ELECTROLYTICALLY INITIATED POLYMERIZATIONS

by

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B. Sc. (Hons.), University of Manitoba, 1967

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE
in the Department
of
Chemistry

SIMON FRASER UNIVERSITY
January, 1969

TO MY PARENTS

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ABSTRACT

The electroinitiated polymerization of tetrahydrofuran was carried out in the bulk. Polymerizations were performed in divided electrolytic cells. The tetrabutylammonium salts were used as the electrolytes.

The polymerizations were initiated at a platinum anode by the passage of electrical current through the cell. The reaction mechanism was shown to be cationic. Polymer was not isolated from the system till 7 or 8 hours after initial current passage. The polymer was characterized by IR and NMR measurements.

The polymerizations required highly purified monomer and electrolyte, involving the use of high vacuum techniques. Polymerizations were attempted in dilute solutions of various solvents but no polymer was isolated in such cases. Studies of the effects of current reversal demonstrated that the polymerization rate could be either slowed or stopped.

Kinetic studies showed that the rate of polymerization was first order with respect to monomer, first order with respect to electrolyte concentration, and one-half order with respect to current. A typical rate determined was 9.34×10^{-5} moles/l.-sec.

A mechanism for the electroinitiated cationic polymerization is also proposed.

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ACKNOWLEDGEMENTS

The author wishes to express his thanks and appreciation to Dr. B. L. Funt for his guidance and helpful criticism during the course of research.

The author would also like to thank Dr. R. A. Young and Mr. V. Hornof for their helpful comments and discussions.

Thanks are also in order to the Simon Fraser Glass Shop for the construction of the glass apparatus used in this research.

INTRODUCTION

GENERAL CONSIDERATIONS

A polymer is a high molecular weight compound built up by the repetition of small chemical units joined by covalent bonds. The repeat units of the polymer, the monomer, may be combined linearly or in a branched or interconnected network. The length of the polymer chain is specified by the number of repeating units in the chain, usually referred to as the degree of polymerization. The molecular weight of the polymer then is the product of the weight of the repeat unit and the degree of polymerization. The length of a chain is determined by various events in the polymerization reaction. The polymer may contain molecules of very many different chain lengths, resulting in a molecular weight distribution. The most remarkable features of high polymers are their mechanical properties - elasticity, tensile strength, deformability, hardness, etc. which differentiates them from other organic molecules.

The processes of polymerization have been divided into two categories known as condensation (step-reaction) and addition (chain reaction).

A condensation polymer is one in which the polymer does not have the same composition as the monomer or monomers from which it was formed, or to which it may be degraded by chemical means. These polymers are formed from bi- or polyfunctional monomers with the elimination of a by-product in a step-wise intermolecular manner.

An addition polymer is one in which the molecular formula of the structual unit is identical with that of the monomer from which the polymer is derived. Addition polymerizations usually proceed by a chain mechanism involving active centers on the end of a growing polymer chain. The active centers may be either free radical, anionic, or cationic in nature. Some initiating species is usually required before the polymerization will proceed.

In our work, we have primarily interested ourselves in cationic polymerization, and the electroinitiation of such polymerizations. Both of these topics will be discussed more extensively later.

The molecular weight and the molecular weight distribution are important quantities to be determined in considering the properties of a polymer. In general, there are two types of molecular weight distribution which are of importance, the number average (M_n) and the weight average molecular weight (M_w). The former is defined as the total weight of polymer divided by the number of moles which it contains. It is really a measurement of the number of molecules present with no regard to size, and thus is very sensitive to low molecular weight species, and may be written as

$$M_n = \frac{\sum_i M_i N_i}{\sum_i N_i}$$

where N_i is the number of i^{th} species and M_i is the molecular weight of the i^{th} species. The weight average molecular weight (M_w) depends not only on the concentration but also on the weight of the particle, where this is written as

$$M_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

where the symbols have same meaning as before.

Viscosity measurments of a polymer give a measure of size of the polymer, and may be empirically related to the molecular weight of a linear polymer by the relation $[\eta] = KM^{\alpha}$ where K and α are empirical constants, both being dependent on the nature of the polymer, and the solvent; M is the molecular weight, and $[\eta]$ is the intrinsic viscosity obtained from a plot of (η_{sp}/c) versus the concentration (c). The nomenclature for intrinsic viscosity measurements is given in Table I.

CATIONIC POLYMERIZATION

Chain reaction (addition) polymerizations occur by several mechanisms. The principal types are:

1. free radical
2. anionic
3. cationic
4. coordination

Table 1. Nomenclature of solution viscosity (1).

Common name	Recommended name	Symbol and equation
Relative viscosity	Viscosity ratio	$\eta_r = \eta/\eta_o \approx t/t_o$
Specific viscosity	....	$\eta_{sp} = \eta_r - 1$
Reduced viscosity	Viscosity number	$\eta_{red} = \eta_{sp}/c$
Inherent viscosity	Logarithmic viscosity number	$\eta_{inh} = (\ln \eta_r/c)$
Intrinsic viscosity	Limiting viscosity number	$[\eta] = (\eta_{sp}/c)_{c=o}$

The steps of an addition polymerization can be briefly described as follows:

1. Initiation: the activation of monomer molecules by an initiator into growing sites.

$$I \longrightarrow I^*$$

$$I^* + M \longrightarrow IM^*$$

2. Propagation: addition of monomer to activated species, increasing the chain length.

$$IM_n^* + M \longrightarrow IM_{n+1}^*$$

3. Chain transfer: reaction of the polymeric active center with monomer or another substance to produce a terminated polymer chain and another active species.

$$IM_n^* + S \longrightarrow IM_n + S^*$$

$$S^* + M \longrightarrow SM^*$$

4. Termination: active center is destroyed.

$$IM_n^* \longrightarrow IM_n$$

Broadly speaking, a cationic polymerization is one in which the active end of the growing polymer molecule is a positive ion. The ion may be a carbonium ion or it may be an oxonium ion. Other possibilities may be the sulfonium or quaternary ammonium ions. The carbonium ion chain carrier is the best known at this time.

The most important group of monomers that are polymerized by carbonium ion processes are the olefins. In general, any monomer whose double bond is not deactivated by strongly electrophilic (electron withdrawing) substituents is capable of initiation by cationic reagents, provided its structure imposes no gross steric hindrance. But because of the great activity of many monomer carbonium ions, various side reactions (5) may predominate over linear addition, and so high polymers have only been obtained for a few systems under narrowly defined conditions of temperature and catalyst. It is usually necessary to work at low temperatures (-100°C) using Friedel-Crafts type catalysts (eg. $AlCl_3$), and using olefins such as isobutylene, that contains a terminal methylene group and that yields a tertiary carbonium ion upon protonation:

$$\overset{R}{\underset{R'}{\rangle}}C=CH_2 + H^+ \longrightarrow \overset{R}{\underset{R'}{\rangle}}\overset{+}{C}-CH_3$$

The vinyl ethers also form an important group of monomers for cationic polymerization. The vinyl ethers are very reactive, and so the polymerizations are usually carried out using milder conditions in order to avoid crosslinking and charring.

One of the few examples in which the oxonium ion is the active propagating species is the polymerization of tetrahydrofuran discovered by Meerwein around 1940 (6). The polymerization of oxacyclobutane also proceeds via an oxonium ion (7).

A. General Features of the Reaction

The nature of the carbonium ion or oxonium ion largely determines the character of the cationic polymerization, i.e. the ease of formation and destruction of the ion, its reactions and rearrangements. The ability of an ion to propagate a chain is determined by its energy - the greater the energy, the less stable the ion. If the ion is of very high stability (low energy) the ion will form easily, but may not be of sufficient energy to react with a certain monomer. Conversely, if the ion is of low stability (high energy) it will be difficult to form, will be easily destroyed, and may yield unwanted side reactions. The tertiary alkyl and styryl carbonium ions, and the tertiary alkyl oxonium ions achieve a reasonable balance of the two extremes. The important quantity to be considered is the energy of formation of the solvated cation which involves the energy of **dissociation** of a polymer-catalyst complex and the energy of solvation of the resulting ions.

When a carbonium ion is involved in the reaction, it is assumed that its concentration is minute, because such ions are very reactive species and few have been detected. The evidence for a carbonium ion propagating species in cationic polymerizations may be seen from the following general characteristics of the reaction:

i) increasing solvent polarity increases rate of reaction.

ii) Friedel-Crafts catalysts (are cationic in nature) are effective initiators.

iii) the monomers have a nucleophilic character.

iv) inhibition by amines and anions.

v) certain monomers which do not polymerize by free radical processes do polymerize in these systems.

In general, oxonium ions are more stable than carbonium ions, and thus oxonium ions are much more easily detected.

The choice of solvent for carrying out a carbonium ion polymerization is restricted by the following requirements:

i) it must not react with the ionic species involved in the polymerization.

ii) it must dissolve the reactants, often at low temperatures.

iii) it should not complex or react with the catalyst sufficiently to retard the reaction.

iv) it must remain fluid at low temperatures often below -100°C.

The most suitable solvents then are low polarity solvents. Normally, however, ionic reactions are favoured by high polarity solvents. But some balance must be achieved, and usually low polarity solvents such as methyl chloride and methylene chloride are used.

Carbonium ion polymerizations are usually favoured by low temperatures, the main reasons being kinetic, but also because a decrease in temperature can increase the dielectric constant. It has usually been found that as the dielectric constant of the solvent is increased, the rate of polymerization is increased markedly, but the molecular weight only moderately, thus showing that the initiation process is the most affected.

B. Mechanism of Cationic Polymerizations

1. Initiation - The common methods of initiating a carbonium ion polymerization can be classified as follows:

- a) Protonation of monomer
  - i) by simple acids
  - ii) by complex acids
- b) Reactions yielding carbonium ions
  - i) reaction of alkyl halides with Friedel-Crafts reagent
  - ii) reaction of iodine with monomer, and other examples
- c) Radiation

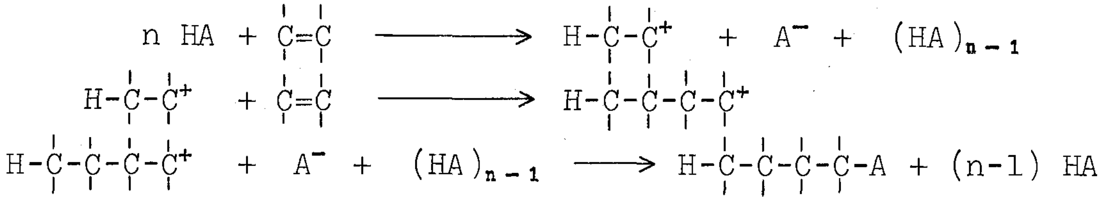
These are now discussed in more detail.

a) protonation of monomer

The requirements for this to occur are that the acid be of sufficient strength to produce the equilibrium concentration of ions required to maintain a reasonable rate of polymerization, and that the acid anion be of sufficiently low nucleophilic character that termination by recombination of ions is not important.

i) by simple acids '

Initiation of the more reactive monomers can sometimes be accomplished with the simple protonic acids. A polymerization mechanism with a high rate of termination is expected.

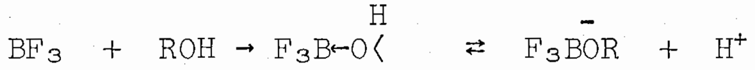


$$n\ HA + C{=}C \longrightarrow H{-}C{-}C^{+} + A^{-} + (HA)_{n-1}$$
$$H{-}C{-}C^{+} + C{=}C \longrightarrow H{-}C{-}C{-}C{-}C^{+}$$
$$H{-}C{-}C{-}C{-}C^{+} + A^{-} + (HA)_{n-1} \longrightarrow H{-}C{-}C{-}C{-}C{-}A + (n{-}1)\ HA$$

Thus the polymerization of olefins by simple acids leads almost invariably to low molecular weight polymer. As reported by Tauber in 1960 (8), anhydrous perchloric acid in ethylene chloride solution will not polymerize 2-butene because of apparent ester formation. Styrene has been polymerized with sulfuric or perchloric acid in ethylene chloride to a molecular weight of only a few thousands (9,10).

ii) complex acids - Lewis acids

The most important of all cationic initiators are the Friedel-Crafts catalysts. The formulation of a mechanism was hampered by the difficulty of envisaging how an ionic reaction could be initiated by a Friedel-Crafts halide like $AlCl_3$. Various theories were proposed (11,12), but it wasn't until 1950 that Evans and Polanyi established that water co-catalysis was involved in the polymerization of isobutene by boron trifluoride (13). No polymerization occurred when the components were pure and dry. The need for a proton source, designated the co-catalyst, in the polymerization of styrene with aluminum chloride has been demonstrated (14,15). The proton necessary for initiation is furnished by an ionic hydrate or some catalyst-co-catalyst complex:



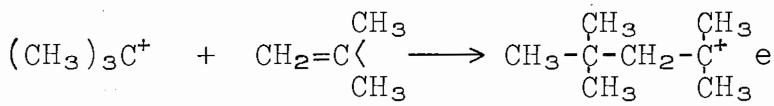
$$BF_3 + ROH \rightarrow F_3B\leftarrow O\langle^{H}_{R} \rightleftarrows F_3\overset{-}{B}OR + H^+$$

The mechanism, then, of hydrogen co-catalyzed systems is as follows, using isobutene as an example:

initiation:

$$H^+ + CH_2{=}C\langle^{CH_3}_{CH_3} \longrightarrow (CH_3)_3C^+$$

propagation:

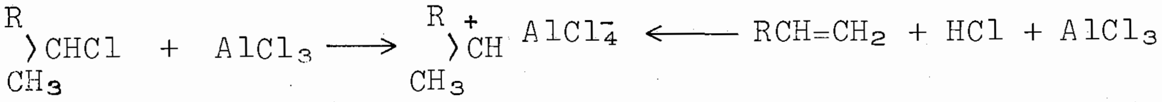


$$(CH_3)_3C^+ + CH_2{=}C\langle^{CH_3}_{CH_3} \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C^+}} \text{ etc.}$$

b) reactions yielding carbonium ions

i) reaction of alkyl halide with Friedel-Crafts reagent

Polymerization may be initiated by carbonium ions, as shown by the polymerization of octyl vinyl ether by triphenylmethyl chloride in ionizing solvents (16), and by the incorporation of alkyl and groups into polymers prepared in solutions of alkyl bromides (17). Reaction of an appropriate alkyl halide with a Friedel-Crafts reagent should lead to the same carbonium ion pair as does protonation of the corresponding olefin. Interactions of this type, "solvent co-catalysis", have been used to explain the non-necessity of water co-catalysis in chlorinated hydrocarbons.



$${}^{R}_{CH_3}\rangle CHCl + AlCl_3 \longrightarrow {}^{R}_{CH_3}\rangle \overset{+}{C}H\ AlCl_4^- \longleftarrow RCH{=}CH_2 + HCl + AlCl_3$$

The process for Friedel-Crafts catalysis can be generally written as:

$$MX_n \cdot AB + CH_2{=}CHY \longrightarrow A-CH_2\overset{+}{C}HY + [MX_nB]^-$$

where MX_n is the Friedel-Crafts catalyst and AB represents the co-catalyst, an ionizable compound whose dissociation may be enhanced by complexing with the catalyst.

ii) iodine and other examples

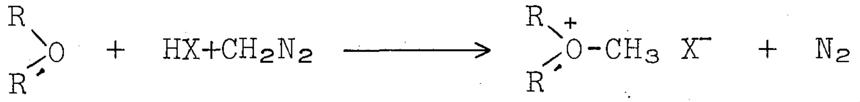
Iodine (18) and iodine chloride (19) and bromide have been used to initiate cationic polymerization. It is postulated that in vinyl ether polymerization, part of the iodine is taken up as a catalytically inactive π complex and that only the I^+ is involved in the actual initiation:

$$2\ I_2 \longrightarrow I^+ + I_3^-$$

$$ROCH{=}CH_2 + I^+ \longrightarrow RO\overset{+}{C}H{-}CH_2I$$

Other initiators reported in the literature are ionic compounds such as $(C_6H_5)_3^+\ BF_4^-$, $NO_2^+\ BF_4^-$, and $CH_3\overset{+}{C}{=}OClO_4^-$ (20).

Oxonium ions, which are prepared by alkylation of an ether acid complex with some very active alkylating agent such as epoxide, diazomethane, or ketene, are also used as initiators:



$$R_2O + HX{+}CH_2N_2 \longrightarrow R_2\overset{+}{O}{-}CH_3\ X^- + N_2$$

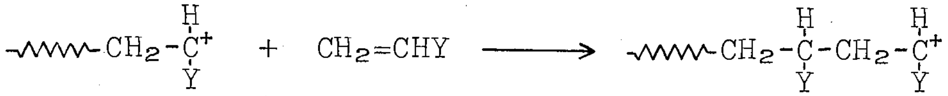
The oxonium ions have been used in the polymerization of THF, oxacylobutane (7), and vinyl ethers (21).

c) high energy radiation

Polymerizations can be initiated by high energy radiations such as gamma rays and fast electrons. Most initiators thus produced are free radical. A few cationic cases have been observed, an example being the polymerization of isobutylene (22) which was initiated by a vacuum ultra-violet source.

2. Propagation

The propagation in olefins may be regarded as an electrophilic attack by the ion at the π electrons, and the ease with which this occurs is governed by the stability of the ion and the basicity of the olefin.



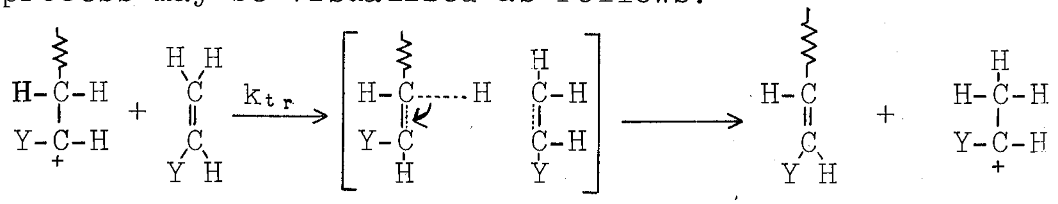
$$\sim\!\sim\!\sim CH_2-\overset{H}{\underset{Y}{C^+}} + CH_2{=}CHY \longrightarrow \sim\!\sim\!\sim CH_2-\overset{H}{\underset{Y}{C}}-CH_2-\overset{H}{\underset{Y}{C^+}}$$

The monomer molecule will be highly polarized in the transition state, and hence the site of addition will be determined by the character of its substituents. Since these are usually electropositive groups, we should expect cationic addition to occur at the least substituted end of the double bond (more stable carbonium ion) giving a regular head to tail structure, as shown by polyisobutene (23). The coulombic energy of interaction between the ion and the dipole induced in the monomer double bond reduces the activation energy for propagation below that for free radical processes, giving, in general, low overall activation energies for ionic polymerizations (24). The nature of the reaction implies that it would be very susceptible to the nature of the groups attached to the double bond, determining not only the structure as mentioned above, but also the rate at which the propagation proceeds.

The reverse of propagation, depolymerization, is not too important in carbonium ion polymerizations because the reactions are carried out well below the ceiling temperatures. In the oxonium ion polymerization of THF, a true equilibrium between polymer and monomer is observed.

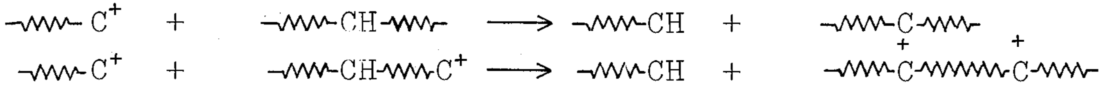
3. Transfer reactions

Monomer transfer appears to be the dominant factor in determining the molecular weight at room temperatures. Reaction between a carbonium ion and monomer can lead to either chain growth or to chain transfer to the monomer, that is, to the transfer of the cation from polymer to monomer with the initiation of one chain, and termination of the other. The process may be visualized as follows:



Here there is a transfer of a proton from the polymer carbonium ion to a monomer molecule, leaving a "dead" polymer with a terminal double bond.

Another type of transfer in which the carbonium ion captures a hydride ion from a dead polymer molecule or from another polymer carbonium ion is called hydride transfer.



$$\sim\!\sim C^{+} + \sim\!\sim CH \sim\!\sim \longrightarrow \sim\!\sim CH + \sim\!\sim \overset{+}{C} \sim\!\sim$$

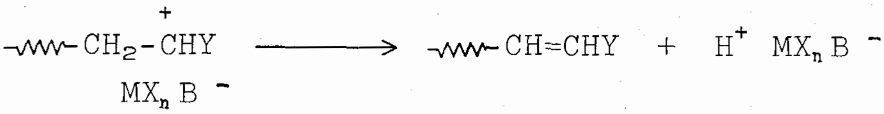
$$\sim\!\sim C^{+} + \sim\!\sim CH \sim\!\sim C^{+} \longrightarrow \sim\!\sim CH + \sim\!\sim \overset{+}{C} \sim\!\sim\!\sim\!\sim \overset{+}{C} \sim\!\sim$$

This brings about formation of highly branched polymers.

4. Termination Reactions

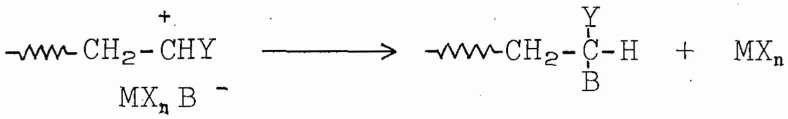
When the growth of a polymer chain is stopped without simultaneous initiation of a new chain, the process is known as termination. Several processes by which termination may proceed are:

i) proton expulsion



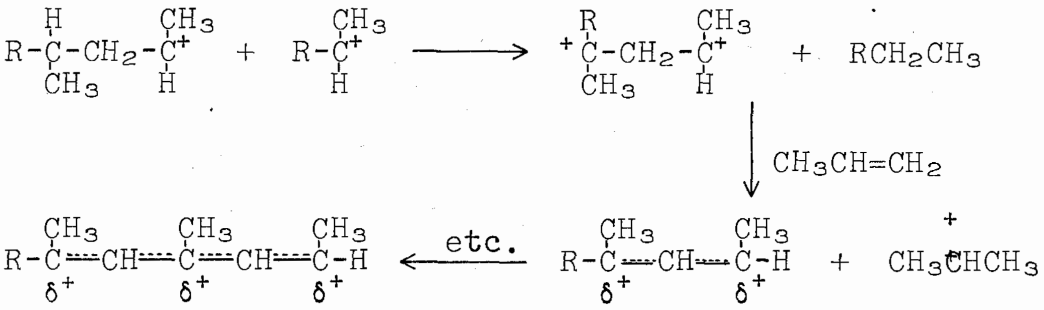
$$\sim\!\sim\!\sim \underset{MX_nB^-}{CH_2-\overset{+}{C}HY} \longrightarrow \sim\!\sim\!\sim CH=CHY + H^+\ MX_nB^-$$

ii) combination with an anion



$$\sim\!\sim\!\sim \underset{MX_nB^-}{CH_2-\overset{+}{C}HY} \longrightarrow \sim\!\sim\!\sim CH_2-\overset{Y}{\underset{B}{C}}-H + MX_n$$

iii) resonance stabilization of multivalent carbonium ions



As a result of hydride transfer, doubly charged carbonium ions are formed, which then react with monomer to form allylic-type carbonium ions, which are so stabilized by resonance as to be incapable of further propagation.

C. Kinetics

Kinetic analyses frequently involve the steady state assumption, that the concentration of active centers is constant. This assumption is valid for many cationic polymerizations, but on the other hand, is not valid for some systems.

Let the catalyst be A, and the co-catalyst RH.

$$A + RH \rightleftharpoons A\text{-}RH \qquad 1)$$

$$A\text{-}RH + M \xrightarrow{k_1} HM^+ \; AR^- \qquad 2)$$

$$HM_x{}^+ \; AR^- + M \xrightarrow{k_p} HM^+_{x+1} \; AR^- \qquad 3)$$

$$HM^+_x \; AR^- \xrightarrow{k_t} M_x + A\text{-}RH \qquad 4)$$

$$HM^+_x \; AR^- + M \xrightarrow{k_{tr}} M_x + HM^+ \; AR^- \qquad 5)$$

If 2) is the rate determining step, then the rate of initiation is $v_1 = k_1 [C][M]$, where C is the catalyst concentration. Since termination is first order, then $v_t = k_t [M^+]$. (M^+ is the concentration of all active centers.) By steady state assumption,

$$\frac{d[M^+]}{dt} = k_1 [C][M] - k_t [M^+] = 0$$

Then $$[M^+] = \frac{k_1}{k_t} [C][M]$$

Therefore, the overall rate is given by

$$v_p = k_p [M^+][M] = \frac{k_p k_1}{k_t} [C][M]^2$$

ELECTROINITIATED POLYMERIZATIONS

A. Scope of Electroinitiation

The generation of various species at an electrode may be utilized to initiate polymerization. The species produced may be such so as to initiate free radical, anionic, cationic, living, and condensation polymerization, depending on their nature. The electrolytic initiation presents a means of controlling the amount of initiator. The potential of the electrode may be regarded as the factor determining the kinds of substances electrolyzed and the current may be regarded as an initiator regulator. The progress of the polymerization after the initiation stage should be similar to conventional polymerization. Electroinitiation, then, is a means of providing some degree of control over the polymerization reaction.

Direct initiation, in which the active initiating species (be it from monomer or additive) is formed by an electrode reaction, is illustrated by the following free radical initiators:

$$CH_3I + e^- \longrightarrow CH_3\cdot + I^- \qquad \text{cathodic}$$

$$(C_2H_5OCO)_3C^- \longrightarrow (C_2H_5OCO)_3C\cdot + e^- \qquad \text{anodic}$$

The electrode may also be considered as a Lewis acid or base of variable strength which might initiate ionic polymerization:

$$X + e^- \longrightarrow X^-$$

$$X^- + M \longrightarrow XM^- \qquad \text{anionic}$$

$$XM^- + M \longrightarrow XMM^- \quad \text{...etc.}$$

$$R \longrightarrow R^+ + e^-$$

$$R^+ + M \longrightarrow RM^+ \qquad \text{cationic}$$

$$RM^+ + M \longrightarrow RMM^+ \quad \text{...etc.}$$

Indirect electroinitiation refers to the electrolytic formation of a species of an essentially chemical initiating system, that is, where the catalytic species generated at the electrode reacts with a second species in the bulk of the polymerization. This is illustrated by the following redox system (25):

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

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

where the $HO\cdot$ radicals may initiate polymerization. The electrolytic reduction of oxygen to hydrogen peroxide, which then polymerizes methyl methacrylate is another example of indirect initiation (26):

$$O_2 + e^{-} + H^{+} \longrightarrow HO_2\cdot$$

$$HO_2\cdot + e^{-} + H^{+} \longrightarrow H_2O_2$$

where $HO_2\cdot$ could initiate the polymerization.

B. Electroinitiated Free Radical Polymerization

1. Cathodic

One of the first polymerizations at the cathode was reported by Wilson in 1949 (27), in which methyl methacrylate was polymerized in aqueous or methanolic sulfuric acid solutions using various cathode materials. It was proposed that free radical centers were produced by the addition of hydrogen atoms, formed at the cathode, to the monomer double bond.

It was later shown by Parravano (28) in 1951 that the polymerization of methyl methacrylate indeed was due to hydrogen atoms produced at the cathode.

Tsvetkov (29) found that stirring of the electrolysis solution decreased the efficiency of the polymerization of methyl methacrylate, as compared to an unstirred solution. He explains this by picturing the polymerization centers as individual droplets whose number is decreased upon stirring, with a consequent increase in rate of termination. He also studied the effects of current density, temperature, and electrode dimensions on the yield of the polymer.

Mentioned previously were the studies of Federova (26) and Kolthoff (25) who, respectively, polymerized methyl methacrylate and acrylonitrile electrolytically.

2. Anodic

Reports of anodic free radical polymerizations are indeed few. The classical method of producing free radicals at the anode is the Kolbe electrolysis. The first success was the polymerization of styrene at the anode reported by Goldschmidt and Stockel in 1952 (30). Polymerizations of vinyl acetate, vinyl chloride, and methyl methacrylate were studied in aqueous solutions with potassium acetate as electrolyte by Smith and Gilde (31).

Breitenbach in 1962 (32) reported the polymerization of methyl methacrylate in acetic acid/acetic anhydride solution saturated with lithium acetate. A more detailed study on methyl methacrylate was done by Funt and Yu (33) using dimethyl sulfoxide, a non-aqueous solvent, in which both monomer and polymer are soluble. The free radical character was demonstrated, as well as the degree of control which could be exerted on the polymerization by the current.

The initiation of methyl methacrylate polymerization by the Kolbe electrolysis of sodium acetate in water, aqueous ethanol, and methanol has been studied by Tsvetkov (34,35). A 50% conversion was obtained in two hours.

C. Electroinitiated Anionic Polymerization

In contrast to free radical polymerizations, anionic polymerizations are not subject to bimolecular termination by the interaction of free radicals. Thus it is to be expected that the molecular weight of the polymer will be much higher, and the electrical efficiencies (the number of monomer units added per faraday) will also be increased.

In 1957, Yang, McEwan, and Kleinberg (36), using magnesium electrodes in anhydrous pyridine, polymerized styrene by an anionic mechanism.

Breitenbach (37) showed that the polymerization of acrylonitrile using a quaternary ammonium salt was anionic, and not free radical as he had previously thought (38).

Funt and coworkers have also carried out some anionic polymerizations. The polymerizations of acrylonitrile (39) showed a first order rate dependence on current and monomer concentration. The polymerization of styrene in dimethylformamide (40) was done using various alkali metal nitrates as the electrolyte. More recently, tetramethylammonium chloride in dimethylformamide was used as a conducting medium for the anionic polymerization of styrene (41) and of methyl methacrylate (42), the former being a first order with respect to current, the latter half order with respect to current.

A recent publication by Laurin and Parravano (43) involves a detailed study of the electrochemical polymerization of 4-vinylpyridine in liquid ammonia. The consequence of the electron transfer to monomer is the formation of radical anions, with subsequent chain growth occurring through an anionic mechanism.

$$e^- + M \longrightarrow \cdot M^- \qquad \text{initiation}$$

$$2\ \cdot M^- \longrightarrow {}^-M\text{-}M^- \xrightarrow{2\ M} {}^-M\text{-}M\text{-}M\text{-}M^- \qquad \text{propagation}$$

The electrolytic polymerization of caprolactam has been recently carried out by Gilch and Michael (44). Though the reaction proceeds via anionic intermediates, the product appears as a condensation polymer.

D. Electroinitiated Cationic Polymerization

The first report of an electroinitiated cationic polymerization came from Breitenbach (32). He studied the polymerization of styrene, isobutyl vinyl ether, and N-vinylcarbazole in nitrobenzene using mostly perchlorate salts, tetraethylammonium perchlorate and silver perchlorate. The following mechanism at the anode was proposed:

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

$$ClO_4\cdot + M \longrightarrow ClO_4^- + M^{+\cdot}$$

Funt and Blain, in attempting to repeat some of Breitenbach's experiments, found several discrepancies. This led to a more detailed and extensive study of the above monomers using various quaternary ammonium salts, in methylene chloride solutions (45). The work showed that the degree of control over the reactions by the current varies greatly with both the monomer and salt. Pulsed current experiments - current ON, current OFF, current ON - showed that a large degree of control could be obtained especially for the polymerization of styrene and isobutyl vinyl ether using tetrabutylammonium perchlorate. Constant current experiments gave reproducible kinetic results.

E. Other Electroinitiated Polymerizations

1. Living polymers

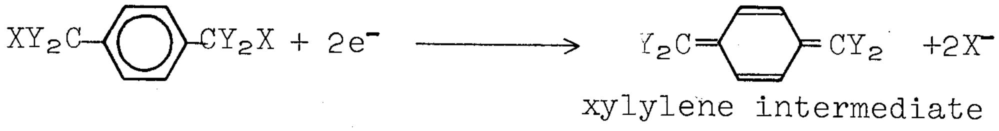
Yamazaki, Nakahama, and Kanbara (46) provided the first report of electroinitiated living polymerizations (polymerization with no termination) using THF as solvent, lithium aluminum hydride or sodium tetraalkylaluminum salts, and α-methylstyrene as monomer. At low temperatures, the characteristic colour of living anions was obtained, and the polymer molecular weight closely obeyed the conventional equation for living polymers

$$\bar{M}_n = \frac{\text{grams of polymer}}{\frac{1}{2} \times \text{faradays passed}}$$

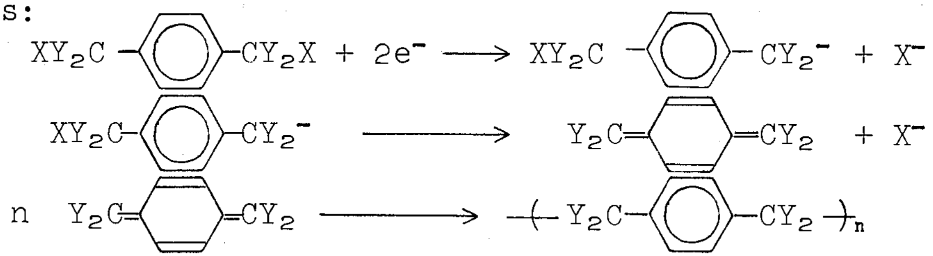
This work has been extended by Funt and coworkers using styrene and isoprene monomers (47,48).

2. Poly-p-xylylenes

A case where an easily polymerized intermediate was produced by electrolysis has been found by Gilch (49), the reduction of p-xylene compounds. Though the overall process appears as a condensation polymerization, kinetic results are in fact consistent with a free radical addition polymerization of a reactive intermediate formed by reduction. The key step in the reaction is not the formation of an intermediate between the reducing agents and the haloxylenes, but rather the process of electron transfer:



It should be possible to carry out the reduction electrolytically. The mechanism for the electrolytic polymerization of α,α′-dihalo-p-xylenes at the cathode is proposed to be as follows:



Various p-xylene compounds polymerized by Gilch are summarized in Table 2.

Covitz (50) more recently has done studies on the reduction of α,α′-dihalo-p-xylenes using the techniques of polarography, controlled potential electrolysis, coulometry, and cyclic voltammetry, to clearly establish the presence of the p-xylylene intermediate. Two mechanisms for the production of the intermediate are proposed with the following concerted mechanism being favoured on a basis of polarographic studies:

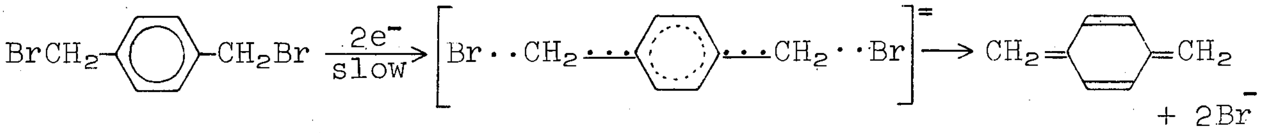


Table 2. Polymerization Conditions for α,α′-halo-p-xylylenes (49).

	p-xylene monomer	Cathode potential, volts	Cathode-anode potential volts	Current density, ma. cm.^{2}	Current efficiency, %
A	α,α′-dichloro-	-1.2	3.0-3.5	1.4-2.7	35
B	α,α,α,α′,α′,α′-hexachloro-	-0.7	3.6-6.0	2.0-5.5	95
C	α,α′, 2-trichloro-	-1.4	3.4-4.0	1.3-3.2	65
D	α,α′-dibromo-	-1.2	2.5-4.5	1.2-3.5	90
E	α,α′-dibromo-2-chloro-	-1.2	2.3-4.2	1.0-3.5	90
F	α,α′-dibromo-α,α,α′,α′-tetrafluoro-	-1.1	4.9-6.0	3.0-6.0	96

Ross and Kelley (51) report the preparation of adherent films of poly-p-xylylenes on aluminum by the electrolysis of solutions of p-methylbenzyltrimethylammonium salts in polar solvent such as dimethylformamide and dimethylsulfoxide. An adherent coating of polymer appears on the aluminum cathode.

The poly-p-xylylenes promise to bring a new dimension to dielectric and electric insulation, to protective and barrier coatings, and so on. The polymers are linear and highly crystalline. Several good reviews on the chemistry, the physical properties, and the applications of the poly-p-xylylenes have been written (52,53,54). The added dimension of producing these polymers by an electrical process where some degree of control may be applied, promises to be very important industrially.

THE POLYMERIZATION OF TETRAHYDROFURAN

A. Introduction

The polymerization of tetrahydrofuran (THF) was first reported by Meerwein (6) around 1939, and later reviewed by him in 1960 (55). The polymerization proceeds via a cationic mechanism, with the catalysts being of the strong acid or Lewis acid type, or their derived salts.

Poly (THF) is a crystalline polymer, and has been prepared either as very low molecular weight polymer (sticky viscous oils), medium molecular weight (waxes) or high molecular weight polymer (tough, rubbery, intractable materials).

The polymer is soluble in solvents like toluene, benzene, ethyl acetate, and chloroform, and from intrinsic viscosity measurements one may obtain molecular weights. X-ray studies (56) have indicated that the crystalline polymer has a planar zig zag conformation. The infra-red, Raman, and NMR spectra have also been reported (56,57,58). The degree of crystallinity has varied from about 30% to 80% depending on method of preparation and molecular weight. (59). The ceiling temperature, above which no polymerization will occur in the bulk, has been reported to be about 83°C. (60).

In considerations of the thermodynamics of ring opening polymerizations of cyclic ethers, the heat of polymerization (ΔH_p) is the main contributor to the free energy of polymerization (ΔF_p). The heat of polymerization is dependent on ring strain and on the amount of crowding of the eclipsed adjacent hydrogen atoms (61). Table 3 shows some of the heats of polymerization for several cyclic ethers. For polymerization to occur, ΔF_p must be negative, and all polymerize except tetrahydropyran. However, upon substitution of the THF ring, ΔF_p becomes positive, and in fact, substituted tetrahydrofurans have not yet been reported to polymerize.

B. Mechanism of Polymerization

1. Initiation

It is generally accepted that the propogating species in cationic THF polymerization is a tertiary oxonium ion, and so initiation must involve the formation of such a

Table 3. Heats of polymerization of some cyclic ethers (62).

Compound	$-\Delta H_p$ (kcal mole)	Polymerized when substituted
ethylene oxide	22.6	yes
oxetane	19.3	yes
tetrahydrofuran	3.5	no
tetrahydropyran	-1.3	no

species (63). Several ways are possible, and they can be grouped as follows:

i) reaction with preformed trialkyl oxonium salts

ii) "in situ" formation of oxonium ion

iii) addition of carbonium ion

iv) hydrogen abstraction

i) Reaction with preformed trialkyl oxonium salts

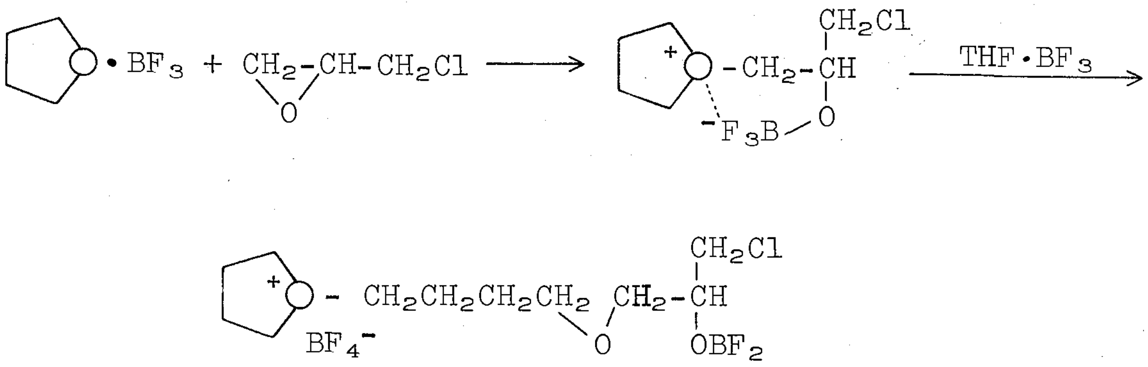
The initiation involves a transfer of an alkyl group from a preformed trialkyl oxonium ion salt to a THF molecule:

This probably occurs by a nucleophilic attack of the THF oxygen atom on a carbon alpha to the oxygen of the trialkyl oxonium ion salt. It has been shown that each mole of initiator will initiate one mole of polymer chains (64). The disadvantages lie in the experimental problems of purification and handling the materials, and in the lability of the salt solutions (65).

ii) "in situ" formation of oxonium ion

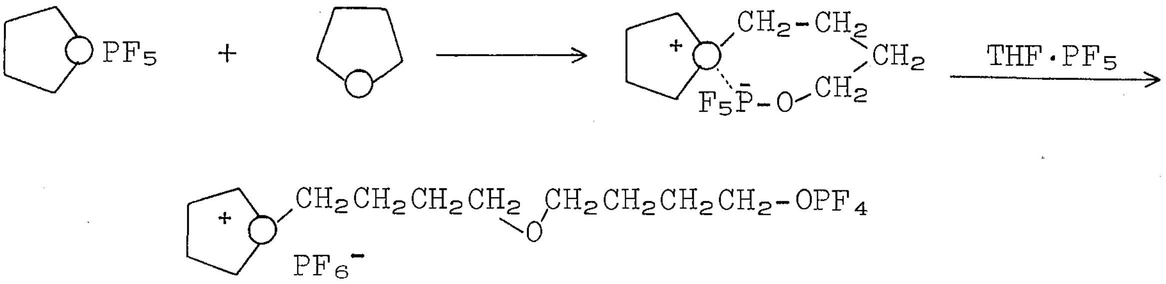
a) in presence of added promotor

The reaction of a metal halide like BF_3 or BF_3 etherate with an epoxide, like epichlorohydrin (ECH) or ethylene oxide, is used as an "in situ" method of providing the oxonium ion, where the Lewis acid component is referred to as the "catalyst", and the epoxides as the "promoter" (66). In a bulk THF system, the Lewis acid would be in the form of a complex with the THF, and this complex then would interact with the promoter to initiate polymerization, as follows:



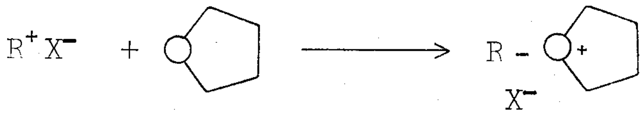
b) in absence of added promoter

For very reactive Lewis acids like PF_5 the THF itself could function as a promoter:



This has been studied by Sims (68) for PF_5, by Lyudvig and coworkers for $SbCl_5$ (69), and by Burrows for BF_3 (70), and it has been found that initiation of this type is a slow process.

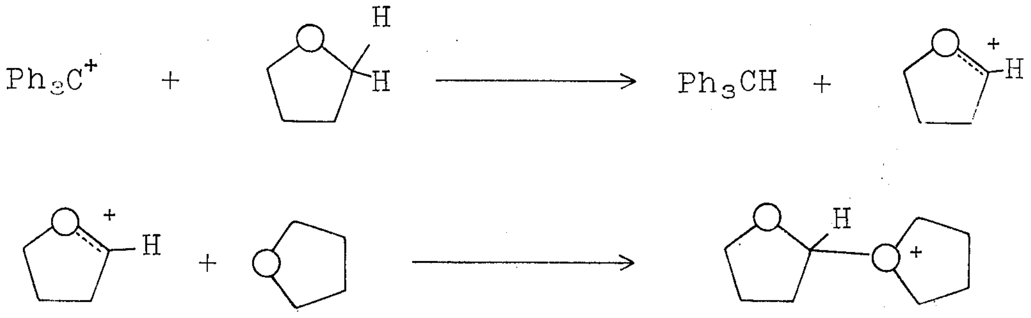
iii) addition of carbonium ion



This type of initiation is not too common because of the instability of the carbonium ion salts. The polymerization using $CH_3COSbCl_6$ as initiator has been carried out recently by Lyudvig et al. (69).

iv) hydrogen abstraction

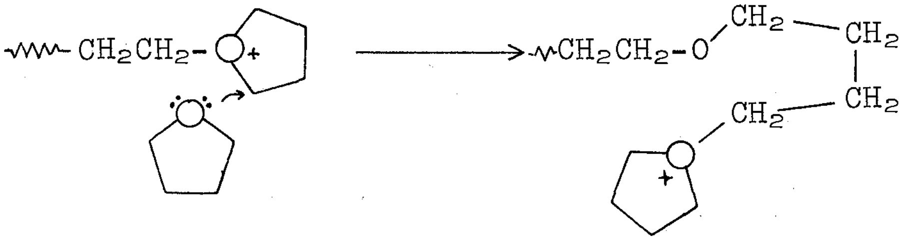
The use of the initiator $Ph_3C^+SbCl_6^-$ was first reported by Bawn, Bell, and Ledwith (71), and prompted a study by Kuntz (58) into the mechanism. The possibilities were either the addition of the Ph_3C^+ cation to THF (in which case one would expect Ph_3C^- endgroups) or the formation of triphenyl methane by hydride-ion abstraction, with the further reaction of the cationic intermediate with THF. By means of an NMR study, they showed that the latter was in fact the correct mechanism:



Studies on another salt, p-chlorophenyldiazonium hexafluorophosphate have confirmed the above hydride-ion abstraction mechanism (63).

2. Propagation

The propagating species in the cationic polymerization of THF is the tertiary oxonium ion. The propagation reaction is considered to be a nucleophilic attack by the oxygen on the monomer with a carbon alpha to the positive oxygen on the oxonium ion.



Some suggestion of the propagation step involving the preliminary opening of the THF ring to produce a carbonium ion has been ruled out by the fact, that if such a mechanism were to occur, then one would expect methyl branches on the chain due to an isomerization from unstable primary carbonium ions to more stable tertiary carbonium ions (72). This has not been observed.

3. Termination and Transfer

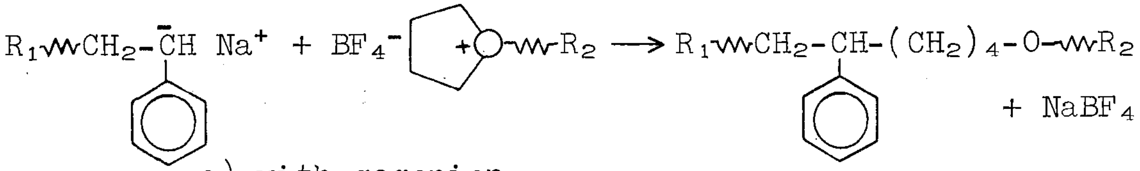
In recent literature (60,71,72) evidence for the "living polymerization" of THF has been given, that is, polymerization without termination. Experimentally, the molecular weight increases with increase in the degree of conversion, and the molecular weight is inversely proportional to the catalyst concentration. Molecular weight distribution data gives $M_w/M_n = 2$, which confirms that the polymerization is of the "living" type (73). To achieve polymerization without termination a very high degree of purity would be required, otherwise, termination can occur. Several termination possibilities are as follows:

a) with impurities

Anything which could react with the cation complex could terminate the reaction, substances like amines, oxygen, acids, and water. Therefore high vacuum work is usually required, although some polymerizations do occur under a nitrogen atmosphere.

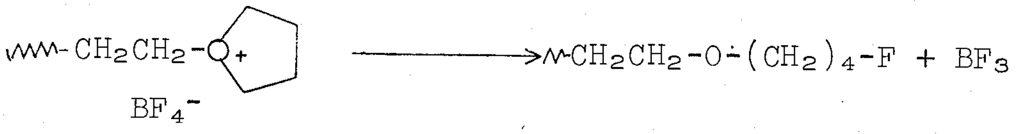
b) with anionic "living" polymer

With the discovery of "living" cationic polymerization of THF, the possiblity of termination with an anionic "living" polymer existed. Berger in 1966 (74) successfully performed a mutual termination of two living systems, in the formation of a polystyrene - poly(THF) block copolymer, with properties quite different than the homopolymers. The mechanism of this "tailor-made" copolymer formation was given as:



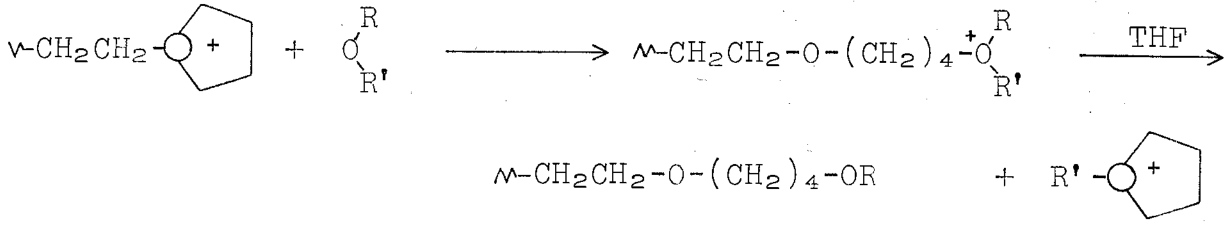
c) with gegenion

The nature of the gegenion determines to a large extent the degree of conversion and the molecular weight of a polymer, and thus the properties of the oxonium ion - gegenion complex are very important. Meerwein (55) has suggested that above room temperature the following termination reaction could occur with the BF_4^- gegenion:



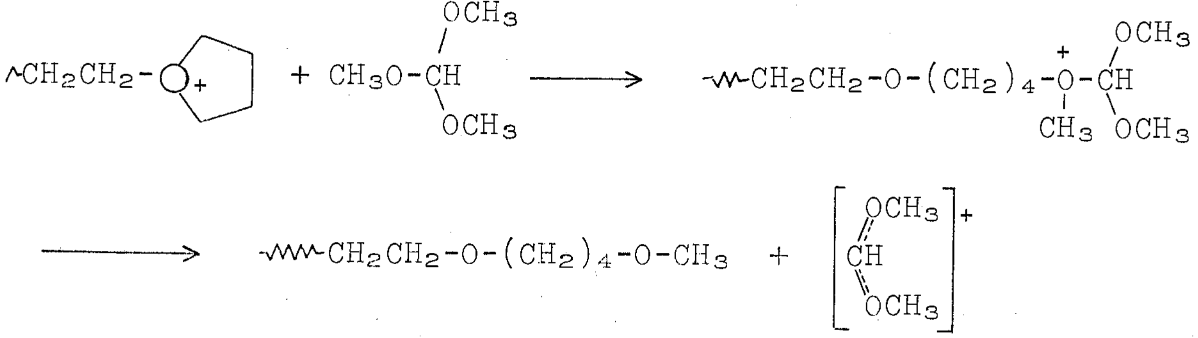
Chain transfer occurs when a growing center reacts such that a new reactive center is produced and the old one is destroyed by the chain transfer agent. Again, the transfer reactions may be grouped as follows:

a) with acyclic ethers

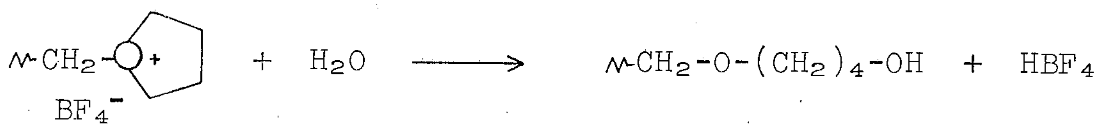


The transfer does not affect the final degree of conversion to the polymer, but does affect the intrinsic viscosity. That is, an overall decrease in molecular weight is noted (63).

b) with an orthoester (63)

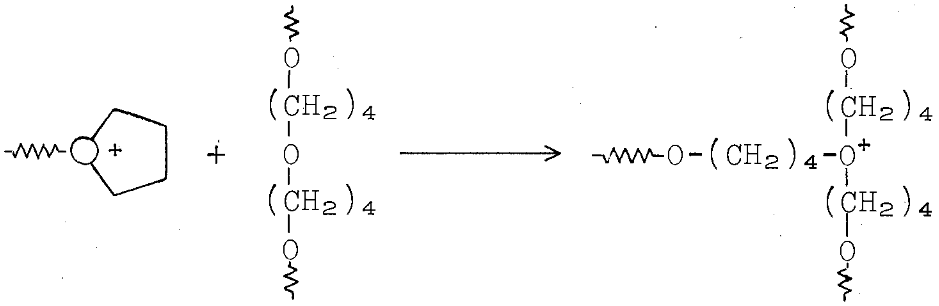


c) with water (72)

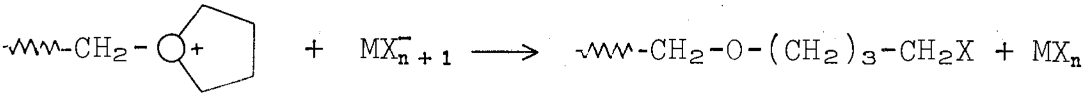


d) with polymer oxygen (75)

After most of the THF monomer has polymerized, a large increase in viscosity of the reaction mixture was noted, which was explained by a chain transfer to polymer:



e) with gegenion



C. Kinetics

Although the kinetics of the polymerization of THF vary somewhat for different catalyst systems, the following discussion is applicable to the majority of systems studied so far.

The process of THF polymerization is a reversible, monomer-polymer equilibrium system. The polymerization rate is proportional to the effective monomer concentration, and takes place as a steady state process of the "living" polymer type. A lowering of the molecular weight with a rise in temperature is explained by an increase of the equilibrium monomer concentration with increase in temperature. The rate is directly proportional to the catalyst concentration. The reaction scheme can then be represented by:

$$\begin{array}{llll} C_O + M_1 & \rightleftarrows & M_1{}^* & \text{initiation} \\ M_1{}^* + M & \rightleftarrows & M_2{}^* & \text{propagation} \\ M_n{}^* + M & \underset{k_d}{\overset{k_p}{\rightleftarrows}} & M_{n+1}^* & \end{array}$$

where C_o is the initiator, M is the monomer, and M^* is the activated monomer.

If it is assumed that the initiation rate is equal to the growth rate, then the concentration of active growing polymers is equal to the concentration of initiator originally there, that is $[M^*] = [C_o]$.

Then the rate is

$$\frac{-d[M]}{dt} = k_p[M][C_O] - k_d[M^*] = [C_O](k_p[M] - k_d)$$

$$\text{At equilibrium, } K = \frac{k_p}{k_d} = \frac{[M^*]}{[C_O][M]_{eq}} = \frac{1}{[M]_{eq}}$$

$$\therefore -d[M] = [C_O](k_p[M] - k_p[M]_{eq})$$

$$= k_p[C_O]([M] - [M]_{eq})$$

Numerous systems have been found to agree experimentally with the above kinetics (64,65,72,76).

Saegusa and coworkers (67,77,78) have determined the concentration of the propagating species by ultraviolet spectroscopy, and thus have been able to calculate a propagation constant. In a polymerization without termination or chain transfer, the concentration of propagating species $[P^*]$ can be determined by:

$$[P^*] = \frac{\text{grams of polymer}}{\text{molecular weight}} \times \frac{1}{\text{volume of system}}$$

However for systems involving some chain transfer or termination, this relation is not valid, and the alternate U.V. method is used. The values of k_p thus determined are of the order of 1.2×10^{-2} to 7.8×10^{-3} liter/mole-sec.

D. Electroinitiation of THF polymerization

The electroinitiation polymerization of THF has not previously been reported. The question then is whether a polymerization catalyst for the polymerization of THF can be generated by an electrical process. Previous work by others (45) in this lab has resulted in the successful electroinitiated cationic polymerization of vinyl ethers using a tetrabutylammonium salt electrolyte. This prompted experiments to polymerize THF cationically, by an electroinitiation process, using tetrabutylammonium salts as the electrolyte. The anions of the salts would be required not to react with the positive growing site, as this results in a high rate of termination and low molecular weight polymers. Therefore it was thought that anions which are used in conventional polymerizations, such as BF_4^-, $SbCl_6^-$, and possibly ClO_4^-, should be good electrolyte anions for the electroinitiation of THF polymerization.

PURIFICATIONS AND EXPERIMENTAL TECHNIQUES

A. Monomers, salts, solvents

Tetrahydrofuran (Fischer Certified) was stirred for 24 hours over fresh calcium hydride using a teflon coated magnetic stirring bar. The tetrahydrofuran (THF) was then transferred onto a vacuum line, where again it was stirred for several hours, opening the flask to the vacuum system at various intervals. A sodium mirror was prepared. A flask with sodium metal was evacuated for an hour or two. With the flask open to the vacuum, the sodium was heated gently until the boiling point was reached, and a bright shiny mirror of sodium was produced on the walls of the flask. The THF was then distilled from the calcium hydride onto the sodium mirror, with which it remained in contact for at least 4 or 5 hours before use. Successive distillations were done onto fresh sodium mirrors if the mirror disappeared.

The salts used for THF polymerization were tetrabutylammonium perchlorate and tetrabutylammonium borofluoride. Tetrabutylammonium perchlorate (Southwestern Analytical Chemicals, polarographic grade, wet with water) was used without further purification, except for drying in a vacuum oven overnight. The salt was placed in the polymerization cell and pumped out under vacuum for a minimum of 6 hours, with gentle intermittent heating.

Tetrabutylammonium borofluoride was prepared by titrating a 25% methanolic solution of tetrabutylammonium hydroxide (Eastman Organic Chemicals) with a 48% aqueous solution of fluoroboric acid (Matheson, Coleman, and Bell) (79). Cold water was added to effect better precipitation of product. The precipitate was collected on a Buchner funnel. The salt was recrystallized twice by dissolving it first in warm methanol, and then precipitated into large volumes of cold water. It was then dried under vacuum at about 70°C. The melting point was 161°C. When placed in a polymerization cell, it was treated the same as tetrabutylammonium perchlorate.

Attempts were made to polymerize THF in various solvents - methylene chloride (Matheson, Coleman, and Bell - spectroquality), nitrobenzene (Matheson, Coleman, and Bell), chlorobenzene (Fisher Certified), and dioxane (Matheson, Coleman, and Bell). These solvents were purified by stirring over CaH_2 for several hours and degassing 2 or 3 times, after which the solvents were distilled into the polymerization cell.

The experiments performed with the p-xylenes involved no purification procedures. The monomers, α,α'-dibromo-p-xylene (Aldrich Chemical Co.), $\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$ - hexachloro-p-xylene (Aldrich Chemical Co.), and $\alpha,\alpha,\alpha',\alpha',2,3,5,6$ - octachloro-p-xylene (Aldrich Chemical Co.) were all used as received. The salts, tetramethylammonium bromide (Matheson, Coleman, and Bell), tetrabutylammonium bromide (Eastman

Organic Chemicals), tetrabutylammonium iodide (Matheson, Coleman, and Bell), and tetrabutylammonium perchlorate (Southwestern Analytical), were all used as received. The solvent, dimethylformamide (Matheson, Coleman, and Bell) was used without further purification.

B. Polymerization Cells

The cells used in the initial bulk polymerization experiments of THF were of the type shown in Figure 1. The volume of the anode solution was approximately 60 - 65 ml. and the cathode solution was approximately 40 - 35 ml. The electrodes consisted of 2.6 cm. x 2.6 cm. square sheets of platinum separated by about 8.0 cm. The electrodes were suspended by platinum wire from a graded lead glass vacuum seal. (On some cells, the platinum wire was silver soldered to a tungsten wire sealed in glass). The fritted glass disc was of medium porosity.

A modification of the cell in Figure 1 allowing samples to be withdrawn was made by putting a sidearm glass tube on the anode compartment. A silicone rubber septum was glued onto the end of the glass tubing, so that samples could be removed by syringe.

A later design for a cell in which viscous polymer was more easily removed is shown in Figure 2. The volumes of anode and cathode solution were both 50 ml. The electrodes were 1 in. square platinum sheets, suspended by platinum wires silver soldered to tungsten wires vacuum sealed in

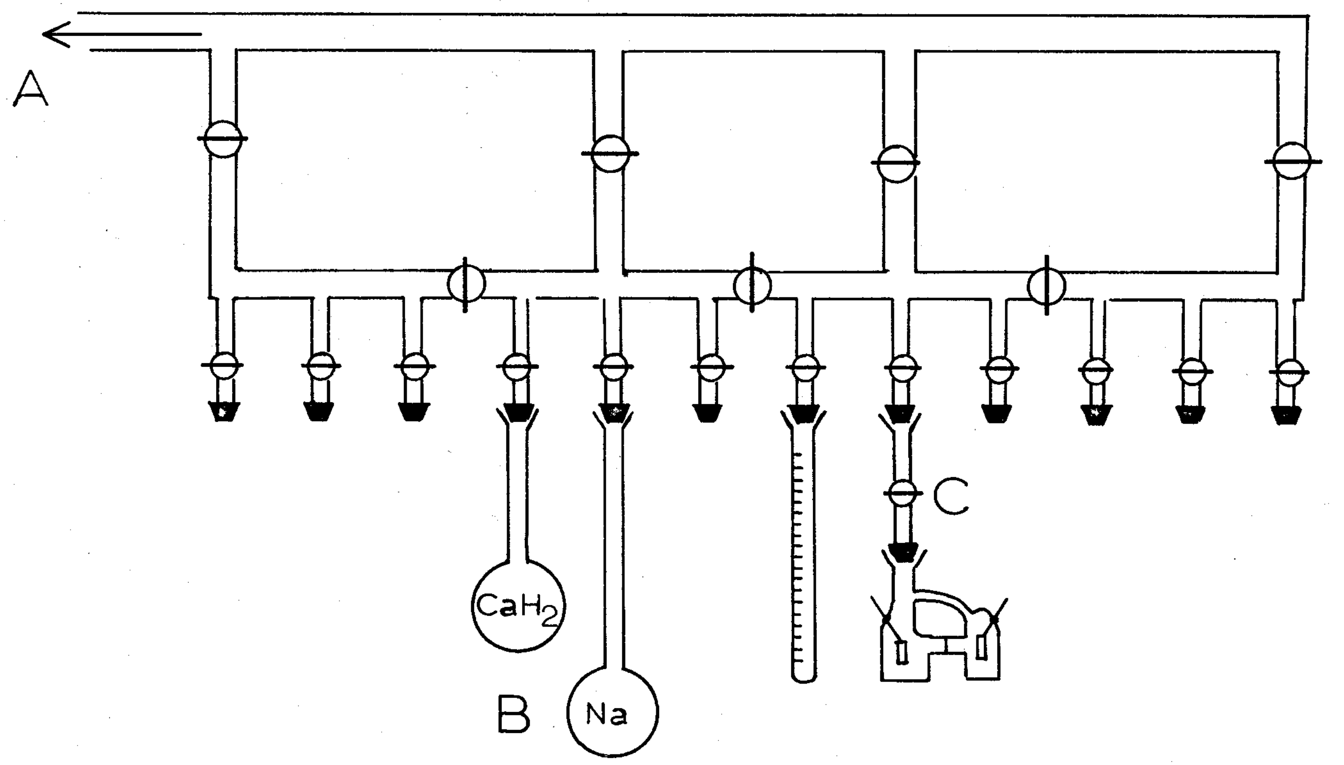

A
CaH$_2$
B
Na
C

Figure 5. The vacuum line.

A - to the vacuum pumps.

B - section of line for solvent purification.

C - ground glass stopcock to remove cells.

a vacuum line shown in Figure 5. A mechanical pump and a mercury diffusion pump in series provided a vacuum of $<10^{-4}$ mm. of mercury, as measured on a Macleod gauge. All stopcocks were ground glass and silicone grease (Dow Corning) was used. One section of the line was used for THF purification (CaH_2,Na mirrors). The remaining sections of the line were used to evacuate the cells and to dry the salts. THF was distilled into measuring cylinders, and from measuring cylinders into polymerization cells. Both liquid nitrogen and acetone/dry ice baths were used in the distillations. By closing stopcock C, the cells could be removed from the vacuum line without releasing the vacuum.

D. Electrolysis Apparatus

The polymerization cells for THF were placed in a thermostated bath at 25±0.5°C. Rotating magnets below the baths allowed the solutions to be stirred by means of teflon coated magnetic bars.

Most THF polymerizations were carried out using a Kepco (Model ABC 1000M) power supply. A circuit was prepared so that constant current electrolyses could be performed. The current could be continuously varied from 0 - 20 ma. An automatic ON-OFF timer was used for electrolyses begun or ended during the night.

Initial experiments on THF were performed with an Ambitrol 4005 power supply. However, the output was limited to 40 volts, and because of the high resistance of our solutions ($\sim$100 K), this limited the currents to about 0.6 ma.

glass. The separation of the electrodes was 9.5 cm. and the fritted glass discs were of medium porosity.

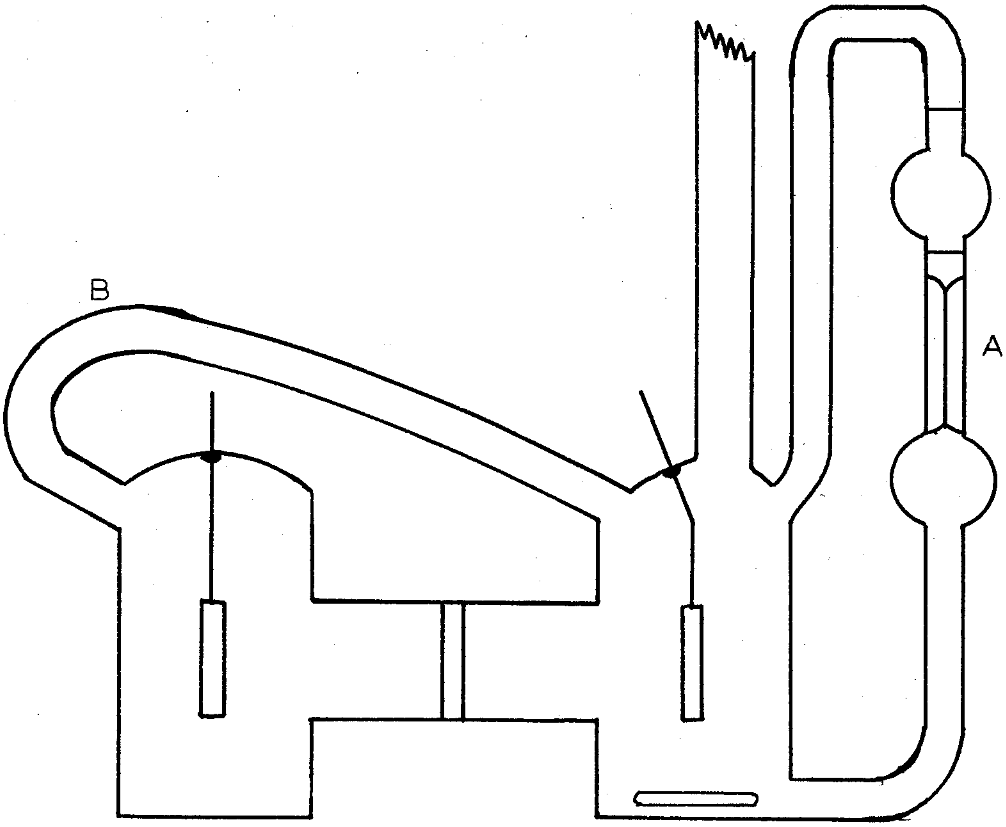
The cells were attached to the vacuum line using a B24 socket-B19 cone adaptor, with a stopcock in between.

Two viscosity cells, as shown in Figure 3 were used, one with a 0.5 mm. bore capilliary, and the other with a 1.5 bore capilliary. The 0.5 mm. bore viscosity cell has anode platinum electrode dimensions of 2.3 cm. x 2.3 cm, and cathode platinum electrode dimensions of 2.3 cm. x 2.3 cm, and volumes of 55 ml. each. The electrodes were separated by 10.5 cm, and were suspended from platinum wires in graded lead glass seals. The 1.5 mm. bore viscosity cell has anode and cathode dimensions of 2.6 cm. x 2.5 cm., with an anode volume of 65 ml. and cathode volume of 60 ml. The electrodes were separated by 11.0 cm. The design of the cell allowed rotation to fill the bulbs of the viscometer without mixing the solutions of the anode and cathode compartments.

The cell used for the polymerization of the p-xylenes is shown in Figure 4. The cathode consisted of a mercury pool, and the anode of a platinum disc separated from the cathode by a fritted glass disc. A calomel reference electrode was placed with the measuring tip near the mercury surface. In this way, a controlled-potential electrolysis could be conducted.

C. Vacuum line and distillations

Final purifications and distillations were done on


B
A

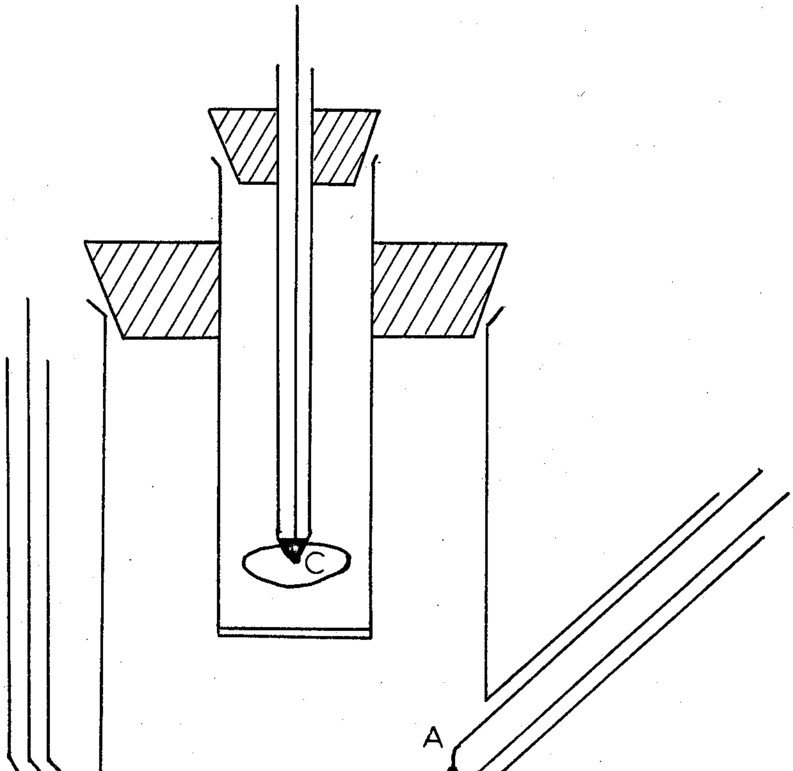

C
A
B

Figure 3. Viscosity Cell for THF polymerization.

A - capillary to measure viscosity.

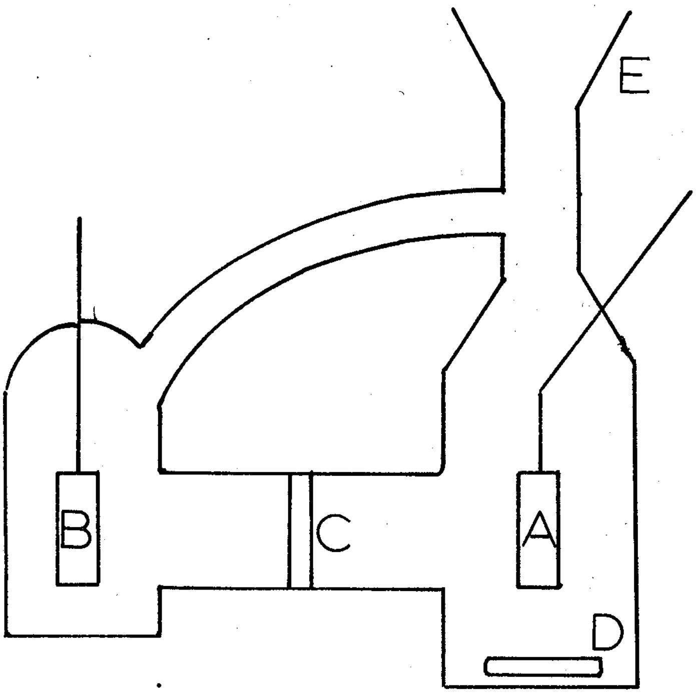
B - glass extension to allow rotation of cell without mixing of the solutions in the anode and cathode compartments.

Figure 4. Polymerization cell for p-xylene experiments.

A - calomel reference electrode.

B - mercury working electrode.

C - platinum counter electrode.


E
B
C
A
D

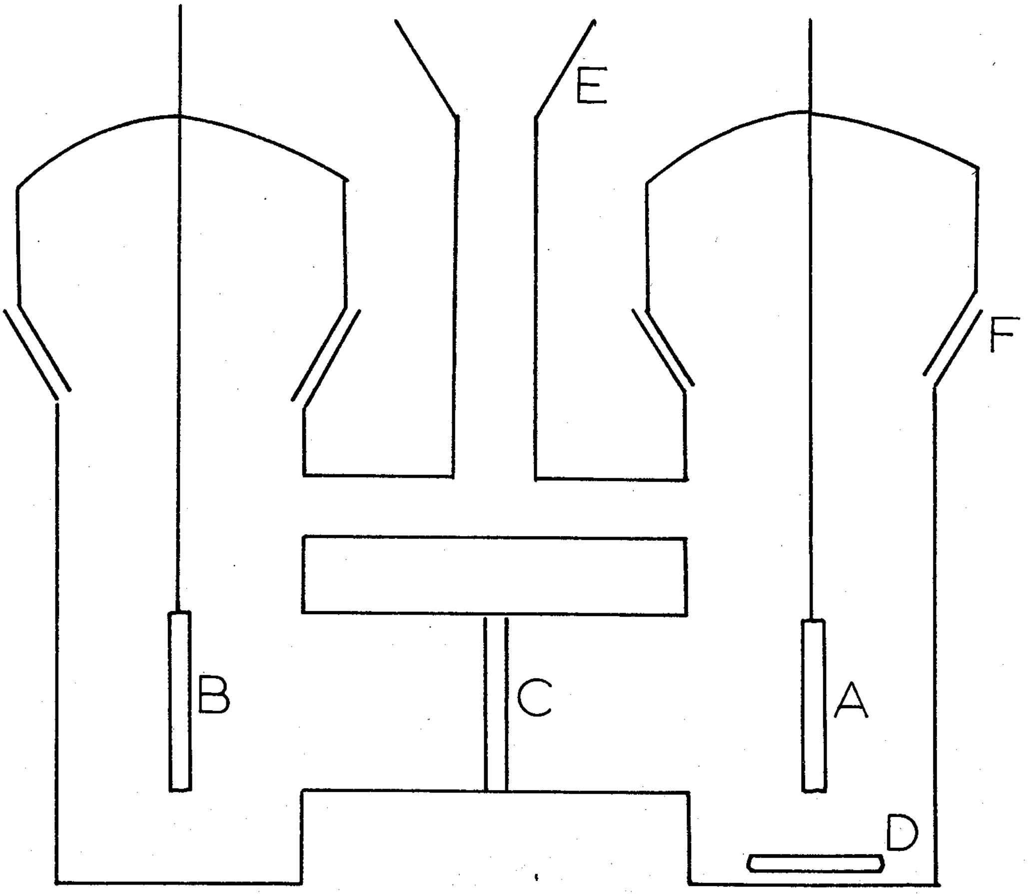

E
F
B
C
A
D

Figure 1. Polymerization cell for THF polymerization.

A - platinum anode.
B - platinum cathode.
C - sintered glass disc.
D - magnetic stirrer.
E - ground glass joint to vacuum line B 19.

Figure 2. Polymerization cell for THF polymerization.

A - platinum anode.
B - platinum cathode.
C - sintered glass disc.
D - magnetic stirrer.
E - ground glass joint to vacuum line B 19.
F - ground glass joint for removing electrodes B 34.

and less.

The power source for the p-xylene electrolyses was a Wenking 61 RH potentiostat. With the potentiostat it is possible to exactly control the potential of the working electrode (cathode) with respect to the reference - a controlled potential electrolyses. Applied voltages were of the order of 1000 mv., with the currents being of the order of 20 - 100 ma.

E. Polymer Characterizations

The polymers of THF were isolated from the polymerization cell by precipitation into large volumes of methanol. The polymer was then dried under vacuum for about 24 hours to remove all traces of methanol and unpolymerized THF monomer.

The measurement of the molecular weight of THF was done by dilution viscosity, using a Ubbelohde type viscometer. The viscosity measurements are independent of the amount of solution used in the viscometer, and successive dilutions are made easily. Measurements were done in a thermostated bath at 25±.05°C. Using solutions of ½% to 1% polymer in benzene, the reduced viscosity was obtained, and by extrapolation to infinite dilution, the intrinsic viscosity $[\eta]$ was obtained. The relation $[\eta] = KM^{\alpha}$ was used to obtain the molecular weight, where $K = 2.98 \times 10^{-4}$ and $\alpha = 0.79$ at 25°C. (80). These values of K and α are those used in a molecular weight determination of an equilibrium polymer conventionally prepared at 25°C, whose distribution may or may not be similar to a polymer prepared by electroinitiation. However, the molecular weights determined will be useful for establishing molecular weight trends and for comparative purposes.

The infra-red spectra and NMR spectra of poly(THF) were also obtained, using a Beckman IR 12 spectrophotometer, and a Varian A-56 60A NMR machine.

Some experiments involved the use of a Micro Tek DSS 161 gas chromatograph. The column used was $\frac{1}{4}$ inch copper tubing, 10 feet long, and filled with 15% carbowax on Chromosorb G DMCS, and was kept at 85°C. The detector, a thermal conductivity unit, was used at 135°C. The injection port was at 115°C. Injections of 1 - 5 micro liters were used.

A series of polymers were sent to Waters Associates, Framingham, Mass. for molecular weight distribution analysis.

The poly-p-xylenes precipitate out of solution upon polymerization. The precipitate was collected and dried under vacuum at 110°C. Viscosity measurements were performed on a poly-p-xylylene polymer in α-chloronaphthlene at 247°C. The intrinsic viscosity was found as before, but no K and α constants are available to determine the molecular weight of the polymer.

EXPERIMENTAL RESULTS

A. Initial Experiments

Constant voltages of 40 volts were applied to cells of the type shown in Figure 1, containing a solution of 1.0 x 10^{-3} moles to 6.0 x 10^{-3} moles of tetrabutylammonium perchlorate ($TBAClO_4$) dissolved in 100 mls. of THF. The initial currents were in the order of 0.5 ma. to 6.0 ma. After 2 or 3 hours a brown coloration was noticed in the stirred anodic compartment. The current was passed for periods of about 24 hours, during which time the current decreased due to a marked increase in the resistance of the solution. In 18 hours, the current decreased from 6.0 ma. to 0.40 ma., as the resistance increased from 85 K to 1700 K. The viscosity of the anodic solution increased during the experiment as could be seen by the reduced speed of the magnetic stirrer. The cell was then opened to the atmosphere and the contents of the anode were poured into large quantities of methanol. The polymer was precipitated out of solution, collected in a beaker, and dried under vacuum for 24 hours to remove all remaining THF monomer and methanol. The yields of polymer were around 2 - 10 grams, and the molecular weights varied from 6,000 to 50,000.

An attempt was made to polymerize THF in the bulk without purification of either the THF or the $TBAClO_4$ salt. A .0586 molar solution of $TBAClO_4$ in THF was electrolyzed for $1\frac{1}{2}$ hours with a current of 11.0 ma. No brown colour was noted in the anode compartment and after 40 hours the anode solution was poured into methanol. No polymer precipitated out of solution.

Blank experiments in which no current was passed also did not yield polymer, regardless of the purity of the monomer or the salt. Even where the salt and monomer were rigorously purified, an increase in the viscosity of the anode solution as measured by a viscosity cell shown in Figure 3 was not noted even after several days, indicating that polymerization did not occur.

Experiments in which rigorous vacuum purifications were used, did yield polymer if nitrogen was let into the system before electrolysis. No apparent loss in yield or decrease in molecular weight as compared to vacuum systems was noted. This led to the possibility of carrying out the polymerizations under an inert atmosphere of nitrogen, employing cells such as shown in Figure 1, but with a sidearm on the anode where samples could be removed by syringe through a rubber septum. Such experiments could be used to measure the degree of conversion with time (section H).

In two particular experiments where currents of 6.0 ma. were passed through THF solutions of .0586 molar $TBAClO_4$ for $2\frac{1}{2}$ hours and 5 hours respectively, no polymer was isolated from the anodic compartment when the solution was precipitated immediately after electrolysis. An experiment was then performed using a cell with a sidearm sampling port, with the same concentration of $TBAClO_4$ in THF, passing 11.0 ma. for 1 hour. Samples of 5 mls. were withdrawn at various intervals after the electrolysis. Samples withdrawn up to 6 hours after the beginning of electrolysis showed only turbidity when syringed into methanol. About 7½ hours after the beginning of electrolysis some polymer was precipitated. However, the quantity was too small for a molecular weight determination or a yield measurement. After 49½ hours the remaining solution was precipitated, giving a polymer of molecular weight 59,200. These experiments suggested that the mechanism may involve slow growth after a fast initiation, with the intermediate production of dimers, trimers, low molecular weight polymers, etc., or may involve slow initiation and slow growth. An attempt was made to see if the intermediates above could be detected by gas chromatography (section D).

Differences in the yield of polymer and molecular weight, were noted in the polymerization of two similar solutions where a current of 11.0 ma. was passed for 1 and 2 hours respectively. The yield for the latter was 66% higher and the molecular weight increased from 46,000 to 54,600. These results suggested that other investigations be carried out on the effects of the time of current passage, and amount of current (section E and G).

To further elucidate the mechanism, polymerization was attempted in the presence of a free radical inhibitor. To the polymerization system of 1.5 grams of $TBAClO_4$ in 80 mls. THF was added 1.00 g. of hydroquinone. A current of 11.0 ma. was passed for one hour. A gas was evolved from the cathode, but no attempt to identify the gas was made. After one hour, crystals appeared on the cathode, and the cathodic solution became bright yellow. The solution in the anode compartment was not as viscous as in polymerizations without hydroquinone. After 62 hours, the contents of the anode compartment were pour-into methanol, yielding 5.32 grams of polymer having a molecular weight of 29,000. Both the yield and molecular weight were less than that normally found for polymerizations without hydroquinone.

An attempt to polymerize THF at low temperatures did not yield polymer. A methanol dry ice bath at -78 °C was used. The resistance of the cell was very high and so only low current was passed through the solution.

Several polymerizations were performed with tetrabutylammonium borofluoride ($TBABF_4$) as the electrolyte. The anode solution became extremely viscous during an electrolysis in which the current was less than 1 ma. for a period of approximately 3 days. The molecular weights of these polymers, in the range of 160,000 to 175,000, were much higher than those prepared from the $TBAClO_4$ salt. The effect of $TBABF_4$ salt concentration is discussed later (section F).

Infra-red spectra of poly(THF) were obtained from solution (CS_2,$CHCl_3$) and from a film of polymer (Figure 6). The latter was prepared by evaporating a few drops of chloroform solution of polymer on a sodium chloride cell. A difference in the spectra between the solution (A) and the film (B) can be noted at 1000 $cm.^{-1}$ The spectra correspond very closely to spectra of poly(THF) prepared by conventional methods (57).

The NMR spectrum of a poly(THF) sample is given in Figure 7. The spectrum shows peaks with chemical shifts of 1.5 ppm. and 3.4 ppm. downfield from tetramethylsilane (0 ppm.). The spectrum is displaced downfield with respect to the spectrum for pure solvent THF, and compares well with spectra given in the literature (58).

B. Viscosity Cell Experiments

A viscosity cell as shown in Figure 3 was used to follow the increase in viscosity with time of the anodic polymerization system. With the 0.5 mm. diameter capillary, measurements were limited by the high viscosities encountered during polymerization to about 7 hours after the beginning of electrolyses. A typical curve is shown in Figure 8 for the polymerization of a .0586 molar solution of $TBAClO_4$ in THF, and a current of 11.3 ma. for one hour. This experiment shows that the polymerization reaction continued after the current was turned off.

A viscosity cell with a larger bore capillary (1.5 mm.) was used to follow the polymerization to longer times. Measure-

Figure 6. IR Spectrum of poly(THF).

A - spectrum of CS_2 solution.

B - spectrum of a film of polymer.

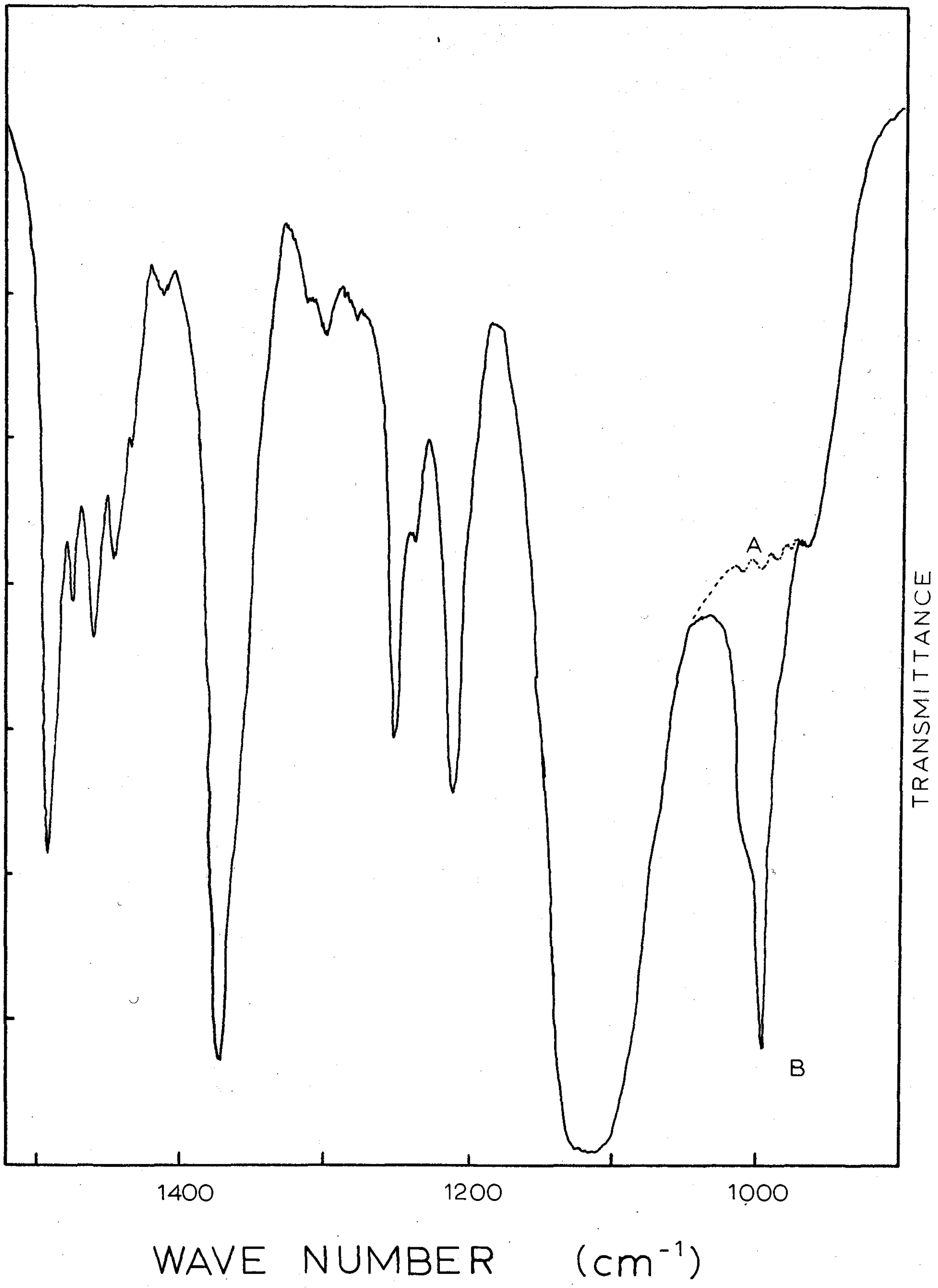
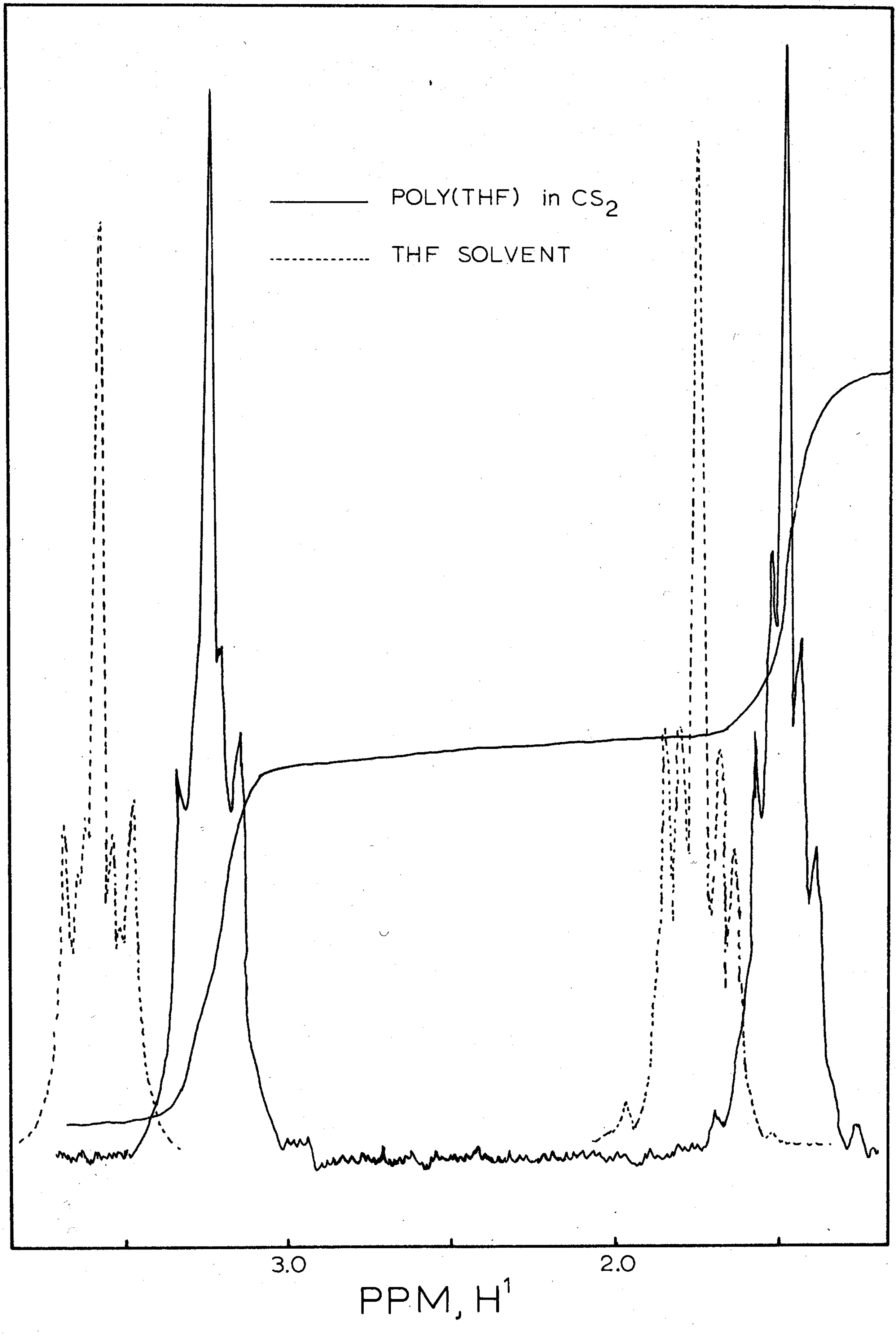

A
B
TRANSMITTANCE
1400
1200
1000
WAVE NUMBER (cm^{-1})

Figure 7. NMR spectrum of poly(THF) and monomer THF.


POLY(THF) in CS_2
THF SOLVENT
3.0
2.0
PPM, H^1

ments could still be made 12.7 hours after the beginning of the electrolyses. A typical curve (Figure 9) shows a smooth increase of the viscosity of the solution with the time of the polymerization. The polymer precipitated at the end of 24 hours had a molecular weight of 58,800.

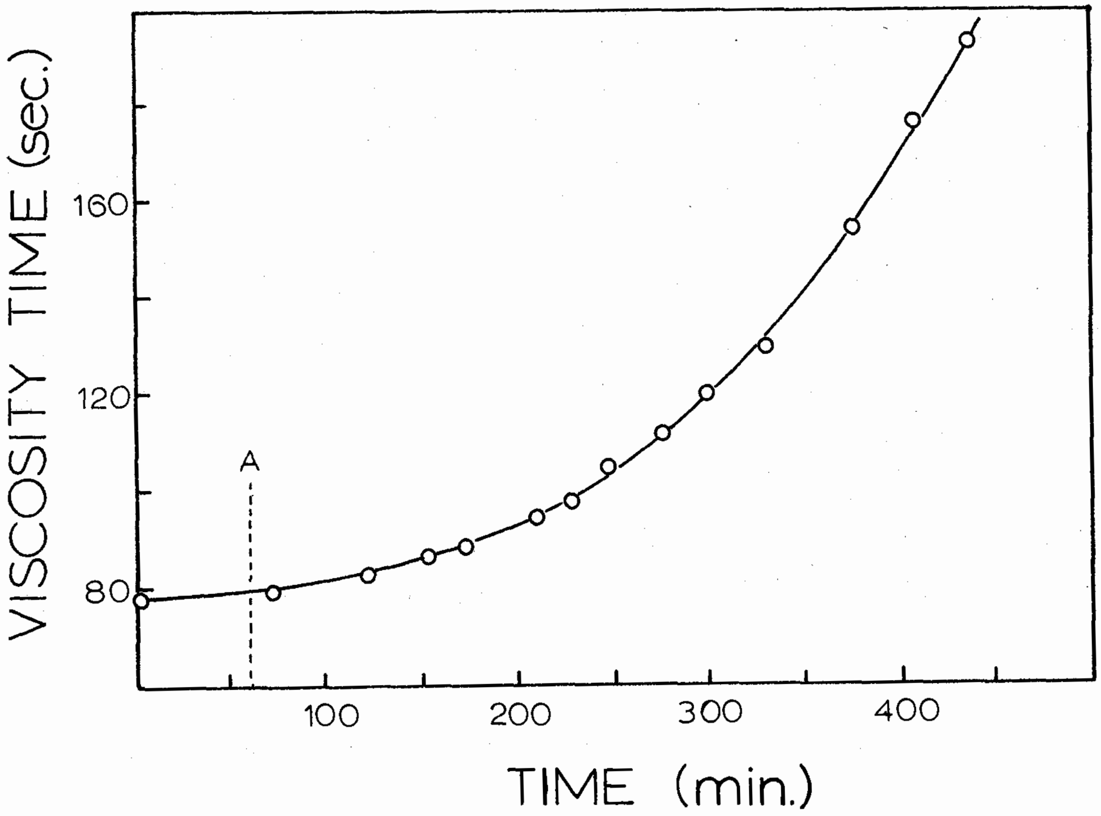
The following experiments were designed to determine the effects of a current reversal. In one case, a .0543 M $TBAClO_4$ solution was electrolyzed for 1 hour at 11.0 ma. The current was turned off, and the viscosity readings were taken for 4 hours after the end of the electrolysis. Then the reverse current was passed for 1 hour at 11.0 ma. Again readings were taken. Figure 10 shows that the viscosity readings reached a steady value for periods up to 24 hours. When the anodic solution was poured into methanol, no polymer was precipitated out. In another experiment, a .0586 M $TBAClO_4$ solution was electrolyzed for 1 hour at 11.0 ma. Viscosity readings were taken for 4 hours after the end of electrolysis. The current was then reversed for ½ hour at 11.0 ma., that is, half the quantity of current passed during initiation. Viscosity readings were taken for another 1½ hours. Then the current was reversed for another ½ hour at 11.0 ma. More viscosity readings were taken at various time intervals. Figure 11 shows that after the first current reversal, the viscosity continued to increase, but possibly at a slower rate than before. After the second current reversal, the polymerization stopped, and no polymer was isolated from the anode compartment.

Figure 8. Reaction trace using viscosity cell (0.5 mm. capillary).

A - current of 11.3 ma. passed for 60 minutes.

Figure 9. Reaction trace using viscosity cell (1.5 mm. capillary).

A - current of 11.3 ma. passed for 60 minutes.


VISCOSITY TIME (sec.)
160
120
80
A
100
200
300
400
TIME (min.)

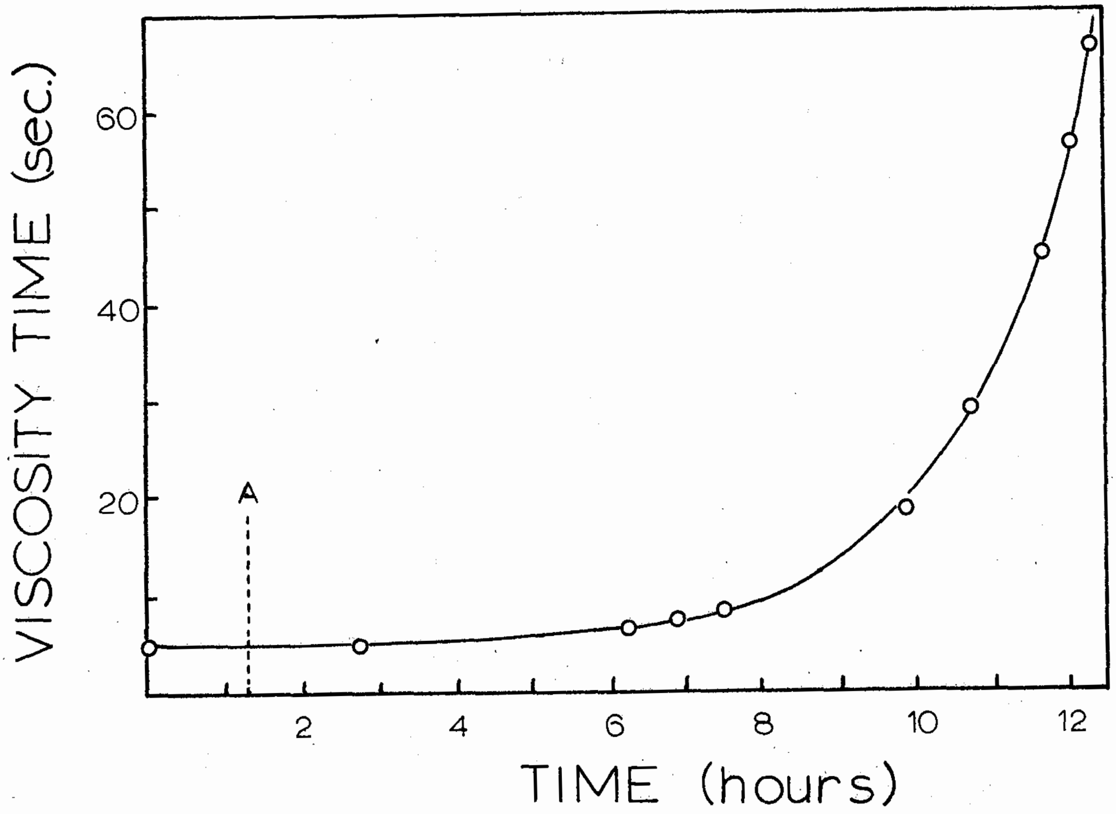

VISCOSITY TIME (sec.)
60
40
20
A
2
4
6
8
10
12
TIME (hours)

Figure 10. Reaction trace showing effects of current reversal (0.5 mm. capillary).

A - current turned off after 11.3 ma. passed for 60 minutes.

B - reverse current of 11.3 ma. turned on.

C - reverse current stopped after 60 minutes.

Figure 11. Reaction trace showing effects of current reversal (0.5 mm. capillary).

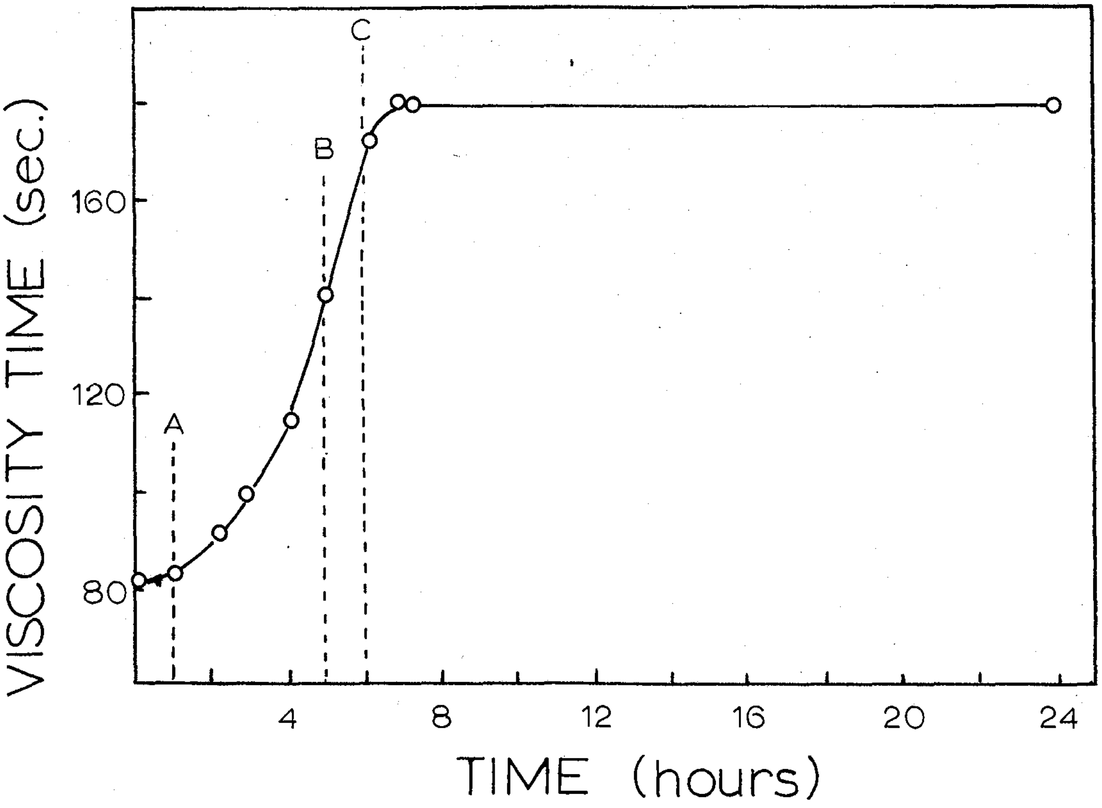
A - current turned off after 11.3 ma. passed for 60 minutes.

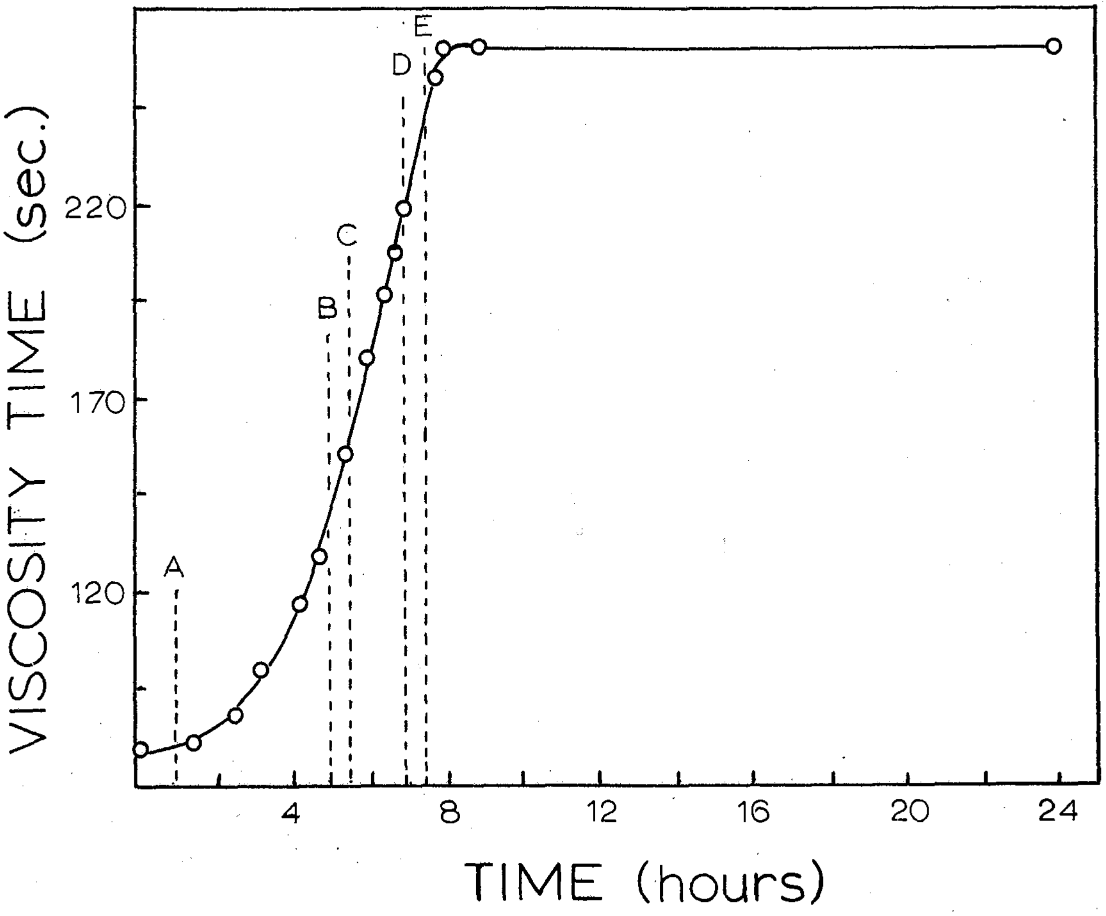
B - reverse current of 11.3 ma. turned on.

C - reverse current stopped after 30 minutes.

D - reverse current of 11.3 ma. turned on.

E - reverse current stopped after 30 minutes.


VISCOSITY TIME (sec.)
80
120
160
A
B
C
4
8
12
16
20
24
TIME (hours)


VISCOSITY TIME (sec.)
120
170
220
A
B
C
D
E
4
8
12
16
20
24
TIME (hours)

C. Solvent-Monomer Systems

In order to do a thorough kinetic study of the polymerization of THF, it would be convenient to perform the polymerization in some medium other than THF itself, that is, a solution rather than a bulk polymerization. It would then be possible to follow the rate of disappearance of monomer with time, possibly with a gas chromatograph. In a bulk polymerization, the viscosity of the system became so high that it was difficult to withdraw samples for analysis. The fact that polymer was not precipitated from the anode compartment till at least 7 or 8 hours after electrolysis, made any measurements of monomer disappearance during the early stages of the reaction difficult. These points demonstrated the desirability of a suitable solvent in which to do the polymerization. Methylene dichloride, a frequently used solvent for cationic polymerizations, was the first choice. Solutions of 20% THF in CH_2Cl_2 by volume were electrolyzed with 10 ma. for periods of over an hour. Black solutions were formed in the anodic compartment and the electrode became coated with a black substance not identified. However, no polymer could be isolated after 24 hours. Other solvents tried were chlorobenzene, nitrobenzene, and dioxane, but in all cases no polymer was isolated.

D. Gas Chromatrograph Studies

A possible mechanism for the polymerization of THF in the bulk was considered to be that of fast initiation followed by a slow stepwise addition of monomer units to the active center. This would imply the formation of dimers, trimers, tetramers, ... and low molecular weight polymer, during the initial stages of the reaction. There was a possibility that these species could be detected with a gas chromatograph. A .0586 M solution of $TBAClO_4$ in THF was electrolyzed for 10 minutes with a current of 10 ma. A microliter syringe was used to withdraw samples periodically from a cell equipped with a sidearm tube. The samples were injected directly into the gas chromatograph. No peaks other than the one due to the THF were found. Another similar experiment was performed, but in this case the 2 ml. samples periodically withdrawn after electrolyses, were syringed into about ½ ml. of methanol to terminate the polymerization. Then, microliter samples were injected into the gas chromatograph. Again no other peaks than those due to THF and methanol were observed. The anode solution was allowed to stand for 21 hours, and then the contents were precipitated into methanol. Isolation of a polymer proved that initiation had indeed ocurred in only 10 minutes of current passage at 10.0 ma.

The gas chromatograph could not be used to follow the degree of conversion of monomer to polymer because the viscosity of the reaction solution became too high for samples to be withdrawn by a syringe even at low degrees of conversion.

E. Effects of time of current passage

A series of polymerizations were carried out using the type of cell shown in Figure 1. The $TBAClO_4$ salt concentration, the total polymerization time, and the total amount of current were held constant. The time of current passage and the current were varied so that the product of the two was a constant, equal to the total amount of charge passed through the system. The concentration of $TBAClO_4$ in THF was .0586 molar. The total amount of current passed in each case was 1.25×10^{-3} faradays. It was thought, that, if the mechanism were a fast initiation - slow growth addition process in which monomer units were added on one at a time to the active center, then differences in yield, molecular weight, and molecular weight distribution result. The results obtained are given in Table 4.

It was expected that if the times of producing the initiating centers was different, and if a slow growth process were valid, then a difference in molecular weight distribution should be noted. That is, if 100 active centers are produced in one hour, the resulting polymer would have a narrower molecular weight distribution than if 100 active centers were produced over a period of 10 hours. The samples were analysed by Waters Associates Inc. by gel permeation chromatography. The molecular weight distributions are described by the number average and weight average molecular weights, and by the ratios of M_w/M_n, as given in Table 4.

A check on the viscosity molecular weight of the polymer about 3 months after polymerization showed a remarkable

Table 4. The effects of time of current passage on yield, molecular weight, and molecular weight distribution in the polymerization of THF.

	current time (min.)	current (ma.)	yield (grams)	M.W. (1)	M.W. (2)	M_n (3)	M_w (4)	M_w/M_n
A	178	11.3	18.7	66,400	27,050	20,450	38,800	1.90
B	339	5.90	18.0	56,500	49,400	16,630	41,040	2.47
C	585	3.45	17.4	-	25,600	13,600	39,240	2.89
D	1440	1.40	12.8	45,300	26,300	22,750	33,480	1.47

(1) - measured 1 week after polymerization (viscosity)

(2) - measured 3 months after polymerization (viscosity).

(3) - measured by gel phase chromatography (Waters Associates Inc.) - 3 months.

(4) - measured by gel phase chromatography (Waters Associates Inc.) - 3 months.

change.

F. Effect of salt concentration

Using 4 equivalent cells of the type shown in Figure 2, THF solutions varying in the concentrations of $TBAClO_4$ were electrolyzed for 2 hours with a current of 5.0 ma. The total time allowed for polymerization was 24 hours, at which point the contents of the anodic compartments were poured into methanol. The yields and the molecular weights are given in Table 5. A plot of yield versus the salt concentration is shown in Figure 12. A plot of the molecular weight versus the concentration is shown in Figure 13.

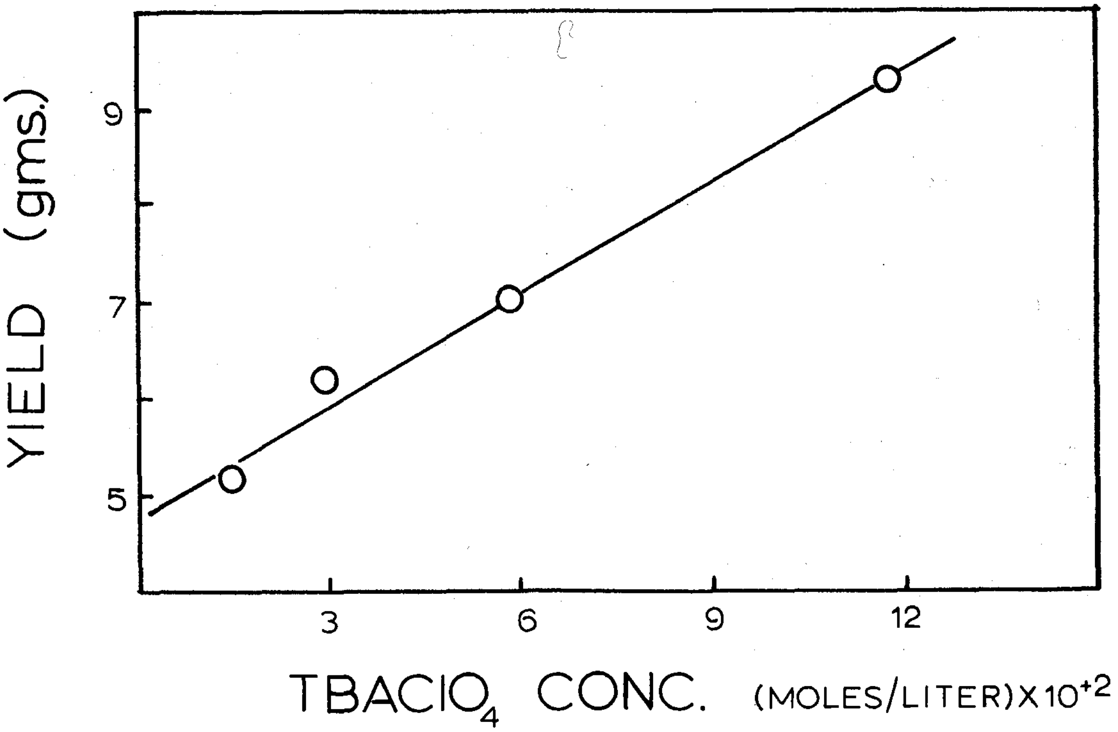
The graphs show a linear increase in both the yield of polymer and the molecular weight with increase in salt concentration. If an equilibrium polymerization is considered, where the monomer and polymer are in equilibrium, a plot of log $([M]_o - [M]_e)([M]_t - [M]_e)$ against time should be linear if the rate dependence on monomer is 1st order. If the time of polymerization is constant, and the rate is assumed to be 1st order with respect to monomer, a plot of the same log term against catalyst concentration should be linear if the rate dependence on catalyst concentration is 1st order. A linear dependence is shown in Figure 14. The value of $[M]_o$ for bulk THF polymerization is 12.3 molar, and the equilibrium concentration $[M]_e = 3.3$ moles/l. at 25°C. (65,71). A mechanism and kinetic expression is proposed later (section I).

Table 5. Effects of $TBAClO_4$ concentration on the yield and molecular weight in the polymerization of THF.

	salt conc. (g/100 cc.)	yield (grams)	M.W.	$[THF]_t$ (moles/l.)
A	4.00	9.30	68,900	9.72
B	2.00	6.94	48,900	10.38
C	1.00	6.20	42,700	10.58
D	0.50	5.16	36,700	10.86

Figure 12. Linear dependence of yield of polymer on $TBAClO_4$ concentration.

Figure 13. Dependence of molecular weight of polymer on $TBAClO_4$ concentration.


YIELD (gms.)
5
7
9
3
6
9
12
TBAClO$_4$ CONC. (MOLES/LITER) X 10^{+2}

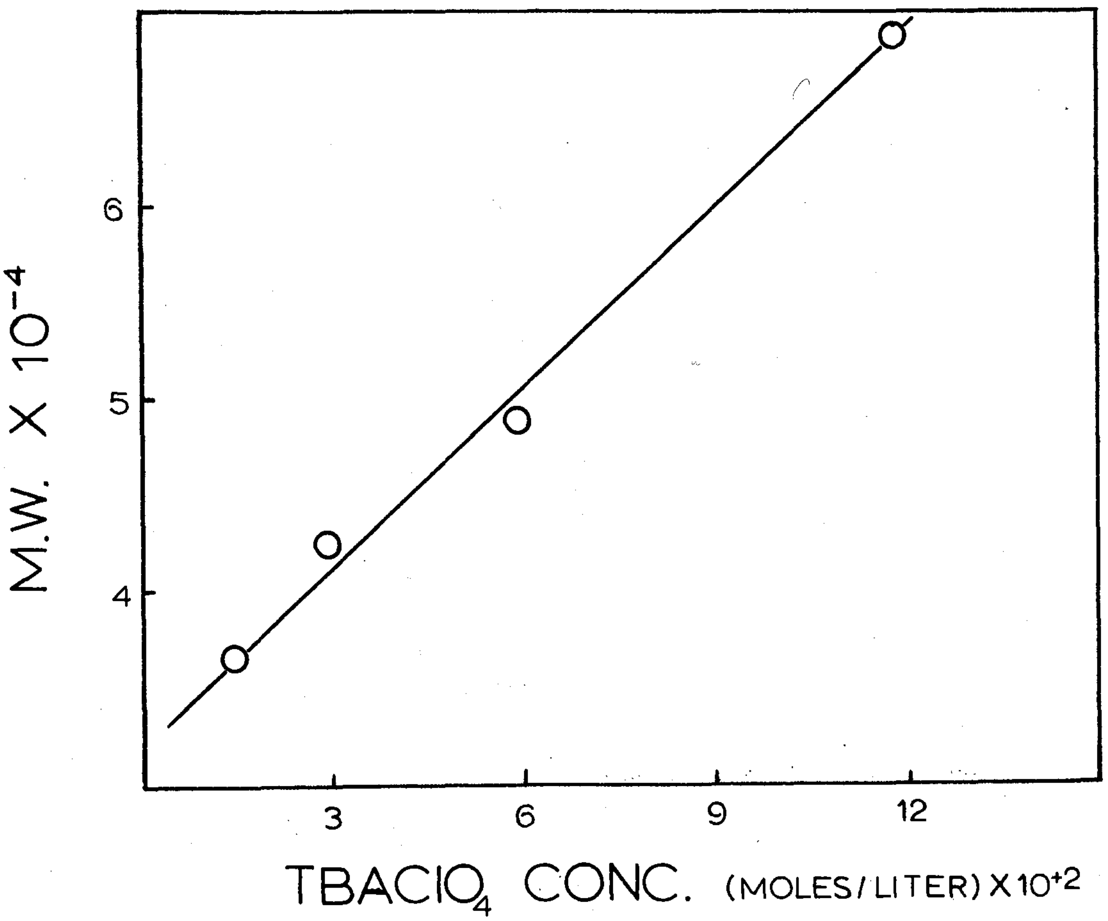
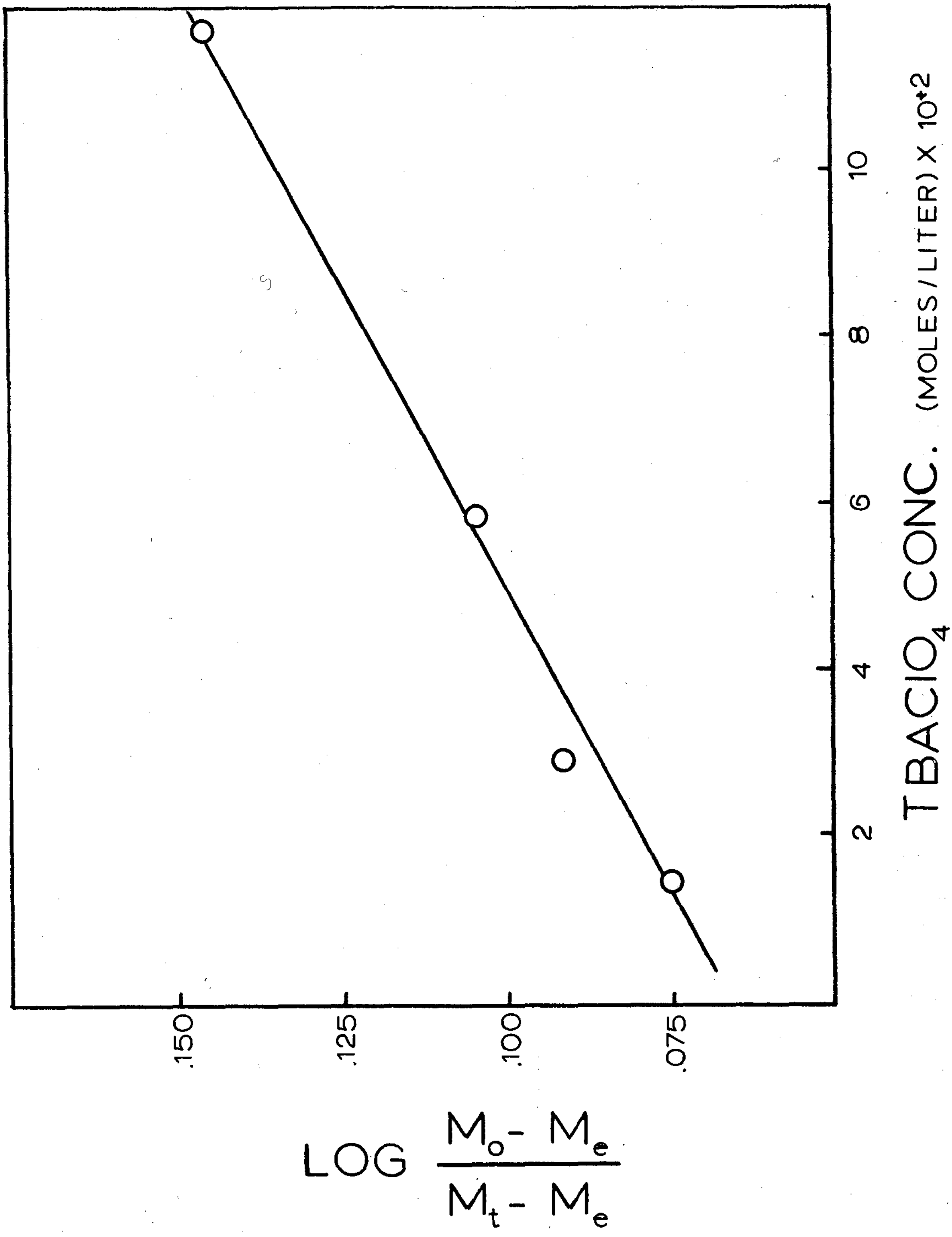

M.W. X 10^{-4}
4
5
6
3
6
9
12
TBAClO$_4$ CONC. (MOLES/LITER) X 10^{+2}

Figure 14. Linear dependence of rate on $TBAClO_4$ concentration.


.150
.125
.100
.075
2
4
6
8
10
TBAClO$_4$ CONC. (MOLES/LITER) X 10^{+2}
LOG $\frac{M_o - M_e}{M_t - M_e}$

ii) $TBABF_4$

The concentrations of $TBABF_4$ were varied in a series of polymerizations. The current passed was 5.0 ma. for 2 hours, and the total polymerization time was 24 hours. A coating of polymer was formed on the electrode, possibly interfering with the polymerization. Referring to Table 6, it is noted that the salt used in D was prepared at a time previous to the salt used in the other three, although by the same method. No straight line relationships existed for plots of yield and molecular weight versus salt concentration here as for the $TBAClO_4$ salt.

G. Effect of current

Polymerizations in which the electrolysis time was varied from $\frac{1}{4}$ hour to 4 hours were carried out in equivalent cells as described in Figure 2. The $TBAClO_4$ salt concentration was maintained at .0586 M, and the total polymerization time was 24 hours, the same for all cells. A current of 10.0 ma. was used in all the polymerizations. The yields and molecular weights of the polymers obtained are given in Table 7. A plot of yield against number of faradays passed is given in Figure 15. A linear plot of yield against (number of faradays)$^{\frac{1}{2}}$ is shown in Figure 16. Figure 17 shows the relationship between the polymer molecular weight and the number of faradays passed.

H. Effects of Time of Polymerization

It was noted previously that polymer could not be

Table 6. Effects of $TBABF_4$ concentration on the yield and molecular weight in the polymerization of THF.

	salt conc. (g/100 cc.)	yield (grams)	M. W.
A	3.00	1.44	190,500
B	2.00	1.64	190,500
C	1.00	1.32	162,000
D	2.00	1.63	151,000

Table 7. Effects of the quantity of current passed on yield and molecular weight in the polymerization of THF.

	current time (hours)	current (ma.)	number of faradays	yield (grams)	M. W.
A	$\frac{1}{4}$	10	$.93 \times 10^{-4}$	1.60	33,100
B	$\frac{1}{2}$	10	1.87	3.97	39,400
C	1	10	3.73	7.34	53,100
D	4	10	14.91	18.00	61,600

Figure 15. Dependence of yield of polymer on the number of faradays passed.

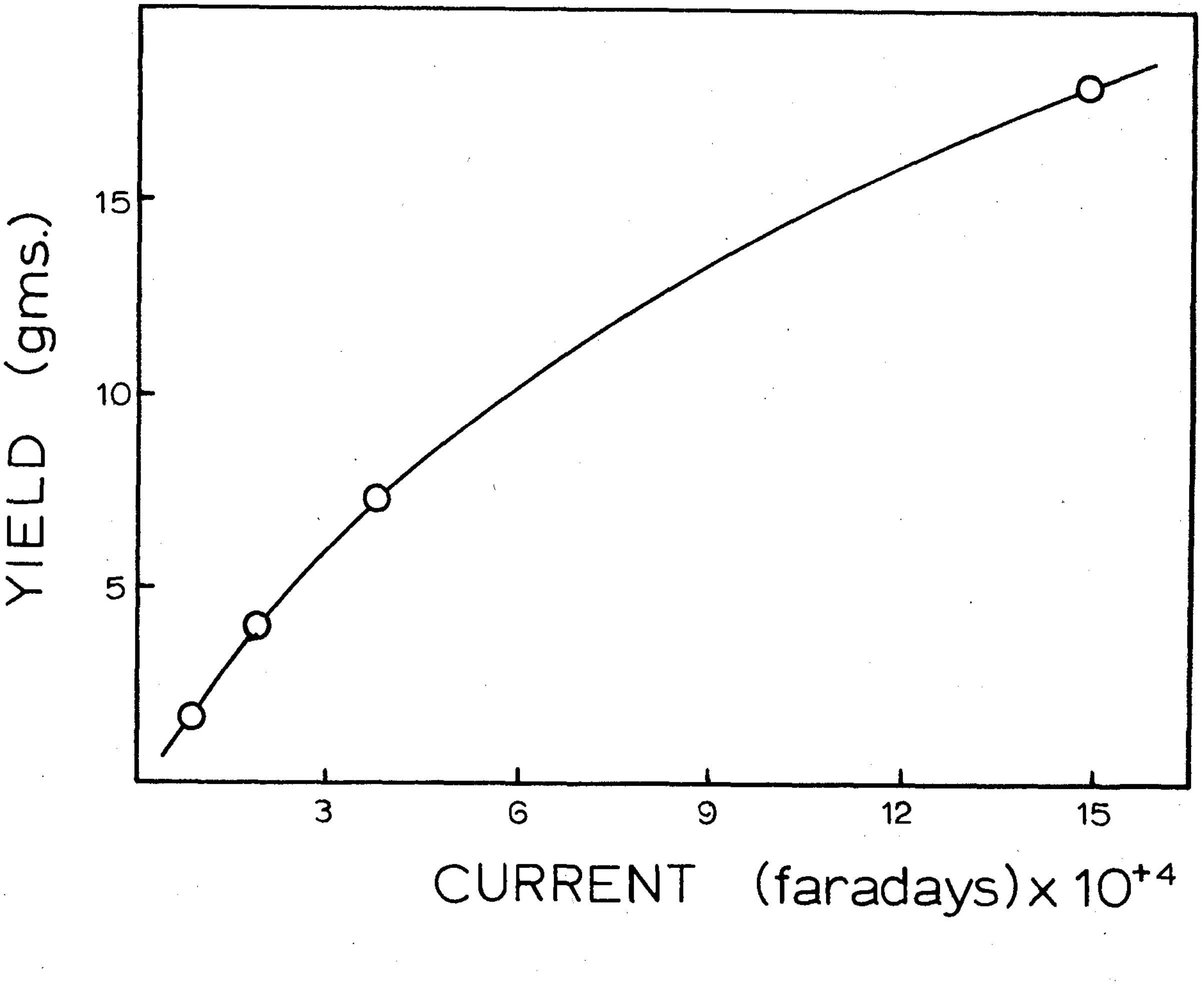

YIELD (gms.)
5
10
15
3
6
9
12
15
CURRENT (faradays) x 10^{+4}

Figure 16. Linear dependence of yield of polymer on the square root of current.

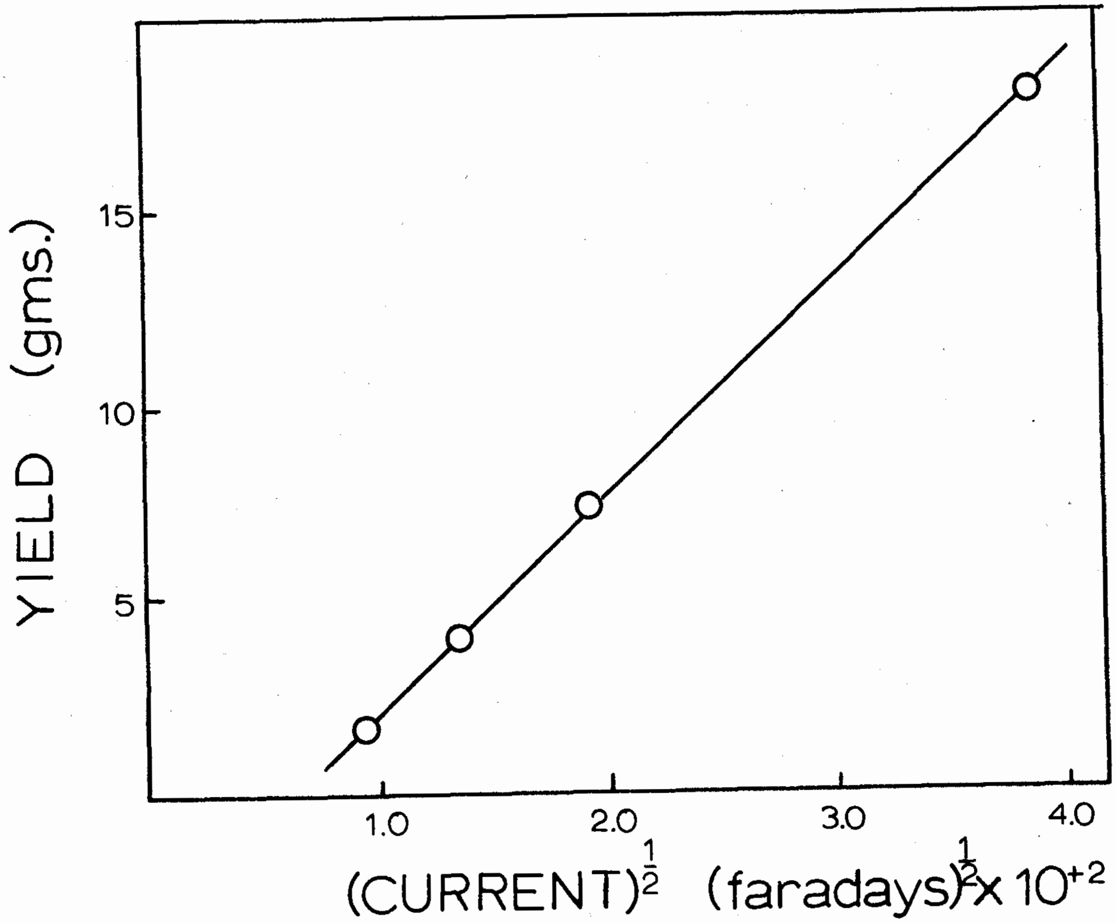
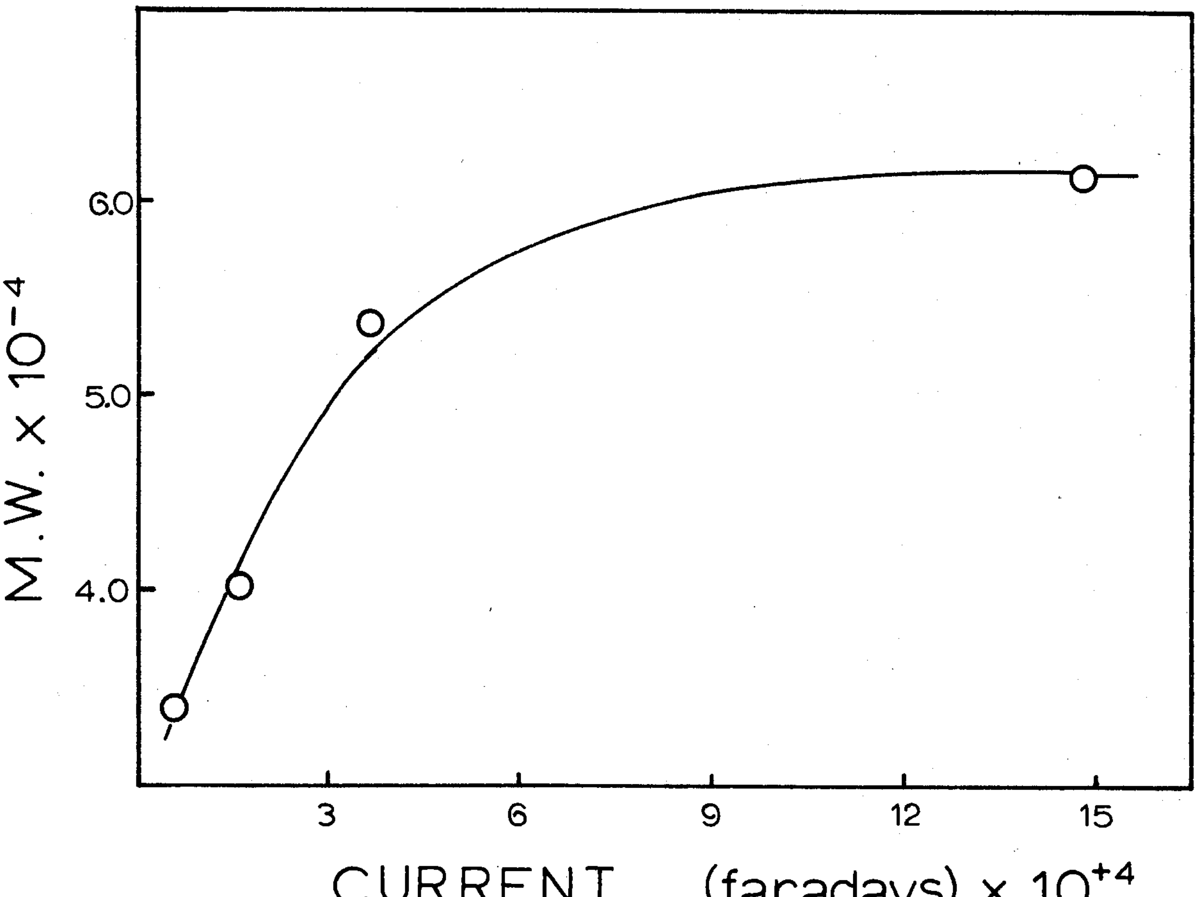

YIELD (gms.)
15
10
5
1.0
2.0
3.0
4.0
(CURRENT)$^{\frac{1}{2}}$ (faradays)$^{\frac{1}{2}}$x 10^{+2}

Figure 17. Dependence of molecular weight of polymer on number of faradays passed.

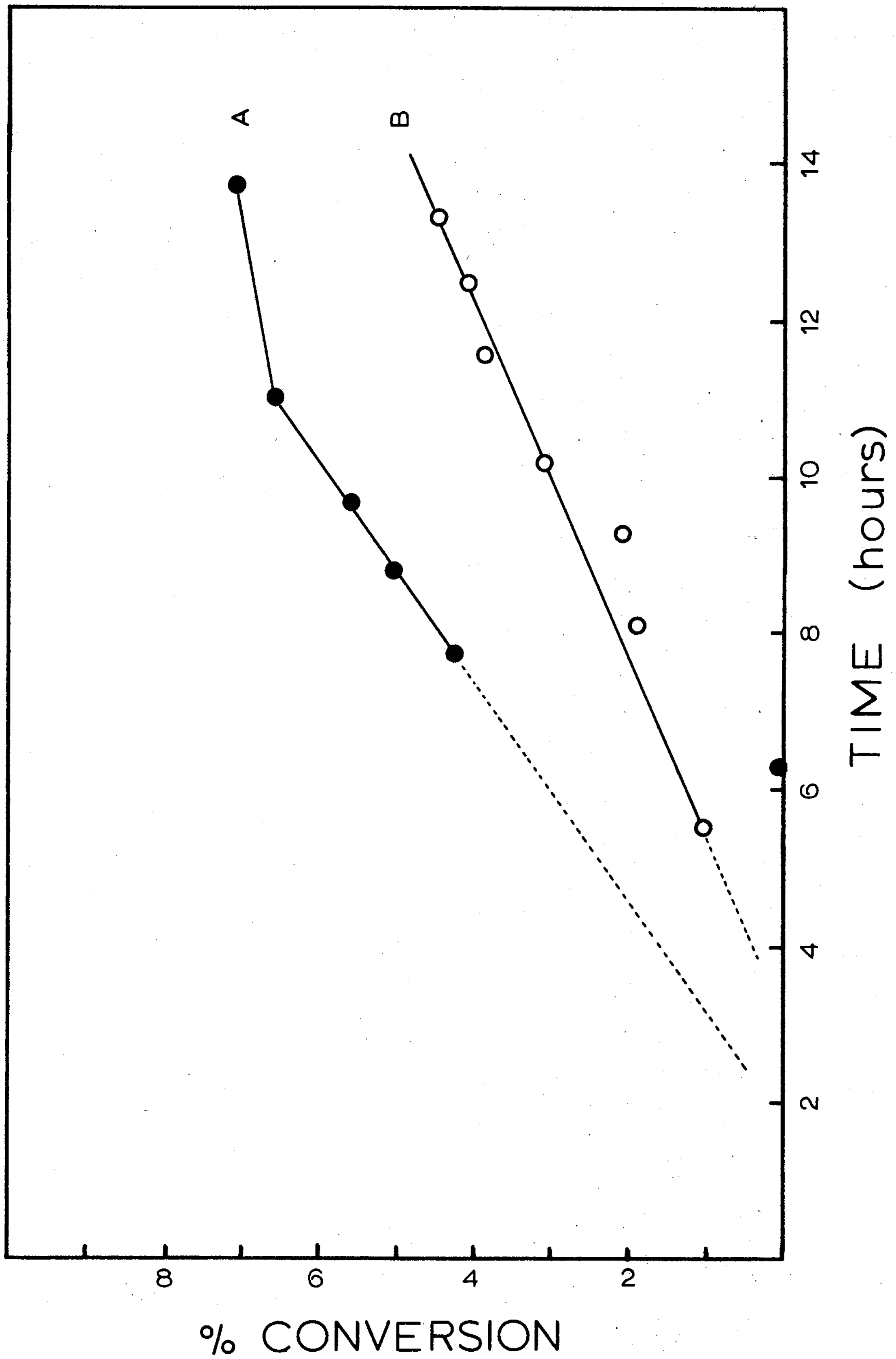

M.W. x 10^{-4}
6.0
5.0
4.0
3
6
9
12
15
CURRENT (faradays) x 10^{+4}

isolated from the anodic compartment if precipitation in methanol was attempted less than 7 or 8 hours after the beginning of electrolysis. Furthermore, gas chromatography did not detect any other substances besides THF monomer and methanol precipitant, casting some doubt on the question of a fast initiation - slow propagation mechanism. An experiment was conducted where 5 ml. samples were withdrawn intermittently after the electrolysis by means of a syringe from a polymerization cell equipped with a sidearm tube. The samples were syringed into pre-weighed beakers containing a little methanol. The samples were then dried under vacuum for about 6 - 12 hours, and the beakers were weighed. From the concentration of salt, the weight of salt in a 5 ml. sample is known. Any increase in weight of the beaker beyond that expected for the salt, would then be due to polymer. Figure 18 shows the results of two such experiments both in which a .0586 M $TBAClO_4$ solution was electrolyzed for 1 hour at 10.0 ma. The graph shows the variation of yield (% conversion) with polymerization time. As can be seen from the curves, the reproducibility of such an experiment was not very good. However, the curves do show an increase in the degree of conversion as the polymerization time increases.

Another series of polymerizations were performed where the polymerization time before precipitation was varied. A current of 5 ma. for 2 hours was passed through THF solutions .0586 M in $TBAClO_4$. The yields and molecular weights of

Figure 18. Linear dependence of conversion on the time of polymerization.

A and B - current of 10.0 ma. passed for 1 hour through .0586 molar $TBAClO_4$ solutions.


A
B
% CONVERSION
2
4
6
8
TIME (hours)
2
4
6
8
10
12
14

polymers precipitated at various times are given in Table 8. A plot of the % conversion against time in hours is given in Figure 19, and a plot of molecular weight against time is given in Figure 20, showing that as the polymerization proceeded, both the yield and the molecular weight increased almost linearly with time. From the conversion-time curve, a rate of polymerization was calculated, and was found to be 9.34×10^{-5} moles/l-sec.

At the time of each precipitation, a monomer concentration was calculated, as given in Table 8. At 25°C, the equilibrium monomer concentration is 3.3 moles/l. (65,71). A plot of log $([M]_o - [M]_e)/([M]_t - [M]_e)$ against time, in Figure 21, shows a 1st order rate dependence on monomer concentration. Figure 22 shows that the molecular weight of the polymer increases linearly as the percent conversion increases.

I. Poly-p-xylylenes

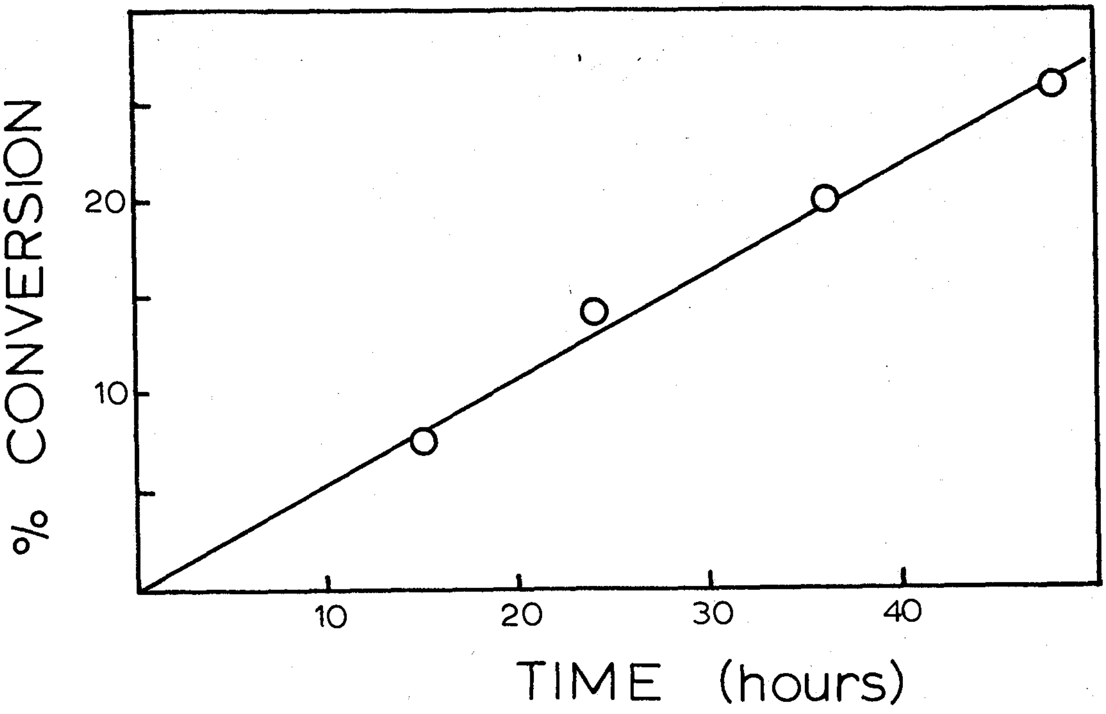
Constant cathodic potentials of -0.9 to -1.4 volts were applied to solutions of α,α′-dibromo-p-xylene, α,α,α,α′,α′,α′-hexachloro-p-xylene, and α,α,α′,α′,2,3,5,6-octachloro-p-xylene in DMF. The tetrabutylammonium salts were used as electrolytes. A general feature of the polymerizations was that the polymers precipitated out of solution during electrolysis. The polymers were produced at the mercury cathode (see Figure 4) which was held at a constant potential. The details and results of the polymerizations are given in

Table 8. Effects of the time of polymerization on yield and molecular weight in the polymerization of THF.

	time of polymerization (hours)	yield (grams)	M. W.	% conversion	$[THF]_t$ (moles/l.)
A	15	3.33	28,800	7.52	8.08
B	24	6.29	49,300	14.2	7.22
C	36	8.82	60,700	19.9	6.56
D	48	11.52	78,200	26.0	5.81

Figure 19. Linear dependence of the conversion on the time of polymerization.

Figure 20. Dependence of the molecular weight on the time of polymerization.


% CONVERSION
20
10
10
20
30
40
TIME (hours)

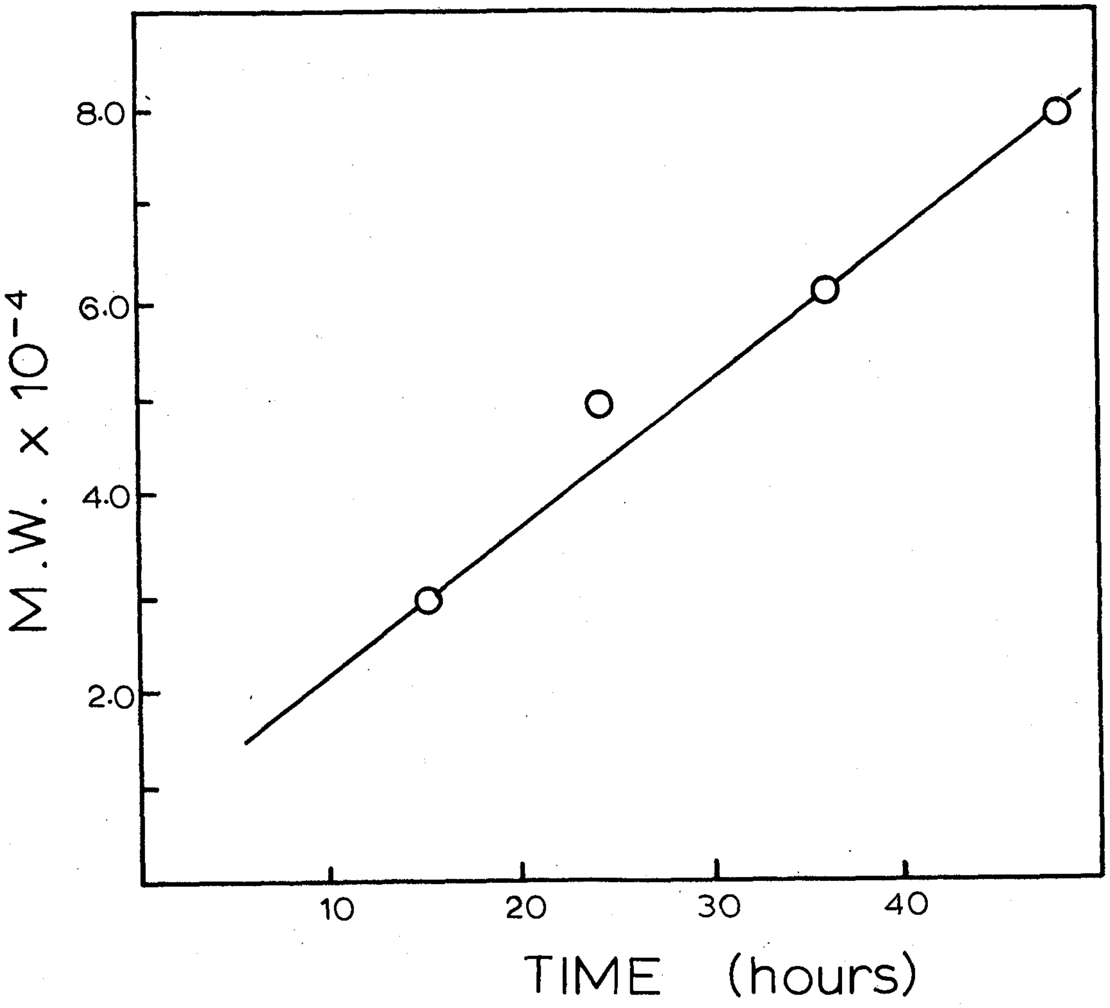

M.W. x 10^{-4}
8.0
6.0
4.0
2.0
10
20
30
40
TIME (hours)

Figure 21. First order dependence of rate of polymerization on monomer concentration.

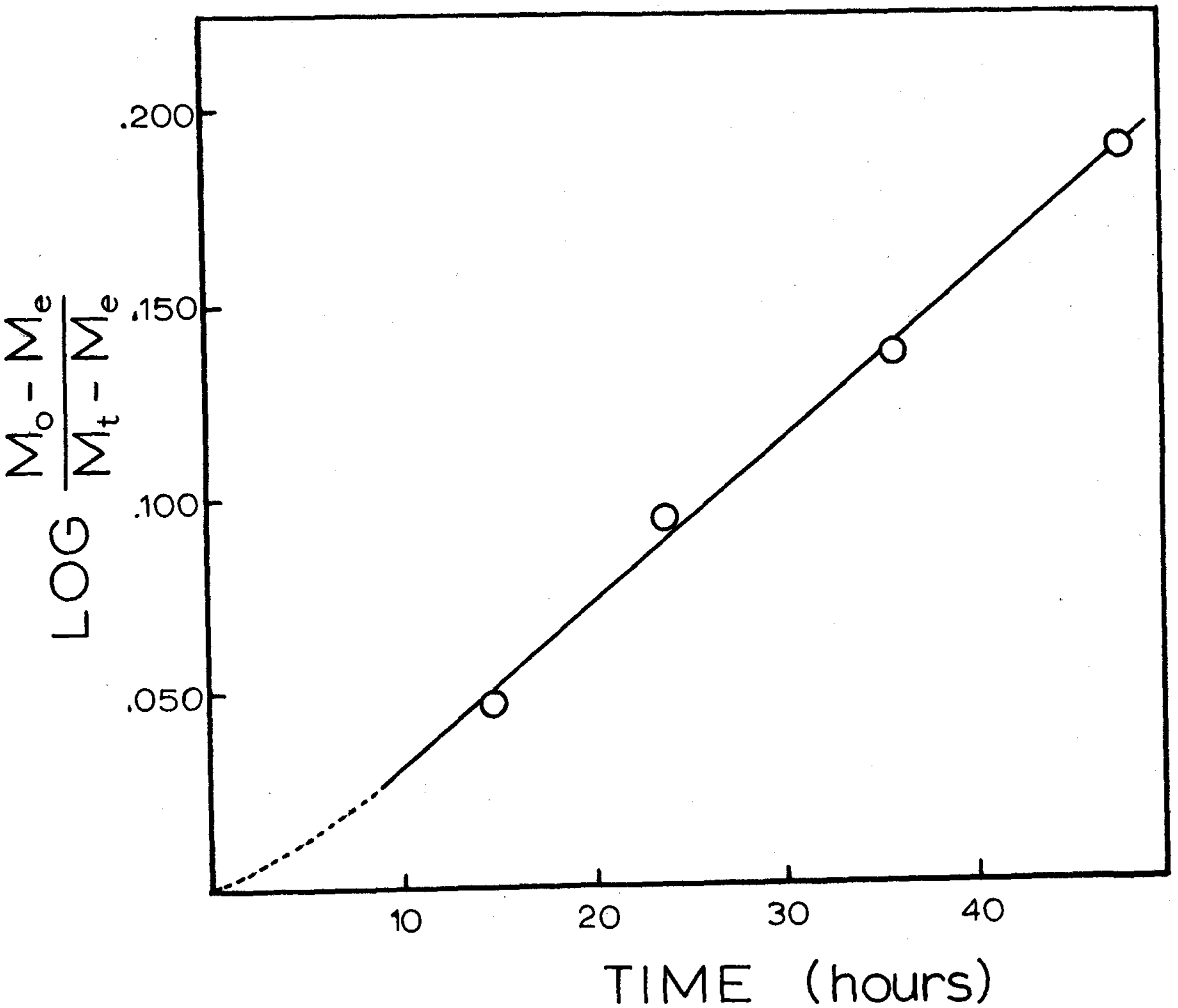

.200
.150
.100
.050
$\mathrm{LOG}\ \frac{M_o - M_e}{M_t - M_e}$
10
20
30
40
TIME (hours)

Figure 22. Dependence of molecular weight on the conversion.

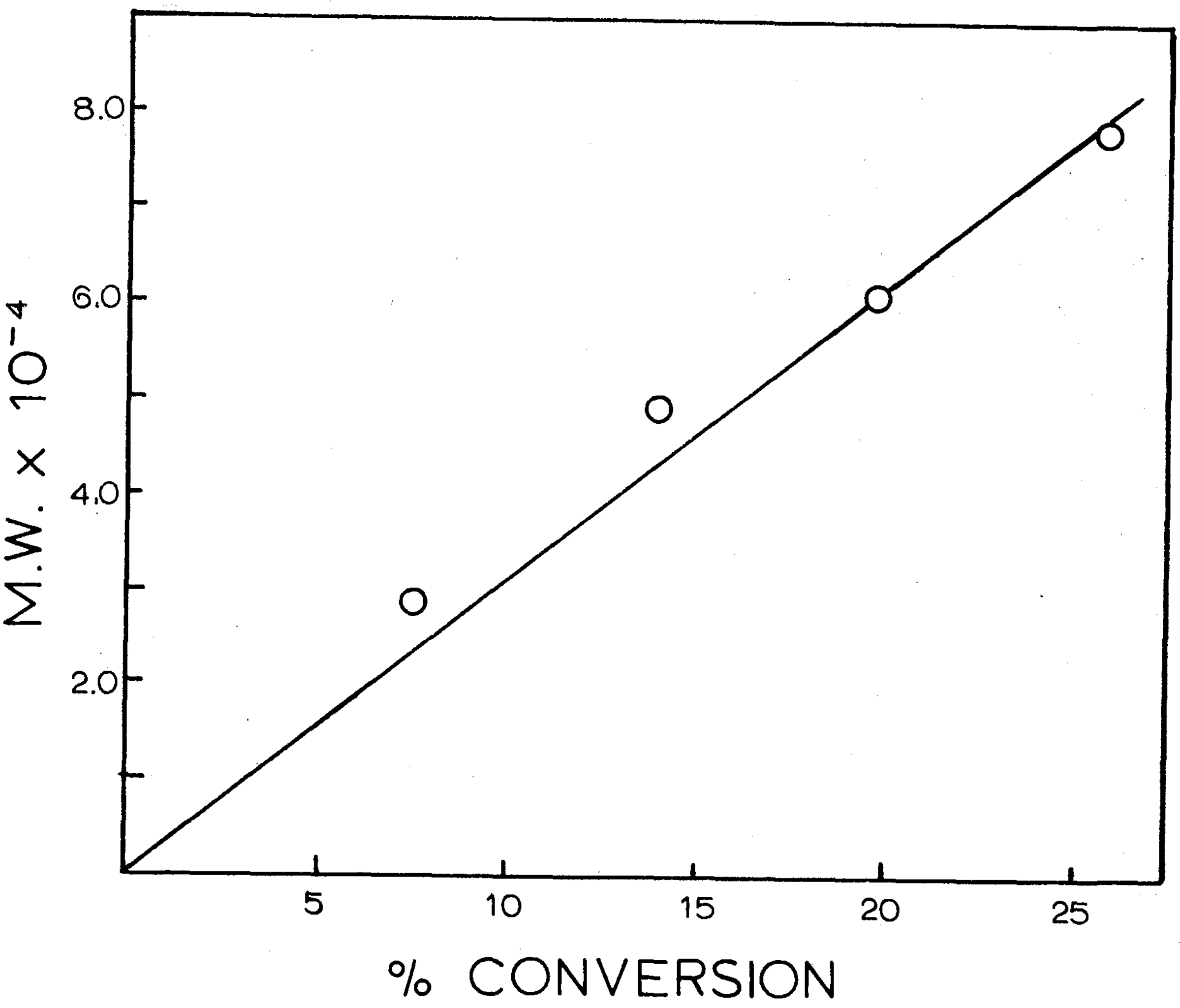

8.0
6.0
4.0
2.0
M.W. × 10^{-4}
5
10
15
20
25
% CONVERSION

Table 9.

The solubility of the polymers was limited to several solvents such as α-chloronaphthalene, benzyl benzoate, and the chlorinated biphenyls, at temperatures greater than 200°C. Upon heating the polymers, they turned brown above 300°C., but did not melt even when heated to 345°C.

The polymerization is thought to proceed via a xylylene intermediate (see electroinitiated polymers, section E). This involves a two electron transfer at the cathode. Thus one monomer unit should add on for every two electrons passed, or one mole of monomer for every two faradays. From the number of faradays passed and the weight of the polymer collected, a current efficiency could be calculated. These values are given in Table 9.

DISCUSSION

A. Initial Experiments

The polymerization of tetrahydrofuran is very dependent upon the purity of the reagents employed. A reaction of the positively charged intermediate with any impurities such as water, oxygen, amines, bases, etc. would destroy the active center, and polymerization would not occur. For this reason extensive drying procedures are necessary for monomer purification, and high vacuum work is essential. At no time did polymerization occur in experiments where the reagents had not undergone rigorous purifications.

Experimental evidence revealed that the electroinitiated

Table 9. Polymerization of some p-xylylenes.

	p-xylene monomer	monomer conc. (moles/l.)	electrolyte conc. (moles/l.)	potential	faradays passed	yield (grams)	current efficiency
A	α,α′-dibromo-	0.095	TBABr .031	-0.9 volts	-	.60	-
B	α,α′-dibromo-	0.105	TMABr .065	-1.4	0.135	.50	71.0%
C	α,α′-dibromo-	0.106	$TBAClO_4$ .036	-1.2	0.099	.32	61.9%
D	α,α′-dibromo-	0.088	TBABr .037	-1.0	0.152	.66	83.3%
E	α,α′-dibromo-	0.136	TBABr .042	-1.0	-	.323	-
F	α,α,α,α′,α′,α′-hexachloro-	0.098	TBABr .036	-1.0	-	~.5	-
G	α,α,α′,α′,2,3,5,6-octachloro-	0.035	TBABr .038	-1.0	0.035	.266	49.4%

polymerization of THF proceeded by a cationic process. Polymer could be isolated only from the anodic compartment of a divided electrolysis cell. Addition of a free radical inhibitor, hydroquinone, still resulted in the formation of polymer at the anode. If polymerization had not occurred, then there would have been doubt as to whether some free radical mechanism has been inhibited, or whether some impurity in the hydroquinone had terminated a cationic polymerization. The rate of the reaction was slowed, however, and accompanied by a decrease in molecular weight of the polymer. When the tetrabutylammonium perchlorate salt is used as electrolyte, radicals may be produced at the anode (81), which may be involved in polymer initiation:

$$ClO_4^- - e^- \xrightarrow{\text{anode}} ClO_4\cdot$$

A reaction of the $ClO_4\cdot$ radical may, in fact, involve a competition process between the inhibitor and the THF monomer so that a reduced rate of polymerization is expected.

A polymerization attempt at a low temperature (-78°C) did not result in polymer production. This is possibly because of thermodynamic considerations, which state, that at room temperature the free energy of polymerization is -0.8 kcal mole, and is just able to polymerize (59). With such a small negative free energy, a large decrease in temperature would prevent polymerization. In fact, Sims (60) reports that even at -35°C, there is no formation of polymer, but at 0°C, the percent conversion is 95% after 14 days.

The infra-red and NMR spectra of the polymer correlate very closely with those in the literature. The solid polymer shows an infra-red absorption at about 1000 cm.$^{-1}$ whereas the solution polymer does not. This band has been identified as being due to the crystallinity of the polymer (57).

The fact that polymer could not be isolated from the reaction vessel till about 7 or 8 hours after the beginning of electrolysis presented a question as to what kind of process was involved. Was the current involved in the production of active centers, all of which initiated polymerization immediately, but was followed by only slow addition of monomer units to the active center? Was the current producing active centers which initiated the polymerization slowly, with the propagation being either slow or fast? Is the current involved in the formation of a monomer (as in the p-xylylene case) which then polymerizes slowly to polymer? A discussion of these proposals in relation to the experimental results should provide some indication as to the actual mechanism involved in the electro-initiated polymerization of THF.

B. Viscosity Cell Experiments

The curves of viscosity against time (Figures 8 and 9) showed a smooth increase in the viscosity of the anodic solution during the course of the polymerization. A small, but definite increase was noted immediately after electrolysis. This indicated that some initiation had taken place during the first hour of the polymerization. Whether all initiation had occurred, and the slow increase was due to slow propagation, or whether it was in fact slow initiation was not known definitely, as both would have resulted in the same curves as given. The 1.5 mm. bore viscosity cell showed that the increase in viscosity continued in an exponential manner even after about 12 hours of reaction. However, the question as to whether the increase in viscosity was due to the increase in the number of molecules of high molecular weight (slow initiation - fast propagation) or whether it was due to all possible active centers slowly increasing in molecular weight by successive monomer additions (fast initiation - slow propagation), involved other experiments discussed later.

The polymerization may be stopped by current reversal. Passing the same amount of current in reverse as was passed during initiation quantitatively stopped the polymerization at a steady value of the viscosity. Reversing the current for one half the original initiation amount did not stop the reaction, but did seem to decrease the rate. Further reversal of the current of again half the original amount stopped the reaction at a steady value of the viscosity. This then provided a control over the polymerization reaction. Control over the molecular weight and or the yield thus seemed feasible. The fact that no polymer was isolated in any of the experiments in which current was reversed indicated the likelihood that termination occurred before very much polymer was initiated or propagated. Very low molecular weight polymers were possibly formed which did not precipitate from solution.

A proposed mechanism for the termination of polymerization due to current reversal involves the following reaction at the "new cathode" (previously the anode during initiation):

$$R_4N^+ + e^- \longrightarrow R_4N\cdot$$

$$R_4N\cdot \longrightarrow R_3N + R\cdot$$

where R_4N^+ is the tetrabutylammonium ion. The $R\cdot$ radicals would likely undergo mutual termination to produce R-R. The tertiary amine produced could terminate the cationic polymerization by reaction of its lone pair of electrons with the positive center of polymerization. This would terminate the growth of polymer, and so the viscosity of the solution should reach a constant value. This was, in fact, observed. The possibility of the above reaction at the cathode has been confirmed by Breitenbach and Gabler (38) and by Finkelstein (83).

C. Solvent - Monomer Systems

Because the high viscosity solutions encountered in bulk THF polymerization present analytical difficulties, it was desirable to effect the polymerization in solution. It was found that solutions of about 20% THF in various solvents did not yield polymer, even though the characteristic brown colour which accompanied all other bulk polymerizations appeared in the anodic compartment. If in fact the brown colour produced in the anode compartment was due to some substance necessary for the initiation of THF polymerization, then the polymerization would be expected to proceed in solution. However, for conventional initiators such as Friedel-Crafts reagents, the polymerization process is a reversible polymerization, with a monomer-polymer equilibrium. The equilibrium monomer concentration does not depend on the monomer concentration or the nature and concentration of the catalyst, but is a function only of the temperature. Therefore, for every temperature there is an equilibrium monomer concentration. If the concentration of monomer in a reaction system does not exceed the equilibrium concentration, then polymerization cannot occur. At 25°C. this concentration has been calculated to be about 3.3 moles/l. (65,71). The 20% THF solutions were below this equilibrium concentration. If in fact the electroinitiated polymerizations did proceed by an equilibrium process, then polymerization would not be expected for such dilute systems.

D. Gas Chromatograph Studies

If a mechanism involving fast initiation with slow propagation were correct for the polymerization of THF, then the polymerization would be expected to proceed by a formation of successive dimers, trimers, tetramers ..... and low polymers. The retention time on a chromatographic column would be expected to be different for these different intermediates, and thus the possibility existed of detecting them. However, no species other than monomer were detected by the chromatograph. It was possible that the limits of detection of the gas chromatograph were exceeded by such measurements. The amount of current passed was approximately 6×10^{-5} faradays, which, if each faraday initiated one mole of active centers, would produce 6×10^{-5} moles of active centers. Assuming for a moment that only dimers would be produced upon growth, then there would be approximately 10^{-7} grams of dimers in a 1 microliter injection volume. The thermal conductivity detector was capable of detecting approximately 10^{-8} grams. However, because the current initiation period was over a period of about 10 minutes, one would expect not only dimers, but also higher species. The concentration, then, of any one species was probably much less than that which the gas chromatograph could detect.

Looking at these results from the point of view of a slow initiation - fast propagation process, the fact that intermediate substances were not detected could be because of a slow production of active monomer species, whose concentration at times immediately after electrolysis would be very low. That is, the number of moles of active monomer would not be equal to the number of faradays passed immediately after electrolysis. In fact, if the propagation were rapid, then the active species would be found as low molecular weight polymers, which probably would not be detected by the chromatograph.

E. Time of Current Passage

Experiments were performed in which the total quantity of charge passed was kept constant, but the time over which it was passed was varied from 3 hours to 24 hours. If a fast initiation - slow propagation mechanism were applicable, then the same number of active monomer units were initiated in all cases. However, taking the two extremes, for a 3 hour initiation, all of the active center had time to slowly propagate for at least 21 hours before precipitation. Where initiation was continued for 24 hours, the active centers produced near the end of the electrolysis would not have had very much time to grow. Thus a decrease in yield would be expected for the latter, and this, in fact, was the case as shown in Table 4. Because of the wide spread of growth times for various active centers produced at different times in the latter case, a broad molecular weight distribution should result, much broader than for the instance where initiation was carried out in 3 hours. This should also result in a lower molecular weight for longer initiation periods, and viscosity measurements immediately after electrolysis confirmed this. The molecular weight distributions, as given by the ratio of M_w/M_n in Table 4, show that the broadness of the distribution is in fact, increasing for longer current passage times. One of the values (D) does not follow the trend of the other three. This is probably due to the fact that not all the polymer initiated near the end of 24 hours could be precipitated. It is later shown, however, that the fast initiation proposal is unlikely (section G).

Considering a slow initiation reaction, the observed yield differences agreed with the argument that centers produced near the end of the 24 hour electrolysis experiment did not have the time to initiate polymerization. Here the molecular weight distribution would depend on whether the propagation was slow or fast. If fast, then very few differences should be expected. The differences observed are small, but significant. A fast propagation step conflicts with previous experiments which showed that high molecular weight polymer could not be isolated till 7 or 8 hours after electrolysis and conflicts with experiments in which the molecular weight increases with the time of polymerization. A slow initiation followed by slow propagation would again predict distributions in which the broadness increased with time of current passage. This trend was observed, except for the case in which the current passage was 24 hours. The evidence presented here lends support to the slow initiation--slow propagation mechanism.

It should be noted that a measurement of the molecular weights of the polymers 3 months after polymerization showed a remarkable decrease in molecular weight over measurements done near the time of polymerization. This may well be due to some degradation reactions occurring, or due to a depolymerization reaction. If the latter occurred, a decrease in weight would have been expected. However, this was not checked.

F. Effect of salt concentration

i) tetrabutylammonium perchlorate

A linear increase of yield with increase in salt concentration is observed in Figure 12, that is, the rate dependence on salt concentration is first order. In an equilibrium polymerization, a plot of log $([M]_0 - [M]_e)/([M]_t - [M]_e)$ against time will give a straight line if the monomer dependence is first order. The time of polymerization is constant in these experiments, and so a plot of the same log term against salt concentration should be a straight line if the rate dependence on salt concentration is first order, as is seen in Figure 14. The molecular weight also shows a linear increase with increasing salt concentration (Figure 13).

For a fast initiation - slow growth process, the yield would be expected to increase only if the salt was involved in the propagation step. If the salt concentration is increased, then the propagation rate would be increased. This would account for an increase in molecular weight as well, if termination was not regarded as being important near the beginning of the polymerization. However, a propagation step involving the salt was not likely in our case.

If a slow initiation process is involved, the salt must be associated with the initiation step, unless propagation is slow also. In the latter case, the salt could possibly be associated with either initiation or propagation. The initiation described here involves a fast production of some active species by the current, with the successive slow reaction of these species with monomer. If the salt is involved in the slow reaction of the active species with monomer, then an increase in salt concentration would increase the rate of initiation and thus increase the yield, as is observed. If the propagation were fast, then one would not expect an increase in molecular weight. If the propagation were slow then the increased initiation rate would allow more polymer to grow for longer periods of time, resulting in a molecular weight increase, as is observed. If sufficient time were allowed for each polymerization to proceed to equilibrium, it is possible that all the polymers would be of approximately the same molecular weight.

Therefore, it appears that the mechanism of slow initiation followed by slow propagation is favoured as observed from a salt concentration variation.

ii) Tetrabutylammonium borofluoride

The yields observed in the polymerizations using $TBABF_4$ were much lower than in the perchlorate polymerizations, but showed remarkable increases in molecular weights. The low yields were possibly due to a coating of polymer formed on the electrode at the time of electrolysis which would not allow any active species produced by the current to get into the bulk. The increased molecular weights were possibly due to an increased rate of propagation. Chain transfer reactions and propagation are highly dependent on the nature of the anion of the salt (80). The borofluoride anion may increase the rate of propagation as compared to the perchlorate anion while at the same time reducing the rate of chain transfer. This would result in an increased molecular weight.

G. Effect of amount of current

The dependence of the rate of polymerization on the amount of current passed is shown in Figure 16, in which the yield is directly proportional to the square root of the current. Both the yield and the molecular weight increase with an increase in the number of faradays of current passed.

Consider a slow initiation - slow propagation mechanism. If the amount of current is increased, the number of active species available to initiate polymerization is increased. This means the rate of initiation is increased. If there are more monomer units initiated, this would result in an increase in yield, as is observed. Because the rate of formation of growing polymer chains is increased, there are more growing polymer chains produced near the beginning of the polymerization. These would have a longer period of time to grow. This would result in an increase in the molecular weight with an increase in the amount of current, as is observed. If a fast propagation were involved, there would be no expected increase in the molecular weight. The experimental results lend more support to the slow initiation - slow propagation mechanism.

H. Effect of Polymerization Time

Experiments involving withdrawal of samples during a polymerization reaction showed that a relationship between the total time of polymerization and yield existed. The data plotted in Figure 18 approximate straight lines for both curves, indicating an increase in yield for increased polymerization time.

Another series of experiments shown in Figures 19 and 20 show linear dependencies of both the percent conversion (yield) and the molecular weight with time. The rate of polymerization calculated from the yield curve was 9.34×10^{-5} moles/l.-sec. This indicates a very slow polymerization reaction. A plot of $\log ([M]_o - [M]_e)/([M]_t - [M]_e)$ against time is a straight line, confirming a first order rate dependence on monomer concentration (Figure 21). Figure 22 shows a straight line plot of molecular weight increasing with conversion. Generally, the latter two relationships are an indication of an almost constant concentration of propagating species which continue to grow without interruption by chain transfer or termination (67). For the above systems, it is then probable that the proposed slow initiation reaction would be completed before the time of 15 hours, the time of the first precipitation. Otherwise the graphs would not be expected to be linear because the concentration of propagating species would not be constant.

A slow initiation in which there is a steady increase in the number of growing chains, would predict an increase in yield as the polymerization proceeded. If the propagation was fast, then the molecular weight would be expected to be approximately constant. But if the propagation is slow, then an increase in molecular weight would be expected as the polymer chains are given more time to grow as is observed. The slow rate of the reaction is comparable to some other systems reported in the literature. In one case, a 75% conversion in the bulk was only reached after a 15 day polymerization time (70).

I. Proposals

To explain the rate dependencies on the salt concentration, the amount of current, and the monomer concentration, a mechanism involving both slow initiation and slow propagation seems likely from previous discussions. Several proposals could be made for the nature of the initiation reaction, one of which could involve an ion-pair type of species, and another in which the nature of the THF molecule is altered so as to make it more susceptible to polymerization. This could occur by some kind of complex formation with the monomer.

The reactions of ion pairs are much slower than the reactions of free ions. If initiation requires the presence of free ions, then any process which increases the number of free ions would increase the rate of polymerization. An increase in salt concentration increases the tendency of ion pair formation, and thus would be expected to decrease the rate of the polymerization. This was not observed experimentally. If the current is involved in a formation of free ions from ion pairs, then an increase in the current could result in an increase in the rate of the reaction, as is observed. A second possibility is that the ion pairs could be involved in the initiation themselves. Then an increase in the salt concentration should result in an increase in the ion pair concentration, and thus lead to the observed increase in rate of polymerization.

Another possiblity is the formation of a complexed monomer which is involved in the initiation reaction. From the observed dependencies of rate on first order monomer concentration, first order salt concentration, and half order in current, the following mechanism may be proposed:

$$\theta + M \longrightarrow \theta M \qquad [\theta M] = [\theta]$$

$$\theta M + 2S \longrightarrow M_1{}^*$$

$$M_n{}^* + M \rightleftharpoons M_{n+1}^* \qquad K = \frac{k_p}{k_d} = \frac{[M_{n+1}]}{[M_n{}^*][M]_e}$$

where θ represents the current or some species generated by it, θM is the complexed monomer, S is the salt, and M is the monomer. The rate is then given by:

$$\frac{-d[M]}{dt} = k_p[M_n^*][M] - k_d[M_{n+1}^*]$$

At equilibrium, $k_d[M_{n+1}^*] = k_p[M_n^*][M]_e$

$$\therefore \frac{-d[M]}{dt} = k_p[M_n^*]([M] - [M]_e)$$

At a point of maximum rate, $\frac{d^2[M]}{dt^2} = 0$

$$\therefore \frac{-d^2[M]}{dt^2} = k_p[M_n^*]\frac{d[M]}{dt} + k_p[M]\frac{d[M_n^*]}{dt} - k_p[M]_e\frac{d[M_n^*]}{dt}$$

$$= 0$$

Simplifying, $\frac{d[M_n^*]}{dt} = k_p[M_n^*]^2$

$$\text{But } \frac{d[M_n^*]}{dt} = k_1[\theta M][S]^2$$

$$= k_1[\theta][S]^2 \qquad \text{where } [\theta M] = [\theta]$$

$$\therefore [M_n^*] = \left(\frac{k_1}{k_p}\right)^{\frac{1}{2}}[\theta]^{\frac{1}{2}}[S]$$

Then $\frac{-d[M]}{dt} = (k_1 k_p)^{\frac{1}{2}}[\theta]^{\frac{1}{2}}[S]([M] - [M]_e)$

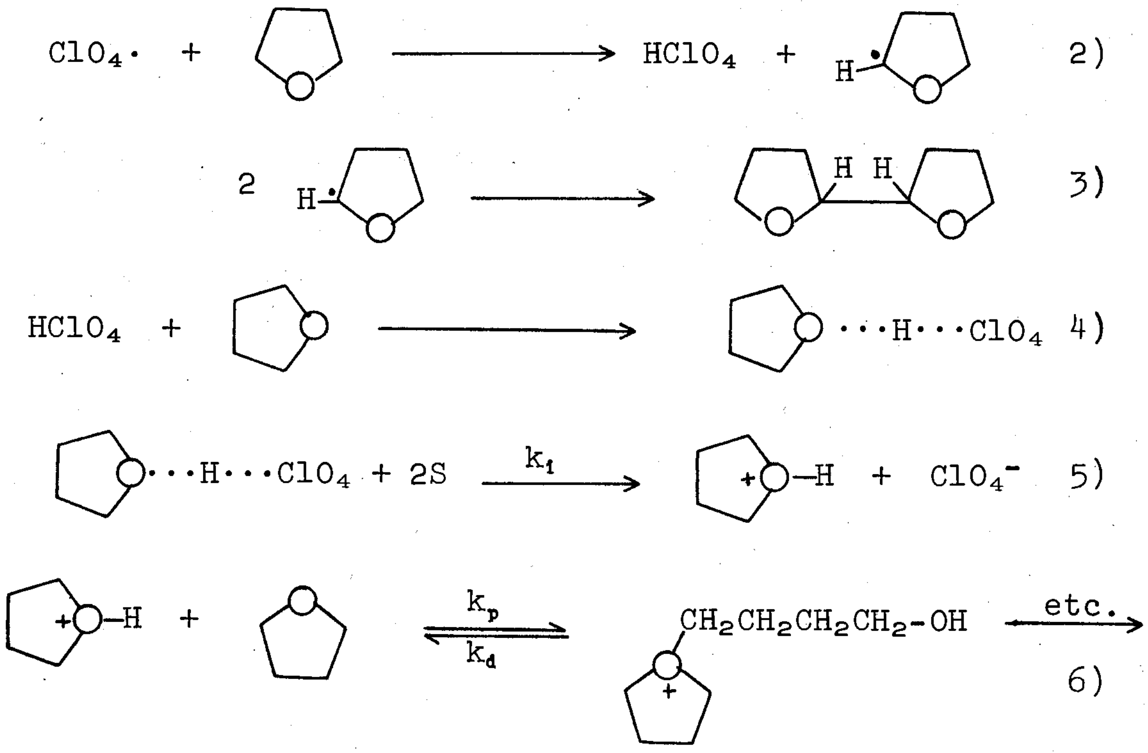
Integrating from $[M]_o$ to $[M]_t$ as t_o goes to t,

$$\ln\frac{[M]_o - [M]_e}{[M]_t - [M]_e} = (k_1 k_p)^{\frac{1}{2}}\int_{t_o}^{t}[\theta]^{\frac{1}{2}}[S]\,dt$$

These kinetic results do, in fact, account for the observed experimental dependencies of the rate on monomer concentration, salt concentration, and the current.

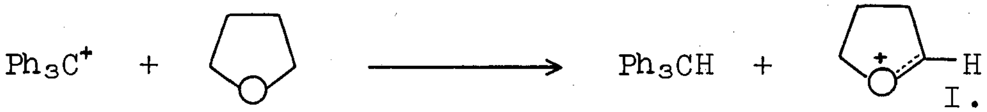
A proposal for a mechanism of the polymerization reaction involving the formation of $ClO_4\cdot$ radicals is as follows:

$$ClO_4^- \; - \; e^- \xrightarrow{\text{anode}} ClO_4\cdot \qquad 1)$$



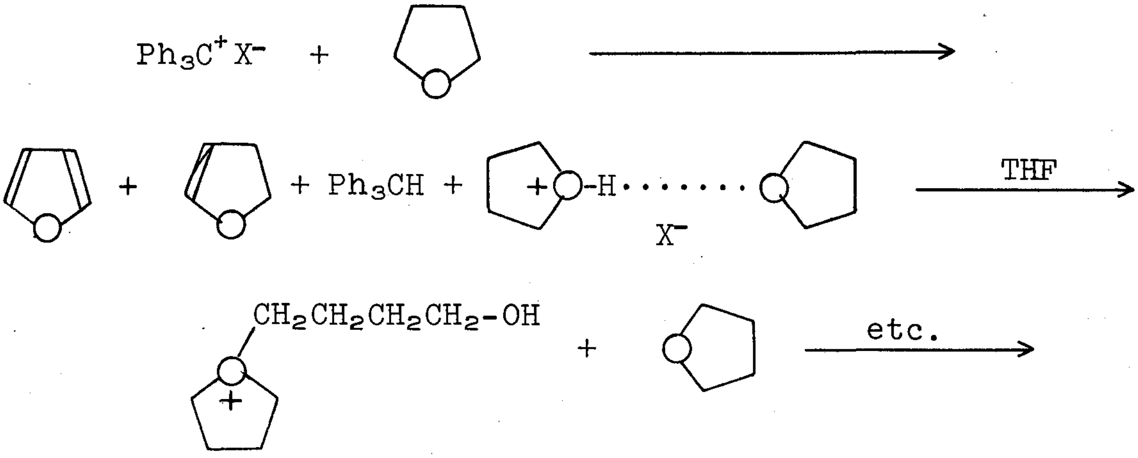
Although sufficient evidence has not been obtained to verify the proposed mechanism, several steps have been previously observed. Maki and Geske have detected electrolytically generated transient free radicals such as $ClO_4\cdot$ by ESR (81). The formation of perchloric acid by hydrogen atom abstraction has been well accounted for in vinyl polymerization (45). The formation of a complex between a protonic acid such as $HClO_4$ and THF has been postulated previously (82). It was suggested that the acid-monomer complex was the actual initiating species in the polymerization. Reactions 4), 5), and 6) would in fact show the observed kinetics, although the function of the salt in reaction 5) is not known at this time.

A very recent publication by Dreyfuss (82) suggests that a protonic acid, furan or dihydrofuran, and hydrogenated carbonium ion are the products of the reaction of trityl salts with THF. The protonic acid complexed with monomer is the true initiator of THF. They claim that the product of the hydride ion abstraction (I):



I.

is an unstable species and readily loses a proton. The net dehydrogenation leads to dihydrofurans and furans. The polymerization may be summarized as follows:



Under the acidic conditions which they employ, these products would be expected to resinify. They attributed a a dark brown colour formed in their reaction vessels to the resins resulting from the formation of furans and dihydrofurans. This brown coloration was also noted in our electrolytically initiated polymerizations of THF in the anodic compartment, and may be due to side reactions of this type.

CONCLUSION

The work reported here constitutes the first electroinitiated polymerization of tetrahydrofuran. The polymerization was performed in the bulk using tetrabutylammonium salts as the electrolytes. The polymer was formed in the anodic compartment of a divided electrolytic cell. Coversions as high as 25% were obtained with the molecular weights ranging from several thousand to as high as 190,000, depending on the electrolyte used.

The first report of electroinitiated cationic polymerization was by Breitenbach (32). However, the only detailed study so far of the kinetics and the control features of electroinitiated cationic polymerization was performed only recently in this lab (45). The work reported here constitutes the first cationic polymerization of a monomer other than a vinyl compound, initiated at the anode.

A polymerization in the bulk does not involve the usual solvent effects encountered in solution polymerizations. Thus the system of only monomer and electrolyte allows a close examination of the features of the polymerization, where solution side effects are not a factor. The bulk polymerization of THF reported here constitutes the first bulk polymerization initiated electrolytically.

The initiation of polymerizations at an electrode are unique in that there is the possibility of achieving a greater degree of control over the rate of polymerization, and in some cases over the molecular weights and molecular weight distributions. Conventional cationic polymerizations are difficult to control. Initiation by an electric current provided some degree of control in our polymerization of tetrahydrofuran. An increase in the amount of current passed resulted in an increase in the rate of polymerization and in the molecular weights. Varying the time over which the current was passed produced polymers differing in their molecular weight distributions. Reversing the current provided a means of slowing or stopping the polymerization, confirming a previous report (45) in which current reversal slowed the rate of polymerization.

An investigation of the kinetics of the polymerization showed that the rate was first order with respect to monomer, first order with respect to electrolyte concentration, and one-half order with respect to the quantity of charge passed. A mechanism was proposed in which the process at the electrode was considered to be the formation of perchlorate radicals. This was followed by hydrogen abstraction from the monomer by the radicals to produce perchloric acid. An acid-monomer complex was then involved in the initiation of polymerization, resulting in a positive oxonium ion growing center. The monomer then reacted with the oxonium ion in a propagation of the polymer.

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