

UNIVERSITY OF MANITOBA

THE ELECTROINITIATED POLYMERIZATION OF STYRENE
IN SOLUTIONS OF QUARTERNARY AMMONIUM SALTS

presented by

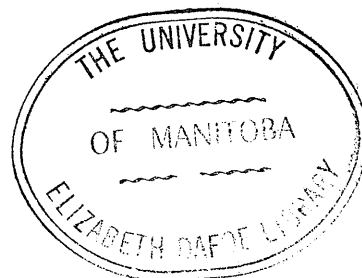
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TO MY PARENTS

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ABSTRACT

The kinetics were studied of the electrically initiated polymerization of styrene in solutions of tetramethyl ammonium salts. The reaction was confined to the cathode and was found to proceed via an anionic mechanism. Free radical inhibitors had little influence on the yield of polymer, but the reaction was quenched by the addition of methanol and water.

The polymerization was investigated at six currents between 10 and 100 ma. and at various initial concentrations of monomer. Kinetic analysis of the data indicated a dependence on the first power of monomer concentration and of current. The initial rate of the reaction decreased with decrease in temperature.

The high electrical efficiencies and molecular weights of 15,000 to 50,000 contrast sharply with previous fruitless attempts to electroinitiate styrene polymerization.

The copolymerization was performed using active styrene and methyl methacrylate. Data differed from the previously reported results in the literature. The reaction mechanism was believed to be anionic.

Besides styrene, methyl methacrylate, acrylonitrile and α -methylstyrene could be successfully polymerized by the electrolysis of tetramethyl ammonium chloride in dimethylformamide.

INTRODUCTION

ADDITION POLYMERIZATION

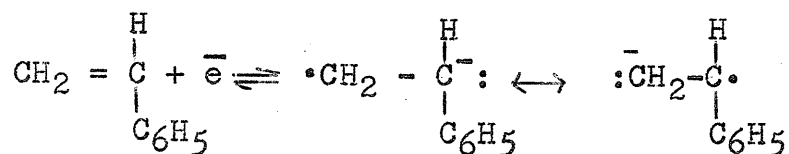
Addition polymerization may be propagated by three distinct types of reactive centres namely, radicals, ions or coordination complexes, and the respective polymerization processes are classified, therefore, as radical, ionic or coordination polymerization. The reaction mechanism of radical polymerization is well known. In spite of familiarity with cationic initiated polymerization for many years, its mechanism is not clear and generally confused by the complex phenomenon of co-catalysts whose fates are not well understood.

Monomers with electron-donating groups attached to the double-bonded carbons form stable carbonium ions and polymerize best by electrophilic substances such as BF_3 , AlCl_3 , SnCl_4 , TiCl_4 etc. Trace amounts of water or methanol or acids serve as co-catalysts. In ion polymerization, reaction often leads to very high rate at ordinary temperature involving enormous difficulty in obtaining kinetic data. A very troublesome feature of the ionic polymerization is the poor reproducibility and concordance of the results.

Very little detailed work on the polymerization of olefins proceeding by an anionic chain mechanism has been reported. Much of the early work has been confined to qualitative studies on the effect of metal gegenion and solvent

on polymer microstructure and copolymer composition. However, base-catalysed polymerizations can be carried out in liquid ammonia, and many early studies were carried out in this solvent (1,2,3). The polymerizations are complicated by chain-transfer to the solvent. Recent work has, therefore, been concentrated on polymerization carried out in hydrocarbons and ethers where chain-termination is absent or negligible if the systems are rigorously purified and the reactions carried out in the absence of moisture or air. The anionic polymerization of acrylonitrile in various systems such as butyl-lithium in petroleum ether (4), metal ketyls in tetrahydrofuran (5), ~~sodio-malonic~~ ^{sodio-malonic} ester in dimethylformamide (6), and quaternary ammonium hydroxide (7) in dimethylformamide have been studied. In almost all the systems the termination step in ^{the} mechanism of the polymerization is believed to be by chain transfer to monomers.

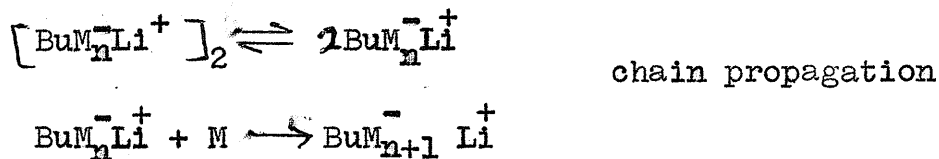
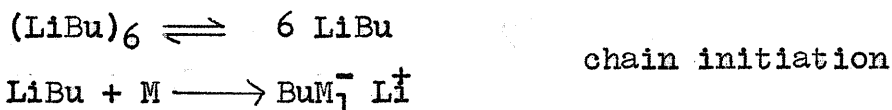
Electron-transfer initiated polymerization of styrene in ethers catalysed by sodium naphthenide was described by Szwarc (8). The reaction mechanism is believed to be



Chain-initiation forms a styrene ion-radical. Any radical ends dimerize quickly and chain propagation proceeds from ionic centres at each end of the chain. Termination is

negligible under ideal conditions (9). If chain-initiation is rapid and chain propagation is slow, the rate of polymerization measured will be that of chain-propagation. In dioxane, propagation occurs at a measurable rate and the polymer formed has the narrow molecular weight distribution expected for rapid initiation. The system styrene-benzene n-butyl-lithium has been extensively studied. Initiation consists of the addition of n-butyl-lithium across the monomer double bond (10). One polymer chain is produced by each initiator molecule. Chain-termination is negligible, but initiation and propagation proceed at comparable rates (11).

The reaction mechanism can be summarized as follows:



First successful electrically initiated anionic polymerization of styrene in dimethylformamide and KNO_3 system was carried out by Funt and Walker (12). They believed that the formation of a radical-ion and its subsequent polymerization most probably represents the reaction path.

TERMINATION OF ANIONIC POLYMERIZATION

The most important mode of termination of a radical

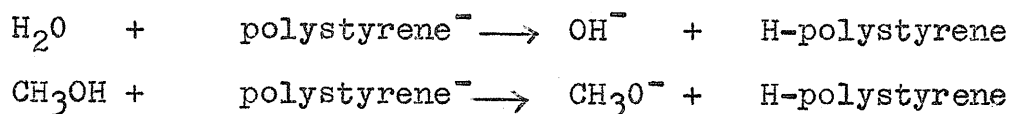
polymerization is the bimolecular interaction of its reactive centres. Radicals rapidly recombine or disproportionate and these reactions annihilate the growing ends. On the other hand, neither recombination nor disproportionation takes place in anionic polymerization, and hence a collision between two ionically growing centers usually does not lead to termination. While the active end of a growing polymeric radical forms single entity, the active end of anionically growing polymers involves two species, a charged terminal atom or terminal group of the polymer and associated with it, an oppositely charged counter ion (gegenion). The interaction between these two entities may lead to termination of polymerization or termination is involved with solvent or substances present in the solution.

Transfer of a proton is a very common mode of termination of anionic polymerization. Indeed, this mode of termination was postulated in the earliest studies of anionic polymerization, e.g., in the polymerization of styrene carried out in liquid NH_3 (1,2,3). In the course of their investigation of styrene polymerization carried out in liquid NH_3 and sodium amide system, Sanderson and Hanser (2) found a constant molecular weight of about 3,000 for the resulting polymer. Its value was unaffected by the concentration of sodium amide and it was not changed appreciably by the extent of the polymerization. This was interpreted by the above workers as evidence for the termination due to a proton trans-

fer from an ammonium molecule to a growing chain, i.e.,



They found one NH_2 group in each polymeric chain, no unsaturation, independence of molecular weight on amide concentration and its increase with increasing styrene concentration. Proton-donating substances e.g., water or methanol easily inhibit the growth of anionic polymerization. The probable reaction takes as follows:



The termination of anionic polymerization can also proceed through isomerization reaction of carbanion ions (13).

A REVIEW OF ELECTROINITIATED POLYMERIZATION OF VINYL COMPOUNDS

Unlike thermal and photoinitiated polymerization of vinyl and related compounds, electroinitiated polymerization has not been thoroughly studied. This is at the very beginning of its progress. However, recently several investigators in different countries have been attracted towards this method of polymerization of unsaturated compounds. An attractive feature of this method of polymerization is the control of reaction rate by controlling current and current density.

Stopping the reaction is a simple matter of switching off the current.

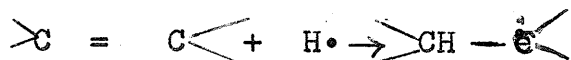
Although a number of reports of polymerization induced by electrolysis of solutions of monomers, are now available a majority of investigations have been confined to the polymerization of methyl methacrylate. This monomer can be easily polymerized by atomic hydrogen generated on the cathode in the electrolysis of water, methanol, acid or other material.

Electroinduced polymerization of monomers was first reported by Wilson in 1949 (14). He polymerized acrylic acid, methyl acrylate and methyl methacrylate in the solution of sulphuric acid in aqueous methanol using ^amercury cathode with a current density of 30 ma/cm². The polymerization was initiated by a cathodic hydrogen that was added to the monomer, followed by the growth of the resulting free radical by further addition of monomer. Parravano (15) whose work was just the revision of Wilson's, found that polymers formed at a mercury cathode after 1.5 hour, at a lead cathode after 2 hours and at a platinum cathode after 24 hours, of electrolysis. Current density of 2.57 ma/cm² was the same in each case. Kern (16) polymerized methyl methacrylate in aqueous hydrogen-chloride, and reported the polymerization of 270 moles of monomer per mole of hydrogen ion discharged. Polymerization of this monomer was also carried out in aqueous hydrochloric

acid at lead cathode (17). It was reported that polymer formation was accelerated by an increase either in the size of the cathode or in current density or in the reaction temperatures. Limiting viscosity of products increased with a decrease in the cathodic current density. Recently the same author (18) studied the effect of the hydrochloric acid and sodium chloride contents of the aqueous phase in cathodic hydrogen-initiated polymerization of methyl methacrylate. He reported that an increase in HCl concentration lowered the polymerization rate, whereas sodium chloride had an inverse effect. The addition of alcohol augmented the polymer yield, while degree of polymerization increased at first and then later fell with increase in concentration of alcohol.

The efficiency of the reaction of atomic hydrogen with monomers varies with the hydrogen over-voltage of the cathode metal (14,15). The atomic hydrogen released from the cathode of the highest over-voltage is the most reactive. Therefore, monomers can be polymerized by atomic hydrogen on cathodes of several metals like Pb, Sn, Pt, Bi, Fe, Al etc., and efficiency of initiation varies in accordance with the hydrogen over-voltage of these metals. No polymerization occurs on cathodes of Cu, Cd, Ni, W, Ta, Mo, Cr, Ag and Zn. A reaction mechanism of the polymerization of monomers initiated by the atomic hydrogen can be shown by the follow-

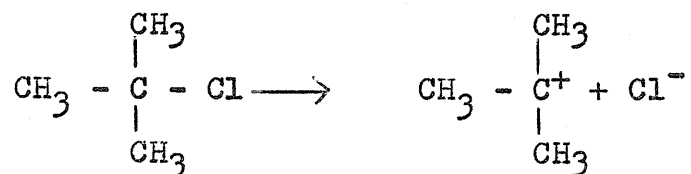
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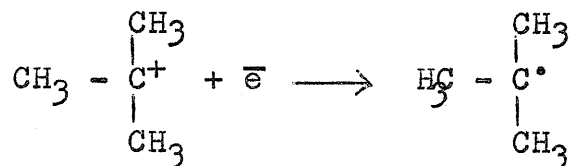
A second type of radical polymerization is due to the production of radicals at the anode by the Kolbe electrolysis of acetates in suitable solvents. Alkyl \dot{R} or alkoxide $R-\overset{\overset{O}{\parallel}}{C}-\dot{O}$ free radicals, produced at the anode, diffuse into the solution to initiate the polymerization. Das and Palit (19) attempted to polymerize methyl methacrylate by anodic discharge of acetate radicals in glacial acetic acid, but did not succeed. However, Smith and Gilde (20) were successful in polymerizing vinyl acetate, methyl methacrylate and vinyl chloride by the electrolysis of potassium acetate in water. Polymerization of methyl methacrylate was also carried out in the solution of lithium acetate in acetic acid and its anhydride with high electrical efficiency, (21). Similar free radical initiation of methacrylate in homogeneous system has been reported (22). These authors used dimethyl sulfoxide and dimethylformamide as solvents and zinc acetate as a source of the free radical. In this system rate of polymerization varied directly with current density while the molecular weight of the polymer varied inversely with current density.

A third type of radical polymerization is due to the

reduction of reducible organic compounds. This method was adopted by Funt and Van Buren (23) to polymerize methyl methacrylate by electrolysis of nonaqueous solution of tertiary butylchloride and tertiary butylammonium chloride in dimethylformamide. The reaction mechanism is believed to be:

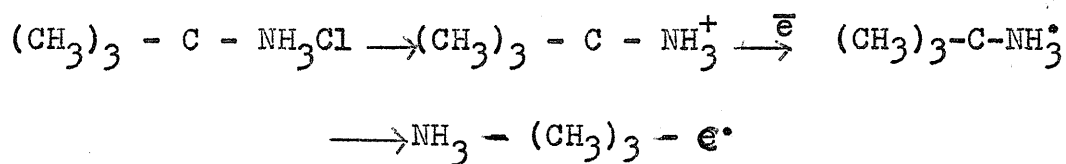


The carbonium ion is reduced to the tertiary butyl radical



The radical thus formed reacts with the monomer to give a monomeric radical which propagates the chain.

Similarly tertiary butylammonium chloride undergoes reduction to form tertiary-butyl-radical.



Tertiary butylchloride serves as an electrosensitizer in this system. The electrical efficiency, expressed in moles of monomer polymerized per Faraday, of the system was found ^{to be the} highest ever recorded for free radical system.

Acrylonitrile

Kolthoff (24) used an indirect electrolytic method to

polymerize acrylonitrile. He reduced an aqueous solution of ferric iron electrolytically in the presence of persulphate, hydrogen peroxide or cumene hydroperoxide. Ferrous ion, formed on the reduction of ferric ion, reacted with the oxidizing agent to produce a free radical and ferric ion. $Fe^{+++} + e \rightarrow Fe^{++}$; $Fe^{++} + H_2O_2 \rightarrow Fe^{+++} + OH^- + OH^\bullet$

The free radical (OH^\bullet) thus formed initiated the polymerization of the monomer.

Breitenbach (21) reported the polymerization of acrylonitrile by electrolysis of tetraethyl ammonium perchlorate as an anionic polymerization. An anionic polymerization was also studied in the presence of sodium nitrate in dimethylformamide (25). It was suggested that the initiation mechanism is direct electron addition from cathode to the monomer. The authors were able to prove that the salt served merely as an electrolyte.

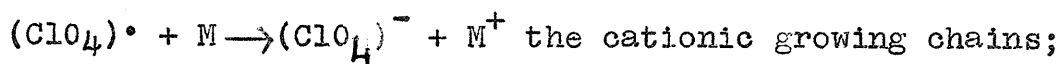
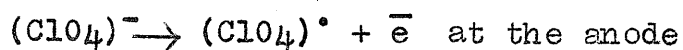
Styrene

In 1952 Goldschmidt and Stockel (26) obtained polystyrene by electrolysis of solutions of monomer in anhydrous fatty acids containing the corresponding fatty acid salts. The major part of the product of the reaction consisted of dimer and trimer, and only 0.098 of a semi-colloid of 3,200 molecular weight was obtained from the electrolysis of a solution containing 20g of styrene. Das and Palit (19) reported a trace of polymer formed under similar conditions

in propylene glycol. A brief note by Yang, McEwen and Kleinberg (27) reported on the initiation of styrene polymerization at the cathode. They electrolysed a pyridine solution of NaI and monomer. An unstated quantity of polymer was obtained with a molecular weight of 1,800. In the light of the present knowledge it is probable that this was the first electrically initiated anionic polymerization.

Breitenbach and Srna (21) were successful in obtaining polystyrene by electrolysis of solutions consisting of acetic acid, acetic anhydride and lithium acetate. 0.8 mole of styrene was polymerized by the passage of one Faraday of electricity. These authors claimed a free radical mechanism.

They also polymerized styrene by a cationic process initiated in a solution of the monomer in nitrobenzene by the anodic discharge of perchlorate and borotetrafluoride ions. A reaction mechanism was proposed as follows:



where M represents the monomer.

Kolthoff and Ferstandig were not successful in obtaining polystyrene with their redox system. Failure to obtain polystyrene was also reported by Friedlander, Swann and Marvel (28). The polymerization of styrene by cathodic hydrogen in the presence of alcohols has been recently reported by

Russian chemists (18). A detailed study of electroinitiated polymerization of styrene by anionic mechanism in dimethylformamide and alkali salt system was made (12). The authors attempted to find out the effects of various parameters on the yield and configurations of the polymers formed in this system. An attempt to polymerize styrene by reducible organic compounds proved unsuccessful (23).

COPOLYMERIZATION

The composition of the copolymer formed from a particular mixture of monomers depends upon whether the mechanism of the polymerization is radical, anionic or cationic. The effect is more pronounced for styrene and M.M.A. It is known that when equimolecular mixture of these two monomers are copolymerized with various types of catalysts, the copolymer initially formed has a composition dependent on the catalyst type (29) as shown in the following table.

Table (a)

| <u>Catalyst type</u> | <u>Copolymer composition</u> | |
|----------------------|------------------------------|----------------|
| | <u>% ST</u> | <u>%M.M.A.</u> |
| Cationic | >99 | <1 |
| Free radical | 51 | 49 |
| Anionic | <1 | >99 |

Therefore, examination of composition of the product has been used in identification of the type of polymerization

promoted by new and unusual initiators.

MOLECULAR WEIGHT

Any method of measurement of molecular weight will give an average value, as polymers normally have a wide molecular size distribution. Two types of molecular weight averages are of considerable importance; number average molecular weight and weight average molecular weight. In computing a number average molecular weight, the molecular weight of each species is weighted by the mole fraction of the particular species in the polydisperse system. The mathematical formulation of this average \bar{M}_n is

$$\bar{M}_n = \sum X_i M_i = \frac{\sum N_i M_i}{\sum N_i} \dots\dots\dots (1)$$

where X_i is the mole fraction of the species, i ; M_i is the molecular weight of the species; N_i is the number of molecules of the species and the summation is carried out over all species of i . Equation (1) shows that the number average molecular weight is the total weight of polymer divided by the number of moles of polymer molecules.

For the weight average molecular weight the molecular weight of each species is weighed by the weight fraction of the species occurring in the polydisperse system, so that

$$\bar{M}_w = \sum W_i M_i = \frac{\sum N_i M_i^2}{\sum N_i M_i} \dots\dots\dots (2)$$

where W_i is the weight fraction of the species and N_i have the same meaning as before.

A third average molecular weight is the so-called Z-average and defined by:

$$M_Z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2} \dots \dots \dots (3)$$

This can be found from the centrifuge measurements.

The turbidity and osmotic pressure measurements give weight average and number average molecular weights respectively. The ratio \bar{M}_w/\bar{M}_n is a measure of the polydispersity of the system.

VISCOMETRY

The viscosity average molecular weight of linear polymer can be computed from limiting viscosity number of the poly sample of any degree of heterogeneity by use of the following equation (30):

$$[\eta] = K M_w^\alpha \dots \dots \dots (1)$$

where K is a constant whose value is independent of the molecular weight but dependent on the polymer, solvent and temperature. α is dependent on shape of the solute molecule. For linear micromolecules α usually lies between 0.5 and unity, so that the viscosity average would lie between a number and a weight average. However, absolute molecular weight cannot be determined by this method unless

the dependence of limiting viscosity number on molecular weight has been established empirically by an absolute method such as osmotic pressure or light scattering.

Weight average molecular weight of polystyrene can be determined by viscometry using the following relationship (31):

$$[\eta]_{\text{benzene}}^{25^{\circ}} = 1.12 \times 10^{-4} \bar{M}_w^{0.73} \text{ for range } 2 \times 10^4 \text{ to } 1.5 \times 10^5$$

Similar measurements in other solvents have been summarized in Table (b) in terms of the parameters defined by the equations:

$$[\eta] = K M_w^{\alpha}$$

$$\log [\eta]_{\text{benzene}} = A + B \log [\eta]_{\text{solvent}}$$

Table (b)

| <u>Solvent</u> | <u>K x 10⁴</u> | <u>_____</u> | <u>A</u> | <u>B</u> |
|-------------------|---------------------------|--------------|----------|----------|
| Benzene | 1.12 | 0.73 | - | - |
| Toluene | 1.16 | 0.72 | 0.025 | 0.01 |
| Methylethylketone | 2.02 | 0.63 | 0.287 | 1.15 |

The viscosity molecular weight relationships hold for a wide range of polystyrenes, and are not markedly influenced by the heterodispersity of the polymer. In view of the experimental difficulties it is well known that the viscosity

method, although it constitutes the simplest and most rapid method of determining the molecular weight of a polymer, cannot be considered to give much better than a useful estimate of the value. For comparative purposes and for assessing molecular weight trends the method has considerable application.

AIM OF RESEARCH

The problem undertaken was to study the kinetics of electroinitiated polymerization of styrene in solution of quaternary ammonium salts in dimethylformamide and to investigate the probable mechanism of polymerization. From this laboratory the successful electroinitiated polymerization of this monomer in solution of alkali metal nitrates was reported, but the question might be asked whether the polymerization was merely a side effect due to the interaction of a deposit of alkali metal on electrode with the monomer, since it is well known that metallic sodium and potassium under appropriate environment are able to initiate the polymerization of styrene. Therefore, the exploratory experiments were performed to find out the salts other than alkali metals, which would initiate the polymerization of styrene. During the course of investigation it was observed that quaternary ammonium salts in dimethylformamide are excellent initiators for the polymerization of styrene. This monomer was previously considered a difficult monomer to undergo polymerization by electroinduced method.

In this system there is no possibility of deposition of an active metal. Satisfactory yields of polymers were obtained. Polymerization proceeded as soon as current was passed. Further investigation proved that this system is amenable to simple kinetic analysis. Therefore, it appeared to merit detailed study of the reaction of polymer formation as a

function of monomer concentration, current, solvent and salts.

A further aim of this work was to discover the most probable mechanism of the reaction path by copolymerization study and to find out the reactivity ratios of styrene and methyl methacrylate in this system, and compare the values with previous reported values in the literature.

PURIFICATION AND PREPARATION OF THE REAGENTS

Styrene, methyl methacrylate and α -methyl-styrene contain small amounts of inhibitors to prevent polymerization during transportation and storage. The inhibitor was removed by passing monomers through a column of chromatographic alumina. Methyl methacrylate and α -methyl-styrene were dried over calcium hydride, then distilled under reduced pressure and the center fractions were collected. Acrylonitrile was dried over BaO and CaSO₄ and distilled under reduced pressure. Every monomer sample, freshly distilled, was stored in the refrigerator for a period not exceeding one week. Just prior to use the monomer was tested to ensure absence of polymer by adding a sample to methanol.

Dimethylformamide (A.R.) was purified by mixing with 10% benzene previously dried over calcium hydride. After standing more than 24 hours the mixture was fractionally distilled and the fraction boiling at 150-152°C was collected over BaO, allowed to stand for 24 hours and redistilled at reduced pressure. Dimethyl sulfoxide was dried over calcium hydride for 24 hours and then fractionally distilled and the portion boiling at 189°C was collected. Benzene was dried over calcium hydride and fractionally distilled and center cuts were collected.

Quaternary ammonium salts were polarographic grade, and were used without purification. Prior to use they were dried in the oven.

Tetramethyl ammonium perchlorate was prepared from its chloride. First tetramethyl ammonium hydroxide was prepared by the addition of alcoholic potash on an alcoholic solution of its chloride, potassium chloride was precipitated out and removed by filtration. When tetramethyl ammonium hydroxide remaining in the solution was treated with perchloric acid, tetramethyl ammonium perchlorate precipitated out as fine crystals which were washed several times with methanol till the filtrate was free from acid and chloride. The tetramethyl ammonium perchlorate thus obtained was dried in vacuum at 70°C.

Tetramethyl ammonium nitrate was prepared by mixing equimolar solution of silver nitrate and tetramethyl ammonium chloride. Silver chloride precipitated and was removed by filtration. Tetramethyl ammonium nitrate remaining in solution evaporated slowly and the residue was dried at 70°C. The prepared tetramethyl ammonium nitrate was tested for presence of chloride and silver salts and negative results were obtained.

POLYMERIZATION

Polymerization was carried out in glass cells which were of a basic test tube type (Figure A). Two platinum electrodes each of dimensions 1" x 1" and spaced 1 cm apart were sealed into a 34/45 inner joint and fitted into an outer joint test tube with a side arm. A magnetic stirring bar agitated the solutions during electrolysis. A bank of four such cells was operated simultaneously in a constant temperature bath at 25°C. One geared motor rotated in a series of magnets which provided uniform and constant stirring for all cells. Samples were withdrawn with hypodermic syringe through a serum cap fitted over the side arm of each cell.

The cells and electrodes were dried and flamed before each polymerization. Constant current supplier was used for low currents. A D.C. line of 250 volts was used to get currents above 15 ma. Both voltage and current were simultaneously recorded by means of servo recorder model EuW-20A and switch gear.

All polymerizations were carried out at 25°C unless otherwise stated.

FIGURE A. Polymerization cell.

- (a) mercury contacts.
- (b) 35/45 ground glass joint.
- (c) platinum electrodes.
- (d) stirring bar.
- (e) rubber cap.

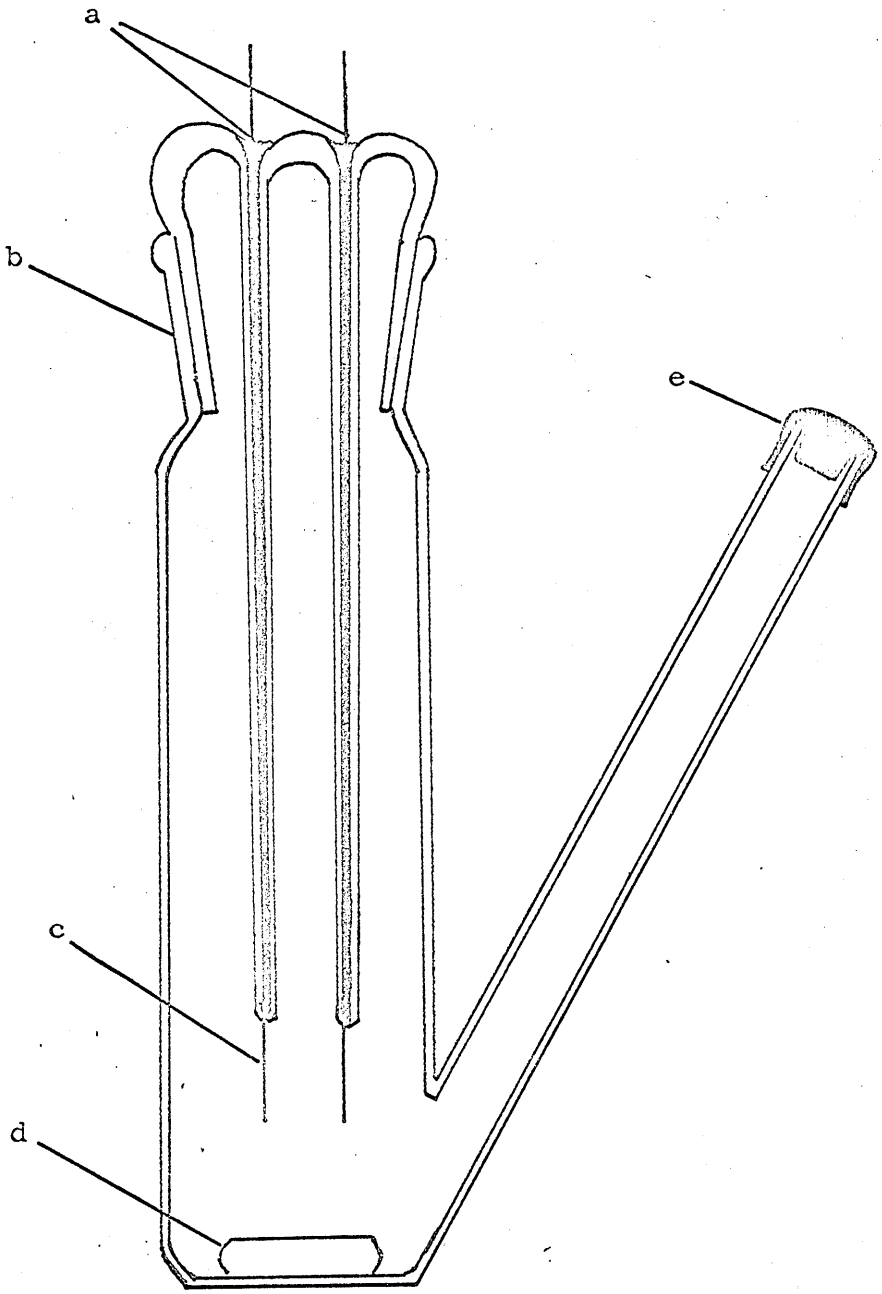


FIGURE A

RESULTS AND DISCUSSION OF EXPLORATORY EXPERIMENTS

Attempts to polymerize styrene by electrolysis of sodium or potassium acetate were made by various workers without success. They reported that low molecular weight polystyrene oil was formed. During the course of our preliminary investigation of electroinitiated polymerization of styrene with various salts and solvents, it was observed that styrene was polymerized by potassium acetate, zinc chloride, silver nitrate and tetramethyl ammonium chloride in dimethylformamide. The molecular weight of polystyrene produced in system composed of potassium acetate and dimethylformamide was found to be 20,000 and yields were also reasonably high. Beside styrene, other monomers like α -methyl-styrene, acrylonitrile, methylmethacrylate were also polymerized. Data are presented in Table I. Attempts to polymerize vinyl acetate, methacrylate and acrylic acid proved unsuccessful in these systems, although these monomers could be easily polymerized by potassium acetate in aqueous systems (20,32).

TABLE I. Formation of polymers of different monomers (40% by volume) in dimethylformamide saturated with potassium acetate. Current 15 ma.

| Monomer | Time (hours) | Weight of polymers (g) |
|-------------------------|--------------|------------------------|
| Acrylonitrile | 22 | 22.90 |
| Styrene | 22 | 11.50 |
| Methylmethacrylate | 22 | 7.00 |
| α -methylstyrene | 22 | 4.00 |
| Acrylic acid | 22 | Nil |
| Methacrylate | 22 | Nil |
| Vinyl acetate | 22 | Nil |

All potassium salts or acetate salts did not give uniform polymer products as shown in Table II. Various other solvents were tested for the polymerization of styrene using potassium acetate and tetramethyl ammonium chloride. Very puzzling results were obtained as shown in Table III.

TABLE II. Relative yields of polystyrene in saturated solutions of different salts in dimethylformamide. (Styrene 40% by volume).

| Salt | Time (hours) | Current ma. | Weight of polymers (g) |
|-----------------------|--------------|-------------|------------------------|
| Potassium acetate | 22 | 15 | 11.5 |
| Potassium nitrite | 22 | 30 | 12.0 |
| Potassium perchlorate | 22 | 15 | 1.0 |
| Potassium thiocyanate | 22 | 30 | 2.9 |
| Potassium fluoride | 22 | 15 | Nil |
| Lithium acetate | 23 | 15 | 0.25 |
| Sodium acetate | 21 | 15 | 1.615 |
| Zinc acetate | 22 | 15 | 0.40 |
| Ammonium acetate | 24 | 15 | Nil |
| Lead acetate | 22 | 15 | Nil |
| Sodium propionate | 22 | 15 | 5.1 |
| Silver nitrate | 24 | 30 | 4.0 |

The inconsistency observed in the data may have been due to the following possible reasons:

1. Solubility of salts in solvent.
2. Complex formation between salt, solvent and monomer.

3. Solvation power and dielectric constant of the solvents.

Although the solubility of potassium thiocyanate in dimethylformamide is greater than that of potassium acetate, the yield of polymers is greater for the latter. It seems possible that one fragment of the salt acts as an initiator or catalyst whereas other behaves as an inhibitor or retarder. Hence the formation of polymer might possibly depend on whether the fragment initiating the polymerization exerts a greater influence than the fragment which inhibits it. Solubility of tetramethyl ammonium chloride in dimethylformamide and dimethylacetamide is almost the same, but no polymers were obtained with the latter solvent. Therefore, the relation between salt solubility and the effectiveness of the salt as an initiator does not in itself account for the observed data.

Of the other possibilities, complex formation would seem more likely. It is possible that salt and solvent form a complex or active species which may be responsible for the polymerization. No detailed interpretation is possible until further evidence is obtained, but this will necessitate a separate study.

TABLE III. Polymerization of styrene (40% by volume) in 23-24 hours in various solvents at 15 ma.

| Solvent | Dilectric constant of solvents | Weight of polymers (g) | Mol. Wt. of Poly |
|---|--------------------------------|------------------------|------------------|
| Electrolyte:- potassium acetate | | | |
| 1. Dimethylformamide | 36.7 | 11.5 | 20,000 |
| 2. Dimethylacetamide | 37.8 | 21.0 | 18,000 |
| 3. Dimethylsulfoxide | 45.0 | 1.0 | 30,000 |
| 4. Acetonitrile | 37.5 | 0.4 | - |
| 5. Acetic acid | 6.15 | 0.8 | 30,000 |
| 6. Propionic acid | 3.44 | 0.8 | 16,000 |
| Electrolyte:- tetramethyl ammonium chloride | | | |
| 1. Dimethylformamide | 36.7 | 20.5 | 21,000 |
| 2. Dimethylacetamide | 37.8 | Nil | - |
| 3. Dimethylsulfoxide | 45.0 | Nil | - |
| 4. Acetonitrile | 37.5 | Nil | - |

KINETIC STUDIES OF POLYMERIZATION OF STYRENE IN SOLUTION
OF TETRAMETHYL AMMONIUM CHLORIDE IN DIMETHYLFORMAMIDE

In all experiments 1.5 g of the salt was added to 100 ml of monomer solution in dimethylformamide. This furnished a saturated solution with some excess salt present. Rates of polymerization were determined gravimetrically. During the course of the reaction 2 ml samples were withdrawn periodically, weighed and their polymer content determined by precipitation in cold methanol. After filtration the residue was washed several times with methanol, dried for 24 hours and weighed to constant weight.

To ensure that polymerization was initiated only electrolytically the reaction mixture containing monomer, solvent and salt was placed in a cell which was placed in the constant temperature bath at 25°C and stirred for 24 hours without current. In such experiments no polymers were ever isolated.

Experiments were performed at various currents between 10 and 100 ma taking 40 volume percent of styrene. Similar experiments were also done with 30 and 20 volume percent of styrene. In other sets of experiments current was kept constant at 15 ma and rates of the reaction were determined for various initial monomer concentrations. The polymers were colorless and amorphous^u. These polymers, so obtained, were used in subsequent molecular weight determination. Experimental rates were generally quite reproducible to within 10-12 percent. However, the rates of polymer formation showed pronounced dependence on the presence of small amounts of water.

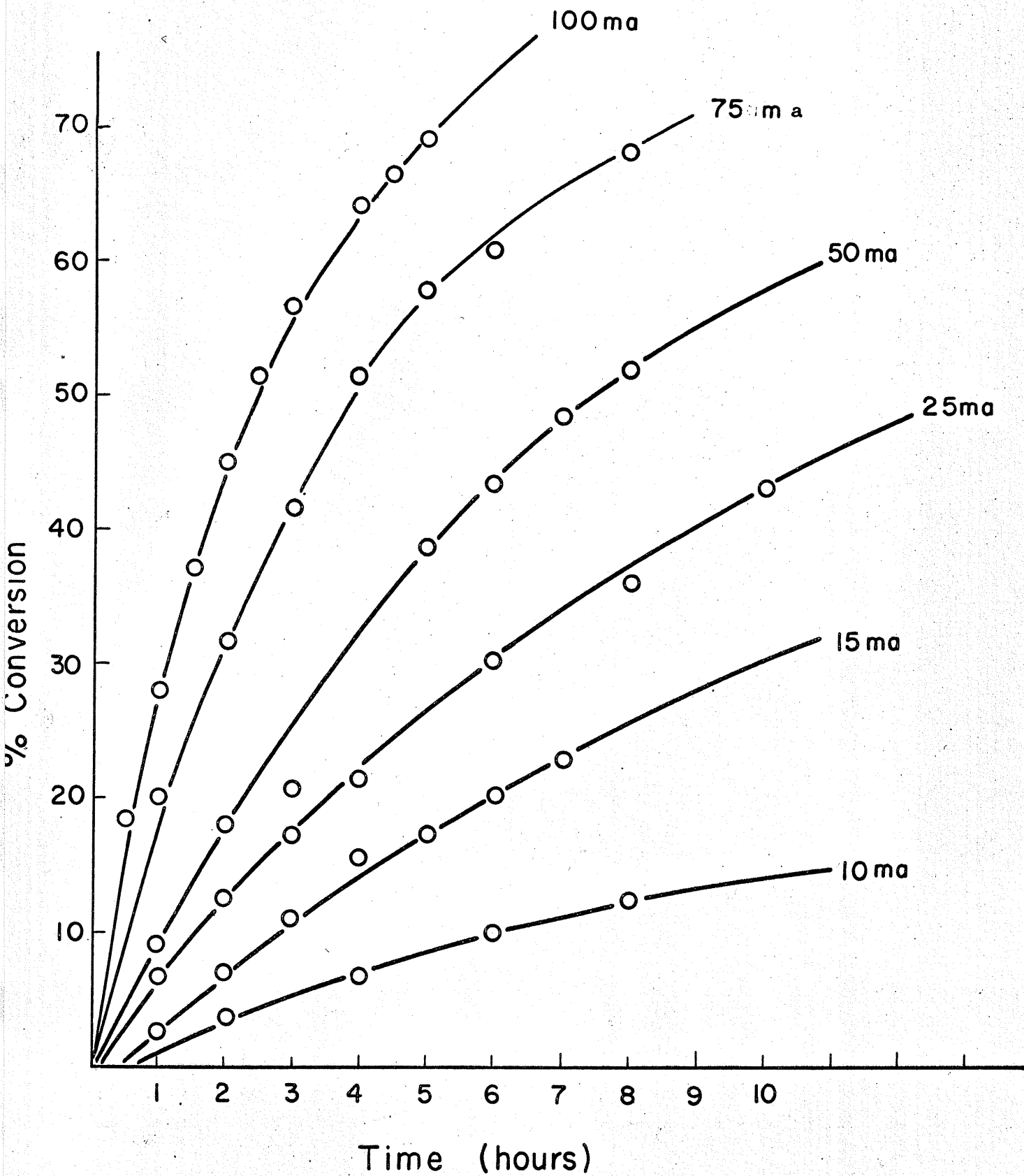


Figure 1

equation with the initial condition that $[M] = [M_0]$ when $t = 0$, we get $\ln [M] = -K t + \ln [M_0]$, where $K = kIC$.

This is an equation of the first order reaction and thus plot of $\ln [M]$ vs time should be a straight line with slope $-K$ and intercept $\ln [M_0]$. This is in agreement with our experimental findings. The data expressed in terms of the logarithmic dependence of unreacted monomer concentration with time, are plotted in Figure 2. Good linearity is observed.

The values of K were determined from the slope of the curves (Figure 2). If the rate constant K is proportional to the current I then a plot of K vs I should be a straight line. In fact, the plot of slope against the inscribed current was found to be linear as shown in Figure 3. This suggests the possibility that all the data for different concentrations could be obtained in a single unified expression. Since the rate constant is a linear function of impressed current, therefore a plot of $\log \frac{[M_0]}{[M]}$ versus times for all data is linear as shown in Figure 5. Similar data for 30 percent styrene are presented in Table IV and Figure 8.

The variation of yield of polymer with time at a constant current of 15 ma, but with initial monomer concentration

FIGURE 2. Logarithmic dependence of monomer concentration on time for a 40 volume percent solution at the inscribed current.

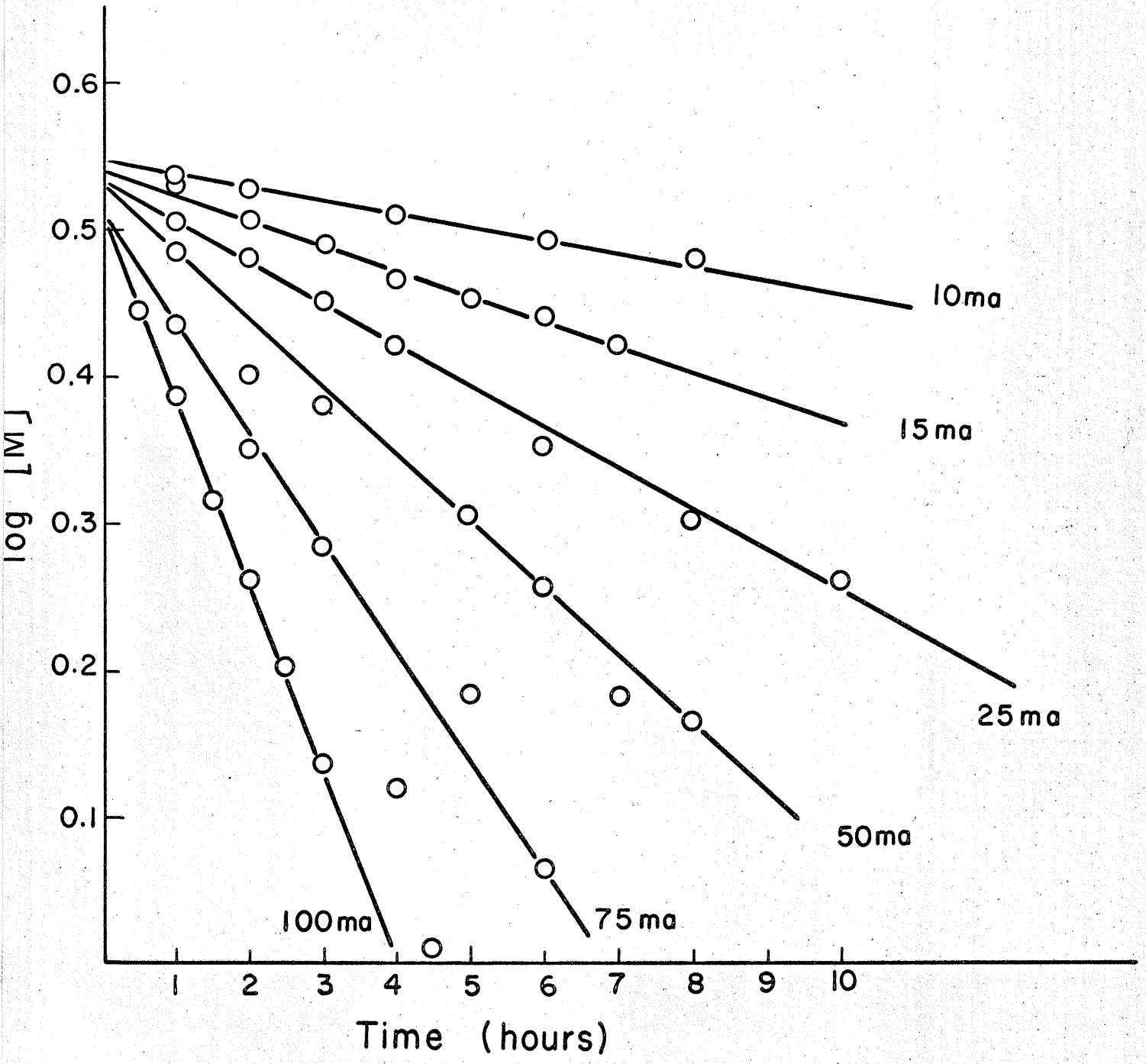


Figure 2

FIGURE 3. Slope (from Figure 2) vs. inscribed current.

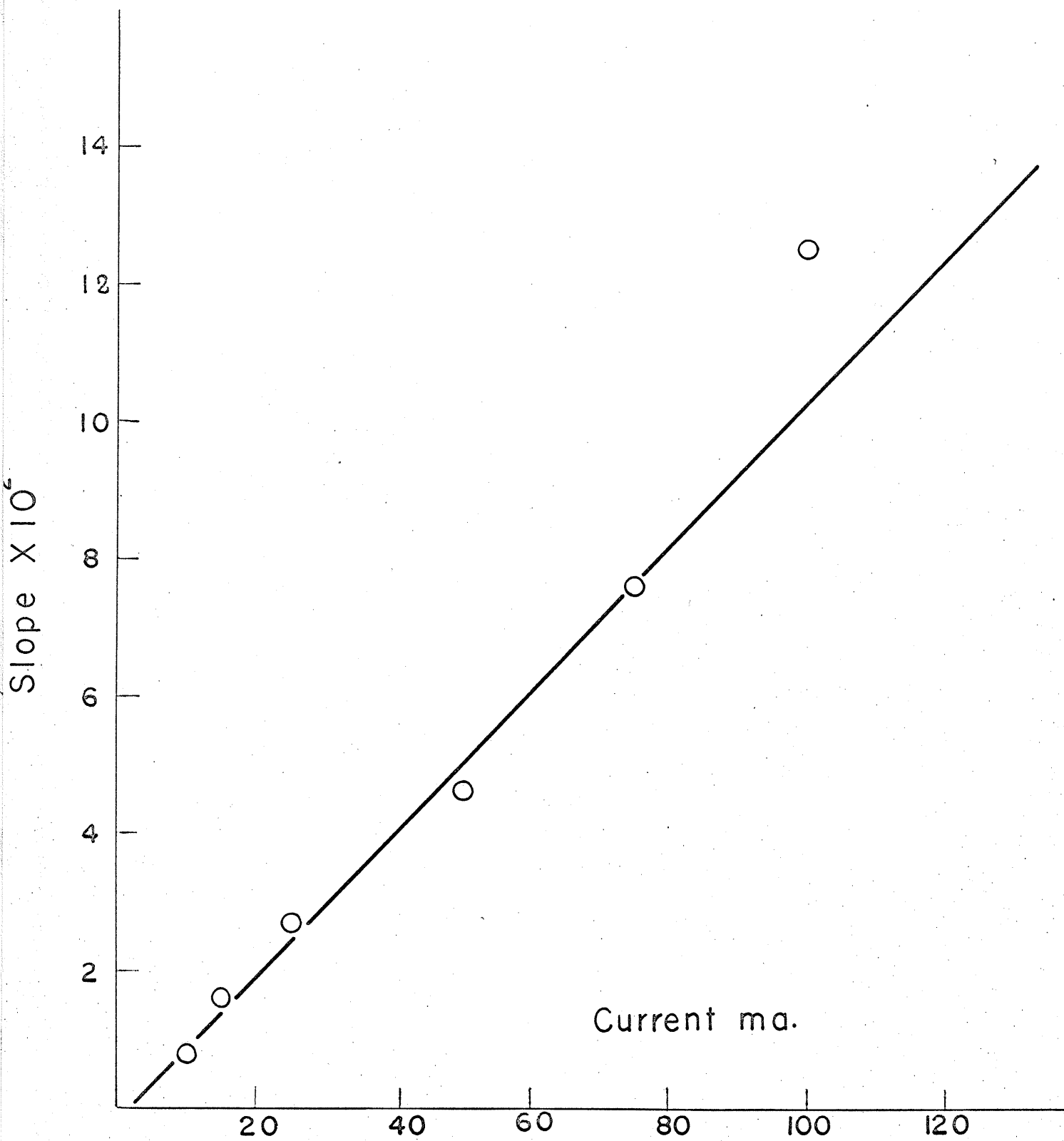


FIGURE 3

FIGURE 4. Initial rate (% conversion) as a function of current for a 40 volume percent solution of styrene in dimethyl formamide containing 1.5 g of tetramethyl ammonium chloride.

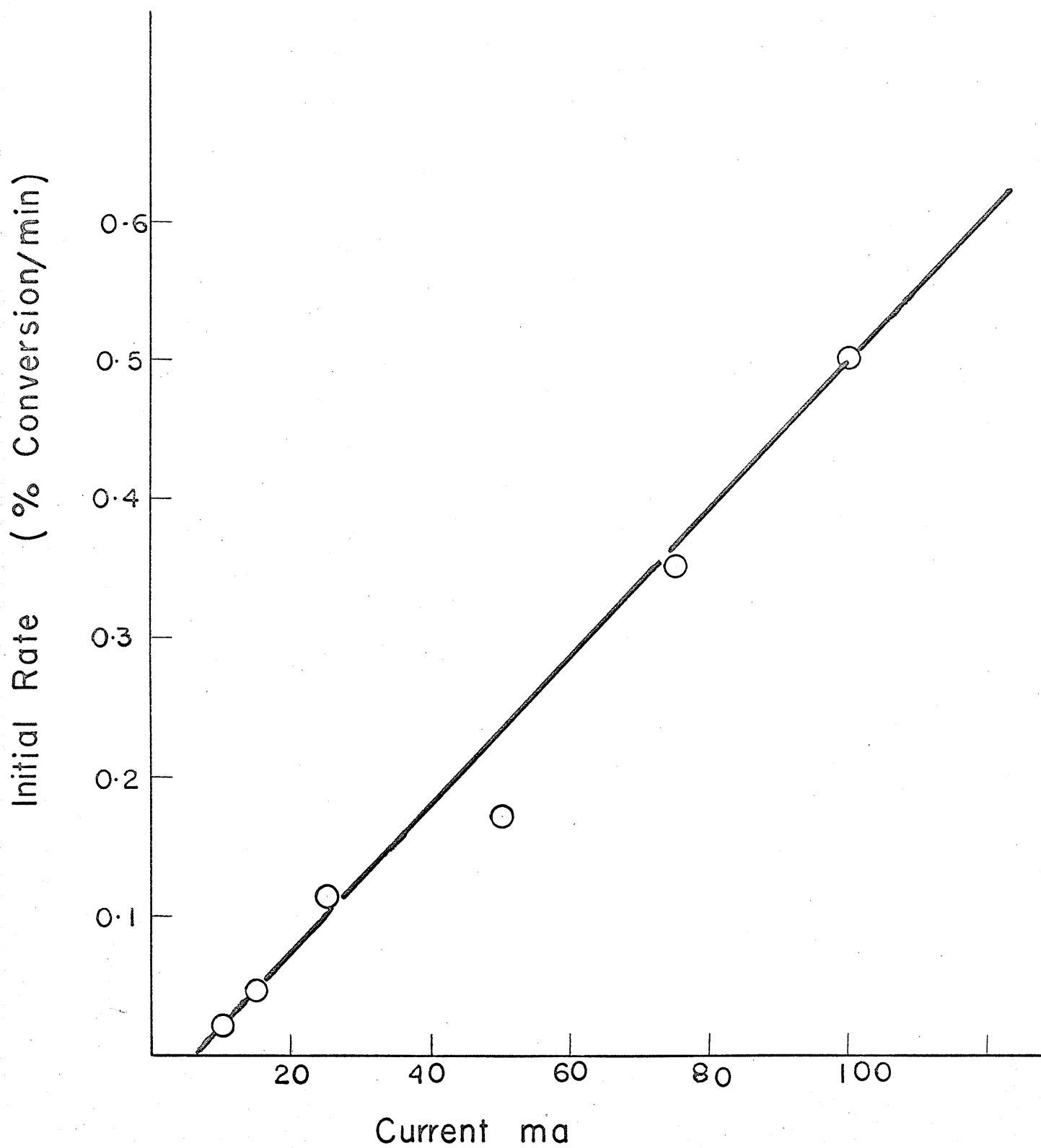


FIGURE 4

FIGURE 5. Dependence of all the data on the proposed relationship with time and current.

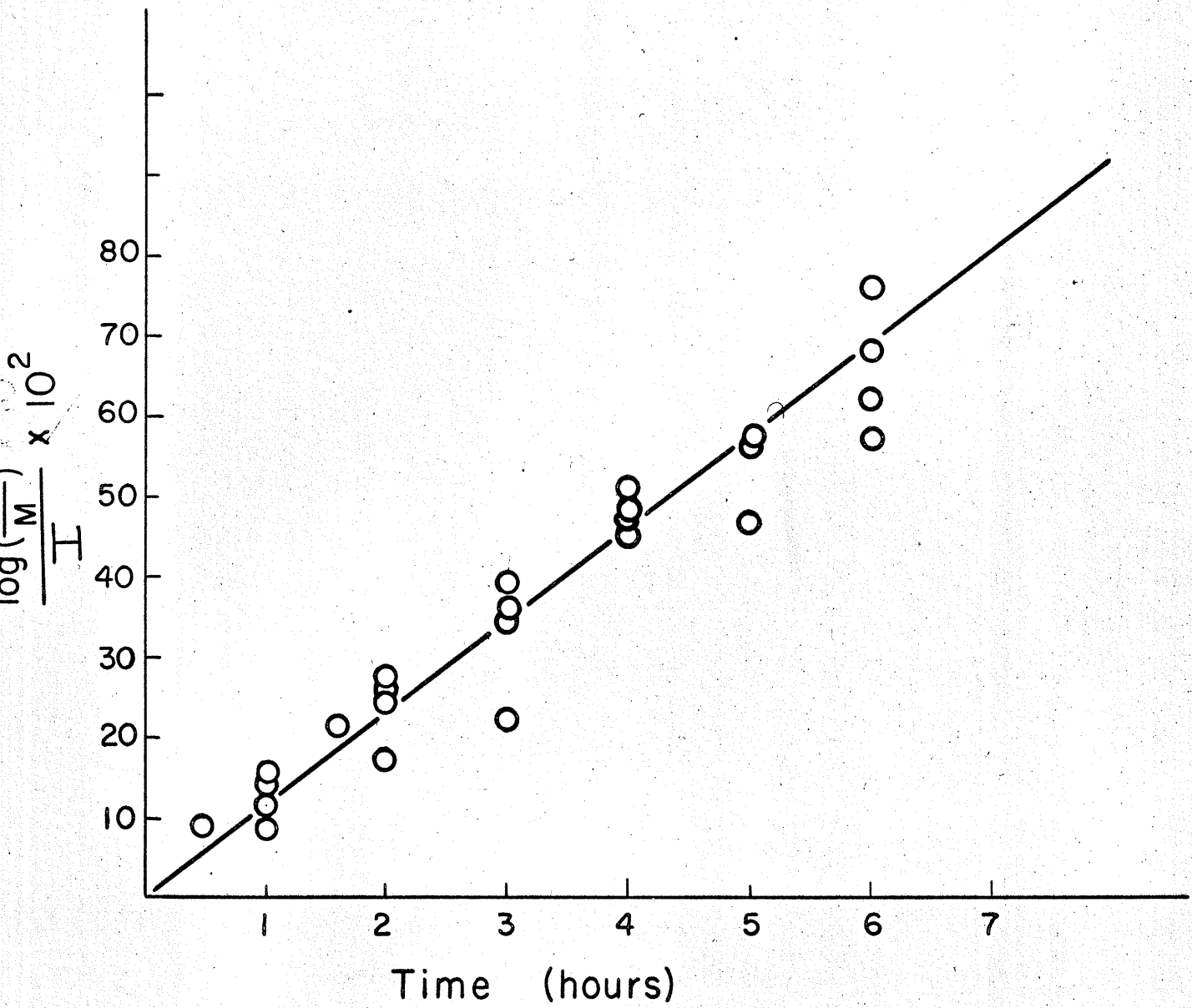


Figure 5

TABLE IV. Polymer formation g per g sample as a function of time and current in dimethylformamide saturated with $(\text{CH}_3)_4\text{NCl}$ styrene 40% (by volume)

| Time of Electrolysis Hours | 10ma. | 15ma. | 25ma. | 50ma. | 75ma. | Time of Electrolysis Hours | 100ma. |
|----------------------------|-------|-------|-------|-------|-------|----------------------------|--------|
| 1 | 0.005 | 0.010 | 0.028 | 0.037 | 0.080 | 0.5 | 0.073 |
| 2 | 0.015 | 0.028 | 0.050 | 0.071 | 0.125 | 1.0 | 0.111 |
| 3 | - | 0.043 | 0.068 | 0.080 | 0.163 | 1.5 | 0.146 |
| 4 | 0.027 | 0.061 | 0.084 | - | 0.204 | 2.0 | 0.176 |
| 5 | - | 0.068 | - | 0.151 | 0.227 | 2.5 | 0.202 |
| 6 | 0.041 | 0.078 | 0.119 | 0.170 | 0.239 | 3.0 | 0.223 |
| 7 | - | 0.089 | - | 0.189 | - | 4.0 | 0.252 |
| 8 | 0.049 | - | 0.142 | 0.203 | 0.268 | 4.5 | 0.258 |
| 10 | - | - | 0.171 | - | - | 5.0 | 0.272 |
| Styrene 30% (by volume) | | | | | | | |
| 1 | | 0.008 | 0.021 | 0.040 | 0.053 | 0.5 | 0.059 |
| 2 | | 0.021 | 0.039 | 0.064 | 0.082 | 1.0 | 0.089 |
| 3 | | 0.035 | 0.060 | 0.084 | 0.111 | 1.5 | 0.107 |
| 4 | | 0.042 | 0.079 | 0.097 | 0.124 | 2.0 | 0.126 |
| 5 | | - | - | 0.109 | 0.127 | 2.5 | 0.140 |
| 6 | | 0.064 | 0.095 | 0.119 | 0.139 | 3.0 | 0.151 |
| 7 | | 0.070 | - | 0.128 | 0.151 | 4.0 | 0.169 |
| 8 | | 0.074 | 0.110 | 0.137 | 0.154 | 4.5 | 0.173 |

of 20 to 70 percent by volume was investigated and the data are shown in Figure 6. A logarithmic dependence on time should be evidenced in a family of curves of the same slope, but of differing intercepts which correspond to the initial monomer concentration. The data are consistent with this point of view and are shown in Figure 7.

The plot of initial rate against current is almost linear, (Figure 4) but does not pass through the origin. The intercept is nearly 6 ma. It was found experimentally that at a current below 5 ma the rate of the reaction was completely negligible and very long inhibition period was noted. It is believed that in this system a current below 5 ma is used up for a long time by non-initiating electrode processes.

LOCUS OF POLYMERIZATION

The locus of polymerization was determined to be the cathode. The reaction was carried out in a divided cell (Figure B) in which the anode and the cathode compartments were separated by a fritted disc; circular platinum electrodes of diameter 2.5 cm. sealed in glass were used as an anode and a cathode electrodes. An equal volume of 25 ml of the reaction mixture was in each compartment. The polymerization was carried out at 15 ma current.

During the first hour 1.29 g of polymer was formed at the cathode, but practically no polymer formed at the anode

FIGURE 6. Polymer formation at inscribed initial monomer concentrations with a current of 15 ma.

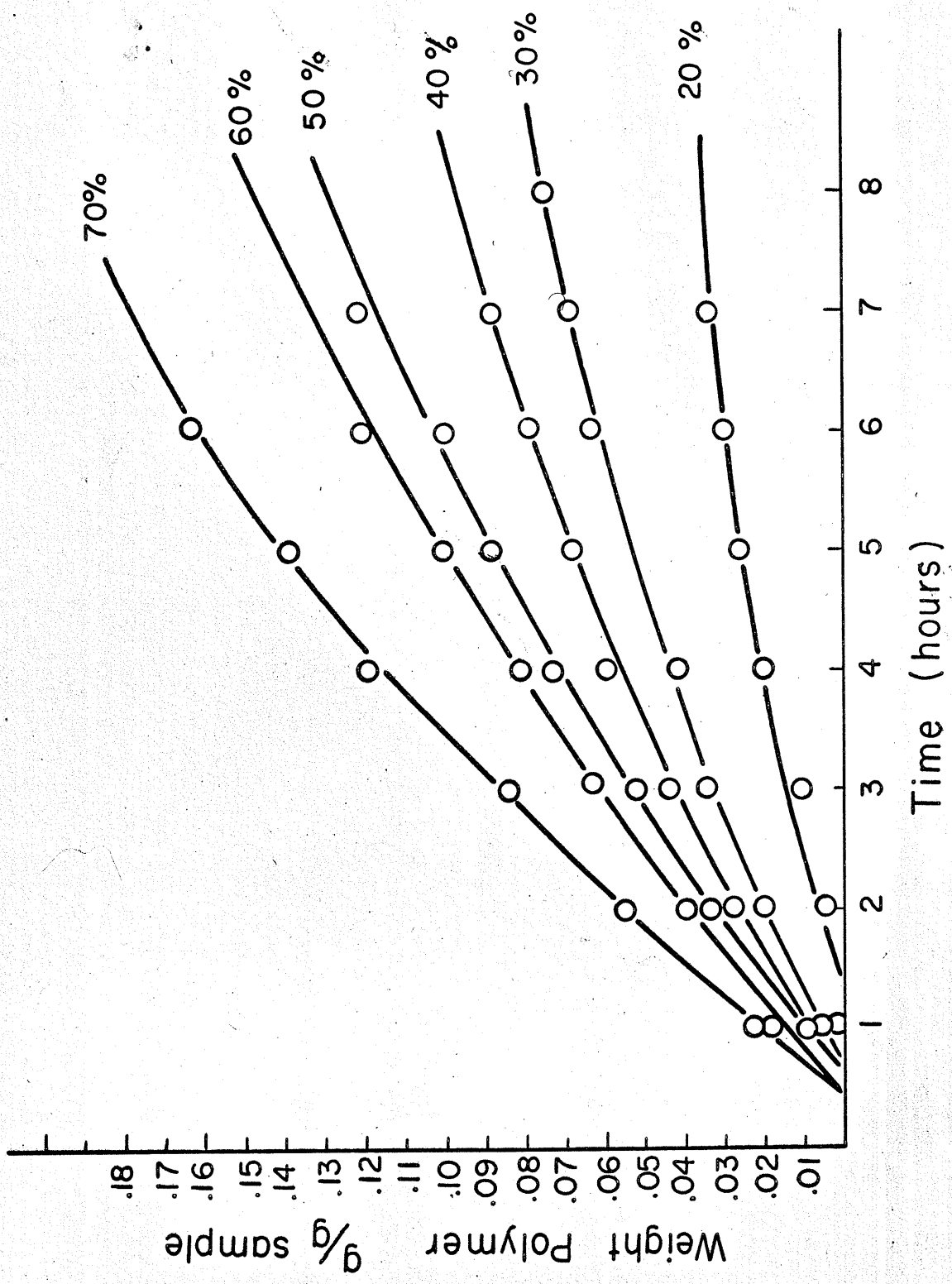
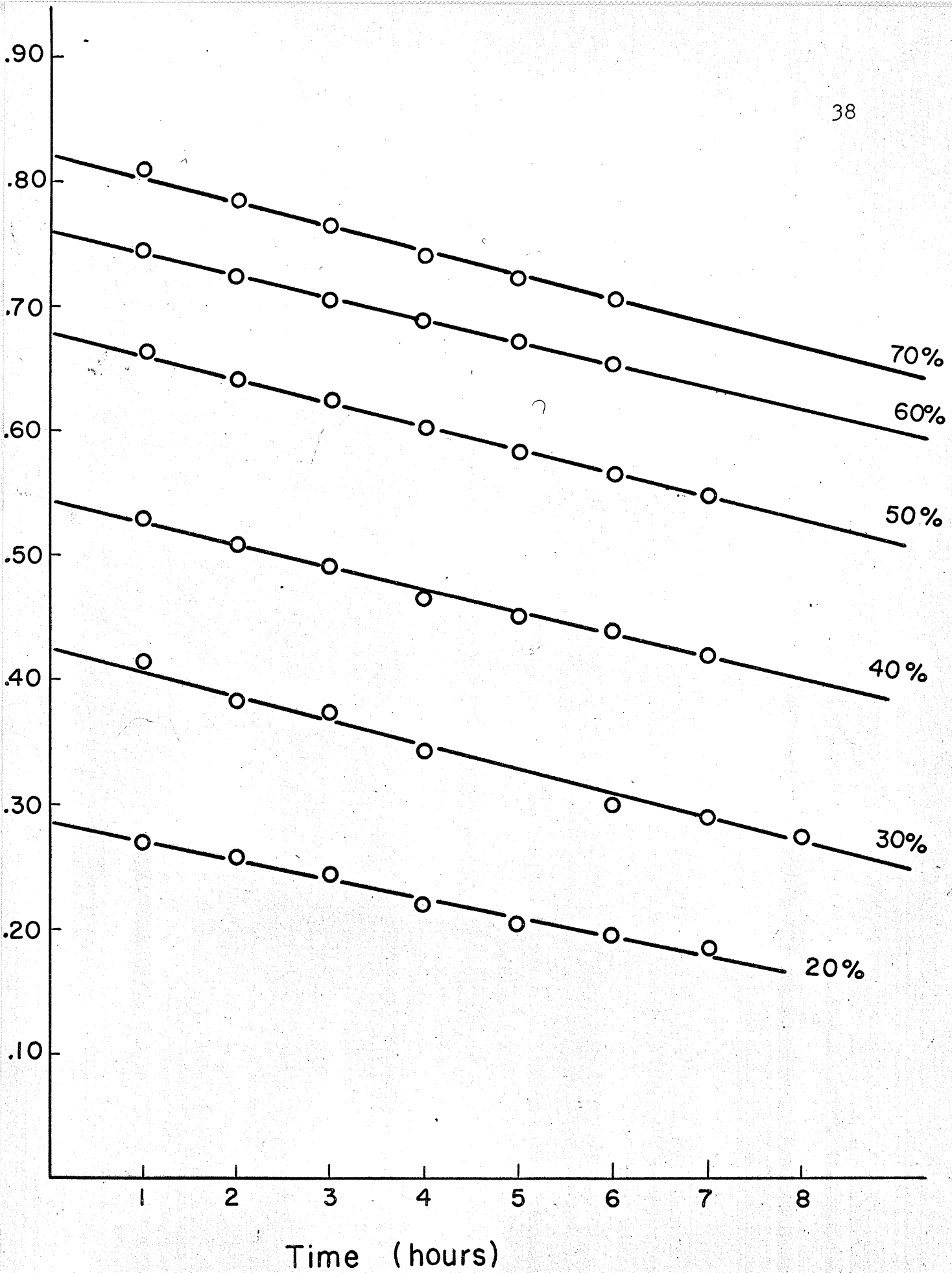


FIGURE 6

FIGURE 7. Logarithmic dependence of polymer formation on time and at the inscribed initial concentrations.



Time (hours)

FIGURE 7

FIGURE B. Divided polymerization cell.

(a) mercury contacts.

(b) sintered glass disc.

(c) platinum electrode.

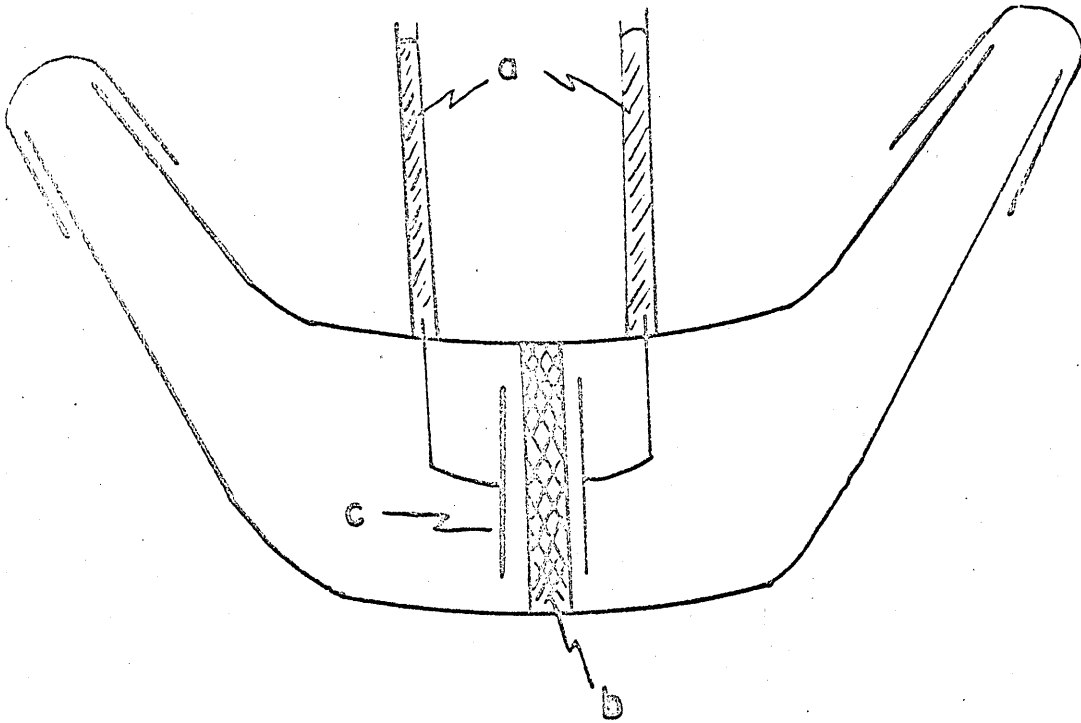


FIGURE B

stages in the reaction. It is believed that this results from diffusion into rather than formation in this region. The same conclusion was reached for polymerization with other anions, i.e., I^- , Br^- , NO_3^- , ClO_4^- or BF_4^- . The data are shown in Table V.

TABLE V. Polymer formation at anode and cathode compartments of a divided cell with 20 vol. percent of styrene in dimethylformamide and current of 15 ma.

| Salt | Time of Electrolysis (min.) | Weight of Cathodic Polymer (g) | Weight of Anodic Polymer (g) |
|------------------|-----------------------------|--------------------------------|------------------------------|
| $(CH_3)_4NCl$ | 30 | 0.503 | .002 |
| $(CH_3)_4NCl$ | 58 | 1.293 | .002 |
| $(CH_3)_4NCl$ | 90 | 1.300 | .224 |
| $(CH_3)_4NClO_4$ | 60 | 0.765 | .002 |
| $(CH_3)_4NNO_3$ | 60 | 0.808 | .002 |
| $(CH_3)_4NBF_4$ | 70 | 1.00 | .002 |

There is little dependence of yield and molecular weight of the polymers and the electrical efficiency upon the anions of the salts. When the polymerization was carried out with salt containing different anions, no considerable difference of yields and molecular weights of polymers were found. Data are given in Table VI. In each case the experimental conditions were the same. There is apparently some correlation between the yield of polymer and the solubility of the salt in this system.

TABLE VI. Effect of salts on polymerization of styrene in dimethylformamide styrene 40% by volume. Current 15 ma.

| Salt | Time of Electrolysis Hours | Weight of Polymer (g) | Moles Styrene Polymerized per Faraday | Limiting Viscosity Number 100 ml/g | Molecular Weight |
|--------------------------------|----------------------------|-----------------------|---------------------------------------|------------------------------------|------------------|
| $(\text{CH}_3)_4\text{NCl}$ | 23.5 | 20.5 | 15.0 | 0.16 | 21,000 |
| $(\text{CH}_3)_4\text{NBr}$ | 23.0 | 24.5 | 18.3 | 0.17 | 23,000 |
| $(\text{CH}_3)_4\text{NI}$ | 23.0 | 25.5 | 18.97 | 0.16 | 21,000 |
| $(\text{CH}_3)_4\text{NClO}_4$ | 23.0 | 25.3 | 18.88 | 0.16 | 21,000 |
| $(\text{CH}_3)_4\text{NNO}_3$ | 23.0 | 26.0 | 19.4 | 0.17 | 23,000 |
| NH_4Cl | 23.0 | 0.5 | 0.37 | - | - |
| NH_4NO_3 | 24.0 | no polymer | - | - | - |

However, the polymer formation completely depends on the cations of the salt i.e., $(\text{CH}_3)_4\text{N}^+$ ion. In an experiment when ammonium chloride was used in place of tetramethyl ammonium chloride relatively small amount of polymer was isolated. This obviously gives evidence that the cathodic discharge of tetramethyl ammonium ion is responsible for the formation of polymer.

ELECTRICAL EFFICIENCY

The electrical efficiency expressed in moles of monomer



polymerized per faraday increased with increase in monomer concentration to very high concentrations. In solution of over 60 volume percent of styrene, the conductance decreased to such an extent that lower currents had to be employed. Data are presented in Table VII. Only at the very highest concentration of 80 volume percent there is a notable decrease in electrical efficiency. This is only due to the considerable decrease in solubility of salt at the highest concentration of styrene since tetramethyl ammonium chloride is not soluble in pure monomer.

TABLE VII. Yield and electrical efficiency at various initial monomer concentrations.

| Styrene Concentration (Volume per cent) | Time of Electrolysis (Hours) | Current (ma.) | Weight Polymer (gms) | Moles Styrene Polymerized per Faraday |
|---|------------------------------|---------------|----------------------|---------------------------------------|
| 10 | 7 | 35 | 2.65 | 2.79 |
| 20 | 7 | 35 | 6.22 | 6.54 |
| 30 | 7 | 35 | 11.8 | 12.4 |
| 40 | 7 | 35 | 13.2 | 13.9 |
| 50 | 7 | 35 | 20.7 | 21.7 |
| 60 | 7.5 | 25 | 22.8 | 31.3 |
| 70 | 23 | 8 | 25.5 | 35.68 |
| 80 | 21 | 2 | 23.0 | 14.11 |

MOLECULAR WEIGHT DETERMINATION

Molecular weights of the polymer were obtained viscometrically using benzene solutions of polymers at 25°C with values of $K = 1.12 \times 10^{-4}$ and $\eta = 0.73$ (31). Ubbelohde viscometer (Figure C) was used to determine the intrinsic viscosity. The polymer samples, used to determine the molecular weight, were purified by dissolving them into methyl ethyl ketone. The solution was filtered and precipitated slowly into cold methanol. Polymers were filtered out, washed several times with methanol, and dried over night at 70°C. The intrinsic viscosities were measured for different concentrations of polymer solution ranged from 0.25 percent to 1 percent by weight. The intrinsic viscosity number was calculated by extrapolating the results to infinite dilution i.e., zero concentration of polymer solutions.

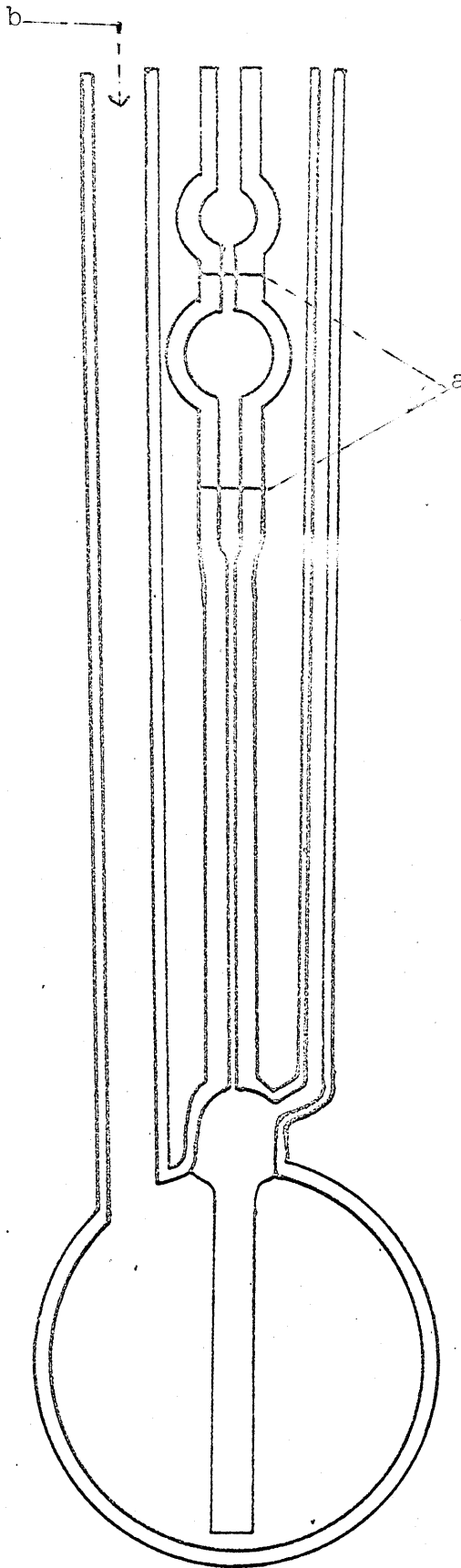
No notable change in molecular weight was found with variation of the currents. The data in Table VIII show maximum possible changes from 14,000 to 21,000 molecular weights between 10 and 100 ma., but the scatter in data indicates that this is the limit of variation.

A four fold increase in monomer concentration (from 20 to 80 percent by volume) gave approximately one and a half fold increase in molecular weight. Between these two extreme concentrations there was a small increase in molecular weight with increase in monomer concentration as shown in Table IX.

FIGURE C. Ubbelohde viscometer.

a. Etched lines.

b. Filling tube.



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FIGURE C

TABLE VIII. Molecular weights of polymers formed at various currents and temperatures.

| Current (ma.) | °C Temperature | Limiting Viscosity Number | Molecular Weight |
|------------------|-------------------|---------------------------------|---------------------|
| 10 | 25 | 0.12 | 14,000 |
| 15 | 25 | 0.16 | 21,000 |
| 35 | 25 | 0.15 | 19,000 |
| 50 | 25 | 0.13 | 16,000 |
| 75 | 25 | 0.13 | 16,000 |
| 100 | 25 | 0.15 | 19,000 |
| 15 | 45 | 0.16 | 21,000 |
| 15 | 0 | 0.22 | 32,000 |
| 15 | -8 | 0.29 | 47,000 |

TABLE IX. Molecular weights of polystyrene produced in various initial concentrations of styrene in dimethylformamide saturated with $(\text{CH}_3)_4\text{NCl}$.

| Concentration of Styrene Volume Percent | Limiting Viscosity Number | Molecular Weight |
|---|------------------------------|---------------------|
| 80 | 0.17 | 23,000 |
| 70 | 0.18 | 25,000 |
| 60 | 0.17 | 23,000 |
| 50 | 0.16 | 21,000 |
| 40 | 0.15 | 19,000 |
| 30 | 0.13 | 16,000 |
| 20 | 0.13 | 16,000 |
| 10 | 0.083 | 8,500 |

However, molecular weight of the polymer decreased substantially when the lowest concentration of monomer was used. It seems, therefore, that at very low concentration of monomer (20 percent by volume) transfer reaction of polymer chain to solvent becomes appreciable. A direct dependence of molecular weight on monomer concentration was obtained in electroinitiated anionic polymerization of acrylonitrile in dimethylformamide and sodium nitrate system (25). In the present work no specified correlation between solvent and monomer ratios, and molecular weights of polymers was observed. The lower electrical efficiency and smaller change in molecular weight with monomer concentration indicate a smaller degree of chain transfer to monomer as would be expected with styrene in contrast to acrylonitrile.

No intensive work was done with systems at low temperatures, but an indication was obtained that the molecular weight apparently increased with decreasing temperature, (Table VIII). Under identical experimental conditions the fact that molecular weights increase as temperatures decrease is well established in most cationic and anionic systems. Apparently the activation energy of chain breaking or terminating is higher than that for propagation so that they can be frozen out at lower temperatures.

INHIBITION AND RETARDATION

The kinetics were investigated in presence of free radi-

cal inhibitors t-butylpyrocatechol and p-benzoquinone, and methanol and water as a chain stopping agent for anionic reactions. Data are shown in Figure 11. Approximately 0.4 to 0.5 weight percent were used in each case and this corresponded to 0.36 molar p-benzoquinone and 0.0249 molar t-butylpyrocatechol and 0.123 methanol. Little over all effect on the rate is exhibited by the free radical inhibitors. However, polymerization was quenched with 0.49 and 0.55 molar methanol and water respectively. It is worthy to note that even at very high concentrations of free radical inhibitors polymerization proceeds although ^{the} rate is suppressed. At very low concentrations of water and methanol polymerization proceeded with ^a feeble rate. The data strongly support the concept of anionic polymerization as the dominant step in the chain addition.

Molecular weights of polymers obtained in the presence of free radical and anionic chain terminator are shown in Table X. Molecular weights considerably decreased in the presence of inhibitors. ~~The~~ data point out that at ^a very low concentration, water and methanol act as retarders reducing the rate and the degree of polymerization.

FIGURE 8. Polymer formation as a function of inscribed current and time for a 30 volume percent solution of styrene in dimethylformamide saturated with tetramethyl ammonium chloride.

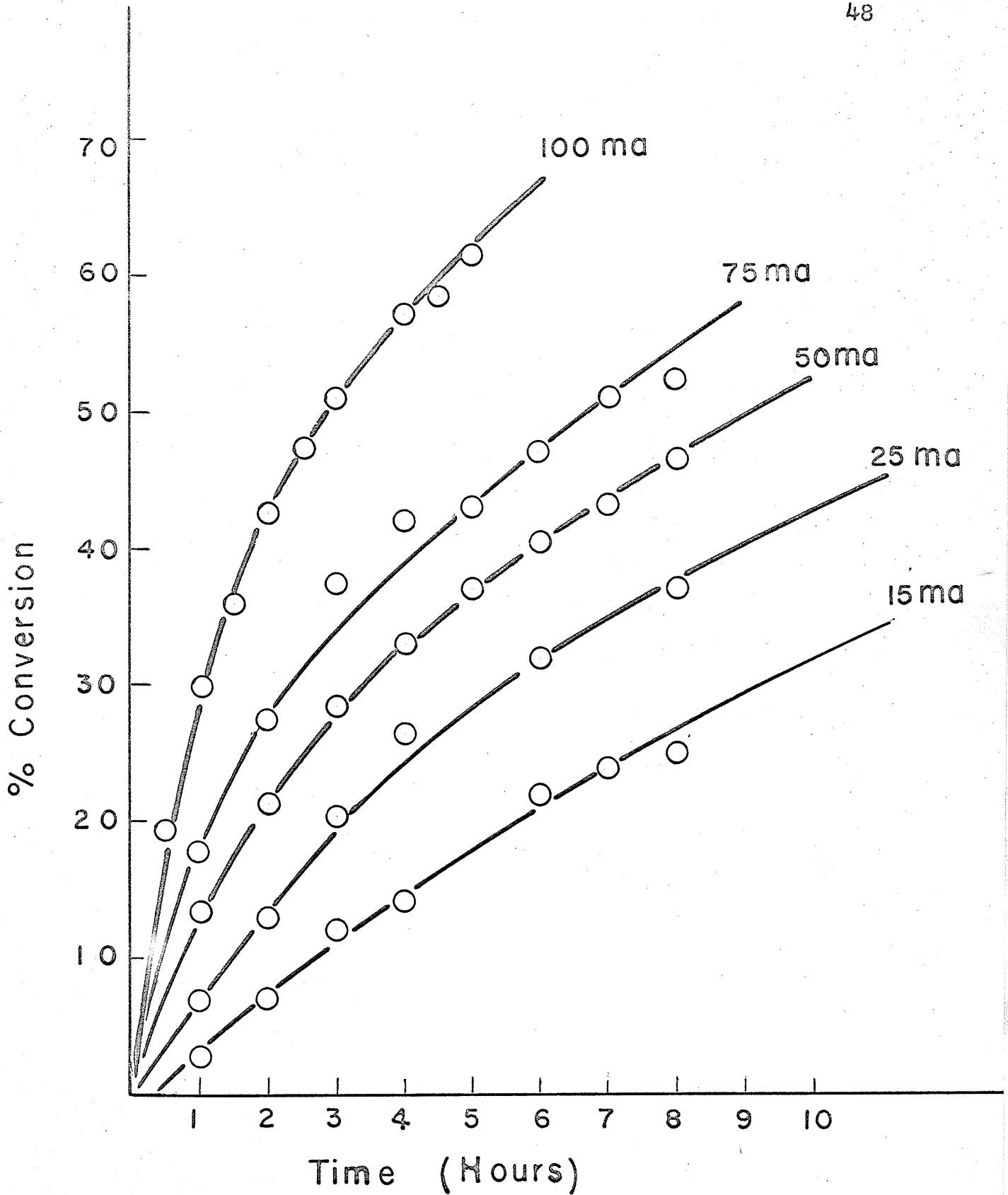


FIGURE 8

FIGURE 9. Rate (% conversion) of polymerization as a function of temperature for a 40 volume percent solution of styrene in dimethylformamide saturated with tetramethyl ammonium chloride at a current of 15 ma.

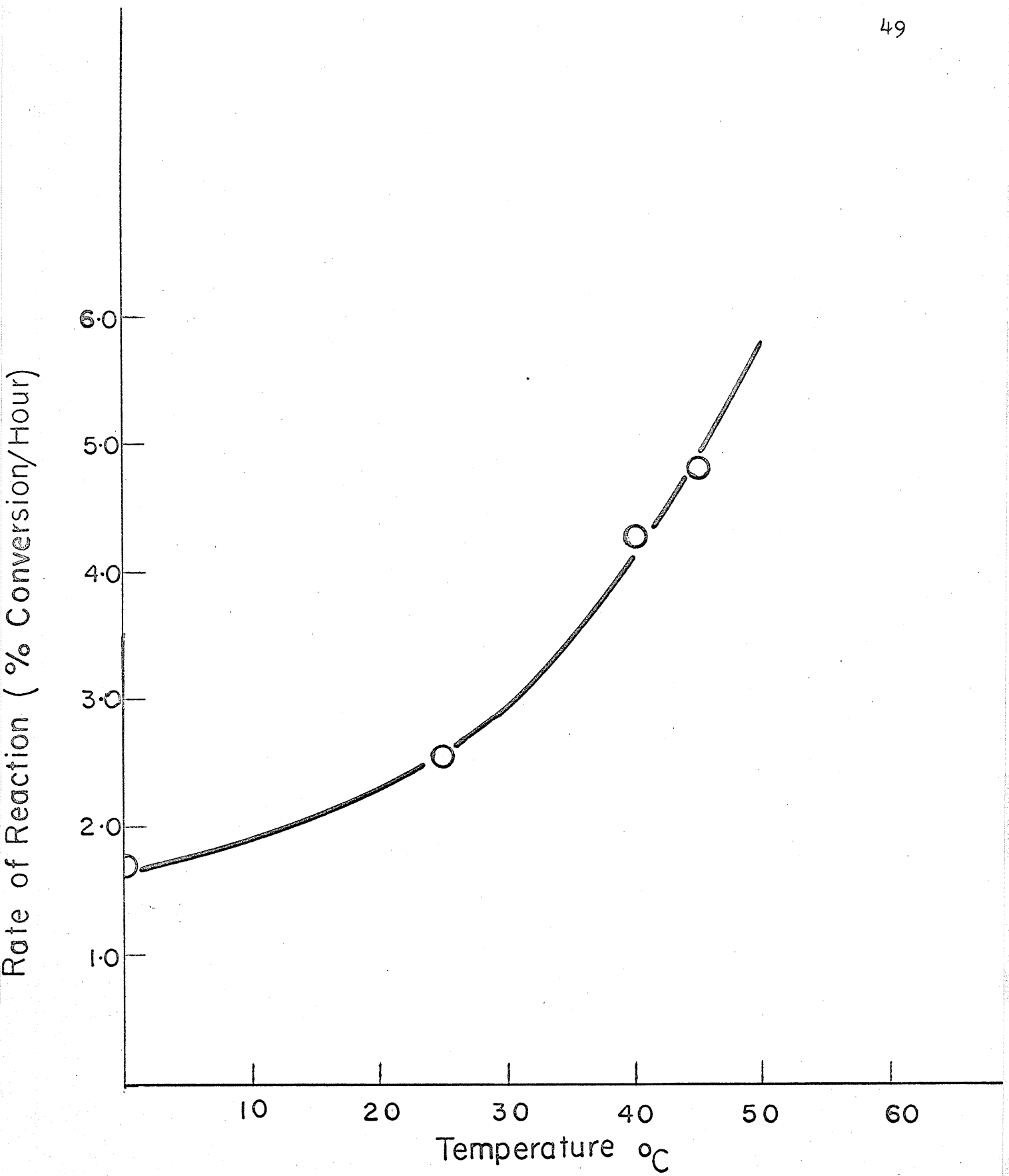


FIGURE 9

FIGURE 10. Efficiency (mole of styrene polymerized per faraday) vs. monomer concentration.

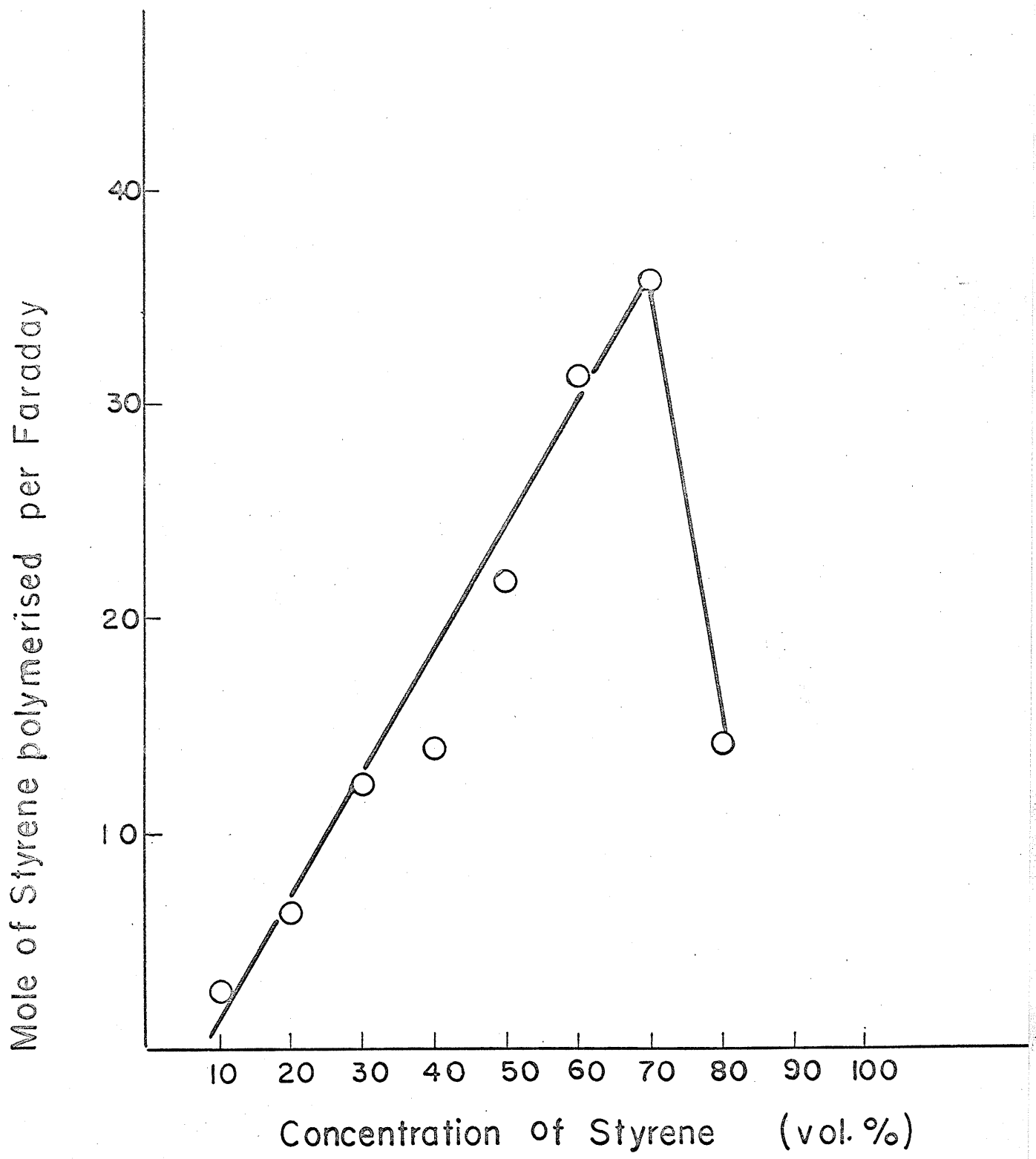


FIGURE 10

FIGURE 11. Effect of various free radical and ionic inhibitors on the rate of polymer formation at a current of 100 ma. and an initial concentration of 40 volume percent styrene.

- A. no inhibitor.
- B. 0.036 M p-benzoquinone.
- C. 0.0249M tertiary butyl pyrocatechol.
- D. 0.123 M methanol.
- E. 0.493 M methanol.

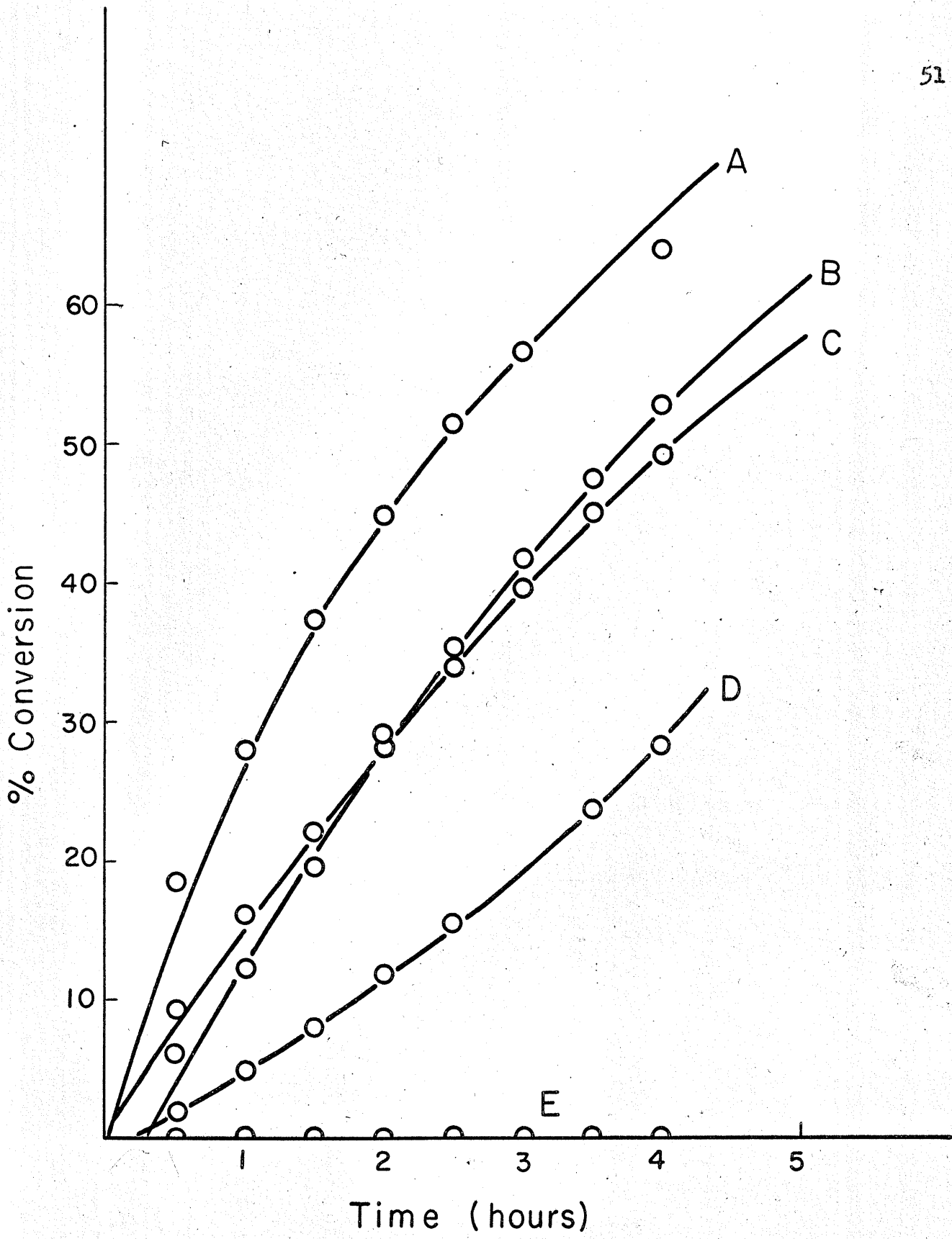


FIGURE 11

TABLE X. Molecular weights of polymers obtained in the presence of radical chain inhibitors and anionic chain terminators. Styrene 40 percent by volume.

| Inhibitor | Viscosity Number | Molecular Weight |
|----------------------|------------------|------------------|
| Methanol | 0.11 | 12,500 |
| T-butyl pyrocatechol | 0.10 | 12,000 |
| P-benzoquinone | - | - |
| Water | 0.085 | 8,500 |

POLYMER FORMATION OF DIFFERENT MONOMERS IN SOLUTIONS OF TETRAMETHYL AMMONIUM CHLORIDE IN DIMETHYLFORMAMIDE

Rates of polymer formation of acrylonitrile, methylmethacrylate and α -methylstyrene were determined under the same experimental conditions as employed for styrene at 15 ma. current. Data are shown in Figure 12. It is apparent from the figure that polymer formations of these monomers are in the following order

acrylonitrile > methylmethacrylate > styrene > α -methylstyrene

Polymerization of acrylonitrile eliminates the possibility of cationic mechanism since acrylonitrile which contains electron withdrawing substituent attached to double bonded carbon atoms and will promote the formation of stable carbanions, is susceptible to anionic polymerization. On the other hand, polymerization of α -methylstyrene rules out the

FIGURE 12. Polymer formation of acrylonitrile (A), methylmethacrylate (B), styrene (C) and -methylstyrene (D) in a saturated solution of tetramethyl ammonium chloride in dimethylformamide and at a current of 15 ma. Concentration of each monomer being 40 volume percent.

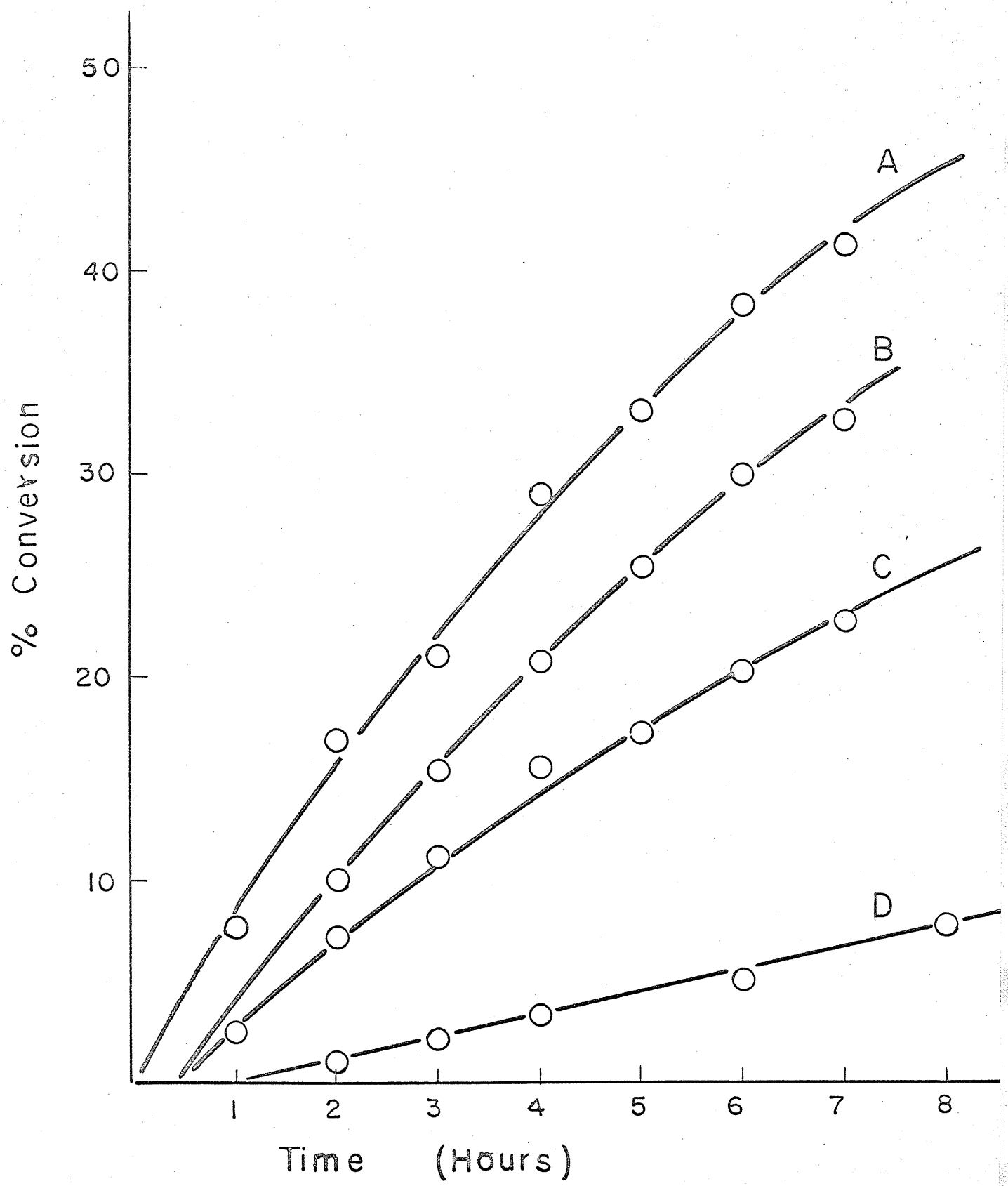


FIGURE 12

radical reaction since it is not successfully polymerized by free radical mechanism. It can be polymerized by a radical initiator only at fairly low temperatures (33).

COPOLYMERIZATION

PROCEDURE

The copolymerization of styrene and methylmethacrylate was conducted at 50 ma. current and 25°C in a saturated solution of tetramethyl ammonium chloride in dimethylformamide. Five copolymerizations were carried out with varying molar concentration ratios of the two monomers. In each case reaction was stopped before the conversion reached 10 percent. Copolymerizations of equimolar mixture of two monomers were also carried out at different conversions to observe the effect of degree of conversion on the copolymer compositions. In the purification of the copolymers by reprecipitation, methyl ethyl ketone was used as solvent and methanol as precipitant. Purification of the copolymers was done at least three times to ensure the complete removal of contamination of active styrene from them. Copolymers were dried at 70°C overnight.

The compositions of the copolymers were determined by tracer method using C¹⁴ tagged styrene. Some experiments were repeated with tagged methyl methacrylate in order to eliminate any systematic error in analysis, but data showed good agreement with the previous results. Data are presented in Tables XI and XII.

TABLE XI. Effect of conversion of feed on compositions of copolymers obtained by polymerization of equimolar mixtures of styrene and methylmethacrylate in saturated solution of $(\text{CH}_3)_4\text{NCl}$ in dimethylformamide.

| Observation No. 3. | Activity of 0.1g active Styrene d.p.m. * | Activity of 0.1g copolymer d.p.m.* | % Conversion of | Weight % of Styrene in copolymer |
|--------------------|--|------------------------------------|-----------------|----------------------------------|
| 1. | 6011 | 1900 | 4.20 | 31.6 |
| 2. | 6011 | 1864 | 11.0 | 31.0 |
| 3. | 6478 | 2027 | 15.58 | 31.3 |
| 4. | 6478 | 2223 | 28.7 | 34.3 |
| 5. | 6478 | 2311 | 34.5 | 35.68 |
| 6. | 6478 | 2407 | 46.5 | 37.2 |
| 7. | 6478 | 2600 | 50.2 | 40.10 |
| 8. | 6478 | 2787 | 56.6 | 43.0 |
| 9. | 6011 | 2604 | 60.0 | 43.3 |

* counting efficiency for every sample was almost the same and hence no efficiency correction was made.

TABLE XII. Copolymerization data.

| No. of Observation | Ml g | M2 (M.M.A*) g | Ml/M2 | Activity of 0.1 g Styrene d.p.m. | Activity of 0.1 g copolymer d.p.m. | Ml (Styrene) in copolymer % | M2 (M.M.A*) Weight % | Ml/M2 |
|--------------------|-------|---------------|-------|----------------------------------|------------------------------------|-----------------------------|----------------------|-------|
| 1. | 13.65 | 23.5 | 0.58 | 6498 | 1068 | 16.5 | 83.5 | 0.20 |
| 2. | 18.20 | 17.86 | 1.019 | 6011 | 1900 | 31.6 | 68.4 | 0.462 |
| 3. | 21.84 | 17.108 | 1.27 | 5544 | 2200 | 39.68 | 60.32 | 0.657 |
| 4. | 22.75 | 14.10 | 1.61 | 6037 | 2844 | 47.11 | 52.89 | 0.89 |
| 5. | 25.48 | 12.22 | 2.085 | 5618 | 3057 | 54.4 | 45.6 | 1.19 |

| No. of Observation | $\frac{F}{f}$ | $\frac{f}{F}$ | $\frac{F^2}{f}$ | $\frac{(F/f)(f-l)}{(f/F^2)}$ | $\frac{(f-l/F)}{(f-l/F)}$ |
|--------------------|---------------|---------------|-----------------|------------------------------|---------------------------|
| 1. | 0.58 | 0.2 | 1.68 | -2.32 | -1.37 |
| 2. | 1.019 | 0.462 | 2.25 | -1.19 | -0.53 |
| 3. | 1.27 | 0.657 | 2.45 | -0.66 | -0.267 |
| 4. | 1.61 | 0.89 | 2.92 | -0.20 | -0.68 |
| 5. | 2.085 | 1.19 | 3.64 | +0.34 | +0.111 |

* Methyl methacrylate.

RESULTS AND DISCUSSION

The copolymerization data for styrene and methyl methacrylate are shown in Figure 13. Their reactivity ratios were determined by the method of Fineman and Ross (34). The copolymer composition equation which relates the polymer composition with the monomer composition is given by:-

$$\frac{dM_1}{dM_2} = \frac{M_1}{M_2} \times \frac{r_1 M_1 + M_2}{r_2 M_2 + M_1} = \left(\frac{m_1}{m_2} \text{ for low conversion} \right) \dots \dots \dots (1)$$

where M_1 (styrene), M_2 (methyl methacrylate) refer to the monomer composition and m_1 (styrene), m_2 (methyl methacrylate) to the polymer composition; r_1 and r_2 denote reactivity ratios of styrene and methyl methacrylate respectively.

Let $f = \frac{m_1}{m_2}$ and $F = \frac{M_1}{M_2}$ then equation (1) can be written as

$$f = F \times \frac{r_1 F + 1}{r_2 + F} \text{ by rearranging terms one obtains:}$$

$$\frac{F}{f} (f-1) = r_1 \frac{F^2}{f} - r_2 \dots \dots \dots (2)$$

A plot of $\left(\frac{F}{f}\right)(f-1)$ as ordinate and F^2/f as abscissa is a straight line whose slope is r_1 and intercept is minus r_2 .

Equation (2) can also be written as:

$$\frac{f-1}{F} = -r_2 \frac{f}{F^2} + r_1$$

In this case the slope is minus r_2 and the intercept r_1 . The two plots based on these equations for styrene and methyl-

FIGURE 13. Mole fraction of styrene in copolymer
vs mole fraction of styrene in feed.

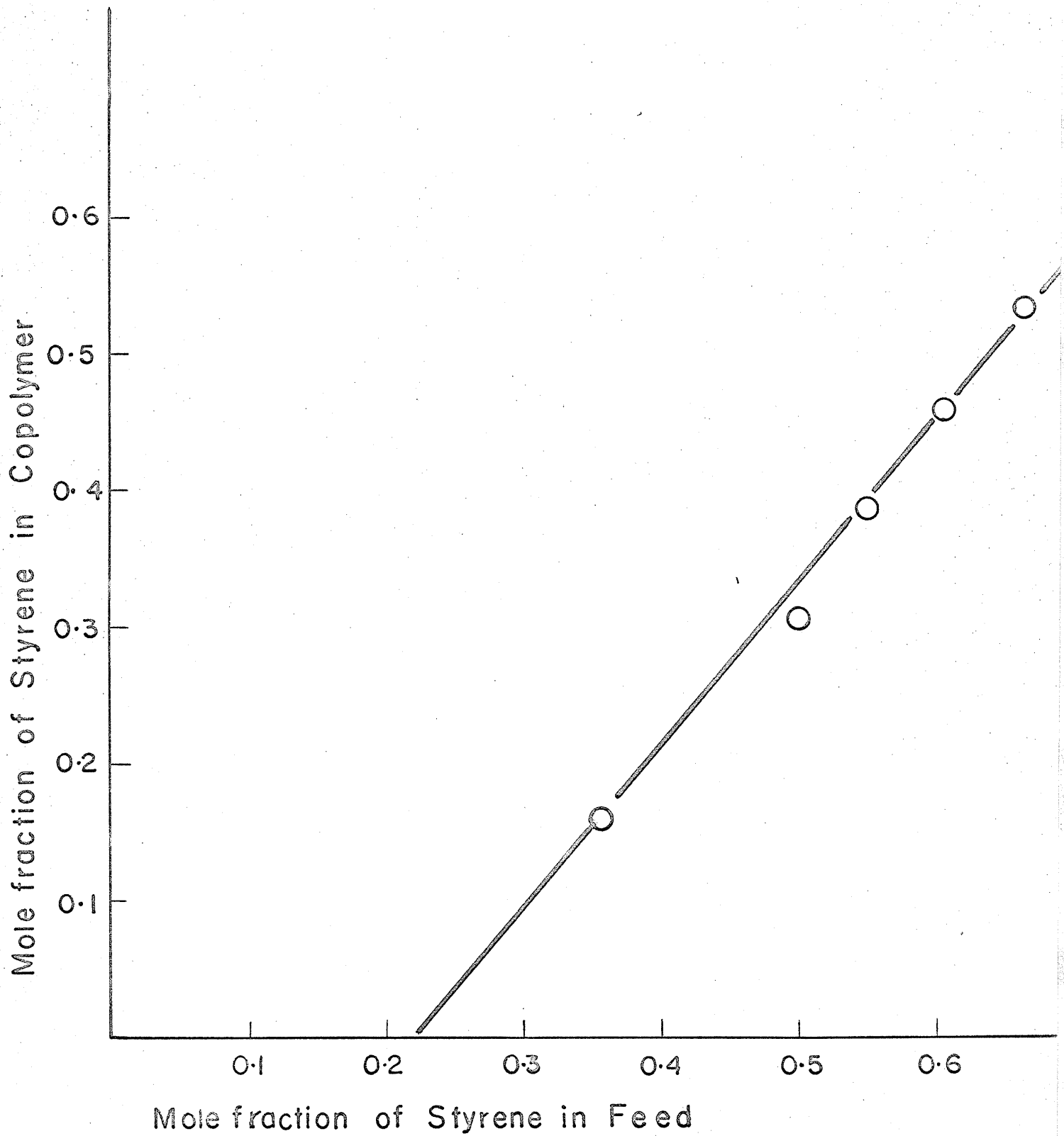


FIGURE 13

methacrylate have been shown in Figure 14 and 15 and yielded $r_1 = 1.6, 1.55$ and $r_2 = 4.85, 4.00$ respectively. The mean values $r_1 = 1.57$ and $r_2 = 4.43$ were then taken.

The formation of polymer solely at one electrode, the inhibitor studies, the smooth rate curves and the constancy of molecular weight with current all point to an ionic mechanism and tend to eliminate a free radical mechanism. Possibility of carbonium ion mechanism has also been eliminated by the experiments which showed that polymerization was completely inhibited by proton donor materials e.g., by water or methanol.

Landler (35) has reported reactivity ratios for the anionic copolymerization of styrene and methyl methacrylate as follows:

$$r_1 = 0.12 \pm 0.05$$

$$r_2 = 6.4 \pm 0.5$$

He suggested that the character of the propagation chain end in anionic polymerization would be independent of which monomer formed the ultimate unit. As a consequence of this the copolymerization equation derived for free radical propagation would reduce to

$$\frac{dM_1}{dM_2} = r_1 \left(\frac{M_1}{M_2} \right) \dots\dots\dots (4)$$

and the product of the reactivity ratios would be unity $r_1 r_2 = 1$, but in our work product of reactivity ratios is much

FIGURE 14. $\frac{F}{f} (f-1)$ vs $\left(\frac{F_0}{f}\right)^2$ for copolymerization of styrene and methyl methacrylate.

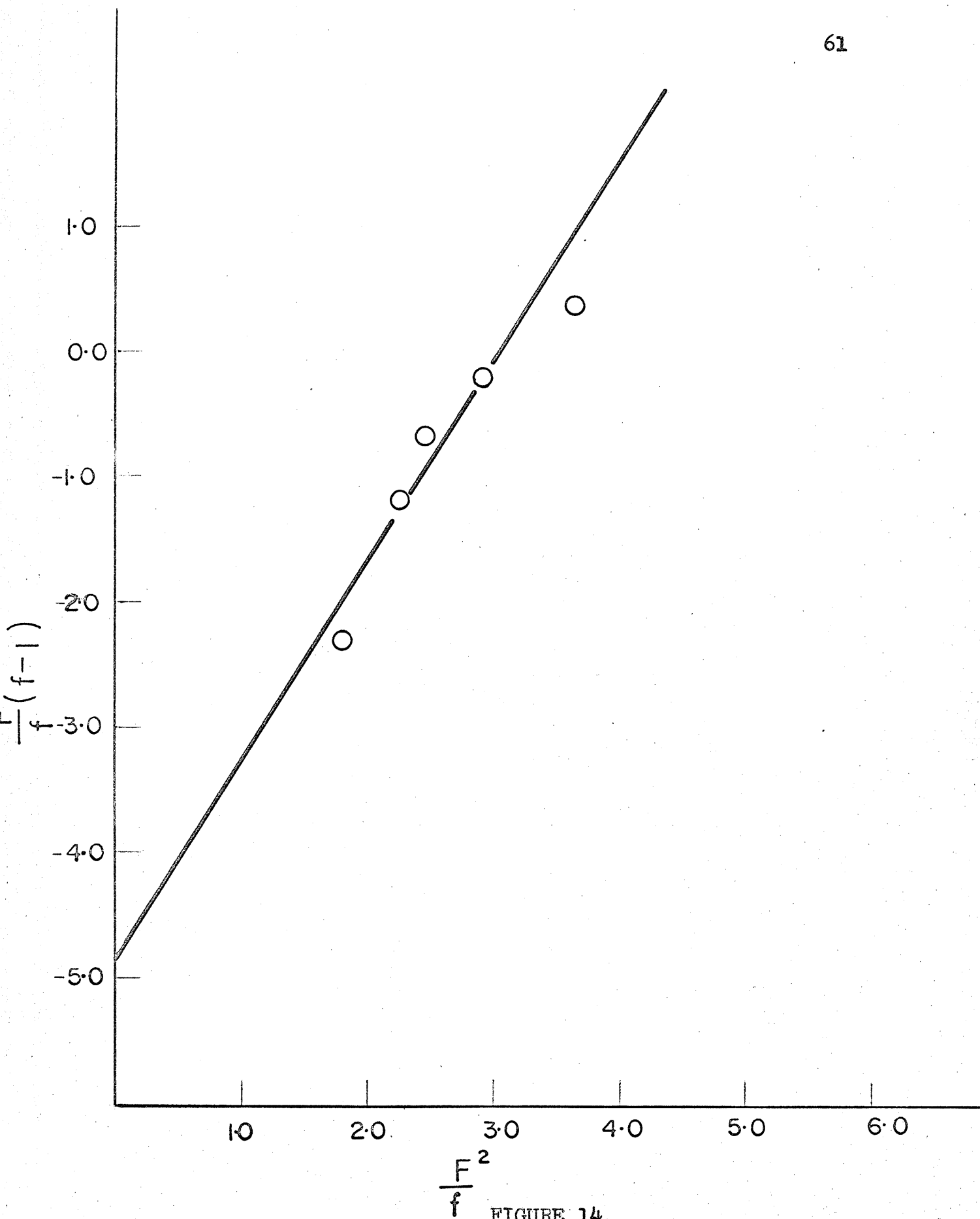


FIGURE 14.

FIGURE 15. $\left(\frac{f-1}{F}\right)$ vs $\left(\frac{f}{F^2}\right)$ for copolymerization of styrene and methyl methacrylate.

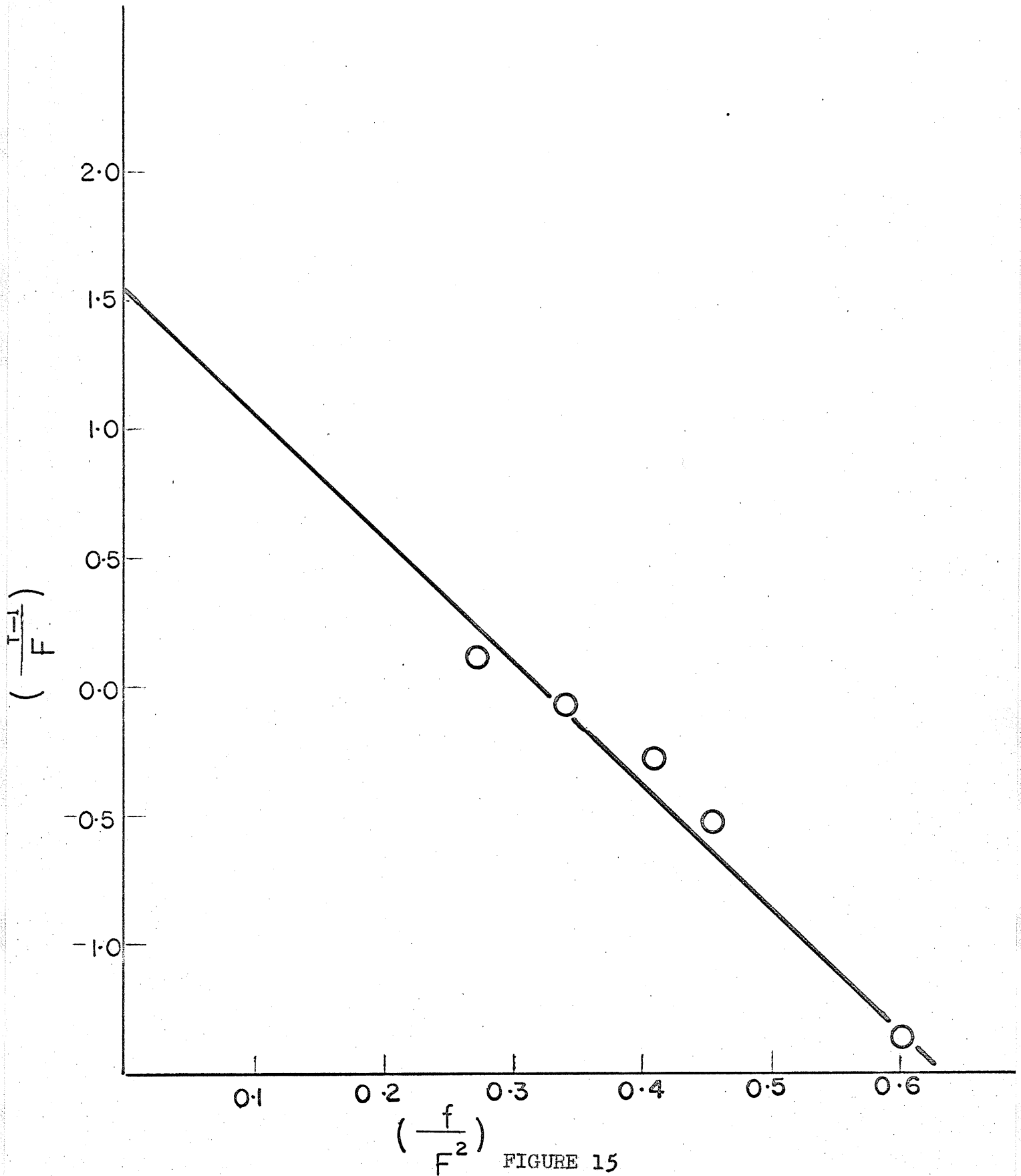


FIGURE 16. $\text{Log } \frac{m1}{m2}$ vs $\text{log } \frac{M1}{M2}$.

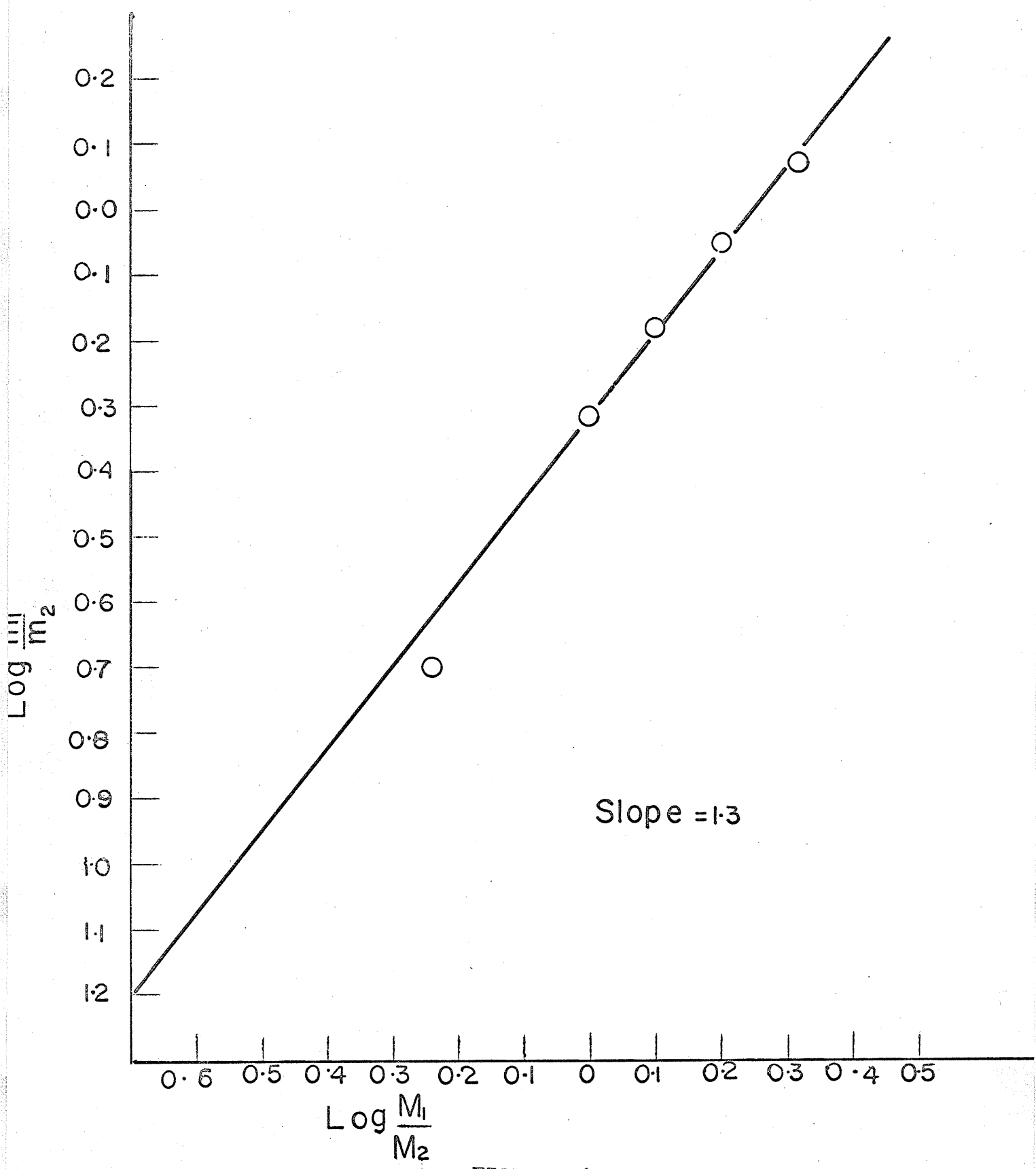


FIGURE 16

greater than one. According to equation (4), if the logarithm of monomer feed ratio is plotted against the logarithm of ratio of monomers in the copolymer formed at low conversion, the slope of the curve should be unity. But in the present work, the logarithm of the monomer feed ratio plotted against the logarithm of the ratio of monomers in copolymers gives a straight line with a slope of 1.3 (Fig.16). Therefore, the electroinitiated copolymerization data for styrene-methyl methacrylate are not in accord with Landler's hypothesis as expressed by eq.(4) (page 60).

Graham (36) has suggested that for styrene and methyl methacrylate the ultimate unit is most important in determining the course of anionic copolymerization. A terminal methyl methacrylate unit can only add another unit of methyl methacrylate but never any styrene. Even if styrene anions are initially formed, they apparently add methyl methacrylate very preferentially. This is attributed to the weak basicity of the methyl methacrylate anion as a chain end, coupled with a need for a strong base to induce anionic polymerization of styrene. Therefore, any styrene found in anionic copolymerization of these two monomers must be incorporated in the initiation and immediately following the propagation steps.

The reactivity ratio of styrene obtained by us shows a significant tendency for the poly (methyl methacrylate) anion and styryl anion to react with styrene. Table XI shows that between 2 and 50 percent conversion of the feed the copolymer

produced by the polymerization of equimolar mixture of styrene and methyl methacrylate contains 31 to 40 percent styrene. Such a large percentage of styrene cannot be incorporated into copolymer during the initiation stage. Therefore, the propagation cannot be completely anionic, but probably has some tendency to add both styrene and methyl methacrylate to the propagating species. It seems, therefore, that polymerization proceeds through radical anion species. Both styrene and methyl methacrylate can add at the radical end of the growing chain and only methyl methacrylate adds to the anion end (37). In such a reaction styrene molecules can be incorporated into the copolymer in both the initiation and propagation steps. This type of mechanism is consistent with the present experimental findings.

In the present work it has been found that product of reactivity ratios of styrene and methyl methacrylate i.e., r_1r_2 is greater than one; but no such result has yet been known in the case of classical free radical or classical anionic polymerization in which the product r_1r_2 is greater than unity.

GENERAL DISCUSSION

No kinetic studies of electroinitiated polymerization of styrene have been reported in the literature. Although Yang, McEwen and Kleinberg polymerized styrene electrolytically in a system composed of sodium iodide, anhydrous pyridine and the monomer, no attempt was made to study the kinetics of the reaction. Probably this was not done due to the low molecular weight of the products. Styrene was successfully polymerized in the solution of silver perchlorate and tetraethyl ammonium borotetrafluoride in nitrobenzene (21), but the authors did not do the kinetic study of the reaction of the polymerization. However, in case of thermal polymerization of styrene kinetic studies were made on several polymerizing systems.

First attempt to study the kinetics of electroinitiated polymerization of styrene was made by Funt and Walker (12). Unfortunately they did not find clearly defined relation to either the current or monomer concentration or salt. In the present work, a clear cut relation between current and monomer concentration is observed. Kinetic studies of electroinitiated polymerization of styrene in a solution of quaternary ammonium salt in dimethylformamide show that the initial rate of the reaction is proportional to the first power of initial monomer concentration and of impressed current provided the current is not below 5 ma. (Fig.4). Rate constant of the

reaction is independent of initial monomer concentration at a fixed current. This is in accordance with the first order of the reaction with respect to the monomer concentration. Furthermore, it increases linearly with increasing current (Fig.3). Deviation is observed at 100 ma. but it is believed to be due to some experimental error. Percent conversion curves with times are smooth and from these curves it is clear that conversion of the monomer increases smoothly with time (Figs. 1 and 8).

In the conventional anionic polymerization of styrene by potassium amide in liquid ammonia (1) the rate of the reaction is seen to be proportional to the square of the monomer concentration and also the rate of the reaction increases with decreasing temperature. However, in our system the rate of the reaction is proportional to the first power of the monomer concentration and the variation of the temperatures over the studied range of 0° to 45°C (Fig.9) has no substantial effect on the rate of the reaction.

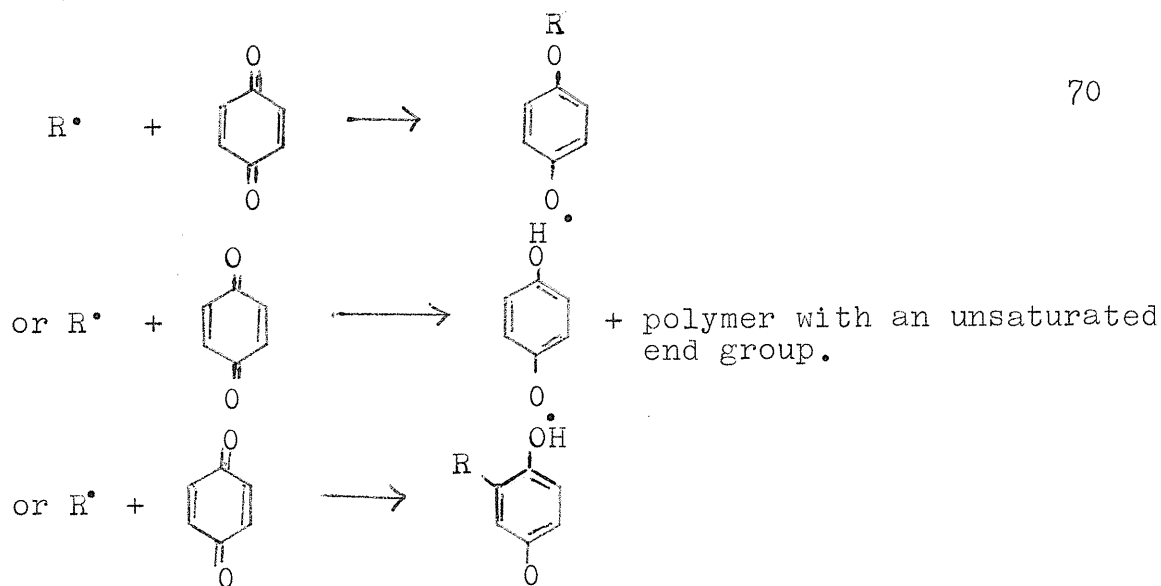
Formation of the polymer commences with the passing of the current. Induction period occurs at a low current. The most probable impurity in this system is a trace of water. Therefore, it is believed that a low current is used up for a long time either by electrolysis of water or by noninitiating electrode processes.

When current is cut off, formation of the polymer ceases i.e., there is no "after-effect" observed. This points out that the initiating species die as soon as current is shut off. The similar phenomenon has been observed in alkali nitrate and dimethylformamide system (12). However, continuation of the polymerization, after the current is switched off, occurs in the polymerization of methyl methacrylate by cathodic hydrogen in aqueous heterogeneous system (17). The author believes that with electrolysis active particles accumulated in the system are capable of initiating polymerization over a long period of time without current. However, he failed to reveal the nature of the active particles. Polymerization of styrene in solution of silver perchlorate in nitrobenzene also showed remarkable after-effect (21). The authors were able to show the existence of living polymers in this cationic system.

When the solution of tetramethyl ammonium chloride is electrolysed, chloride ion Cl^- and tetramethyl ammonium ion $(\text{CH}_3)_4\text{N}^+$ are formed. There are good reasons to believe that polymerization is not initiated by chloride ion since the polymers form solely at the cathode (Table V) and polymer yields and molecular weights are independent of the anions of the salt (Table VI). The mechanism of the reaction, therefore, appears to be independent of anions. This result is a direct contrast to that obtained by Breitenbach (21). The author reported that the mechanism of reaction changes with change of

anions of the salt. When styrene is initiated by electrolysis of tetraethyl ammonium borotetrafluoride in nitrobenzene, polymer forms only in the anode compartment. He assumes that the cathodic process is initiated by anodic discharge of borotetrafluoride ions. However, when styrene is polymerized in the solution of tetramethyl ammonium borotetrafluoride in dimethylformamide, practically no polymer forms in the anode compartment. An identical experiment using ammonium chloride instead of tetramethyl ammonium chloride gives relatively small amount of polymer. No polymer is isolated with ammonium nitrate (Table VII). Therefore, it is worthy noting that polymer formation is quite dependent on the cation but independent of anion of salt. It appears that $(\text{CH}_3)_4\text{N}^+$ ion is responsible for the successful polymerization.

It is well known that the classical radical polymerization is completely quenched by the addition of small amount of p-benzoquinone or tertiary butyl pyrocatechol or other radical inhibitors. Inhibitor reacts with active species to give a product that is too weak to initiate a polymer chain. Possible reaction between a polymer radical and p-benzoquinone which have been proposed are:



The radical produced in each of the above reaction will be resonance stabilized by contribution from structures in which the odd electron is situated on the aromatic nucleus.

In the present system the possibility of polymerization induced absolutely by a free radical reaction is ruled out by experiments which show that formation of polymers proceed in the presence of high concentration of the radical chain inhibitors like p-benzoquinone and t-butylpyrocatechol (Fig.11). However, yield and molecular weight of polymer decrease in the presence of inhibitors as is obvious from Fig.11, and Table X. The decrease in yield indicates either the reaction is occurring through a radical anion mechanism, or free radical and anion occurring simultaneously. On the other hand polymer formation is completely inhibited by water, ^{and} methanol which are chain terminators for the anionic polymerization. The complete inhibition of the reaction by the proton donor material supports the concept of anionic propagation as the dominant step in the chain addition. Rela-

tively small quantities of water and methanol act as transfer agents reducing the rate of the reaction and molecular weight of the polymer (Table X).

This anionic mechanism is further substantiated by the increase of molecular weight of polymers with decrease in temperatures (Table VIII). The fact that molecular weights increase as the temperatures decrease is well established in most cationic and anionic systems since the activation energy of chain breaking or terminating is higher than that for propagation. The propagation step involves the approach of anion to a neutral molecule in a medium of low dielectric constant, and so apparently no activation energy is necessary. The termination step, on the other hand, requires the rearrangement of reactive species and thus involves an appreciable activation energy. Similar result has been observed in the conventional anionic polymerization of the styrene (1) i.e., molecular weight increases with decreasing temperature. The molecular weights of the polymers are roughly independent of the current (Table VIII). Unlike this work, the molecular weights of poly-styrene formed in solution of potassium nitrate in dimethylformamide decrease with increasing current, and decreasing temperature (12). The electroinitiated free radical polymerization of methyl methacrylate with zinc acetate in dimethyl sulfoxide molecular weight of the polymer decreases with increase in current, but that of

acrylonitrile in dimethylformamide initiated by anionic mechanism (25) is independent of current.

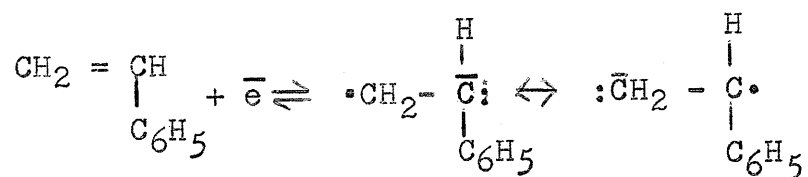
It is apparent from Table (IX) that the molecular weights of the polymers slightly depend on the initial styrene concentration provided the monomer concentration is not below 20 percent by volume. Direct dependence of the molecular weight of the polymer has been observed in the electroinitiated polymerization of acrylonitrile (25).

The electrical efficiency of the polymer formation of the styrene initiated by the electrolysis of the solution of tetramethyl ammonium chloride is the highest of all previously reported values. The efficiency increases linearly with increase in monomer concentration, but starts decreasing when the monomer concentration increases above 70 percent by volume (Fig.10). This is only due to the remarkable decrease of the salt solubility at the highest concentration of the monomer.

The copolymerization studies have shown that polymer formation proceeds via a radical-anion species as previously discussed, but the concept of pure anionic propagation cannot be ruled out completely since it is possible that the electrolysis of the reaction mixture involves some unknown phenomenon that affects the course of the copolymerization.

From the above discussion it is obvious now that the reaction has most of the characteristics of the anionic

mechanism. It is reasonable to believe that the polymerization proceeds through an electron exchange mechanism yielding a propagating species which is radical anion e.g.,



However, it is difficult to comprehend whether the monomer molecule is getting the electron directly from the electrode or from an intermediate initiator. A direct initiation by electrons supplied by the cathode was assumed in the polymerization of styrene by electrolysis of sodium iodide in anhydrous pyridine at magnesium electrodes (27). If radical ion does not dimerize, then the radical ion species probably propagate at each of the unlike ends giving in the same molecule a growing anionic end and a growing free radical. On dimerization of radical ends pure anionic polymerization results. In view of this situation the general kinetic features of the mechanism are similar to those exhibited in acrylonitrile system (25). The kinetic schemes can be written as follows:



If we assume that availability of electrons is proportional to the impressed current i.e.,

$$\bar{e} \propto I \quad \text{or} \quad \bar{e} = KI$$

Rate Constant

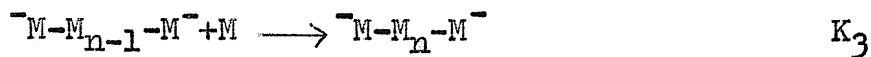


where I is the current.

Dimerization of the radical ion to dianion:



Propagation of dianion:



Chain transfer of dianion:



Propagation of anion:



Transfer of anion:



The rate of propagation is

$$R_p = K_3 [^-M-M_{n-1}-M^-][M] + K_5 [M_{n-1}^-][M]$$

$$\text{or } R_p = K_3 [\text{ion site}][M]$$

where (ion site) refers to the concentration of polymeric negative ions assuming a dianion affords two sites and a monoanion one.

If we assume that the rate determining step is the dimerization of radical ions to form dianions, then the rate of the reaction is to be

Rate = $\frac{1}{2}K_2 [M^{\cdot-}]^2$ and from steady state condition, i.e., rate of formation and rate of disappearance of the ions are equal.

Then,

$$\frac{dM^-}{dt} = K_1 [M] (I) - \frac{1}{2} K_2 [M^-]^2 = 0$$

or

$$\text{Rate} = K_1 [M] (I).$$

This relation satisfies our experimental results.

Rate of termination or chain transfer is given by

$$R_t = K_6 [\text{ion site}] [M]$$

and hence the degree of polymerization is

$$\text{D.P.} = \frac{R_p}{R_t} = \frac{K_3}{K_6} \frac{[\text{ion site}] [M]}{[\text{ion site}] [M]}$$

= constant.

It is apparent from Table IX that molecular weight of the polymer is little dependent on initial monomer concentration provided it (monomer concentration) is not too low. Therefore, the role of chain transfer to monomer is not appreciable. This view is also substantiated by electrical efficiency. If we suppose that chain transfer takes place with solvent or with some electrode products:



Therefore, degree of polymerization:

$$\begin{aligned} \text{D.P.} &= \frac{K_3}{K_7} \frac{[\text{ion site}] [M]}{[\text{ion site}] [SH]} \\ &= \frac{K_3}{K_7} \frac{[M]}{[SH]} \end{aligned}$$

Hence, in this case molecular weight must be a function of the ratio of monomer to solvent concentration, but this is not in agreement with our experimental observation. However, probable explanation of the observed data is that when monomer concentration is greater than that of solvent in the reaction mixture transfer reaction of the growing chain takes place with the monomer otherwise with the solvent.

The order of reactivity in an anionic polymerization is to be nitrile conjugated olefins > carbonyl conjugated olefins > styrene, paralleling the ease of addition of other negative ions and is probably accounted for by the resonance stabilization of the resulting carbanions (29). This order of reactivity of the monomers has been observed in the system composed of $(\text{CH}_3)_4\text{NCl}$ dimethylformamide and monomer. From Figure 12 it is obvious that the rate of the reaction is in the following order:

acrylonitrile > methyl methacrylate > styrene > α -methylstyrene

The polarizing forces of substituents in the aforesaid monomers have been shown in the following table.

Table C.

| <u>Monomer</u> | <u>Polarizing forces of substituents in dynes according to C.C. Price (38).</u> |
|-------------------------|---|
| Acrylonitrile | -CN: + 1.80 |
| Methyl methacrylate | -COOCH ₃ : + 1.23 |
| Styrene | slightly negative |
| α -methylstyrene | -CH ₃ : - 0.39 |

From Table C and Figure 12 it seems that the increasing tendency of monomer to enter anionic induced polymerization is accompanied by increasing polarizing forces of the substituents. However, this is not an unequivocal justification.

SUMMARY

1. Some exploratory experiments were performed with various monomers, salts and solvents.
2. Electroinduced polymerizations of styrene, α -methylstyrene, acrylonitrile and methylmethacrylate were conducted in the solution of tetramethyl ammonium chloride in dimethylformamide.
3. System consisting of styrene, dimethylformamide and quaternary ammonium salts was found amenable to simple kinetic analysis, and a systematic study was undertaken of the rate of polymerization of styrene as a function of monomer concentration, current, solvent and salt. Kinetic study yielded clearly defined relation to the current and the monomer concentration.
4. Locus of polymerization was found to be the cathode.
5. Polymer formation was quenched by water and methanol.
6. Reaction mechanism appeared to be independent of anions of the salt.
7. Copolymerization data were observed to be different from those of classical free radical or anionic mechanism.
8. Molecular weights of polystyrene were found reasonably high being dependent on temperature but independent of current.
9. Dominating role of dimethylformamide in the polymerization of styrene with quaternary ammonium salts was not understood.

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