ELECTROSENSITIZED FREE RADICAL POLYMERIZATION

by

PAULA REIGH VAN BUREN

A Thesis Submitted to the

Faculty of Graduate Studies and Research

in Partial Fulfillment of the

Requirements for the Degree of

Master of Science

University of Manitoba

April, 1964

TO MY PARENTS.

ACKNOWLEDGMENTS

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Polymer was produced when an electric current was passed through a solution of methyl methacrylate, dimethylformamide and tertiary butyl ammonium chloride. The addition of small amounts of tertiary butyl chloride to the above system caused the reaction rate to increase up to six fold. These phenomena were termed electrosensitization. The reaction took place at the cathode and was completely free radical in nature. Efficiencies of the system are among the highest ever recorded for free radical systems.

Osmometry, an absolute number average method, was used to calibrate the molecular weights of the polymer formed.

LIST OF ABBREVIATIONS

Those symbols and abbreviations that will be used in the thesis without further clarification are:

A.C.: alternating current

$(CH_3)_3CCl$: tertiary butyl chloride

$(CH_3)_3CNH_3Cl$: tertiary butyl ammonium chloride

D.C.: direct current

g/cm^3: grams per cubic centimeter

kfr: rate constant for a chain transfer reaction

kpc: " " " the reaction of R1· with M

kp1: " " " " " " R1· " M

kp2: " " " " " " R2· " M

kpr: " " " " " " Rr· " M

kpm: " " " " " " M " M·

ktrs: " " " " combination of Rr· with Rs·

kt'rs: " " " " disproportionation or Rr· and Rs·

M: a monomer molecule

M· : a monomer radical

$\overline{M}_n$: number average molecular weight

$\overline{M}_w$: weight average molecular weight

Mi: the molecular weight of a polymer molecule containing i monomer units

Ni: the number of polymer molecules containing i monomer units

Pr: a polymer molecule containing r monomer units

Ps: a polymer molecule containing s monomer units

Rc• : a radical formed from a catalyst molecule

R1• : a radical containing Rc• plus a monomer unit

R2• : a radical containing Rc• plus two monomer units

Rr• : a radical containing Rc• plus r monomer units

Rs• : a radical containing Rc• plus s monomer units

Rn• : a radical containing Rc• plus n monomer units.

PURPOSE OF THE RESEARCH

A large number of polymerizations occur by a free radical mechanism. Various methods have been used to produce the initial free radicals, and these will be reviewed later in this work. A method which is receiving increasing attention is the electrolytic production of free radicals.

The electrolysis of complex materials usually produces free radicals. The concentration of the radicals at the electrode surface will be high. Thus they will have a strong tendency to dimerize. If the lifetime of these radicals is sufficiently long, they will be able to diffuse into the bulk of the monomer containing solution and initiate polymerization.

The electrolytic production of free radicals has many advantages over the older methods of producing them. Methods employing the thermal decomposition of either the monomer or a catalyst added to the monomer solution may be used only over a restricted temperature range, otherwise the rate of polymerization will be either inconveniently slow or fast. The control of these experiments is also difficult once they are under-way, because thermal transfer is slow. In general the reaction can be stopped only by the addition of an inhibitor. On the other hand, electrical processes are controlled with ease. The production of free radicals may be increased or decreased by varying the current. Stopping the reaction is a simple matter of turning off the current. The electrical process can be programmed, varied and measured with ease.

Most studies of electroinitiated polymerization have dealt with

radicals produced as the direct result of the electrolysis. The purpose of this investigation was to see if an indirect production of radicals could increase the efficiency of a given electroinitiated polymerization.

If a solution containing a monomer, solvent, salt, and reducible organic compound is electrolysed, the organic compound will be reduced under the influence of the applied potential. Free radicals will be among the products of the reaction. The reducible organic compound could be thought of as an electrosensetizer by analogy to the role of photo-sensitizers in photolysis.

Electroinitization experiments in which a reducible organic compound is used could be compared to photoinitiation experiments in which diacetal (1), azo initiators (2), and benzoin (3) were used as photo-sensitizers. These compounds, instead of monomer molecules, absorbed the incident illumination and broke down to form radicals which then initiated the polymerization.

In 1951 (Kolthoff (4), used an indirect electrolytic method to initiate the polymerization of acrylonitrile. He reduced ferric ions to ferrous at the cathode. These ions then reacted with persulfate or peroxide molecules in the solution to produce free radicals:

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

$$Fe^{++} + HOOH \longrightarrow Fe^{+++} + OH^- + HO\cdot$$
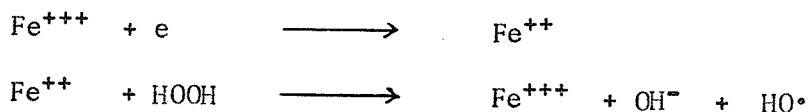
The polymer formed coated the electrode, since an aqueous system was used, causing difficulties. A few experiments were tried with homogeneous systems, using aqueous methanol, but no polymer was thus obtained.

In 1956, Loveland, in a Canadian Patent (6) claims to have polymerized

ethylene and other low molecular weight olefins at atmospheric pressure by passing an electric current through a divided cell which contained a solvent and an electrolyte in both compartments, and in addition a reducible organic compound and an olefin in the cathode compartment. The molecular weights of the polymers thus formed ranged from ten to one hundred thousand and could be controlled by the current density on the cathode. It appears that no further work has been done along these lines.

The present investigation represents an attempt to employ electro-sensitization in the polymerization of vinyl monomers in homogeneous organic solutions. It is thus an amplification of the fragmentary studies outlined above in that it is intended to extend Kolthoff's studies to homogeneous systems employing reducible organic compounds. It also can be considered to represent an extension of Loveland's work to the vinyl family of monomers in organic systems at atmospheric pressure.

INTRODUCTION

Historically, the development of the theory of polymerization reactions took many years. In 1920, Staudinger proposed a free radical chain mechanism for the polymerization of styrene (6). He considered that the activation of a monomer molecule resulted in the opening of the double bond, and that this molecule then reacted with monomer molecules to give intermediates. The initiation step was slow, but the subsequent growth reactions were relatively rapid. He simply wrote the intermediates with free valences at both ends of the molecule. Monomer molecules added on until such a large molecule was formed that the reverse reaction took place. He later modified this view.

Another theory at that time was that polymerization occurred by a stepwise reaction, in which the intermediate species have approximately the same reactivity as the initial monomer. This is true for condensation polymerizations, but not for vinyl polymerizations.

The first clear example of a free radical mechanism for a polymerization reaction appears to be that given by Taylor and Jones in 1930 for the polymerization of ethylene induced by the decomposition of mercury diethyl (7).

In 1934 Whitmore proposed the first ionic mechanism, and by the 1940's, workers could clearly distinguish between free radical and ionic mechanisms.

Also by this time the stepwise reaction mechanism was discarded in favor of the free radical chain mechanism. The most convincing evidence

in favor of the free radical over the stepwise reaction was that:

(1) polymerization was initiated by substances known to give free radicals on decomposition or by photoexcitation and (2) detailed analysis of the kinetics of polymerizations shows them to be in accord with theoretical expectations based on a radical mechanism.

SIMPLE KINETICS OF FREE RADICAL POLYMERIZATIONS

The kinetics of a free radical polymerization must take into account three types of component reactions: (1) the initiation, that is the slow formation of radicals, (2) the propagation, the radicals' rapid growth, and (3) the termination, causing the cessation of growth. Generally a fourth type of reaction may take place in polymerizations: that is chain transfer. In this reaction the activity of a polymer radical is transferred to some other molecule, either monomer, solvent, or some other foreign molecule present in the reaction mixture. In some systems this reaction is negligible, whereas in others, transfer reactions are very significant.

Three simplifying assumptions are usually made in the calculation of the kinetics of free radical polymerizations. The first is that radical reactivity is independent of radical size. Therefore, in a kinetic analysis, a single velocity constant will characterize all the propogation steps occurring in the polymerization. This makes calculations much easier. Although the validity of such calculations has been questioned, on the basis of experimental results which comply with the equations so derived it was felt that the assumption was justified.

The second assumption is that the average chain length is great. A more correct statement of this assumption is that the total rate of reaction of monomer can be set equal to the rate of reaction of monomer in the propagation steps alone. Monomer consumed in the initiation and transfer reactions is neglected. In most free radical reactions the kinetic chain length, that is the number of monomer molecules consumed per chain started, and the molecular chain length, that is the number of monomer molecules consumed per inactive polymer molecule formed, are great, so this assumption leads to valid equations for most systems.

The last approximation is the use of the stationary state method. This involves the assumption that the concentration of radicals remains constant during the polymerization. In other words the rate of change of radical concentration is much less than the rate of polymerization. If the rate of change of radical concentration equals zero in a good approximation, then the radical concentration and therefore the reaction rate are functions of time only in so far as reactant concentrations and initiation rates are functions of time. This relationship has been observed experimentally and thus the stationary state method was adopted. Later, evaluation of velocity constants and direct studies contrasting stationary and non-stationary phases of various reactions have also shown that this method is applicable to most systems.

To illustrate how the above assumptions are used to derive the kinetics of a polymerization a simple kinetic scheme must first be postulated:

$$\text{catalyst} \longrightarrow 2\ R_c^\bullet \qquad \text{rate} = I$$

$$R_c^\bullet + M \xrightarrow{\ kpc\ } R_1^\bullet \qquad\qquad \text{Initiation}$$

$$R_1^\bullet + M \xrightarrow{\ kp1\ } R_2^\bullet$$

$$R_2^\bullet + M \xrightarrow{\ kp2\ } R_3^\bullet \qquad\qquad \text{Propagation}$$

$$R_r^\bullet + M \xrightarrow{\ kpr\ } R_{r+1}^\bullet$$

$$R^\bullet + M \xrightarrow{\ kfr\ } P_r + M^\bullet \qquad\qquad \text{Transfer}$$

$$\text{then}\quad M^\bullet + M \xrightarrow{\ kpm\ } R_2^\bullet$$

$$R_r^\bullet + R_s^\bullet \xrightarrow{\ ktrs\ } P_{r+s} \qquad\qquad \text{Termination: by combination}$$

$$R_r^\bullet + R_s^\bullet \xrightarrow{\ kt'rs\ } P_r + P_s \qquad\qquad \text{by disproportionation}$$
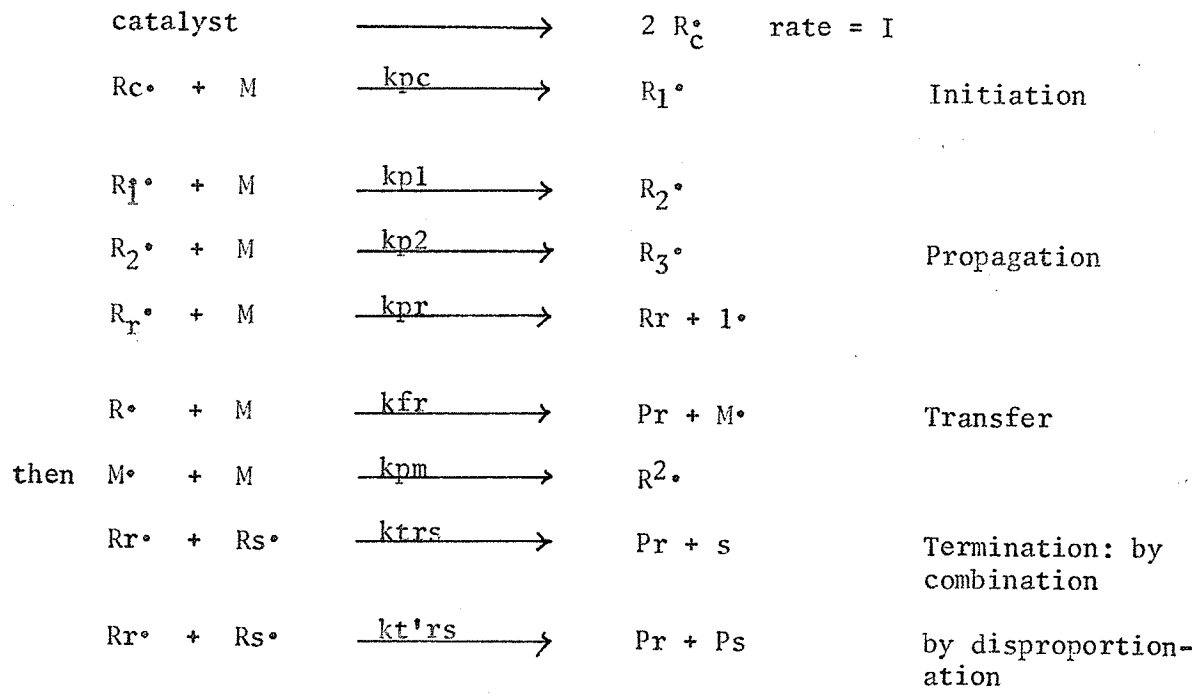
According to the first assumption the velocity coefficients for a given type of reaction are independent of the radical size. Therefore the propagation coefficients are all equal, as are the termination and transfer coefficients.

Secondly, the chain length is assumed to be great and therefore the rate of consumption of monomer is equal to the rate of propagation, That is:

$$\frac{-dM}{dt} = \sum_n kp\ [R_n^\bullet][M]$$

Finally we assume that a stationary state is set up so that the rate of change of radical concentration is zero. For example:

$$\frac{d[R_1^\bullet]}{dt} = kpc[R_c^\bullet][M] - (kp + kf)[R_1^\bullet][M] - (kt + k't)[R_1^\bullet]\sum_n [R_n^\bullet] = 0$$

If we derive all such expressions for rates of change of all radicals and set each equal to zero then add all the equations we get the simple result:

$$I = (kt + kt') \left\{ \sum_n [R\cdot n] \right\}^2$$

i.e. the rate of iniation is equal to the rate of termination. Terminations involving catalyst or single monomer radicals are neglected since if the chain length is great the concentration of these radicals is negligible compared to the concentration of polymer radicals.

The rate of the reaction, as given by the rate of disappearance of monomer is:

$$\frac{-d[M]}{dt} = \sum_n kp[R\cdot n] [M]$$

Substituting for $\sum_n [R\cdot n]$ from above:

$$\frac{-d[M]}{dt} = kp[M] \left\{ I/(kt + kt') \right\}^{1/2}$$

The reaction rate is first order with respect to monomer concentration. Absolute values for the individual velocity constants cannot be obtained from stationary state measurements above. Various other experimental techniques must be employed to determine these values.

METHODS OF FREE RADICAL PRODUCTION

Several methods are used to produce free radicals which will initiate polymerization. Most monomers will polymerize upon being heated. Such polymerizations take place by free radical mechanisms but the exact nature of the initiating species is not known. A study of the kinetics of such reactions for many monomers is difficult because the reaction rate

is relatively low and appears to be dependent on the previous history of the monomer.

Another method of initiating polymerization is by adding, to a monomer solution, a catalyst which will decompose to give free radicals. The rate of the reaction will depend on the catalyst concentration as well as the temperature. It can be deduced from the kinetics of free radical polymerizations that the rate is proportional to the square root of the catalyst concentration.

Polymerizations can be initiated by exposing monomers to γ-rays, β-rays or slow neutrons. Studies have shown the mechanism to be free radical (8) (9). Fairly detailed results are available from γ- and β-ray experiments. In these studies solvents must be carefully chosen to avoid side reactions which inhibit the polymerization.

For many years workers have been studying photoinitiated polymerizations. Such reactions were attractive because of the ease with which they could be started or stopped. Most studies to find individual rate coefficients have used photoinitiated polymerizations. The overall rate of the reaction is proportional to the square root of the intensity of the illumination.

There are two types of photopolymerizations: sensitized and unsensitized. In the former case the reaction mixture contains a catalyst which, on being exposed to the incident illumination, decomposes to form radicals. Unsensitized reactions depend on monomer decomposition alone.

ELECTROINITIATION

For many years the Kolbe electrolysis has been known as a useful method of producing symmetrical alkanes from aliphatic carboxylic acids. The reaction scheme is the following:

$$RCO_2- \longrightarrow RCO_2\cdot + e^-$$

$$RCO_2\cdot \longrightarrow R\cdot + CO_2$$

$$2R\cdot \longrightarrow R-R$$
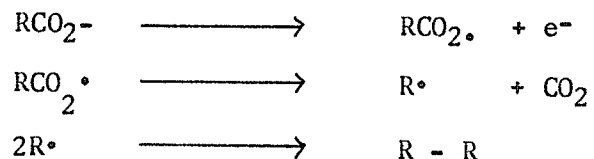
The above electrolysis could serve as a source of free radicals in solution.

In 1952 Goldschmidt and Stockel (10) electrolysed sodium acetate in acetic acid solution containing styrene. The styrene was converted mainly into dimer and trimer at the anode, but some low molecular weight polymer was formed. Acrylonitrile was dimerized similarly.

In 1959, Lindsey and Peterson (11), as well as Smith and Gilde (12), reported anodic dimerization of butadiene and isoprene initiated by acetate radicals.

In 1960, Smith and Gilde (13) obtained high molecular weight polymers in a heterogeneous aqueous system from methyl methacrylate, vinyl acetate and vinyl chloride by anodically generated acetate radicals.

In 1962, Breitenbach and Srna (14) polymerized methyl methacrylate and acrylonitrile by discharge of acetate ions in acetic anhydride.

In all the above cases an insoluble coating of the polymer formed on the anode, insulating it from further flow of current. Therefore yields were low. In many cases molecular weights were low also.

In 1962, Funt and Yu (15) polymerized methyl methacrylate in a

homogeneous organic medium by the discharge of acetate ions at the anode. Polymer of high molecular weight was formed and since it remained dissolved in the solution it did not interfere with the electrode process.

The simplest free radical capable of initiating polymerization is atomic hydrogen. In 1949 Wilson (16) was first to get electrolytically initiated polymerization. Atomic hydrogen was the initiating species. He found that the hydrogen liberated at a mercury cathode did not reduce methyl methacrylate and acrylic acid, but caused these compounds to polymerize.

In 1950 Palit (17) tried to polymerize methyl methacrylate in propane -1, 2- dial solution with acetate free radicals generated in the Kolbe electrolysis. He found no polymer at the anode, but poly (methyl methacrylate) was obtained at the cathode. He attributed this to initiation by hydrogen or sodium atoms.

Various metals have been used as cathodes. Dineen, Schwan and Wilson (18); Kern and Quast (19); and Parrovano (20) have all reported a dependence of the efficiency of initiation on overvoltage of the cathode material. Lead, tin, mercury, platinum, bismuth, iron and aluminum caused initiation in order of effectiveness, whereas no polymerization resulted when cathodes were of copper, cadmium, nickel, tungsten, tantalum, molybdenum, chromium, silver, or zinc. It is thought the hydrogen atoms formed from a high overvoltage material have a greater reactivity and thus a greater probability of efficiently adding to the double bond. The above results are in complete agreement with this idea.

In 1960, Tsvetkov (21) using a lead cathode, found that the yield of poly (methyl methacrylate) varied directly with the size of the electrodes, the current density and the temperature.

MOLECULAR WEIGHTS

Determination of the molecular weights of polymer samples is difficult for two reasons. First, due to the large size of polymer molecules, ordinary molecular weight determinations cannot be used. Also, in a polymer sample there will be a distribution of molecular weights since propagation and termination reactions are random in nature.

Two methods used in this study to determine the molecular weights of polymers are viscometry and osmometry. Here again a difficulty arises. Two different average molecular weights may be obtained for a polymer sample, the number average and the weight average. Defined mathematically, these averages can be expressed as follows:

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

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

A molecular weight determined by measurement of any colligative property, such as osmotic pressure, will be the number average molecular weight. Flory (22, 23) has shown the viscosity average of a heterogeneous polymer lies between the number average and the weight average. The exact relationship depends on the conditions of propagation. Thus the molecular weight of a polymer sample will depend on the method used in determining it.

In this study the molecular weights were determined by osmometry and viscosity.

OSMOTIC PRESSURE

Osmotic pressure may be defined as follows. If a solution and solvent are separated by a membrane permeable to solvent molecules only, a pressure must be applied to the solution in order to make the rate of flow of solvent molecules through the membrane the same in both directions. This pressure is known as the osmotic pressure. It is due to the difference in chemical potential of solvent on both sides of the membrane. The relationship between the chemical potential (μ) and osmotic pressure (π) is:

$$\Delta \mu = \pi V$$ where V is the molar volume of the solvent.

Solutions of increasing degrees of dilution must obey Raoult's Law with increasing accuracy. As the mole fraction tends to zero the following will be true:

$$\pi V \longrightarrow -RT \ln X_1 = RT X_2$$

X_1 - mole fraction of solvent

X_2 - mole fraction of solute

If C_2 is the concentration of solute in g/cm^3 of solution which on increasing dilution becomes g/cm^3 of solvent, $X_2 \longrightarrow C_2 V/M_2$ where M_2 is the molecular weight of the solute. Thus at infinite dilution the Van't Hoff limiting law holds true:

$$M_2 = \frac{RT}{(\pi/C_2)_0}$$

VISCOSITY

The first attempt to estimate molecular weights from viscosity data was made by Staudinger (24). He stated that the molecular weight, [M], of a linear polymer was directly proportional to the intrinsic viscosity, [n], in dilute solution:

$$n = KM$$

The expression now used was developed by Huggins (25, 26)

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

where K is a constant independent of molecular weight but dependent on polymer solvent and temperature, and α depends on the shape of the molecules varying from zero for spheres to two for rigid rods. When a series of molecular weights has been determined for a particular polymer by some absolute method such as osmometry, values for K and α in the expression

$$n = KM^{\alpha}$$ may be determined. Since viscosity measurements are relatively easy to perform, this method can then be used to establish molecular weights.

EXPERIMENTAL

Purification and Synthesis of Chemicals

Methyl methacrylate monomer (Matheson, Coleman and Bell) contains small amounts of phenolic inhibitor to prevent polymerization during shipping and storage. Just prior to use, the monomer was passed through an absorption alumina column to remove this impurity, then distilled under reduced pressures. Monomer thus purified was stored for not more than two weeks at $-25°C$.

Dioxane was dried over potassium hydroxide pellets and distilled.

Dimethylformamide (Fisher Certified Reagent) was mixed with a 10% volume of benzene dried over calcium hydride. The benzene-water azeotrope was removed by distillation at atmospheric pressure. The middle portion was collected at $152°C$, stored over barium oxide for forty-eight hours, decanted, and distilled at reduced pressures.

Methyl ethyl ketone (Matheson, Coleman and Bell) was distilled. The fraction boiling at $79° - 80°C$. was collected.

Tertiary butylchloride was synthesized from tertiary butyl alcohol (Fisher Certified Reagent) and hydrochloric acid by the method given in Laboratory Experiments in Organic Chemistry (27). The product was washed with a dilute sodium carbonate solution, then with distilled water, dried over anhydrous calcium chloride and distilled. The fraction boiling at $49.5° - 50°$ was collected.

Tertiary butyl ammonium chloride was synthesized by bubbling dry hydrogen chloride gas through a solution of tertiary butyl amine (Eastman Organic Chemicals) in absolute ether. The salt was filtered out and allowed to dry.

Polymerizations

Polymerizations were carried out in a cell of simple design as shown in figure 1. Samples were withdrawn with a needle and syringe from the side arm which was covered with a rubber serum cap. The electrodes were one inch square platinum spaced 1.5 centimeters apart. Current was supplied by a D.C. source. The reaction cells were kept in a constant temperature bath at $25^{\circ}C$. An ice-water bath was employed for reactions done at $0^{\circ}C$. The reaction mixtures were stirred at a constant rate with magnetic stirrers. In all experiments the reactant solution was saturated with the salt tertiary butyl ammonium chloride.

Dioxane was first used as a solvent for systems containing either methyl methacrylate or styrene, tertiary butyl ammonium chloride and tertiary butyl chloride. The conductance of these solutions is extremely low. The highest currents that could be passed through these systems were one milliampere or less. No polymer was obtained from these systems.

Small amounts of water were added to the dioxane monomer solution to increase the solubility of the salt in this solution, and thus to increase the conductance of the solutions. This did not bring about the desired result. The conductance remained prohibitively low even when the solutions were saturated with water.

FIGURE 1. Simple polymerization cell

        (a) mercury contacts

        (b) 35/45 ground glass joint

        (c) platinum electrodes

        (d) stirring bar

        (e) rubber cap
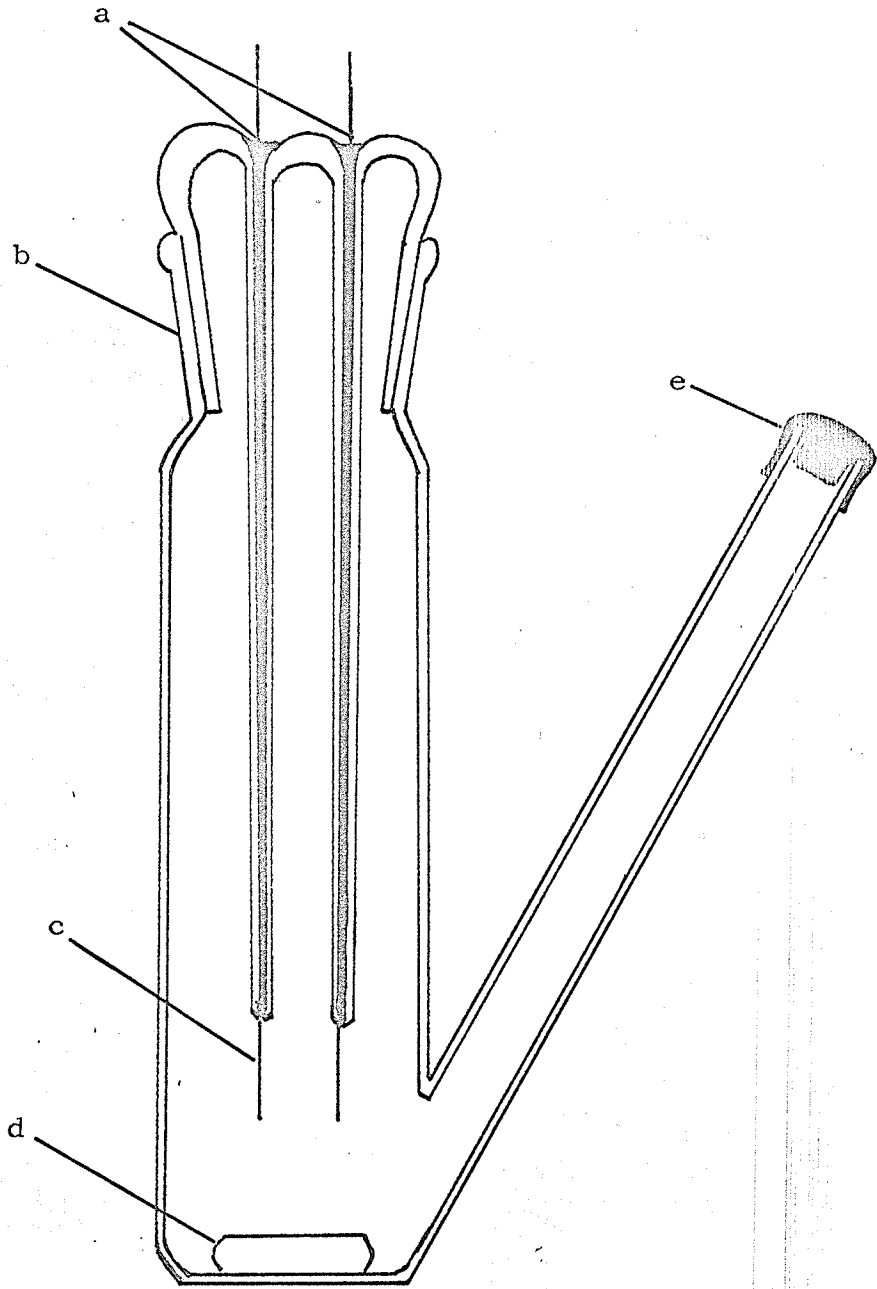
Two solvents of higher dielectric constant were then tried: dimethylformamide and dimethyl sulfoxide. No polymer was obtained when these solvents were used with styrene or vinyl acetate. With methyl methacrylate as monomer and dimethylformamide as solvent, polymer was obtained. Thus the system studied contained the monomer methyl methacrylate, dimethylformamide as solvent, the salt tertiary butyl ammonium chloride, and the reducible organic compound tertiary butyl chloride.

An experiment was carried out in which a current of 20 milliamperes was allowed to pass through two cells, each containing the same amounts of salt, solvent, monomer, and reducible organic compound. One cell had, in addition, one gram of benzoquinone in it.

Experiments were carried out to find what effect the concentrations of monomer and reducible compound and the current density had on the rate of the reaction. In these experiments 3 millilitre samples of the reaction mixture were withdrawn at intervals during the reaction. The samples were weighed, then the polymer in them was precipitated in methanol. The precipitates were then centrifuged, dried in vacuum for twenty-four hours and weighed.

Divided cell experiments were carried out in a cell with two compartments separated by a disc of sintered glass (Figure 2). When radioactive methyl methacrylate was used for these experiments it was placed in the cathode compartment. Samples were counted in a Tri-Carb liquid scintillation counter for ten minutes. The average of four ten minute counts was used.
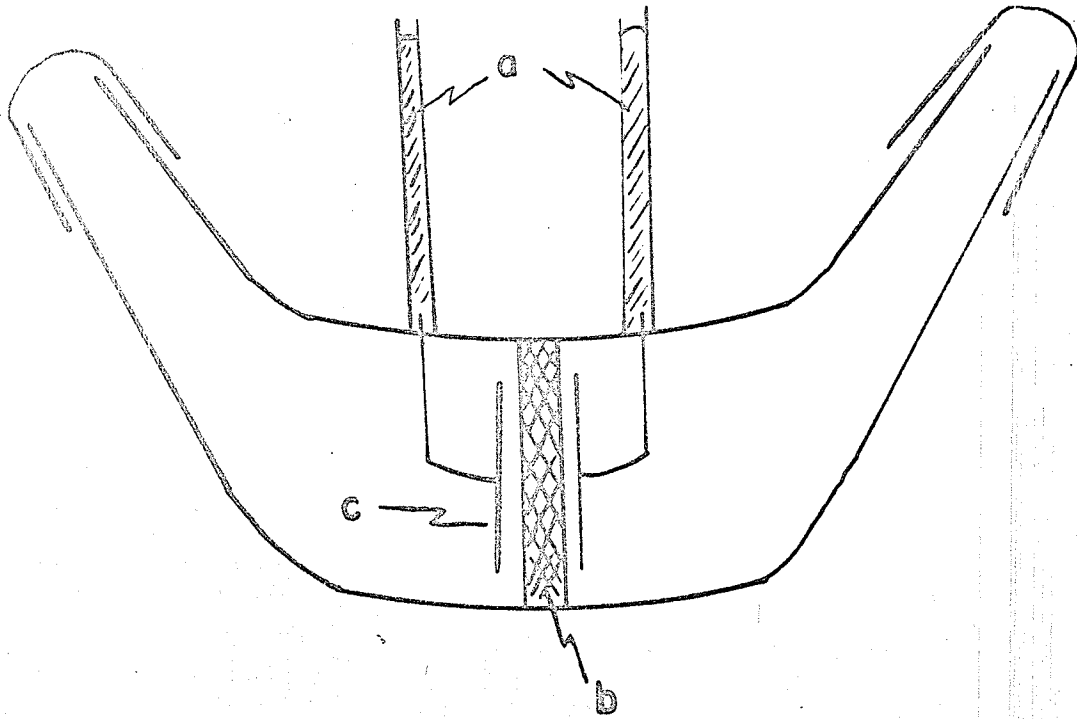
An experiment in which the current was 5 milliamperes A.C. was tried but no polymer was produced.

FIGURE 2. Divided polymerization cell

         (a) mercury contacts

         (b) sintered glass disc

         (c) platinum electrode

Salt Solubility

The solubility of tertiary butyl ammonium chloride in solutions containing 50% by volume of methyl methacrylate, 0, 2, 4, 6 and 8% of tertiary butyl chloride and 50, 48, 46, 44, 42% of dimethylformamide, respectively, was determined. Excess salt was added to solutions of the proper composition, then the solutions were stirred for about an hour and a half. The undissolved salt was filtered off and three 5 millilitre portions of each of the solutions were placed in weighed evaporating dishes. The samples were left to dry at atmospheric pressure for twenty-four hours, then under vacuum for another twenty-four hours, and the evaporating dishes weighed again.

Molecular Weights

i) Viscometry

The intrinsic viscosities of the samples were determined by means of an Ubbelohde viscometer (Figure 3). All measurements were made at 25 $\pm$ .02°C.

ii) Osmometry

Number average molecular weights of polymer samples were determined by osmotic pressure measurements. Modified Zimm-Meyerson osmometers were used (Figure 4). The osmometers were placed in a constant temperature bath at 25 $\pm$ .02°C. The heights of the solutions in the capillaries were read to $\pm$ .001 centimeter with a cathetometer

Number 300 gel-cellophane membranes were used in the osmometers. The membranes were conditioned to the solvent by a method previously found

satisfactory (28). The membranes, which had been stored in water, were
placed succesively in each of the following solutions for fifteen minutes:

  25% ethanol, 75% water

  50% ethanol, 50% water

  75% ethanol, 25% water

100% ethanol,   0% water

  75% ethanol, 25% methyl ethyl ketone

  50% ethanol, 50% methyl ethyl ketone

  25% ethanol, 75% methyl ethyl ketone

   0% ethanol, 100% methyl ethyl ketone

The osmotic pressures of solutions of five different concentrations
were measured for each sample. A hypodermic syringe with a long needle was
used to introduce the solutions into the osmotic cell. The cells were sealed
with a tight fitting metal positioning rod. A drop of mercury was placed
between the metal and the glass to insure that the seal was leakproof.

At least twelve hours were allowed for the equilibrium to be reached.
In all cases the equilibrium was arrived at from above the final pressure
in order that no error be introduced into the final result due to a "flapping"
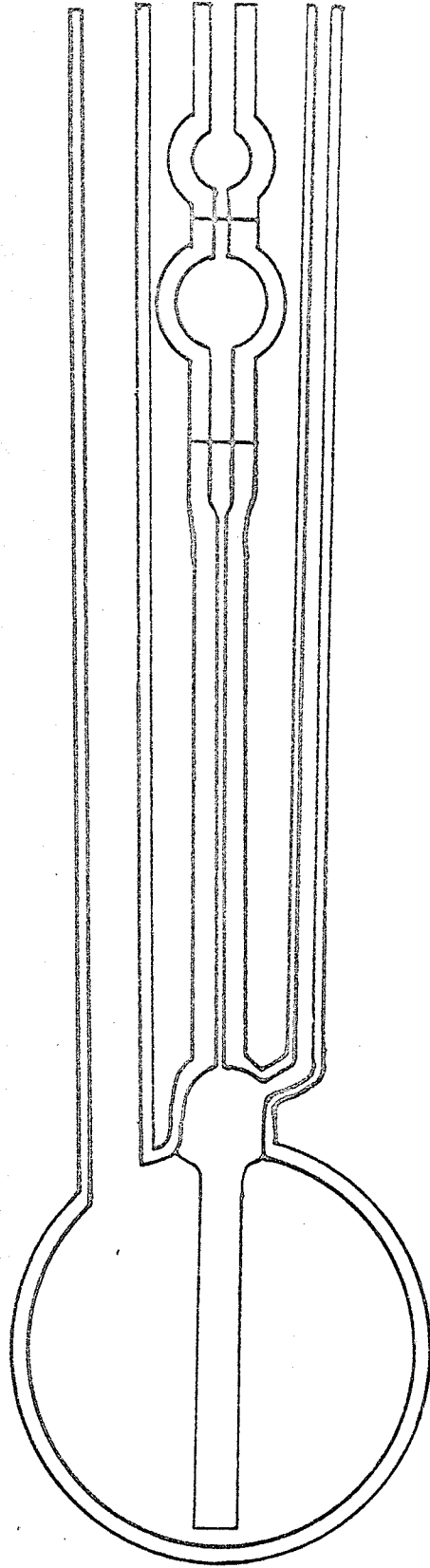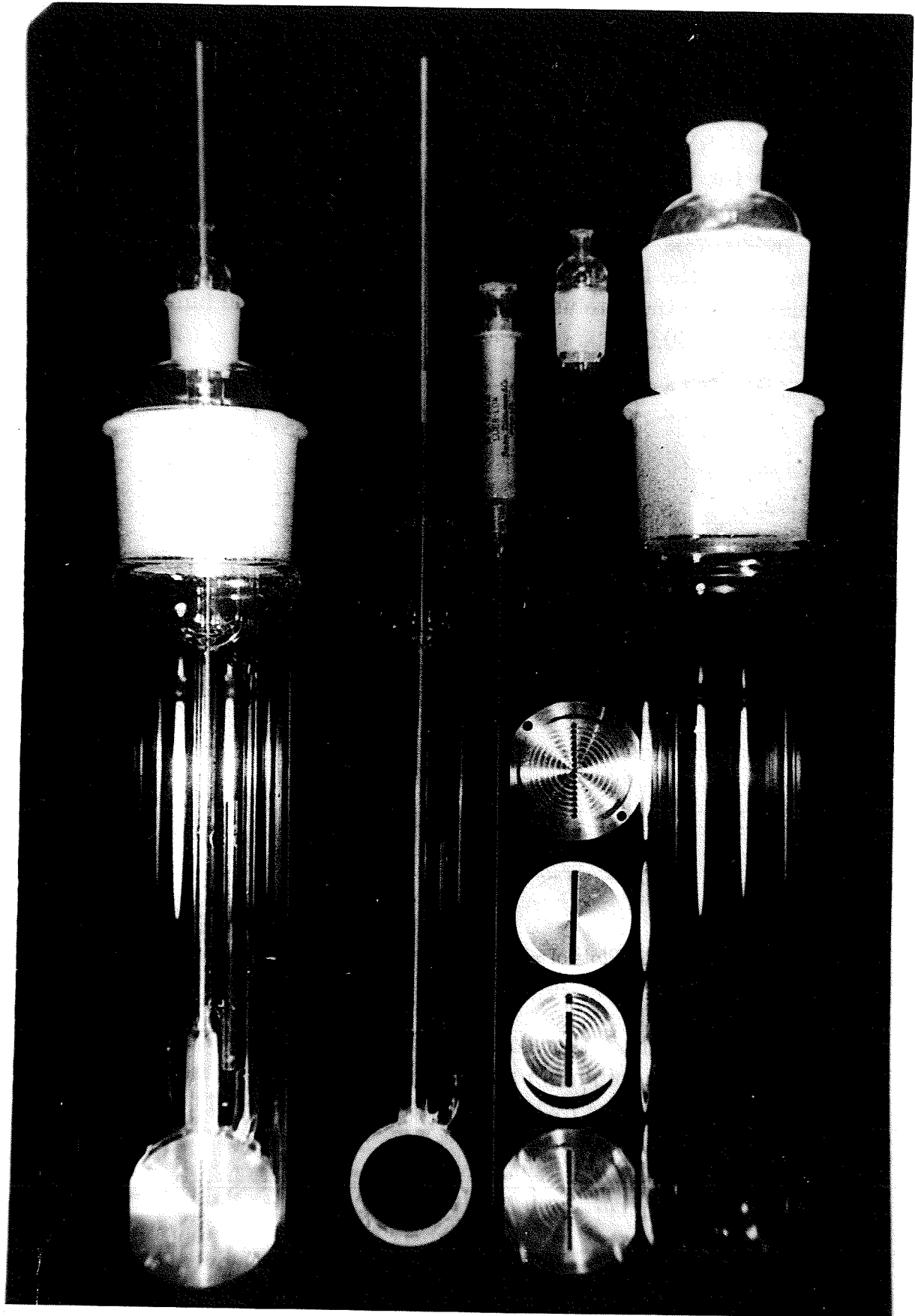of the membrane between its supports.

FIGURE 3. Ubbelodhe viscometer

FIGURE 4. Modified Zimm-Meyerson Osmometer

RESULTS AND CALCULATIONS

Kinetic Studies

Figure 5 shows a plot of yield of polymer in grams per millilitre versus time. The current for the three experiments was five milliamperes. Each cell contained 50% by volume of methyl methacrylate. There was 0, 2, and 3% of tertiary butyl chloride and 50, 48 and 47% of dimethylformamide in cells 1, 2, and 3, respectively. The rates of the reactions were evaluated from the graphs and are given in parentheses beside each curve.

Kinetic runs were done at five, ten, fifteen and twenty milliamperes. Reaction solutions had concentrations of 2, 4, 6 and 8% by volume of tertiary butyl chloride for each current used. For these runs the yield in grams of polymer per gram of reaction solution was plotted against the time. The plots for the reactions done at ten milliamperes are shown in figure 6.

A kinetic run was also done at 3.5 milliamperes. Concentrations of tertiary butyl chloride in these reaction solutions were 0, 0.5, 1, and 2% by volume.

Table 1 shows the rates of reaction, as obtained from the graphs, of the various reaction solutions at different currents.

To insure that polymerization was initiated only electrolytically, reaction solutions containing various concentrations of monomer, solvent, and reducible organic compound, were placed in the reaction cells and stirred for periods up to fifty hours. No current was passed through these solutions and no polymer was ever produced in such experiments.

TABLE 1

Rates and efficiencies for various
reaction solutions at various currents.

(Induction periods were not included in the calculation of these efficiencies.)

Current (ma.)	% $(CH_3)_3CCl$ (by volume)	Rate x10^{-3} (grams/gram hour)	Efficiency in % (moles of polymer per Faraday)
3.5	0	1.2	1.7
3.5	0.5	1.3	0.9
3.5	1.0	4.8	2.8
3.5	2.0	5.1	4.1
5.0	0	1.0	0.9
5.0	2.0	6.4	2.6
5.0	4.0	5.8	2.2
5.0	6.0	1.5	2.3
5.0	8.0	0.9	1.2
10.0	2.0	2.9	1.3
10.0	4.0	5.8	1.8
10.0	6.0	6.9	1.7
10.0	8.0	5.1	1.8
15.0	2.0	0.6	0.3
15.0	4.0	4.2	1.8
15.0	6.0	5.4	1.4
15.0	8.0	4.3	1.7
20.0	2.0	4.2	1.0
20.0	4.0	3.0	0.7
20.0	6.0	3.5	0.7
20.0	8.0	5.7	1.3

FIGURE 5. Yield (grams per gram of reaction solution) versus time at

5 ma. Rates of reactions given in parentheses. Per cent by

volume of $(CH_3)_3CCl$ is shown by each curve.

YIELD × 10^3

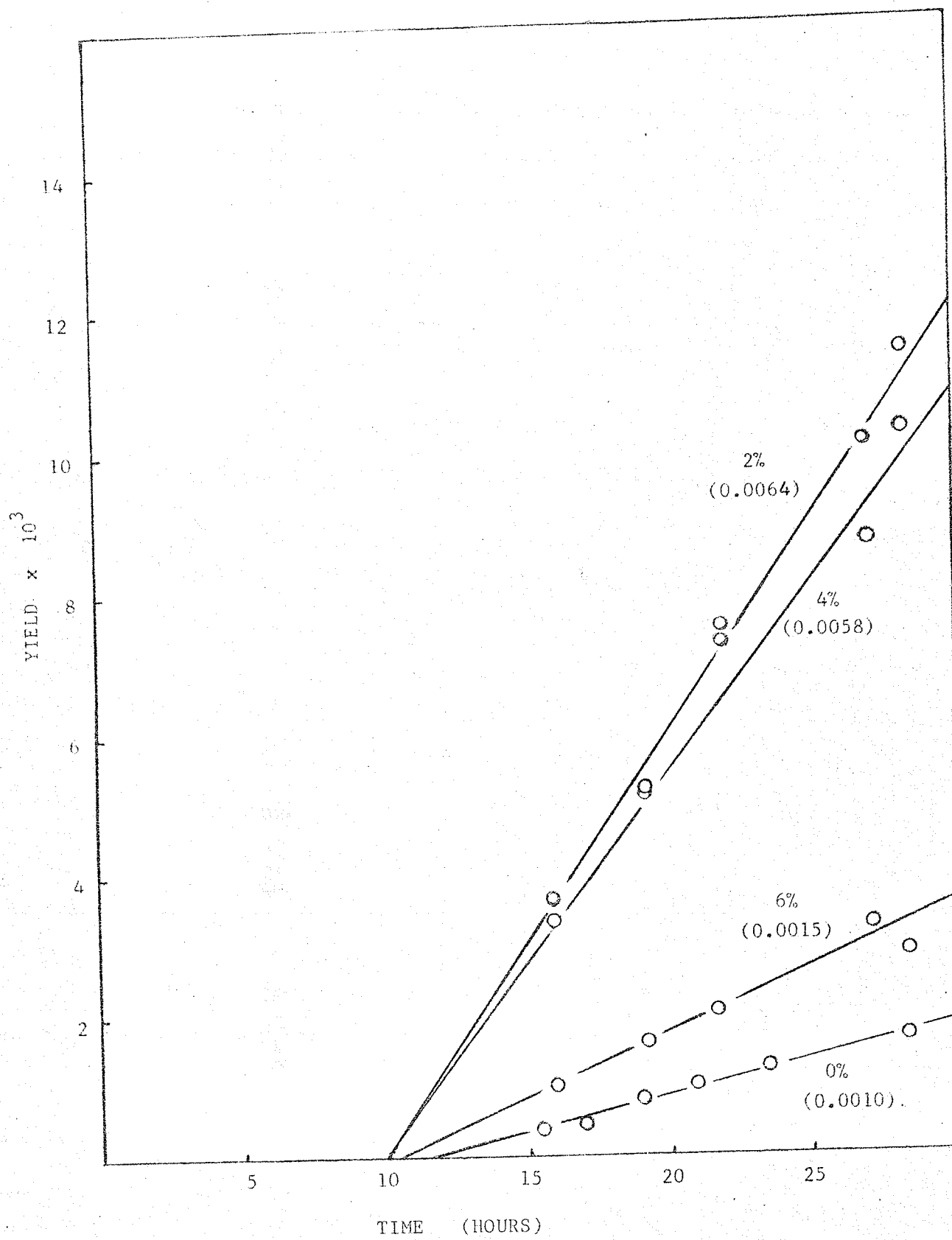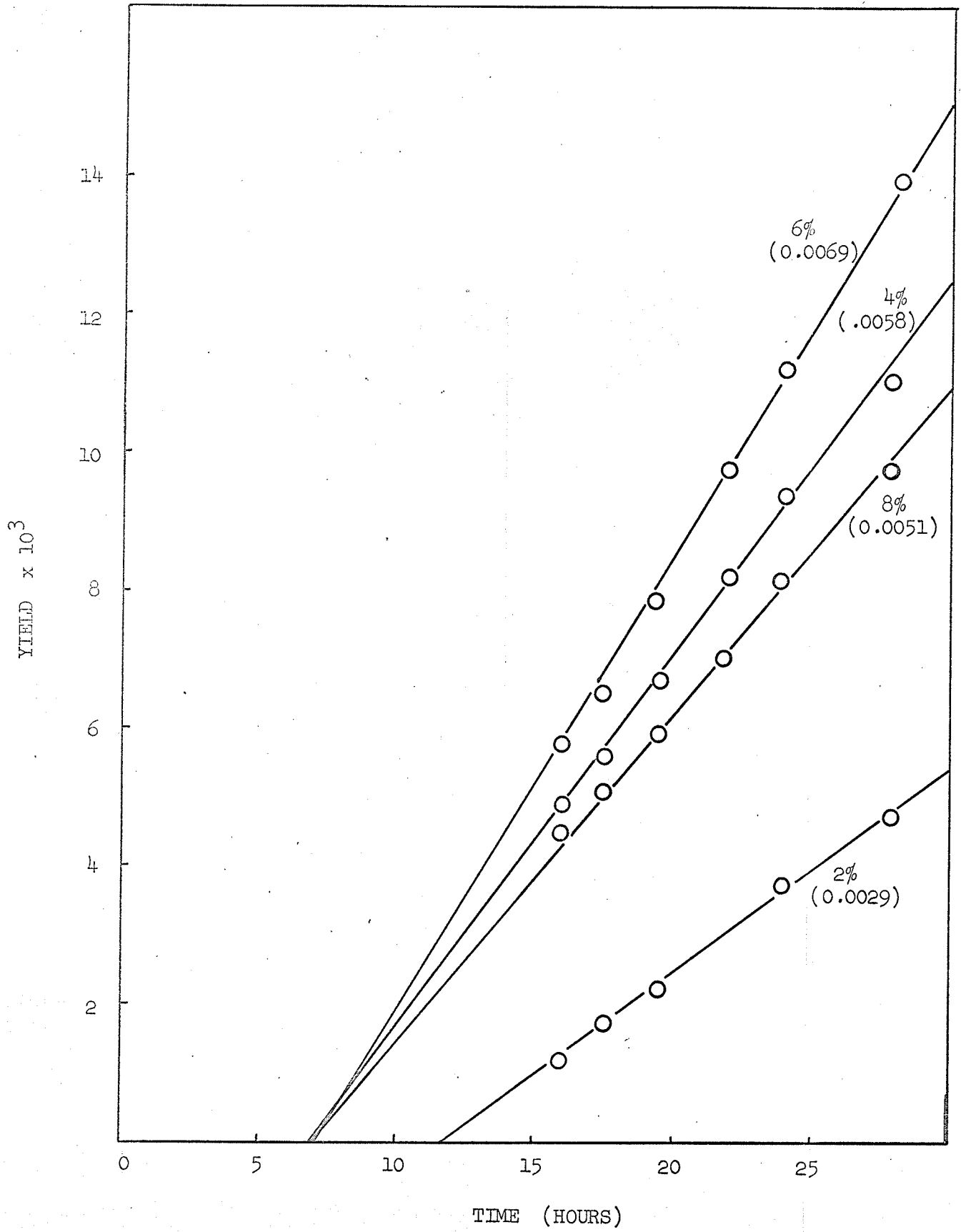TIME (HOURS)

2%
(0.0064)

4%
(0.0058)

6%
(0.0015)

0%
(0.0010)

FIGURE 6. Yield (grams per gram of reaction solution) versus time at 10 ma. Rates of reactions given in parentheses. Per cent by volume of $(CH_3)_3CCl$ is shown by each curve.

6%
(0.0069)

4%
(.0058)

8%
(0.0051)

2%
(0.0029)

YIELD x 10^3

TIME (HOURS)

Two identical reaction solutions containing 50% methyl methacrylate, 6.25% tertiary butyl chloride and 43.75% dimethylformamide, were placed in identical reaction cells, then one gram of benzoquinone was added to cell I. A current of twenty milliamperes was passed through both cells. After twenty hours cell I contained no polymer, while cell 2 contained 3.7 grams of polymer.

Reactions at 0°C produced virtually no polymer.

Table 1 shows the efficiency of the reactions given by:

efficiency = moles of polymer produced per faraday.

Experiments were carried out using reaction solutions containing 30, 40, and 50% methyl methacrylate, 2% tertiary butyl chloride and 68, 58 and 48% dimethylformamide. Currents of five and twenty milliamperes were employed. The results are summarized in table 2. All solutions were saturated with salt.

Divided Cell Experiments

All experiments carried out in the divided cell were done at a current of five milliamperes. The reaction solutions contained 50% methyl methacrylate, 49% dimethylformamide and 1% tertiary butyl chloride. After twenty hours the yield of polymer in the cathode compartment was .1 gram of polymer per millilitre and in the anode compartment was .03 grams per millilitre. When radioactive methyl methacrylate (240,000 counts per minute per gram) was used in the cathode compartment, the activity of the polymer from this compartment was 130,000 counts per minute per gram and for the polymer in the anode compartment the activity was 120,000 counts per minute

TABLE 2

Reaction rates for different monomer concentrations

Current (ma.)	Monomer concentration (% by volume)	Rate $\times 10^{-3}$ (grams/gram hour)
5.0	30	1.0
5.0	40	2.1
5.0	50	6.4
20.0	30	4.6
20.0	40	5.6
20.0	50	6.8

TABLE 3

Salt solubility

$(CH_3)_3C\ Cl$ concentration (% by volume)	(moles/litre)	$(CH_3)_3CNH_3CCl$ concentration (Moles/litre) $\times 10^{-2}$
0	0	3.43
2	.216	3.29
4	.433	3.06
6	.649	2.92
8	.865	2.69

per gram. A third experiment showed that after twenty hours the monomer in the cathode compartment was only two thirds as active as the original monomer and that the monomer in the anode compartment had half this activity.

Salt Solubilities

Table 3 shows the solubilities of the tertiary butyl chloride in different reaction solutions.

Molecular Weights

Figure 7 shows a typical plot of specific viscosity/concentration versus concentration. The extrapolation of these plots to zero concentration gives the intrinsic viscosity, n_i, of the solution, which is then used in the equation:

$$n_i = K M^\alpha$$

Flow times of the solutions and the pure solvent were measured, then specific viscosities of the solutions were calculated from the equation:

$$n_s = \frac{n - n_0}{n_0}$$

where n_s = specific viscosity

n_0 = viscosity of the solvent

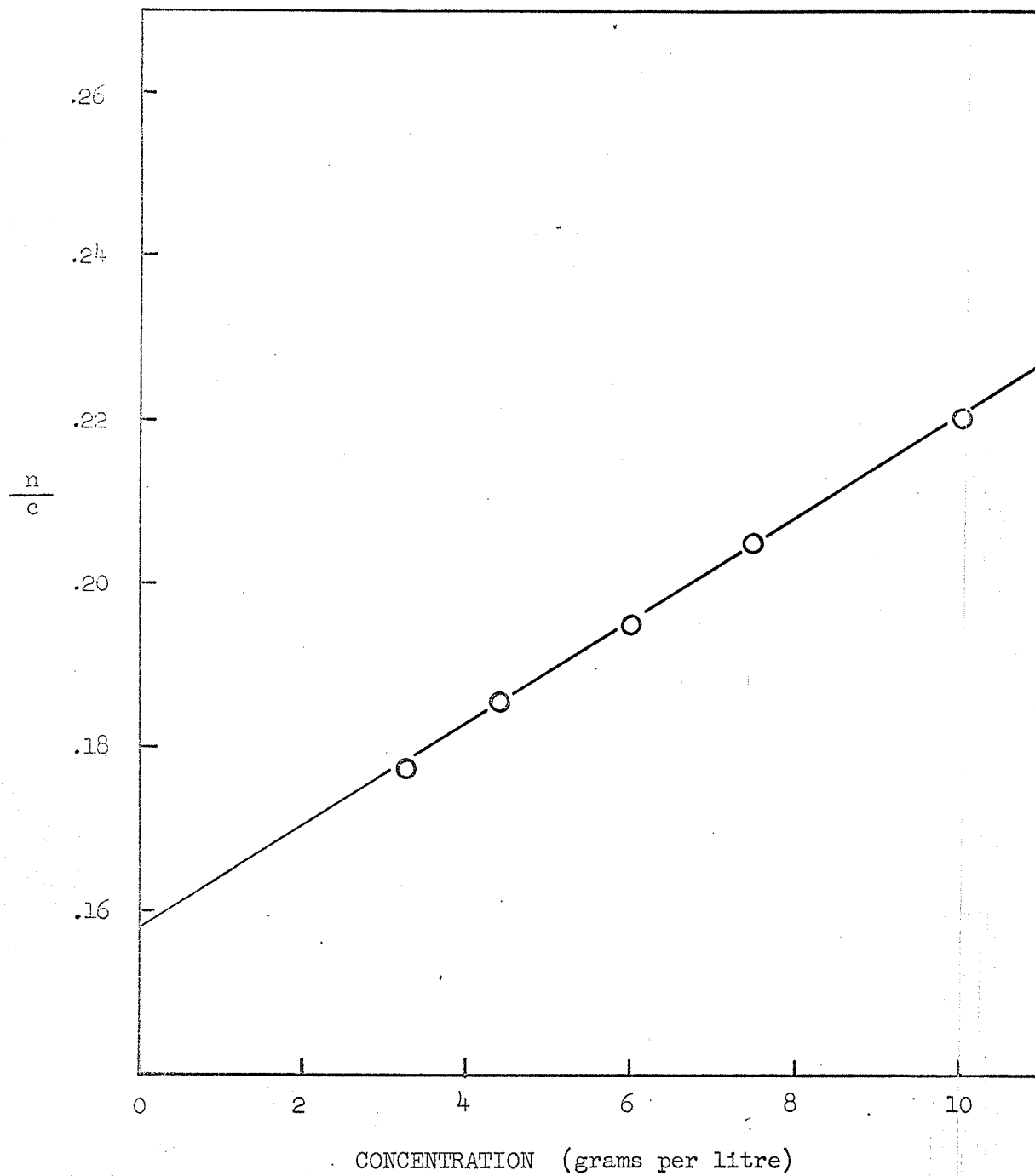n = viscosity of the solution.

Number average molecular weights were calculated using the formula $M = \frac{RT}{(\pi/C)_0}$. When π is expressed in centimeters of solvent, and C in grams

FIGURE 7. Specific viscosity/concentration versus concentration.

Concentration is expressed in grams of poly(methylmethacrylate)

per litre of methyl ethyl ketone.

CONCENTRATION (grams per litre)

of polymer per 100 millilitres of solvent, the constant, R, becomes equal to $\frac{848}{d}$ where d is the density of the solvent at the temperature of the measurement. For these experiments the temperature was 298°K. The density of methyl ethyl ketone is .805 g/ml. Therefore the formula for the molecular weight becomes

$$M = \frac{316,450}{(\pi/C)_0}$$

A plot of the reduced osmotic pressure (π/C) versus concentration is shown in figure 8.

A log log plot of intrinsic viscosity versus molecular weight is shown in figure 9. The slope of this curve is α and the intercept is the value of K for the relationship

$$n = KM^\alpha$$

The plot in figure 9 was used to obtain molecular weight values from intrinsic viscosity values (see table 4).

TABLE 4

Intrinsic viscosities and molecular weights.

Current ma.	% $(CH_3)_3CL$ by volume	Intrinsic viscosity	Molecular Weight
3.5	0	.085	40,000
3.5	0.5	.123	62,000
3.5	1.0	.198	110,000
3.5	2.0	.130	68,000
5.0	2	.184	98,000
5.0	4	.191	105,000
5.0	6	.102	50,000
5.0	8	.097	47,000
10.0	2	.113	55,000
10.0	4	.158*	82,000
10.0	6	.180	96,000
10.0	8	.136	70,000
15.0	2	.065	28,000
15.0	4	.070	32,000**
15.0	6	.115	55,000
15.0	8	.085	40,000
20.0	2	.100	48,000
20.0	4	.104	50,000
20.0	6	.109	53,000
20.0	8	.100	48,000

 * Shown in Figure 7

** Shown in Figure 8

FIGURE 8. Osmotic pressure/concentration versus concentration.

Concentration is expressed in grams of poly(methylmethacrylate)
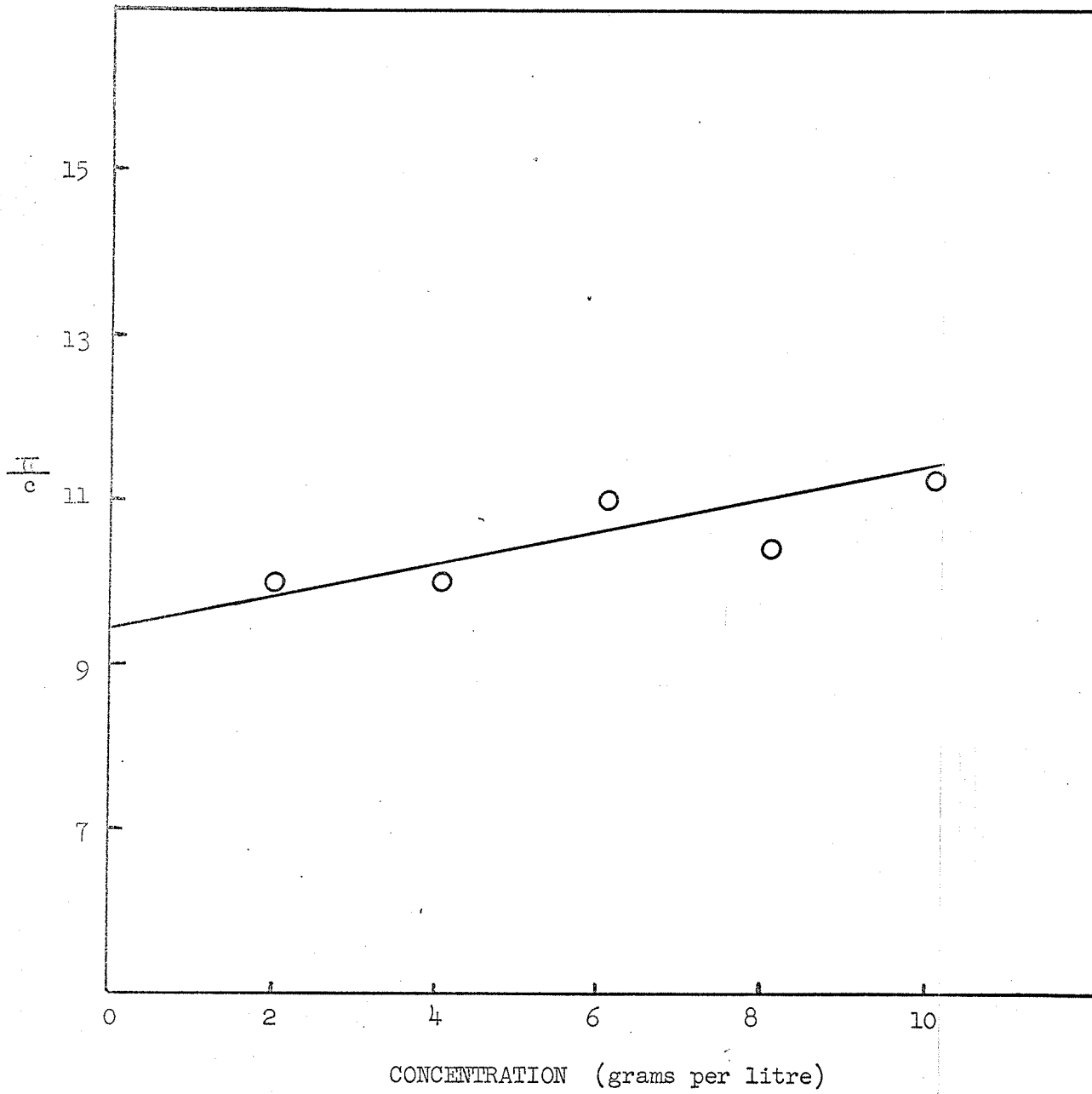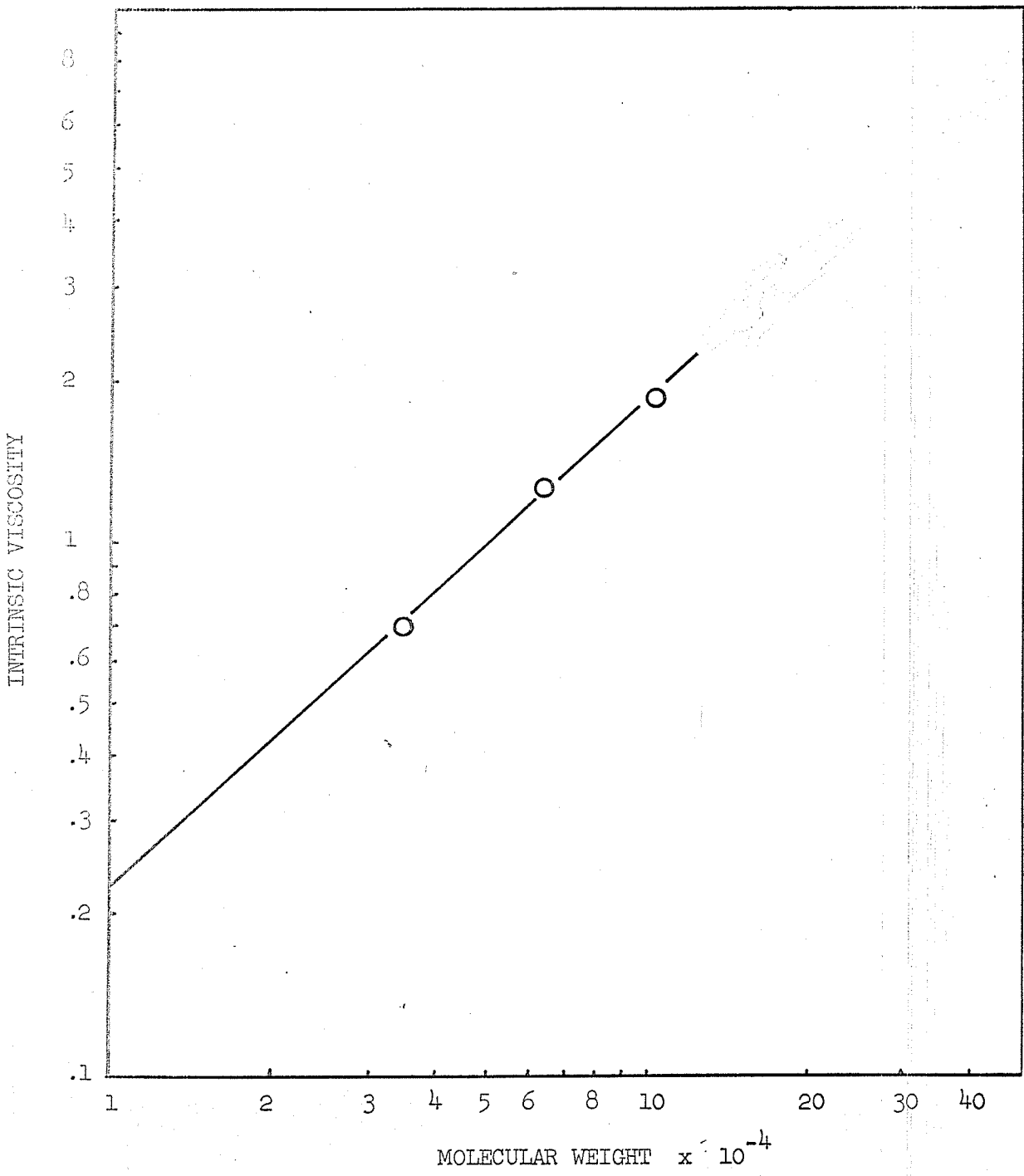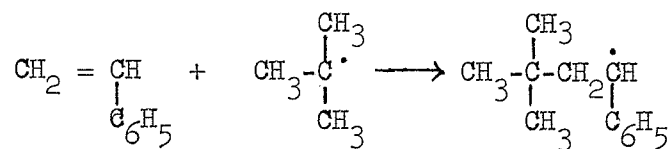
per litre of methyl ethyl ketone.

CONCENTRATION (grams per litre)

FIGURE 9. Log. log. plot of intrinsic viscosity versus molecular weight

INTRINSIC VISCOSITY
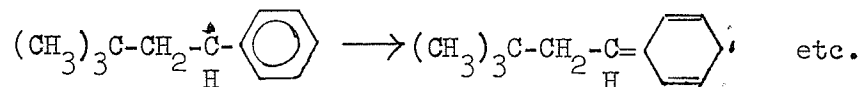
MOLECULAR WEIGHT   x 10^{-4}

DISCUSSION

The purpose of this research was to discover whether the efficiency of a polymerization reaction could be improved by adding a reducible organic compound to the reaction mixture, and if such an effect were found, to study the kinetics of the reaction. It was found that for the system tertiary butyl ammonium chloride, methyl methacrylate, and dimethylformamide, the rate of polymerization was increased sixfold when the reducible organic compound tertiary butyl chloride was added in small amounts. An increase in rate produces an increase in efficiency of the system. A kinetic analysis of this system, however, proved to be disappointing because no clearcut dependence on current, and monomer or tertiary butyl chloride concentration could be found.

Of the three monomers used in the experiments, only methyl methacrylate was found to polymerize. This could be explained in terms of monomer and radical stability. Styrene monomer is least stable and thus the initiating radicals will quickly attack it as shown:

$$CH_2 = \underset{C_6H_5}{\overset{|}{CH}} \quad + \quad CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\cdot \quad \longrightarrow \quad CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2\underset{C_6H_5}{\overset{\cdot}{\underset{|}{CH}}}$$

The new radical will be resonance stabilized:

$$(CH_3)_3C-CH_2-\underset{H}{\overset{\cdot}{\underset{|}{C}}}-\langle\bigcirc\rangle \quad \longrightarrow \quad (CH_3)_3C-CH_2-\underset{H}{\overset{}{\underset{|}{C}}}=\langle\bigcirc\rangle \cdot \quad etc.$$

Thus it will terminate quickly by combination with another radical, and the low molecular weight products formed will not precipitate in methanol.

Vinyl acetate is a very stable monomer and the relatively stable tertiary butyl radical is probably not reactive enough to initiate this monomer.

The reactivity of the radical produced when methyl methacrylate is initiated, as well as that of the monomer itself, is intermediate to styrene and vinyl acetate. Therefore under these conditions only this monomer will react.

The reaction rate varied with the amount of reducible organic compound present. As the concentration of the compound increased, the rate increased to a certain peak value at the optimum concentration, after which tha rate fell off quite rapidly. This could be explained by the fact that the higher the concentration of the reducible compound, the higher will be the concentration of radicals in solution. More kinetic chains are initiated and the rate of the reaction increases. However, as the radical concentration increases still more, the rate of termination will increase and thus the overall rate will decrease. The possibility of a primary radical termination of a chain becomes much greater. The dimerization reaction would also increase in importance. Thus the molecular weights of polymers formed at higher tertiary butyl chloride concentrations should be lower, and this effect is noted.

It has been shown that the solubility of the salt in the reaction mixture decreases with increasing tertiary butyl chloride concentration. This will cause a corresponding decrease in the conductance of the solution.

Another factor which would lower the rate at higher concentrations of reducible compound is the formation of low molecular weight oils, which

would not be precipitated out in methanol. The formation of such oils would reduce the amount of monomer in the solution but would not show a corresponding increase in the yield of precipitated polymer.

The reaction rate varied with the current passing through the solution. The optimum value of the current for these experiments would be close to ten milliamps. Reaction rates increased with increasing current up to this value and again fell off. The explanation of this effect would be the same as the above argument for the effect of tertiary butyl chloride concentration. Again, a general trend to lower molecular weights is noted for higher currents.

It would appear that the concentration of the reducible compound and the current density are factors which work together and the effect of one cannot be separated from that of the other. Since both these factors influence the concentration of radicals in the solution, the difficulty in distinguishing their effects is understandable.

As in all free radical polymerizations, the rate of the reaction was found to increase with increasing monomer concentration but the dependence was found to be complex. At 5 milliamperes the rate depended on $[M]^{5/2}$, whereas at 20 milliamperes the rate depended on $[M]$. This could be explained by two effects. At 20 milliamperes the measured rate is probably not in fact, the true rate. Low molecular weight products which would form do not precipitate in methanol and thus do not count in the yield of polymer. Another factor which would influence the rate at 20 milliamperes is the diffusion of initiator fragments into the bulk of

the reaction solution. This process might be rate controlling as the concentration of radicals at the electrode is increased.

The rates of the reactions at 20 milliamperes were at first unexpected. At constant monomer concentration, the rate is high at either low or high concentrations of the reducible organic compound. At low concentrations, the rate is high because only small amounts of low molecular weight material are formed. At intermediate concentrations, the rate appears lower since an increasing amount of monomer is used up in reactions producing low molecular weight materials. As the concentration of the reducible organic compound increases, the true rate of the reaction steadily increases and thus the yield of polymer also shows an increase.
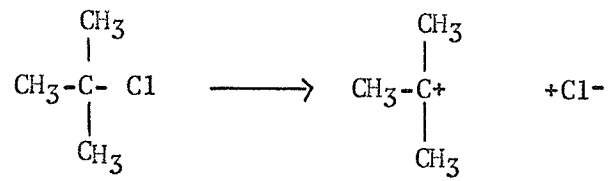
Free radical reactions are known to be inhibited by p-benzoquinone. The polymerization of methyl methacrylate in this system was completely inhibited by the addition of benzoquinone to the reaction solution, thus this reaction must be completely free radical in nature. If any ionic polymerization took place as well as free radical, the presence of the quinone would not have affected it and a small yield would have been noted.

Experiments in which the divided cell was used were rather disappointing, since the sintered glass disc did not prevent all diffusion from one side of the cell to the other. The fact that three times as much polymer was found in the cathode compartment as in the anode compartment suggested that most of the reaction took place at the cathode, but whether polymer had also formed at the anode or whether it had diffused over to the anode compartment, possibly after becoming charged, was not known. When radio-
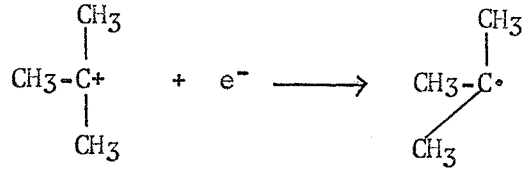
active methyl methacrylate was used, polymer in both compartments was found to have approximately the same activity. The activity had been totally in the cathode compartment at the beginning of the experiment. Either monomer diffused through to the anode and then reacted, or polymer already formed, diffused through. In the last experiment it was observed that the monomer activity in the cathode compartment was still twice the activity in the anode compartment after twenty hours. Since the polymer on both sides of the cell had approximately the same activity, it is not possible that it was formed separately at both electrodes. The highest activity that polymer formed at the anode could be expected to have would be half the activity of polymer at the cathode. Therefore, the polymer must form at the cathode.

The proposed initiation steps are the following:
tertiary butyl chloride reacts to give the tertiary butyl carbonium ion

$$
\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH_3-C-Cl}} \longrightarrow \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH_3-C+}} \quad +Cl^-
$$

The carbonium ion is reduced to the tert.-butyl radical

$$
\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH_3-C+}} \quad + \quad e^- \longrightarrow \underset{CH_3}{\overset{\overset{CH_3}{|}}{CH_3-C\cdot}}
$$

The radical then attacks monomer

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\bullet \quad + \quad CH_2 = \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\underset{\underset{\displaystyle O-CH_3}{|}}{C=0}}{|}}{C}} \quad \longrightarrow CH -\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\underset{\underset{\displaystyle O-CH_3}{|}}{C=0}}{|}}{C}}\bullet$$
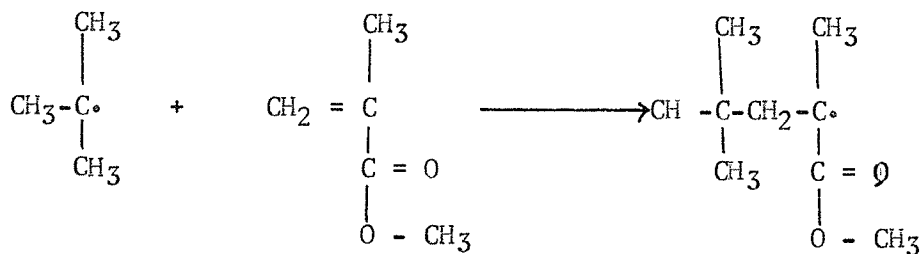
The salt, tertiary butyl ammonium chloride can also be reduced to the tertiary butyl radical.

$$(CH_3)_3-C-NH_3Cl \quad \longrightarrow \quad (CH_3)_3-C-NH_3^+ + Cl^-$$

$$(CH_3)_3-C-NH_3^+ \quad + e^- \longrightarrow (CH_3)_3-C-NH_3\bullet$$

$$(CH_3)_3-C-NH_3\bullet \quad \longrightarrow NH_3 \quad + \quad (CH_3)_3-C\bullet$$
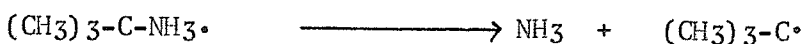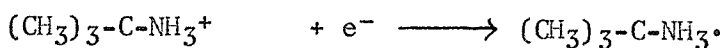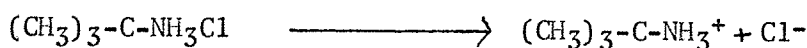
Thus salt alone can initiate the polymerization. Since there are about ten times as many moles of tertiary butyl chloride as tertiary butyl ammonium chloride in the solution, reactions in which initiation takes place only as a result of salt decomposition will be much less efficient.

The two different methods used to determine molecular weights in this work are complimentary. Viscosity measurements are quickly and easily accomplished. However there is an amount of uncertainty in obtaining values of the molecular weights from known intrinsic viscosities. Values used for the constants K and α in the formula $n = KM^\alpha$ must be those determined by some other worker. These values will depend on the molecular weight distribution in this worker's polymer samples.

The distribution depends on how the polymer was formed, and since the types of reaction systems vary, the distribution should also vary. Therefore in this work osmometry was used as an absolute method of determining

the molecular weights. The measurements are time consuming and exacting, so osmotic measurements were not made on every sample. Once a few have been done it is possible to plot the logarithm of the intrinsic viscosity against the logarithm of the molecular weight and from this graph obtain all the other molecular weight values.

We may conclude from this work that electrosensetization of electro-initiated polymerization can be accomplished by the addition of reducible organic compounds. Though many studies have been made of photosensetized photoinitiated reactions, their counterpart in the electrolytic field has been almost entirely neglected. Only two studies (4) (5) can be considered to deal with these phenomena. Both have many drawbacks.

Kolthoff's work was done mainly with aqueous systems, thus his choice of monomers was restricted to those which are at least partially soluble in water. Many important monomers must be totally neglected due to their insolubility. He tried to overcome this shortcoming by using emulsion systems but the only monomer that would polymerize under these conditions was acrylonitrile, which would also polymerize in the aqueous system.

Loveland's work, as stated in his patent, does not seem to have been carried very far. He gives no figures to indicate the efficiency of the system. Another shortcoming typical of patent coverage is that no attempt is made to explain the phenomena observed or postulate a likely mechanism by which the reaction could occur.

Though just one monomer was used in the present study other monomers could be made to polymerize by the proper choice of reducible compound.

The factors influencing this choice would be the ease with which the compound can be reduced to a radical and the reactivity of the radical thus formed. For less reactive monomers, radicals of greater reactivity would be chosen. Varying the solvent and the salt would also be expected to influence the efficiency of the reaction. The results of this research would seem to indicate that a further study of electrosensitization would be worthwhile.

SUMMARY

1. It was found that methyl methacrylate was polymerized by passage
    of an electric current through a solution of methyl methacrylate,
    dimethylformamide, and tertiary butyl ammonium chloride.

2. Electrosensitization of the above system was accomplished by the
    addition of small amounts of tertiary butyl chloride. This
    increased the reaction rate up to factors of six.

3. The efficiencies of this system are among the highest recorded
    for free radical reactions.

4. Unlike many electroinitiated reactions, this reaction was completely
    free radical in nature.

5. The reaction was found to take place only at the cathode.

6. An absolute number average method was used to calibrate the molecular
    weights of the polymers formed.

BIBLIOGRAPHY

1. Mackay, M. H. and Melville, H. W., Trans. Faraday Soc., 45, 323, (1949).

2. Bengough, W. I. and Melville, H. W., Proc. Roy. Soc. A., 225, 330, (1954).

3. Chinmayanandam, B. R. and Melville, H. W., Trans. Faraday Soc., 50, 73, (1954).

4. Kolthoff, I. M., and Ferstandig, L. L., J. Polymer Sci., 6, 563 (1951).

5. Loveland, J. W., Can. Patent 566, 294, (1956).

6. Staudinger, H. Ber., 53, 1073, (1920).

7. Taylor, H. S. and Jones, W. H., J. Amer. Chem. Soc., 52, 1111, (1930).

8. Seitzer, W. H., Goeckerman, R. H., and Tobolsky, A. V., J. Amer. Chem. Soc., 75, 755, (1953).

9. Barb, W. G., Disc. Faraday Soc. 12, 127, (1952).

10. Goldschmidt, S., and Stockl, E., Chem. Ber., 85, 630, (1952).

11. Lindsey, R. V., and Peterson, M. L., J. Amer. Chem. Soc., 81, 2073 (1959).

12. Smith, W. B., and Gilde, H. G., J. Amer. Chem. Soc., 81, 5325 (1959).

13. Smith, W. B., and Gilde, H. G., J. Amer. Chem. Soc., 82, 659 (1960).

14. Breitenbach, J. W., and Srna, Ch., Pure Appl. Chem., 4, 245 (1962).

15. Funt, B. L., and Yu, K. C., J. Polymer Sci., 62, 359 (1962).

16. Wilson, C. L., Record Chem. Progress, 10, 25 (1949).

17. Palit, R. S., and Das, M. N., Sci. and Culture (Calcutta), 16, 34 (1950). Ref. Chem. Abst., 45, 3189h (1951).

18. Dineen, E., Schwan, T. C., and Wilson, C. L., Trans. Electrochem. Soc., 96, 226 (1951).

19. Kern, W., and Quast, H., Makromol. Chem., <u>10</u>, 202 (1953).

20. Parrovano, G., J. Amer. Chem. Soc., <u>73</u>, 628 (1951).

21. Tsvetkov, N. S., Vyrokomol. Soedir., <u>3</u>, No. 4, 549 (1961).

22. Flory, P. J., J. Amer. Chem. Soc., <u>65</u>, 372 (1943).

23. Schaefgen, J. R. S., and Flory, P. J., J. Amer. Chem. Soc. <u>70</u>, 2709 (1948).

24. Staudinger, H. and Heuer, W., Ber., <u>63</u>, 222 (1930).

25. Huggins, M. L., J. Phys. Chem., <u>42</u>, 911 (1938).

26. Huggins, M. L., J. Phys. Chem., <u>43</u>, 439 (1939(.

27. Adams, R. and Johnson, J. R., Laboratory Experiments in Organic Chemistry, MacMillan Company, (1958).

28. Williams, F. D., M. Sc. Thesis, University of Manitoba (1960).