1.9	12,000
Vinyl acetate	Dimethyl sulfoxide zinc acetate	15	66	no polymer	-
Vinyl acetate	Acetic acid Acetic anhydride Potassium acetate	15	72	10.5	-
Vinyl acetate	Acetic acid Acetic anhydride Lithium acetate	15	48	2.5	-

Pre-electrolysis, Stirring and Electrode Spacing

The effect of pre-electrolysis and vigorous stirring on the yields of the polymerization of methyl methacrylate with zinc acetate as initiator was fully investigated. It was found that the former increased the yield of the polymer by 63.5%, the latter only by 28.6%. The spacing of the electrodes had a remarkable influence on the yield of the polymer. The shorter the distance, the greater was the yield. The results are tabulated in Table 6.

TABLE 6

Effect of pre-electrolysis, stirring and electrode spacing on yield of polymer.

	Current (ma)	Time (hrs)	Yield (gms)	% increase or decrease
Standard	15	24	2.20	
Pre-electrolysis	15	24	3.61	+ 63.5
Stirring	15	24	2.83	+ 28.6
Electrode spacing (double)	15	24	1.82	- 17.3

Alternating current

An experiment was conducted to polymerize methyl methacrylate by alternating current. Polymer of a high molecular weight 1.85×10^6 was obtained. This molecular weight is approximately five or six times greater than that of polymer formed by direct current. However, the yield of this polymer was very low. With a current of 40 ma and a time period of 43 hrs., only 1.2 gm of polymer, 4% conversion of monomer, was obtained.

Current and Current Density

The effect of current and current density on the yield of the polymer was studied. It was found that an increase in the current density reduced the yield of the polymer whereas an increase in current increased the yield of the polymer. From Table 7, it can be seen that the yield of polymer is inversely proportional to the current density but directly proportional to the square of current.

TABLE 7

Relative effect of current and current density on the yield of the polymethyl methacrylate with zinc acetate as initiator.

Time (hrs)	Current (ma)	Electrode surface area (cm^2)	Current density (ma/cm^2)	Yield (gms)
18	10	23.9	.42	2.03
18	10	14.9	.67	1.13
18	15.9	23.9	.67	3.22

KINETIC STUDIES

In all the kinetic experiments, the same electrode surface area was used. Hence the current density changes were directly proportional to the change in current. Since the yield of the polymer is found to be inversely proportional to current density but directly to the square of current, the net effect in the system employed can be expressed in terms of current. Thus all the results have been interpreted only on the basis of current changes.

Current, Time and Yield

The system monomer, dimethyl sulfoxide and zinc acetate was chosen for a detailed study of the phenomenological aspect of the kinetics.

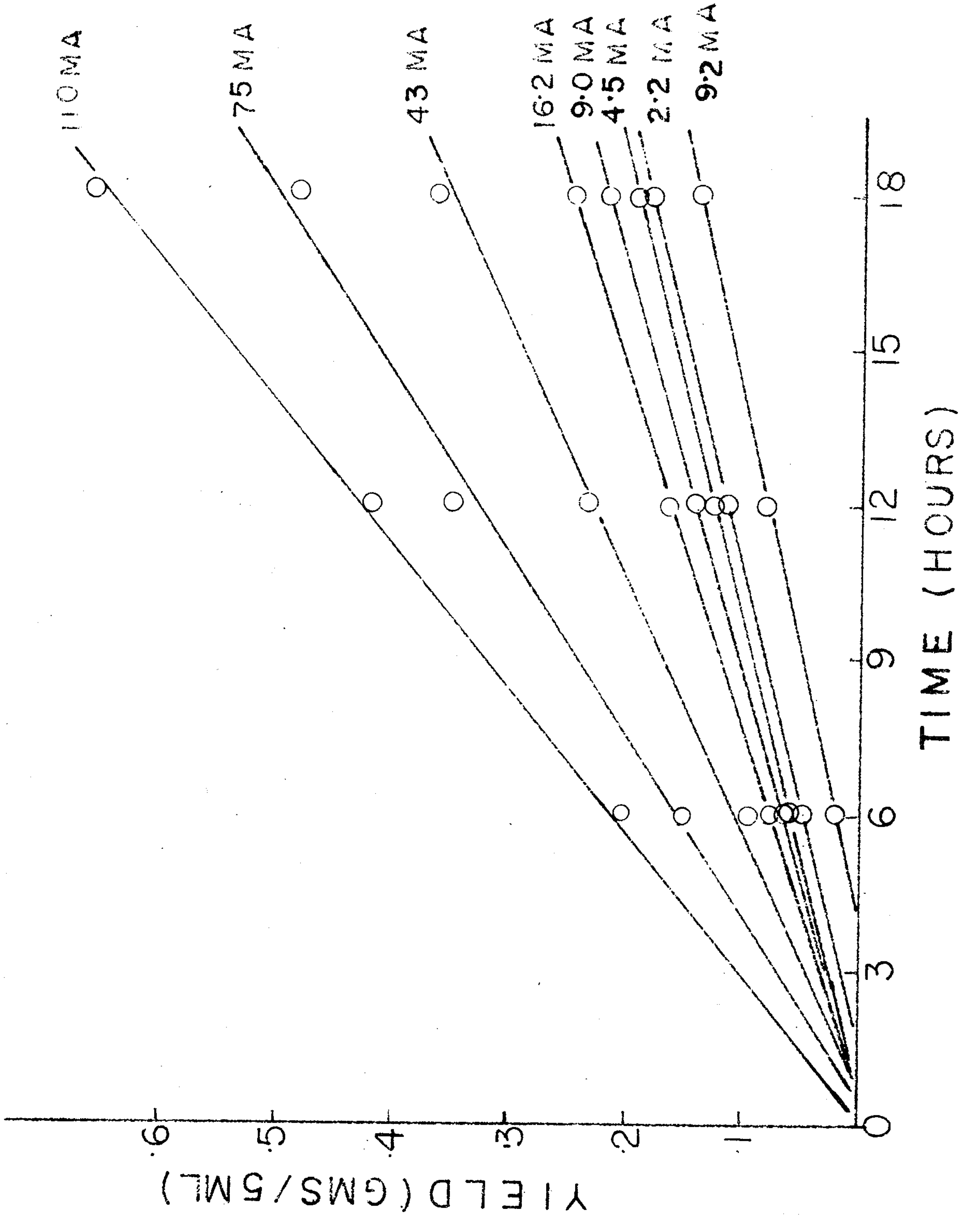
Experiments were conducted at 8 values of current from 1 ma to 110 ma in cylindrical cells with graphite electrodes and samples were withdrawn at intervals for analysis. The results are summarized in Table 8 and Figure IV.

TABLE 8

Yields of polymer at different values of current.

Current (ma)	Current density (ma/cm^2)	Yield of polymer gms per 5 ml. sample time 6 hrs.	12 hrs.	18 hrs.
.92	.038	.019	.082	.141
2.2	.092	.048	.115	.180
4.5	.188	.058	.126	.196
9.0	.378	.065	.143	.219
16.2	.676	.075	.164	.250
43.0	1.79	.095	.238	.365
75	3.14	.154	.354	.482
110	4.60	.205	.423	.662

FIGURE IV. Effect of time and current on the relative yields of polymethyl methacrylate.


YIELD (GMS/5ML)
.1
.2
.3
.4
.5
.6
0
3
6
9
12
15
18
TIME (HOURS)
110 MA
75 MA
43 MA
16·2 MA
9·0 MA
4·5 MA
2·2 MA
9·2 MA

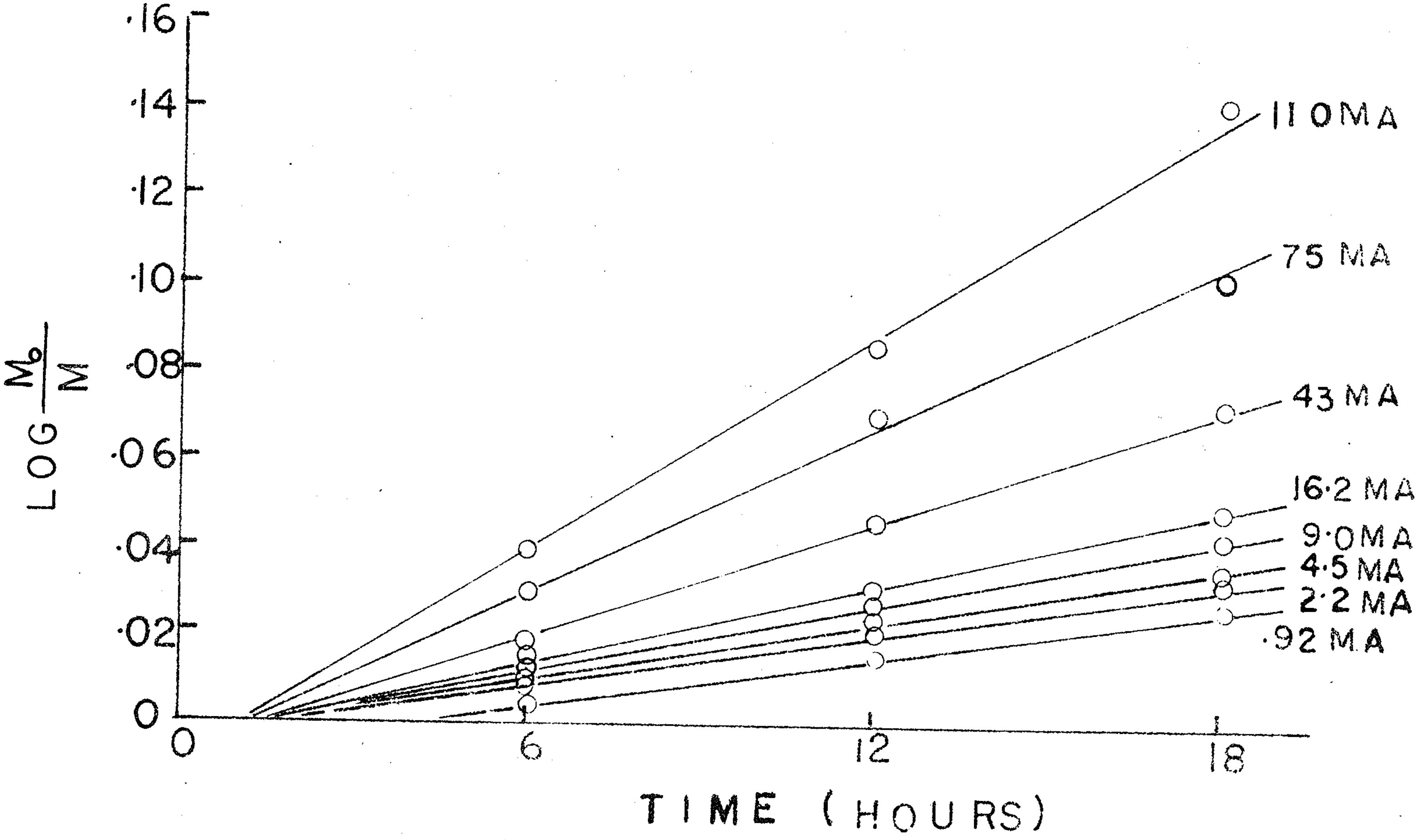
It is evident the yield of the polymer increases linearly with time and is a function of current. The apparent small induction period which is particularly evident in the experiments performed at low values of current is probably due to traces of impurity. This is confirmed by the observation that pre-electrolysis of the solvent and salt system reduces this induction time. It was further found that the addition of traces of water increased the induction period and reduced the yield of polymer.

A cursory examination of Figure IV could suggest a zero order dependence on monomer concentration. However, calculating from the data of Table 8, a plot of log $\frac{M_o}{M}$ versus t (Figure V) shows a first order reaction is actually present. M_o and M represent concentrations of monomer initially and at time t respectively.

Rate, Molecular Weight and Current

The slopes of the individual yield versus time curves give the rates of the reaction. These are tabulated in Table 9, together with the molecular weights determined from viscosity measurements for samples obtained after 18 hours of

FIGURE V. A plot of log $\frac{M_o}{M}$ versus t.


·16
·14
·12
·10
·08
·06
·04
·02
0
LOG $\frac{M_0}{M}$
0
6
12
18
TIME (HOURS)
110 MA
75 MA
43 MA
16·2 MA
9·0 MA
4·5 MA
2·2 MA
·92 MA

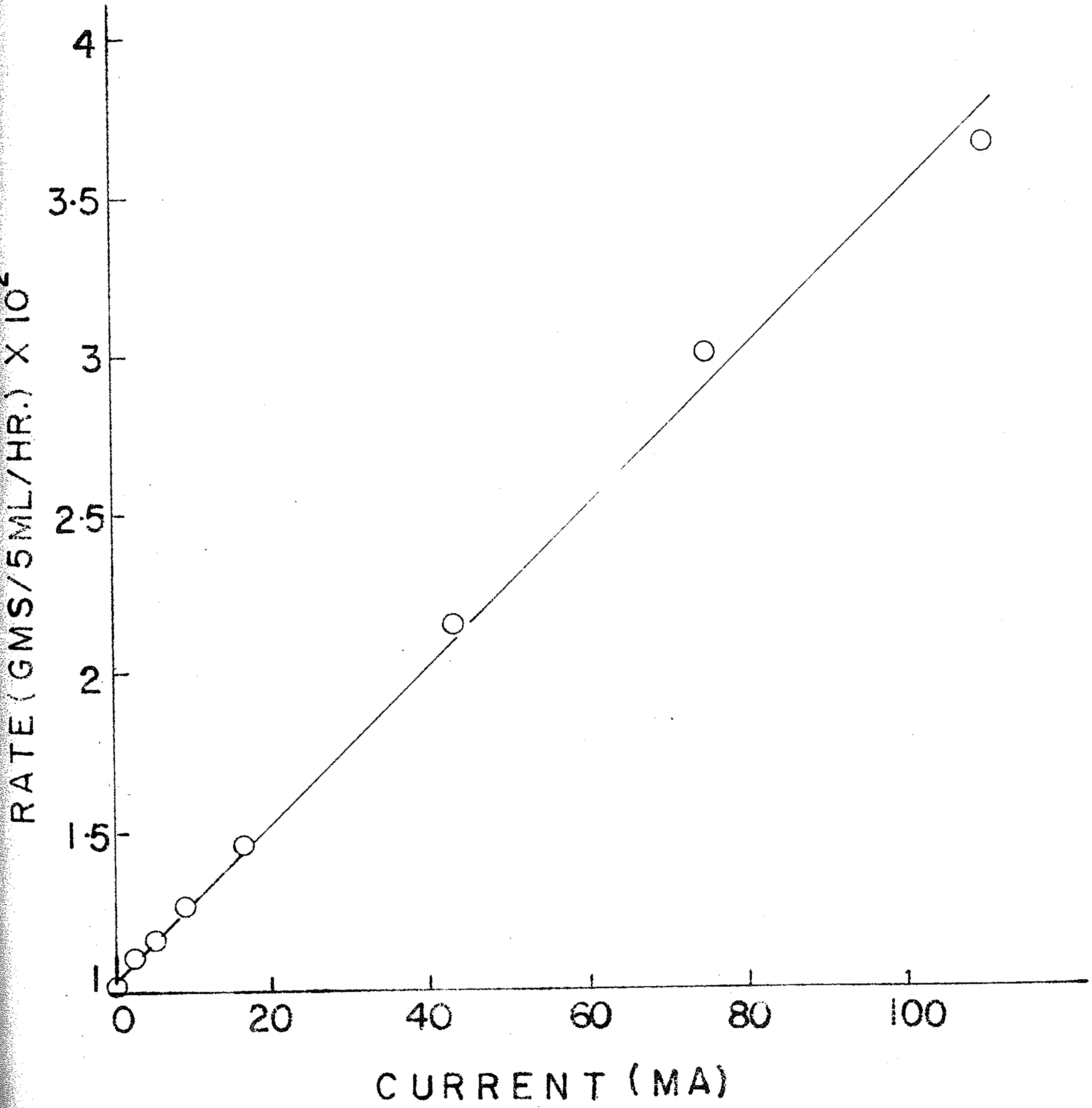
electrolysis. A plot of these rates of reaction versus current for sample withdrawn at 18 hrs is shown in Figure VI. It is seen that the rate is linearly dependent on the current, in contrast to the square root dependence normally obtained by thermally initiated free radical reactions.

TABLE 9

Influence of current on the rate of formation and molecular weight of polymer.

Current (ma)	$\frac{dp}{dt}$ (gms/5ml/hr)	Intrinsic viscosity (decilitre/gm)	M.W. x 10^{-5}	1/M.W. x 10^{6}
0.92	.0100	1.39	10.00	1.00
2.2	.0110	1.28	9.00	1.11
4.5	.0115	1.18	8.00	1.25
9.0	.0126	.81	4.60	2.18
16.2	.0145	.78	4.30	2.32
43.0	.0214	.62	3.02	3.32
75.0	.0300	.52	2.38	4.15
110.0	.0366	.43	1.80	5.50

FIGURE VI. Linear dependence of rate of polymerization on the impressed current.


4
3·5
3
2·5
2
1·5
1
RATE (GMS/5ML/HR.) X 10^2
0
20
40
60
80
100
CURRENT (MA)

The relationship between molecular weight and current is shown in Figure VII. It is obvious that the molecular weight of the polymer varies inversely with current since a plot of the reciprocal of the molecular weight versus current gives a linear relationship.

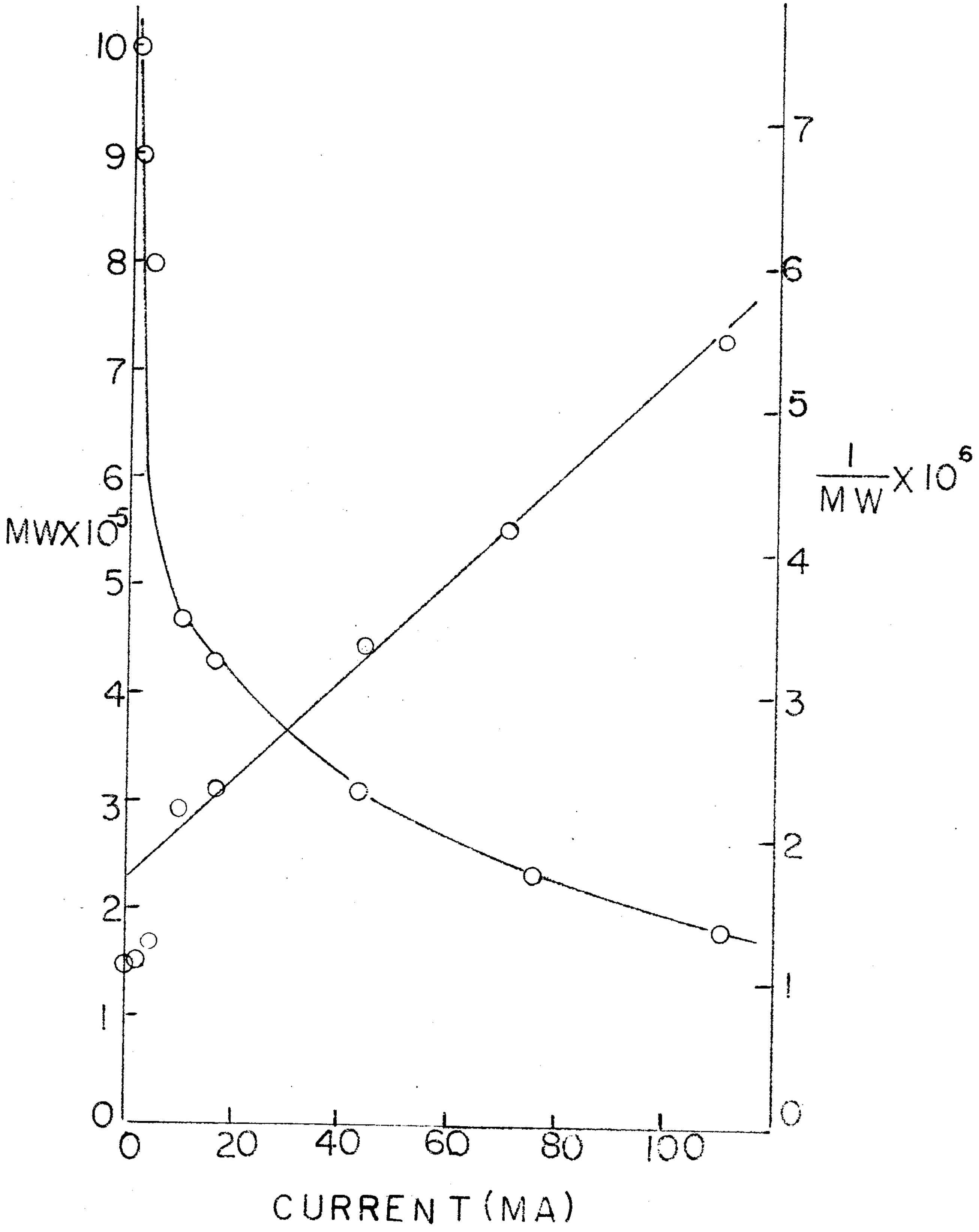
Efficiency of Initiation

The efficiency of initiation is defined as fractions of the primary radicals which initiate the formation of chains. It can be determined from a knowledge of the numbers of moles of polymer produced, the molecular weight and number of faradays passed. As a sample calculation, at a current of .92 ma and a time period of 18 hrs, the total polymer formed is 1.83 gm. That is, $0.92 \times 60 \times 60 \times 10^{-3} \times 18/9.56 \times 10^{4} = .62 \times 10^{-3}$ faradays produce $\frac{1.83}{1.0 \times 10^{6}}$ moles of polymer. Since the polymer is terminated by unlike radicals as shown in rate scheme (p. 85) each polymeric molecule contains only one initiating radical

$$\therefore \text{ the efficiency} = \frac{1.83}{1.0 \times 10^{6}} \times \frac{1}{.62 \times 10^{-3}} = 2.95 \times 10^{-3}$$

or .295%

FIGURE VII. Variation of molecular weight (left axis) and reciprocal of molecular weight (right axis) with impressed current.


MWX10^5
0
1
2
3
4
5
6
7
8
9
10
1/MW X 10^6
0
1
2
3
4
5
6
7
0
20
40
60
80
100
CURRENT (MA)

The results are summarized in Table 10 and Figure VIII.

In most of electro-initiated polymerizations, the efficiency of the system is expressed in terms of current efficiency. The latter is defined as either the number of grams of polymer formed or number of moles of monomer consumed per faraday of current. Using this definition, a plot of yield of polymer (gms) per faraday versus current is shown in Figure IX.

TRACER STUDIES

Reaction Mechanism

To determine the type of polymerization mechanism, equal volumes of methyl methacrylate and styrene were copolymerized in a divided cell. The mole ratio of styrene to methyl methacrylate was .93 to 1. Since the monomer reactivity ratios (r_1, r_2) of styrene and methyl methacrylate in a free radical mechanism are respectively 0.52 and .46 (57a), the theoretical mole fraction of styrene in the copolymer formed is .498 as calculated from the copolymerization equation.

$$F_1 = (r_1f_1^2 + f_1f_2)/(r_1f_1^2 + 2\ f_1f_2 + r_2f_2^2)$$

TABLE 10

Influence of current on the efficiency of initiation.

Current (ma)	No. of faradays passed x 10^3	Total polymer formed (gms)	Polymer formed (gms)/faraday x 10^{-3}	Moles of polymer formed/faraday x 10^3	% Efficiency
.92	.62	1.83	2.95	2.95	.295
2.2	1.48	2.32	1.57	1.75	.175
4.5	3.03	2.55	.84	1.05	.105
9.0	6.08	2.86	.47	1.02	.102
16.2	10.08	3.29	.33	.77	.077
43.0	28.90	4.74	.16	.53	.053
75	56.40	6.26	.12	.51	.051
110	71.10	8.60	.12	.66	.066

FIGURE VIII. Variation of efficiency of initiation with current.

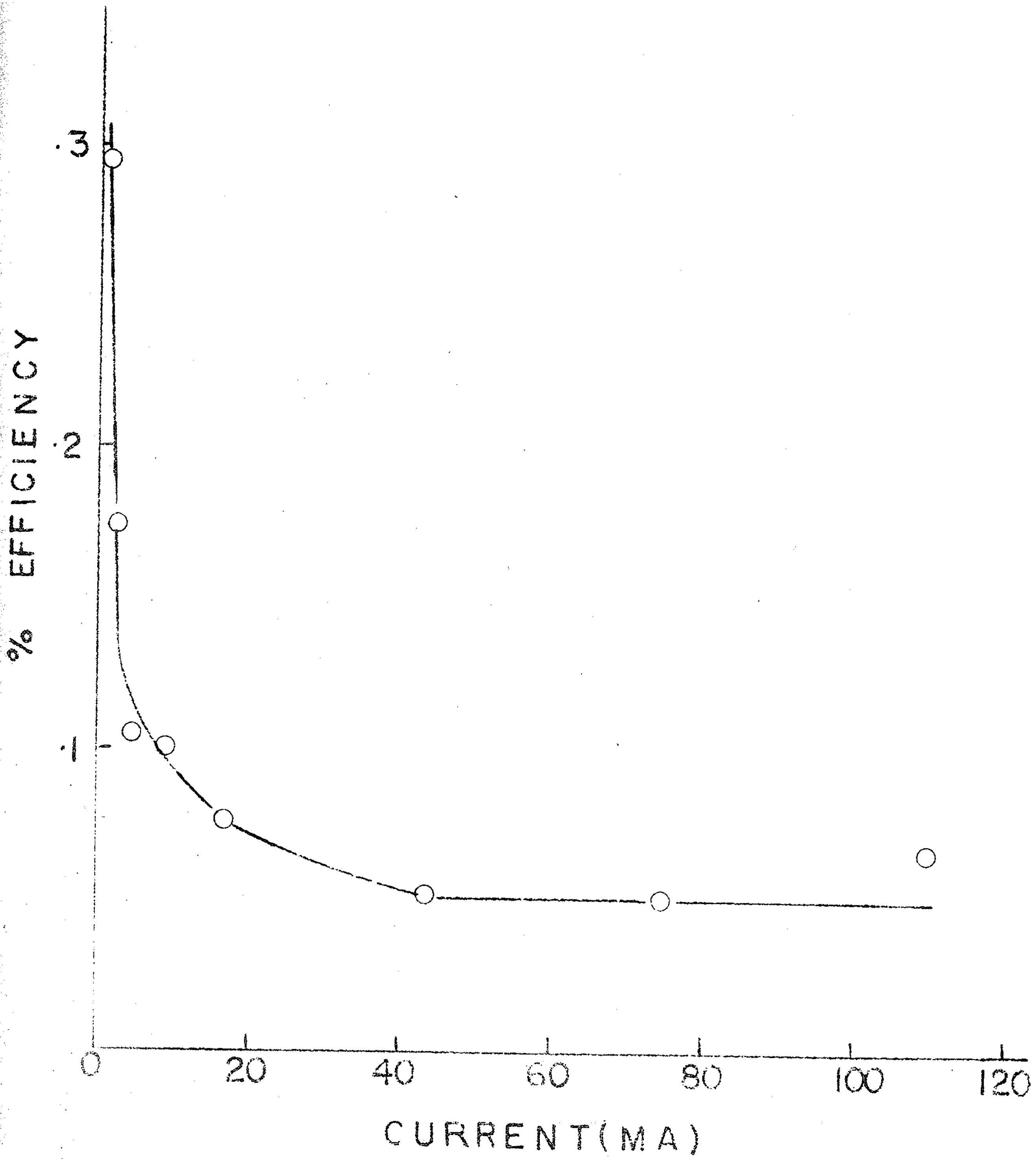
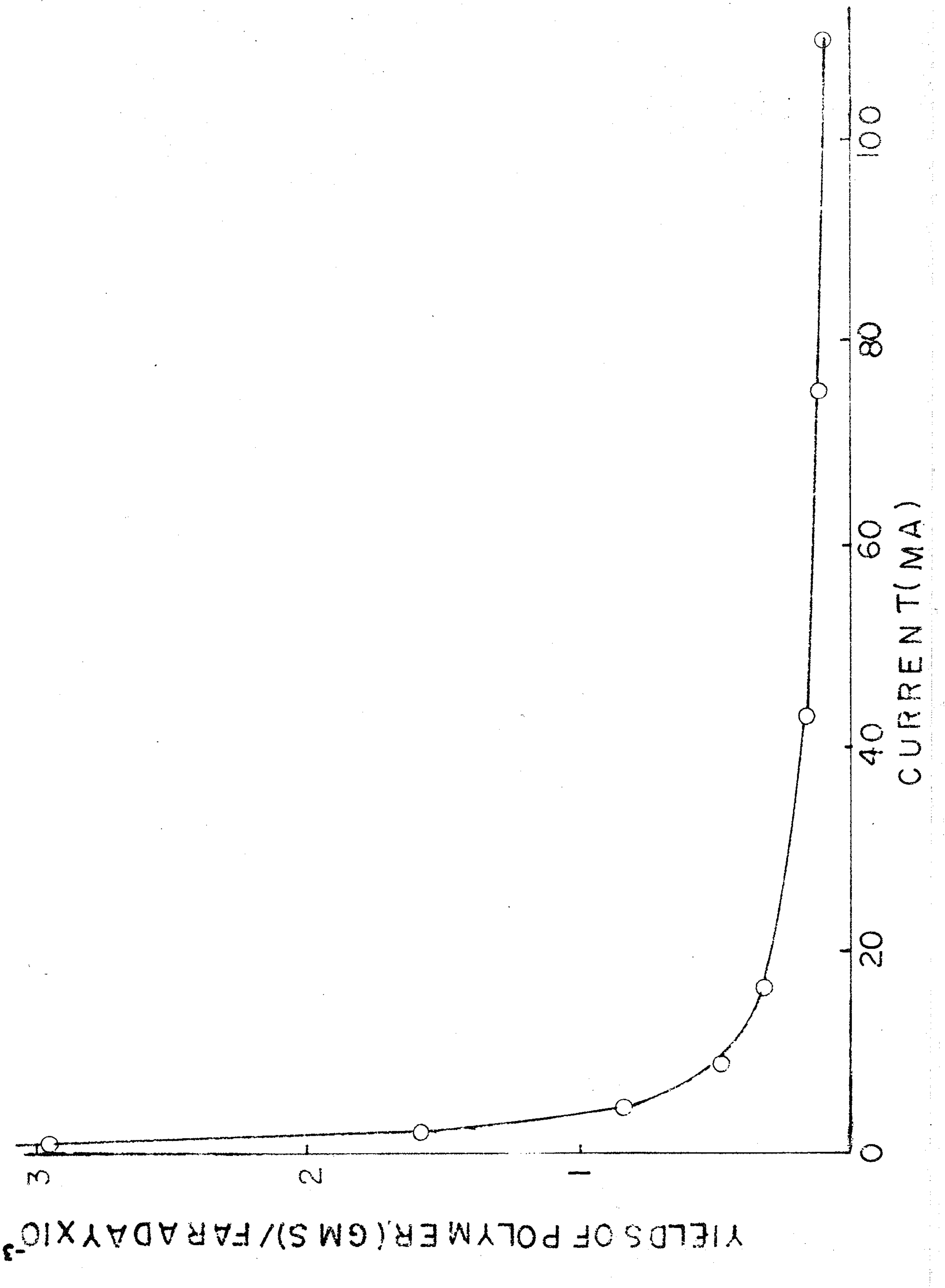

·3
·2
·1
% EFFICIENCY
0
20
40
60
80
100
120
CURRENT(MA)

FIGURE IX. A plot of the yields of polymer (gms)/faraday versus current.


CURRENT(MA)
0
20
40
60
80
100
YIELDS OF POLYMER,(GMS)/FARADAY X10^{-3}
1
2
3

where f_1 and f_2 represent mole fraction in monomer feed

$$(e.g., f_1 = 1 - f_2 = \frac{M_1}{M_1 + M_2})$$

r_1 and r_2 = reactivity ratio of monomers M_1 and M_2 respectively.

F_1 = mole fraction of M_1 in the copolymer.

The equation above is only valid however if the final monomer mole ratio of styrene and methyl methacrylate is changed only slightly from the initial monomer mole ratio.

In our experiments, the copolymer isolated from both anode and cathode compartments were found to be 50.4 and 54.5 mole % of styrene respectively. The results are tabulated in Table 11 and strongly indicates a free radical mechanism occuring at both electrodes

TABLE 11

Copolymerization of equal volume mixture of styrene and methyl methacrylate.

	Original counts/ min of 0.1 gm styrene	Final counts/ min of 0.1 gm of copolymer	mole % of styrene in copolymer
Anode	5900	3067	50.4
Cathode	5900	3228	54.5

Initiating Species

Experiments with C^{14} labelled zinc acetate in C_1 and C_2 positions were undertaken to determine the initiating species of the polymerization. It was found that 92.8% of the polymer was initiated by the methyl radical CH_3 and only 7.3% was induced by acetoxy radical $CH_3COO\cdot$. The result is shown in Table 12.

TABLE 12

Determination of the relative percentage of the initiating species.

Initiators	Total activity of initiators (counts/min)	Activity of 0.1 gm anodic polymer (counts/min)	Normalized counts/min of 0.1 gm polymer	Relative % of initiating species
Zinc Acetate-2-C^{14} (2.97 gm)	2.83×10^7	7420	13290	$CH_3\cdot$ 92.8
Zinc Acetate-1-C^{14} (3.0 gm)	5.08×10^7	963	963	$CH_3COO\cdot$ 7.2

The relative percentage of the initiating species was calculated from the relative activity of the polymer formed in the zinc acetate-1-C^{14} and zinc acetate-2-C^{14} systems. Using zinc acetate-1-C^{14}, both $CH_3\cdot$ and $CH_3COO\cdot$ radicals formed will provide an active group whereas in the case of zinc acetate-1-C^{14}, only the $CH_3COO\cdot$ radical is active. The difference in counts/min of the polymer is a measure of methyl radical concentration. To avoid incorporation of highly active solution into the polymer, the latter was reprecipitated four times before counting.

DIOXANE SYSTEM

In the dimethyl sulfoxide and zinc acetate system, the yields of the polymer were comparatively low and the plating out of metals sometimes complicated the reaction. A system which partially overcomes these difficulties is highly desirable and for this purpose dioxane, which is miscible with water and organic compounds, was employed as a solvent to furnish a homogenous medium for kinetic studies. Concentrated nitric acid was used as the electrolyte to conduct the current. The applied voltage was very low ranging from 0.5 to 2 volts. In preliminary experiments, voltages up to 10 V were used in conjunction with other monomers.

EFFECT OF MONOMER AND SOLVENT

Various experiments were performed to polymerize different vinyl compounds in the dioxane system with concentrated nitric acid as initiator. Graphite and platinum electrodes were used. The results are summarized in Table 13.

It was found that the esters of methacrylic acid gave the best yields of polymer but nevertheless, they were sticky and extremely difficult to handle. Thus methyl methacrylate was chosen as the monomer for kinetic studies.

Styrene and other similar types of monomer formed a heterogenous system with the dioxane-nitric acid mixture. Many other solvents were used instead of dioxane in order to achieve a homogenous medium. The results are presented in Table 14.

Stirring

The effect of stirring on the yield and molecular weight of the resultant polymer was investigated. It was

TABLE 13

Relative yields of polymer in 21 hours in dioxane system with different monomers containing 50% of monomer, 37.5% solvent, and 12.5% HNO_3 by volume.

Monomers	Current (10 ma)	Initial voltage (volts)	Yield (gms)	Electrode
Ethyl acrylate	10	1.4	23.0	graphite
Butyl acrylate	10	1.4	15.2	"
Methyl methacrylic acid	10	2.2	3.6	"
Acrylonitrile	10	.9	1.3	"
Acenaphthylene	10	.8	11.6	"
Vinyl acetate		no polymer		"
Butyl vinyl ether		no polymer		"
Styrene		no polymer		"
Methyl methacrylate		no polymer		"
Methyl methacrylate	9.5	3.75	7.4	platinum
Styrene	15	4.2	3.1	"

TABLE 14

Influence of solvent on yields of polymer in a divided cell containing 50% of MMA, 37.5% solvent, 12.5% HNO_3 in 24 hours.

Solvents	Current (ma)	Voltage (volts)	Yield (gms)	
			Cathode	Anode
Dimethyl formamide	10	8.0	.475	.523
Dimethyl sulfoxide	10	28.0	.862	.288
Dimethyl ether	10	65.0	.770	.350

found that at a current of 10 ma and a time period of 9 hours, stirring nearly doubled the yield but the molecular weight was decreased by half. The results are presented in Table 15.

TABLE 15

Effect of stirring on the yield and molecular weight of the resultant polymer.

	Yield (gms)	Molecular wt. x 10^{-5}
Standard	3.22	1.22
Stirring	6.30	.66

KINETIC STUDIES

It has been shown that the electro-induced polymerization of methyl methacrylate in a non-aqueous medium dimethyl sulfoxide is 1st order dependence on current. It was of interest to investigate the behaviour of the same monomer in a homogenous aqueous system of dioxane and nitric acid. Experimental conditions were the same as before with a slight change in the design of electrolytic cells. Platinum electrodes having an area of 1 sq. in. were used instead of carbon.

Current, Time and Yield

A series of experiments were performed in which the current was kept at a constant value throughout. The milliamperage used was between 1 to 100 ma and samples were withdrawn at intervals for analysis. The volume employed initially was 100 ml and contained 50 ml of monomer, 37.5 ml solvent and 12.5 ml initiator. The results are summarized in Table 16.

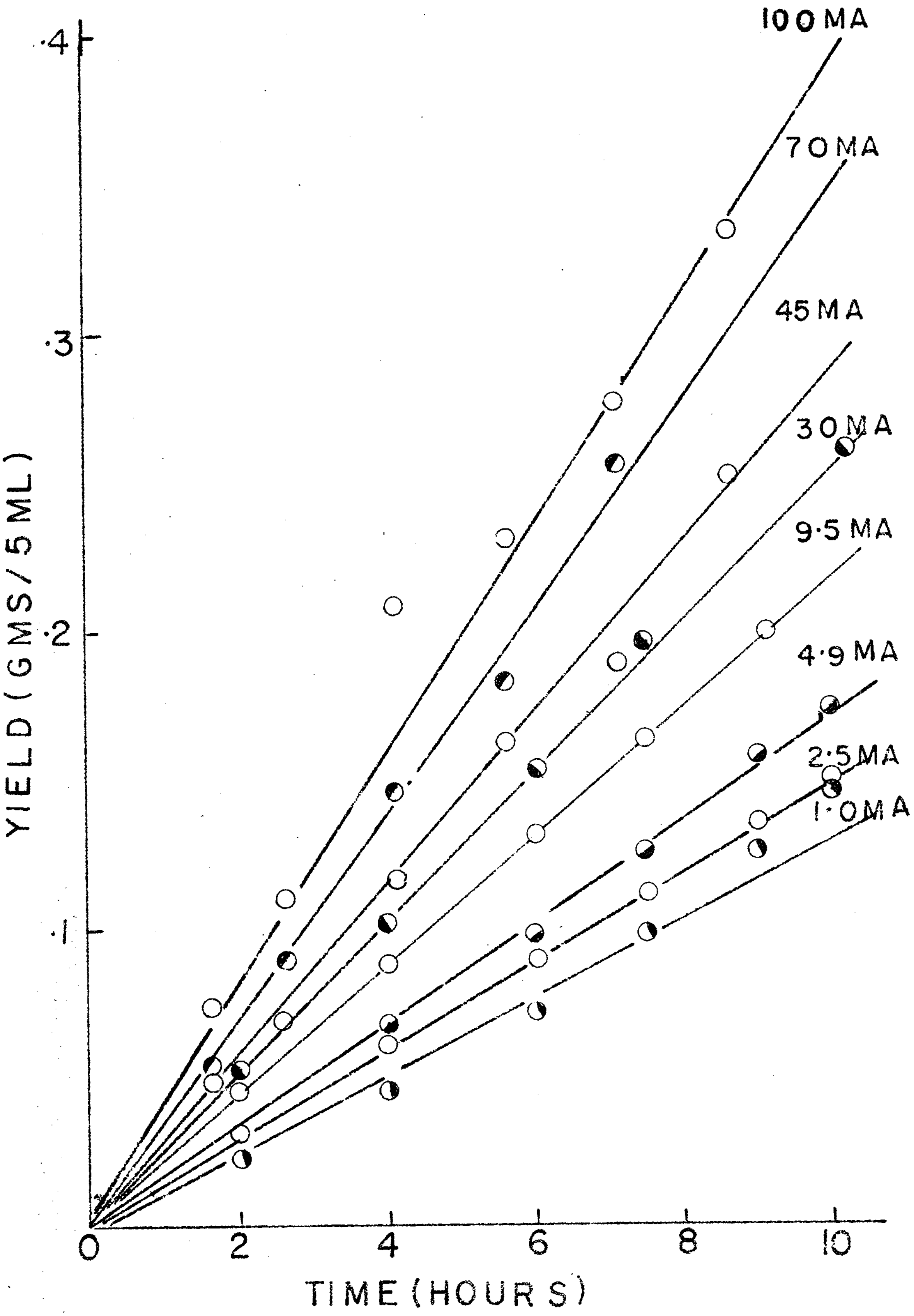
TABLE 16

Yield of polymer at different values of current.

Current (ma)	Current densities (ma/cm^2)	Yield of polymer gms/5 ml sample					
		2 hrs	4.10 hrs	6 hrs	7.30 hrs	9 hrs	10 hrs
1.0	.153	.0212	.0437	.0709	.0979	.1252	.1405
2.5	.388	.0301	.0602	.0898	.1101	.1350	.1500
4.9	.697	.0452	.0674	.0936	.1251	.1673	.1746
		2 hrs	4.02 hrs	6.02 hrs	7.28 hrs	9.10 hrs	10.16 hrs
9.5	1.470	.0450	.0875	.1320	.1630	.1999	-
30	4.650	.0515	.1013	.1534	.1955	-	.2604
		1.38 hrs	2.38 hrs	4.08 hrs	5.38 hrs	7.08 hrs	8.38 hrs
45	6.97	.0472	.0669	.1161	.1632	.1890	.2526
70	10.80	.0546	.0885	.1408	.1824	.2564	-
100	15.30	.0745	.1099	.2097	.2312	.2765	.3390

The yield versus time curves shown in Figure X were corrected for induction period or very minor traces of polymer formed by thermal polymerization at room temperature. It

FIGURE X. Yields of polymer as a function of time and current.


100 MA
70 MA
45 MA
30 MA
9·5 MA
4·9 MA
2·5 MA
1·0 MA
·4
·3
·2
·1
0
2
4
6
8
10
YIELD (GMS/5 ML)
TIME (HOURS)

is apparent that the yield of the polymer is a function of current and increases linearly with time. Confirmation that the system obeys the first order kinetics with respect to monomer concentration is shown in the graph of log $\frac{M_o}{M}$ versus t (Figure XI) where a linear relationship between these functions is observed.

Rate, Molecular Weight and Current

The reaction rates at different current strengths were estimated from the slopes of the yield versus time curves and are presented in Table 17 together with the molecular weight determined from viscosity measurements.

It is seen in Figure XII that the molecular weight varied inversely with the current. The molecular weight trend of this polymer was towards lower values than that of the polymer initiated by zinc acetate in the dimethyl sulfoxide medium under the same current.

The rate of reaction was not directly proportional to the current as indicated by Figure XIII. However a plot of the reaction rate against square root of current in Figure XIV shows a linear relationship.

FIGURE XI. A plot of log $\frac{M_o}{M}$ versus t. M_o and M represent monomer concentration initially and at a time t.

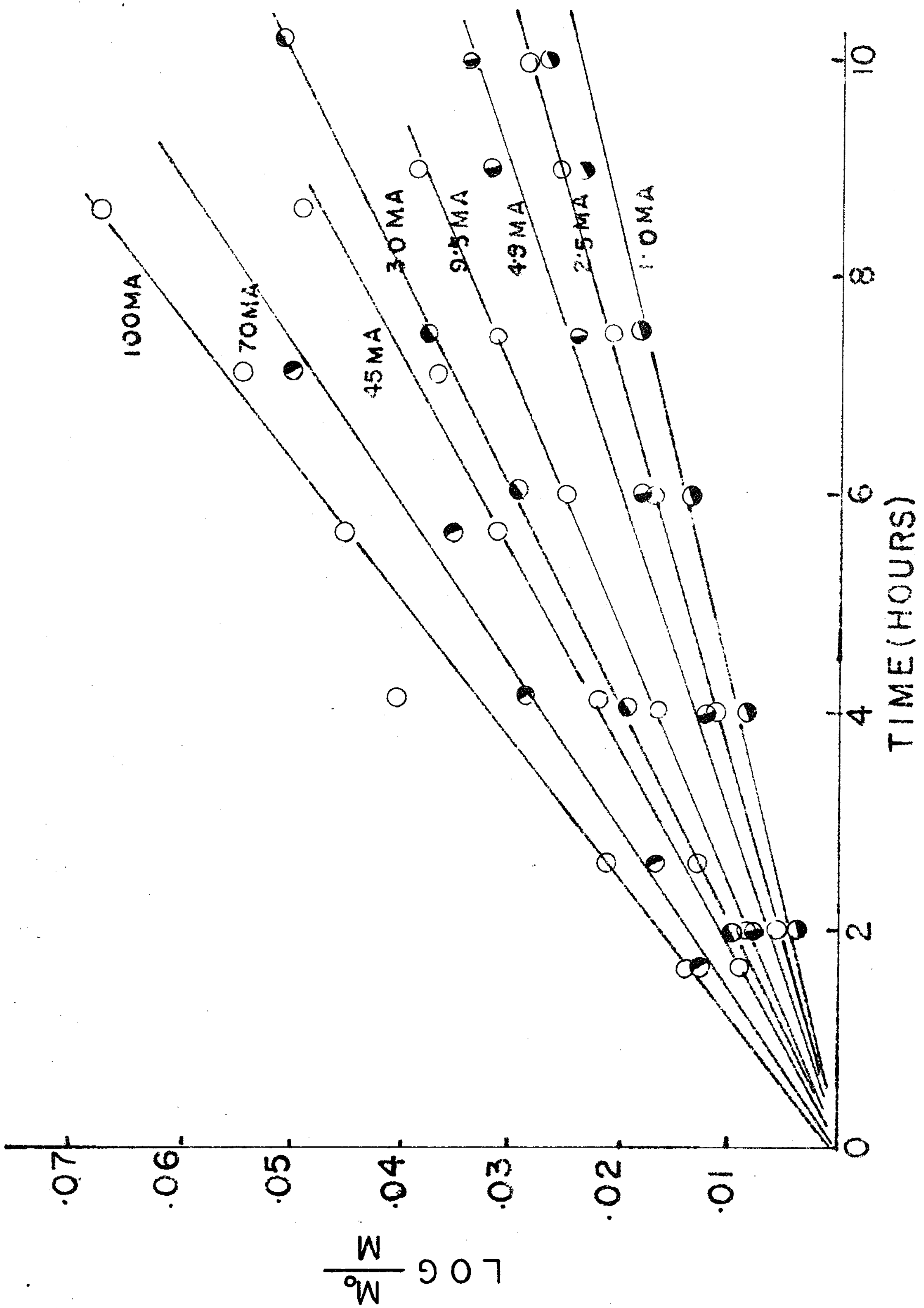

LOG $\frac{M_0}{M}$
.07
.06
.05
.04
.03
.02
.01
0
2
4
6
8
10
TIME (HOURS)
100MA
70MA
45 MA
30 MA
9·5 MA
4·9 MA
2·5 MA
1·0 MA

TABLE 17

Influence of current on rate of formation and molecular weight of methyl methacrylate polymer.

Current I (ma)	$\sqrt{I}$	$\frac{dp}{dt} \times 10^2$ (gm/5 ml/hr)	Intrinsic viscosity (decilitre/gm)	M.W. x 10^{-5}	$\frac{1}{M.W.}$ x 10^6
1.0	1.00	1.30	.610	3.08	3.25
2.5	1.58	1.50	.390	1.57	6.38
4.9	2.12	1.74	.379	1.50	6.68
9.5	3.09	2.05	.330	1.22	8.20
30	5.48	2.57	.274	1.01	9.90
45	6.71	2.88	.226	.775	12.70
70	8.36	3.50	.188	.548	22.20
100	10.00	3.98	.086	.204	49.00

Current Efficiency

The number of grams of polymer obtained or moles of monomer consumed per faraday is called current efficiency. The relative efficiencies of the reactions were determined by calculation of the yield per faraday and plotting these against the current. The results are summarized in Table 18 and Figure XV (calculated from data in Table 16).

FIGURE XII. Variation of molecular weight with impressed current.

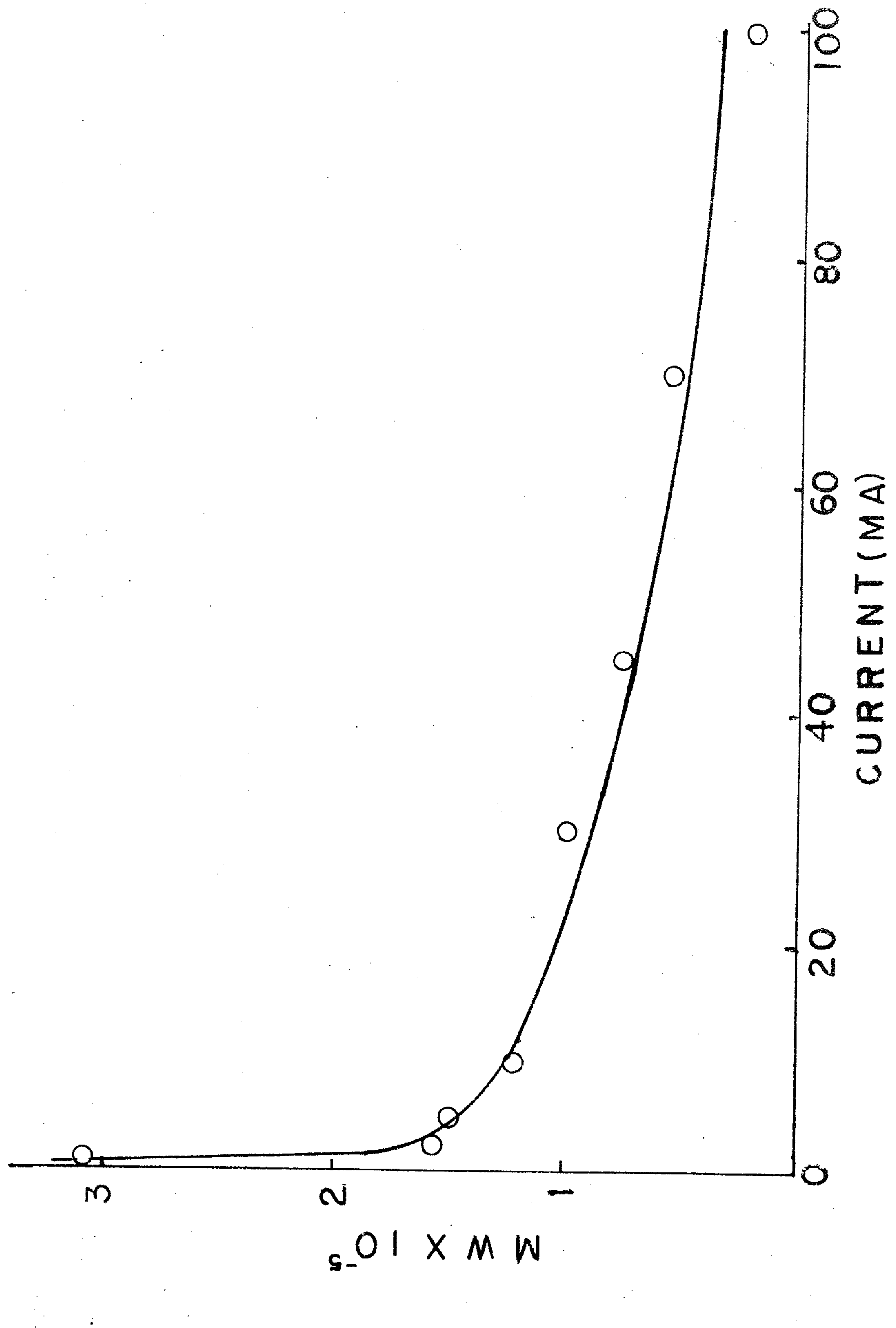

CURRENT (MA)
0
20
40
60
80
100
M W X 10^{-5}
1
2
3

FIGURE XIII. Rate of polymerization as a function of current.

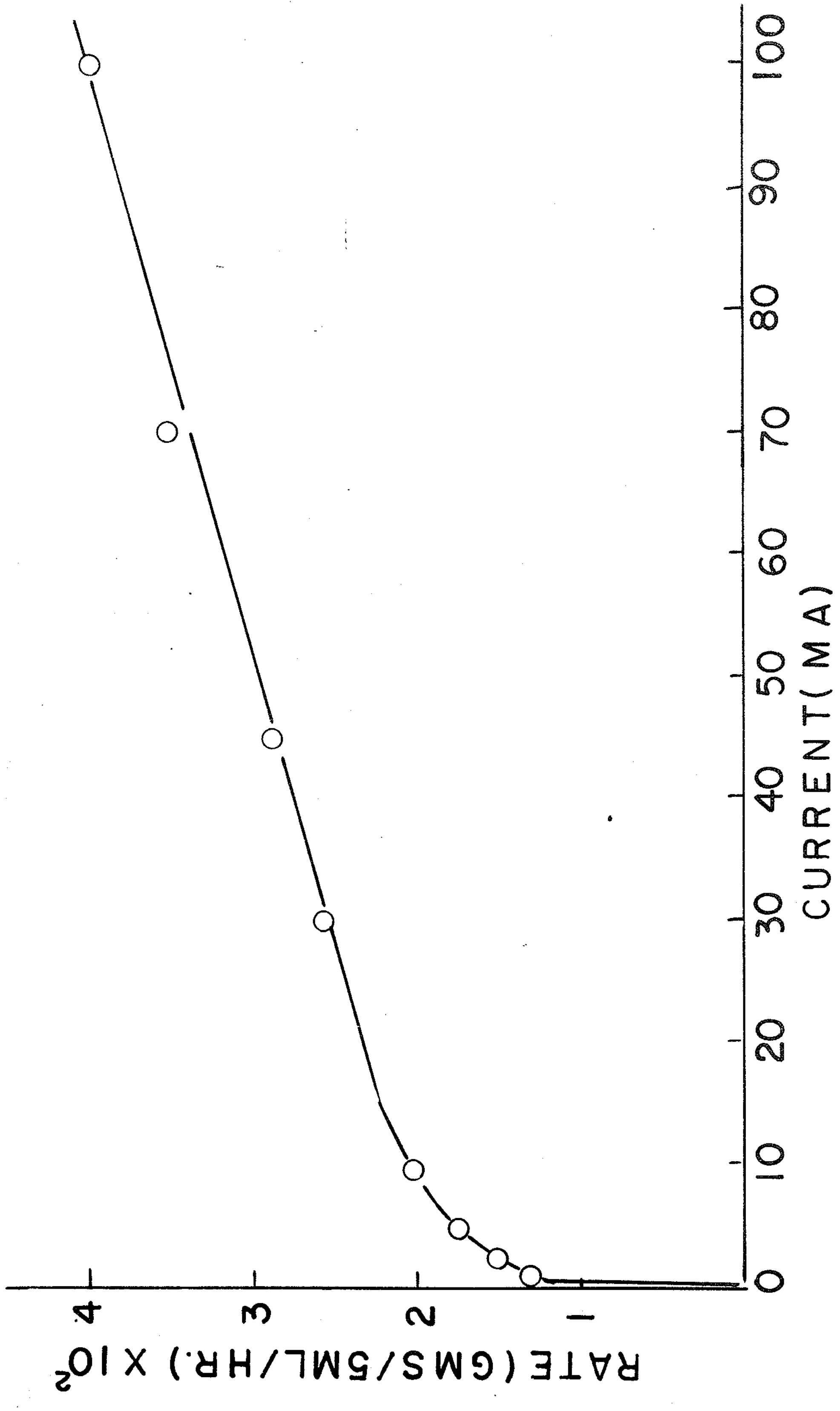

RATE (GMS/5ML/HR.) X 10^2
1
2
3
4
CURRENT(MA)
0
10
20
30
40
50
60
70
80
90
100

FIGURE XIV. Rate of polymerization as a function of the square root of current.

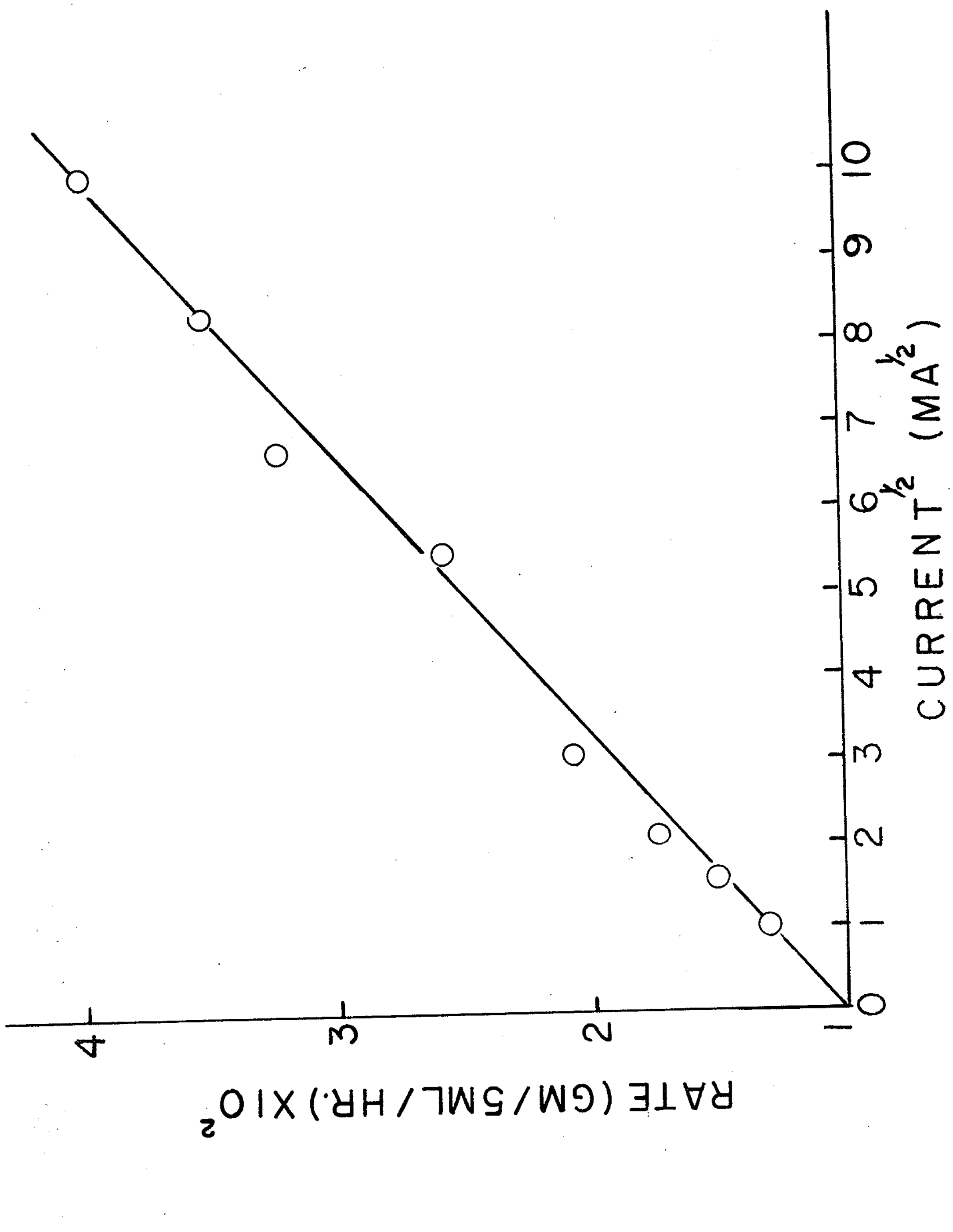

RATE (GM/5ML/HR.) X10²
1
2
3
4
0
1
2
3
4
5
6
7
8
9
10
CURRENT^½ (MA^½)

TABLE 18

Relative efficiencies of the reaction at different current strengths.

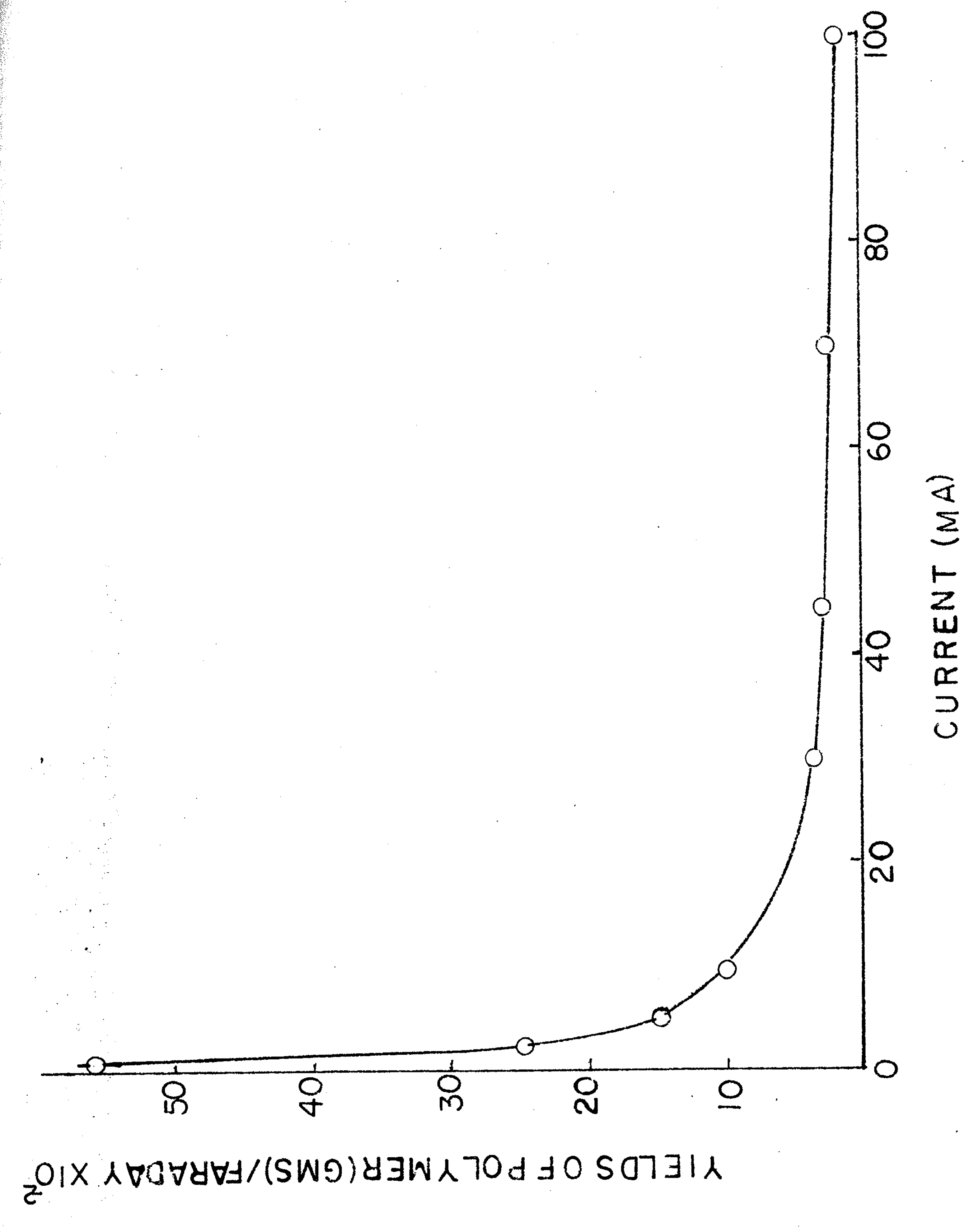
Current (ma)	Time (min)	No.of faradays passed x 10^{-3}	Total yield of polymer (gms)	Yield of polymer (gms) per faraday x 10^{-2}
1.0	600	.37	2.11	55.6
2.5	600	.93	2.25	24.2
4.9	600	1.84	2.65	14.4
9.5	550	3.28	3.20	9.8
30	616	11.60	3.92	3.3
45	518	14.60	3.79	2.6
70	428	18.80	4.11	2.2
100	518	32.50	5.07	1.6

TRACER STUDIES

Reaction Mechanism

The type of reaction mechanism in the dioxane and concentrated nitric acid system was determined by analysis of copolymer composition in the anode and cathode. It was

FIGURE XV. Efficiency (yield per faraday) versus current.


CURRENT (MA)
0
20
40
60
80
100
YIELDS OF POLYMER(GMS)/FARADAY X10^{2}
10
20
30
40
50

found that the anodic polymer contained 49.5 mole % of styrene and the cathodic polymer 43.8 mole %. The results are tabulated in Table 19 and they show the presence of only a free radical mechanism in the anode, seen by comparing the experimental mole % of styrene in the polymer (49.5%) to that calculated from p. 53 for a theoretical free radical mechanism 49.8 mole % of styrene. The mole % of styrene obtained from polymer in the cathode compartment suggests the occurrence of both the free radical and ionic mechanism.

TABLE 19

Copolymerization of equal volume mixture of methyl methacrylate and C^{14} labelled styrene.

	Activity of 0.1 gm of styrene (counts/min)	Activity of 0.1 gm of copolymer (counts/min)	Mole % of styrene in copolymer
Anode	4.94×10^3	2.5×10^3	49.5
Cathode	4.94×10^3	2.2×10^3	43.8

COPOLYMERIZATION

When an equimolar mixture of styrene and methyl methacrylate is initiated by free radicals, the resulting polymer will contain approximately equal proportions of both monomers (58). A cationically polymerized styrene-methyl methacrylate mixture will contain predominantly styrene (57), whereas anionically initiated styrene and methyl methacrylate will compose chiefly of methyl methacrylate (59)(57). However, it must be realized that the relative mole fractions of the monomer in the copolymer are true only if the polymerization proceeds at low conversion.

The determination of propagation mechanism with different initiators was accomplished by copolymerization experiments in dimethyl formamide solutions saturated with the salt under investigation. The reactions were conducted in a divided cell with an anode and cathode compartment. Only the cathodic polymer was examined for the styrene composition. The results are summarized in Table 20.

It was found that cations such as K^+, Li^+ etc., which have a higher decomposition potential than the monomer were able to initiate polymerization cathodically. The type of the mechanism appeared to be predominantly free radical and tended to increase in anionic character at higher valency.

TABLE 20

The effect of salts on the characteristics of cathodic polymer in the dimethyl formamide system.

Initiator	Counts/min 0.1 gm styrene x 10^3	Counts/min 0.1 gm cathodic polymer x 10^3	Wt. % of styrene in cathodic polymer	Mole % of styrene in cathodic polymers	% of free radical	% of anionic	% of conversion
$KClO_4$	5.06	2.232	44.6	43.5	87.5	12.5	36.30
KCNS	6.45	2.85	44.2	43.2	86.6	13.4	9.70
$K_2Cr_2O_7$	6.45	2.60	40.3	39.4	78.9	21.1	14.60
$NaNO_3$	5.16	-	-	-	-	-	-
LiAc	5.06	2.64	52.0	51.0	100	0	2.16
$AgNO_3$	6.45	1.63	25.3	24.6	48.8	51.2	1.04
NH_4Ac	5.22	2.62	50.1	49.1	98.6	1.4	1.10
$TlNO_3$	6.45	1.895	29.4	28.7	56.9	43.1	0.35
$ZnCl_2$	6.45	2.76	42.8	41.9	83.9	16.1	1.12
$Zn(NO_3)_2$	6.45	-	-	-	-	-	-
$Sr(NO_3)_2$	6.45	1.89	29.3	28.6	56.7	43.3	12.80
$AlCl_3 6H_2O$	5.06	1.688	33.6	32.7	65.3	34.7	.70
$SnCl_4 6H_2O$	5.16	3.30	66.0	65.1	68.5	31.5	.75

(cationic)

TABLE 20 (cont'd)

Initiator	Counts/min 0.1 gm styrene x 10^3	Counts/min 0.1 gm cathodic polymer x 10^3	Wt. % of styrene in cathodic polymer	Mole % of styrene in cathodic polymers	% of free radical	% of anionic	% of conversion
$NiCl_2$			no polymer				
$CoCl_2$			no polymer				
$CuCl_2$			no polymer				
$FeCl_3$			no polymer				
$CrCl_3$			no polymer				

Usually in tracer studies, the polymer was reprecipitated four or five times to avoid absorption of activity from the reaction mixture. Since the initiation of the polymerization in this particular case was both free radical and anionic, the resultant polymer was a mixture of a high molecular weight polymer due to the free radical process, and a very low molecular weight polymer due to the anionic process. In other words, reprecipitation constituted fractionation of polymer and the counts/min of the polymer increased after each reprecipitation. The change of counts/min in the cathodic copolymer initiated by potassium thiocyanide furnished the best example and the result is shown in Table 21. Hence the polymer used for counting was only precipitated twice and the result may be affected to a certain degree.

TABLE 21

Influence of reprecipitation on the counts/min of the polymer.

No. of precipitations	Counts/min of 0.1 gm cathodic polymer
1st	2850
2nd	3260
3rd	3970
4th	4700

The percentage of polymer formed by the free radical mechanism and that formed by the ionic mechanism of the concurrent process was calculated for a typical system. A monomer feed of 0.93:1 of styrene and methyl methacrylate was used. The calculation was based on the assumption that for a free radical polymerization, the copolymer contained exactly 49.8 mole % or 50.8 % weight of styrene (p. 53) and for an anionic reaction, only 1 mole % or 1.04 weight % of styrene.

e.g. activity of 0.1 gm C^{14} labelled styrene

= 6450 counts/min.

activity of 0.1 gm of cathodic copolymer initiated by KCNS

= 2850 counts/min.

$$\therefore \text{ weight \% of styrene} = \frac{2850}{6450} \times 100 = 44.2\%$$

$$\therefore \text{ mole \% of styrene} = \frac{\frac{.442}{104.14}}{\frac{.442}{104.14} + \frac{.558}{100.1}} \times 100 = 43.5\%$$

Let x be the fraction of 1 gm of cathodic polymer initiated by a free radical mechanism

$$\therefore \quad .508x + (1 - x)\,0.0104 = .442$$

$$\therefore \quad x = .866$$

∴ 86.6% of the cathodic polymer was produced by the free radical mechanism and the remainder was produced by anionic mechanism.

REDUCIBLE ORGANIC COMPOUNDS

Cathodic reduction of organic compounds such as ketones, aldehydes, nitro-compounds, imine and imidic esters, carboxylic acid, amides and imides was thoroughly discussed by Allen (33). The intermediate species present during the electrolytic reduction of ketones and aldehydes were shown to be free radicals (74) which were able to initiate polymerization. Since most of the reducible organic compounds were non-electrolytes and could only provide a medium of very low conductance, cupric chloride, which was claimed to facilitate reduction, was added as electrolyte. A survey was carried out in which many carbonyl compounds, unsaturated acids and aliphatic hydrocarbons were used as the reducible organic compounds. The yield of the polymer was very low and no further work was attempted in this direction. The solvent used was dimethyl formamide and the monomers employed were styrene and methyl methacrylate. The current applied, was generally 15 ma depending on experimental conditions and the resistance of the solution. The results are tabulated in Table 22.

TABLE 22

The effect of different reducible organic compounds on the yields of the cathodic polymer in the dimethyl formamide at 15 hrs and a monomer concentration of 50% by volume.

Reducible organic compounds	Solvent	Current (ma)	Yield (gms)	Monomer
Acetophenone 15%	Dimethyl formamide	15	.270	Methyl Methacrylate
Benzophenone 16.7%	"	"	.320	"
Butyl aldehyde 25%	"	"	.455	"
Tertiary butyl chloride	"	"	.305	"
Acetoxime 10%	"	"	0.020	"
Cinnamic acid 10%	"	"	0.033	"
Triphenyl methane 16.7%	"	"	no polymer	"
Tertiary butyl bromide 25%	"	12	"	Styrene
Stilbene	"	15	"	"

DISCUSSION

SALT AND SOLVENT SYSTEM

Kolbe electrolysis as a source of free radical has been reported in the early literature (66) and the mechanism of the reaction is believed to be as follows.

$$RCOO^- \xrightarrow{-e} RCOO\cdot \longrightarrow R\cdot + CO_2$$

The radical then dimerizes to form the hydrocarbon

$$R\cdot + R\cdot \longrightarrow R - R \quad (64)(65)$$

Application of the active intermediate species as initiators of polymerization of vinyl compounds have received limited attention (42)(43)(44)(45)(48). The investigators were content to show that radicals could activate the double bond and no greater effort was spent in pursuit of the reaction mechanism or other prominent factors that might, to a certain extent, control the propagation step.

In our present studies, we have examined the electroinitiated polymerization of methyl methacrylate in a homogenous organic medium of high dielectric constant and conveyed the results of our investigations on the effects of current, initiating salt, solvent, electrode material, pre-electrolysis, stirring and electrode spacing on the yield and molecular weight of the resultant polymer.

It is seen in Figure VII that the molecular weight of the polymer varies inversely with the current and its reciprocal shows a linear dependence. As a rule, the molecular weight of the polymer depends upon the rate of termination which is in turn controlled by the concentration of the radicals in the reaction medium. Since the concentration of radicals is dependent on the current, it is reasonable to believe that the comparatively small number of radicals generated at low current will interact with the monomer molecules and have a longer life-time. Hence a polymer of higher molecular weight is expected at low current.

On the whole, the high molecular weights of the polymer obtained under our polymerization conditions are in sharp contrast to discouragingly low values reported in the literature. The dependence of the molecular weight on current changes indicates the possibility of programming molecular weight distribution by judicious control of the current-time relationship.

The influence of current on the yields of polymer is shown by Figure IV and the proportionality between polymerization rate and first power of current is illustrated by Figure VI. The 1st order dependence on monomer concentration is observed in Fig. V. It is understood that the rate of polymerization is governed by the concentration of both initiators and monomer. Hence the yield of polymer is expected to be higher at either higher currents or monomer concentration.

The establishment of the types of reaction mechanism occurring in the anode and cathode compartment and the determination of the initiating species is based upon tracer studies. In copolymerization experiments, with an equal volume mixture of methyl methacrylate and C^{14} labelled styrene, the anodic copolymer contained 50.4 mole % of styrene while that of the cathode contained 54.5 mole %. This strongly suggests the free radical processes at both electrodes.

It has been generally accepted that the initiating species during electrolytic oxidation of acetate ions is the methyl radical $CH_3\cdot$ (43)(44)(45). However, in our experiment with C^{14} labelled acetate in C_1 and C_2 positions, the relative percentages of $CH_3\cdot$ and $CH_3COO\cdot$ that contributed to the initiation were 92.8% and 7.2%. Some of the acetoxy radical generated at the electrode surface must initiate the monomer molecules before they have the chance to decompose into methyl radicals.

Since the reaction mechanism is predominantly free radical and the rate of polymerization is linearly dependent on current as well as monomer concentration, a simple kinetic scheme shown in Table 23 is proposed.

TABLE 23

Kinetic Scheme

$$q + R^- \xrightarrow{k_e} R_1\cdot$$

$$R_1\cdot \xrightarrow{k_d} R_2\cdot$$

$$R\cdot_2 + M \xrightarrow{k_i} M\cdot$$

$$M\cdot + M \xrightarrow{k_p} M\cdot$$

$$M\cdot + R_1\cdot \xrightarrow{k_t} P$$

where q is electronic charge, R^-, $R_1\cdot$, $R_2\cdot$, M, P are salt ion, radicals, monomer and polymer respectively.

The rate of the reaction

$$-\frac{dM}{dt} = k_p [M\cdot][M] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

since

$$\frac{dR_1\cdot}{dt} = k_e i [R^-] - k_d [R\cdot_1] \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

$$\frac{dR_2}{dt} = k_d [R_1\cdot] - k_i [R_2\cdot][M] \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

$$\frac{dM\cdot}{dt} = k_i [R_2\cdot][M] - k_t [M\cdot][R_1\cdot] \quad \ldots\ldots\ldots\ldots \quad (4)$$

and at steady state, the rate of the concentration of radical intermediates is zero (that is, $\frac{dR_1\cdot}{dt} = 0$, $\frac{dR_2\cdot}{dt} = 0$, $\frac{dM\cdot}{dt} = 0$)

$\therefore$ by adding (2),(3),(4).

$$M\cdot = \frac{k_e i [R^-]}{k_t [R_1\cdot]}$$

$$\therefore \frac{dM}{dt} = k_p [M] \frac{k_e i [R^-]}{k_t [R_1\cdot]}$$

The term $k_t[M\cdot][R_1\cdot]$ is omitted in step (2) since it is much smaller in comparison to rate of formation of $R_1\cdot$. In step (4), the term $k_p[M\cdot][M]$ is cancelled out eventually and is not included in the expression. The postulation of the termination of unlike radicals is reasonable because of the preponderance of the initiating radicals near the electrodes even at low current. The concentration of radical $R_1\cdot$ is considered to be large, constant and controlled by rate of diffusion.

It was stated previously the majority of the methyl radicals produced dimerize to form ethane (66, 65). Studies of the Kolbe reaction have revealed that at higher currents, approximately 90% of all the radicals dimerize (67) but the rate of dimerization decreases at lower values (68, 69). It can be predicted that the efficiency of radicals as initiators of polymerization will be the inverse of their rate of dimerization. That is, there will be a higher efficiency of initiation at lower currents. Figure VIII illustrates the variation of initiation efficiency with current. It is in full agreement with the above postulate.

Figure XI indicates the current efficiency of the system at different values of current. With a current of 7 ma, six moles of monomer were consumed per faraday of current passed. This value is comparatively lower than that reported by Breitenbach (10 moles of monomer/faraday). In both cases, acetate ions were employed as initiator.

The products obtained as a result of anodic and cathodic electrolysis are influenced to a marked degree by the nature of the medium. Sometimes even the rate and order of the reaction may be affected (70)(71)(72). Since the ability of the solvent to separate positive and negative charges is governed by the dielectric constant, it is reasonable to assume that an inorganic salt such as zinc acetate may be completely ionized in medium of high dielectric constant but exists as an ion pair $SZn^{++}(2Ac)^{-}$ in low dielectric solvents. In other words, the conductivity of the medium and electrode potential are controlled by the solvent employed. During anodic oxidation, free ions can be discharged much easier and more radicals will be formed. It is expected that higher yields of polymer will be obtained in high dielectric medium. The prediction is supported by experimental evidence shown in Table 2.

The influence of the salts on the yields of the polymer is still uncertain. It may depend upon the reactivity of the radicals or ion radicals generated during electrode processes, diffusion of active intermediate species, electrode potential, solvent employed and nature of the monomers. With some of the salts used, a cationic reaction at the anode (48), anionic in the cathode (52)(53) or a superimposed free radical and ionic processes in one electrode may take place (48). Table 3 shows the variation of yields of polymer with different salts. Since the experiments were conducted in non-divided cells, the amount of the polymer formed is subjected to an additional factor - the competitive reaction that takes place in both electrodes.

It has been reported (37)(39)(40) that during the electro-induced polymerization of methyl methacrylate in aqueous medium, the efficiency increased with increasing hydrogen over-potential on the electrode. In the system we employed, this relationship does not hold. It is probably due to the difference of the initiating species. In former cases, active hydrogen was used but in our work, methyl radicals were employed. However there are changes in the yields of the polymer with different electrode materials as shown in Table 4.

Since pre-electrolysis shortens the induction period of the system by removal of impurities and stirring gives a more even distribution of radicals, the yield of the polymer increases with respect to the above effects as indicated by Table 6.

However, Tsvetkev (76) observed that agitation lowered the yield of the polymer during polymerization of methyl methacrylate by cathodic hydrogen. This is probably due to the decrease of hydrogen voltage by stirring which in turn affects the efficiency of the system.

The influence of electrode spacing as shown in Table 6 is an indication of the control of reaction rate by the electrode potential. It was found that the shorter the distance between the electrodes, the higher is the yield. During electrolytic oxidation or reduction, a certain electrode potential is required and if, at any instant the potential is changed, the nature and yield of the products will be affected.

DIOXANE AND NITRIC ACID SYSTEM

Initiation of polymerization by the cathodic discharge of hydrogen in aqueous medium, with acids as initiator, has been reported in the literature (37)(38)(39)(40). The system employed is generally of a heterogenous nature and the polymer obtained is insoluble. However, in our present investigation of polymerization of methyl methacrylate, the above defects are removed by the use of dioxane as a solvent, which is miscible in all respects with organic liquids and water, and thus provides a homogenous system for kinetic studies. The concentration of water which may to some extent disturb the homogenity of the reaction medium is reduced to a minimum by using concentrated nitric acid as the initiator. It may be argued that by using concentrated nitric acid, ploymer is formed without passing a current but special care was taken to dilute the acid with dioxane, to 25% of its original strength, before addition of the monomer.

The molecular weight of the polymer obtained is actually an average value from both the electrodes since the experiment was conducted in non-divided cell and the polymerization is believed to be initiated by cathodic hydrogen as well as an active intermediate species of nitrate ions during electrolytic reduction and oxidation. It has been shown that initiation by cathodic hydrogen produced 30% of the total yield. In general, the molecular weight trend from 20,000 to 300,000 is much lower and the current efficiency is almost twice that of the dimethyl sulfoxide and zinc acetate system. The inverse current and molecular weight relationship is still maintained. The higher the current, the lower is the molecular weight as shown in Figure XII.

The types of reaction mechanism was determined by analysis of the copolymer in both electrodes. Table 19 shows that anodic polymer contained 49.5 mole % of styrene while that of the cathode contained 43.8 mole %. It is reasonable to believe that the polymerization at the anode proceeds through a free radical mechanism while a superimposed process of both anionic and free radical initiation takes place in the cathode. It has been shown that an electron supplied at the cathode can either be used to discharge a cation to form a free radical (40)(37) or it can be added to a monomer to form an ion radical (48)(54) which is able to propagate in either direction depending upon the experimental conditions.

Kinetically, the yield of the polymer is a function of current and increases linearly with time. The rate of the reaction is the slope of the time versus yield curve. A plot of reaction rates versus square root of current shows a linear relationship. This is in contrast to the first power dependence on current in the system of dimethyl sulfoxide and zinc acetate. However, the 1st order dependence on monomer concentration is maintained. The total yields of polymer are those produced from both of the electrodes which in turn are governed by their respective reaction mechanisms. The two processes that occur at the anode and cathode may interfere or compete with each other. As a result, the yield and molecular weight of the polymer may be affected.

COPOLYMERIZATION

It has been shown that the electron supplied by the cathode in the electrolytic reduction may add directly to the monomer to form an ion-radical, (48)(54), or discharge the cation to form a radical (37) or electro-plate the metal. (73). The relative concentrations of these active intermediate species and their potentialities of initiation depend on the nature of monomer, on the cation, and on the solvent employed. If the cation has a higher decomposition potential than the monomer, the ion-radical will be dominant.

In our copolymerization studies, we have investigated the reactivities of different cations to initiate the polymerization and the types of reaction mechanisms which result. Table 20 shows that certain cations such as K^+, Li^+ etc., were able to induce the polymerization and the reaction is predominantly free radical. Since the initiating species is the ion-radical, the styrene monomer is more susceptible to free radical polymerization due to its resonance structure and it is reasonable to believe that polymerization will proceed through the radical end.

REDUCIBLE ORGANIC COMPOUNDS

The product obtained from cathodic reduction of organic compounds is governed by the electrode potential. At relatively high cathodic potential, the intermediate species during reduction of ketone is a highly reactive radical (74). The application of reducible organic material to the polymerization of a vinyl monomer was first studied by Loveland (75). However in our present work, we investigated the effect of different reducible compounds on the yield of polymer in the system of dimethyl formamide. Table 21 indicates that carbonyl compounds such as ketones and aldehydes gave reasonable yields of polymer while others such as acetoxime, cinnamic acid, triphenyl methane, stilbene, tertiary butyl chloride only formed minor trace of polymer. It is believed the energy required for the formation of free radical except for the case of ketone and aldehyde is much higher than experimental conditions employed (66). The experiments conducted in this field were exploratory and our main interest was to see whether polymer can be formed by active intermediate species during cathodic reduction.

CONCLUSION

Methyl methacrylate was polymerized in a homogenous organic medium composed of a solvent of high dielectric constant, an ionizable salt and the monomer. The yield and molecular weight of the polymer are found to increase with solvents of high dielectric constant, inert electrode materials, shorter electrode spacing, pre-electrolysis and with stirring. The influence of varying the inorganic salts or the monomer were also investigated but the results only show that the polymer is some function of the nature of these starting materials. The use of alternating current instead of direct current increased the molecular weight and decreased the yield of the polymer. From the kinetic studies, the yield of the polymer is seen to be linearly dependent on the time and the rate of reaction is directly porportional to the current. The first order dependence on monomer concentration is confirmed by the plot of log $\frac{M_o}{M}$ versus t. The type of reaction mechanism presentwas proved to be free radical with the initiating species predominantly the methyl radical. The current efficiency though low is found to be in line with that reported by Breitenbach (48). However, the major improvement in the system employed is the high molecular weight of the polymer obtained and the control of molecular weight distribution by current adjustment.

The system of dioxane and concentrated nitric acid has also been studied. The rate, molecular weight, and current relationship of this second homogenous system follows a similar trend to that in the former. However the current efficiency is doubled. It increased with decrease of current. At a constant current of 1 ma, 55.6 moles of monomer were consumed per faraday. The molecular weight is found to be lower and the rate of the reaction is proportional to the square root of the current. Again, the reaction mechanism is found to be free radical at the anode but with a superimposed process of free radical and anionic at the cathode. The advantage of both systems is their homogenity which enabled these studies of kinetics to be undertaken.

In the copolymerization experiments, the reactivity of the cation is found to dominate the nature and extent of the polymerization.

The use of reducible organic compounds to induce polymerization of vinyl compounds was found to produce very low yields of polymer.

It can be seen that methyl methacrylate-dimethyl sulfoxide - zinc acetate and methyl methacrylate - dioxane - nitric acid, both form systems in which electro-initiated polymer may be formed. They provide a basis for the production of controlled molecular weight polymers and a medium in which kinetics of polymerization reactions are easily studied.

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