ELECTRO-INITIATED POLYMERIZATION IN A FLOW SYSTEM

presented by

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To my Parents

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ABSTRACT

The flow system method of kinetic study was applied to the electro-initiated polymerizations of acrylamide, acrylonitrile, and methyl methacrylate in various systems. The cases of both plug and stirred flow were examined with several different flow reaction cells containing different electrode materials (platinum, stainless steel, gold). Problems arising from heterogeneity were encountered in all trials in which polymer was produced except those involving the stirred flow anionic polymerization of methyl methacrylate in N,N-dimethylformamide with tetrabutylammonium iodide as conducting salt. Rates of polymerization found in the flow runs with this system were comparable to those determined in static runs with a similar system for a 40 volume-% monomer concentration, but fell off much more rapidly at intermediate conversions than rates for static runs with a 20 volume-% monomer concentration. Several reasons for the discrepancy were suggested.

Efforts towards the condensation polymerization of long-chain dicarboxylic acids (sebacic acid, suberic acid, 1,10-decanedicarboxylic acid) to polyethylene by the Kolbe reaction resulted in an insoluble substance formed at the anode upon electrolysis of a partially-neutralized methanolic solution of the acids at platinum electrodes. I.R. spectra of the substance obtained suggested no polymethylene chains were present.

I. ELECTRO-INITIATED POLYMERIZATION IN A FLOW SYSTEM

A. INTRODUCTION

1. THEORY OF FLOW SYSTEMS.

When a flow system is used in a kinetic experiment, the procedure is to pass a gas or liquid at a known rate of flow through a reactor, in which the reactants are activated by some means. The material emerging (outflow solution) is then analyzed to determine the amount of reaction that occurred in the reaction compartment. The order of the reaction and the rate constant can then be calculated if experiments are done over a range of flow rates and concentrations.

There are two types of flow systems. In the first, there is no stirring in the reactor, and the flow through it is sometimes spoken of as "plug flow". In the second, stirring is effected which is sufficiently vigorous to render the solution in the reactor homogeneous.

Plug Flow:

The case of plug flow is shown schematically in Figure 1. The reaction mixture passes through the reactor with a volume rate of flow (expressed, for example, in milliliters per hour) equal to "u". Consider a slab of volume dV in the reactor, and suppose that the reaction rate "v" depends on the concentration of only one reactant. In this example of a 1st order reaction, the rate of disappearance of the controlling reactant would be

$$v = -\frac{dc}{dt} = kc$$

where "c" is the number of moles per unit volume (reactant concentration),

and "k" is the 1st order rate constant in units of time^{-1}. The number of moles of reactant disappearing in the reactor in unit time in a volume dV is then kcdV.

After the reaction has been proceeding for a sufficient time, a steady-state condition is established in which the concentration of reactant in the slab of volume dV is constant with time. Three processes actually contribute to the steady state as follows (see Figure 1):

(a) Molecules of reactant enter the slab by the left face, the number of moles entering in time interval dt being ucdt.

(b) Molecules leave the slab by the right face, the number of moles doing so in time interval dt being u(c - dc)dt.

(c) Molecules disappear in the slab of volume dV by chemical reaction; for the 1st order case the number of moles disappearing in time interval dt is kcdVdt.

The steady-state relationship for the slab is obtained by equating the rate of entry of reactant into the slab (by process a) to the rate of removal (by processes b and c). If this is done one gets

$$ucdt = u(c - dc)dt - kcdVdt$$

which reduces to

$$-\frac{dc}{c} = \frac{k}{u}dV$$

Choosing u constant and integrating over the entire volume of the reactor from $V = 0$ and $c = c_i$ (initial or inflow reactant concentration) at the reactor entrance to $V = V_o$ and $c = c_f$ (final or outflow reactant concentration) at the reactor exit, we arrange the intended integration as

FIGURE 1.

PLUG FLOW – SCHEMATIC DIAGRAM.

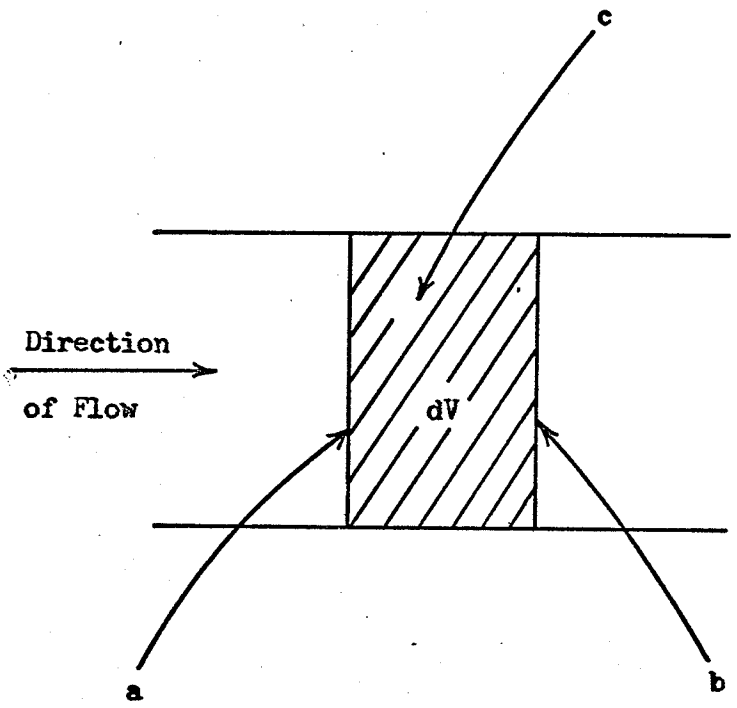
(a) ucdt moles enter in time interval dt

(b) u(c – dc)dt moles leave in time interval dt.

(c) kcdVdt moles disappear by chemical reaction in time interval dt in volume dV

Figure 1.

PLUG FLOW - SCHEMATIC DIAGRAM.



$$-\int_{c_i}^{c_f} \frac{dc}{c} = \frac{k}{u}\int_{0}^{V_o} dV$$

which, upon integration, yields

$$\ln \frac{c_f}{c_i} = -\frac{kV_o}{u} \quad .$$

It may be noticed that the above equation becomes identical with that associated with a static 1st order system if $\frac{V_o}{u}$ is replaced by t. This quantity $\frac{V_o}{u}$ is known as the residence time or contact time and is the average time that a molecule takes to pass through the reactor.

The residence time (t_r) may be varied by changing u, the flow rate, or by varying V_o, the reactor volume. Usually, the reactor volume is fixed and the flow rate varied.

By using a high flow rate and a small reactor volume, one can do kinetics of reactions that are too rapid for convenient study in a static system.

The integrated rate equation for a flow system for a certain order reaction may be obtained from that describing a static system if one replaces the reaction time "t" in the static rate equation with the residence time "t_r".

It has been implicitly assumed that there is no volume change during the course of reaction in the hypothetical flow system discussed (eg. gas evolution, solid precipitation, etc.). Any such change would cause the flow rate to vary throughout the reactor and erroneous measurements to be made. These volume changes may be taken account of in the derivation of the rate equations (1), but the resulting equations are very cumbersome, therefore flow system work has been restricted largely to homogeneous reactions.

Stirred Flow:

In the case of a stirred flow reactor, in which the solution in the reactor is homogeneous, the reactor as a whole is considered rather than a thin slab. If the same symbols used in the plug flow derivation are allowed to represent the same quantities and the rate of entry of reactant into the reactor is equated to the sum of the rates of removal as before, we get

$$uc_i = vV_o + uc_f$$

or, rearranging,

$$v = \frac{u(c_i - c_f)}{V_o} \quad .$$

The measurement of c_i and c_f at a given flow rate thus allows the reaction rate to be calculated. The order of the reaction and the rate constant can then be determined by working at different initial concentrations and feed rates. Usually, however, it is the integrated rate equation which is tested by the data and not the above differential form.

2. ELECTRO-INITIATED POLYMERIZATIONS OF INTEREST IN THE FLOW STUDIES:

All electrolytic polymerizations of vinyl monomers attempted with the flow system method were of either the free radical or anionic type and had been investigated previously by various workers using the static method.

Free Radical Polymerizations:

a. Acrylamide (AAm):

G. S. Shapoval and V. I. Shapoval used the system 10% AAm in water with potassium persulfate ($K_2S_2O_8$) as electrolyte and reported high yields (50-100%) and high molecular weight products (intrinsic viscosity 1 to 4.5) at current densities of 20-110 microamperes/cm.^{2} for amalgamated silver, 20-100 for nickel, and 20-90 for platinum electrodes after approx. 3 hours electrolysis at room temperature (2).

Polarographic tests in the presence of AAm confirmed the initiation potential of the reducible persulfate anion.

A number of experiments were performed to obtain information about the kinetics of the electrochemical polymerization process. Two characteristics of electrochemical initiation were apparent: a constant rate of initiation, and use of a layer near the electrode as a site of initiation.

Cathodic reduction of the persulfate anion resulting in formation of the sulfate ion-radical which could then initiate a chain was suggested as the initiation mechanism; this mechanism is as follows:

(1) $S_2O_8^{=} + e \longrightarrow SO_4^{=} + SO_4^{-}\cdot$

(2) $SO_4^{-}\cdot + M \longrightarrow \cdot MSO_4^{-}$

(3) $\cdot MSO_4^{-} + M \longrightarrow \cdot MMSO_4^{-}$, etc.

where M is a molecule of monomeric AAm and $SO_4^{-}\cdot$ is the sulfate ion-radical.

b. Acrylonitrile (AcN):

The aqueous, free radical electro-polymerization of AcN in several systems by Kolthoff and Ferstandig (3) is an excellent example of the indirect electrochemical initiation of polymerization in which the initiating species (be it an ion or radical) is produced by a non-electrode reaction between a primary, non-initiating species produced at the electrode by electron transfer to or from a charged or neutral substrate, and a second substrate.

The radical-generating redox activation systems they used were:

(1) $Fe^{+3} + e \longrightarrow Fe^{+2}$

then (2) $Fe^{+2} + H_2O_2 \longrightarrow Fe^{+3} + OH^{-} + HO\cdot$

or (3) $Fe^{+2} + S_2O_8^{=} \longrightarrow Fe^{+3} + SO_4^{=} + SO_4^{-}\cdot$

where ferric ion is the first substrate, ferrous ion is the primary, non-initiating species formed by reduction of ferric ion, persulfate ion or hydrogen peroxide is the second substrate, and the sulfate ion-radical or the hydroxyl radical is the species initiating free radical polymerization.

Anionic Polymerizations:

Unlike the free radical polymerizations, anionic polymerizations are usually limited to nonaqueous media. Such reactions offer higher current efficiencies than those possible with free radical systems.

a. AcN:

Funt and Williams (4) investigated the polymerization of AcN in N,N-dimethylformamide (DMF) saturated with sodium nitrate.

Static kinetic runs at 30°C were carried out at six different currents from 0.9 to 125 milliamperes using 37 mole-% AcN, then at nine different initial monomer concentrations with a fixed current of 15 ma. A 1st order dependence on monomer concentration was observed.

When 37 mole% AcN in DMF saturated with $NaNO_3$ was electrolyzed in a divided cell, the amount of cathode polymer far exceeded the amount of anode polymer. This relative yield could be accounted for by an anionic polymerization mechanism.

The anionic character of the polymerization of AcN when $NaNO_3$ was used as electrolyte was further substantiated by copolymerization studies of AcN with Methyl methacrylate (MMA). When an equimolar mixture of AcN and MMA is polymerized by a free radical mechanism, the resulting copolymer should contain both species in approx. equal amounts. If the polymerization is anionic, then the mixture should contain predominantly AcN (5,6). A cationic polymerization would be manifested by a difficulty in forming any polymer at all (7).

When a solution containing 54.1 wt.-% MMA and 45.9 wt.-% AcN in DMF

saturated with $NaNO_3$ was actually polymerized, the polymer formed was 100% AcN, suggesting that the propagation mechanism was anionic.

Data for other salts than $NaNO_3$ indicated a possibility of free radical and ionic polymerization at the same electrode.

The nature of the chain-initiating step was investigated through polarographic measurements, and the authors concluded that probable chain initiation is by direct electron addition to a molecule of monomer to produce an ion-radical of the type

$$CH_2\overset{H}{\underset{R}{C}}:- \longleftrightarrow -:CH_2\overset{H}{\underset{R}{C}} \quad .$$

Two of these ion-radicals may then combine to form the dianion

$$-:\overset{H}{\underset{R}{C}}CH_2CH_2\overset{H}{\underset{R}{C}}:-$$

which is able to propagate anionically at both ends.

It is conceivable that if combination did not occur under certain conditions, the ion-radical could initiate free radical propagation from one end and anionic propagation from the other.

b. MMA:

The electro-initiated, anionic polymerization of MMA in DMF with several different quaternary ammonium salts was reported by Funt and Bhadani (8).

Static runs were performed with 40 volume-% MMA in DMF saturated with tetramethylammonium chloride (NMe_4Cl) at seven different currents from 10 to 120 ma., also with seven different initial monomer concentrations

(from 20-80% MMA by volume) at a fixed current of 15 ma. A 1st order dependence on monomer concentration was found in all cases.

Several runs were also carried out at 15 ma. for a period of 23 hours using 40 volume-% MMA in DMF and various tetra-alkyl ammonium salts (1 g. per 100 ml.). Polymer yield appeared to be independent of the anion of the salt, while the cation exerted a marked influence on the amount of polymer formed. Runs with tetrabutylammonium salts produced considerably more polymer than runs with tetramethylammonium salts, both with the same anion. No mechanism was postulated, however.

Polymer was observed to form at the cathode, free radical inhibitors such as p-benzoquinone and p-tert-butylcatechol did not affect the yield of polymer, and electrolysis of a mixture containing styrene and MMA in a 1:1 molar ratio and NMe_4Cl in either dimethylsulfoxide or dimethylacetamide yielded MMA homopolymer. The above evidence points unmistakeably towards an anionic reaction mechanism similar to that postulated by Funt and Williams (4)

The rate constants were found to depend on the square root of the current, however, unlike previous polymerizations studied in this laboratory (9). The authors stated that such a phenomenon could be accounted for if one postulated association (in which ion pairs consisting of quaternary ammonium cations and growing polymer chains associate to form complexes) in the process of chain propagation.

3. KINETICS IN A SYSTEM OF VARYING VOLUME - THE VOLUME EFFECT.

Whenever a flux-type reactant activator such as electrical current or electromagnetic radiation is used in systems where the reactor volume may vary while the activator is fed in at a constant rate, the "volume effect" may be encountered.

Consider the two hypothetical electro-polymerization cells in Figure 2 charged with the same monomer solution, both of which are equivalent with respect to electrode area and current passing, but whose reactor volumes are different, being 100 ml. and 50 ml.

Obviously, at any time "t" after the current has been switched on, the concentration of polymer in the smaller volume will be two times that in the larger volume, provided the total amount of polymer produced per Faraday is the same. This would be exactly the case for a "0" order reaction, whereas for a reaction 1st order with respect to monomer, the more rapid depletion of monomer in the smaller volume would cause the relative concentration factor for the two idealized cells to be somewhat less than two.

During an actual kinetic run using a cell similar to those just discussed, samples of solution varying from 2 to 5 ml. in volume may be withdrawn at different times for analysis. The solution volume at the time of removal of the last sample may be as little as 60-70% of the volume started with, depending on the size and number of samples taken.

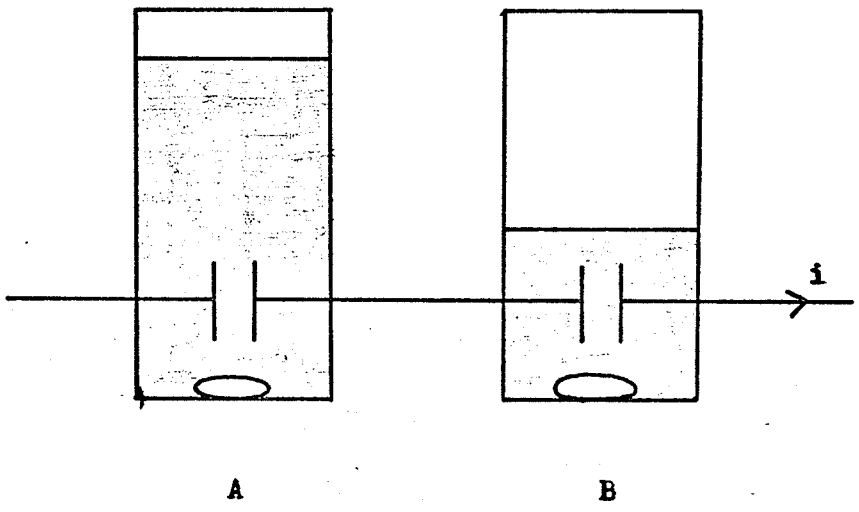
As a result, polymer is being produced in a smaller and smaller volume all the time, and the nature of the reaction solution (in particular the polymer and monomer concentrations) in contact with the electrodes is not what it would have been had the volume been fixed. If the reaction

FIGURE 2.

TWO HYPOTHETICAL STATIC ELECTRO-POLYMERIZATION CELLS.

	Cell A	Cell B
Volume reaction solution	100 ml.	50 ml.
Initial monomer concentration	M	M
Current passing	i	i
Polymer concentration at time "t"	x	2x

FIGURE 2.



rate is sensitive to this concentration difference, a "volume effect" is present.

If the course of reaction is arbitrarily assumed to be independent of the rate of change of composition of reaction solution induced by a decreasing reaction volume, one may apply corrections for the volume decrease to the sample analyses to arrive at data for a volume-invariant reaction under the same conditions.

There is no justification for making such an assumption for a reaction unless experimental evidence is obtained showing that the additional rate of increase of polymer concentration (or rate of decrease of monomer concentration) caused by a decreasing reaction volume over and above the rate of production of polymer by chemical reaction has no effect on the reaction rate. Unless such a procedure is followed, the above assumption would be invalid.

Assuming a volume effect does exist for a particular reaction, it is mathematically possible to correct the data from a kinetic run of varying reaction volume provided sample withdrawal is temporally regular and to arrive at results for a volume-invariant run, but such corrections are quite lengthy, hence the most convenient way to assess the significance of the volume effect would be via comparisons between experimental kinetic runs free of and vulnerable to the volume effect.

There are two experimental methods of doing kinetics which circumvent the volume effect. The first method is to do one kinetic run to evaluate one polymer concentration at a given reaction time, that is, doing one kinetic run to get one point on a curve. The chief disadvantage of this

sequential method is that the runs are always done with slightly differing solutions. The method lacks reproducibility due to the susceptibility of electro-initiated polymerizations to inhibition by trace impurities as evidenced by the occurrence of different inhibition times under supposedly identical conditions.

The second way to obtain kinetic data free of the necessity of correction is to use a flow system. Here, since it is the outflow solution which is sampled and analyzed, the data is implicitly free of the volume effect. By comparing the kinetic parameters for a system subjected to both static and flow studies, it should be possible to determine whether a volume effect of significant proportion in the static system has in any way camouflaged the true kinetic picture.

B. EXPERIMENTAL

1. PREPARATION OF MATERIALS.

Monomers:

Eastman (Practical) and Matheson, Coleman, and Bell (Practical) acrylonitrile monomer was purified by drying over CaO for several days. It was then fractionally distilled at reduced pressure in the apparatus shown in Figure 3.

Methyl methacrylate monomer from Eastman Chemicals and Matheson, Coleman, and Bell was stirred over CaH_2 for several days, stored in a cold room at approx. 0°C, and fractionally distilled in vacuo at room temperature (20-25°C) immediately prior to use.

Solvents:

Before use, Fisher Certified Grade N,N-dimethylformamide was stirred over CaH_2 for several days and fractionally distilled under vacuum at approx. 40°C. The distilled DMF was stored in a dry box under positive nitrogen pressure prior to preparation of the reactant solutions.

Salts:

Tetramethylammonium chloride (Matheson, Coleman, and Bell) was purified by dissolving in methanol, precipitating with an excess of ether, and drying in a vacuum dessicator for several hours (10).

A new bottle of tetrabutylammonium iodide (Eastman Chemicals) was opened and kept continuously in a dry box under positive nitrogen pressure.

Other reagents were used without purification unless otherwise stated.

2. APPARATUS.

Fractional Distillation Apparatus: (Figure 3)

Essentially the same apparatus was used for all distillations, the only components changed being the source of heat to the distillation flask (water bath for MMA and AcN; mantle for DMF), and the different receivers and distillation flasks. A two-way stopcock (a) which was part of and integral with a specially constructed adapter, and a three-way stopcock (b) enabled control of the vacuum and exclusion of air from the system to be effected when receivers were changed. Vacuum was supplied by a rotary mechanical pump protected by cool and cold traps.

Flow System Apparatus:

A flow system apparatus consists of two principal components: the means of producing and controlling a flow (the drive assembly), and a component through which the reactant liquid is forced to flow by the drive assembly and within which a reaction is caused to occur by some activator (the reaction cell).

a. The Drive Assembly:

In previous papers reporting the use of flow systems, a constant pressure head device was inevitably used to produce a uniform and controllable flow rate (11,12).

In the present work, constant and reproducible flow rates were achieved by employing a 100 cc. B-D Yale Luer-Lok syringe clamped and driven by a 1" micrometer coupled via an extensible drive shaft to an

FIGURE 3.

A SIMPLE APPARATUS FOR IN VACUO FRACTIONAL DISTILLATION OF HYGROSCOPIC MONOMERS AND SOLVENTS.

(a) two-way stopcock

(b) three-way stopcock

(c) adapter

(d) nitrogen

(e) receiver

(f) condenser cooling water

(g) condenser

(h) thermometer

(i) fractionation column

(j) distillation flask

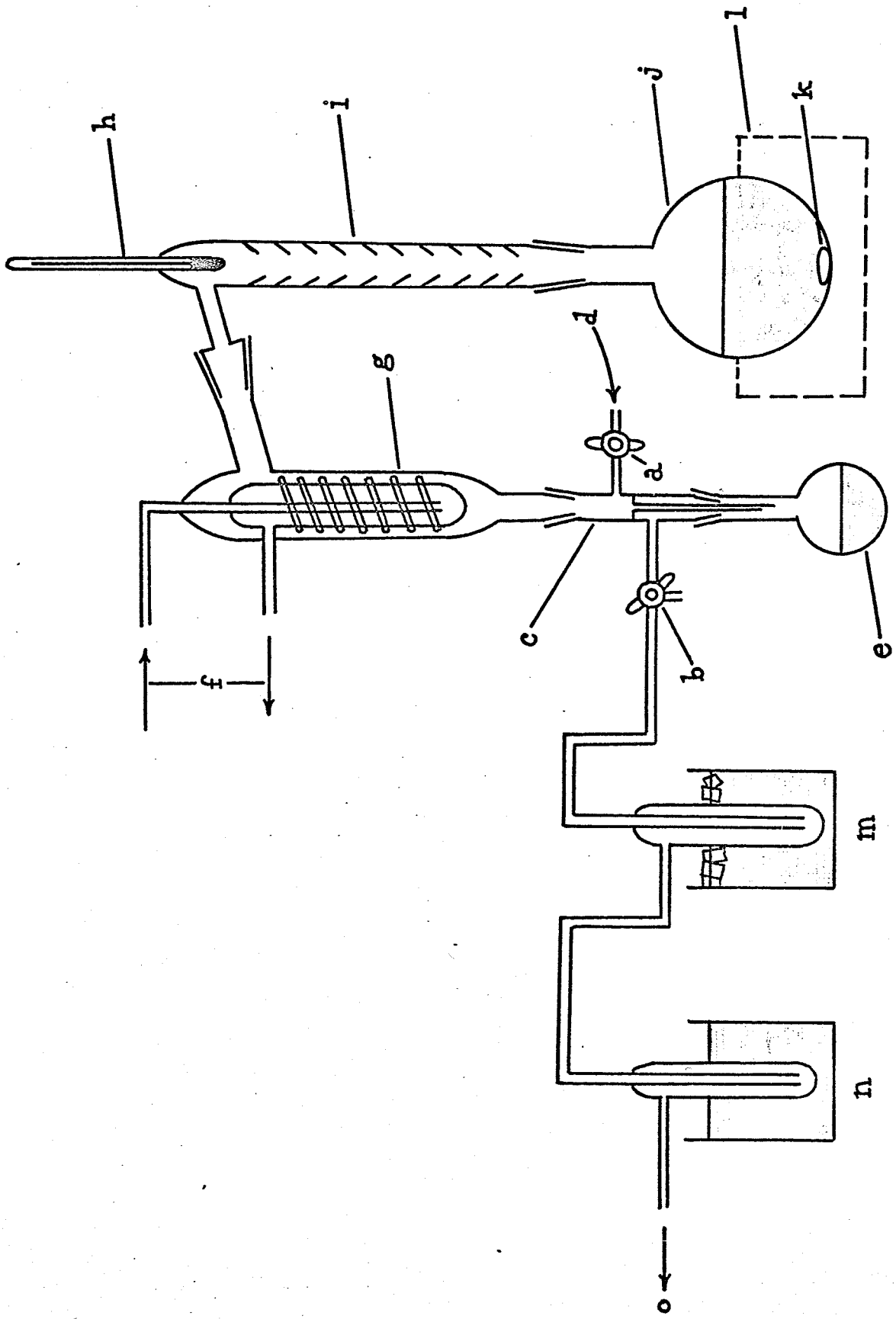
(k) stirring magnet

(l) source of heat to distillation flask (varies)

(m) cool trap (ice water)

(n) cold trap (liquid nitrogen)

(o) vacuum line


h
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j
l
k
d
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e
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o

adjustable ratio gear reducer, which was driven in turn through interchangeable Meccano gears by a 10 r.p.m. synchronous motor.

The reduction of the gear box alone varied from about 8:1 to about 50:1, but the range could be improved by installing additional gears between it and the drive motor (Figure 4).

Flow rates were related to micrometer speed in the following way: the syringe was filled with water at 25°C, clamped into place, and the motor switched on. Several portions of water were collected in stopwatch-measured intervals of time. By weighing the water collected and knowing the density at 25°C, the volume of water expelled from the syringe in the measured time and hence the flow rate (in ml./sec. or ml./hr.) corresponding to this particular micrometer speed could be calculated. It was then a simple matter to calculate the flow rate at another micrometer speed when the ratio was varied.

Using the 100 cc. syringe, flow rates obtainable, using only the adjustable ratio gear box for reduction, varied from 10-60 ml./hr. The same syringe used in the calibration of the flow rates was used for the flow runs.

The throw of the micrometer and the size of the syringe both exercised control over the total amount of solution which could be expelled from the syringe with this type of drive assembly. Using the largest syringe which was suitable and available (100 cc.) and the 1" micrometer, the maximum volume that could flow was approx. 25 ml.

Since 2 ml. samples were desired for analysis and volumes of comparable magnitude had to flow through the reaction cell and become waste while the

FIGURE 4.

FLOW SYSTEM DRIVE ASSEMBLY.

(Semi-schematic - top view)

(a) to flow cell

(b) syringe

(c) reactant solution

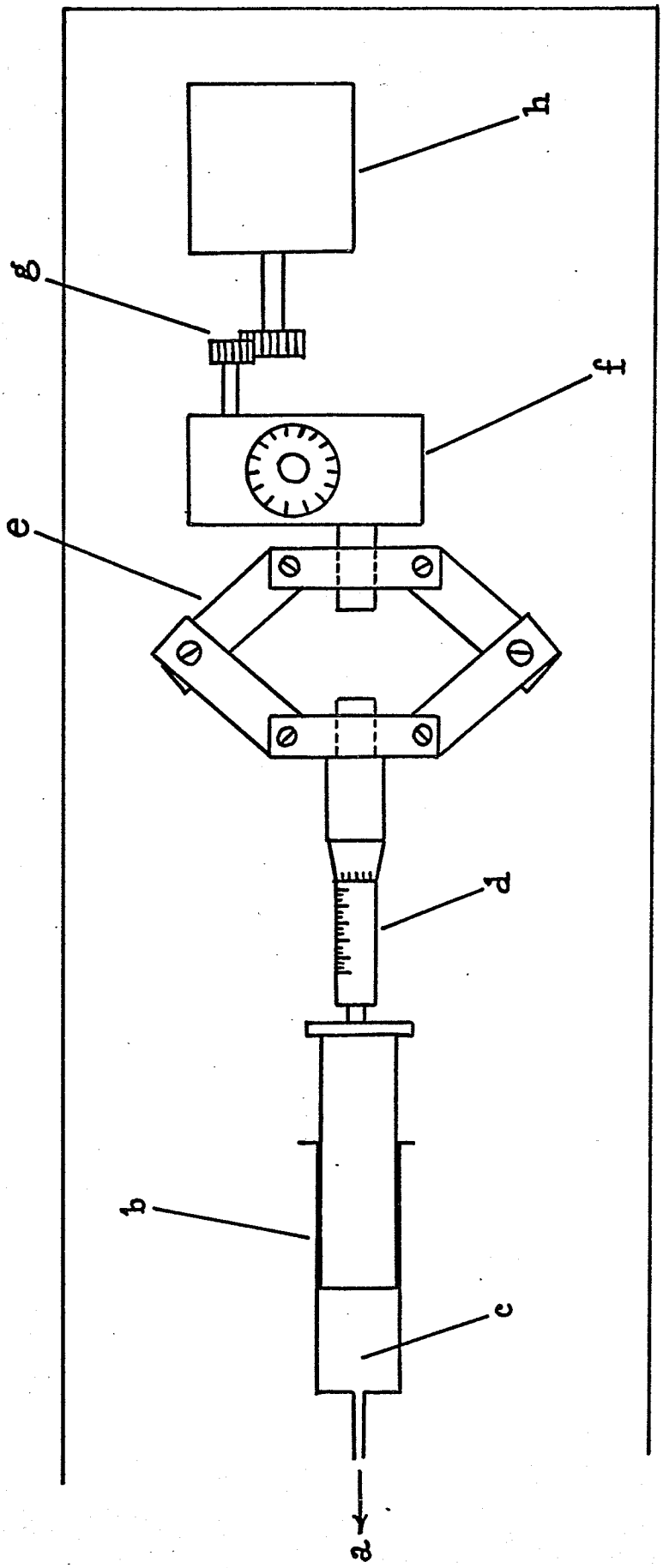
(d) micrometer

(e) extensible drive shaft

(f) adjustable ratio gear reducer

(g) secondary reduction gears

(h) constant speed electric motor


h
g
f
e
d
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c
a

steady-state condition was being re-achieved after a change in the flow rate, it was found that five was the maximum number of 2 ml. samples containing different concentrations of polymer it was possible to collect using the above apparatus. More would be possible with a larger micrometer and/or a larger syringe.

b. Reaction Cells:

Both plug and stirred flow cells have been used in conjunction with the drive assembly just described.

(i) Plug Flow Cells:

The plug flow cells employed have all been concentric in design, since this arrangement prevents the existence of "dead spots" in the reactor, where a small parcel of solution could become temporarily immobile and cause erratic data on product formation. Three plug flow cells varying in design and construction material were fabricated, only one of which exhibited suitable operation.

The first plug flow cell (Figure 5) was fashioned from glass tubing and had as electrodes a platinum wire concentric with a 1" X 1" platinum square bent to form a cylinder. Electrical connections were via mercury side-tubes, and the entire cell was enclosed by a water jacket through which water at 25°C could be circulated by a constant temperature pump (controlled by a rheostat) immersed in a 10-12 liter water reservoir.

Disadvantages of this cell which became apparent after several trial runs were inability to be taken apart and cleaned, insufficient area of electrodes to enable passage of currents of the order of 5-10 milliamperes

FIGURE 5.

PLUG FLOW CELL I.

(Cross-sectional side view)

(a) inflow solution tube)
) small-diameter teflon tubing
(b) outflow solution tube)

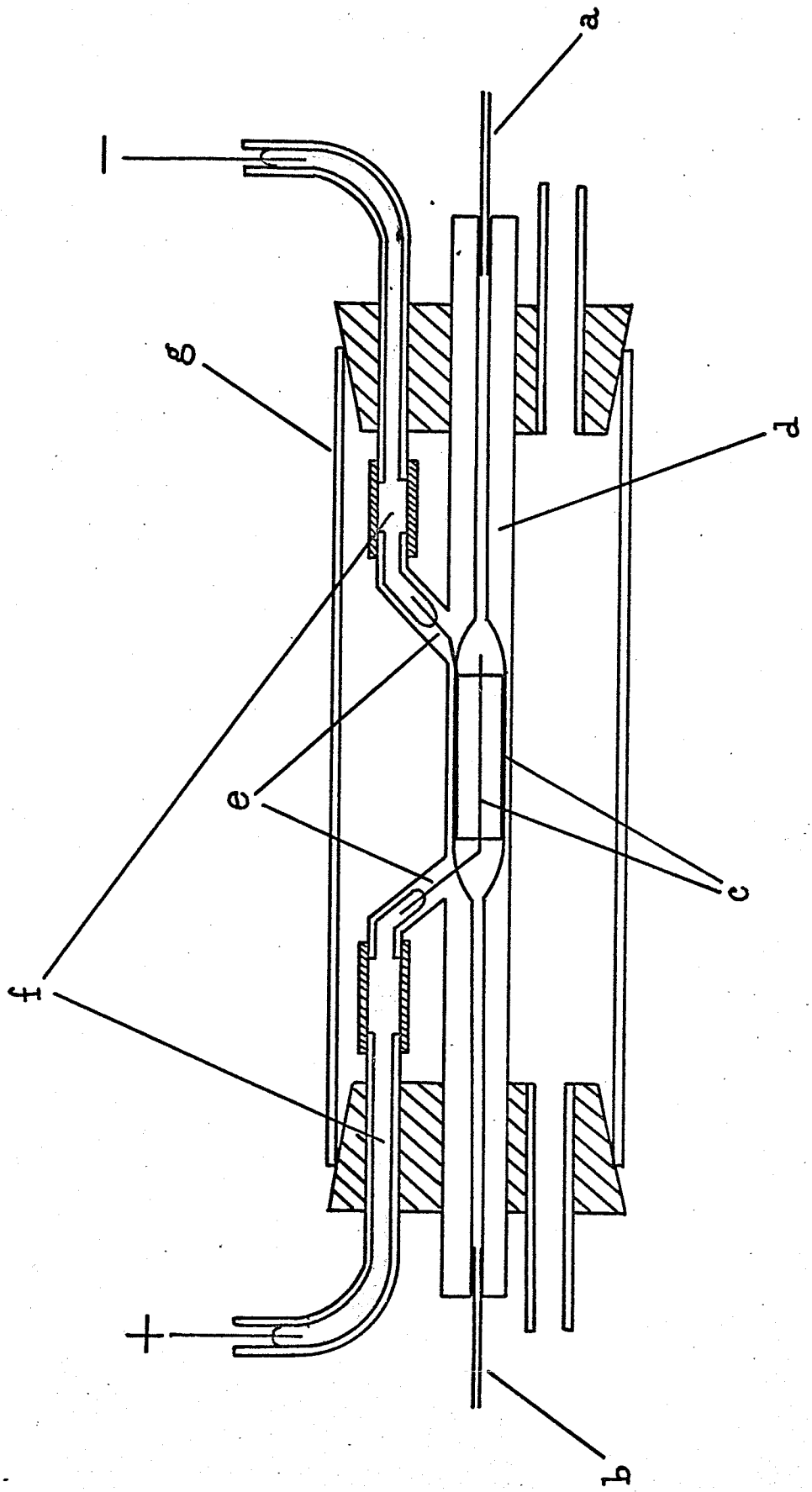
(c) platinum electrodes

(d) glass tubing

(e) platinum wire connections to electrodes

(f) mercury side-tubes

(g) water jacket


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without application of excessive voltages, and difficulty in determining the reactor volume (needed in order to calculate the residence time). Despite these handicaps, this cell showed, in the few times it was used, a handling convenience and rugged dependability.

Plug flow cell II (Figure 6) was the least successful operationally of all the cells used. It consisted of a glass rod concentric with a glass tube, both of which were coated with a very thin layer of platinum by firing a special paint, which when applied to a glass surface and fired at high temperature in an oxidizing atmosphere leaves such a coating. Un-platinized glass beads on the rod held it away from the tube wall and prevented short-circuiting of the electrodes.

Teflon end plugs through which small-diameter teflon tubing was passed were installed at either end of the glass tube. A water jacket was fitted, and friction electrical connections were made from the electrodes to two connecting posts via platinum wires.

The electrode area in this cell appeared quite adequate, but like the previous cell discussed it could not be disassembled for cleaning.

In the disastrous first and only trial with this cell, the platinum coating stripped off the glass and rendered the cell unserviceable.

The last but most successful plug flow cell from an operational point of view was comprised of a stainless steel rod inside and concentric with a stainless steel tube (Figure 7). Teflon end-pieces ensured the fluid-tightness of the cell and could be unscrewed, thus facilitating a thorough cleaning of the cell compartment after each run, which had been a disadvantage of earlier cells. The generous area of the electrodes (approx. 2 $in.^2$)

FIGURE 6.

PLUG FLOW CELL II.

(Cross-sectional side view)

(a) inflow tube)
) small-diameter teflon tubing
(b) outflow tube)

(c) glass tube (platinized inside)

(d) platinized glass rod

(e) glass beads (unplatinized)

(f) water jacket

(g) teflon end-plugs

(h) binding posts and electrical connections

FIGURE 6.

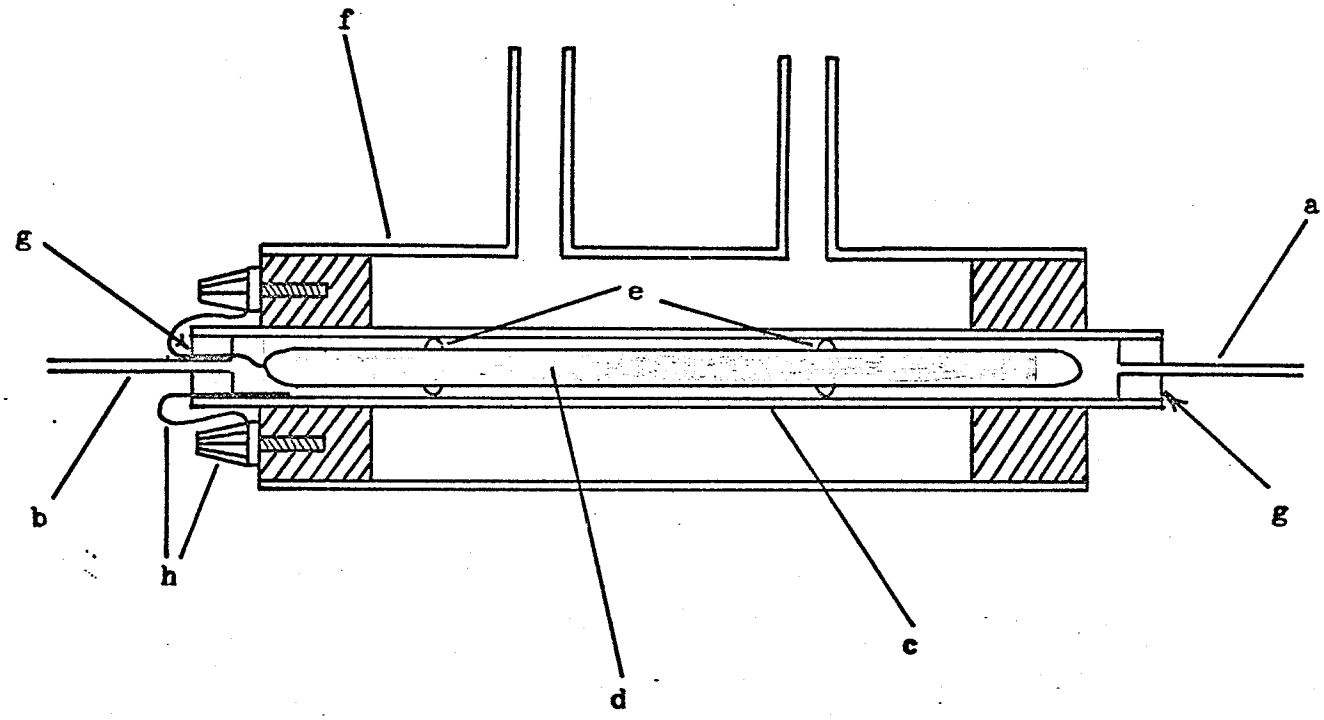


FIGURE 7.

PLUG FLOW CELL III.

(Cross-sectional side view)

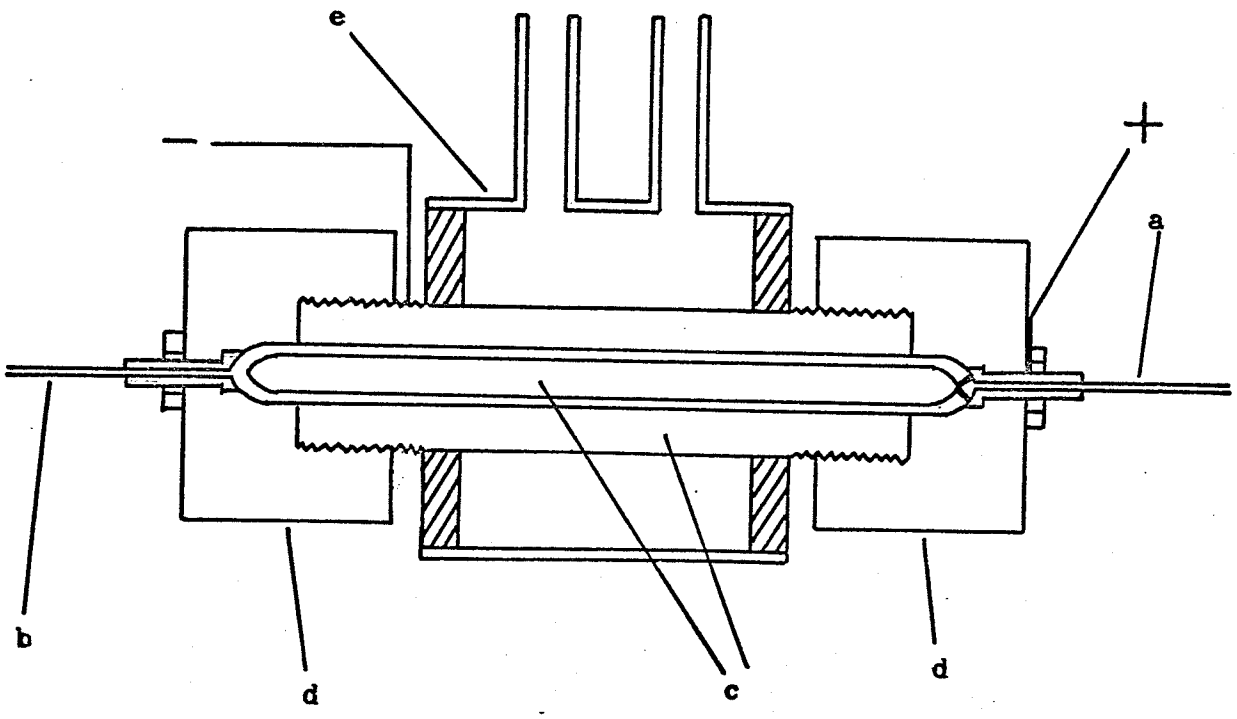
(a) inflow solution tube)
) small-diameter teflon tubing
(b) outflow solution tube)

(c) stainless steel electrodes

(d) teflon end-plugs

(e) water jacket

FIGURE 7.



kept voltages low and in so doing prevented possible corrosion of the stainless steel electrodes. Again, a water jacket was standard equipment.

The volume of the reactor in the above cell was found by calculation to be 0.552 cc., using the measured dimensions of the machined parts involved.

(ii) Stirred Flow Cells:

Only one stirred flow cell was constructed (Figure 8), but it has proven so convenient to use and successful with the systems examined that no others were deemed necessary.

The cell reaction compartment was defined by two gold disc electrodes 1" in diameter fastened to the top and bottom of a piece of teflon shaped like a doughnut. In the reactor was a micro stirring magnet 1.5 cm. long to agitate and thereby make homogeneous any solution in the reactor. Inlet and outlet tubes (cut-off No.17 B-D Yale Luer-Lok syringe needles attached to small-diameter teflon tubing) were led in through the electrode spacer. The upper part of the cell contained a chamber through which water at 25°C was circulated in contact with the upper gold electrode (cathode).

Eight 4/40 brass screws held the cell together and provided a means of hanging it above a magnetic stirrer. The screws were narrowed on the lathe at certain positions along their lengths and fitted with approx. $\frac{1}{8}$" long collars of polyethylene tubing to prevent shorts between the anode (bottom gold electrode) and cathode, since all screws were connected to the anode. Stainless steel washers were fitted to the extreme top and bottom of the unit to prevent gouging and deformation of the teflon parts when the screws were tightened.

FIGURE 8.

STIRRED FLOW CELL.

(Cross-sectional side view)

(a) inflow tube

(b) outflow tube

(c) gold disc electrodes

(d) teflon electrode spacer

(e) stirring magnet

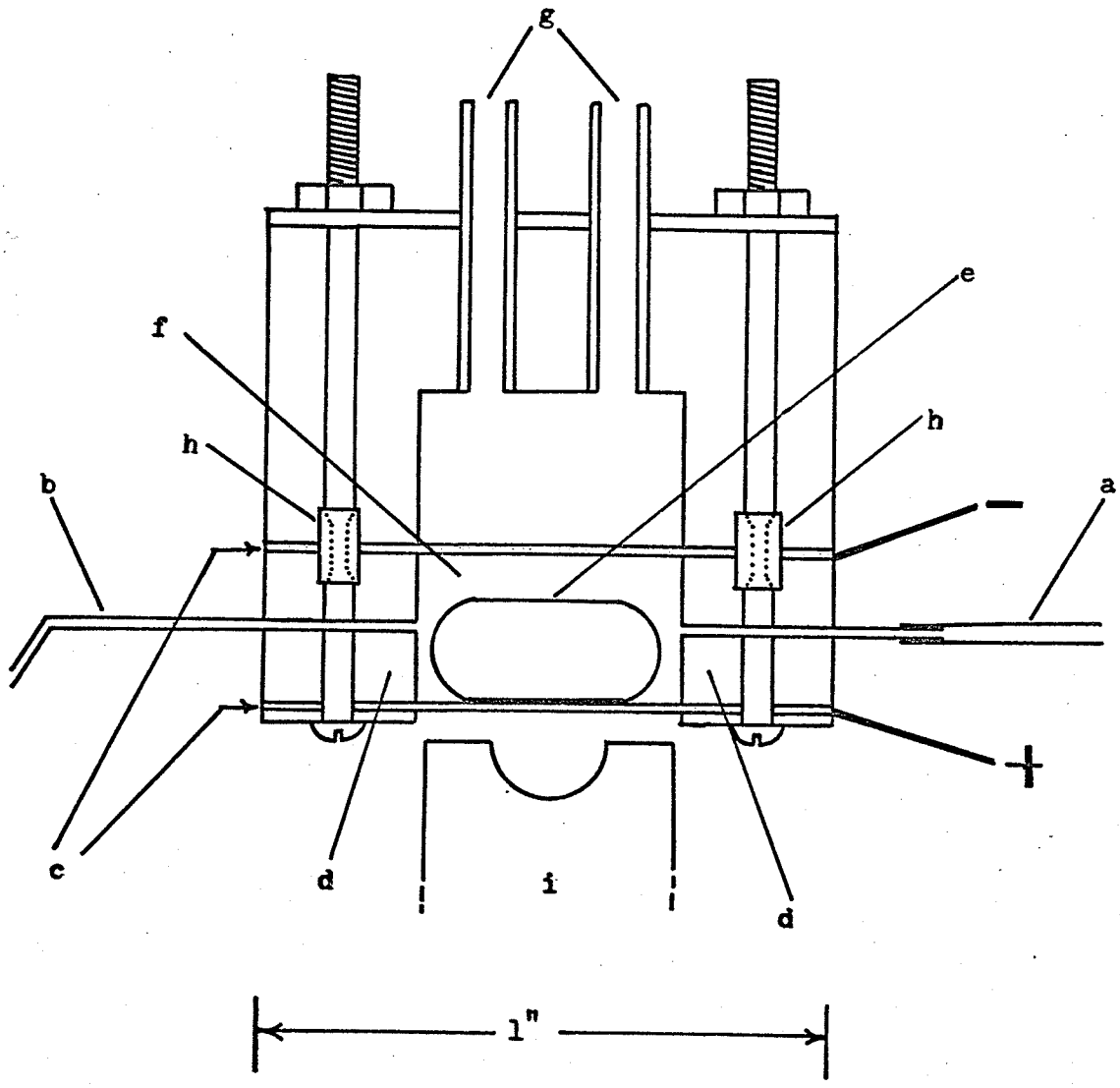
(f) reaction compartment

(g) water inlet and outlet tubes

(h) polyethylene collars

(i) magnetic stirrer

FIGURE 8.



The volume of the reactor in the above cell was found by filling with water and weighing and was 0.698 cc.

A stripped-down and modified conventional variable-speed magnetic stirrer was used to activate the stirring magnet in the cell, and a special bracket was constructed (Figures 9a and 9b) to hold the latter as close as possible to the driving magnet and also to facilitate electrical connections between the electrodes and the source of current. The above bracket, along with the magnetic stirrer, was secured to the same base as the drive assembly.

Current Sources:

Currents of 2-5 ma. were obtained using a constant current supply built by the Radio and Electrical Laboratories of the National Research Council and described in previous work in this laboratory (13).

Currents of 7-20 ma. were obtained from a high-voltage current stabilizer constructed in the Physics Department of the University of Manitoba and described in previous work in this laboratory (14).

A Power Designs constant current supply furnished currents from 25-500 ma. (maximum voltage 70 V.).

For low currents in the 200-300 microampere range, a 2 volt storage battery in series with the cell and a large resistance was employed.

3. POLYMERIZATION PROCEDURE.

Essentially the same procedure was followed whether the system was free-radical or anionic or whether the cells were of the plug or stirred flow type; the only components of the apparatus changed were the flow cells

FIGURE 9a.

STIRRED FLOW CELL (FRONT VIEW).

FIGURE 9b.

STIRRED FLOW CELL (SIDE VIEW).

(a) bracket

(b) stirred flow cell

(c) outflow tube

(d) magnetic stirrer

(e) water inlet and outlet tubes

FIGURE 9a.

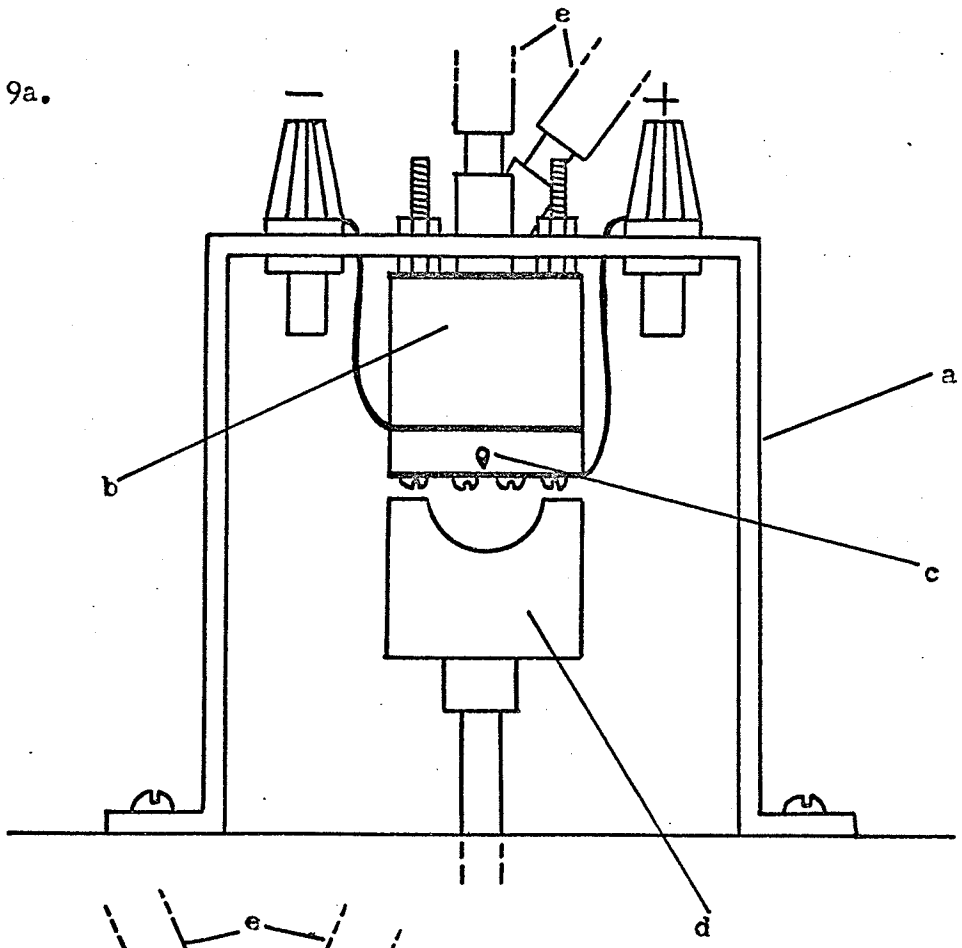
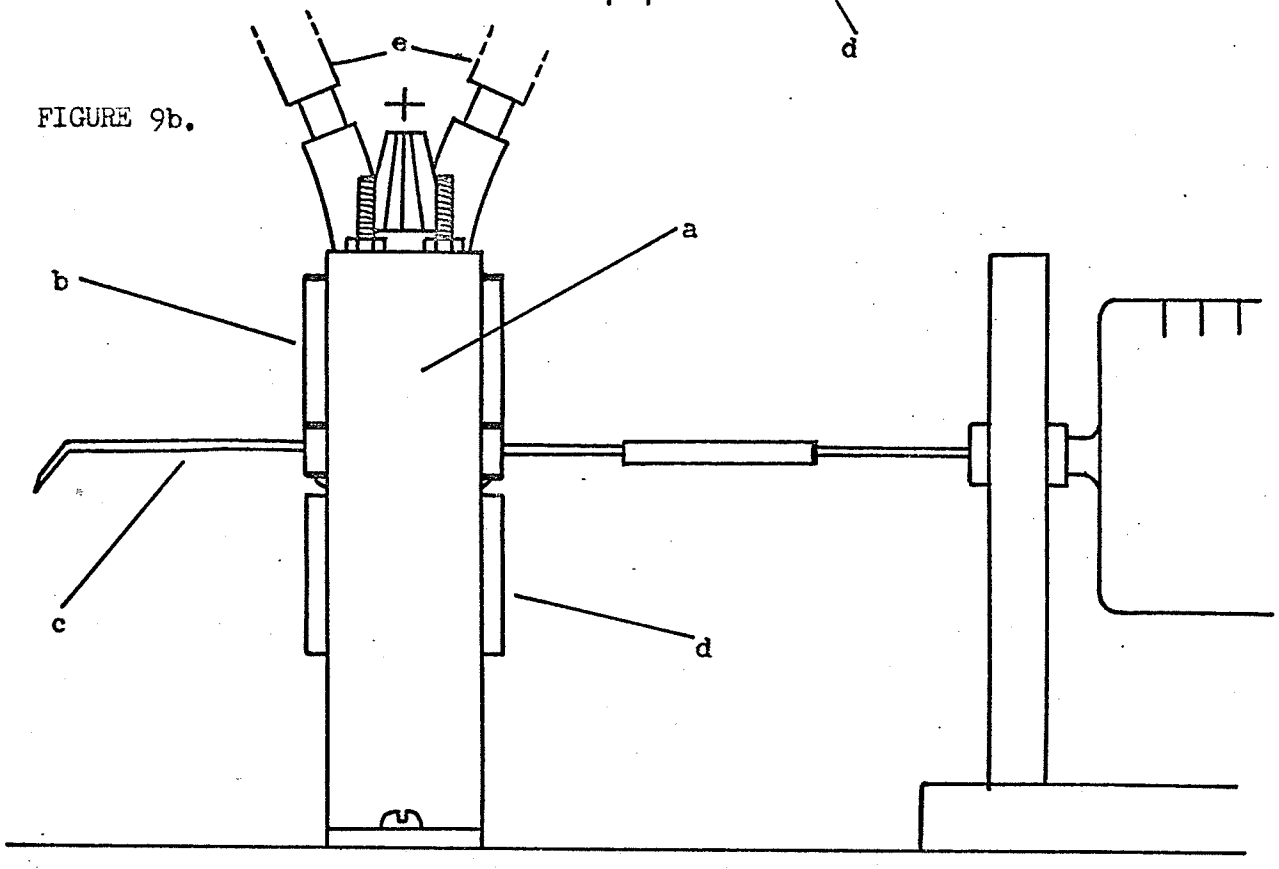


FIGURE 9b.



and the secondary reduction gears between the gear box and drive motor.

Approx. 20 ml. of monomer solution prepared in the dry box under positive nitrogen pressure and contained in a serum-capped flask was drawn into the syringe. The syringe was then held vertically (needle up) and air bubbles eliminated. With the syringe in this position, the flow cell was attached (also in the vertical position, in line with the axis of the syringe) and the plunger slowly pushed in, filling the reactor of the flow cell with monomer solution. The syringe and flow cell were then clamped into horizontal position for a flow run.

The outflow solution tube of the flow cell was immersed in the monomer solution in the flask and the syringe plunger drawn completely back to contact the micrometer. The flask was removed, and connections made to the flow cell for current and water. The apparatus was now in a position to begin a flow run.

The thermostatted water was circulated, and the drive assembly activated (current off). As soon as solution emerged from the outflow tube (at this point using the stirred flow cell the stirring was begun), the current supply was switched on and adjusted to give the desired current at a preset flow rate. Approx. 2 ml. of outflow solution was collected in a 3" test tube (used as outflow receivers in all runs), then the 2 ml. of sample 1 was collected in another test tube. The first volume collected was called a sweep because during the time of its collection, the steady-state condition was being approached in the reactor. During a run, sweeps alternated with samples. In all flow cells used, the sweep volume was several times the reactor volume.

Once the first sample was collected, the reduction ratio was changed and a second sweep collected, followed by the second sample, etc. During a run, five sweeps and five samples were usually collected.

As previously stated, the flow rate at any micrometer speed could be calculated from the drive assembly calibration data. As the reactor volume was known for any given flow cell, it follows that the residence time = reactor volume/flow rate could be calculated for any micrometer speed.

Micrometer speeds were measured indirectly as follows. T_{2rev} (i.e. the time required for two revolutions of the micrometer or a distance moved forward of 0.050") was the time quantity worked with. The two-revolution times were measured twice: once during the sweep collection at a given reduction ratio, and again during the sample collection at the same ratio. The times were measured with a stopwatch and were found to be constant at a given reduction ratio.

After the collection of five samples the current, water, and drive were shut down (stirring left on if using stirred flow cells) and the outflow solution tube dipped into a suitable solvent for the polymer (water for acrylamide, DMF for acrylonitrile, methyl ethyl ketone for methyl methacrylate). By moving the syringe plunger back and forth, the reactor was flushed clean of reaction solution. Fresh solvent was then employed for a final rinsing. Where possible, the cell was taken apart and cleaned further.

4. ANALYSIS.

AAm:

Analysis of aqueous acrylamide monomer was by standard iodine double bond titration (15).

Poly-AcN and Poly-MMA:

Analysis was by polymer precipitation of 2 ml. aliquots in approx. 25 ml. cold methanol. The solid polymer was filtered onto No.541 Whatman filter paper pre-dried in an oven at 70-80°C for several hours and weighed. The polymer and filter paper were then dried in an oven at 70-80°C for several hours and weighings again carried out.

C. RESULTS AND DISCUSSION

1. FREE RADICAL ELECTRO-POLYMERIZATIONS.

As stated in the introductory section, G. S. Shapoval and V. I. Shapoval reported high rates of polymerization of monomeric acrylamide in aqueous media initiated by electro-reduction of persulfate ion at very low current densities (below 100 microamperes per square centimeter) using a number of different electrode materials.

The above system was subjected to several blank static runs duplicating the conditions under which the Russians worked - room temperature, 10% monomer concentration, and current density approx. 40μamps./cm.^{2} (260μamps./in.^{2}).

With no current passing, 100 ml. of 10% aqueous AAm solution containing 1 g. $K_2S_2O_8$ exhibited polymerization to a colourless jell after $2\frac{1}{2}$ hours from the time of addition of $K_2S_2O_8$ to the monomer solution.

Another static run with 100 ml. of 1% AAm solution containing 0.01 g. $K_2S_2O_8$ was a satisfactory blank and showed no evidence of thermal polymer formation 3 hours after addition of the salt.

The conductance of the solution in the latter run was too low to enable passage of currents of the desired magnitude without evolution of hydrogen. The conductance was enhanced by increasing the salt concentration by a factor 100, and a flow run with current carried out using plug flow cell I. Little or no polymer was formed even at high residence times as evidenced by only slight cloudiness when the sweeps were poured into methanol.

By doing a flow run with a secondary initiated system similar to that employed in a paper by Kolthoff and Ferstandig (see p.7, Section A) comprising OF

10% aqueous acrylamide solution 0.001 Molar in $K_2S_2O_8$, 0.1 Molar in $Fe_2(SO_4)_3$, and 0.15 Molar in H_2SO_4, it was hoped to reduce the molecular weight of the Poly-AAm, thus preventing the formation of a gel and enabling quantitative evidence for thermal polymerization to be accumulated.

In the above flow run (at a current of 146μamps.) a gel did not form, and four samples at different residence times plus a blank outside the flow system were collected and analyzed by precipitating 2 ml. aliquots in methanol. After weighing the precipitated polymer, it was discovered that almost the same amount of polymer was present in all four flow samples while only a trace (approx. 1 milligram) was detected in the blank (Table 1).

TABLE 1.

POLY-AAm CONCENTRATION IN OUTFLOW SOLUTION AT DIFFERENT RESIDENCE TIMES AT A CURRENT OF 146μAMPS.

SAMPLE	RESIDENCE TIME (Min.)	MILLIGRAMS POLY-AAm PER 2 ML. SAMPLE
1	1.70	80.0
2	2.24	78.4
3	3.43	86.0
4	5.88	87.1
BLANK	----	1.1

The above data appear contradictory. The absence of polymer in the blank would seem to imply that thermal polymerization did not occur, while the insensitivity of polymer concentration in the outflow samples to changes in residence time would seem to indicate that thermal polymerization did take place.

Using the same system just described, two flow runs were attempted with plug flow cell III at 3.75 and 10.0 ma. When poly-AcN concentration in the outflow solution was plotted against residence time for the two runs, two fairly smooth curves were obtained (Figure 10).

As would be expected, the concentration of polymer was greater at longer residence times and higher currents. Initial rates were of the same order of magnitude for similar currents as those reported by Funt and Williams (4).

When the flow cell was taken apart for cleaning after a run, a considerable amount of solid, yellowish-white poly-AcN was always discovered in the reactor compartment.

Since the flow system treatment is based on the assumption that the reaction is homogeneous, it was decided not to continue flow studies with the above system.

Methyl Methacrylate:

a. Plug Flow Studies:

The kinetics at 25°C of the system 40 volume-% MMA in DMF saturated with tetramethylammonium chloride (NMe_4Cl) were reported by Funt and Bhadani (8). Seven different currents from 10-120 ma. were used at constant initial monomer concentration, and the initial monomer concentration also was varied at constant current, rendering a fairly complete description of the rates of polymerization at different reaction variables.

Four flow runs at 25°C with the system 40 volume-% MMA in DMF saturated with NMe_4Cl were completed using the stainless steel plug flow cell (III), two runs at each of 10 and 15 ma.

FIGURE 10.

POLY-AcN CONCENTRATION IN OUTFLOW SOLUTION VS. RESIDENCE TIME FOR A PRE-ELECTROLYZED 37 MOLE-% SOLUTION OF AcN IN DMF SATURATED WITH $NaNO_3$, AT TWO DIFFERENT CURRENTS AND $30^{\circ}C$.

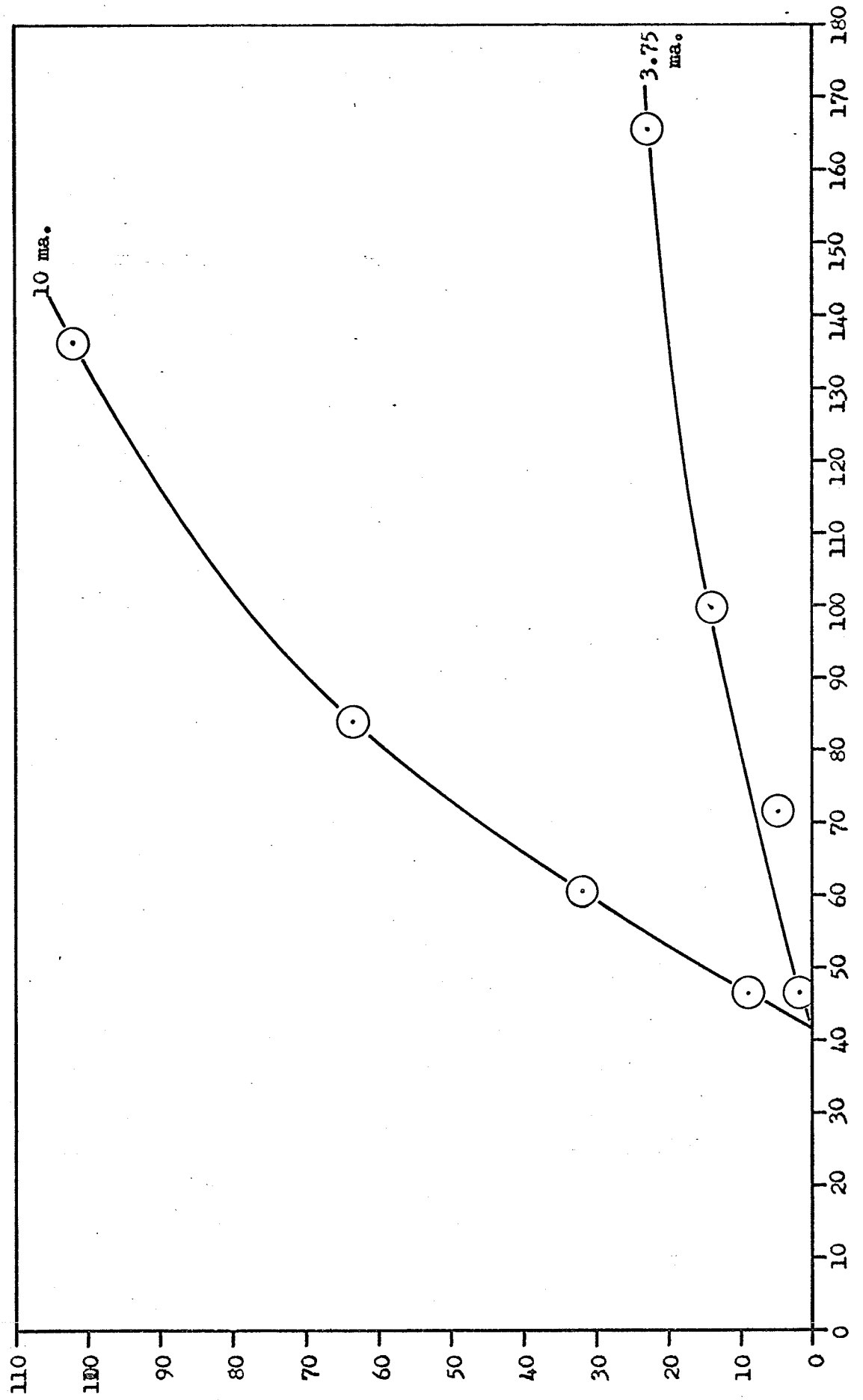

10 ma.
3.75 ma.
Residence time (sec.)
Mg. Poly-AcN per 2 ml. Outflow Solution
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180

FIGURE 10.

Plots of poly-MMA concentration in the outflow solution vs. residence time for the four runs (Figure 11) showed the direct dependence of poly-MMA concentration on residence time and current, but such dependence was seen to be more qualitative than quantitative if one noticed the irregular distribution of points and conflicting slopes of curves obtained for the same current.

As with the AcN system, undissolved, sticky polymer was detected in the reactor when the cell was opened.

b. Stirred Flow Studies:

Whereas in plug flow cell III the electrode area had been approx. 2 $in.^2$, in the stirred flow cell the electrode area was only 0.27 $in.^2$ As a result, in order to pass currents of the order of 10 ma. through the system described in the previous section, excessively high voltages (approx. 300 V.) were required. At such high voltages, the outflow solution was blackish and contained solid debris, probably due to decomposition of some part of the cell.

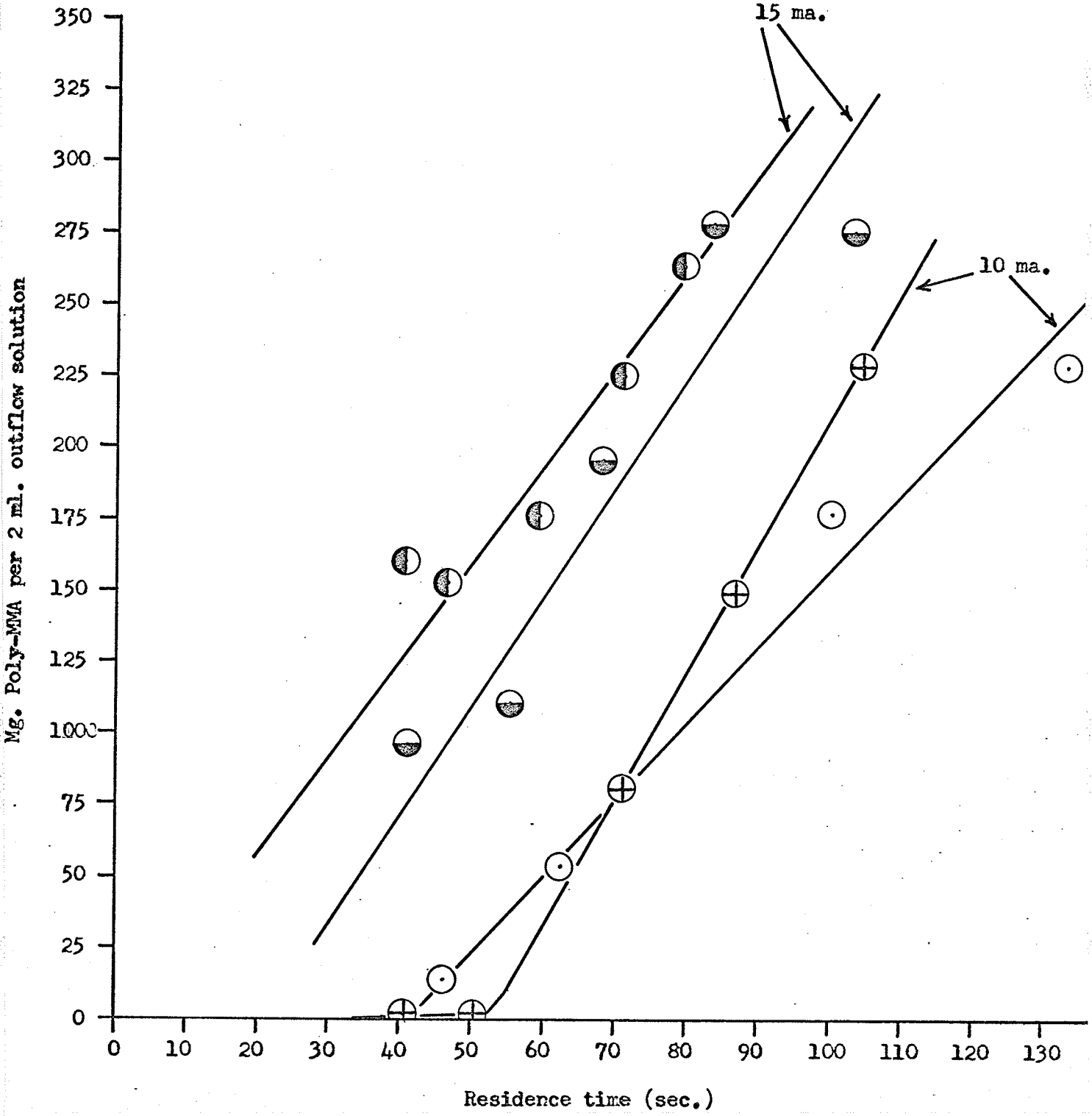
In order to reduce the voltage required to produce the desired currents, several tetrabutylammonium salts, which are in general more soluble than the tetramethylammonium salts, were tried. It was found that approx. 0.3 g. of tetrabutylammonium iodide (NBu_4I) dissolved in 100 ml. of 40 volume-% MMA in DMF furnished a solution with a conductance enabling the passage of currents up to 20 ma. without exceeding 125 volts.

In the theoretical development of rate equations for flow systems, it is assumed that a steady-state condition exists in the reactor which manifests itself in a constant concentration of product in the outflow solution at a fixed residence time. In order to be able to pursue flow studies effectively

FIGURE 11.

POLY-MMA CONCENTRATION IN OUTFLOW SOLUTION VS. RESIDENCE TIME FOR 40 VOLUME-% MMA IN DMF SATURATED WITH NMe_4Cl FOR CURRENTS OF 10 and 15 MILLIAMPERES (25°C).

FIGURE 11.


15 ma.
10 ma.
Mg. Poly-MMA per 2 ml. outflow solution
Residence time (sec.)
0
25
50
75
100
125
150
175
200
225
250
275
300
325
350
0
10
20
30
40
50
60
70
80
90
100
110
120
130

on a particular system, therefore, the steady-state condition must be verified as having been achieved.

This was done for the MMA - DMF - NBu_4I system as follows. At constant current and residence time, several outflow samples were analyzed for polymer content. The procedure was followed in two runs at 15 ma. with different residence times. The results are shown in the following table:

TABLE 2.

POLY-MMA CONCENTRATION IN OUTFLOW SOLUTION AT 15 ma. FOR TWO RUNS AT DIFFERENT BUT CONSTANT RESIDENCE TIMES.

SAMPLE	MG. POLY-MMA PER 2 ML. OUTFLOW SOLUTION	
	RUN 1 (t_r = 65.8 sec.)	RUN 2 (t_r = 98.8 sec.)
1	17.2	78.4
2	22.7	69.4
3	19.4	80.5
4	----	76.5
5	----	75.1
MEAN	19.8	76.0
DEVIATION	±2.0	±3.0

The polymer concentration, as seen above, was quite constant, hence a steady-state was assured.

Four stirred flow runs were then carried out using the above system at four different currents (5, 10, 15, and 20 ma.). When the poly-MMA concentration in outflow solution vs. residence time and 1st order plots were

made, two families of straight line curves were obtained (Figures 12 and 13), suggesting the reaction was 1st order under these conditions. Inhibition times were not shown on the graphs for the sake of clarity (to eliminate crossover), but were as follows:

TABLE 3.

INHIBITION TIMES FOR STIRRED FLOW RUNS AT 25°C WITH 40 VOLUME-% MMA IN DMF WITH NBu_4I AS CONDUCTING SALT, AT DIFFERENT CURRENTS.

CURRENT (ma.)	INHIBITION TIME (sec.)
5	12
10	39
15	23
20	18

For a 1st order reaction, the rate equation in integrated form is suggested to be

$$\ln \frac{M_f}{M_i} = -\frac{k'}{V} t = kt$$

where k' is a volume-independent quantity having units of volume x time^{-1}, and is found by multiplying the volume-dependent rate constant "k" by the volume throughout which the polymer is distributed by stirring (reactor volume).

A comparison of the values of k and k' obtained by static and flow studies of similar systems is given in the following table. The volume-dependent rate constants were determined graphically from the slope of the 1st order plots at the different currents.

FIGURE 12.

POLY-MMA CONCENTRATION IN OUTFLOW SOLUTION VS. (RESIDENCE TIME - INHIBITION TIME) FOR A 40 VOLUME-% SOLUTION OF MMA IN DMF WITH NBu_4I AS CONDUCTING SALT, AT DIFFERENT CURRENTS AND 25°C.

FIGURE 12.

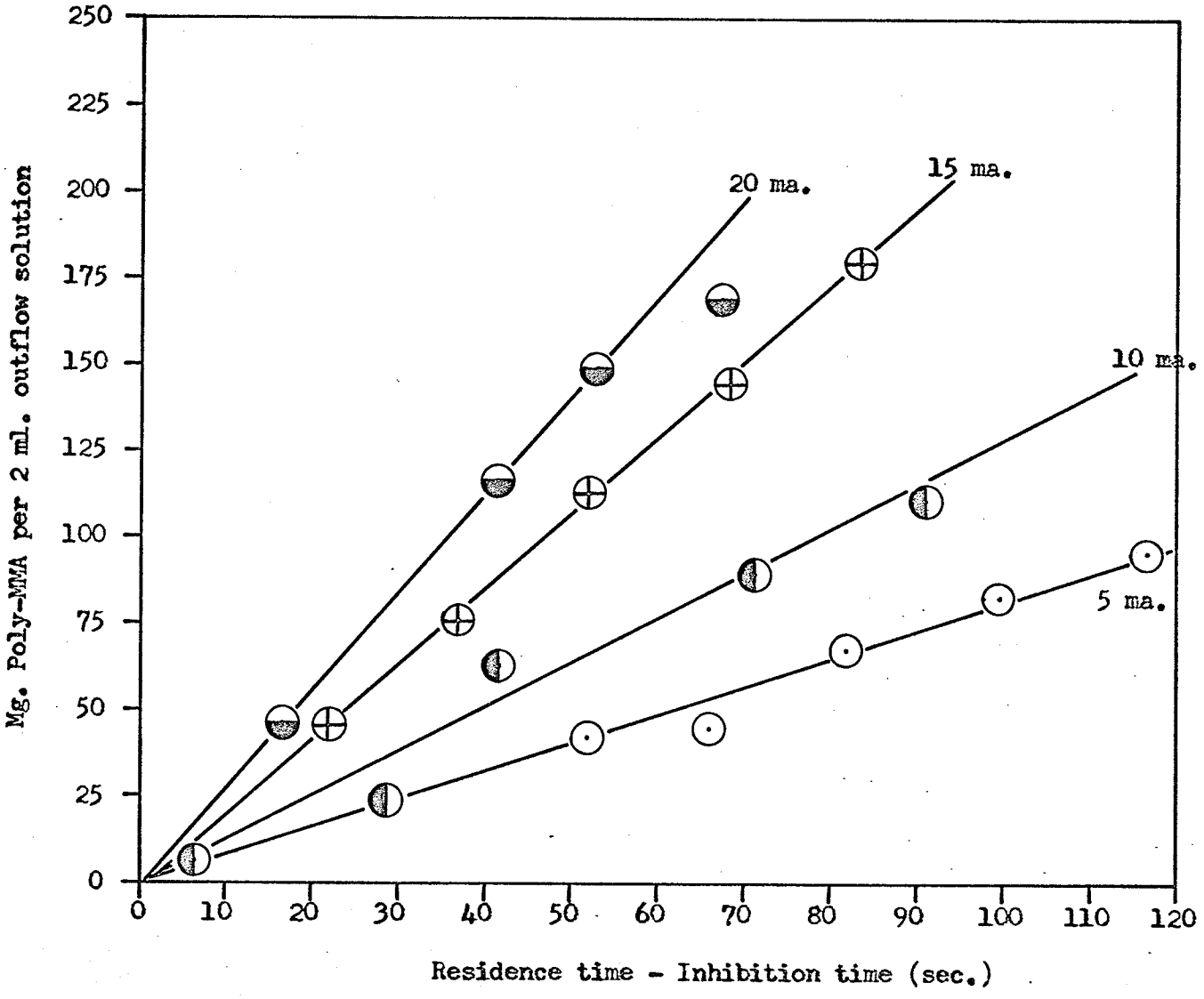

250
225
200
175
150
125
100
75
50
25
0
0
10
20
30
40
50
60
70
80
90
100
110
120
20 ma.
15 ma.
10 ma.
5 ma.
Mg. Poly-MMA per 2 ml. outflow solution
Residence time - Inhibition time (sec.)

FIGURE 13.

LOG (MMA CONCENTRATION) VS.(RESIDENCE TIME - INHIBITION TIME) FOR 40 VOLUME-% MMA IN DMF WITH NBu_4I AS CONDUCTING SALT, AT DIFFERENT CURRENTS AND 25°C.

FIGURE 13.

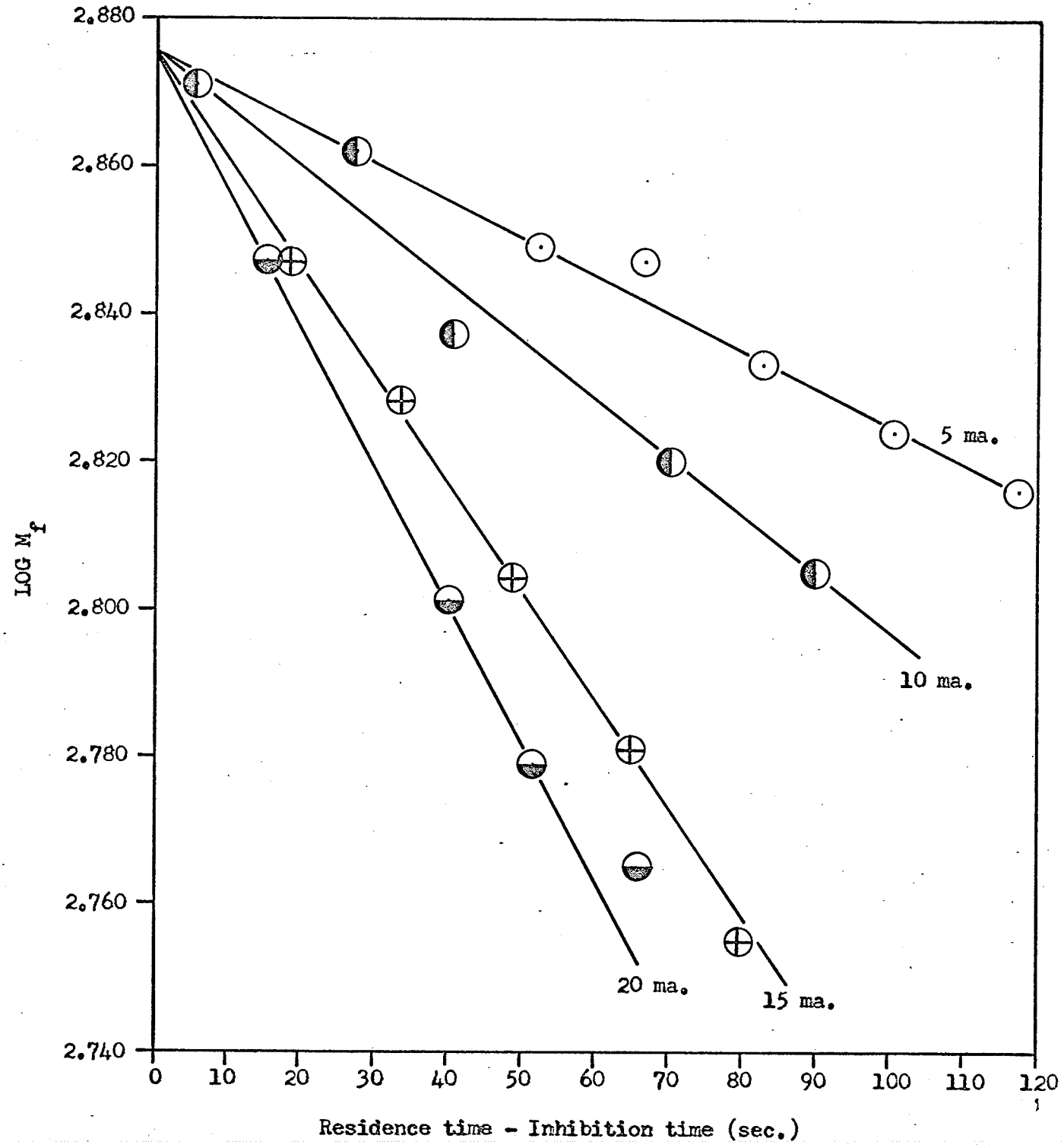

2.880
2.860
2.840
2.820
2.800
2.780
2.760
2.740
LOG M_f
0
10
20
30
40
50
60
70
80
90
100
110
120
Residence time - Inhibition time (sec.)
5 ma.
10 ma.
15 ma.
20 ma.

TABLE 4.

VOLUME-DEPENDENT (k) AND VOLUME-INDEPENDENT (k') RATE CONSTANTS OBTAINED BY STATIC AND FLOW STUDIES OF THE 40 VOLUME-% MMA IN DMF SYSTEM.

CURRENT	k		$k' = k \times$ reactor vol.[1]	
	STATIC	FLOW	STATIC	FLOW
5 ma.	——	4.2 $hr.^{-1}$	——	2.9 $ml./hr.^{-1}$
10	.046	6.5	4.6	4.6
15	.054	12.4	5.4	8.7
20	——	15.5	——	10.9
25	.065	——	6.5	——

[1] Static reactor volume = 100 ml.
Flow reactor volume = 0.70 ml.

As is seen, data is available for static-flow comparison for only two currents, but in both cases the k' for the flow system is greater than that for the static system. The reason for this is probably that the conducting salt used in the static runs was NMe_4Cl, while the conducting salt used for the flow runs was NBu_4I. Bhadani also reported that a tetrabutylammonium salt gave a much better poly-MMA yield than a tetramethylammonium salt at 15 ma. with the same system (8).

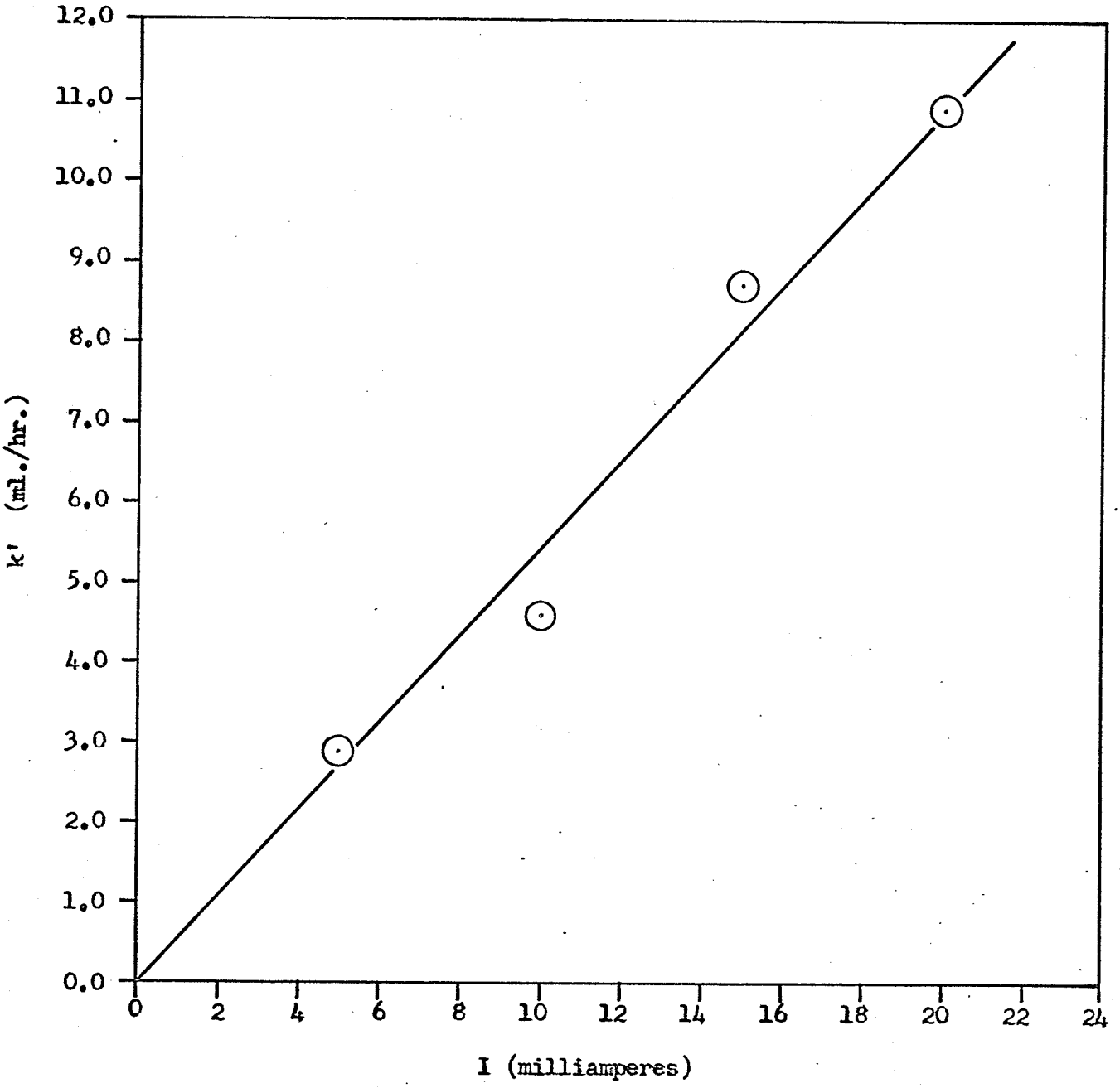
If the flow-determined k or k' is plotted against the first power of the current (Figure 14), a straight line through the origin is indicated, suggesting a 1st order dependence on current rather than a half-power dependence, which was found by Bhadani in static experiments with the same system (8).

The initial electrical efficiencies (moles monomer polymerized per Faraday) have been calculated for both static and flow studies and are

FIGURE 14.

VOLUME-INDEPENDENT RATE CONSTANT VS. FIRST POWER OF CURRENT FOR THE SYSTEM 40 VOLUME-% MMA IN DMF WITH NBu_4I AS CONDUCTING SALT, AT 25°C.

FIGURE 14.


12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
k' (ml./hr.)
0
2
4
6
8
10
12
14
16
18
20
22
24
I (milliamperes)

given in the following table.

TABLE 5.

INITIAL ELECTRICAL EFFICIENCIES (E) FOR STATIC AND FLOW RUNS AT DIFFERENT CURRENTS.

CURRENT	E_{stat} (moles/Faraday)	E_{flow}
5 ma.	——	58.4
10	46.3	45.3
15	34.9	57.6
20	——	54.0
25	26.2	——

Again, the above phenomenon could perhaps be attributed to the use of NBu_4I as conducting salt in the flow runs as opposed to NMe_4Cl in the static runs. As one can see, the initial electrical efficiencies in the flow runs were generally higher than those encountered for the static runs and did not exhibit a definite decrease with increasing current, remaining high and fairly constant from 5 to 20 ma.

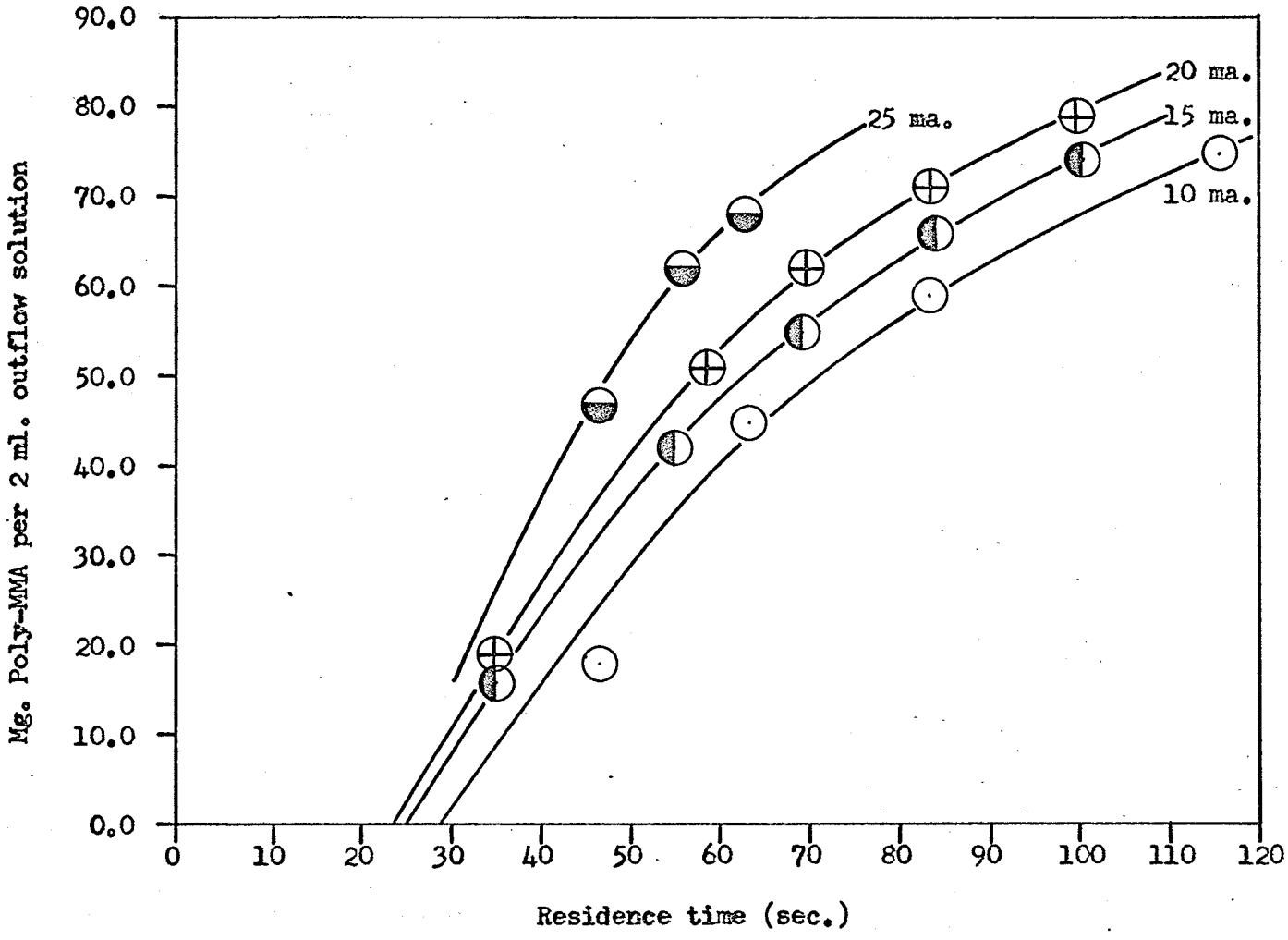
Four stirred flow runs with the system 20 volume-% MMA in DMF with NBu_4I (approx. 0.3 g./100 ml. solution) as conducting salt were also carried out at currents of 10, 15, 20, and 25 ma. When polymer concentration in the outflow solution was plotted against residence time, a family of smooth curves was obtained (Figure 15).

Neither the 1st order plots nor the 2nd order plots of the data from the above runs yielded straight lines, however. A differential plot of the

FIGURE 15.

POLY-MMA CONCENTRATION IN OUTFLOW SOLUTION VS. RESIDENCE TIME FOR 20 VOLUME-% MMA IN DMF WITH NBu_4I AS CONDUCTING SALT, AT DIFFERENT CURRENTS AND 25°C.

FIGURE 15.


90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
0
10
20
30
40
50
60
70
80
90
100
110
120
Mg. Poly-MMA per 2 ml. outflow solution
Residence time (sec.)
25 ma.
20 ma.
15 ma.
10 ma.

run at 20 ma. suggested the order of reaction with respect to monomer approached and maintained fifteen at approx. 17% conversion. In contrast, Bhadani (8) observed 1st order behaviour in a static run with 20 volume-% MMA in DMF saturated with NMe_4Cl, at 15 ma.

One explanation which could possibly account for the extraordinary dropoff in rate encountered in the stirred flow runs involves discussion of stirring. According to unpublished data by Bhadani, a lesser rate of reaction occurs in the living polymerization of isoprene when moderate stirring is employed than when it is absent. With the vigorous stirring effected in the flow reactor, perhaps there would be a further analogous dropoff in rate from that observed for the moderately stirred static runs.

The reason for the decrease in rate with increase in solution agitation could be that the electrolysis products formed at the anode are oxidizing agents and as such, possible terminators of growing anionic chains. Vigorous stirring would enable the chain-terminating species to spread throughout the reactor, work in close to the cathode, and be presented with a much larger number of attackable sites than if they were confined to the immediate vicinity of the anode as would be the case for no stirring.

For example, the iodine generated at the anode by the reaction

$$2\,I^- - 2e \longrightarrow I_2$$

could be spread throughout the reactor by stirring and terminate growing anionic chains (partially) in the following manner:

$$I_2 + -:\!\overset{H}{\underset{R}{C}}\!-CH_2\sim\sim CH_2-\!\overset{H}{\underset{R}{C}}\!:- \longrightarrow I^- + I-\!\overset{H}{\underset{R}{C}}\!-CH_2\sim\sim CH_2-\!\overset{H}{\underset{R}{C}}\!:-$$

growing anionic chain (dianion)

partially terminated chain

At higher monomer concentrations, perhaps the rate did not exhibit a pronounced dropoff as stirring was varied from moderate (static) to vigorous (flow) because the terminating species were not able to compete with the increased number of monomer molecules available for combination with the ionic ends of a growing chain.

Another reason why the rate of polymerization seemed to become low rapidly could be that analysis was of polymer, not of monomer. It was assumed that all of the monomer participating in chain growth polymerized to high molecular weight poly-MMA (i.e. that

$$\text{(I) MONOMER CONCENTRATION AT TIME "t"} = \text{INITIAL MONOMER CONCENTRATION} - \text{HIGH POLYMER CONCENTRATION AT TIME "t"}$$

If the degree of polymerization had been approx. 4, this low molecular weight polymer would not have precipitated in methanol, hence would not have appeared in the polymer analysis. The monomer concentration at time "t" would have appeared higher than it actually was, but the rate would have dropped off according to the true, lower concentration of monomer at time "t".

The second reason is compatible with the first, for at low monomer concentration quick termination would result in low molecular weight product and cause erroneously high monomer concentrations to be recorded, while at higher monomer concentrations termination would not be so widespread and the amount of high polymer relative to the amount of low polymer formed would render equation (I) above valid.

II. ELECTROLYTIC CONDENSATION POLYMERIZATION OF DICARBOXYLIC ACIDS

A. INTRODUCTION

In 1834, Michael Faraday (16) reported the formation of a hydrocarbon from electrolysis of an acetate solution. Fifteen years later, Kolbe identified this hydrocarbon as ethane and undertook a thorough study of the reaction named after him (17).

The normal Kolbe reaction, which can be represented as

$$2\ C_nH_{2n+1}COO^- - 2e \longrightarrow C_{2n}H_{4n+2} + 2\ CO_2$$

is sometimes accompanied by side-reactions, the principal one being the Hofer-Moest reaction, which results in the formation of an alcohol $C_nH_{2n+1}OH$ (18). Conditions favouring the formation of Hofer-Moest product are the use of alkaline solutions and presence of certain inorganic salts.

A free radical mechanism is now generally accepted for the Kolbe reaction. The initial step is the discharge of carboxylate ion at the anode forming a carboxylate radical, which then breaks down into carbon dioxide and an alkyl radical:

$$RCOO:^- \longrightarrow RCOO\cdot + e$$
$$RCOO\cdot \longrightarrow R\cdot + CO_2$$

Depending on the reaction conditions, the alkyl radical may combine (couple) with another alkyl radical to produce an alkane (normal Kolbe product):

$$R\cdot + R\cdot \longrightarrow R\text{-}R$$

or react with a molecule of water to give the alcohol (Hofer-Moest product):

$$R\cdot + HOH \longrightarrow ROH + H\cdot$$

The occurrence of other by-products present in minor quantities can also be accounted for by the free radical mechanism.

Not all monocarboxylic acids undergo coupling, however. Among those which do not are aromatic carboxylic acids and α-substituted carboxylic acids. Up until 1959, the formation of coupled products or cycloalkanes was never observed in the electrolysis of dibasic acids. Products obtained from these aqueous electrolyses of acids from malonic to sebacic were saturated and unsaturated acids with the loss of one carbon atom, and olefines with the loss of two carbon atoms, as well as lower degradation products. A summary of such work up to 1942 was given by Fichter (19).

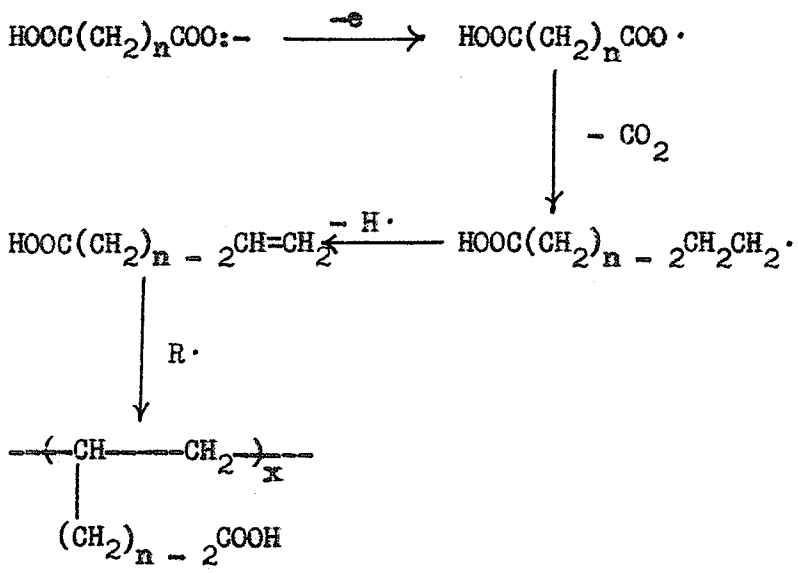
In 1959, W. E. Garrison Jr. (20) discovered the formation of both benzene-soluble, low molecular weight polymers and insoluble, probably highly cross-linked materials from the electrolysis of methanolic solutions of certain long chain dicarboxylic acids and their ammonium salts.

Electrolyses of the ammonium salts of malonic, succinic, glutaric, and β,β-dimethylglutaric acids yielded no polymer insoluble in boiling methanol.

Methanol-insoluble polymers were obtained by the electrolyses of adipic, azelaic, sebacic, and hexadecane-1,16-dicarboxylic acids and were separable into benzene-soluble and benzene-insoluble fractions.

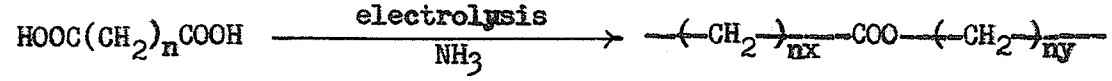
Analytical results on the insoluble material which showed that very little decarboxylation had taken place, and I.R. spectra displaying the absence of the doublet at 720-740 $cm.^{-1}$ characteristic of a long polymethylene chain, indicated that no significant amount of coupling had occurred. The spectra also indicated the presence of carboxylic acid groups absorbing at 1712 $cm.^{-1}$ and ester linkages at 1735 $cm.^{-1}$

Accordingly, Garrison suggested the following mechanism for the formation of the benzene-insoluble material, involving polymerization of an α-olefine formed by the abstraction of a hydrogen radical from an alkyl radical to give a low molecular weight polymer containing free carboxyl groups. The polymer could then be cross-linked by means of the carboxyl group remaining at the end of the hanging chain.



Interesting features of the I.R. spectra of the benzene-soluble material were a methylene doublet at 721 and 732 $cm.^{-1}$ and an ester peak at 1734 $cm.^{-1}$

With the above results in mind, Garrison postulated the following mechanism for the formation of the benzene-soluble material:



These benzene-soluble polymers had molecular weights below 1000, and were not investigated further.

B. EXPERIMENTAL

1. PREPARATION OF MATERIALS.

Sebacic acid (Eastman Organic Chemicals) and suberic acid and 1,10-decanedicarboxylic acid (Aldrich Chemicals) were used without purification. Practical methanol was used directly in all experiments.

2. APPARATUS.

Electrolytic Cells:

Simple test-tube type reaction cells of approx. 150 ml. volume fitted with 1 $in.^2$ platinum electrodes and small magnetic stirring bars were used, and have been described in previous papers from this laboratory (4,8). The cells were immersed in thermostat baths during the passage of current.

Current Source:

A transistorized Power Designs constant current supply enabling the passage of 25 to 500 ma. up to a voltage of approx. 66 V. was used for all experiments.

3. EXPERIMENTAL PROCEDURE.

Approx. 5 g. of each acid was dissolved in 100 ml. methanol and filtered into the electrolysis cell for each respective experiment. A solution of one pellet of NaOH in approx. 10 ml. water was added to partially neutralize the acid and improve the conductivity, then electrolyses carried WERE out with as large a current as possible.

Any methanol-insoluble films encountered were scraped off the anode, as their formation greatly decreased the current, as found in Garrison's work.

At the end of the period of electrolysis, they were then either transferred onto an NaCl plate in a beaker of absolute ether or allowed to dry and incorporated into a KBr pellet in order to determine the I.R. spectra.

Solubility tests on the insoluble anode material were carried out with concentrated aqueous NaOH and HCl, toluene, dimethylsulfoxide, and DMF. Several melting point determinations were also attempted.

C. RESULTS AND DISCUSSION

An insoluble, whitish film was observed on the anode for all acids after 15-60 minutes of electrolysis. Formation was most rapid for 1,10-decanedicarboxylic acid.

The initial currents were usually of the order of 400-500 ma., smaller by a factor 10 than those used by Garrison.[20] The current fell to 100-200 ma. when the film formed on the anode and caused the voltage required to maintain a higher current to exceed that able to be applied with the apparatus used. When the film was scraped off, the current again rose to a high value, but gradually decreased as another anodic film was formed.

Some of the anodic material was rinsed with absolute ether (in which it did not dissolve) and dried, giving a light brown, resilient, paper-like substance which did not melt below 200°C and which was insoluble in concentrated aqueous NaOH, HCl, dimethylsulfoxide, toluene, and DMF.

I.R. spectra of films and KBr mulls of the anode material from experiments with all three acids were not very sharply defined, but showed no characteristic poly-methylene doublets in the 700-800 $cm.^{-1}$ region. Peaks occurred between 1700 and 1750 $cm.^{-1}$, indicative of carboxylic acid groups and ester linkages. The spectra are very similar to those described by Garrison for his benzene-insoluble material.[20]

From the above evidence, one can only conclude that linear polymers were not obtained from the electrolysis of partially-neutralized methanolic solutions of the three dicarboxylic acids mentioned.

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