

ELECTROLYTICALLY INITIATED
CATIONIC POLYMERIZATION



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by
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TO MY PARENTS

ABSTRACT

Electrolytically initiated cationic polymerizations were carried out in divided electrolytic cells. Quaternary ammonium salts were used as electrolytes in methylene chloride solutions of the monomers.

Isobutyl vinyl ether was successfully polymerized using tetrabutylammonium tetrafluoroborate as the electrolyte. The reactions were started by relatively small pulses of current applied to the solution. The rates of polymerization appeared to depend on the amount of current passed after terminating impurities were removed by the current or by species generated by the current. Further forward pulses increased the rates of polymerization while reverse pulses decreased the rates. A first order dependence of the rates on the monomer concentration was demonstrated.

The electroinitiated polymerization of isobutyl vinyl ether with tetrabutylammonium perchlorate as the electrolyte was also carried out using a relatively small initial pulse of current. The reaction was slowed and stopped before 100% conversion of monomer to polymer by a termination reaction. This termination was probably caused by impurities in the system. The final yields of polymer varied with respect to the magnitude of the initial current pulse in accordance with a relation derived assuming a first order dependence of the rate on the monomer and catalyst concentrations.

The anodic polymerization of isobutyl vinyl ether was also carried out using tetrabutylammonium hexafluorophosphate as the electrolyte. As with the tetrafluoroborate salt, the first portion of the initial current pulse was used to remove impurities.

The polymerization of styrene was carried out using constant currents of various magnitudes. When tetrabutylammonium perchlorate was used as the electrolyte, a very reproducible behaviour was found. Rate constants for the reaction at 0°C., 25°C. and 40°C. were found and the corresponding activation energy was calculated. The effect of current reversal in slowing the reaction was investigated.

With tetrabutylammonium tetrafluoroborate as the electrolyte in styrene polymerizations the reaction was much less reproducible. This behaviour was probably due to impurities in the solution.

Reaction curves were also obtained for the electropolymerization of styrene using tetrabutylammonium hexafluorophosphate as the electrolyte. This system appeared to be very sensitive to impurities in the reaction medium.

A study of the nature of the anodic reactions producing active centers and of the cathodic reactions producing terminating substances was attempted using cyclic voltammetry. Some evidence was obtained suggesting that the direct anodic oxidation of isobutyl vinyl ether did not occur in the system using tetrabutylammonium tetrafluoroborate as the electrolyte.

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INTRODUCTION

Electroinitiated cationic polymerization involves both conventional cationic polymerization chemistry and the electrochemistry of nonaqueous solutions. The electrochemical reactions of interest produce cationically active species at the anode, either by oxidation of the salt to form a product resembling a conventional catalyst, or by oxidation of the monomer. The ensuing reactions should be similar to those encountered in conventional cationic polymerizations.

Two of the most characteristic features of many cationic polymerizations are the rapidity and unpredictability of the reactions under all but the purest conditions. A major goal prompting the marriage of electrochemistry and cationic polymerization was, therefore, the possibility of achieving a larger degree of control over the rates of polymerization. Ideally, the rate of reaction could be controlled by the magnitude of the impressed current in reactions with effective termination processes, and by the total amount of current passed where no termination was present. The cathode, effectively a base of variable strength, might remove the acidic active centers by direct interaction or indirectly by the production of basic substances. Thus, an electroinitiated polymerization would not be limited in character by the com-

position of the initial preparation of the reaction.

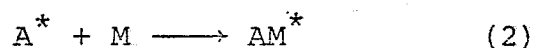
In this work, attempts were made to demonstrate the amount of control possible in some electroinitiated cationic polymerizations of vinyl monomers. Interpretations of the course of these reactions on the basis of conventional polymer kinetics and reaction mechanisms also proved possible.

Finally, some investigations of the character of the electrode reactions involved were attempted. As a background to this work, the current state of knowledge of conventional cationic polymerization is discussed in addition to previous studies on both cationic and other types of electroinitiated polymerizations. Furthermore, some studies of the oxidation of aromatic hydrocarbons and of the perchlorate and tetrafluoroborate anions in organic media are mentioned.

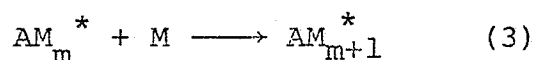
Cationic Polymerization

Addition polymerization is a chain reaction consisting of many fast, identical reactions generated by a small number of initiator or catalyst molecules. Four basic types of reactions are possible:

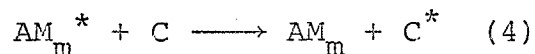
(i) initiation: the conversion of a small number of monomer molecules into active species which can serve as loci of polymerization.



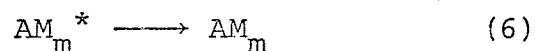
(ii) propagation: the addition of the active species to a monomer molecule, producing another active center on a chain one monomer unit longer.



(iii) chain transfer: the reaction of a polymeric active center with the monomer or other substance in the solution to produce a dead polymeric chain and another active species.



(iv) termination: the reaction which destroys the kinetic chain by eliminating the active center.



These reactions control the rate of formation, the structure and the size of the polymer molecules.

Addition polymerizations are classified according to the electronic configuration and charge of the active center involved. The principal types are:

- (i) free radical
- (ii) anionic
- (iii) cationic
- (iv) coordination catalysts (Ziegler-Natta)

In the cationic addition polymerization of vinyl monomers, the active center is usually considered to be an ion with a positive charge. Except where there are specific effects due to the supporting medium, the carbon atom on which the charge resides is usually planar with three covalent bonds and an empty p-orbital perpendicular to the plane. This species is a carbonium ion. Where conjugation is possible the charge is spread over a number of carbon atoms as in allylic carbonium ions.

A. Initiation

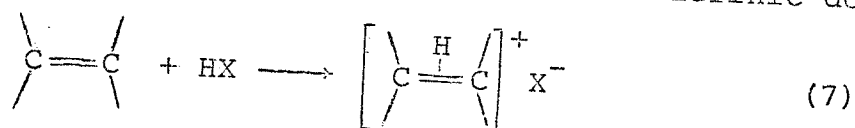
The initiation step in cationic polymerization has generally been considered to consist of the formation of carbonium ion active centers. These initiators, usually acidic substances, can be classified into four main groups:

- (i) classical protonic acids: HCl , H_2SO_4 , HClO_4
- (ii) Lewis acids: SnCl_4 , BF_3
- (iii) substances capable of oxidizing the monomer to radical cations
- (iv) other carbonium ion generators: isobutyl perchlorate, I_2 , ionizing radiation.

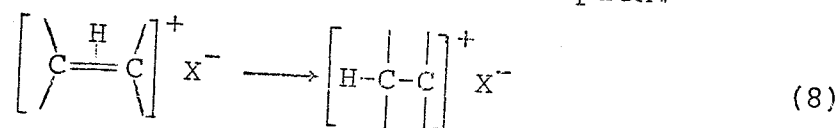
Because the initiation reactions in our polymerizations may involve mechanisms related to all four groups above, the activities of these initiators are discussed below.

(i) Protonic Acids

Initiation by protonic acids bears a strong relation to the addition of hydrogen halides to olefins and to the acid-catalyzed hydration of olefins. All of these reactions have been considered to involve the protonation of the olefinic double bond to form a carbonium ion. Various lines of evidence have shown that this reaction does not occur as a fast, reversible step (1,2,3,4). A mechanism more compatible with experimental evidence involves a fast, reversible equilibrium between unprotonated olefin and a loosely-bonded π -complex of a proton with the olefinic double bond:



The rate-determining step is postulated to be the intramolecular rearrangement of the π -complex to form the carbonium ion, sometimes called a σ -complex:

(ii) Lewis Acids

The most extensively used cationic polymerization initiators are Lewis acids. They generally produce polymers of higher molecular weight than those formed by protonic acid catalysts, especially at low temperatures. The metal halides used are usually those of Group III and d-transition

metals.

The problem of cocatalysis has been associated with Lewis acid catalysts. Earlier work suggested that in some cases, Lewis acids could function as initiators without the aid of cocatalysts while in others a cocatalyst was necessary. Anomalous results were frequently reported, adding to the confusion. Addition of water to a particular system might have increased the rate in one instance and decreased it in another.

More recent work has shown that the anomalies arose from a lack of rigor in the reaction preparations. As a result, variable, small but catalytic amounts of water were present and the reactions appeared to occur without a cocatalyst, although the observed rates varied considerably. The need of a cocatalyst was demonstrated only when catalyst, monomer and solvent, mixed in a state of high purity, exhibited no polymerization (5). This was not accomplished until sophisticated high vacuum techniques were used to handle the materials and proper methods of drying enabled the reduction of water content to 10 millimoles per liter or less. The effect of a chosen cocatalyst could then be determined.

It has now been demonstrated that a cocatalyst is necessary for initiation with almost all Friedel-Crafts catalysts. Perhaps the most spectacular demonstration of

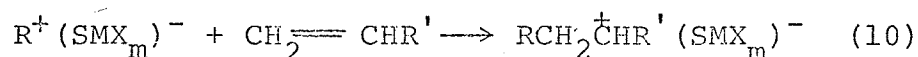
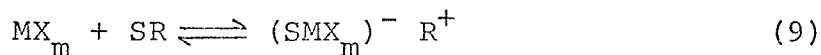
this was the successful distillation of styrene onto, and then from aluminum chloride, an extremely powerful catalyst (6).

Cocatalysts commonly used in cationic polymerization include alcohols, water, protonic acids and hydrocarbon halides. Some cocatalysts, such as water, inhibit the reaction when present in large amounts relative to the catalyst concentration. If the system can be dried perfectly and there is no other potential cocatalyst in solution, the observed rate rises from zero, as water is added to the system, to a maximum at a cocatalyst - catalyst ratio that is specific for each polymerization system. Thereafter, any further increase in water concentration retards the reaction to a degree dependent on the excess of water present. However, other cocatalysts, such as alkyl halides, do not inhibit the reaction even when present as the solvent. A good example of cocatalytic behaviour is contained in the study of the stannic chloride polymerization of styrene in various solvents reported by Colclough and Dainton (7).

Although some catalyst-cocatalyst pairs combine to form stable catalytic species, in many cases the corresponding complex acids have never been detected. For example, combinations of aluminum chloride with hydrogen chloride and boron fluoride with hydrogen fluoride might be expected to produce the complex acids $\text{H}^+(\text{AlCl}_4)^-$ and $\text{H}^+(\text{BF}_4)^-$. The

existence of these acids has never been demonstrated except in the presence of proton accepting bases (8). Double bonds can act as stabilizing bases for these types of systems, which might explain their strong polymerization initiating ability and their activity in ordinary Friedel-Crafts reactions in the presence of alkenes. A number of mechanisms have been proposed for the activity of these catalytic systems (9, 10).

In general, the activity of Friedel-Crafts catalysts is not well understood. In polymerization, the production of the carbonium ion could result from an attack by the monomer on a monomer-catalyst-cocatalyst complex, an attack by the cocatalyst on the catalyst-coordinated monomer or a rearrangement of a monomer-catalyst-cocatalyst complex. Alternatively, initiation by proton donation, as with protonic acids, could occur with cocatalysts having active hydrogens. Whatever the detail of the mechanisms, it has been shown in a number of cases that a part of the cocatalyst molecule is incorporated into the polymer, suggesting the following generalized reaction scheme:



where MX_m is the Lewis acid, SR is the cocatalyst and R is the part of the cocatalyst that adds to the double bond to

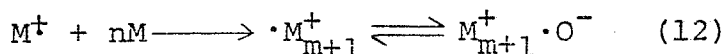
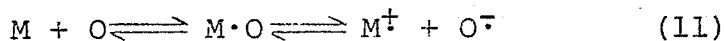
produce the cationic propagating species.

(iii) Oxidation of Monomer

Some compounds can act as cationic polymerization initiators by directly oxidizing monomeric double bonds to form radical-cations. This process is analogous to the production of radical-anions by the sodium naphthyl reduction of monomer molecules (11). Like radical-anions, the radical-cations are expected to dimerize into dicarbonium ions or add to monomer molecule to form polymeric species with separated ionic and free radical ends. Catalysts for these reactions include some Lewis acids and organic molecules with marked electron-acceptor character due to the attachment of many cyano, chloro or other electron attracting groups. Some examples are tetracyanoethylene, 1,4,5,8-tetrachloroanthraquinone, 2,3-dichloro -5,6-dicyanobenzoquinone (12), tropylium salts (13) and antimony pentachloride (14,15). These have been used in the polymerization of N-vinylcarbazole (12,13), alkyl vinyl ethers, styrene and other monomers (13). Szwarc (13,14) recently studied the oxidation and dimerization of 1,1-diphenylethylene.

The mechanism that has been advanced (12,13,14) to explain the activity of these catalysts involves the reversible formation of a coloured charge-transfer complex, $M \cdot O$, between catalyst and monomer. This species is in equilibrium

with the radical cation, $M^{\cdot+}$:



A review of polymerizations initiated by the oxidation of monomeric double bonds to radical-cations has recently appeared (16).

(iv) Other Carbonium Ion Generators

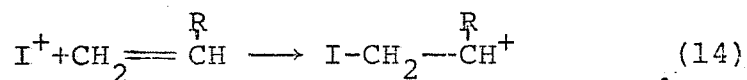
Many initiators of this class form carbonium ion growth centers by direct addition of part of the catalyst to a monomer molecule. Termination in no case regenerates an initiator molecule and therefore the term catalyst is inapplicable to these systems.

Acyl and alkyl perchlorates (17) and tetrafluoroborates (18) dissociate to form acylium and carbonium ions which can readily add to double bonds to initiate cationic polymerization. Because of the simplicity of their mode of initiation, these initiators along with perchloric acid (19) have been suggested for fundamental studies of cationic polymerization rather than syncatalytic systems whose mode of activity is not well understood.

Solutions of triphenylmethyl halides initiate polymerizations most probably by ionizing to form a triphenylmethyl carbonium ion (20). This initiator is especially active

with liquid sulfur dioxide, a specific ionizing solvent for the triphenylmethyl cation.

Iodine (21,22,23,24), iodine chloride and iodine bromide (25) have been studied as cationic polymerization initiators. The activity of these substances is thought to arise from ionization of the diatomic molecules and addition of the cation to the monomeric double bond:



(v) Implications of the Above Initiating Behaviour on Electroinitiated Cationic Polymerization

The initiation reactions possible in electro-initiated cationic polymerizations will probably be related to initiation by the catalysts described above. Like conventionally initiated cationic systems, the electroinitiated reactions will probably vary from very complex to very simple behaviour. However, it is possible that the electro-initiation of cationic polymerizations will not only provide some measure of control over the initiation process but will also simplify the initiation behaviour.

The production of conventional protonic acids at the anode would provide a relatively simple initiation especially

if the acids were strong and formed active centers in an effectively instantaneous reaction. In cases where no termination was possible, the number of active centers present would be proportional to and in cases with 100% electrode efficiency equal to the amount of current passed.

The production of a Lewis acid at the anode would probably provide a more intricate initiating behaviour. A cocatalyst must either be added or be present as an impurity. If adventitious water were responsible for cocatalytic activity, the first quantities of Lewis acid produced would probably not be very effective for initiation as water in large excess over the Lewis acid would retard the reaction. Also, higher hydrates than those responsible for initiation may form because of the excess of water, eg., inactive $\text{SnCl}_4 \cdot 3\text{H}_2\text{O}$ instead of active $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$ (7). However, as more Lewis acid was produced, the rate would rise as more of the active hydrate was formed and/or as the catalyst-water ratio was increased. When the latter ratio reached the value at which the maximum rate for the concentration of cocatalyst present occurred (maximum amount of syncatalyst formed), the rate would become independent of any further current passed, provided the Lewis acid-water syncatalyst was the only catalyst possible. Thus, the reaction rate at any time would not be a simple function of the amount of current passed but also a function of the

catalyst-cocatalyst ratio. Therefore, a very complex initiation behaviour would result unless water was completely removed from the system and a cocatalyst which could not retard the reaction was added. Alternatively, an electrode reaction simultaneously producing catalyst and cocatalyst in equimolar amounts would also simplify the initiation behaviour because the catalyst-cocatalyst ratio would be constant throughout the catalyst production.

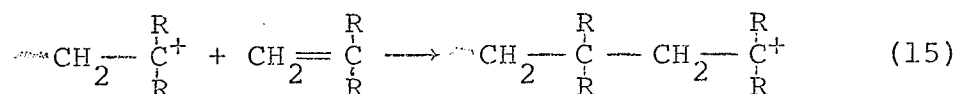
An initiation proceeding by direct oxidation of the monomer at the electrode would be analogous to initiation by monomer oxidation described above. A carbonium ion would be produced directly and an anion from the electrolyte would function as the counterion. Thus, the active center would be equivalent to that produced by the conjugate protonic acid of the electrolyte anion.

Finally, it may also be possible to initiate cationic polymerizations by the electrolytic production of initiators of the types described above in (iv). Although it is difficult to imagine the formation of triphenylmethyl chloride or acyl and alkyl perchlorates and tetrafluoroborates at an electrode, iodine, a good cationic catalyst, may be produced on the electrolysis of an iodide salt.

B. Propagation

The cationic propagation reaction involves the

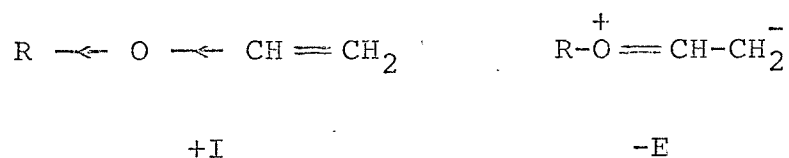
addition of a carbonium ion or cationically active center to the monomeric double bond:



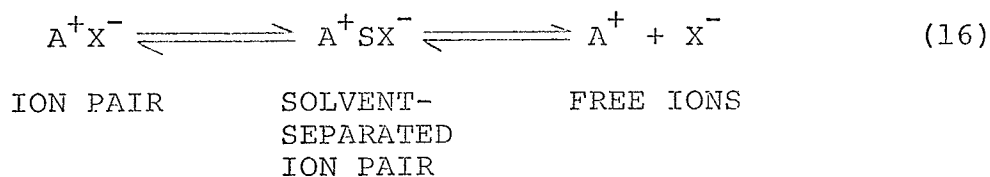
This reaction is a major factor in controlling the overall rate of polymerization and in cases where initiation is fast and termination absent, it is the only rate-controlling reaction. The mechanism of this reaction determines the microstructure of the resulting polymer and both the rate and mechanism are governed by the reaction conditions and monomer structure.

The extent of the predominance of propagation over all other modes of reaction of the active center determines the average size of the resulting polymeric molecules. Therefore the monomeric double bond must be the locus of greatest cationic affinity in the medium. Since the addition of a cationic center to an olefin is an electrophilic reaction, monomers susceptible to this type of reaction have relatively negative double bonds. Thus, the relative rates of polymerization of para-substituted styrenes increase with the electron-releasing ability of the para-substituent, i.e. in the order $\text{Cl} < \text{H} < \text{CH}_3 < \text{OCH}_3$. In the very active vinyl ethers, an electron-releasing mesomeric effect, -E, greatly predominates over an electron-withdraw-

ing inductive effect, + I :



Studies of simple carbonium ion reactions in organic chemistry have suggested that some easily dissociated compounds, such as triphenylmethyl chloride, unimolecularly dissociate into carbonium ions through two distinct intermediates proposed by Winstein et al (26). These intermediates are known as contact ion pairs and solvent-separated ion pairs. The equilibria between these ionic forms are represented as follows:



The carbonium ions and their counterions in polymerizing systems also exist in these ionized forms, the relative quantities of which are determined by the temperature and the specific solvation ability of the solvent for each of these species. As the rate and mechanism of propagation should differ for each of these ionic forms, a very complicated polymerization behaviour on changes of solvent or temperature may occur.

In practice, great changes in propagation rate

constants do occur on changing solvents. Thus, for the polymerization of styrene with perchloric acid as initiator (19), the propagation rate constant at 25°C dropped from 17.0 liters/mole-sec. to 0.0012 liters/mole-sec. on changing the solvent from ethylene chloride to carbon tetrachloride. In the polymerization of isobutene by titanium tetrachloride (27), complications in kinetic behaviour with changes in temperature have been attributed to ionic equilibria between ions and ion pairs.

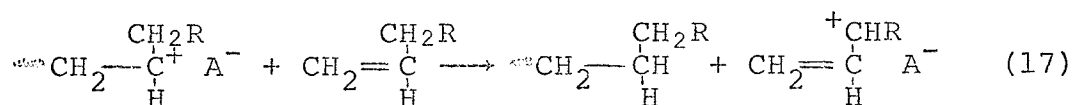
The carbonium ion counterions can also exert a great influence on the propagation reaction. For example, in the polymerization of styrene in ethylene dichloride at 25°C., the propagation rate constant with an I_3^- counterion was 0.003 liters/mole-sec. with an activation energy of 6.5 kcal/mole (18). However, on changing the counterion to perchlorate, the reaction was found to have a rate constant of 17.0 liters/mole-sec. and an activation energy of 9.6 kcal/mole (28).

C. Transfer and Termination

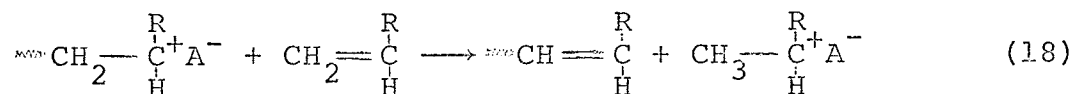
Under the terms transfer and termination are classified all reactions limiting the molecular weight obtained in a polymerization reaction. If a reaction results in a dead polymer chain and a species capable of promoting the growth of a new chain it is termed chain transfer. If it produces

a dead polymer chain and an inactive species incapable of initiating further chain growth it is considered to be a termination reaction. While chain transfer usually occurs at a rate comparable to that of propagation and does not affect the rate of polymerization, termination can have an important effect on the rate and is included in the overall rate constant. Molecular growth-stopping reactions are more important in cationic than in any other type of vinyl polymerization. As a result, the molecular weights produced by cationic mechanisms are generally lower.

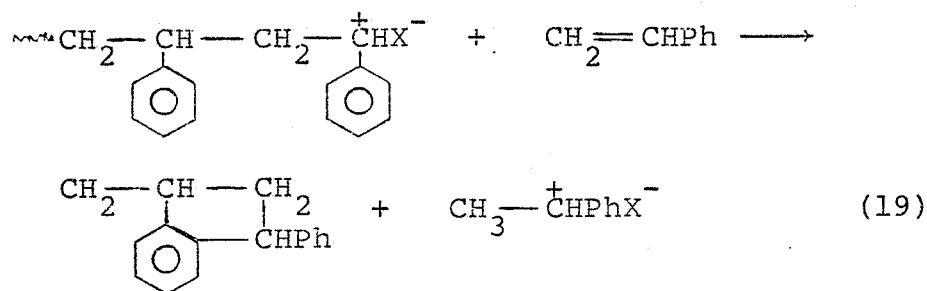
Chain transfer to monomer is the most important molecular size-limiting reaction in cationic polymerization. The principal mechanisms proposed for this process are hydride abstraction:



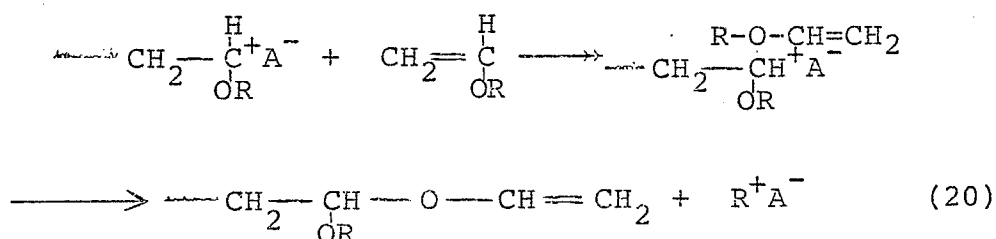
and proton donation:



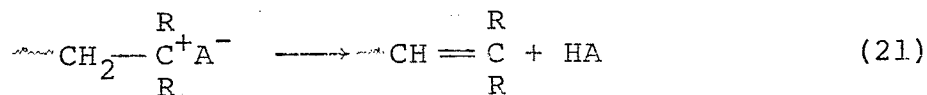
Mechanisms applicable to specific monomers have been proposed. For some aromatic monomers such as styrene, a Friedel-Crafts alkylation of the aromatic ring on the penultimate monomer unit is possible (19):



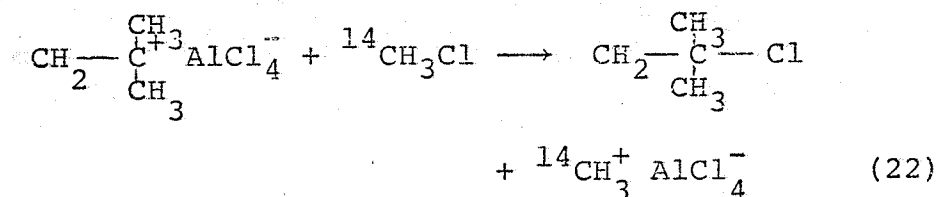
For vinyl ethers a mechanism involving the ether oxygen atom has been proposed (29):



Species other than monomer can be involved in transfer processes. Transfer can occur to the counterion producing the original initiating acid (30):



This reaction can be unimolecular or bimolecular, depending on the separation of the ions. Chain transfer to polymer (31) produces branching while transfer to aromatic solvents (32) produces detectable end groups such as tolyl groups in toluene. Transfer to halogenated aliphatic solvents has been verified by the detection of radioactivity in the polymer when radioactive solvent is used (33):

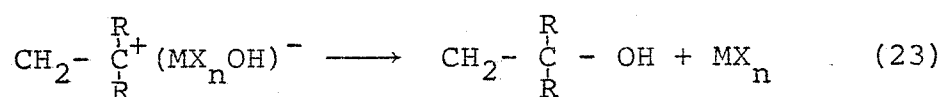


Transfer processes in cationic polymerization usually possess relatively high activation energies. Lower temperatures can therefore "freeze out" these reactions resulting in higher molecular weights.

Especially in Brønsted acid-catalyzed polymerizations, termination can take place by means of a simple combination of the anion with the growing polymer end to form a bond. The importance of this process decreases with a decreasing nucleophilicity of the anion and therefore with an increasing acid strength of the initiator. Thus, the polymerization of styrene by the very strong perchloric acid appears to have no true termination reaction (19). In the sulfuric acid polymerization of styrene, the termination reaction has the rather high activation energy of 13.5 kcal/mole, possibly because of the poor nucleophilicity of the bisulfate anion (34). When hydrobromic acid is used as initiator, termination assumes great importance because of the possibility of the formation of a relatively stable carbon-bromine bond (35).

With Lewis acid-cocatalyst combinations, a wider variety of termination reactions are possible. In some

systems, termination is unimportant (22,36,37). In other cases termination involving the consumption of initiator may occur (38). However, the most common mode of termination is a combination of the active end with a cocatalyst fragment. In the case of water-cocatalyzed systems, a terminal alcoholic group is formed:



D. Kinetics

Kinetic analyses of addition polymerizations have often utilized the steady-state assumption to simplify the kinetic expressions involved. This assumption, that the concentration of active centers is constant, is applicable to reactions in which the rate of change of the concentration of active centers is negligible compared with their rates of formation and disappearance (39). This is termed a stationary-state of the First Kind and is applicable to a number of cationic systems. The assumption also applies to systems which possess virtually instantaneous initiation and no termination. This is called a stationary-state of the Second Kind.

For many cationic polymerizations, the steady-state assumption is invalid. In some cases, the rate of termination never attains the rate of initiation, resulting in an

increasing number of growing polymer chains during the reaction and sigmoid-shaped reaction curves (40,41). In other systems, the polymerization ceases before all the monomer has been consumed (40), suggesting a complete consumption of catalyst or cocatalyst by a termination reaction. A very involved and complete analysis of the latter type of system was derived by Pepper for the polymerization of styrene by sulfuric acid (34).

The rate of cationic polymerization is usually first order in both monomer and active center concentrations.

$$-\left(\frac{d(M)}{dt}\right) = k_p (M_n^+) (M) \quad (24)$$

Where termination involves the combination of a carbonium ion and a counterion of a propagating ion pair, it is usually unimolecular in active center concentration:

$$R_t = k_t (M_n^+) \quad (25)$$

In polar solvents, initiation is often first order in catalyst concentration, only:

$$R_i = k_i (C) \quad (26)$$

However, the kinetic expression for this reaction is often more complicated. This is particularly true for reactions in media of low dielectric constant where the solvating ability of the solvent for the ions or ion pairs is not great. In

these cases, the formation of propagating ions can be assisted by the most polar or polarizable molecules in solution, often the catalyst or the monomer. The kinetic dependence of the initiation reaction is then greater than one on the catalyst concentration and greater than zero on the monomer concentration.

The general kinetic equation for a cationic reaction exhibiting a stationary-state of the First Kind can be expressed as (42):

$$-\left(\frac{d(M)}{dt}\right) = \frac{k_p k_i}{k_t} (M) F\{(C) (Co-cat.), (M)\} \quad (27)$$

where (Co-cat.) is the concentration of the cocatalyst, if one is needed and $F\{(C), (Co-cat.), (M)\}$ is a function of the catalyst, cocatalyst and monomer concentrations. The overall rate constant, $\frac{k_p k_i}{k_t}$, may have a positive or negative activation energy depending on the relative sizes of the termination activation energy and the sum of the initiation and propagation rate constants.

E. Degree of Polymerization

The number-average degree of polymerization is the average number of monomer units in the polymeric chains of a polymer sample. It can be expressed as the ratio of the rate of propagation to the sum of the rates of molecular chain-terminating reactions including termination and

transfer:

$$\overline{DP} = \frac{R_p}{R_t + R_{tn}} \quad (28) .$$

F. Carbonium Ions and Pseudocationic Polymerization

It had been assumed for many years that the chain-carrying species in polymerizations initiated by Lewis Acids and protonic acids were carbonium ions. However, in the majority of cases, the carbonium ion character of active species was inferred from the nature of the catalyst and supported only indirectly by kinetic evidence. Electrical conductivity measurements were seldom carried out to ascertain the presence of ions during polymerizations. Observations of carbonium ion spectra were often reported but seldom under polymerization conditions. In addition there was a failure to recognize the kinetic complications that may arise in ionic polymerization systems due to equilibria between ions and ion pairs in the low dielectric media used.

True cationic behaviour has been established in a number of systems. The polymerization of isobutene with titanium tetrachloride and water in methylene chloride (27) shows an apparent change in the mechanism of propagation as the temperature is lowered from +18°C to - 91°C. This behaviour has been attributed to predominantly ion pair

propagation at higher temperatures and free ion propagation at lower temperatures.

Recently Sukurada, Ise and coworkers have reported cogent experimental evidence for the existence of propagating ions and ion pairs in some ionic polymerizations. They found that the application of electric fields of strengths of up to 2.0 K.V./cm. across some cationic polymerization systems increased the rates of polymerization and that the increase was proportional to the strength of the field. This effect was ascribed to a field-facilitated dissociation of ion pairs to free ions, a well-known phenomenon in weak electrolyte solutions (43,44). Apparently the free cations propagated at a higher rate than ion pairs, a phenomenon which has been demonstrated for anionic systems (45). In this work it was satisfactorily demonstrated that the field accelerations did not arise from electroinitiation or from joule heating by the passage of current. Accelerations proportional to the electric field strength were found in the iodine-initiated polymerization of p-methoxystyrene (46), α -methylstyrene (47) and isobutyl vinyl ether (48) in ethylene chloride. A field acceleration was also found in the polymerization of styrene by boron trifluoride etherate in ethylene chloride (49) and of α -methylstyrene by iodine in nitrobenzene (50). However, no field effect could be detected in the free radical polymerizations of styrene and

methyl methacrylate in ethylene dichloride initiated by azobisisobutyronitrile and benzoylperoxide (46), indicating that the accelerations due to the electric field only occur in ionic polymerization systems. To clarify the effect of the dielectric constant of the medium on the acceleration, Sakurada, Ise and Hayashi (49) studied the electric field acceleration of the polymerization of styrene by boron trifluoride etherate in ethylene chloride as a function of dielectric constant. The results of this work indicated that at sufficiently large or small degrees of dissociation, an electric field does not affect the rate of polymerization.

The carbonium ion theory for the polymerization of styrene by perchloric acid in chlorinated solvents was the first to be challenged. This reaction, originally studied by Pepper et al (19,34), was found to be very reproducible even with water concentrations equal to ten times that of the catalyst. The rate law observed up to 95% conversion was:

$$-\left(\frac{d(M)}{dt}\right) = k(\text{HClO}_4)_0 (M)_t \quad (29)$$

where $(M)_t$ is the monomer concentration at time t and $(\text{HClO}_4)_0$ is the initial catalyst concentration. After 100% conversion of monomer to polymer, a further charge of monomer resulted in polymerization with approximately the same rate constant. The logarithm of the observed rate constant was found to vary linearly with the reciprocal of

the dielectric constant for most solvents used. In ethylene chloride at 25°C. a rate constant of 17.0 liters/mole-sec. and an activation energy of 8.3 kcal/mole were found.

Pepper concluded from this evidence that:

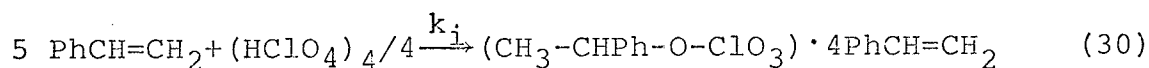
- a) the active species involved in the propagation reaction were carbonium ions formed on protonation of the monomer by perchloric acid,
- b) the number of carbonium ions equaled the number of equivalents of acid added,
- c) initiation was instantaneous and there was no termination, and
- d) the measured rate constant was that of propagation alone.

Gandini and Plesch (51,52) reported the same general phenomena for the perchloric acid polymerization of styrene in methylene chloride. A rate constant of 10.7 liters/mole-sec. and an activation energy of 12 kcal/mole were found. However, the absorption peak at 424 m μ , attributed to the polystyryl carbonium ion, was not present during the polymerization. Moreover, conductivity measurements demonstrated that no significant concentration of free ions was present during the polymerization. Although propagating ion pairs could have been responsible for the polymerization, estimates of the equilibrium constant between ion pairs and free ions under the experimental conditions used (53) indicated that a

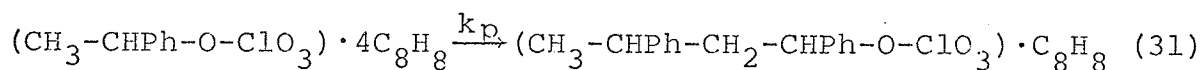
significant change in free ion concentration would occur in the range of acid concentration used, precluding the observed first order dependence on the acid concentration. Gandini and Plesch also noted that as 100% conversion was approached both the 424 mμ absorption and the conductivity grew together.

On the basis of the above evidence, Plesch proposed that non-ionic esters, with polar, covalent bonds between the perchlorate and carbonium ions, were the active centers in this reaction. This ester would require stabilization by four styrene molecules and could not exist in the absence of styrene. The proposed reaction scheme was:

Initiation (instantaneous):



Propagation:



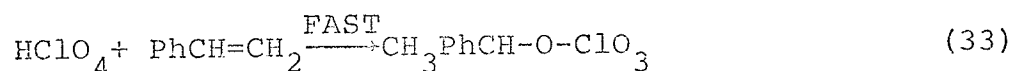
$$R_p = k_p (\text{HClO}_4)_o (\text{PhCH} = \text{CH}_2) \quad (32)$$

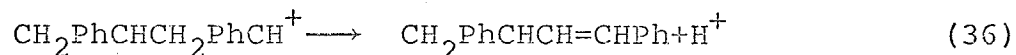
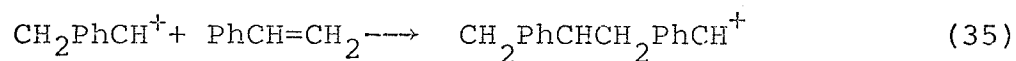
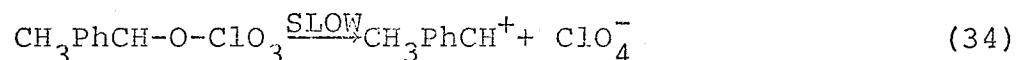
When the styrene was virtually all consumed, the ester would decompose to form polystyryl carbonium ions, explaining the increase in conductivity, the appearance of the 340 mμ Absorption peak and a very rapid consumption of the remaining monomer. The latter reaction was considered to be truly

cationic, while the reaction consuming the bulk of the monomer was termed "pseudocationic".

Shortly after the "pseudocationic" theory appeared, considerable doubt was cast on the possibility of the existence of simple benzyl-type carbonium ions in this medium. Even in strongly acidic solutions such as $\text{SbF}_5\text{-FSO}_3\text{H-SO}_2$ no evidence for the formation of these ions could be gained (54,55,56). In addition, theoretical calculations and experimental evidence suggested that the major absorption for the polystyryl ion should be found in the 300 to 320 $\text{m}\mu$ range (57). Spectroscopic studies by Higashimura et al (58) supported these conclusions. Finally Bywater and Worsfold (59) and later Bertoli and Plesch (60) demonstrated unequivocally that the 420 $\text{m}\mu$ absorption was not due to polystyryl cations but to diphenyl-substituted carbonium ions derived from cyclized end groups formed at the end of the polymerization.

Bywater and Worsfold proposed a carbonium ion mechanism compatible with the experimental evidence. They postulated that the bulk of the perchloric acid did indeed form an ester with the monomer, but that the polymerization proceeded by carbonium ions formed by a slow ionization of the ester, the rate-determining step:





The polymerization would exhibit normal cationic transfer and termination reactions. Moreover, it would be a steady-state polymerization of the First Kind and not of the Second Kind as proposed by Pepper.

In a further study of this system, Gandini and Plesch (61) reported further evidence suggesting that the ions formed after the end of the polymerization were not benzyl but indanyl and various phenyl alkyl carbonium ions. Clear kinetic and thermal evidence was shown for the stabilization of their proposed ester by four styrene molecules.

As yet the identity of the propagating species in the perchloric acid-styrene system had not been definitely established. However, it is difficult to reconcile any carbonium ion theory with the absence of any effect of large quantities of water while polymerizations known to proceed through carbonium ion intermediates are seriously affected. It can therefore be stated that this factor and the evidence cited above have shown that carbonium ions do not exist in large concentrations approaching that of the perchloric acid

during the bulk of the polymerization.

Electroinitiated Polymerization

In electroinitiated polymerization, a species which can serve as an active center of polymerization is produced at an anode or cathode. Monomer, salt or some other substance present in the solution may be involved in the electrode reaction which can produce a radical or ionic species. The potential of the electrode can provide a degree of control over the kinds of substances that are electrolyzed and the current can regulate the amount of initiator being produced. The ensuing polymerization reactions follow the same behaviour as the equivalent conventionally-initiated polymerizations. The major advantage of electropolymerization lies, therefore, in a greater degree of control over the initiation process. This situation is analogous to that of photoinitiated polymerization in which the frequency and intensity of the incident radiation can be varied to regulate the kinds of bonds to be broken and the rate of initiator production.

A. Cathodic Free Radical Polymerizations

One of the first electroinitiated polymerization studies was reported by Wilson and coworkers in 1949 (62). Insoluble poly(methyl methacrylate) was produced at a

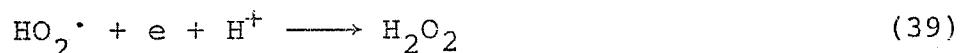
cathode when current was passed through methanolic aqueous solution of sulfuric acid and monomer. Hydrogen atoms produced at the metal cathode were thought to initiate the reaction by adding to the monomeric double bond thereby producing free radical active centers. Various metals (Pb, Sn, Pt, Bi, Fe, Al) used as cathodes were found to produce polymer with efficiencies varying in accordance with their hydrogen overpotentials. A number of metals would not produce polymers.

Parravano (63) polymerized methyl methacrylate by hydrogen atoms produced both electrolytically and by the chemisorption of hydrogen on metallic surfaces. He established that the polymerization did indeed arise from hydrogen atoms. However, the efficiency of conversion from hydrogen atoms to free radicals was found to be very low.

Tsvetkov (64) cathodically polymerized methyl methacrylate in aqueous hydrochloric acid solutions. In this work, it was unexpectedly found that stirring decreased the efficiency of the electropolymerization. In later work (65) the influence of acid concentration and the additions of salts and alcohols were studied. The first aqueous electropolymerization of styrene was accomplished when methyl alcohol was added to increase the solubility of the monomer. Additions of methyl and ethyl alcohol to aqueous methyl methacrylate systems increased the polymerization efficiency of this

monomer because of the greater homogeneity of the reactions under these conditions.

Although earlier reports had claimed that methyl methacrylate had been polymerized by hydrogen atoms generated at a lead cathode in acid solution (62,66,67), Fedorova (68,69,70) provided strong evidence that the polymerization would not proceed in the absence of oxygen. He proposed that oxygen was reduced at the lead electrode in the following manner:

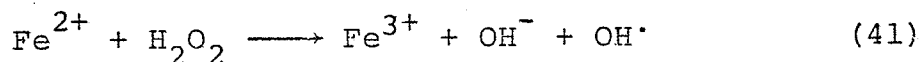


$\text{HO}_2^\cdot$ could be the initiating species for the radical polymerization.

A characteristic phenomenon observed in a number of hydrogen atom initiated electropolymerizations was an "after" polymerization continuing for many hours after the cessation of current (66,67). Since no new radicals were formed during this period, the reaction probably arose from long-lived radicals whose mutual termination was prevented by heterogeneous effects (71).

A further type of cathodic free radical polymerization was reported by Kolthoff and coworkers (72) who polymerized acrylonitrile by means of a ferric-ferrous redox couple. Ferric ions were reduced at the cathode to ferrous ions,

which reduced hydrogen peroxide, potassium persulfate or cumene hydroperoxide to produce free radicals. A possible reaction scheme is:



B. Anodic Free Radical Polymerizations

The classical method of anodic free radical production is the Kolbe electrolysis. This involves the oxidation of monobasic aliphatic acids to produce alkyl free radicals which can dimerize to produce symmetrical alkanes.

Free radicals produced by the Kolbe electrolysis were first utilized for the initiation of radical polymerizations by Goldschmidt and Stöckel in 1952 (73). A low molecular weight polystyrene oil was produced on the passage of current through acetic acid solutions of sodium acetate and styrene. However, Friedlander et al (63) failed in an attempt to form substantial quantities of poly(styrene) and poly(acrylonitrile) by the electrolysis of solutions of these monomers and potassium laurate.

Smith and Gilde (74) studied the electrolysis of methanolic solutions of potassium acetate with butadiene and isoprene. They found products resulting from the addition of methyl and acetoxy radicals to monomer molecules and the subsequent dimerization of the various radicals present. No

polymer was formed because the diene radicals were greatly resonance stabilized and would not attack the diene further. In a later study (75) these authors reported the polymerization of vinyl acetate and methyl methacrylate on the passage of current through aqueous solutions of these monomers and potassium acetate. The use of potassium acetate - $2C^{14}$ resulted in the presence of large amounts of radioactivity in the polymer. This was advanced as evidence for initiation by methyl or acetoxy radicals produced by the electrolysis of the acetate anion. Funt (76) has noted that the level of activity found in the polymer by these authors would indicate that 470 methyl and/or acetoxy fragments were incorporated per molecule of polymer. This unreasonable result was probably due to insufficiently thorough polymer purification procedures. However, studies by Funt and Hnatowich (77) support the conclusion that radioactivity is indeed incorporated into the polymer.

Funt and Yu (78) studied the electroinitiated polymerization of methyl methacrylate in dimethyl sulfoxide. Zinc acetate and several other salts were used as electrolytes. Both monomer and polymer were soluble in this non-aqueous solvent. As a result there was no polymeric coating of the electrode and the system remained homogeneous throughout. This allowed a well-defined kinetic study of this reaction. The homogeneous polymerization of vinyl pyrroli-

done in methyl alcohol using potassium acetate as the electrolyte was also studied (79).

Goerring et al. (80,81) reported that haloolefins such as tetrafluoroethylene, trifluorochloroethylene and difluorodichloroethylene would electrolytically polymerize with ease at one atmosphere pressure in hydrogen fluoride-potassium fluoride and trifluoroacetic acid-potassium trifluoroacetate-trifluoroacetic anhydride solutions. This is significant because haloolefins are especially difficult monomers to polymerize by ordinary means.

Tsvetkov and Koval'chuk (82) have studied the initiation of methyl methacrylate polymerization by the Kolbe electrolysis of sodium acetate in water and aqueous ethyl alcohol, methyl alcohol, acetone and ethylene glycol solutions. The highest rate was found in the aqueous glycol solution in which 50% conversion could be achieved in two hours. A more recent study by the same authors (83) reported a further study of the anodic polymerization of methyl methacrylate in aqueous ethylene glycol.

C. Anionic Electroinitiated Polymerization

A general feature of electroinitiated free radical polymerization has been the very low efficiency of chain initiation. The great concentration of free radicals produced at the electrode enhanced the chance of wastage

through radical combination. Although an increase of current increased the rate of polymerization, the molecular weight would be reduced.

In contrast to free radical systems, anionic polymerizations are not subject to bimolecular termination. As a result, the molecular weights are normally independent of current and the electrical efficiencies are many orders of magnitude greater in anionic systems.

Yang, McEwan and Kleinberg in 1957 (84) reported an electropolymerization that was probably anionic in character. They used magnesium electrodes in a pyridine solution of sodium iodide and styrene to produce low molecular weight polystyrene.

Breitenbach (85) reported the cathodic electropolymerization of acrylonitrile using a tetrabutylammonium perchlorate salt. This reaction was originally believed to be free radical in character, initiated by ethyl free radicals produced by the electrolysis of the cation:



However, a later publication by the same author (86) demonstrated the anionic nature of the reaction by means of co-

polymerization studies with methyl methacrylate and acrylonitrile.

Funt and Williams (87) reported the anionic formation of low molecular weight poly(acrylonitrile) at the cathode in dimethylformamide with a sodium nitrate electrolyte. The rate was first order in both current and monomer concentration. A mechanism involving reduction of the monomer at the electrode and dimerization of the resulting radical-anions to propagating dianions was proposed.

Funt and Laurent (88) studied the relative yields obtained with different alkali metal nitrates in the anionic electropolymerization of styrene in dimethylformamide. Funt and Bhadani reported the use of tetramethylammonium chloride in dimethylformamide for the anionic polymerizations of styrene (89) and methyl methacrylate (90). In both systems the rates exhibited a first order dependence on monomer concentration and a first order dependence on current for styrene. The rate equation for methyl methacrylate was half order in current.

Several studies on the electrolytic reduction of acrylonitrile have been reported. Murphy and coworkers (91) compared the electrolytic and sodium metal reductions of this monomer. Baizer et al. (92,93) conducted polarographic investigations on the conditions favourable to hydrodimerization over polymerization in acrylonitrile reduction. The

presence of proton-donating materials such as water or acetonitrile favoured the simple reductive coupling reaction which can be considered a termination at a very early stage of polymerization. Conversely, the polymerization reaction is favoured by low water and high monomer concentrations.

The low-temperature anionic electropolymerization of 4-vinylpyridine in liquid ammonia and in bulk has been reported (94). Alkali metal and tetraalkylammonium salts were used as electrolytes in a divided cell. The polymer formed was insoluble and was coloured orange-red.

D. Electroinitiated Living Polymers

The work of Michael Szwarc (11,95) has shown that under certain conditions, organic carbanions formed by the reduction of olefinic monomers are not terminated and can exist indefinitely. The persistence of the active species in the electroinitiated anionic polymerizations described above was inherently impossible because of the facility of their reaction with the solvents employed.

The first report of the electrolytic formation of "living" organic anions from a monomer was published by Yamazaki (96). Tetrahydrofuran was found to be suitable as a solvent because of its chemically inactive character and its ability to form conducting solutions. α -methylstyrene was used as the monomer and lithium aluminum hydride and

sodium tetraalkylaluminum were used as electrolytes. A divided cell effected the separation of the red carbanions formed at the cathode from terminating agents formed at the anode. No polymer was formed at room temperature because of the low ceiling temperature of the monomer, but on reducing the temperature to -78°C , polymer was formed with a viscosity-determined molecular weight nearly equal to that given by the equation:

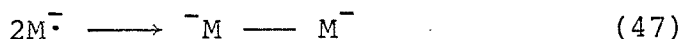
$$\bar{M}_n = \frac{\text{Grams of Monomer}}{\frac{1}{2} \times \text{Faradays Passed}} \quad (45)$$

This suggested a strong resemblance of this reaction to the conventional formation of "living" polymers (11).

The mechanism proposed by Yamazaki involved the reduction of monomer to radical-anions either directly at the electrode or by alkali metal formed at the cathode:



This was followed by a dimerization to form a dianion:

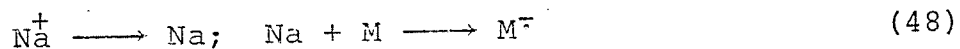


Funt, Bhadani and Richardson (97) formed living α -methylstyrene carbanions in tetrahydrofuran using $\text{NaAl}(\text{C}_2\text{H}_5)_4$, NaBPh_4 and KBPh_4 as electrolytes. The formation and destruction of the living ends could be followed quantitatively by observation of the intensity of the 340

mp absorption peak of the carbanion. It was shown that the destruction of these ions on the reversal of current proceeded at the same electrical efficiency as their formation. Again, no polymer was produced until the solution containing the "living" ends was cooled below room temperature. This study demonstrated that the "living" end population could be varied at will and that the concentration of carbanions could be determined spectrophotometrically.

Funt, Bhadani and Richardson (98) also reported the first study of "living" anionic polymerization with electrolytic control. Styrene was the monomer used in this study. Funt and Kubota (99) have demonstrated methods of tailoring molecular weight distributions and explored copolymerization possibilities in "living" anionic polymerization.

Yamazaki et al (100) recently reported the electro-initiated anionic polymerization of α -methylstyrene in a tetrahydrofuran solution of sodium tetraethylaluminum. The observed molecular weights suggested that the polymer molecules had two "living" ends. Termination with carbon dioxide produced polymer containing carboxyl groups. The yellow living anion of butadiene was also electrolytically formed. Polarographic results indicated that sodium discharge occurred before the reduction of the monomer and therefore the mechanism proposed for initiation was:



The half wave potentials of a number of monomers in dimethoxyethane solutions of tetrabutylammonium perchlorate were also reported in this work.

E. Electroinitiated Cationic Polymerization

The electroinitiated cationic polymerization of vinyl monomers was first reported by Breitenbach (101). Current passed through a solution of tetraethylammonium tetrafluoroborate in an acrylonitrile-styrene mixture produced almost pure polystyrene in the anode compartment of a divided cell, clearly suggesting a cationic mechanism. Poly(styrene) also formed at the anode on electrolysis of a nitrobenzene solution of styrene and tetraethylammonium tetrafluoroborate.

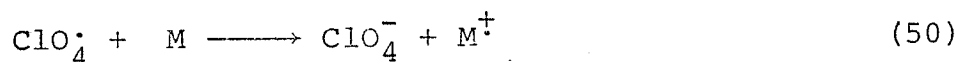
Tetraethylammonium perchlorate proved to be an effective electrolyte for the anodic electropolymerization of styrene, isobutyl vinyl ether and N-vinylcarbazole.

The solubility of silver perchlorate in pure monomers allowed the passage of current without the presence of solvent. Polymers of styrene and isobutyl vinyl ether formed at the anode on electrolysis of silver perchlorate solutions in the monomers with and without nitrobenzene. Similarly, poly(N-vinylcarbazole) was produced in nitrobenzene solution.

A remarkable feature of these polymerizations was the current efficiency. For example, 2700 moles of isobutyl

vinyl ether could be polymerized per electrochemical equivalent passed through a solution of this monomer and tetrabutylammonium perchlorate in nitrobenzene. The efficiency was even greater using silver perchlorate as the electrolyte: 0.1 moles of isobutyl vinyl ether could be polymerized with 0.2 microequivalents of current.

A pronounced after-effect was noted in systems containing the silver perchlorate salt. Addition of a nitrobenzene solution of N-vinylcarbazole to a fully electropolymerized nitrobenzene solution of styrene and silver perchlorate produced a fast polymerization with a great evolution of heat without further passage of current. Breitenbach suggested that a type of "living" polymer was present in this cationic system. Breitenbach proposed the following mechanism for the anodic production of cationically active centers:



In this work, no guarantee of the absence of a blank (polymerization before current passage) was given for most of the results reported. This is especially important for the silver perchlorate systems as this salt has been known to polymerize 2-ethylhexyl vinyl ether (102) and styrene

(103) without current passage. Although subsequent work by Burton and Praill (104) demonstrated that pure, dry silver perchlorate would not function as a catalyst, Breitenbach gives no definite assurance that the salt used in his work was sufficiently dry. This may also apply to the tetraethylammonium perchlorate and tetrafluoroborate salts. However, even in the absence of a blank, the passage of current could have simply removed an impurity in the solution that prevented polymerization initiation by the salt itself.

Breitenbach did not report any reaction curves nor did he examine the effect of current reversal on the rate of reaction. The true electroinitiated character of these reactions, the degree of electrolytic control over the rates and perhaps the kinetics of the reactions could best be demonstrated by following the reaction throughout its course and examining the effects of varying amounts of current on the rate. Nevertheless, Breitenbach's results strongly support a cationic-like mechanism for these polymerizations and indicate that the reactions were probably electrochemically initiated.

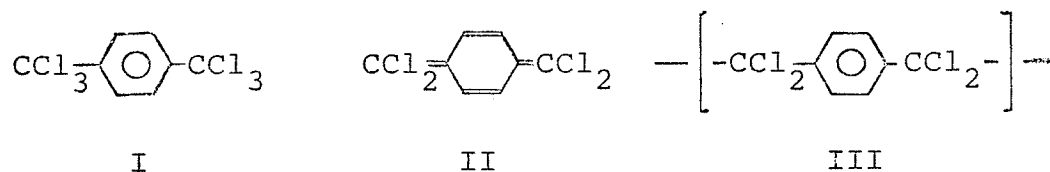
F. Other Electroinitiated Polymerizations

In all of the electropolymerization reactions mentioned above, the initiation and in some cases the termination reactions were subject to electrolytic control. A

number of attempts have been made to control each successive propagation step. The addition of one monomer unit to the polymer chain would result from a single electron transfer. This could be termed electrocondensation polymerization. The great disadvantage of this type of polymerization is that like conventional condensation polymerization, the efficiency of the reaction must be very high for high polymer formation to occur.

Gilch and Michael (105) studied the electrolytically initiated condensation polymerization of caprolactam. This reaction occurred through anionic intermediates formed when a current was passed through a solution of an alkali salt and an isocyanate activator in the monomer melt.

Gilch (106) and Covitz (107) have reported the electrolytic reduction polymerization of p-xylene compounds. For example, the controlled potential reduction of hexachloro-p-xylene, I, in aqueous p-dioxane appeared to produce $\alpha, \alpha, \alpha', \alpha'$ -tetrachloro-p-xylene, II, as an intermediate which subsequently formed polytetrachloro-p-xylylene, III.



The polymer was extremely insoluble and could not be properly characterized. This reaction cannot strictly be termed an electrolytic condensation polymerization because the

transfer of electrons did not add the monomer units to the chain but produced an easily polymerizable intermediate.

The electrolytic formation of apparently stereoregular polymers has recently been reported by Shapoval et al (108). Electrolysis of phenyl isocyanate with tetrabutylammonium iodide in dimethylformamide using a divided cell and a nickel cathode produced a film of poly(phenyl isocyanate) at the cathode. X-ray diffraction demonstrated that the polymer was crystalline. It was proposed that the molecules became orientated during macromolecular chain growth on the electrode surface.

Oxidation of Hydrocarbons

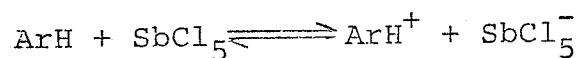
Most of the work on the electrochemical oxidation of hydrocarbons has been done on condensed aromatic ring systems with platinum electrodes and in acetonitrile. In polarographic studies it has been noted that as the size and resonance of the molecule increases, the anodic half wave potential becomes less positive. Much of the early work (109,110,111) suggested that unlike the reduction of hydrocarbons, which resulted in the production of stable radical-anions, two or more electrons were removed on oxidation. However, more recent work (112,113) has shown that after the removal of one electron from the parent hydrocarbon, rapid, irreversible chemical reactions of unknown character produce

a product that can oxidize without a change in potential. At rapid cyclic voltammetric scan rates, the reverse sweep was completed before these chemical reactions occurred and the electrochemical reaction appeared to be a reversible one-electron oxidation producing a radical-cation which was stable during the time necessary for sweep reversal.

Bard et al. (114) studied the oxidation of aromatic compounds in methylene chloride by cyclic voltammetry. The radical-cations appeared to be much more stable with respect to the coupled chemical reaction in methylene chloride than in acetonitrile. In the latter solvent, the radical-cation of 9,10-diphenylanthracene rapidly disappeared as it was stirred away from the electrode surface. In methylene chloride, however, this hydrocarbon could be quantitatively oxidized to produce relatively large quantities of radical cations which were stable for days in sealed tubes at liquid nitrogen temperatures. Bard's results also indicated that the stability of the radical-cations increased with substitution in positions of high electron density. Thus, although cations of 9,10-diphenylanthracene and 1,3,6,8-tetraphenylpyrene are stable, those of anthracene and tetracene are rapidly removed by coupled chemical reactions.

Lewis and Singer (115) have studied the chemical oxidation of aromatic hydrocarbons by antimony pentachloride in methylene chloride. Because of the high electron affinity

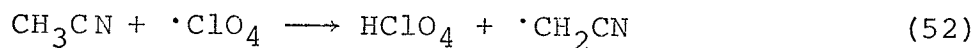
of the metal compound and the polarity of the solvent, a variety of previously unreported aromatic radical-cations were formed and the ESR spectra of these species were observed. Radical-cations of 9,10-dimethylantracene, perylene and naphthacene were satisfactorily formed in air and at room temperature whereas for other parent hydrocarbons it was necessary to exclude air. Well-resolved ESR spectra were observed for the more stable radical-cations but very broad lines were observed for less stable systems possibly due to electron exchange between the radical cations and diamagnetic dipositive ions. Thus, tetraphenylethylene formed a purple radical-cation which exhibited a well-resolved ESR spectrum. However, the green trans-stilbene radical-cation spectrum at 25°C. was very broad and weak. The oxidation reaction proposed in this work was:



The Electrochemical Oxidation of ClO_4^- and BF_4^-

The first detection of transient species electrolytically generated by the oxidation of the perchlorate anion was reported by Maki and Geske in 1959 (116). Current was passed through acetonitrile solutions of sodium or lithium perchlorate in a divided cell with a platinum wire electrode. An ESR spectrum consisting of four equally spaced lines of

equal intensity was interpreted as arising from a perchlorate radical, $\text{ClO}_4\cdot$, formed on the oxidation of the perchlorate anion. The following reaction scheme was suggested:



No spectrum for the $\cdot\text{CH}_2\text{CN}$ radical was detected and therefore the subsequent reactions of this species were assumed to be very rapid.

Billon (117,118) studied the electrochemical oxidation of sodium, lithium and tetrabutylammonium perchlorates on a platinum electrode and in acetonitrile. Again the ESR spectrum of the perchlorate radical but not the $\cdot\text{CH}_2\text{CN}$ radical was found. The half-life of the perchlorate radical was estimated to be 2 seconds. The oxidation of the perchlorate anion took place at +2.4V. relative to a $\text{Ag}/\text{AgNO}_3 10^{-2}\text{M}$ (acetonitrile) reference electrode. Using a divided cell, Billon demonstrated that the anodic oxidation produced an acid in 98% yield.

Billon also studied the oxidation of tetrabutylammonium tetrafluoroborate in acetonitrile. The discharge of the tetrafluoroborate anion also occurred at +2.4 to +2.5 V. relative to the $\text{Ag}/\text{Ag}^+ 10^{-2}\text{M}$. reference electrode, however,

no ESR signal for the BF_4 radical was detected, possibly because of a very short half-life for this radical.

PURIFICATIONS AND EXPERIMENTAL TECHNIQUES

Monomers

The purifications of isobutyl vinyl ether and styrene were identical. The monomer was washed several times with an approximately equal volume of 10% aqueous potassium hydroxide. This was followed by preliminary drying with calcium chloride and then thorough drying by stirring with calcium hydride. The monomer was then fractionally distilled under slightly reduced pressure onto fresh calcium hydride. The first and last 20% of the distillate were discarded. The remaining liquid was passed through a column of activated alumina to free it of traces of inhibitor and then degassed and stored over calcium hydride on a vacuum line with continuous stirring effected by a teflon coated magnetic stirring bar. Immediately before use, the monomer was cold distilled by liquid nitrogen under high vacuum into a calibrated tube from which a measured volume was cold distilled into the reaction vessel.

N-vinylcarbazole (Matheson, Coleman and Bell) was dissolved in hot, freshly distilled hexane and filtered. The solution was cooled until crystals of the monomer formed. The precipitate was filtered and this procedure was repeated twice. The monomer was then dried at 40°C. in a

vacuum desiccator and then pumped in the reaction vessel on a high vacuum line immediately before use.

Solvents

Methylene chloride (Fisher Certified) was washed with concentrated sulfuric acid five or six times or until the acid layer remained colourless. This was followed by six or seven washings with distilled water and then rough drying over calcium chloride. The liquid was then stirred over calcium hydride for several days and then fractionally distilled, discarding the initial and final 20% by volume distilled. The resulting liquid was passed through a column of activated alumina onto fresh calcium hydride and alumina and then degassed and stored on a vacuum line with constant stirring by a teflon-coated magnetic stirring bar. Immediately before use, the methylene chloride was distilled under high vacuum into a measured cylinder from whence a measured quantity was distilled into the reaction vessel.

Salts

Tetrabutylammonium tetrafluoroborate was prepared by adding a filtered aqueous solution of ammonium tetrafluoroborate (Alfa Inorganics) dropwise to a solution of tetrabutylammonium bromide (Eastman) in a large volume of water. The required salt precipitated and was filtered on a Buchner

funnel. It was then dissolved in a small quantity of acetone and filtered dropwise into a fairly large quantity of water to produce a precipitate. The latter step was repeated once and as a result a considerable amount of salt was lost as the tetrabutylammonium tetrafluoroborate is not completely insoluble in water. However, this step served to eliminate the very water soluble tetrabutylammonium bromide and/or ammonium tetrafluoroborate from the required salt. The remaining salt was reprecipitated several times from freshly distilled ethyl acetate. The melting point was $161.0 - 162.0^{\circ}\text{C}$. It was subjected to high vacuum pumping with intermittent slight heating in the reaction cell for 12 to 24 hours before use.

Tetrabutylammonium perchlorate (Southwestern Analytical Chemicals, Polarographic Grade, wet with water) was taken as received and dried with gentle heating in a vacuum desiccator for several days. It was then placed in the reaction vessel and pumped with intermittent heating under high vacuum for from 12 to 24 hours before use.

Tetrabutylammonium hexafluorophosphate was prepared by metathesis by adding an aqueous solution of tetrabutylammonium bromide dropwise through a filter paper into 65% aqueous hexafluorophosphoric acid. The required salt precipitated and was collected in a Buchner funnel. The salt was then recrystallized three times from freshly distilled

ethyl acetate.

Tetrabutylammonium iodide (Matheson, Coleman and Bell) was taken as received and pumped under high vacuum in the reaction vessel for at least 12 hours before use.

Reaction Vessels

The cell shown in Figure 1 was used for pulsed experiments with isobutyl vinyl ether as monomer. The typical amount of solution added to the cell was approximately 95 ml. with 74 ml. in the anode compartment and about 21 ml. in the cathode compartment. The anode consisted of a 1 inch square sheet of platinum while the cathode was a circular sheet of platinum, 1 cm. in diameter. The electrodes were 7.5 cm. apart and were suspended by platinum wires attached by silver solder to tungsten wires which were vacuum sealed in the glass. The silver solder was situated in the wells above the electrodes and thus were never in contact with the liquid. A well protruding into the liquid was sealed into the top of the anode compartment and was filled with mercury before the reaction. A 10,000 ohm thermistor (Veco) placed in the well quickly detected minute temperature changes in the anolyte. The thermistor bridge circuit is also shown in Figure 1.

The cell shown in Figure 2 was used for constant current experiments with styrene as monomer. The amount of

FIGURE 1. A: Polymerization cell for pulsed experiments.
stopcock 1: for addition of nitrogen
stopcock 2: for attachment of reaction
vessel to vacuum line
stopcock 3: capillary stopcock for sampling

a: the cathode - a 1 cm diameter circular
sheet of platinum
b: the anode - a 1 inch square sheet of
platinum
c: teflon - coated magnetic stirring bar
d: filling tube
e: thermistor well

B: Thermistor bridge circuit

a: 10,000 ohm thermistor
b,c,d: precision 10,000 ohm resistors
e: variable resistor
f: voltmeter

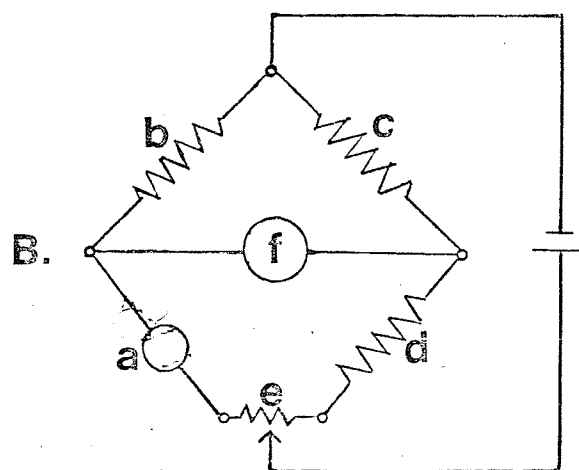
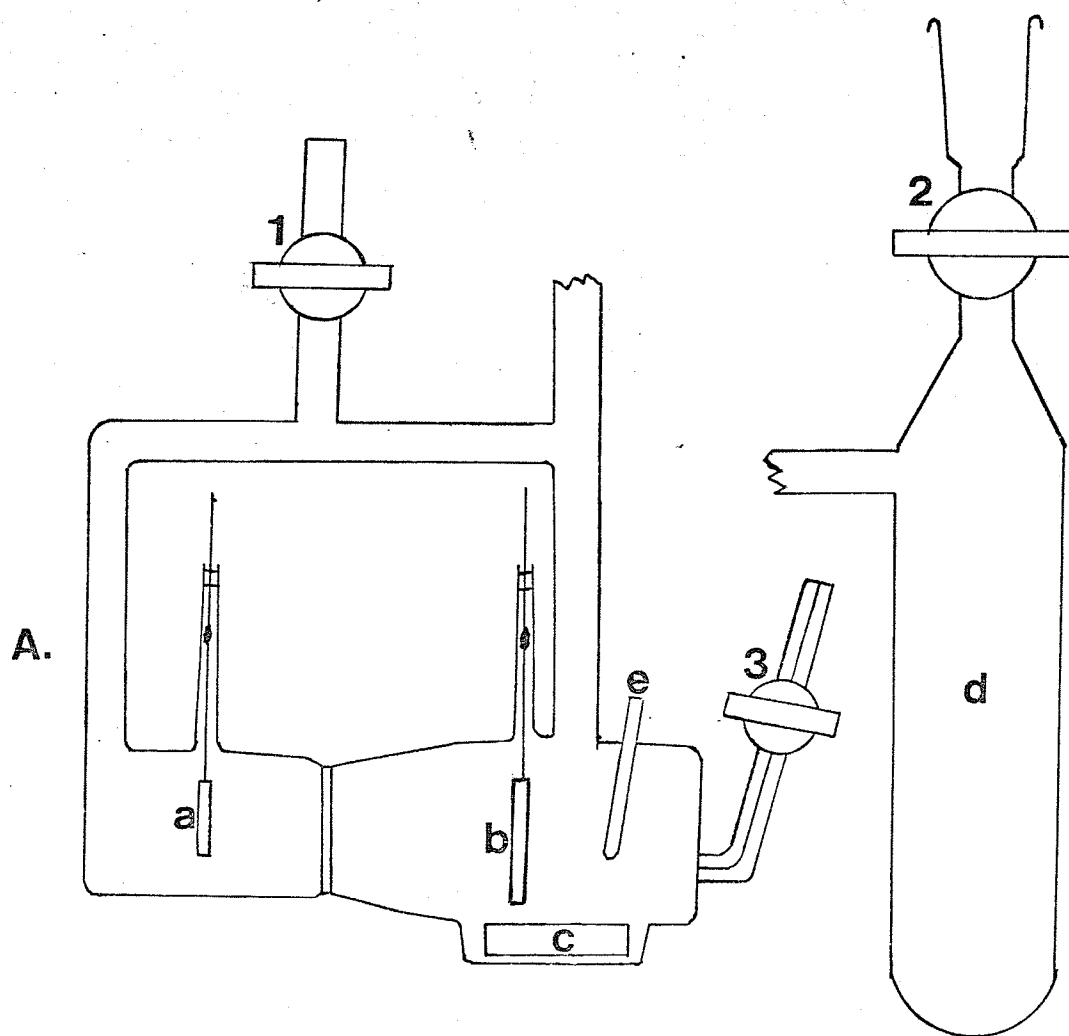
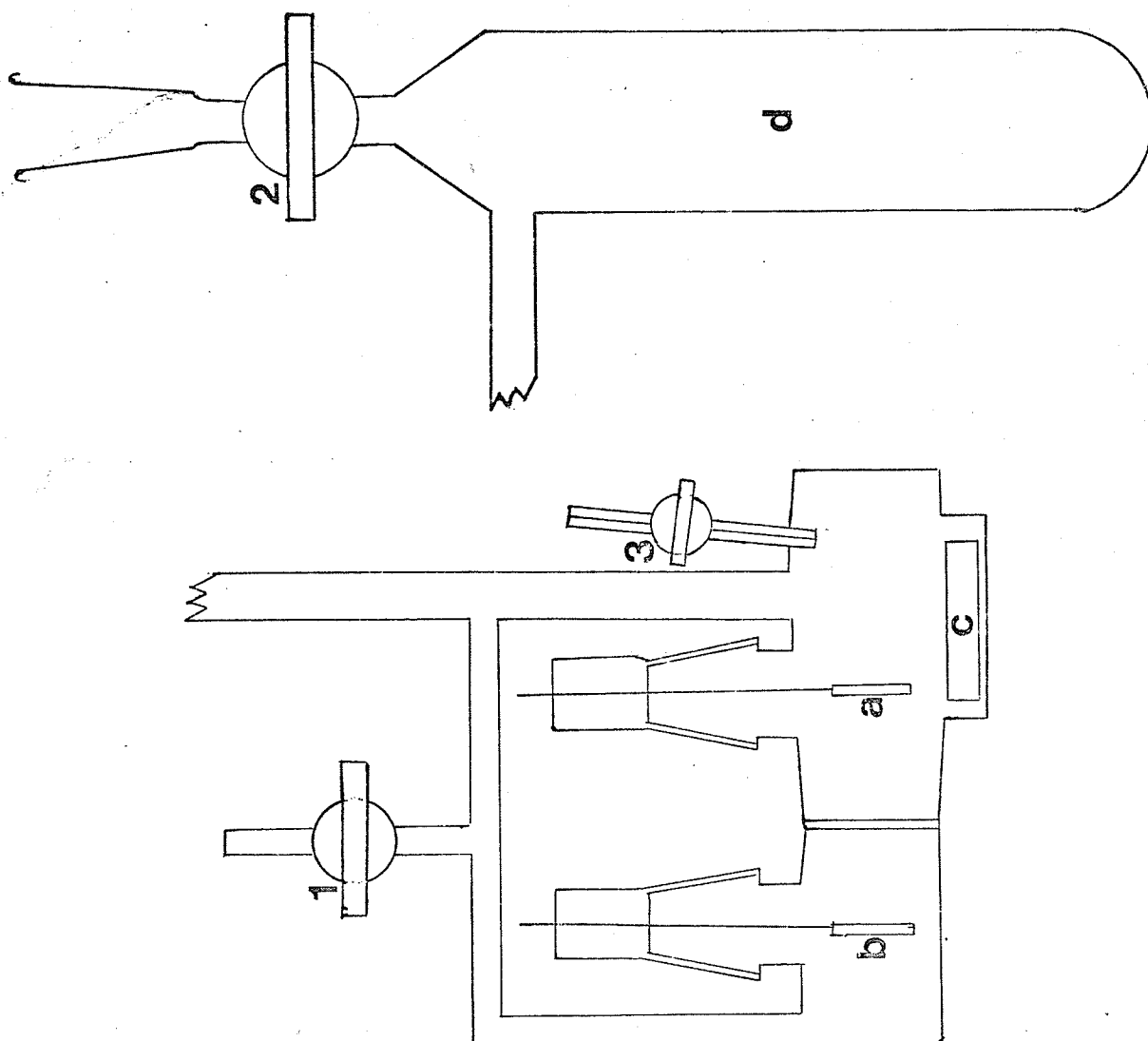


FIGURE 2. Polymerization cell for constant current experiments

- stopcock 1: for addition of nitrogen
- stopcock 2: for attachment of reaction vessel to vacuum line
- stopcock 3: capillary stopcock for sampling

- a: the anode - a 1 cm. diameter circular sheet of platinum
- b: the cathode- a 1 cm. diameter circular sheet of platinum
- c: teflon - coated magnetic stirring bar
- d: filling tube
- e: 24/25 ground glass joints



solution added to the cell in a typical experiment was approximately 198 ml. with 157 ml. in the anode compartment and 41 ml. in the cathode compartment. Both the anode and cathode consisted of circular sheets of platinum, 1 cm. in diameter and 6.5 cm. apart. Because large amounts of solid material formed on the anode during continuous current experiments, the electrodes were made removable to facilitate the cleaning of the electrodes and examination of the insoluble products. The electrodes were therefore suspended on inverted B24/29 outer ground glass joints by means of a platinum wire joined by silver solder to tungsten wire sealed to the glass of the ground glass joint. These electrode assemblies could be vacuum sealed with stopcock grease to upward facing B24/29 inner ground glass joints, attached to the top of the two electrode compartments which were separated by a 3 in. diameter sintered glass divider of fine porosity. A 1 mm. vacuum capillary stopcock to be used for sampling the anolyte was also attached to the top of the anode compartment.

Vacuum Grease

The vacuum grease (Dow Corning) was placed in a glass container and dried for several days in a vacuum dessicator at 100°C.

The Vacuum Line

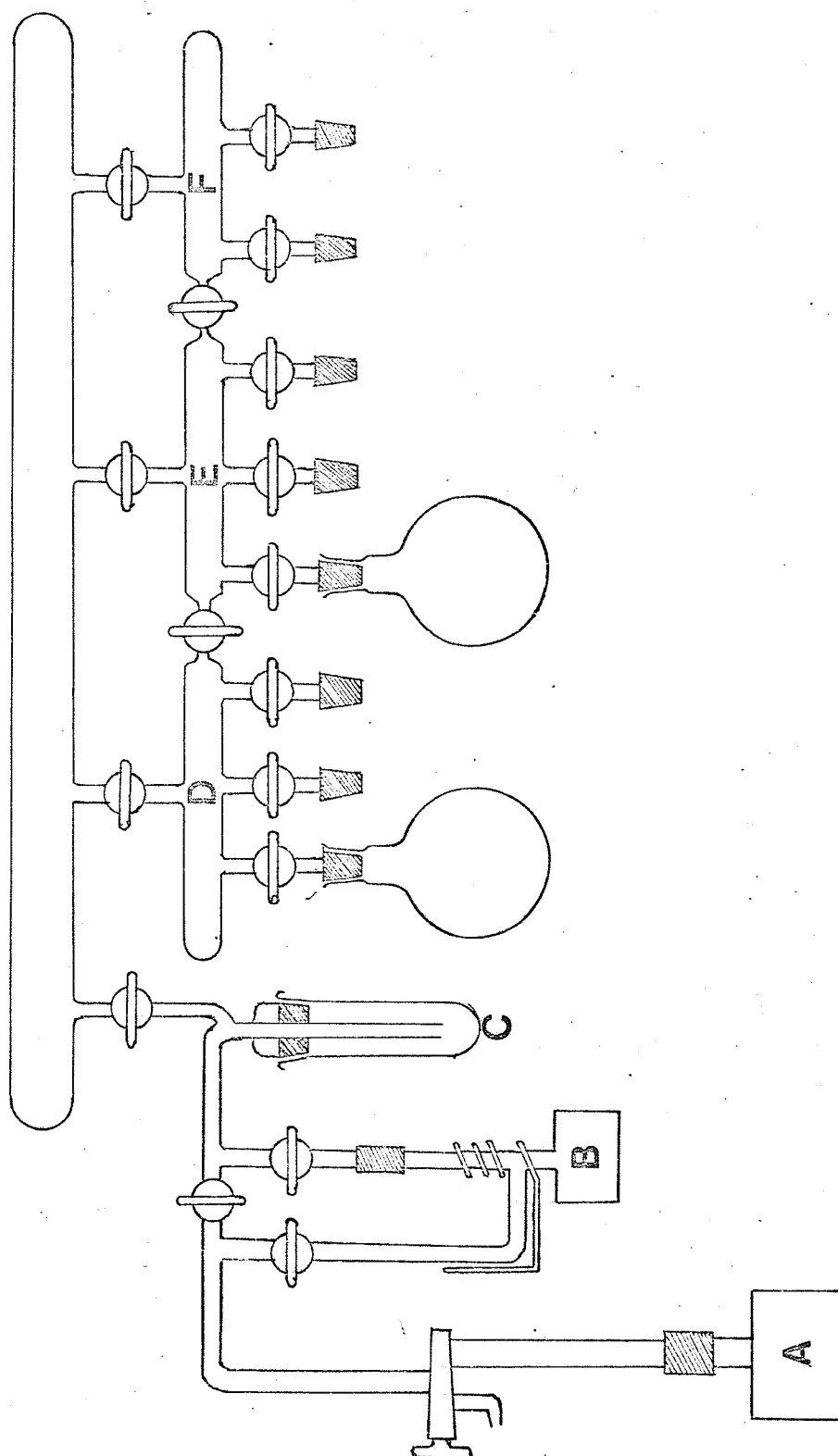
The reaction solutions were prepared on the vacuum line shown in Figure 3. A vacuum of 10^{-4} mm. of mercury was obtained using a mechanical vacuum pump, A, and an oil diffusion pump, B. The latter was filled with DC702 Silicone Fluid. The pumps were protected by the liquid nitrogen trap, C. Parts D, E and F of the vacuum line were used for the purification of monomer, the purification of solvent and the pumping and filling of the reaction vessel, respectively.

Preparation of the Reaction Solution

Flasks of solvent and monomer were attached to sections D and E of the vacuum line. The liquids were degassed and stirred with calcium hydride for several days. Calibrated tubes were attached to sections D and E and the reaction vessel containing the required salt was attached to section F. The whole system was pumped for from 12 to 24 hours with intermittent heating. Monomer and solvent were cold distilled into the calibrated tubes and then into the filling tube of the reaction vessel. The vacuum stopcock above the filling tube was closed and the cell was removed from the vacuum line. The frozen liquid was thawed and mixed by means of a small teflon-coated stirring bar. The cell was tipped to allow the solution to flow into the

FIGURE 3. The high vacuum line.

- A: mechanical vacuum pump
- B: oil diffusion pump
- C: liquid nitrogen trap
- D: section of vacuum line for monomer purification
- E: section of vacuum line for solvent purification
- F: section of vacuum line for the pumping and filling of the reaction vessel



reaction vessel. Nitrogen, passed through tubes of Drierite, activated molecular sieve, and activated silica gel, was added through stopcock 1 in the cells shown in Figures 1 and 2. Nitrogen was then passed for 30 seconds through the reaction vessel with stopcocks 1 and 2 opened. A slight nitrogen pressure was applied to the cell and the stopcocks were closed. On opening the capillary stopcock, 3, the nitrogen pressure in the cell forced a sample of the anolyte solution into the capillary above stopcock. Therefore, a gas chromatographic sample could be removed from the capillary without the syringe needle touching the reaction solution. For each sample taken in this manner, it was necessary to flush all the liquid from the previous sample remaining in the capillary tube and stopcock. For this reason a total of 0.06 ml. from the cell in Figure 1 and 0.50 ml. from the cell in Figure 2 were removed for each sample taken.

Gas Chromatography

Samples removed from the reaction cells during a polymerization were analyzed for residual monomer by injection into a Micro Tek DSS 161 gas chromatograph. For the analysis of styrene reaction solutions, a column of $\frac{1}{4}$ inch copper tubing, 4 feet long and filled with 25% apiezon L on Chromosorb G DMCS was used with a flow rate of 85 ml. of helium per minute, a column temperature of 88°C. and injec-

tion and detector (thermal conductivity) temperatures of 92°C. For isobutyl vinyl ether polymerizations, a column of ¼ inch copper tubing, 10 feet long and filled with 15% carbowax on Chromosorb G DMCS was used with a flow rate of 60 ml. of helium per minute, a column temperature of 78°C. and injection and detector temperatures of 82°C. The area of the peaks for solvent and monomer were used as a measure of the amounts injected. The areas were measured by cutting out the peaks and weighing them. The solvent peak was used as an internal standard and calibration curves were made up by plotting concentration in moles per liter against the chromatographic Response, R, defined as:

$$R = \frac{\text{peak weight of monomer}}{\text{peak weight of solvent}}$$

A reproducibility of about ±1.0% was obtained.

Molecular Weights

The polymers were isolated by pouring the reaction mixture into a large volume of cold methanol. The precipitated polymer was redissolved in methyl ethyl ketone, reprecipitated two times from cold methanol and then dried in a vacuum dessicator at 70°C. for several days. The viscosity of solutions of the polymers in benzene were measured using an Ubbelohde viscometer. Reduced viscosities for polymer concentrations 0.25% to 1% by weight were measured

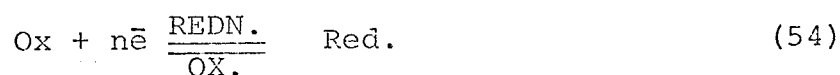
and the limiting viscosity number, (η) , was calculated by extrapolating these results to infinite dilution. The number average molecular weight, M , for styrene polymers were calculated using the expression (34):

$$(\eta) = KM^a$$

where $K = 4.37 \times 10^{-4}$ and $a = 0.66$ at $25 \pm 0.01^\circ\text{C}$.

Cyclic Voltammetry

Cyclic voltammetry is an electroanalytical technique in which a finite current flows resulting in electrolysis, as opposed to potentiometry where no significant current flows. As in other forms of electrochemistry, there can be considered to be an oxidation-reduction couple in solution between the oxidized and the reduced forms of a component of the solution:



The Nernst Equation gives a relation between the electrode potential and the solution composition:

$$E = E^\circ + \frac{RT}{nF} \ln \frac{a_{\text{ox.}}}{a_{\text{red.}}} \quad (55)$$

where n is the number of electrons transferred, E is the indicating electrode potential, E° is the standard electrode potential at unit activity of the components of the couple,

and the activity of a component is $a = C'f$, where C is the concentration and f is the activity coefficient. Potential sweep chronoamperometry is a controlled potential technique in which the electrolysis of the anolyte occurs at a stationary electrode in an unstirred solution. Cyclic voltammetry is potential sweep chronoamperometry in which the potential is swept back and forth across the region of interest. This technique has the advantages of fast scan, high sensitivity and better resolution than polarography. Because of the use of inert metal electrodes (silver, gold), it has a wide range for oxidation and reduction. However, the electrolysis can cause surface contamination. Because the electrolysis occurs at a stationary electrode in an unstirred solution, the only means of mass transport for uncharged species is diffusion.

At the start of the potential sweep in cyclic voltammetry there is no passage of current until the oxidation or reduction potential of a substance in solution is reached. The current then rises and the first 10% of the current rise is controlled by the kinetics of the electron transfer. As the current rises above the 10% limit, the solution around the electrode is depleted of the electrolyzed substance and the current becomes more and more controlled by diffusion until finally a peak is obtained. If the sweep is reversed and the system is reversible, oxidation of the reduced

species takes place and a reverse peak is obtained at a more positive potential than the forward peak but with a peak height equal to that of the forward peak. The peak height is directly proportional to the concentration of the electroactive species.

Figure 4 shows the cell used for cyclic voltammetry. The working electrode consisted of a 1/16 inch diameter platinum wire sealed in glass while the reference electrode was a simple silver wire sheathed in a glass capillary. This reference electrode avoided the risk of contamination from conventional reference electrodes. The counter electrode was a platinum disk.

Before an experiment, the electrodes were washed with dilute nitric acid, water, acetone and finally high purity ether. After the whole cell was baked overnight in an oven at 70°C., the salt was added and the cell and salt were pumped under high vacuum for 12 hours. 30 ml. of solvent were cold distilled into the cell. The solution was thawed, mixed and finally thermostated at 25°C. with an electric heating tape wrapped around the part of the cell not immersed in water to prevent condensation. The electrodes were connected to the circuit shown in Figure 5 and the potential of the working electrode was scanned over a suitable voltage range. The potential of the working electrode was controlled relative to the reference electrode by means of

FIGURE 4. Cell used for voltammetry.

- a: silver wire - reference electrode
- b: platinum wire sealed in glass-
working electrode
- c: platinum disk - counter electrode
- d: 34/35 ground glass joint
- e: to vacuum line.

- R: connection to reference electrode
- W: connection to working electrode
- C: connection to counter electrode

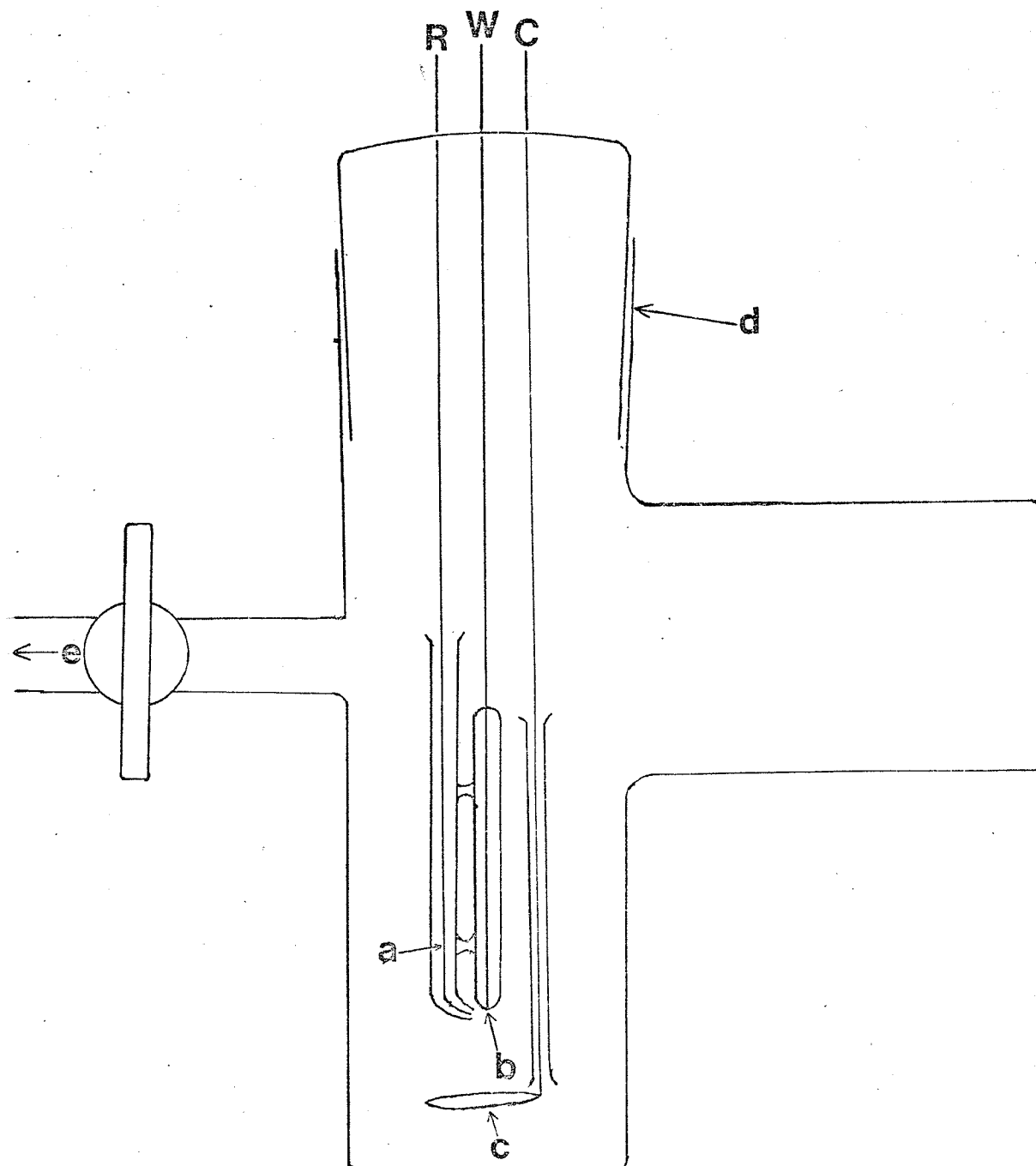
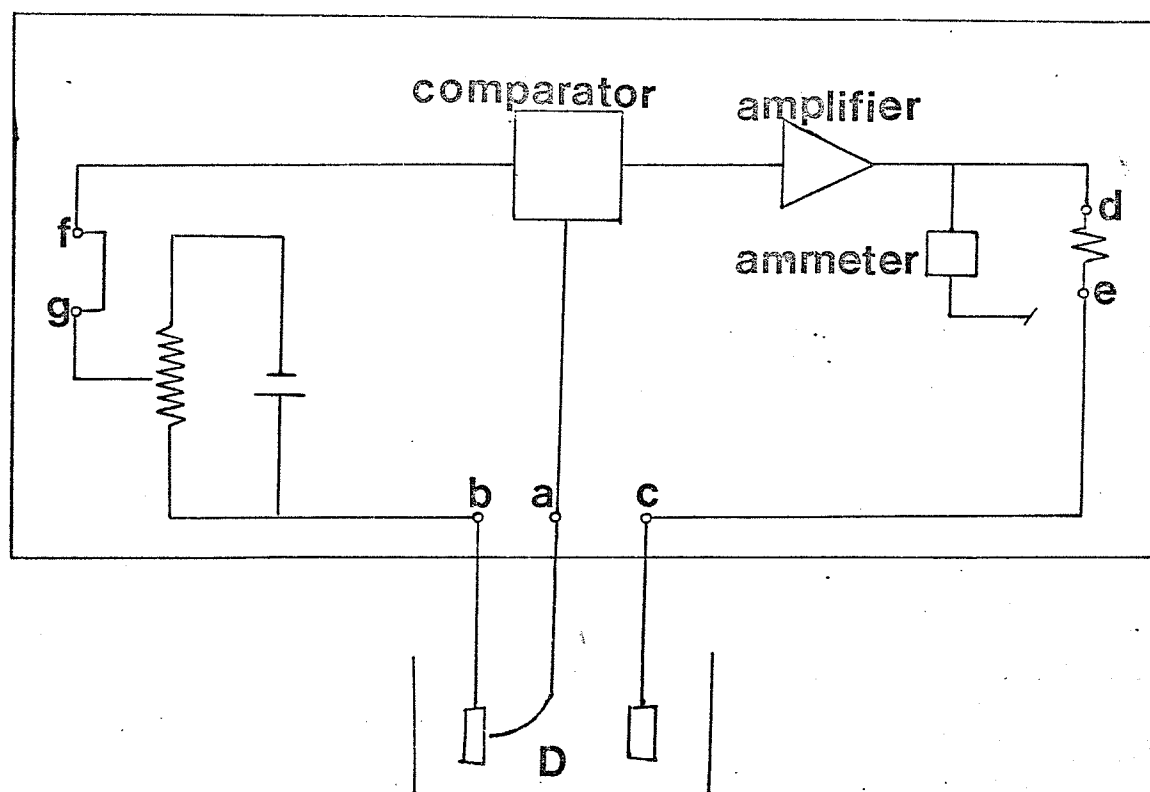
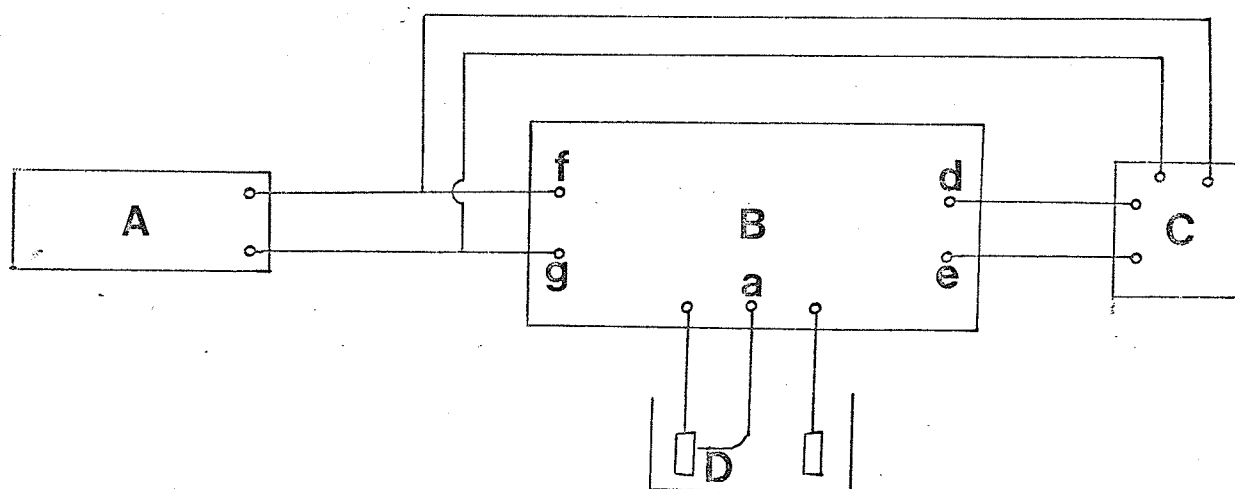


FIGURE 5. Circuit for cyclic voltammetry.

A: triangular wave generator
B: Wenking potentiostat
C: X-Y recorder
D: electrolysis cell

a: reference electrode
b: working electrode
c: counter electrode
de: external current recorder, across Re
fg: external voltage source



a Wenking 61 RH electronic potentiostat. A Hewlett Packard 3300A function generator with a 3304A sweep/offset plug-in unit was used as an external voltage source to produce a triangular wave pattern as required by cyclic voltammetry. A Moseley Autograf 7030A X-Y recorder was used to record the current-potential curves (voltammograms). The potential of the working electrode relative to the reference electrode was applied to the X-axis while a voltage proportional to the current flowing was applied to the Y-axis.

EXPERIMENTAL RESULTS

Initial Experiments - Undivided Cells

In undivided cell experiments, constant currents of from 0.5 to 2.0 ma. were passed through stirred solutions of isobutyl vinyl ether and tetrabutylammonium tetrafluoroborate in nitrobenzene and ethylidene chloride. At 1.0 ma. and using solutions of approximately 1.5 molar monomer concentration, roughly 4 gms. of polymer was produced per hour.

Rate studies were attempted in ethylidene chloride; however, no correlation between the magnitude of the impressed current and the observed rate was found. The effect of a current increase was unpredictable; the rate of polymerization in some cases increased, remained constant or even decreased. Invariably the reaction did not cease when the current passage was terminated but gradually slowed down and stopped after fifteen to thirty minutes. Induction periods of variable lengths were also observed. Solid insoluble material formed on the anode during the passage of current and after about 60 minutes of current, a gas, presumably formed by the anodic reaction, became trapped under this thickening insoluble coating.

It was assumed that the above anomalous results could be attributed to terminating agents produced at the cathode.

The cathodic products formed at a clean electrode so that they could be quickly mixed into the bulk of the solution by the stirring. Therefore, an increase of current would have immediately increased their rate of appearance in the bulk of the solution. On the other hand, the initiating species were produced under a layer of insoluble material on the anode, and this coating could have delayed their infusion into the bulk of the solution. The after-effect, i.e. the polymerization occurring after the current was stopped, could have been due in part to the gradual diffusion of the initiator through the electrode coating.

To avoid the difficulties described above, all further experiments were carried out in cells divided into anode and cathode compartments to effect the separation of the anodically produced initiator and the termination agents formed at the cathode.

Pulsed Experiments

Reactions initiated by the application of current pulses were carried out in the divided cell shown in Figure 1. A constant potential of 15 volts was applied across the cell during the current passage which lasted for only a small fraction of the total reaction time. Methylene chloride and isobutyl vinyl ether were used as solvent and monomer in all these experiments. Invariably a temperature of

25°C $\pm$ 0.1 degrees centigrade was employed.

Reactions in the divided cell contrasted sharply with those in undivided cells. Polymer formed only in the anode compartment and termination reactions were much less important. A continuous current increased the rate exponentially when isobutyl vinyl ether was used as the monomer resulting in virtual 100% polymerization in a few minutes. For these reasons the reactions were initiated by a relatively short pulse of current and the ensuing reaction was followed by sampling at suitable intervals. As an induction period was present in many of these reactions, a thermistor was used to detect the beginning of the chain reaction. The heat of the polymerization produced a sharp deflection of the recorder in the thermistor bridge circuit. The heating produced by the current passage was negligible.

Slight polymerization took place before current passage with all the salts used in pulsed experiments. This was demonstrated by the slight cloudiness due to precipitated polymer when a small amount of the reaction solution was added to a large volume of methyl alcohol. However, when these reaction mixtures were allowed to remain without current being passed for up to eighteen hours, no change in monomer concentration was detectable by gas chromatography. When current was finally passed through these blank mixtures, polymerization proceeded normally.

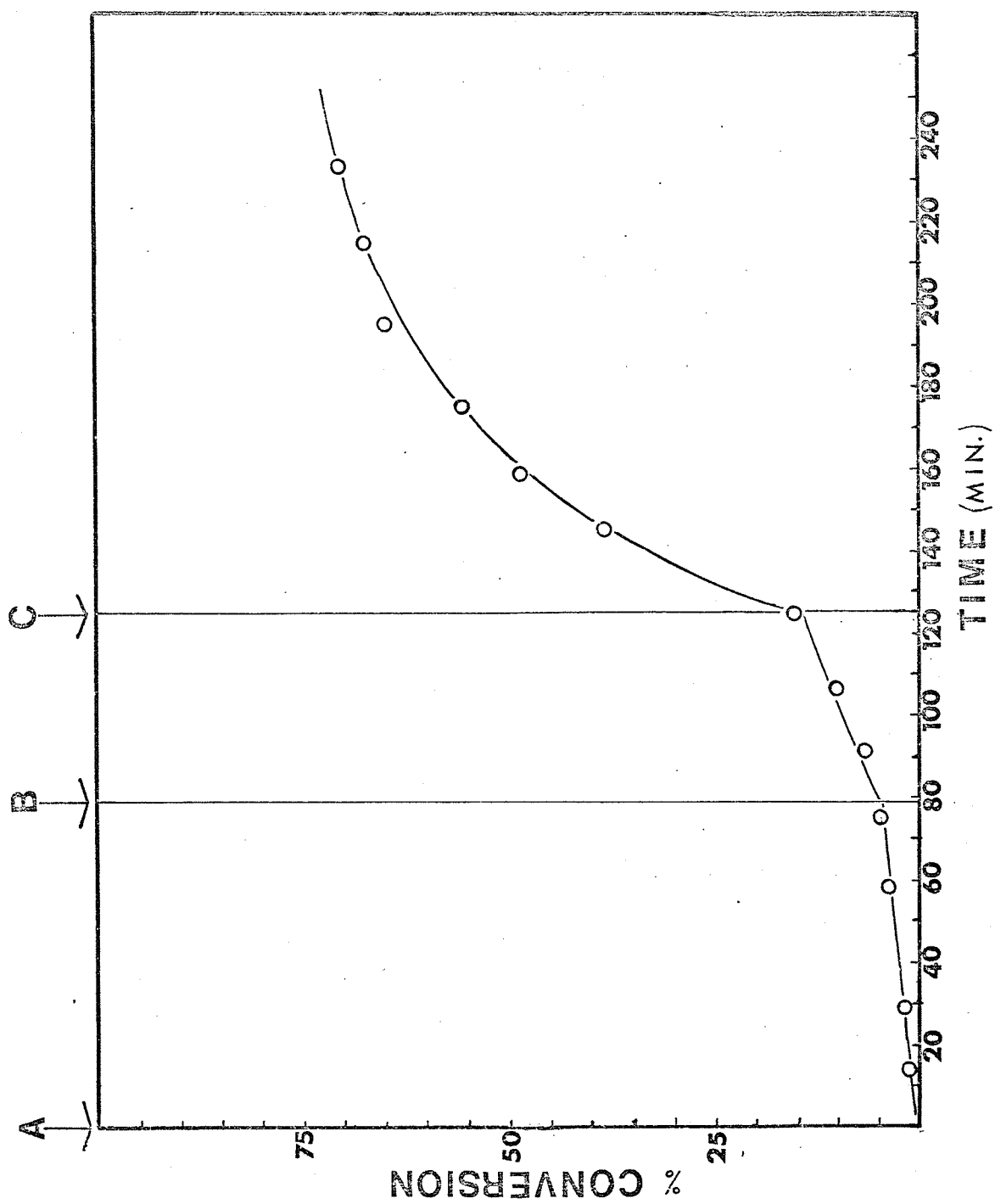
The polymerization of a solution of 0.5 molar isobutyl vinyl ether and 15.2 millimolar tetrabutylammonium tetrafluoroborate in dimethylformamide was attempted in a divided cell. No polymerization took place in this basic solvent. Methylene chloride was used as solvent in all experiments described below.

(i) Tetrabutylammonium Tetrafluoroborate

Reactions were initiated by the passage of a current through a solution of about 15 milliequivalents of tetrabutylammonium tetrafluoroborate per liter of solution. Poly (isobutyl vinyl ether) of an intrinsic viscosity of 0.087 deciliters per gram in benzene at $25.0 \pm 0.01^\circ\text{C}$. was formed. Figure 6 shows the course of a reaction begun by an initial current pulse at A. The rate of monomer conversion with time was approximately linear. A further pulse at B produced a faster and again approximately linear rate. At point C a further forward pulse of current was applied, initially resulting in a much faster rate of polymerization. However, the rate after point C decreased much more rapidly than could be explained by the depletion of monomer and contrasted sharply with the linear rates of monomer conversion between A and B or B and C.

The rapid slowing of the rate of reaction at later reaction times was a general feature of polymerizations of

FIGURE 6. Reaction trace for the polymerization of
0.421 moles/liter isobutyl vinyl ether in
methylene chloride.
Electrolyte: 15.2 milliequivalents/liter
tetrabutylammonium tetrafluoroborate
Amounts of current passed:
A: 5.14 microFaradays/liter, forward
B: 0.914 microFaradays/liter, forward
C: 1.36 microFaradays/liter, forward



isobutyl vinyl ether with tetrabutylammonium tetrafluoroborate. This effect was attributed to flow through the sintered glass divider caused by sampling. For reasons explained in the Experimental section, relatively large volumes of 0.06 mls. were necessarily removed with each sample from a total volume of 70 ml. of anolyte. This resulted in a slight lowering of the liquid level in the anode compartment which in turn probably caused catholyte liquid to flow through the sintered glass divider and mix with the anolyte. Since the catholyte was unstirred, the terminating substances produced at the cathode could only reach the divider by diffusion and by the slight flow of the solution toward the divider caused by sampling. This explains why the rate was affected only after a number of samples were removed.

Figure 7 shows a polymerization started by a forward pulse at A, stopped by a reverse pulse at B and restarted by a second forward pulse at C. Again the rate of monomer conversion with time after A was approximately linear while that after C was slowed, probably by the sampling effect explained above. After the reverse pulse at B the reaction slowed gradually and did not stop instantaneously while the forward pulse at C appeared to affect the rate immediately.

The reaction shown in Figure 8 was started by a forward pulse at A and again an approximately linear rate of

FIGURE 7. Reaction trace for the polymerization of
0.417 moles/liter isobutyl vinyl ether in
methylene chloride.
Electrolyte: 15.2 milliequivalents/liter
tetrabutylammonium tetrafluoroborate
Amounts of current passed:
A: 5.83 microFaradays/liter, forward
B: 1.45 microFaradays/liter, reverse
C: 1.83 microFaradays/liter, forward.

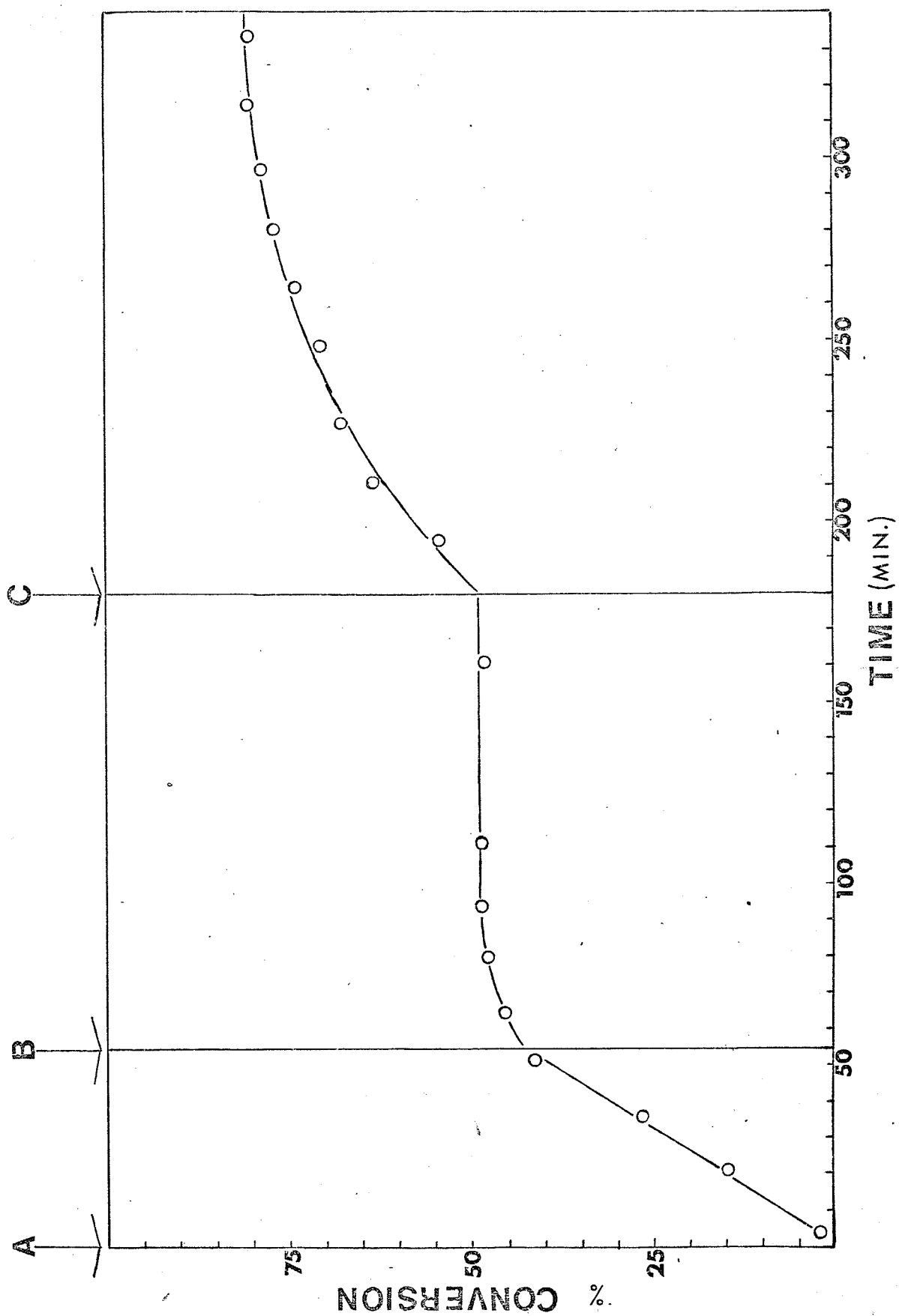
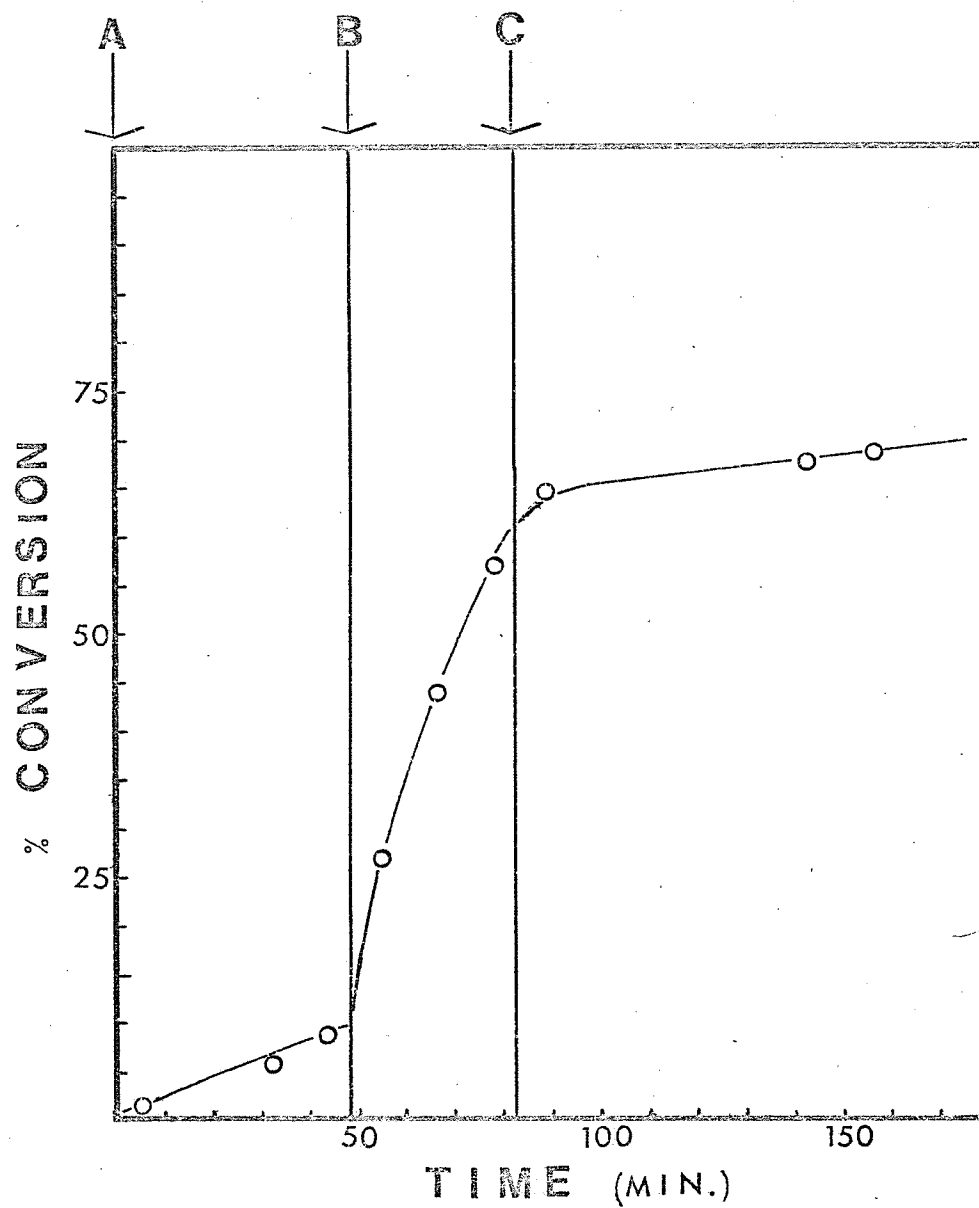


FIGURE 8. Reaction trace for the polymerization of
0.585 moles/liter isobutyl vinyl ether in
methylene chloride.
Electrolyte: 15.2 milliequivalents/liter
tetrabutylammonium tetrafluoroborate
Amounts of current passed:
A: 7.41 microFaradays/liter, forward
B: 1.50 microFaradays/liter, forward
C: 1.51 microFaradays/liter, reverse.

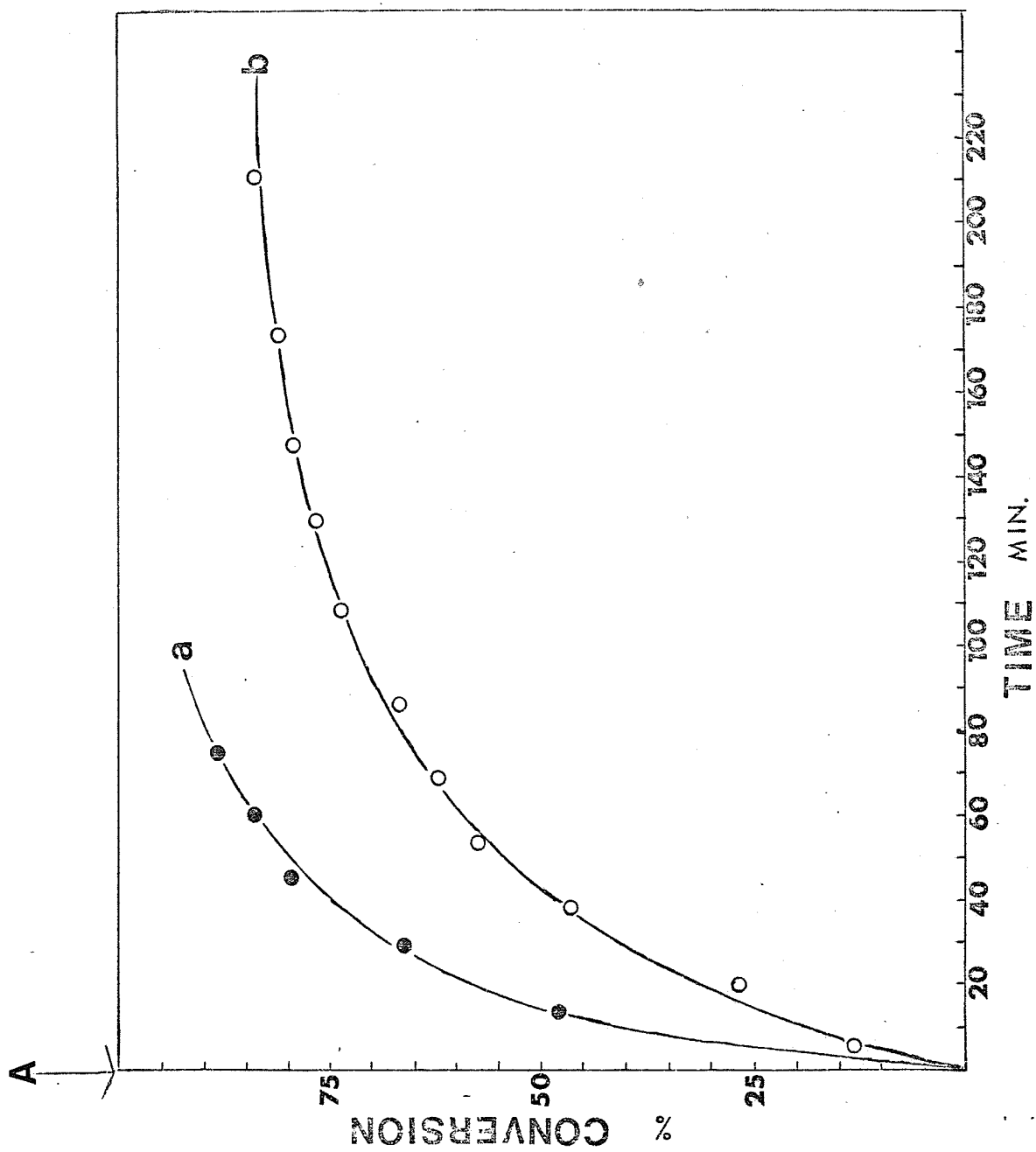


monomer consumption with time ensued. A further forward pulse at B increased the rate greatly and the full effect of this forward current on the rate was virtually instantaneous. A reverse pulse at C slowed the rate to a relatively small value, but again the effect of the reverse pulse on the rate was not instantaneous.

In all the polymerizations of isobutyl vinyl ether using this salt, the initial pulse of current at A was much larger than subsequent pulses whose effect on the rate was proportionally much greater. Most of the initial pulse was apparently used to remove terminating agents present in the solution. The initial current passed which removed impurities from the solution and did not cause significant polymerization will be termed the induction current. After polymerization commenced (as indicated by a signal from the thermistor bridge described in the experimental section), a further 1.0 to 1.5 microFaradays per mole were allowed to pass through the solution in order to generate reasonable reaction rates. An attempt was made to correlate the initially observed rate with the amount of current passed after the thermistor bridge recorder deflection. However, no reliable correlation could be found. As a result, the actual initiator concentration due to the first current pulse could not be accurately determined.

Figure 9 shows the course of two reactions started by

FIGURE 9. Reaction traces for the polymerization of 0.328 moles/liter isobutyl vinyl ether in methylene chloride.
Electrolyte: 15.2 milliequivalents/liter tetrabutylammonium tetrafluoroborate.
Amounts of current passed at A:
Curve a: 8.34 microFaradays/liter, forward
Curve b: 7.27 microFaradays/liter, forward.

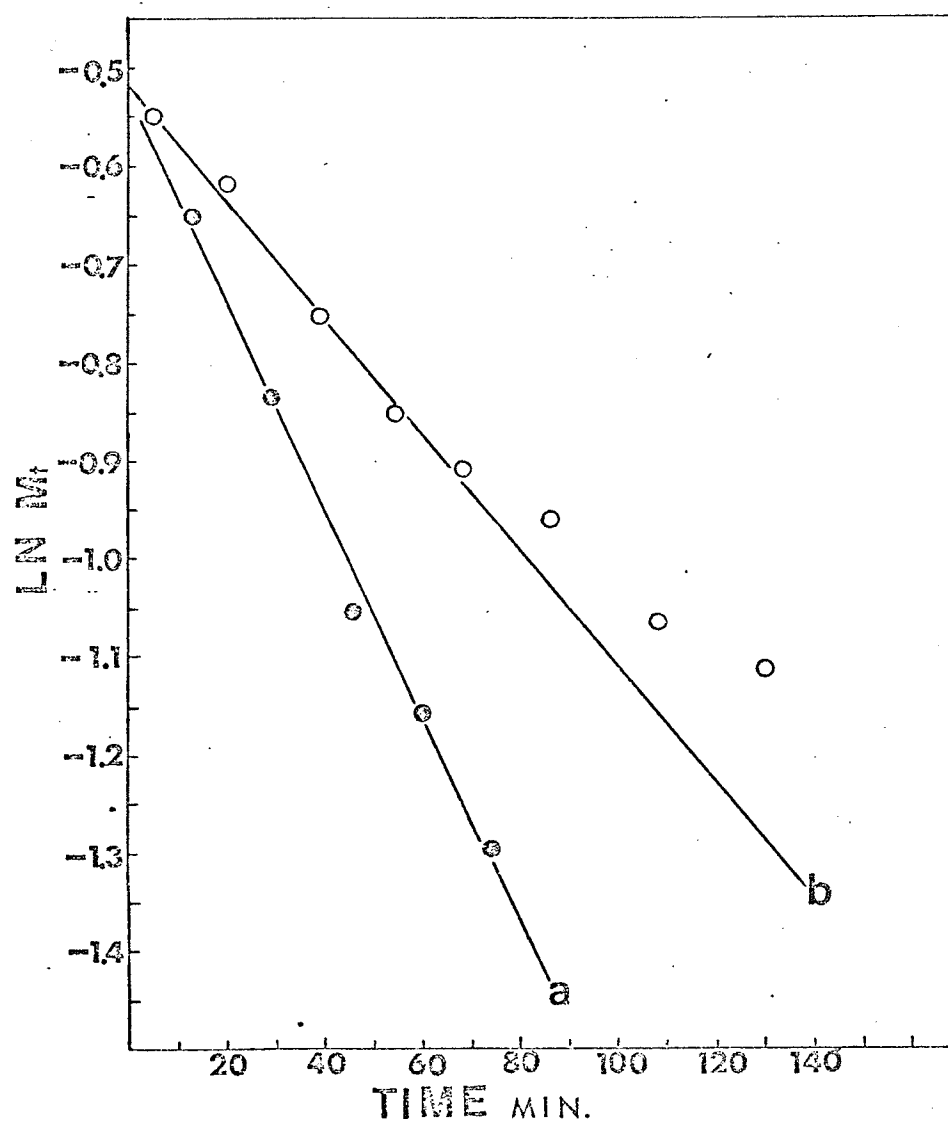


initial current pulses at A and followed for a considerable portion of the conversion of monomer to polymer. The plots of the logarithms of the monomer concentrations against the corresponding times are shown in Figure 10. Straight lines were obtained for the first five samples taken in both these reactions. Later samples taken in reaction b exhibited a deviation from a first order plot, probably due to the flow of cathodically-produced terminator from the cathode compartment. However, a first order dependence on monomer concentration is evident up to 88% conversion in reaction a and 62% conversion in reaction b.

In all the above polymerizations in divided cells using tetrabutylammonium tetrafluoroborate as the electrolyte, an insoluble anodic film was produced on passage of current, as in the undivided cell experiments. However, the amount of this substance formed was much smaller than in undivided cell experiments where the current was applied continuously. This material was found to be insoluble in boiling methyl ethyl ketone, benzene or methyl alcohol.

On the passage of current through the isobutyl vinyl ether solutions, a green electrolysis product formed on the anode when polymerization began. This green product did not form when only salt and solvent were electrolyzed. In one experiment, a cell with removable electrodes was used and the solution was not stirred during the current passage.

FIGURE 10. Logarithmic dependence of monomer concentration on time for the reactions shown in Figure 9.



Under these conditions, the green product formed under the insoluble film formed on the anode and persisted for up to 20 seconds after the current passage was terminated. However, the colour disappeared immediately when the electrode was exposed to the atmosphere.

Electrolysis of tetrafluoroborate salt and solvent.

0.25 grams of tetrabutylammonium tetrafluoroborate in 60 ml. of solvent were electrolyzed in the anode compartment of a divided cell with a total of 5 milliFaradays per liter of anolyte passed. A current of 0.45 ma. was used. 6 ml. of the anolyte were syringed into a solution of isobutyl vinyl ether in methylene chloride making a total volume of 210 ml. and a monomer concentration of 0.445 moles per liter. Complete polymerization was effected in about 3 minutes with an attendant evolution of much heat. Assuming a one to one relationship between the number of electrons passed and the number of initiating species present in the solution, the maximum concentration of initiator in the polymerizing solution would have been 0.14 millimoles per liter. However, no indication of the efficiency of the anodic production of initiator was obtained.

The electrolysis of tetrabutylammonium tetrafluoroborate in methylene chloride, similar to the electrolysis described above, was conducted with the passage of 3.7

milliFaradays per liter of anolyte. Addition of up to 10 ml. of the anolyte to 174 ml. of a 0.40 molar solution of isobutyl vinyl ether in toluene, resulting in a solution with a maximum initiator concentration of 0.20 microFaradays per liter, resulted in no polymer formation over a 24 hour period.

(ii) Tetrabutylammonium Perchlorate

The electropolymerization of isobutyl vinyl ether in methylene chloride with tetrabutylammonium perchlorate as the electrolyte exhibited a markedly different character than the polymerizations using the tetrafluoroborate salt. Polymerization began almost immediately when the current pulse was applied, suggesting that at most only a small portion of the current was used in an induction period. This was supported by a large amount of heating shown by a marked change of resistance of the thermistor from five to seven seconds after the beginning of the current passage. Thus, initiation appeared to be effectively instantaneous on passage of current. Polymer of an intrinsic viscosity of 0.030 deciliters per gram in benzene at 25°C. was formed in this reaction.

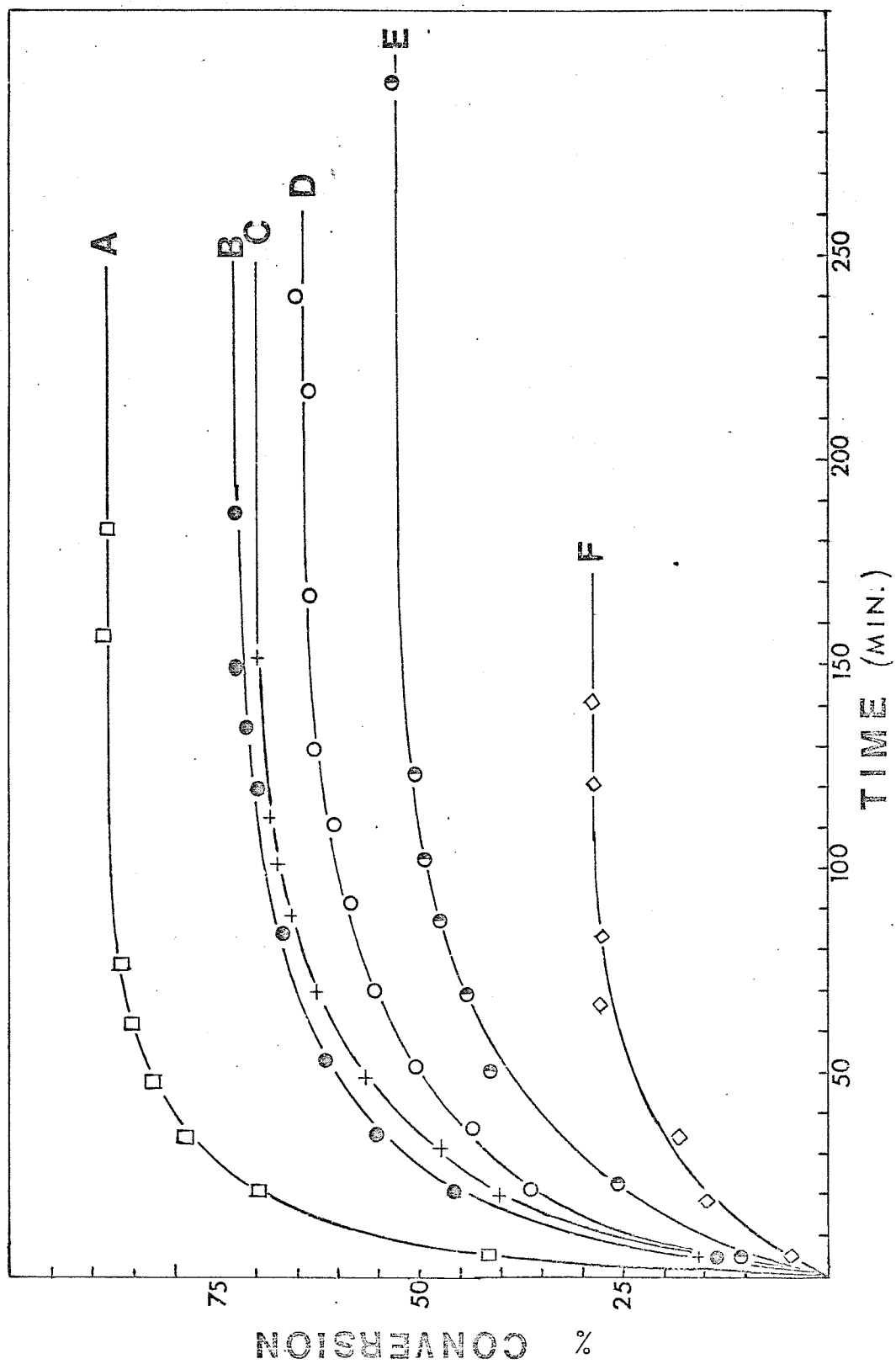
The reaction curves obtained for this system are shown in Figure 11. Since the initially very rapid polymerization slowed rapidly and stopped before 100% conversion of

FIGURE 11. Reaction traces for the polymerization of isobutyl vinyl ether in methylene chloride at 25°C.

Electrolyte: 15.2 milliequivalents/liter tetrabutylammonium perchlorate

Amounts of current passed at A and the initial monomer concentrations:

A:	3.41 microFaradays/liter;	$(M)_0 = 0.332$	moles/ liter.
B:	2.12 microFaradays/liter;	$(M)_0 = 0.331$	moles/ liter.
C:	2.01 microFaradays/liter;	$(M)_0 = 0.336$	moles/ liter.
D:	1.92 microFaradays/liter;	$(M)_0 = 0.339$	moles/ liter.
E:	1.37 microFaradays/liter;	$(M)_0 = 0.334$	moles/ liter.
F:	1.45 microFaradays/liter;	$(M)_0 = 0.344$	moles/ liter.

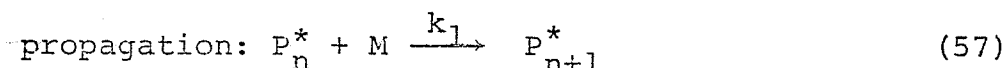
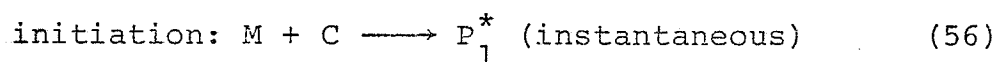


monomer to polymer, a very effective termination reaction was in effect. This termination might be attributable to a property of the reaction itself or to an impurity in the solution.

Curves A to E of Figure 11 exhibit initial rates and final degrees of conversion which increase with the total amount of current passed in the initial pulse. These reactions employed approximately equal amounts of salt giving concentrations of 15.2 milliequivalents per liter. In each case the salt had been pumped under high vacuum for from 12 to 24 hours. Curve F shows a reaction for which salt had been pumped under high vacuum for only 2 hours. It exhibited a much lower initial rate and a much lower final degree of conversion.

The reaction curves obtained for this system bear a strong resemblance to those obtained by Hayes and Pepper for the sulfuric acid polymerization of styrene in ethylene chloride (34). For their system it was postulated that initiation was instantaneous and that the reaction was slowed rapidly and stopped by a termination reaction involving the combination of a carbonium ion growing center with the bisulfate counterion to form a sulfate ester. A kinetic scheme analogous to that used for the sulfuric acid polymerizing system was derived by the author for the data shown in Figure 11. Since the initial pulse was of only 13 to 30 seconds duration

and the stirring was rapid, the reaction was assumed to be primarily homogeneous. It was also assumed to be first order in monomer concentration and first order in the number of equivalents of current passed per liter, which was equal or proportional to the amount of catalyst produced by the current. The following kinetic scheme was proposed:



where M is the monomer and P^* is the active species. Possible chain transfer reactions were neglected in this scheme because their effect on the overall rate would be negligible for high polymer formation. The rate of disappearance of the active species could be expressed as:

$$\frac{dP_t^*}{dt} = k_2 P_t^* \quad (59)$$

$$\text{Then } P_t^* = P_0^* \exp(-k_2 t) = C_0 \exp(-k_2 t) \quad (60)$$

where $C_0 = P_0^*$ = the amount of current passed per liter of anolyte at $t=0$. The rate equation for the disappearance of monomer would then be:

$$-\frac{dM}{dt} = k_1 M_t P_t^* = k_1 M_t C_0 \exp(-k_2 t) \quad (61)$$

Integration of this equation from $t=0$ to t gives

$$\ln \frac{M_0}{M_t} = \frac{k_1}{k_2} C_0 (1 - \exp(-k_2 t)) \quad (62)$$

where M is the monomer concentration.

At $t = \infty$:

$$\ln \frac{M_0}{M_\infty} = \frac{k_1}{k_2} C_0 \quad (63)$$

Figure 12 shows the plot, for the reactions shown in Figure 11, of $\ln(M_0/M_\infty)$ against the total number of Faradays passed per liter of anolyte in the initial current pulse, which was assumed to be equal or proportional to the actual initiator concentration. A straight line was obtained with a slope giving a value for k_1/k_2 of 6.7×10^5 liters per mole and an intercept on the C_0 axis of 2.27 microFaradays per liter. A summary of the results obtained for this system is shown in Table 1.

The termination found in this system could not have arisen from a flow through the sintered glass divider of the cell. There was a very small induction period in the current passage so that the amounts of cathodically produced terminating agents were probably comparable to the amounts of initiating species produced at the anode. Therefore a large percentage of the catholyte would have had to flow into the anode compartment to stop the reaction. Furthermore relatively few samples were removed, precluding a very great

FIGURE 12. Linear dependence of $\ln(M_0/M_\infty)$ on Co , the amount of current passed at $t=0$, per liter of anolyte for the reactions in Figure 11.

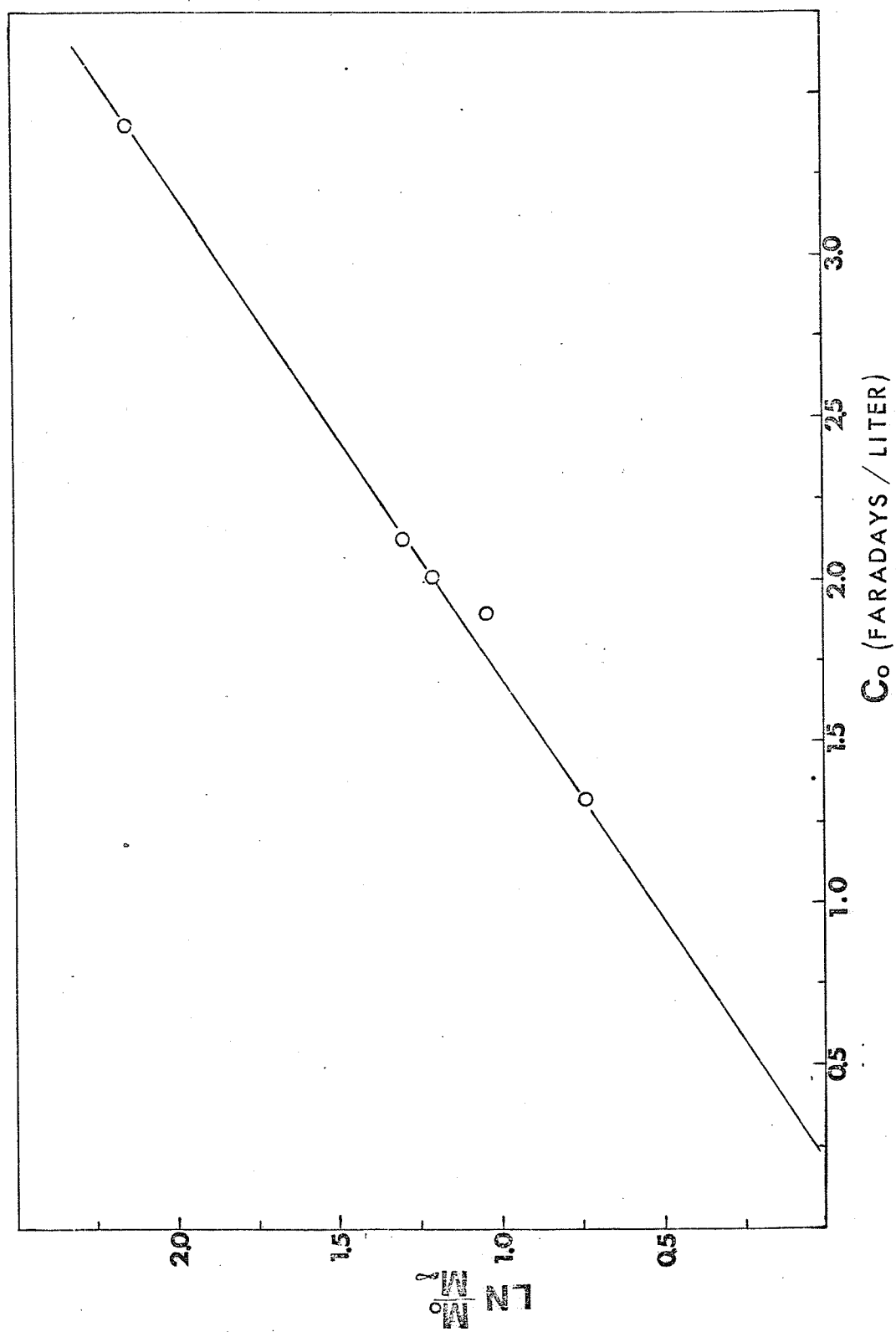


TABLE 1. Initial and Final Monomer Concentrations with Current Pulses of Various Magnitudes in Methylene Chloride Solutions of Tetrabutylammonium Perchlorate and Isobutyl Vinyl Ether.

CURVE	CURRENT PASSED FARADAYS/MOLE $\times 10^6$	INITIAL MONOMER CONCENTRATION MOLES/LITER	FINAL MONOMER CONCENTRATION MOLES/LITER	LN $\frac{M_0}{M_\infty}$
A	3.41	0.332	0.039	2.137
B	2.12	0.311	0.085	1.294
C	2.01	0.336	0.101	1.204
D	1.92	0.339	0.121	1.027
E	1.37	0.334	0.157	0.755

volume change of the anolyte.

As in the polymerization of isobutyl vinyl ether using the tetrafluoroborate salt, the passage of a current through the solution produced a green colour across the inner face of the anode. However, the green colour was more intense for this reaction and was not accompanied by the formation of an insoluble anodic coating.

(iii) Tetrabutylammonium Hexafluorophosphate

The passage of a current of 0.77 ma. through a solution of 14.3 milliequivalents per liter of tetrabutylammonium hexafluorophosphate and 0.339 moles per liter of isobutyl vinyl ether in methylene chloride produced soluble polymer after an induction current similar in magnitude to that found in the polymerizations with tetrabutylammonium tetrafluoroborate salt. A translucent insoluble film formed on the anode during the passage of current. This material was insoluble in boiling methyl ethyl ketone, benzene and methylalcohol and appeared to be formed in much larger quantities than the film formed with the tetrafluoroborate salt. However, no green colour was noted at the anode during the current passage. Because of the induction current, no rate curves were obtained for this reaction.

(iv) Tetrabutylammonium Iodide

The passage of a current of 1.0 ma. through a solution of 15.0 milliequivalents per liter of tetrabutylammonium iodide and 1.2 moles per liter of isobutyl vinyl ether in methylene chloride produced no polymer in the cathode or anode compartments although the initially colourless anolyte acquired a faint red colour, presumably due to the production of iodine by the oxidation of the iodide ions. No depletion of monomer was detected by gas chromatography.

Constant Current Experiments

Isobutyl vinyl ether was a difficult monomer to handle in electroinitiated cationic polymerizations due to the rapidity of its reaction. Styrene proved to be more docile since it exhibited a much slower rate. Using this monomer, experiments could be conducted using a constant current without producing an explosively fast polymerization.

In all of the following systems, a very slight amount of polymer formed before the passage of current, shown by a very slight cloudiness that formed when a small amount of the solution was added to methanol. However, no change in monomer concentration could be detected by gas chromatography in any of these systems when left over a period of 18 hours. Polymerization occurred in these blank solutions as soon as

the current was passed.

The reaction vessel used for constant current experiments is shown in Figure 2. Because the anolyte volume was about 157 ml. and the total volume removed per sample was only 0.05 ml., no effects due to flow of catholyte into anolyte were expected or observed.

(i) Tetrabutylammonium Perchlorate

When a current was passed through a solution of the perchlorate salt and styrene in methylene chloride, polymer was formed only in the anode compartment. Again a green colour formed across the inner face of the anode during the passage of current. However, no insoluble polymeric film formed on the anode. Instead only a very thin brown coating was formed which did not resemble a film. The reaction appeared to begin as soon as current was passed, i.e., there was no significant induction current. The soluble polymer formed at 25°C. had an intrinsic viscosity of 0.029 dl. per gram in benzene at 25°C. equivalent to a number average molecular weight of approximately 570.

Reaction curves at three different currents and three different monomer concentrations at 25°C. are shown in Figures 13 and 14. Sigmoid-shaped curves were invariably found for these reactions. This characteristic has been a feature of polymerizations in which steady-state concentrations

FIGURE 13. Reaction traces for the polymerization of styrene in methylene chloride at 25°C.

Electrolyte: 15.0 milliequivalents/liter
tetrabutylammonium perchlorate

Magnitude of current and initial monomer
concentrations:

a: 1.454 milliamperes; $(M)_0 = 0.388$ moles/liter

b: 0.987 milliamperes; $(M)_0 = 0.449$ moles/liter

c: 0.658 milliamperes; $(M)_0 = 0.449$ moles/liter

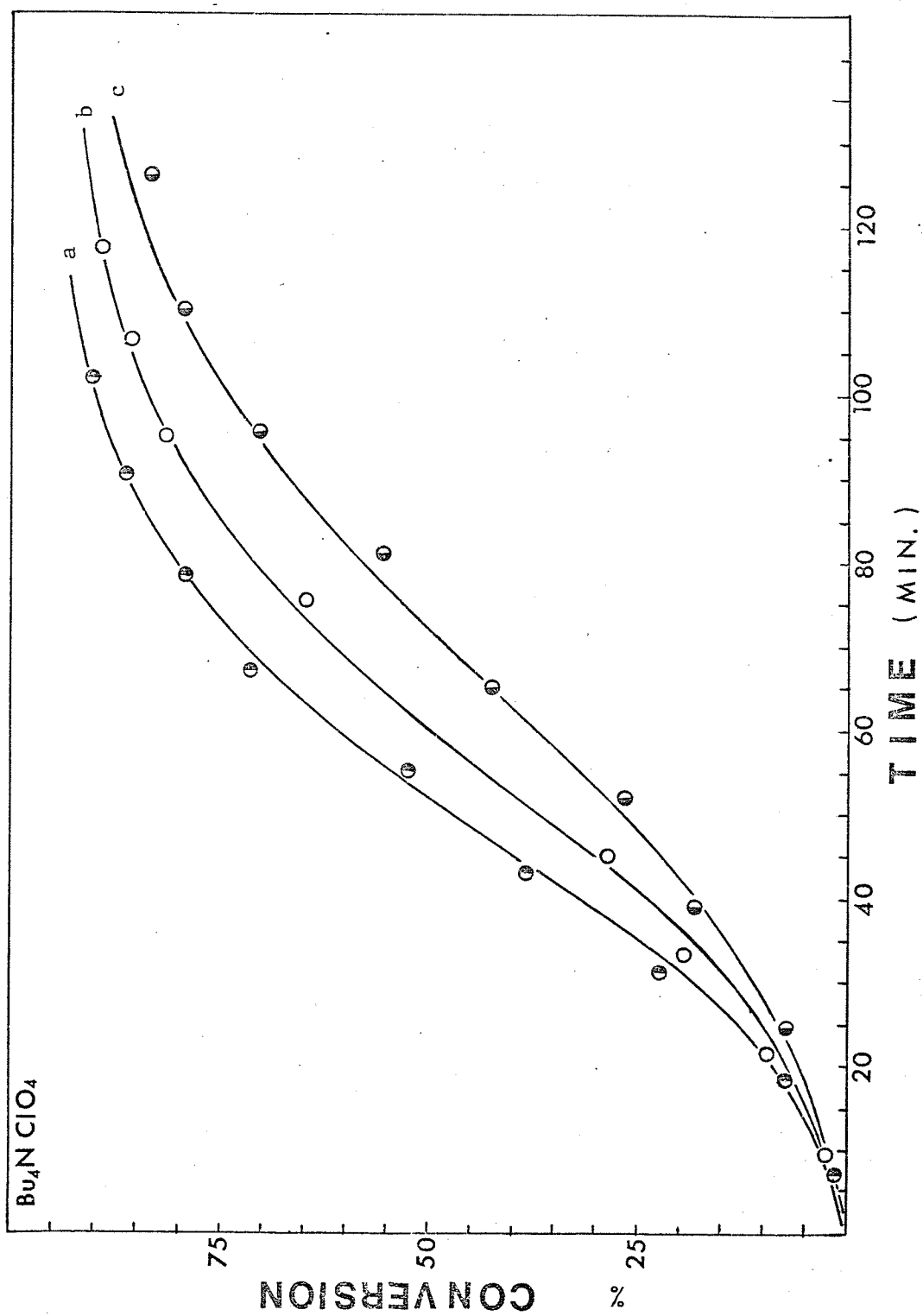
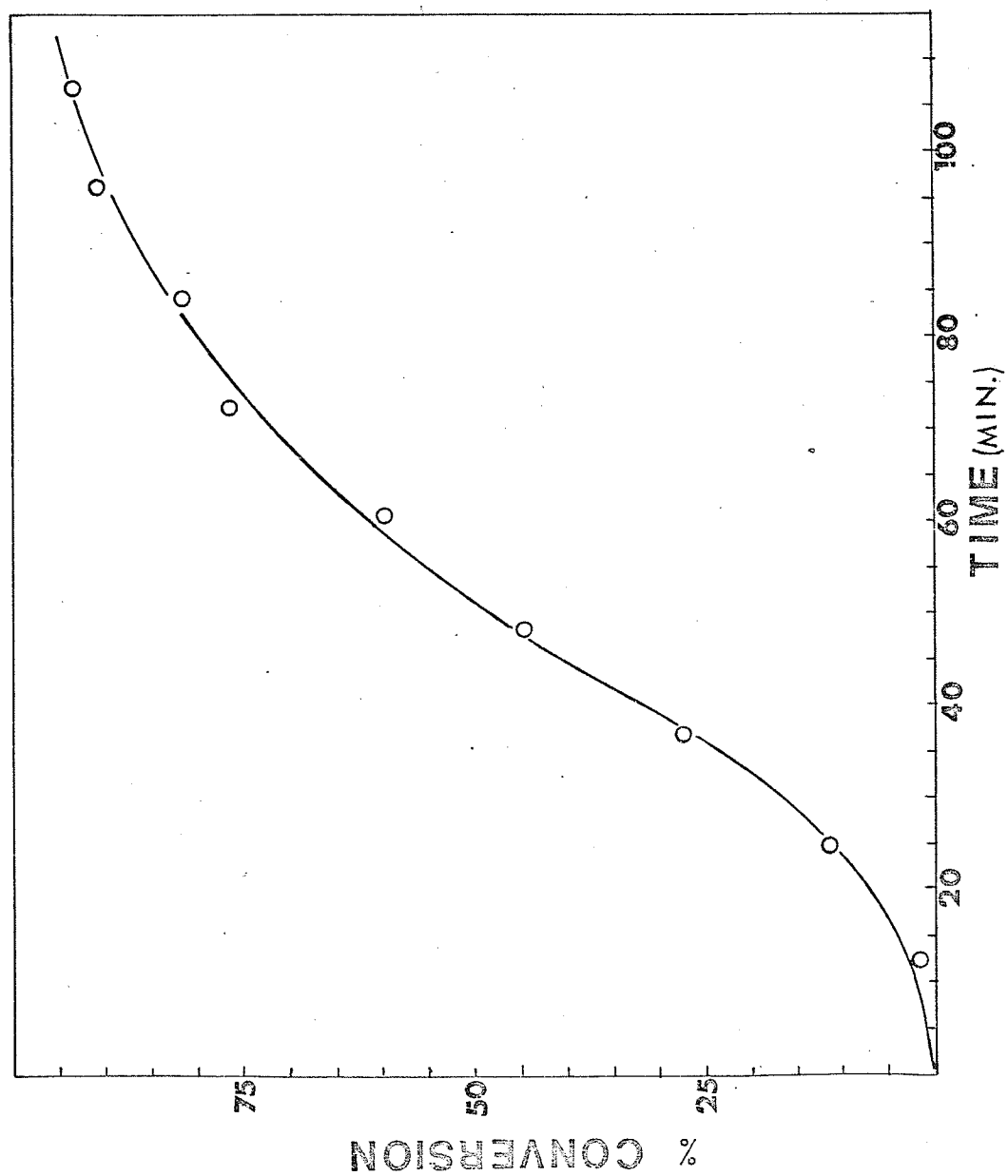


FIGURE 14. Reaction trace for the polymerization of
styrene in methylene chloride at 25°C.
Electrolyte: 15.0 milliequivalents/liter
tetrabutylammonium perchlorate
Magnitude of current: 0.987 milliamperes
Initial monomer concentration= 0.739 moles/liter



of active polymerization centers were not present because the production of active centers occurred throughout the reaction while termination was either absent or much slower than initiation.

Using the above observations and by analogy with the conventional polymerization of styrene by perchloric acid (19), the derivation of a kinetic relation to fit this system was carried out using the following assumptions:

a) at any time t , the reaction rate was directly proportional to the first powers of the initiator and the monomer concentrations existing at that time.

b) the total amount of active centers present at any time t was directly proportional to the total amount of current passed at that time.

c) no termination occurred in this polymerization.

d) there was no induction current in this system.

$$(\text{RATE})_t = -\left(\frac{dM}{dt}\right)_t = k_p (C^*)_t (M)_t \quad (64)$$

$$(C^*)_t = \frac{1}{96,493} \int_0^t i dt = \frac{it}{96,493} \text{ moles,} \quad (65)$$

if i is in amperes.

$$\text{Then } -\left(\frac{dM}{dt}\right)_t = k_p (M)_t (C^*)_t = \frac{k_p i}{96,493} (M)_t \quad (66)$$

$$\text{Writing } K = \frac{k_i}{96,493} \quad (67)$$

$$- \int_{M_o}^{M_t} \frac{d(M)}{(M)} = K \int_0^t t dt \quad (68)$$

$$\ln \frac{(M)_o}{(M)_t} = \frac{1}{2} K t^2 \quad (69)$$

A plot of $\ln\{(M)_o/(M)_t\}_t$ against t^2 should give a straight line with a slope equal to $\frac{1}{2} K$ from which the rate constant, k_p , could be obtained.

In practice straight lines were obtained at all currents and monomer concentrations used. The plots for reactions at 25°C. are shown in Figure 15 and Figure 16. The slopes of the curves were found by linear regression analysis and the corresponding rate constants calculated. The results are summarized in Table 2. The rate constant found at 25±0.1 °C. and its mean deviation are 1.56±0.05 liters/mole-sec.

Polymerizations were also carried out at 0°C. and 40°C. and the plots of $\ln\{(M)_o/(M)_t\}$ against t^2 for these reactions were also found to be straight lines. The rate constants were found to be 0.50 liters/moles-sec. at 0°C. and 3.05 liters/mole-sec. at 40°C. These results are also summarized on Table 2. The reaction curves for 0°C. and 40°C. are shown in Figure 17 and the corresponding kinetic plots are shown in Figures 18 and 19.

FIGURE 15. Linear dependence of $\ln(M_0/M_\infty)$ on t^2 ,
the time in seconds squared for the
reaction in Figure 14.

FIGURE 16. Linear dependence of $\ln(M_0/M_\infty)$ on t^2 ,
the time in seconds squared for the
reactions in Figure 13.

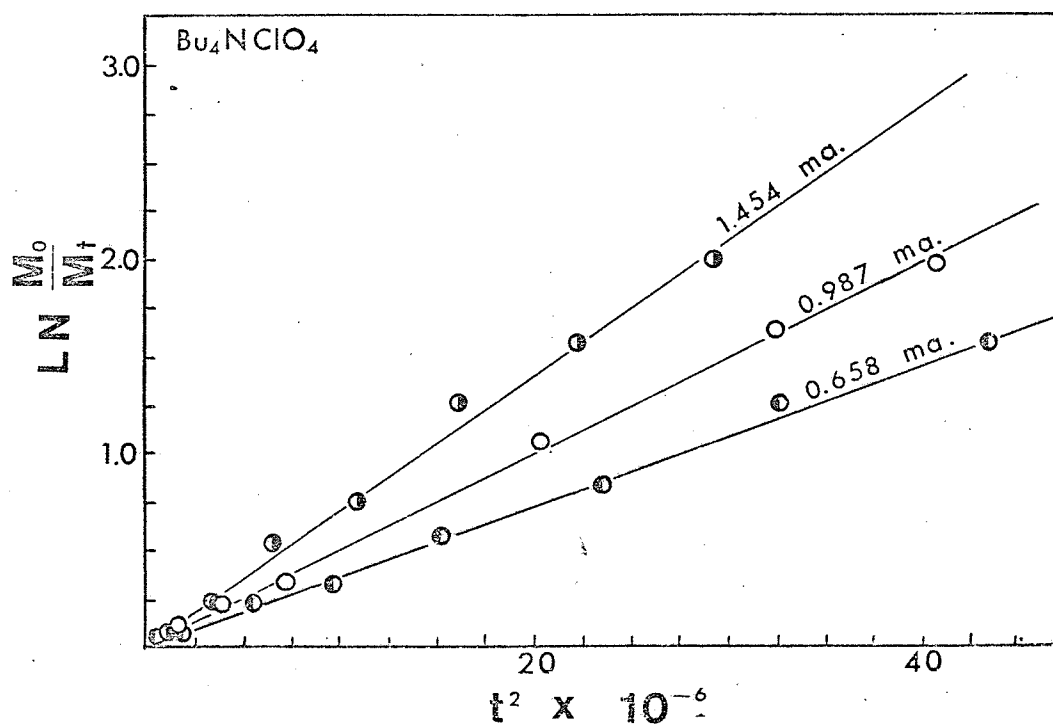
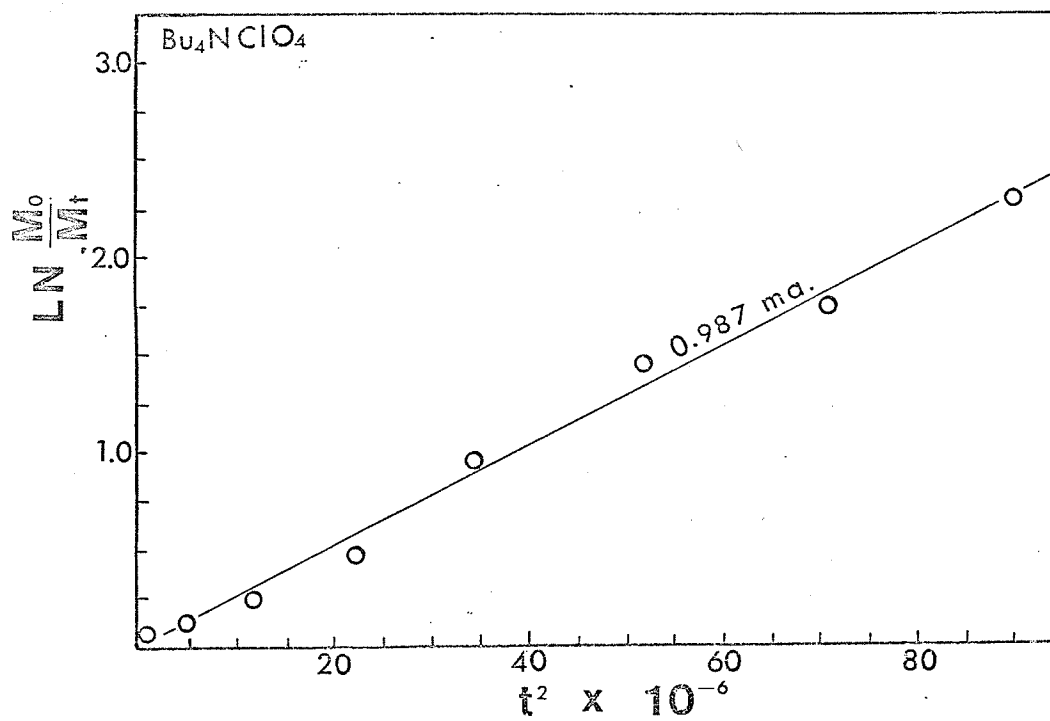


TABLE 2. Rate Constants for the Polymerization of Styrene with Bu_4NClO_4 .

APPROXIMATE POTENTIAL ACROSS ELECTRODES (VOLTS)	CURRENT ma.	TEMPERATURE $^{\circ}\text{C}$	MONOMER CONCENTRATION M/L	SLOPE $\times 10^8$	RATE CONSTANT L/M-SEC.
13.8	0.987	25	0.449	4.91	1.51
15.2	1.454	25	0.388	7.81	1.50
11.1	0.658	25	0.449	3.60	1.65
15.0	0.987	25	0.739	5.13	1.57
24.0	1.974	0	0.588	3.24	0.50
10.2	0.658	40	0.494	6.70	3.05

FIGURE 17. Reaction traces for the polymerization of styrene in methylene chloride.
Electrolyte: 1.50 milliequivalents/liter tetrabutylammonium perchlorate.
O - 1.454 milliamperes; $(M)_0 = 0.588$ moles/liter; temperature = 0°C.
● - 0.658 milliamperes; $(M)_0 = 0.494$ moles/liter; temperature = 40°C.

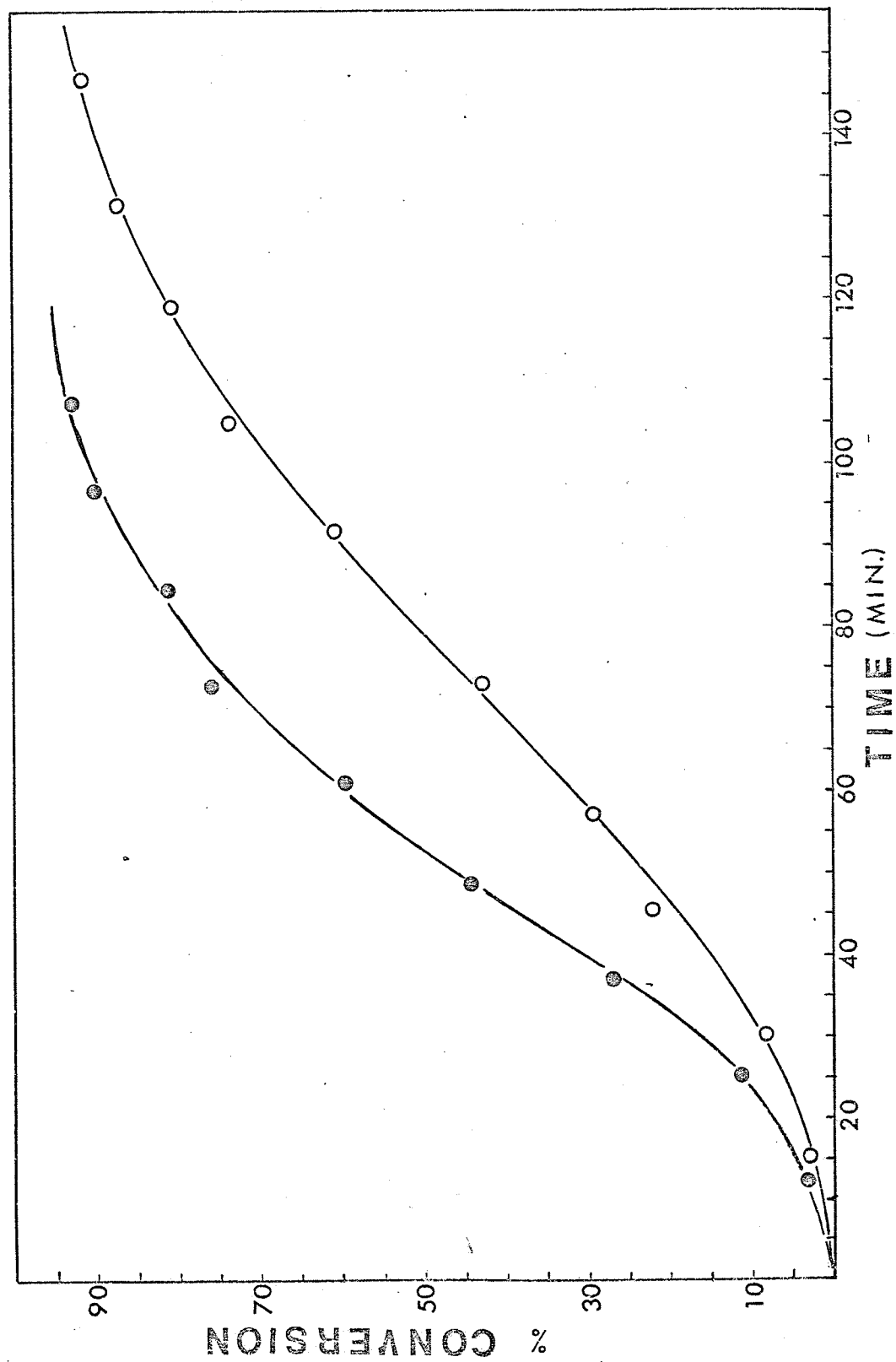
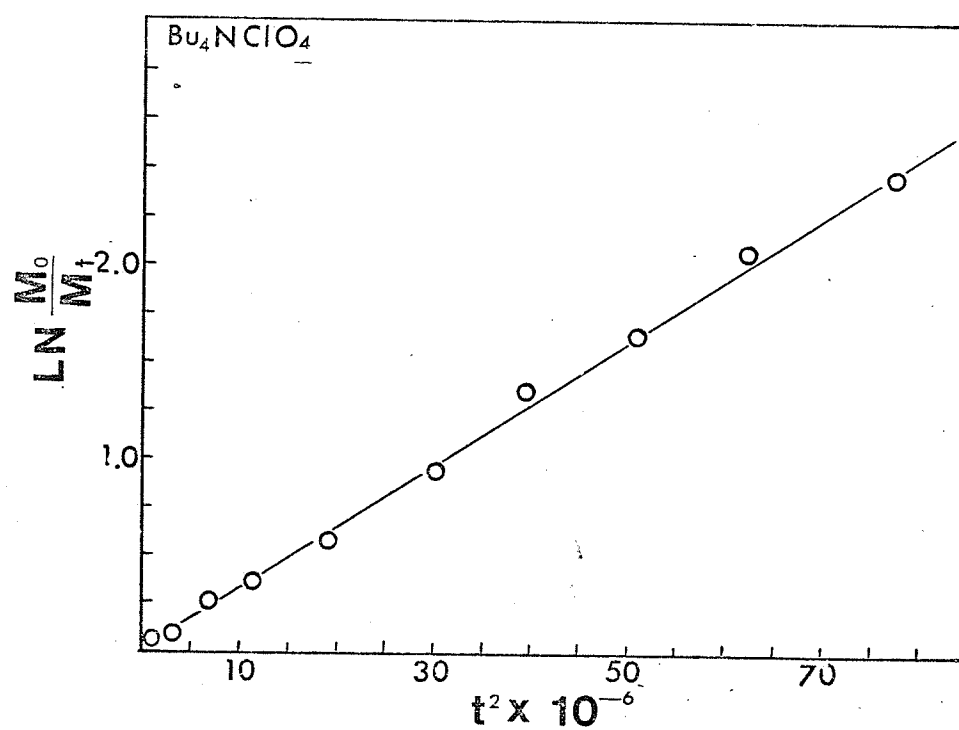
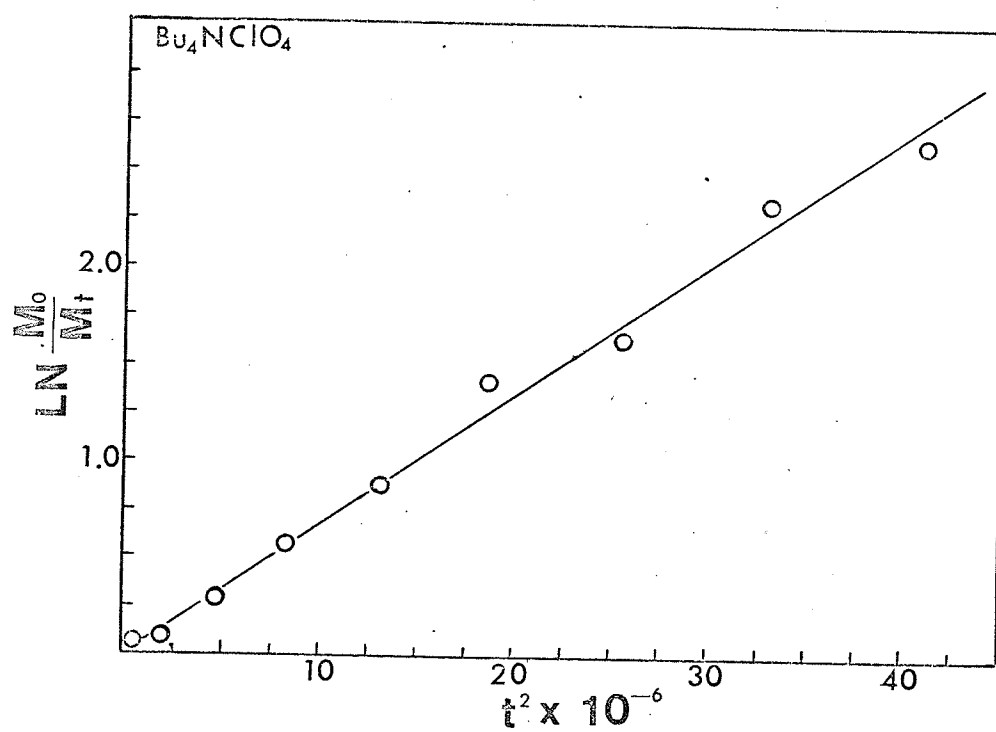


FIGURE 18. Linear dependence of $\ln(M_0/M_\infty)$ on t^2 ,
the time in seconds squared for the
reaction in Figure 17 at 40°C.

FIGURE 19. Linear dependence of $\ln(M_0/M_\infty)$ on t^2 ,
the time in seconds squared for the
reaction in Figure 17 at 0°C.



Polymer formed at 0°C. had an intrinsic viscosity of 0.030 deciliters per gram corresponding to a molecular weight of 615. The intrinsic viscosity of the polymer formed at 40°C. was 0.026 deciliters per gram corresponding to a molecular weight of 480. Only 10% of the polymer formed at 25°C. and 1.5% of the polymer formed at 40°C. were isolated.

Activation Energy. According to the Arrhenius theory, the rate constant can be expressed in the form:

$$k = A e^{-E/RT} \quad (70)$$

where E is the activation energy of the reaction, R is the gas constant, T is the absolute temperature and A is the pre-exponential factor. In logarithmic form this becomes:

$$\log k = \frac{-E}{2.303 RT} + \text{constant} \quad (71)$$

A plot of the logarithm of the rate constant against the reciprocal of the absolute temperature should give a slope from which the activation energy may be obtained.

The Arrhenius plot for the rate constants in Table 2 is shown in Figure 20. The slope of the straight line obtained was found to be -3.83×10^3 by linear regression analysis, corresponding to an activation energy of 7.6 kcal/mole.

Current Reversal. Figure 21 shows the effect of current reversal on the styrene-perchlorate-methylene chloride

FIGURE 20. Plot of $\ln k$ versus $\frac{1}{T}$ for the polymerization of styrene in methylene chloride with tetrabutylammonium perchlorate at 0°C., 25°C. and 40°C.

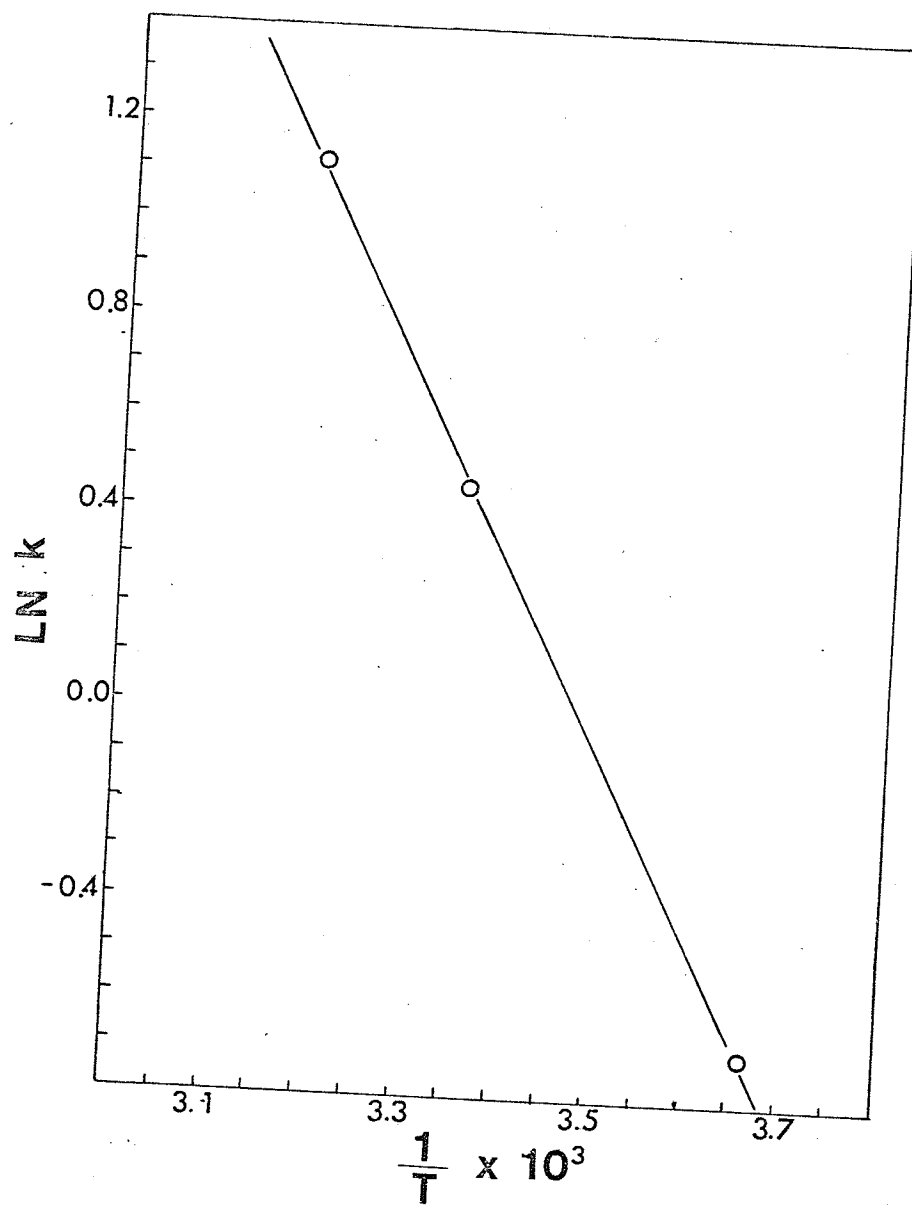
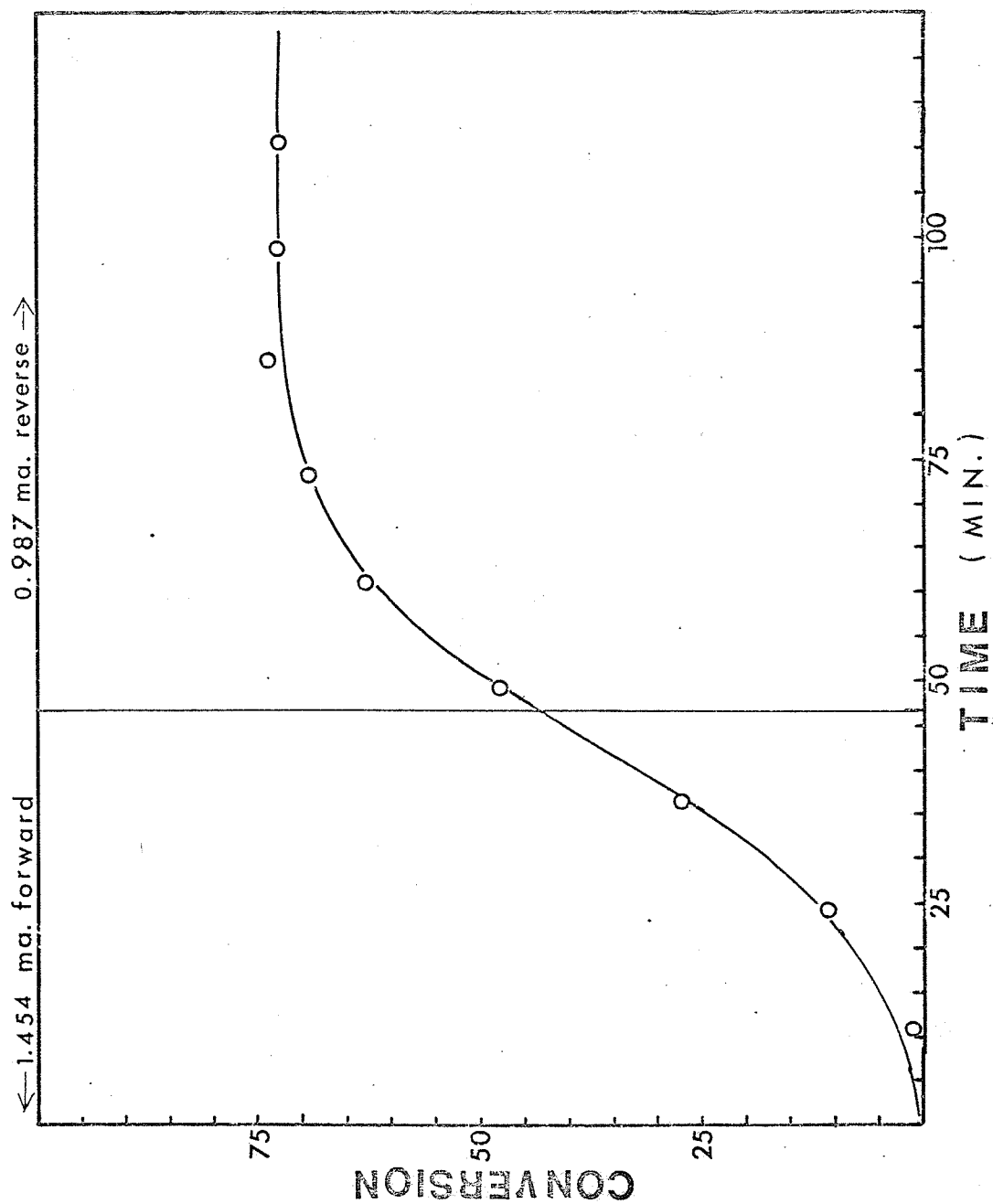


FIGURE 21. Reaction trace for the polymerization of 0.559 moles/liter styrene in methylene chloride with current reversal at $t = 47$ minutes.
Forward current = 1.454 milliamperes.
Reverse current = 0.987 milliamperes.



system. Current was passed for 47 minutes in the forward direction at a rate of 1.454 ma. giving a total of 4.25×10^{-5} Faradays. In this region the curve has a shape characteristic of other constant current experiments. The current was reversed at 47 minutes and passed at a rate of 0.987 ma. An inflection point appeared in the curve at the point at which the current was reversed. The reaction then slowed down and stopped at a constant final monomer concentration. Apparently products from the cathodic reaction terminated the polymerization reaction.

If the efficiency of the reverse reaction was equal to that of the forward reaction, the amount of terminating products produced after 69 minutes 14 seconds of the reverse reaction should have been sufficient to just stop the polymerization. However, it can be seen from Figure 21 that the polymerization stopped well before this time. A rough estimate showed that it had stopped at approximately 45 minutes, suggesting that the reverse reaction was about 50% more efficient than the forward reaction. However, this estimate of the relative efficiency of the reverse reaction must be regarded as a minimum value since the terminating agents did not necessarily react instantaneously with the active centers. Previously described experiments on pulsed current reversal in the isobutyl vinyl ether-tetrafluoroborate system have shown that the effect of the current reversal was not instan-

taneous in that case.

(ii) Tetrabutylammonium Tetrafluoroborate

Figure 22 shows the type of reaction curves obtained in the electropolymerization of styrene with the tetrafluoroborate salt. Again sigmoid-type curves were obtained as with the perchlorate salt. However, in this system the reaction often did not appear to begin accelerating as soon as the current passage had begun. The length of the period before the acceleration and the overall shape of the reaction curve varied between reactions even if the same currents were used. A single batch of salt was used for many of these reactions. The poly(styrene) formed had an intrinsic viscosity of 0.079 deciliters per gram in benzene at 25°C. corresponding to a number average molecular weight of 2600. Only 70% of the polymer formed in these reactions were isolated after purification.

Plots of $\ln\{(M)_0/(M)_t\}$ against t^2 are shown in Figure 25. Instead of straight lines, curves were obtained. One or more of the assumptions used for the perchlorate salt case were therefore not valid for this system, possibly due to variable amounts of impurities in the solution. Obviously rate constants could not be obtained from these data.

No green colour was noted on the anode in this system. Instead an insoluble brown solid material formed on the anode.

FIGURE 22. Reaction traces for the polymerization of styrene in methylene chloride at 25°C.
Electrolyte: 15.8 milliequivalents/liter
tetrabutylammonium tetrafluoroborate
a: 1,457 milliamperes; $(M)_0 = 0.559$ moles/liter
b: 1,457 milliamperes; $(M)_0 = 0.554$ moles/liter
c: 0.987 milliamperes; $(M)_0 = 0.567$ moles/liter

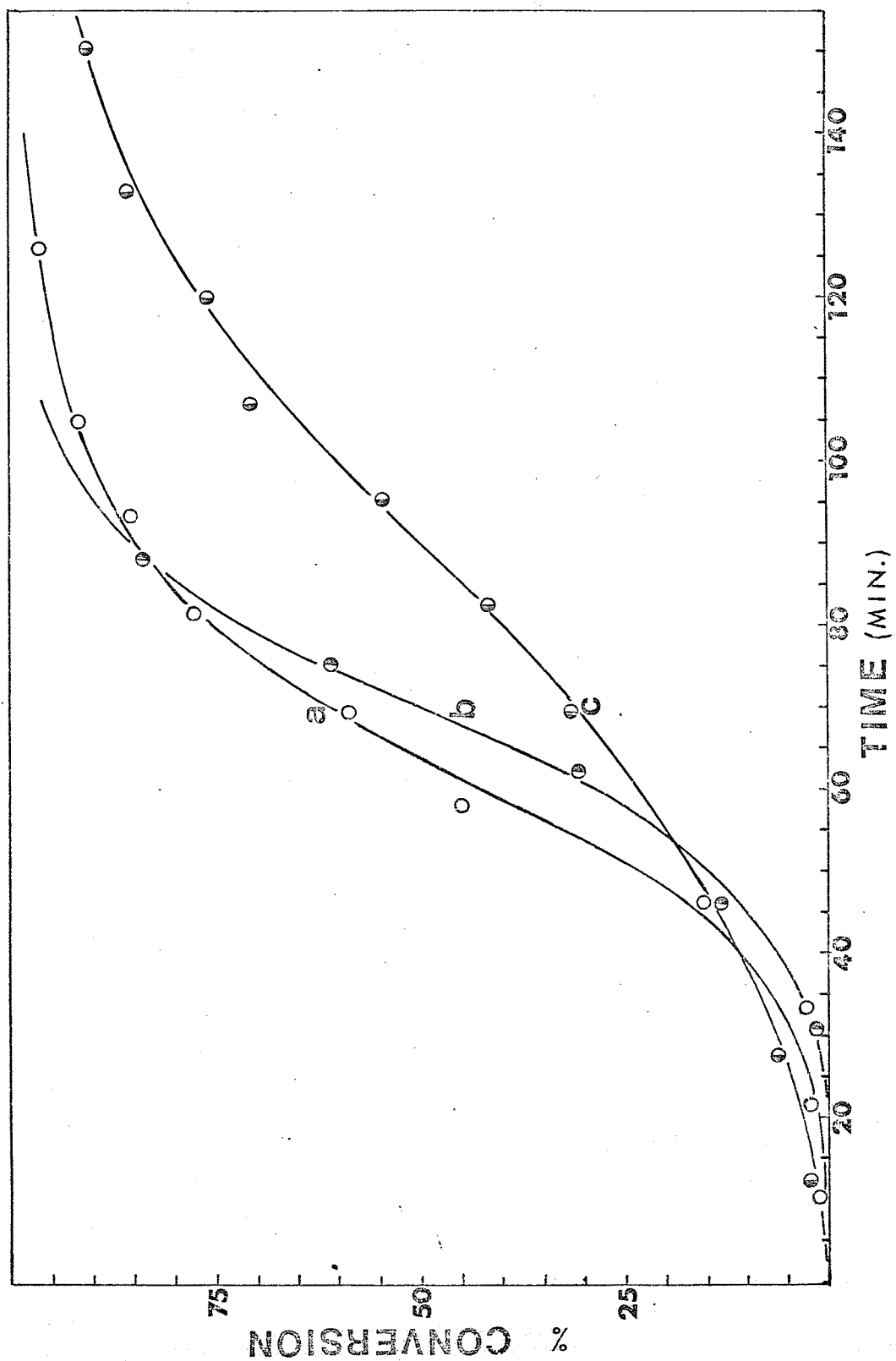


FIGURE 23. Reaction traces for the polymerization of
styrene in methylene chloride at 25°C.
Electrolyte: 9.49 milliequivalents/liter
tetrabutylammonium hexafluorophosphate
Current = 2.00 milliamperes
(M)₀ = 0.551 moles/liter

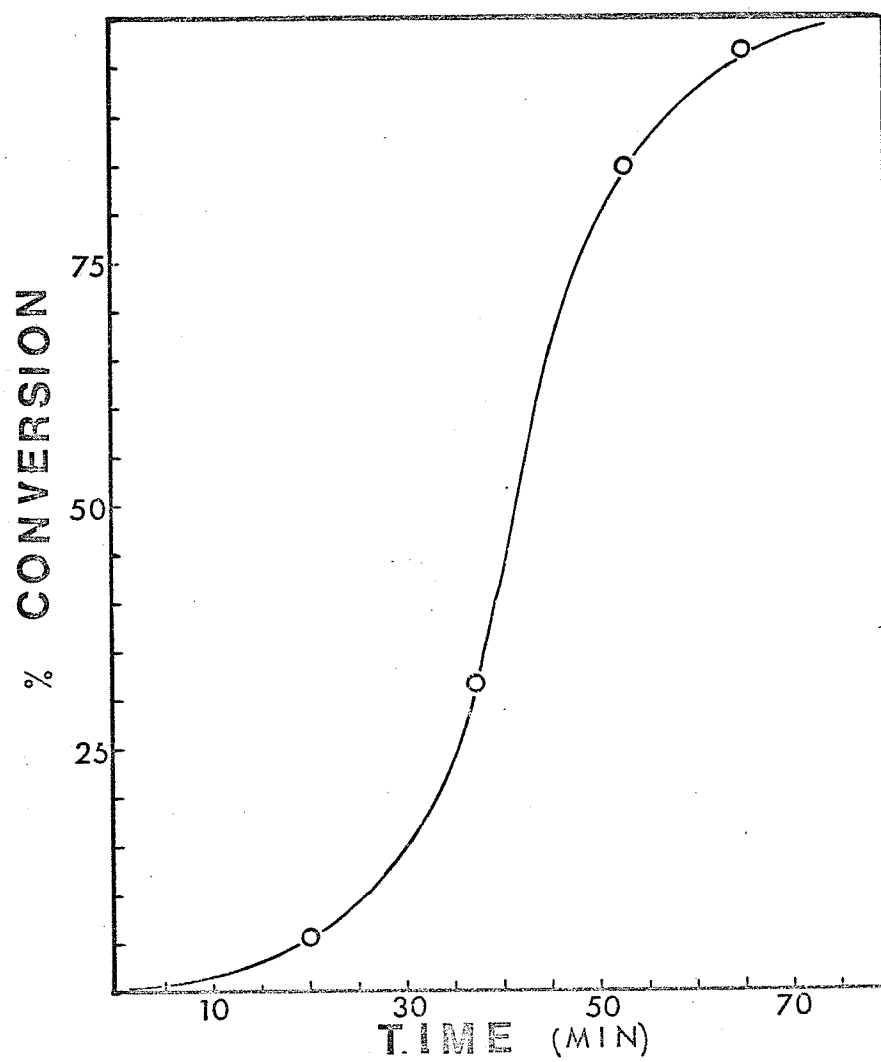
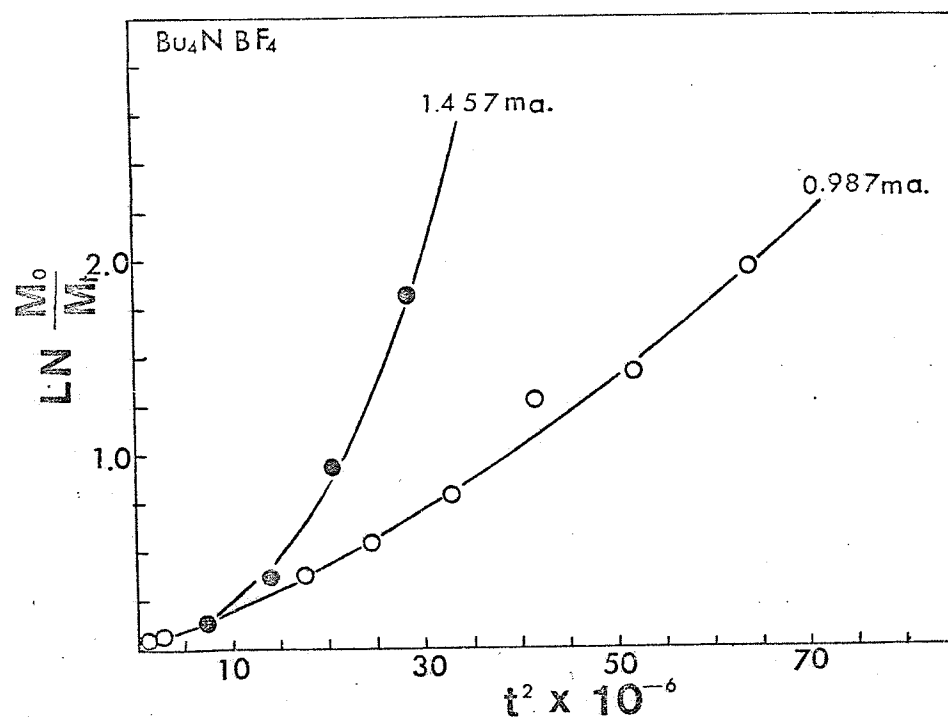
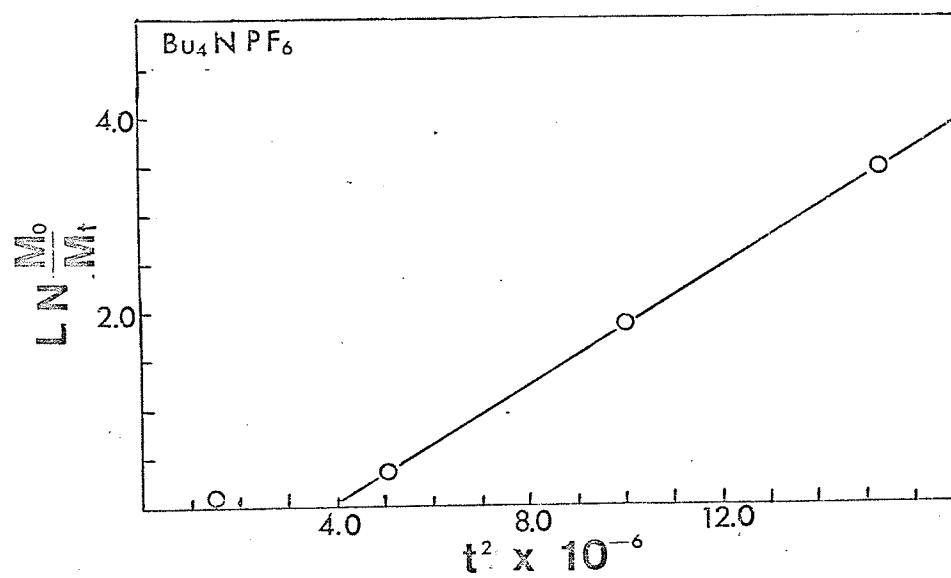


FIGURE 24. Plot of $\ln(M_0/M_\infty)$ versus t^2 ,
the time in seconds squared for
the reaction shown in Figure 23.

FIGURE 25. Plots of $\ln(M_0/M_\infty)$ versus t^2 ,
the time in seconds squared for
two reactions shown in Figure 22.



It was granular in form and did not resemble a film. Its properties were not investigated but it appeared to be degraded polymeric material.

N-vinyl Carbazole. N-vinyl carbazole also polymerized when current was passed through a methylene chloride solution of this monomer and the tetrafluoroborate salt. An intense green colour formed on the anode during the current passage. A slight amount of insoluble material formed on the anode. No reaction curves were obtained for this monomer.

(iii) Tetrabutylammonium Hexafluorophosphate

Figure 23 shows that sigmoid reaction curves were also obtained for the electropolymerization of styrene using the hexafluorophosphate salt. From this curve it appears that the reaction started as soon as the passage of current had begun. However, a plot of $\ln\{(M)_0/(M)_t\}$ against t^2 for this curve, shown in Figure 24, shows that although a straight line was obtained for later points, the curve does not extrapolate to zero. The slope of this straight line could not be used to derive a rate constant since the kinetic analysis derived for the perchlorate salt is only valid if there is no significant induction current.

In general, attempts to obtain reaction curves for the electropolymerization of styrene with this salt as an electrolyte met with greatly varying degrees of success. Results

varied from reaction curves of the type shown in Figure 23 to experiments in which no polymerization would occur at all, even if the same batches of salt, solvent and monomer were used. In other attempts a very slow polymerization would occur during a current passage of up to 140 minutes at 1.5 ma. after which the polymerization accelerated rapidly. These varied results suggested that the polymerization of styrene on electrolysis using the hexafluorophosphate salt was very sensitive to adventitious impurities in the reaction solution.

The poly(styrene) formed in the reaction shown in Figure 23 had an intrinsic viscosity of 0.0808 deciliters per gram in benzene at 25°C. corresponding to a number average molecular weight of 2700. About 70% of the polymer formed in this reaction was isolated after purification.

Voltammetry

Cyclic voltammetric studies were attempted on some of the above polymerization systems to determine the identity of the species directly oxidized at the electrode. These experiments were conducted in the cell shown in Figure 4.

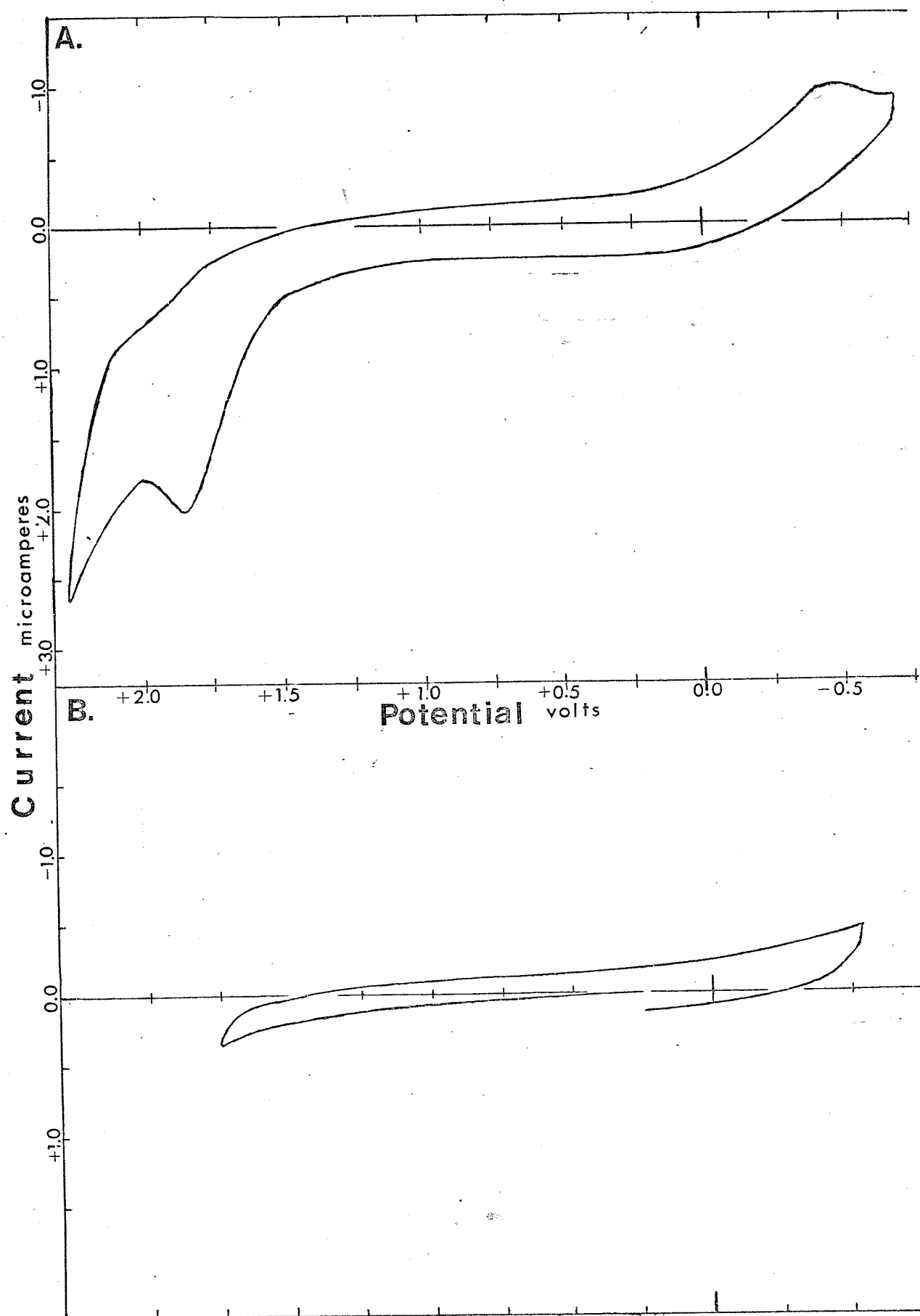
(i) Isobutyl Vinyl Ether - Tetrabutylammonium Tetrafluoroborate

Figure 26A displays the current-potential scan for a solution of tetrabutylammonium tetrafluoroborate in methylene

FIGURE 26. Current-potential scans of a solution of 93.0 milliequivalents/liter tetrabutylammonium tetrafluoroborate in methylene chloride.

A: to + 2.3 volts; scan speed = 0.05 Hz;
current sensitivity = 1 microampere/inch.

B: to + 1.5 volts; scan speed = 0.01 Hz;
current sensitivity = 1 microampere/inch.



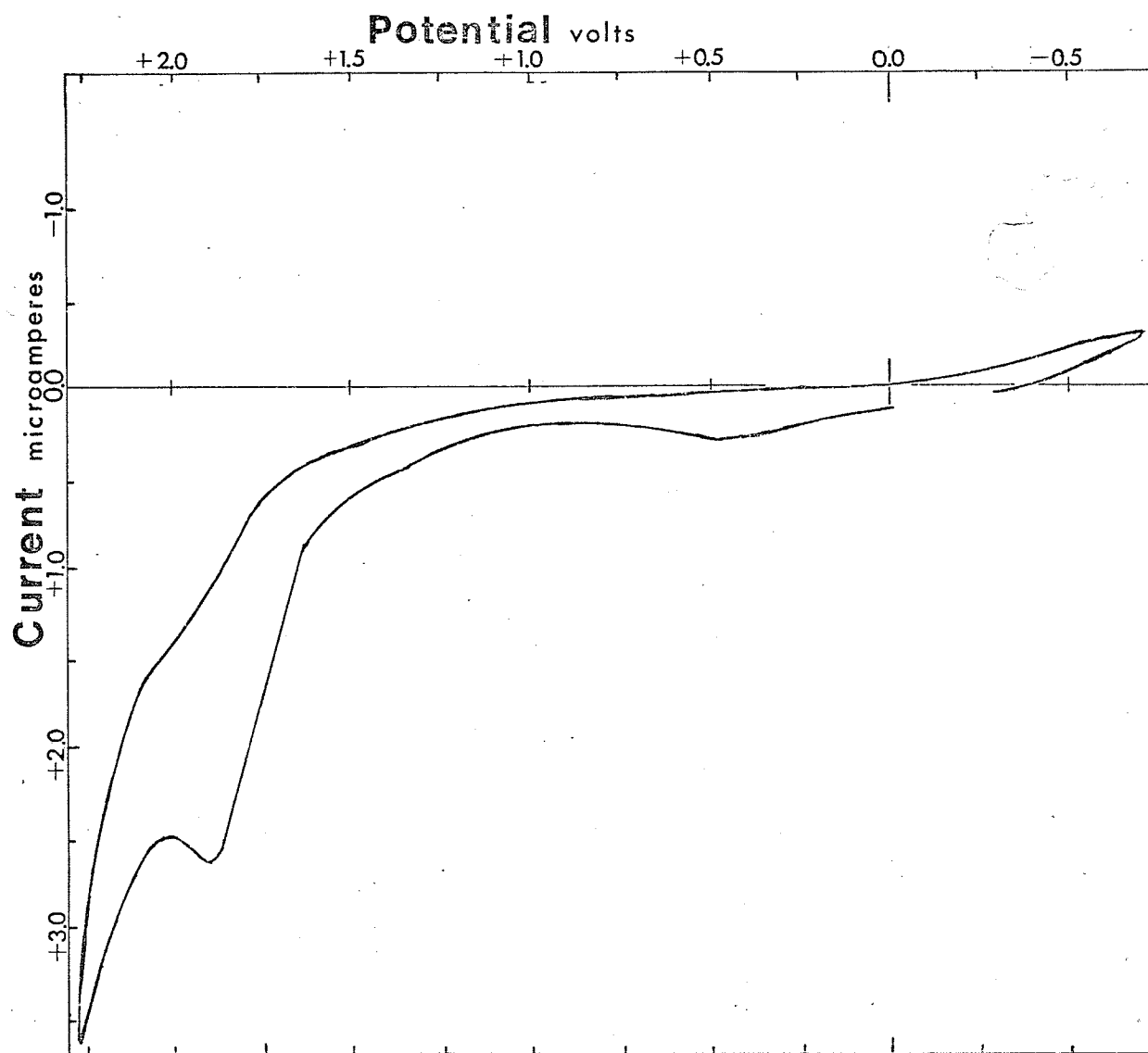
chloride. When the potential was scanned in a positive direction, the current due to the oxidation of the salt increased rapidly at about + 1.5 volts. The peak in the anodic current at about + 1.85 volts was probably due to an impurity in the solution. When the potential sweep was reversed and scanned to negative potentials, a peak appeared at - 0.45 volts. This peak grew as the scan was moved to more anodic potentials. Figure 26B shows that when the potential was not scanned to sufficiently positive potentials to oxidize the salt to a significant extent, the peak at - 0.45 volts disappeared. This suggests that the two peaks arose from the reduction of the electrolytic oxidation products. The various features of the scan shifted slightly in potentials as more and more scans were applied. These effects were probably due to electrode contamination occurring in the oxidation process.

When sufficient isobutyl vinyl ether was added to the solution to make a concentration in monomer of 3.47 millimoles per liter, the scan shown in Figure 27 resulted. The anodic portion of the scan did not change significantly; however, the peak at - 0.5 volts obtained in the absence of monomer no longer appeared.

(ii) Methylene Chloride - Tetrafluoroborate - Tetrahydro-
furan

The cyclic voltammetric scan of a solution of tetra-

FIGURE 27. Current-potential scan to +2.3 volts of a solution of 93.0 milliequivalents/liter tetrabutylammonium tetrafluoroborate and 3.47 millimoles per liter isobutyl vinyl ether in methylene chloride
Scan speed = 0.01 Hz; current sensitivity = 1 microampere/inch



butylammonium tetrafluoroborate in tetrahydrofuran was attempted with and without the presence of methylene chloride. The purpose of this experiment was to determine if methylene chloride was reduced at more positive potentials than the tetrabutylammonium ions. Small concentrations of methylene chloride in tetrahydrofuran as solvent were used in order to obtain a peak due to the reduction of methylene chloride in the cathodic scan of this solution. Tetrahydrofuran was chosen as the solvent because of the similarity of its dielectric constant ($\epsilon=7.4$) to that of methylene chloride ($\epsilon=8.9$), the solvent used in the study of electroinitiated cationic polymerization. However, the addition of 10 millimoles per liter of methylene chloride to a solution of 35 milliequivalents per liter tetrabutylammonium tetrafluoroborate in tetrahydrofuran did not result in a reduction peak in the cathodic current but did shift by + 0.75 volts the potential at which the cathodic current began rising rapidly in the scan to negative working electrode potentials. As it was not certain that this shift was due to the reduction of methylene chloride or simply a shift in the potential at which the salt was reduced, this result was considered to be equivocal.

DISCUSSION

Pulsed Experiments(i) The Tetrabutylammonium Tetrafluoroborate - i - Butyl Vinyl Ether System

In the electroinitiated polymerization of isobutyl vinyl ether in methylene chloride solutions of tetrabutylammonium tetrafluoroborate, an initiator which induced the polymerization was electrolytically generated at the anode. During the induction current, i.e., the initial passage of current which did not effect polymerization, the initiator or the polymeric active centers produced by it quickly reacted with impurities in the solution. Rapid polymerization began only when current was passed after the removal of the impurities. The original source of these impurities may have been any or all the components in the solution: the salt, solvent or monomer. However, as it was found in practice that the salt was relatively difficult to purify, it was considered to be the probable source.

Termination agents in cationic polymerization are usually basic substances capable of reacting with and destroying the electrophilic active centers. Therefore, any tri-butylamine, a common impurity in this salt, would have acted as an effective terminating agent. Residual bromide ion from the tetrabutylammonium bromide used in the preparation of the

tetrafluoroborate salt could also have been responsible. Finally residual water, which is known to inhibit many true cationic polymerizations, could have caused the termination reaction. Whatever the impurities, their concentrations as estimated from the approximate quantity of charge passed in the induction current, were very small, i.e., in the order of 4 to 5 micromoles/liter. However, this was larger than the amount of initiator needed to effect very rapid polymerization and as a result, the end of the induction current and the beginning of the rapid chain reaction could not be accurately determined. Therefore, no accurate measure of the amount of catalyst present could be obtained.

The reactions displayed in Figures 6 to 8 dramatically illustrate the control of the current over the rate of reaction. The rate appeared to depend on the total amount of current passed in the forward direction after the induction current period, demonstrating that the current did not simply remove the impurities and allow the salt to initiate the polymerization. The efficiency of the reverse current, i.e., current passed after the reversal of electrode polarity, in decelerating the reaction relative to that of the forward current in accelerating the reaction, could not be accurately determined. However, in the reaction trace shown in Figure 8, the forward pulse at B appeared somewhat less efficient than the equal reverse pulse at C since the deceleration

resulting from the reverse pulse was greater than the acceleration due to the forward pulse. However, this difference may be attributable to flow of the catholyte through the sintered glass divider.

It has been suggested (119) that some purportedly electrcinitiated polymerizations might actually be only an acceleration, caused by the application of an electric field across the solution, of a slow polymerization occurring without the passage of current. In the reactions displayed in Figures 6 to 8, no current was flowing and the electric field across the solution was zero during the bulk of the polymerization. Therefore, the rapid reaction could not have been due to electric field effects. Moreover, the absence of a blank demonstrated that no significant amount of polymerization took place in the unelectrolyzed solution of salt, solvent and monomer.

The production of initiator at the anode resulted from the oxidation of salt or monomer. Cyclic voltammetric potential scans of methylene chloride solutions of tetrabutylammonium tetrafluoroborate were observed in the presence and absence of monomer to determine if isobutyl vinyl ether was oxidized at a less positive potential than the salt. At the low concentration of monomer used, 3.47 millimoles/liter, direct oxidation of the monomer at the anode should have resulted in a peak in the anodic current at a less positive

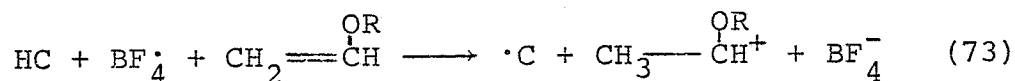
potential than that for salt discharge. The very similar appearance of the anodic scan in the presence or absence of monomer demonstrated that the monomer was not directly oxidized at the electrode. However, the disappearance of the peak at - 0.5 volts in the cathodic scan following the salt oxidation in the presence of monomer suggests that either the monomer reacted with the product of the salt oxidation or that the product was not formed in the presence of monomer. Although the identity of this substance has not been established in this work, it is reasonable to expect the formation of an acid product on oxidation of the tetrafluoroborate anion as was found for the perchlorate anion oxidation (117, 118). If an acidic product was also formed in the presence of the monomer, the basic double bond could have absorbed the acid and made it unavailable for reduction.

A number of initiation mechanisms are compatible with the above evidence. The initial oxidation of the tetrafluoroborate anion could have proceeded in a fashion analogous to that proposed for the oxidation of the perchlorate anion (117,118):



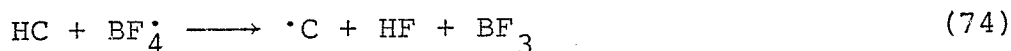
In the presence of the basic monomeric double bond, the tetrafluoroborate radical might have abstracted a hydrogen atom from some hydrocarbon in solution (solvent, monomer or polymer)

to form an initiating carbonium ion and the original tetrafluoroborate anion:

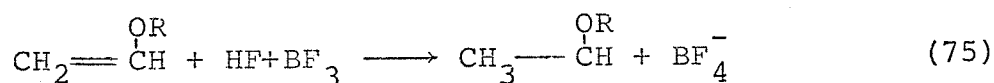


The carbonium ion would probably exist as an ion pair or an ester with a tetrafluoroborate anion.

An alternative reaction of the tetrafluoroborate radical was the abstraction of a hydrogen atom from a hydrocarbon to form hydrofluoric acid and boron trifluoride:

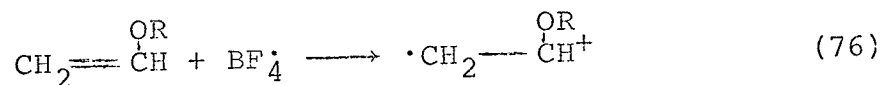


The boron trifluoride might have formed a cationic initiating complex with residual water in the system and this complex plus the hydrofluoric acid could have protonated the monomer to form propagating carbonium ions, although because of the possibility of the formation of a stable carbon-fluorine bond, the hydrogen fluoride might be expected to simply add to the monomeric double bond. In any case this scheme can be considered to involve the electrolytic formation of a Lewis acid which formed an initiating complex with an impurity. However, a further possibility exists if hydrogen fluoride and boron trifluoride were formed; these products may have acted as a catalyst-cocatalyst pair in a manner similar to that proposed by Olah et al. (36):



According to this mechanism, catalyst and cocatalyst were simultaneously produced in equimolar amounts at the anode. The possibility of either of the initiation reactions involving the production of hydrogen fluoride and boron trifluoride is supported by the observation of gases trapped under the thick, insoluble anodic coating after long electrolysis in undivided cells. This gas may have consisted of boron trifluoride and hydrogen fluoride produced by anodic oxidation of the tetrafluoroborate ion. However, the identity of these gases was not investigated in this work.

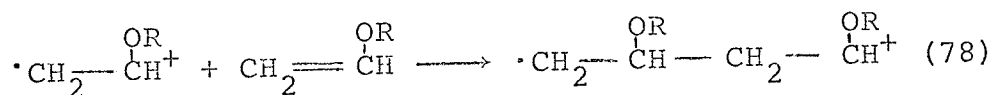
A further alternative reaction of an electrolytically produced tetrafluoroborate radical is the oxidation of the monomer to a radical cation:



This is analogous to the reduction of α -methylstyrene monomer to a radical-anion by electrolytically formed sodium metal (100). Like radical-anions, radical-cations could have either dimerized to dicationic species:

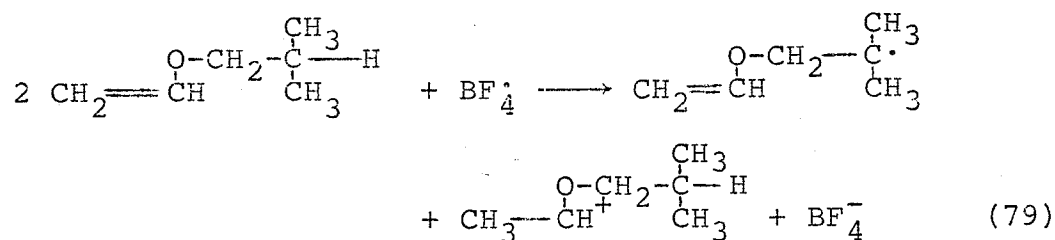


or added monomer to form separated cationic and free radical ends:



In the latter case, polymerization would likely take place only from the cationic end as isobutyl vinyl ether has never been found to polymerize by a free radical mechanism.

Initiation mechanisms involving hydrogen atom abstraction from hydrocarbons in solution could have produced free radicals on the monomeric or polymeric side-chains or on the polymeric backbone. Dimerization of these radical species may have resulted in the formation of crosslinked polymer, explaining the highly insoluble polymer-like film that coated the anode during the passage of current. One possible mode of hydrogen atom abstraction from the monomer is:

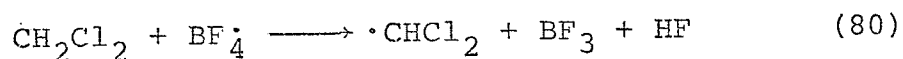


However, the insoluble anodic products could also have arisen from monomeric radical-cation reactions similar to the uncharacterized, solid-producing reactions observed in the oxidation of aromatic hydrocarbons (109,110).

The similarity of the colour of transient green product noted at the anode during the passage of current to colours of radical-cations produced by antimony pentachloride (115) suggests that isobutyl vinyl ether radical-cations may have been formed. The immediate disappearance of the colour

on exposure to air was similar to the behaviour of radical-cations prepared by Lewis and Singer (115) who found that only radical-cations of highly conjugated hydrocarbons such as 9,10-dimethylantracene, perylene and naphthacene were stable in air and at room temperature.

The occurrence of polymerization on the addition of small quantities of the anolyte of an electrolyzed solution of tetrabutylammonium tetrafluoroborate in methylene chloride to a solution of isobutyl vinyl ether in methylene chloride demonstrated that an acid with cationic initiating ability was formed on oxidation of the salt. This acid may have arisen from the abstraction of hydrogen atom from a solvent molecule by an electrolytically formed tetrafluoroborate radical. The character of the acid produced has not been investigated but it was likely equivalent to the acid solution produced on mixing hydrogen fluoride and boron trifluoride in equimolar amounts in methylene chloride solution. A possible overall reaction would be:



The identity of the acids present was not investigated further as it was felt that the reactions and products in the presence of monomer may differ considerably from those in the absence of monomer.

The absence of polymerizing reactions when the anolyte from an electrolyzed solution of electrolyte and methylene

chloride was added to a solution of the monomer and toluene demonstrated that the acids in the anolyte solution could not catalyze the polymerization of isobutyl vinyl ether in a medium of low dielectric constant. This behaviour has also been observed in the attempted polymerizations of styrene by hydrochloric acid and sulfuric acid in toluene (120).

The plot of $\ln(M)$ against t , the time in minutes, displayed in Figure 10, shows that the polymerization exhibited a first order rate dependence on monomer concentration up to approximately 90% conversion, provided no flow through the sintered glass disk occurred. This is compatible with a propagation reaction first order in both monomer and active center concentration, a common phenomenon in cationic polymerization. The kinetic equation for propagation can therefore be written:

$$-\frac{d(M)}{dt} = k_p (M^*) (M) \quad (81)$$

If the current formed initiating substances which reacted to form active centers after the passage of current was terminated, the kinetic equation for initiation can be written:

$$R_i = k_i (C)^x \quad (82)$$

where $(C)^x$ is the concentration of initiator to the unknown power x . This initiation reaction would necessitate the existence of a termination reaction since the reaction did not

accelerate when current was not applied. Because termination reactions in cationic polymerization are first order in active center concentration, the kinetic equation for termination can be written:

$$R_t = k_t (M^*) \quad (83)$$

If the stationary-state assumption is applied, the rates of initiation and termination can be equated giving the following expression for the active center concentration:

$$(M^*) = \frac{k_i}{k_t} (C)^x \quad (84)$$

The overall rate equation could then be expressed as:

$$-\frac{d(M)}{dt} = \frac{k_i k_p}{k_t} (C)^x (M) = k (C)^x (M) \quad (85)$$

and the reaction would be an example of a stationary-state of the First Kind. However, if the active centers were produced virtually instantaneously on passage of current, the concentration of catalyst produced would have been equal to the concentration of active centers, giving the overall rate equation:

$$-\frac{d(M)}{dt} = k_p (C)^x (M) \quad (86)$$

and the reaction would be a stationary-state of the Second Kind. Therefore, a first order dependence of the rate on monomer concentration is compatible with both of the above

stationary-state theories.

Because the concentration of tetrafluoroborate anions from the salt was much greater than the concentration of active centers, the most likely counterion for a carbonium ion active center was the tetrafluoroborate anion. Even if the catalysts were hydrofluoric acid and/or boron trifluoride and the original counterions were F^- and $(BF_3OH)^-$, they would have been replaced by tetrafluoroborate anions if an equilibrium existed between ion pairs and free ions. The work of Sakurada, Ise and coworkers on the electric field acceleration of cationic polymerization showed that such equilibria did exist in ethylene chloride solutions for the polymerization of isobutyl vinyl ether by iodine (48) and the polymerization of styrene by boron trifluoride etherate (49). As the dielectric constant of methylene chloride solutions is similar to ethylene chloride solutions, the existence of ion-ion pair equilibria in this electroinitiated system is plausible. Therefore, the true counterions of the active centers would have been tetrafluoroborate ions. Because tetrafluoroborate anions are very stable and are very poor nucleophiles, they are unlikely to participate in any termination reactions, as has been found for the very poorly nucleophilic perchlorate ion (19). Since no other component of the solution is known to destroy cationic active centers, it is plausible that no natural termination reaction was present and that the system exhibited a

stationary state of the Second Kind.

Integration of equation (85) gives:

$$\ln(M) = -k(C)^x t + \text{constant} \quad (87)$$

The slope of the straight line obtained on plotting $\ln(M)$ against t would be equal to $-k(C)^x$. However, the concentration of catalyst, (C) , was unknown in every experiment and hence, k and x could not be determined.

From Figures 6 and 8, it is evident that the rate of reaction of the polymerizing solutions increased almost instantaneously when current was passed in a forward direction through the solution. On the contrary, after the reverse pulses at B in Figure 7 and at C in Figure 8, the reaction gradually slowed down over a period of fifteen (Figure 8) to thirty (Figure 7) minutes. This behaviour suggests that the initiation reaction at the anode was virtually instantaneous and produced active centers directly while the cathodic reaction produced basic substances which reacted gradually with the active centers in solution.

(ii) The Tetrabutylammonium Perchlorate-i-Butyl Vinyl Ether System

The behaviour of this polymerization system resembled the "flash polymerizations" of isobutene catalyzed by aluminum trichloride (121,122) and of styrene by sulfuric acid in ethylene chloride (34). A given dose of initiator very rapidly produced a corresponding yield of polymer with no sig-

nificant amount of subsequent reaction. In both of these conventional polymerization systems a termination reaction inherent in the system resulted in a depletion of catalyst or cocatalyst causing the reaction to stop.

In the electroinitiated cationic polymerization of isobutyl vinyl ether with tetrabutylammonium perchlorate, a natural termination reaction could only involve the combination of the perchlorate counterion with the carbonium ion to form a stable ester incapable of promoting further polymerization. Considering the poor nucleophilicity of the perchlorate anion, this possibility must be considered unlikely. Moreover, the polymerization of styrene by perchloric acid in methylene chloride at 25°C (52), a reaction having either carbonium ions with perchlorate counterions or active polystyryl perchlorate esters as propagating species, exhibited no terminating reaction. A perchlorate ester of the very stable poly(isobutyl vinyl ether) carbonium ion would probably be very active and/or very unstable with respect to decomposition to carbonium ions. For these reasons, the author believes that the termination was due to adventitious impurities.

In this electroinitiated reaction, there were two observed effects of termination reactions. Firstly, the x-intercept in the plot of $\ln\{(M)_0/(M)_\infty\}$ against $(C)_0$ suggested that the first approximately 2.3 microFaradays of current passed per liter of solution produced initiator that was effectively immediately

destroyed by reaction with termination agents in the solution. Secondly, the rapid slowing of the rate of polymerization occurring after the pulse indicated the presence of a termination reaction that destroyed the active centers during the polymerization. Because the plot in Figure 12 gives a straight line that extrapolates to a definite x-intercept, the effectiveness of these termination reactions was very reproducible when reactions were prepared under similar conditions. Otherwise a considerable scatter would have occurred.

The effectiveness of the termination reaction that slowed and stopped the rapid polymerization was apparently reduced to a minimum by subjecting the salt to extensive vacuum pumping before the addition of monomer and solvent, suggesting further that the termination was due to impurities. This treatment probably removed volatile terminating agents from the salt. Considering the hygroscopic nature of the salt, the most likely impurity was water. Because the same concentration of salt was used in each reaction, the termination occurring after the pumping could reasonably be attributed to reproducible amounts of water remaining in the salt. As amines are common impurities in tetraalkylammonium salts, the initiator formed during the induction current was possibly used to destroy minute quantities of tributylamine from the salt. However, it is possible that the two termination effects

originated from the same impurity.

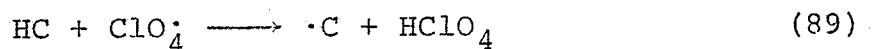
The reaction traces A to E in Figure 11 show that by varying the magnitude of the initial current pulse, a great amount of control over the initial rate and final degree of conversion was possible in this reaction under constant conditions of preparation and reaction. Since no electric field was applied across the solution for the bulk of the reaction, the rapid polymerization was not due to the electric field acceleration of a very slow polymerization occurring without the passage of current (119). Moreover, the absence of a significant amount of polymer formation over periods of up to 18 hours without the passage of current demonstrated that the reaction was not initiated by the salt or other component in the unelectrolyzed solution.

Billon (118) has shown that in acetonitrile solution, the anodic oxidation of the perchlorate anion occurred at approximately the same electrode potential as the oxidation of the tetrafluoroborate anion. Some authors (116,118) have also detected by means of ESR spectroscopy the perchlorate radical produced at the anode, presumably by the following reaction:

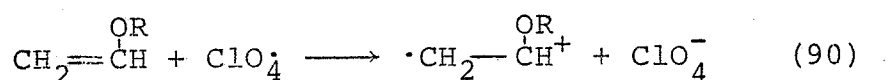


In a methylene chloride solution of monomer, polymer and tetrabutylammonium perchlorate this radical may have abstracted a hydrogen atom from any or all these components to form

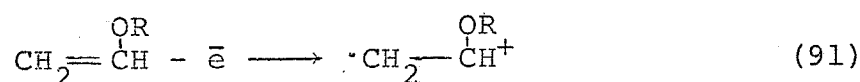
perchloric acid, a strong cationic initiator:



or it may have oxidized the monomeric double bond to form a radical-cation:



However, it is also possible that the monomer was oxidized directly at the anode:



Again a radical cation formed by either of the above mechanisms could have either dimerized to a dicationic species or added monomer to form separated free radical and cationic ends.

With any of the above possible initiation reactions, the result would be virtually equivalent to the addition of perchloric acid to the monomer solution. However, the use of an electric current to generate the active species allows precise control and accurate programming of the addition of very small quantities of catalyst to the reaction solution, i.e., micromoles of catalyst per liter.

As in the electropolymerization of isobutyl vinyl ether with tetrabutylammonium tetrafluoroborate as electrolyte, a transient green colour formed on the anode during the

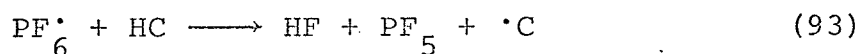
passage of current. However, in this case the colour was more prominent, covered the whole inner face of the electrode and was not accompanied by the formation of an insoluble solid on the anode. This suggests that in this system, radical-cations were formed either by direct oxidation at the anode or on oxidation by perchlorate radicals and that no crosslinking hydrogen atom abstractions from the monomer or polymer occurred.

As is shown in Figure 12, a straight line was obtained when $\ln \{(M)_0/(M)_\infty\}$ was plotted against $(C)_0$, the number of Faradays of current passed in the initial current pulse. If the dependence of the rate of polymerization on the monomer concentration had been to any power other than unity, a plot with $\ln \{(M)_0/(M)_\infty\}$ as ordinate would not have given a straight line. Moreover, according to the derivation of this kinetic relationship, shown in the result section (p.92), the abscissa should be the concentration of catalyst to whatever power the concentration of catalyst is taken in the rate equation. Although the range of initial monomer concentrations used in these reactions was not great, the plot in Figure 12 indicates that the rate of polymerization was first order in both catalyst and monomer concentrations. This could be demonstrated only because the termination was reproducible under the conditions used and could be treated as a termination unimolecular in active center concentration and inherent in the polym-

erization system. However, the significance of the value obtained for the ratio of the rate constants of propagation and termination, $k_1/k_2 = 6.7 \times 10^5$ liters per mole, is rather dubious and can only be regarded as a measure of the relative rates of propagation and termination by impurities.

(iii) Tetrabutylammonium Hexafluorophosphate

The possibilities for initiation reactions for this salt are similar to those suggested above for the tetrafluoroborate salts. However, no transient green colour was noted on the anode during the passage of current and a relatively great amount of insoluble film formed on the anode, suggesting that no radical-cations were formed at the anode and that the majority of the active centers were produced by crosslinking hydrogen atom abstraction reactions:

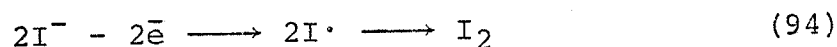


If the Lewis acid potassium pentafluoride was formed as a result of the electrode reactions, it could have acted as a polymerization catalyst with the hydrogen fluoride or adventitious water as cocatalyst.

(iv) Tetrabutylammonium Iodide

The absence of polymerization on electrolysis of solu-

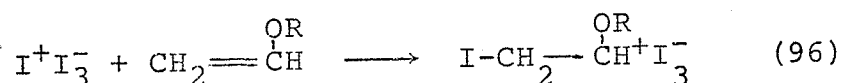
tions of tetrabutylammonium iodide and isobutyl vinyl ether in methylene chloride is not surprising even though iodine, a well-known polymerization catalyst for vinyl ethers, was apparently produced at the anode, presumably by the following reactions:



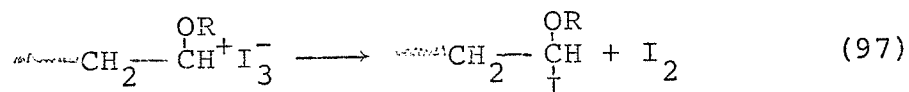
It is generally assumed that in all the polymerizations initiated by iodine the initial active species is the iodonium ion, I^+ , formed by the dimerization of two iodine molecules:



Initiation occurs by addition of the iodonium ion to the olefin to form a carbonium ion:



In conventional systems with iodine, this carbonium ion can then add monomer until termination occurs by abstraction of an iodide anion from the counterion:



However, in the electroinitiated system, a large concentration of iodide ions from the electrolyte existed in solution. Therefore, any carbonium ions formed would likely have been quickly destroyed by a simple combination of the iodide anion with the carbonium ion, preventing the formation of high polymer.

Constant Current Experiments

(i) The Tetrabutylammonium Perchlorate - Styrene System

The polymerization of styrene in the anode compartment by the electrolysis of methylene chloride solutions of the monomer and tetrabutylammonium perchlorate was subject to the greatest amount of control of all the polymerizations in this study. The reaction was very reproducible even when different batches of salt, solvent and monomer were used. The straight lines obtained in the plots of $\ln\{(M)_0/(M)_t\}$ against t^2 and the consistent value of 1.56 liters/mole-sec. $\pm 3\%$ at 25°C . obtained for the rate constant in reactions with different currents and monomer concentrations supported the validity of the assumptions that the amount of catalyst at any time was proportional to the total amount of current passed, that termination of the active centers was absent and that the rate of polymerization was proportional to the first powers of the catalyst and monomer concentrations. If the rate had been proportional to the square or the square root of the catalyst concentration, a plot of $\ln\{(M)_0/(M)_t\}$ against t^3 or $t^{3/2}$, respectively, would have given a straight line. A dependence of the polymerization rate on the monomer concentration to any power other than one would not have given a straight line with $\ln\{(M)_0/(M)_t\}$ as ordinate. Thus, this reaction appears to qualitatively

resemble the conventional polymerization of styrene by perchloric acid in chlorinated solvents.

If a termination reaction, unimolecular in active center concentration, was present in this system, the kinetic rate equation for the increase in active center concentration could be expressed as:

$$\frac{d(M^*)}{dt} = -k(M^*) + i \quad (98)$$

where i is the current in Faradays per second, (M^*) is the concentration of active centers and k is the rate constant for the termination reaction. Rearranging this equation:

$$\frac{d(M^*)}{dt} + k(M^*) = i$$

Consider $\frac{d}{dt}\{e^{kt}(M^*)\} = e^{kt}\left\{\frac{d(M^*)}{dt} + k(M^*)\right\}$

$$= ie^{kt}$$

Therefore $e^{kt}(M^*) = \int_0^t ie^{kt} dt$

and $(M^*) = ie^{-kt} \int_0^t e^{kt} dt$

$$= (ie^{-kt}) \left(\frac{e^{kt} - 1}{k} \right)$$

$$= \frac{i}{k} (1 - e^{-kt})$$

Substituting this equation for the active center concentration into the expression for the rate of decrease in monomer concen-

tration we have:

$$-\frac{d(M)}{dt} = k_p (M^*) (M) = \frac{ik_p}{k} (1 - e^{-kt}) (M)$$

Rearranging $-\frac{d(M)}{(M)} = \frac{ik_p}{k} (1 - e^{-kt}) dt$

On integration from $t=0$ and the initial monomer concentration, $(M)_0$, to $t=t$ and the monomer concentration at time t , $(M)_t$, we have:

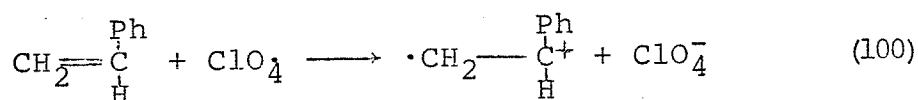
$$\ln \frac{(M)_0}{(M)_t} = \frac{ik_p}{k} \left(t + \frac{e^{-kt} - 1}{k} \right) \quad (99)$$

Therefore, the presence of a termination reaction would have necessitated the dependence of the integrated rate equation on a much more complicated function of time than was observed. Therefore, no termination of active centers occurred in this system if initiation was instantaneous on current passage.

The electroinitiated character of this polymerization is beyond question. The absence of a significant amount of polymer in blank experiments demonstrated that polymer formation did not occur before current had passed. Moreover, the precise control of the current over the course of the polymerization showed that the reaction did not result from initiation by some component in solution after the impurities had been removed by the passage of current. Although an electric field was applied across the solution between the electrodes during the entire polymerization process, an acceleration

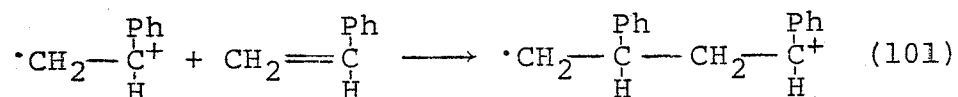
effect of the electric field (119) could not have accounted for the increase in the rate of reaction as current was passed. It is, in fact, unlikely that the electric field could have affected the rate of propagation at all since the proportion of the total anolyte volume between the electrodes was very small and the maximum electric field applied in any of these experiments was 4 volts/cm., much weaker than the fields employed by Sakurada, Ise and coworkers (46,47,48,49, 50).

The mechanism of the primary electrode reaction at the anode was not elucidated but it likely involved the oxidation of a perchlorate ion to a perchlorate radical or the direct oxidation of the monomer to a propagating radical-cation. Again an electrolytically formed perchlorate radical could either abstract a hydrogen atom to form perchloric acid as initiator or oxidize the monomer to form a radical-cation:



The possibility of the formation of radical-cations in the electrolysis was again supported by the observation of a green colour, similar to that of conventionally produced radical-cations, across the inner face of the anode. Furthermore, the absence of an insoluble anodic coating may be an indication that crosslinking or degrading hydrogen atom abstractions did not occur in the initiation process.

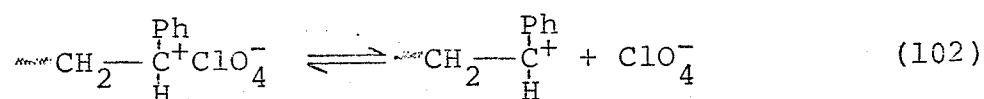
If radical-cations were formed at the anode, they may have dimerized to form a difunctional propagating species or they may have added monomer to form separated free radical and cationic or styryl perchlorate ester ends:



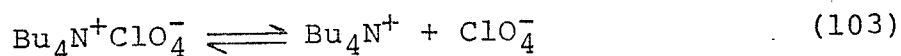
Unlike isobutyl vinyl ether, styrene can also polymerize by free radical mechanisms. Hence, the possibility exists that besides the cationic or pseudocationic propagation, free radical addition of monomer may have occurred. However, electroinitiated free radical polymerizations are much less efficient and much slower than acid polymerizations of this monomer and therefore any free radical addition would probably be negligible. Furthermore, because the reaction obeys the kinetic relationship of Equation (69), no significant amount of termination of the effective active centers occurred. Although some electroinitiated free radical polymerizations have exhibited polymerization for hours after the termination of current passage apparently due to long-lived free radicals (66,67) the heterogeneity of these systems was probably responsible for the absence of a rapid bimolecular termination reaction (71). In all systems studied in the work discussed here, organic, homogeneous solutions were used and free radical active centers would have been terminated during the course of the reaction. Therefore, within the ex-

perimental error in this electroinitiated polymerization of styrene, effectively all the polymerization must occur through non-free radical active centers.

With any of the possible modes of reaction shown above, the net result would have been the formation of polystyryl carbonium ions with perchlorate counterions or propagating perchlorate esters of polystyryl carbonium ions. Thus, the propagating species were probably identical to those formed in the perchloric acid polymerization of styrene in methylene chloride solution, investigated by Gandini and Plesch (51,52). However, in the conventional polymerization, the propagation rate constant at 0°C. was found to be 2.65 liters per mole-sec. with an activation energy of $E_p = 11.6 \pm 0.2$ kcal per mole. These values differ considerably from the values $k_p = 0.50$ liters per mole-sec. at 0°C. and $E_p = 7.6$ kcal per mole found in the electroinitiated reaction. The reasons for this discrepancy have not been elucidated in this work. The principal difference in the electroinitiated system was the presence of the salt. On a carbonium ion theory of propagation, the presence of an excess of perchlorate anions in solution would reverse the equilibrium between ion pairs and free ions in the direction of ion pairs:



Because a propagation reaction through free carbonium ions occurs faster than propagation through ion pairs, the rate of polymerization and therefore the propagation rate constant would be lowered. The much lower activation energy in the electroinitiated polymerization could be explained by a positive enthalpy of dissociation of the salt ion pair:



$$K = \frac{(\text{Bu}_4\text{N}^+)(\text{ClO}_4^-)}{(\text{Bu}_4\text{N}^+\text{ClO}_4^-)} \quad (104)$$

The concentration of free perchlorate ions would increase with temperature causing the lowering of the rate constant by the free perchlorate ions to become more effective at higher temperatures, resulting in a lower observed activation energy for the polymerization. However, it has been well documented (123) that the equilibrium constants for ion-ion pair equilibria in methylene chloride solution increase with falling temperatures, i.e., have a negative heat of dissociation. As a result, ionic equilibria cannot be invoked to explain the discrepancy.

A wastage of electrolytically produced perchlorate radicals through a reaction with some constituent of the solution which does not produce active centers could provide a plausible explanation of the rate constants found for this electroinitiated system. If this wastage reaction possessed

a higher activation energy than the reaction producing the active centers, the low activation energy for the electro-initiated polymerization could be explained. However, this study produced no evidence about the character of any possible wastage reactions.

(ii) The Tetrabutylammonium Tetrafluoroborate - Styrene System

As in the cationic electropolymerization of styrene with the perchlorate salt, the sigmoid-shaped curves obtained using tetrabutylammonium tetrafluoroborate salt as the electrolyte showed that the concentration of initiator increased as the current was passed through the solution. However, the irreproducibility of the reaction curves shown in Figure 22 and the curved lines obtained in the plots shown in Figure 25 demonstrated that the assumptions successfully applied to the cationic electropolymerization of styrene with the perchlorate salt did not apply to the electropolymerization of styrene with tetrabutylammonium tetrafluoroborate as the electrolyte.

This behaviour was very probably due to impurities in the reaction medium. These impurities may have reacted with and terminated the active centers. The concentration of these impurities would have diminished as more current was passed allowing the reaction to accelerate. The presence of variable amounts of this impurity in solution would explain

the difference in shape between curves for reactions run at identical currents, such as curves a and b of Figure 22.

It is also possible that an impurity acted as a cocatalyst with boron trifluoride formed at the anode. If this impurity also inhibited the reaction at lower catalyst concentrations, the rate at any time would be a function of both the total amount of catalyst produced and also the cocatalyst-catalyst ratio as explained on page 12. In that case, the difference between curves a and b in Figure 22 could have resulted from different initial concentration of the cocatalyst impurity.

The possibilities for anodic initiator-producing reactions in the cationic polymerization of styrene with the tetrafluoroborate salt are similar to those suggested for the polymerization of isobutyl vinyl ether with this salt. Besides monomer oxidation processes, either directly at the anode or through a tetrafluoroborate radical intermediate, hydrogen atom abstractions such as those suggested in reactions (73) and (74) may have produced the active species or the initiator. The production of insoluble granular material may be an indication of the presence of crosslinking or degrading hydrogen atom abstraction reactions at the electrode.

(iii) The Tetrabutylammonium Hexafluorophosphate Styrene System

The sigmoid curve shown in Figure 23 demonstrated that

for the electropolymerization of styrene with tetrabutylammonium hexafluorophosphate the concentration of active centers in the anolyte solution again increased as current was passed through the solution. However this system appeared even more sensitive to impurities than the tetrafluoroborate-styrene polymerization system as virtually no polymerization would occur during the induction current period while the reaction accelerated relatively suddenly when the impurities were eliminated by reaction with the initiator or with active centers produced by the initiator.

The sudden onset of polymerization and buildup of active centers is illustrated by the kinetic plot in Figure 24. According to this plot of $\ln\{(M)_0/(M)_\infty\}$ against t^2 , very little of the reaction occurred until about $t^2 = 4.0 \times 10^6 \text{ sec}^2$ after which the reaction accelerated rapidly. The straight line obtained after this point suggests that in this region the reaction obeyed the assumptions used in deriving Equation (69). If the reaction did obey these assumptions, the reaction rate was first order in both monomer and catalyst concentration and no termination took place after about $t^2 = 4.0 \times 10^6 \text{ sec}^2$. However, this behaviour is also compatible with a system in which the rate of production of active centers from anodically produced catalyst is equal to their rate of termination. Although this result serves as a tentative indication that the reaction possessed these characteristics,

it must be admitted that the amount of data obtained for this system is scant and that a more complete study would be necessary to definitely establish these characteristics.

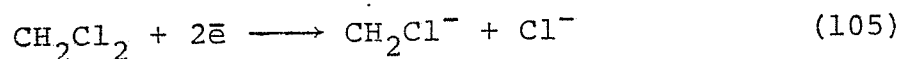
The catalyst-producing reactions suggested in Equations (92) and (93) for the polymerization of isobutyl vinyl ether with this salt are also applicable to the corresponding polymerization of styrene. Moreover, the oxidation of the monomeric double bonds to radical-cationic species is again a possibility, although no transient green colour was noted at the electrode. The formation in this system of an insoluble residue on the anode may again be an indication of crosslinking or degrading reactions, possibly hydrogen atom abstractions occurring at the anode.

Cathodic Reaction

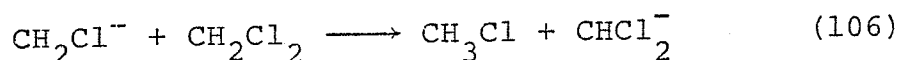
The cathodic reaction produced substances which destroyed active centers of polymerization formed at the anode. These substances may have arisen from the reduction of the salt, the monomer or the tetrabutylammonium cation.

Wawzonek and Duty (124) studied the electrolytic reduction of chlorinated hydrocarbons in dimethylformamide and acetonitrile using tetrabutylammonium bromide as the electrolyte. The reduction of methylene chloride to methyl chloride occurred before the salt discharge in dimethylformamide but not in acetonitrile. A possible reduction scheme

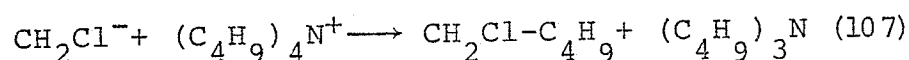
for methylene chloride is:



The carbene anions and/or the chloride ions could have reacted with and terminated the electrophilic active centers. The carbene anions could also have abstracted protons from the methylene chloride to form another terminating carbanion species:

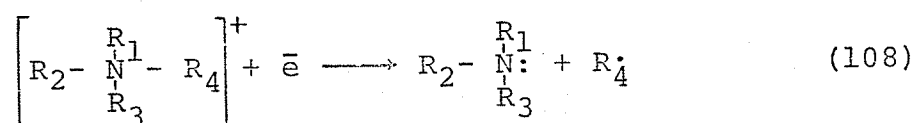


or reacted with the tetrabutylammonium cation:



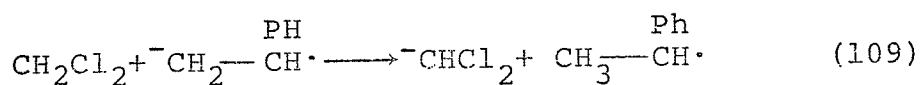
producing tributylamine, a chain-terminating species.

The reduction of the tetrabutylammonium ion would produce a substance capable of destroying electrophilic active centers. Finkelstein et al. (125) reported the reduction of quaternary ammonium cations at aluminum and platinum electrodes in the highly aprotic solvent, N,N-dimethylacetamide. The products were invariably an amine and a hydrocarbon. For example, the reduction of benzyldimethylanilinium trifluoroacetate in N,N-dimethylacetamide produced dibenzyl and dimethylaniline. The reaction proposed was:

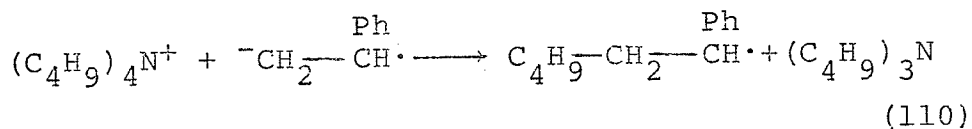


The formation of tri-n-butylamine by the cathodic reduction of the tetra-n-butylammonium cation in dimethylformamide has been verified by gas chromatography (126). The formation of this amine on current reversal in cationic initiated polymerization would result in the destruction of one active center for each molecule of amine formed and therefore for each electron passed.

A final possibility for the cathodic reaction would involve the electrolytic reduction of the monomeric double bond to form a radical-anion which would be basic enough to eliminate electrophilic active centers. This reaction is more likely for the styrene monomer than for isobutyl vinyl ether as the latter molecule has a relatively negative double bond. The anionic species would not likely exist for long in the medium used as it probably would have either abstracted one of the relatively acidic methylene chloride protons:



or reacted with the tetra-n-butylammonium cation to produce tri-n-butylamine:



The destruction of living anions by this cation has been observed (127). Either carbanionic or tri-n-butylamine species

would terminate electrophilic active centers.

Whichever component of the reaction mixture was reduced it is clear that the passage of one electron would result in the destruction of a maximum of one active center. Therefore, because it was observed that the cathodic reaction was at least 50% more efficient than the anodic reaction, it appears that the forward current did not produce active centers at 100% efficiency.

CONCLUSION

A unique feature of all electroinitiated polymerizations is the possibility of achieving a greater degree of control over rates and in some cases the molecular weights and molecular weight distributions than is possible in the corresponding conventionally initiated polymerizations. It is likely that in electroinitiated cationic addition polymerization, control will be restricted to the rates only, even in systems in which no termination occurs ("living" cationic polymerizations), because chain transfer, a reaction over which the electric current can have no control, normally is the prime factor regulating the molecular weights. Although Breitenbach's report on electroinitiated cationic polymerization (101) was indicative of the possibilities of these reactions, his results were not thorough. The work reported here constitutes the first detailed study of the kinetics and of the control features of electroinitiated cationic polymerization.

This work has demonstrated that the degree of control of the electric current over the reactions varied greatly from system to system. These differences appeared to depend on both the monomer and salt chosen. The degree of control was greatest for both styrene and isobutyl vinyl ether when tetrabutylammonium perchlorate was used as electrolyte. With

styrene, the control imposed by the forward current was as great as has ever been found for any electroinitiated polymerization system. Reproducible rate constants have been found along with an activation energy which allows the estimation of rate constants over a narrow temperature range. Although neither the rate constant at 0°C. nor the activation energy compared with the values found for the conventional perchloric acid polymerization system, they can be regarded as apparent values for the electroinitiated system under the conditions used. The discrepancy may have arisen from a wastage of the primary electrode products (perhaps the perchlorate radical) by reactions, of an as yet unknown character, not yielding initiators or active centers. Alternatively, the presence of electrochemical side reactions may have been responsible. Whatever the reactions, the difference in rate constants at 0°C. would have required the wastage of 80% of the current passed at this temperature with an increasing degree of wastage as the temperature was increased, presumably because the side reactions possessed a higher activation energy than the reaction producing active centers. The observation that the efficiency of the cathodic reaction in producing terminating agents was a minimum of approximately 50% greater than the forward reaction supports this concept. However, it must be emphasized that the apparent wastage of current cannot be due to termination after active centers have

been produced as this would preclude the observed dependence of the reaction on the kinetic relation given by equation (69). This work does emphasize that unlike electroinitiated anionic polymerization (97,98) where one electron in the forward direction produces an active center and one electron in the reverse direction destroys an active center, the amount of current passed in electroinitiated cationic polymerization is not necessarily a direct measure of the number of active centers produced.

The control over polymerizations using tetrabutylammonium perchlorate was not as great when isobutyl vinyl ether was used as the monomer. This was partially related to the rapidity of the reaction but was primarily due to the effect of termination reactions. However, under constant conditions of preparation and reaction, the importance of the termination appeared to be reproducible, allowing predictable initial rates and final yields.

The treatment of the tetrabutylammonium perchlorate salt in the polymerizations of isobutyl vinyl ether and styrene were identical although substances (possibly water) remaining in the salt did not affect the styrene polymerization but caused termination in the isobutyl vinyl ether polymerization. This lends support to the possibility that the active centers in the styrene system were equivalent to those formed in the perchloric acid polymerization of styrene

which are also unaffected by the presence of water. However, even small amounts of water would be expected to cause termination, as was found in the isobutyl vinyl ether polymerization with the perchlorate salt, if the active centers were true carbonium ions. Therefore, this difference between the two monomers may have been an indication that the isobutyl vinyl ether polymerization occurred through carbonium ion active centers while the styrene polymerization proceeded through pseudocationic active centers as in the perchloric acid polymerization of styrene (52). This situation would parallel the polymerizations of styrene (128) and isobutene (27) by titanium tetrachloride and water in methylene chloride which appear to exhibit pseudocationic and true cationic behaviour, respectively.

The possibilities for reactions involved in electrical initiation with the perchlorate salt as the electrolyte were relatively simple because the oxidation of the perchlorate anion was very unlikely to produce a Lewis acid catalyst. On the contrary, the oxidation of either the tetrafluoroborate or the hexafluorophosphate anions was not so clear-cut because of the possibility of producing Lewis acids. With each of these anions a cocatalyst, hydrogen fluoride, may have been produced in equivalent amounts or the Lewis acid may have formed a complex with an impurity such as water, present in the solution. The former case would probably be kinetically

equivalent to the production of a protonic acid, as with the perchlorate salt, and the counterions would be the tetrafluoroborate and the hexafluorophosphate anions in the respective systems. As explained in the Introduction, a Lewis acid forming a catalytic complex with a cocatalyst such as water in solution would probably result in a very complex kinetic behaviour as not only the catalyst concentration but the catalyst-cocatalyst ratio would change throughout the passage of current. The variable shape of the reaction curves obtained for the electropolymerization of styrene with tetrabutylammonium tetrafluoroborate as the electrolyte may result from such a cocatalytic behaviour.

The results of this work have indicated that the key to a rigorous study of electroinitiated cationic polymerization lies principally in the character and purity of the electrolytic salt. The less nucleophilic and more inert the anion of the salt, the greater the chance that a "living" cationic polymerization will result on electrolysis. The perchlorate anion is the most advantageous found to date while the iodide ion represents the other end of the spectrum: an ion which can combine with the active center to form a stable, inactive bond before polymerization can occur. The tetrafluoroborate and hexafluorophosphate anions possess the required stability and poor nucleophilicity. It has been shown in this work that the observed behaviours of the polymerization

of styrene with the hexafluorophosphate salt and of the polymerization of isobutyl vinyl ether with the tetrafluoroborate salt are entirely compatible with "living" cationic character with no termination.

In many studies of conventional cationic polymerizations, reactions have been followed by dilatometry. Although this method allows a great degree of experimental rigour, it was found virtually impossible to apply this method to the systems studied in this work because of the necessity of dividing the cell into two compartments. However, the use of silver salts such as silver perchlorate and silver tetrafluoroborate would eliminate the necessity of a sintered glass divider because the cathodic reaction would simply produce metallic silver. This metal would not interfere with the electrophilic active centers formed at the anode. The use of a dilatometer would allow the reactions to be followed without sampling and therefore the reactions could be carried out under rigorous high vacuum conditions. Although these salts when wet will polymerize monomers without the passage of current, the added purification capabilities with the dilatometer may allow a more thorough drying of the salt.

This work has demonstrated that under the proper conditions, a large degree of control over the rate of reaction is possible in electroinitiated cationic polymerizations and has provided some insight into the character of these reac-

tions. The kinetic behaviour of a number of electroinitiated cationic systems has been elucidated. Furthermore, the suitability of hexafluorophosphate salts as electrolytes for these reactions has been discovered.

Although considerable speculation has been given on the character of the reactions producing active centers at the anode, it must be admitted that the evidence submitted here is not sufficient to establish the nature of these reactions. Although the transient green colour produced at the anode in many of these systems was very similar to the colours of radical-cations produced by antimony pentachloride (115), it may also have been due to other species such as to charge-transfer complexes between the monomer and electron acceptor substances formed at the anode. In future work on electroinitiated cationic polymerization, a great deal of attention should be given to the primary electrode processes and the transient intermediates that are formed by them.

REFERENCES

1. Long, F.A. and M.A. Paul, Chem. Rev., 57, 971 (1957).
2. Boyd, R.H., R.W. Taft, Jr., A.P. Wolf and D.R. Christman, J. Am. Chem. Soc., 82, 4729 (1960).
3. Boyd, R.H., R.W. Taft, Jr., A.P. Wolf and D.R. Christman, J. Am. Chem. Soc., 82, 4732 (1960).
4. Burstall, M.L. and F.E. Treloar, in The Chemistry of Cationic Polymerization, P.H. Plesch, Ed., MacMillan, New York, 1963, p. 3.
5. Burstall, M.L. and F.E. Treloar, in The Chemistry of Cationic Polymerization, P.H. Plesch, Ed., MacMillan, New York, 1963, p.241.
6. Jordan, D.O. and F.E. Treloar, J. Chem. Soc., 737 (1961).
7. Colclough, R.O. and F.S. Dainton, Trans. Faraday Soc., 54, 886 (1958).
8. Brown, H.C. and W.J. Wallace, J. Am. Chem. Soc., 75, 6279 (1953).
9. Roberts, R.M., Chem. Eng. News, 43 (4), 96 (1965).
10. Kennedy, J.P. and A.W. Langer, Jr., Fortschr. Hochpolymer Forsch., 3, 508 (1964).
11. Szwarc, M., M. Levy and R. Milkovich, J. Am. Chem. Soc., 78, 2656 (1956).
12. Scott, H., G.A. Miller and M.M. Labes, Tetrahedron Letters, 1963, 1073.

13. Bawn, C.E.H., C. Fitzsimmons and A. Ledwith, Proc. Chem. Soc. 1964, 391.
14. Fleischfresser, B.E., W.J. Cheng, J.M. Pearson and M. Szwarc, J. Amer. Chem. Soc., 90, 2172 (1968).
15. Penczek, S., J. Jagur - Grodzinski and M. Szwarc, J. Amer. Chem. Soc., 90, 2174 (1968).
16. Gossi, Y., Kagaku Kyoakaishi 25 (5), 381 (1967); CA 68: 13406r.
17. Longworth, W.R. and P.H. Plesch, Proc. Chem. Soc., 1958, 117.
18. Olah, G.A., H.W. Quinn and S.J. Kuhn, J. Amer. Chem. Soc., 82, 426 (1960).
19. Pepper, D.C. and P.J. Reilly, J. Polymer Sci., 58, 639 (1962).
20. Kursanov, D.N., M.E. Volpin and I.S. Akren, Doklady Akad. Nauk. SSSR, 120, 531 (1958).
21. Eley, D.D. and J. Saunders, J. Chem. Soc., 1952, 4167.
22. Kanoh, N., T. Higashimura and S. Okamura, Makromol. Chem., 56, 65 (1962).
23. Trifan, D.S. and P.D. Bartlett, J. Amer. Chem. Soc., 81, 5573 (1959).
24. Okamura, S., N. Kanoh and T. Higashimura, Makromol. Chem., 47, 19 (1961).
25. Eley, D.D. and J. Saunders, J. Chem. Soc., 1954, 1668.

26. Winstein, S., C. Clippinger, A.H. Fainberg, R. Heck and G.C. Robinson, J. Amer. Chem. Soc., 78, 328 (1956).
27. Biddulph, B.H., P.H. Plesch and P.P. Rutherford, J. Chem. Soc., 1965, 275.
28. Kanoh, N., A. Gotoh, T. Higashimura and S. Okamura, Makromol. Chem., 63, 115 (1963).
29. Imanishi, Y., T. Higashimura and S. Okamura, Chem. High Polymers, Japan, 19, 154 (1962).
30. Plesch, P.H., J. Polymer Sci., 12, 481 (1954).
31. Imanishi, Y., S. Matsuchita, T. Higashimura and S. Okamura, Makromol. Chem., 70, 68 (1964).
32. Plesch, P.H., J. Chem. Soc., 1953, 1653.
33. Kennedy, J.P., I. Kirshenbaum, R.M. Thomas and D.C. Murray, J. Polymer Sci. A, 1 331 (1963).
34. Hayes, M. and D.C. Pepper, Proc. Roy. Soc., A263, 63 (1961).
35. Plesch, P.H., Ed., Cationic Polymerization and Related Complexes, Academic Press, New York, 1954, p.75.
36. Olah, G.A., H.W. Quinn and S.J. Kuhn, J. Am. Chem. Soc., 82, 426 (1960).
37. Eley, D.D. and J. Saunders, J. Chem. Soc., 1954, 1668.
38. Fontana, C., J. Chem. Soc., 1954, p.121.
39. Bamford, C.H., W.G. Barb, A.D. Jenkins and P.F. Onyon, Kinetics of Vinyl Polymerization by Radical Mechanisms, Butterworths, London (1958).

40. Fontana, C.M. and J. Kidder, J. Amer Chem. Soc., 70, 3745 (1948).
41. Plesch, P.H., J. Chem. Soc., 543 (1950); 3355 (1952).
42. Burstall, M.L. and F.E. Treloar, in The Chemistry of Cationic Polymerization, P.H. Plesch, Ed., MacMillan, New York, 1963, p.120.
43. Wien, M., Ann. Physik 83 (1927) 327.
44. Onsager, L., J. Chem. Phys., 2, 1934, 599.
45. Sukurada, I., N. Ise, H. Hirohara and T. Makino, J. Phys. Chem., 71, 3711 (1967).
46. Sakurada, I., N. Ise and T. Ashida, Makromol. Chem., 95 (1966), 1.
47. Sakurada, I., N. Ise, Y. Tanada and Y. Hayashi, J. Poly. Sci. A-1-4, 2801 (1966).
48. Sakurada, I., N. Ise and S. Hori, Kobunshi Kagaku, 24, 145 (1967); CA 68: 13449g.
49. Sakurada, I., N. Ise and Y. Hayashi, J. Makromol. Chem., 1967, A1, 1039.
50. Sakurada, I., N. Ise and Y. Tanaka, Polymer, 8, 625 (1967).
51. Gandini, A. and P.H. Plesch, Proc. Chem. Soc., 1964, 240.
52. Gandini, A. and P.H. Plesch, J. Chem. Soc. 1965, 4826.
53. Am. Chem. Soc. Div. Polymer Chem., Polymer Preprints, 7, No. 2, 492 (1966).
54. Deno, N.C. Progr. Phys. Org. Chem. 2, 129 (1964).

55. Olah, G.A., J. Am. Chem. Soc. 86, 932 (1964).
56. Olah, G.A., M.B. Comisarow, C.A. Cupas and C.U. Pittman, J. Am. Chem. Soc. 87, 2997 (1965).
57. Bywater, S., A.F. Johnson and D.J. Worsfeld, Can. J. Chem. 42, 1255 (1964).
58. Higashimura, T., N. Kanoh and S. Okamura, J. Macromol. Chem., 1, 109 (1966).
59. Bywater, S. and D.J. Worsfeld, Can. J. Chem., 44, 1671 (1966).
60. Bertoli, V. and P.H. Plesch, Chem. Commun. 625 (1966).
61. Gandini, A. and P.H. Plesch, Eur. Polymer J., 4, No.1, 55 (1968).
62. Dineen, E., T.C. Schwan and C.L. Wilson, J. Electrochem. Soc., 96, 226 (1949).
63. Goldschmidt, S. and E. Stockel, Chem. Ber., 85, 630 (1952).
64. Tsvetkiv, N.S., Polymer Sci. (USSR), 3, 570 (1962).
65. Tsvetkov, N.S. and Z.F. Glotova, Polymer Sci. (USSR), 5, 49 (1964).
66. Parravano, G., J. Am. Chem. Soc., 73, 628 (1951).
67. Kern, W. and H. Quast, Makromol. Chem., 10, 202 (1953).
68. Fedorova, A.I., I.V. Shelepin and N.B. Moiseeva, Dokl. Akad. Nauk. Uz. SSR, 1, 138, 165 (1961).
69. Fedorova, A.I., K.-T.Li and I.V. Selepin, Russ. J. Phys. Chem. 38, 920 (1964).

70. Shelepin, I.V. and A.I. Fedorova, Zhur. fiz Khim., 38,
2676 (1964).
71. Funt, B.L., Makromol. Rev., Interscience, New York, 1967,
p.38.
72. Kolthoff, I.M. and L.L. Ferstandig, J. Polymer Sci. 6,
563 (1951).
73. Friedlander, H.Z., S. Swann and C.S. Marvel, J. Electro-
chem. Soc., 100, 408 (1953).
74. Smith, W.B. and H.G. Gilde, J. Am. Chem. Soc., 81, 5325
(1959).
75. Smiht, W.B. and H.G. Gilde, J. Am. Chem. Soc., 82, 659
(1960).
76. Gandini, A. and P.H. Plesch, Eur. Polymer J., 4, No.1,
42 (1968).
77. Hnatowich, D., M.Sc. thesis, University of Manitoba(1964).
78. Funt, B.L. and K.C. Yu., J. Polymer Sci., 62, 359 (1962).
79. Funt, B.L. and F.D. Williams, Polymer Letters, 1, 181
(1963).
80. Goerrig, D., H. Jonas and W. Moschel, West German Pat.
935, 867 (1955).
81. Goerrig, D. and H. Jonas, West German Pat. 937, 919 (1956).
82. Tsvetkov, M.S. and E.P. Koval'chuk, Uisn. L'viv Derzh.
Univ. Ser. Khim., 8, 24-7 (1965); CA66:65878z.
83. Tsvetkov, M.S. and E.P. Koval'chuk, Uisn. L'viv Derzh.
Univ. Ser. Khim., 9, 72-5 (1967); CA66: 6587.

84. Yang, J.Y., W.E. McEwen and J. Kleinberg, J. Am. Chem. Soc., 79, 5833 (1957).
85. Breitenbach, J.W. and H. Gabler, Monatsch., 91, 202 (1960).
86. Breitenbach, J.W., C. Srna and O.F. Olaj, Makromol. Chem., 42, 171 (1960).
87. Funt, B.L. and F.D. Williams, J. Polymer Sci. A, 2, 865 (1964).
88. Funt, B.L. and S.W. Laurent, Can. J. Chem., 42, 2728 (1964).
89. Funt, B.L. and S.N. Bhadani, Can. J. Chem., 42, 2733 (1964).
90. Funt, B.L. and S.N. Bhadani, J. Polymer Sci. A, 4191 (1965).
91. Murphy, M., M.G. Carangelo, M.B. Ginaine and M.C. Markham, J. Polymer Sci., 54, 107 (1961).
92. Baizer, M.M., J. Electrochem. Soc., 111, 215 (1964).
93. Baizer, M.M. and J.D. Anderson, J. Org. Chem., 30, 1351 (1965).
94. Laurin, D. and G. Parravano, J. Polymer Sci., B, 4, 797 (1966).
95. Szwarc, M., Nature, 178, 1168 (1956).
96. Yamazaki, M., S. Nakahama and S. Kambara, J. Polymer Sci. B, 3, 57 (1965).
97. Funt, B.L., S.N. Bhadani and D. Richardson, J. Polymer Sci. A-1, 4, 2871 (1966).

98. Funt, B.L., S.N. Bhadani and D. Richardson, Can. J. Chem., 44, 711 (1966).
99. Funt, B.L. and H. Kubota, unpublished results.
100. Yamazaki, N., I. Tanada and S. Nakahama, Kogyo Kagaku Zasshi, 70, (11), 1978 (1967); CA68: 115133s.
101. Brectenbach, J.W. and C. Srna, Pure Appl. Chem., 4, 245 (1962).
102. Eley, D.D. and A.W. Richards, Trans. Far. Soc., 45, 425 (1949).
103. Salomon, G., J. Chem. Soc., 1954, 62.
104. Burton, H. and P.F.G. Praill, J. Chem. Soc., 1953, 837.
105. Gilch, H. and D. Michael, Makromol. Chemie, 99, 103 (1966).
106. Gilch, H.G., J. Polymer Sci., 4, 1351 (1966).
107. Covitz, F.H., J. Amer. Chem. Soc., 89, 5403 (1967).
108. Chapoval, G.S., E.M. Skobeta and N.P. Markova, Dokl. Akad. Nauk SSSR, 173 (2), 392 (1967); CA 68, (11894d).
109. Lund, H., Acta Chem. Scand., 11, 1323 (1957).
110. Loveland, J.W. and G.R. Dimeler, Anal. Chem., 33, 1196 (1961).
111. Pysh, E.S. and W.C. Yang, J. Am. Chem. Soc., 85, 2124 (1963).
112. Peover, M.E., "Electroanalytical Chemistry - A Series of Advances", Vol. II, A.J. Bard, Ed., Marcel Dekker, Inc., New York, N.Y., 1967, Chapter 1.

113. Peover, M.E. and B.S. White, J. Electroanal. Chem.,
13 (1967) 93.
114. Phelps, J., K.S.V. Santhanam and A.J. Bard, J. Am. Chem.
Soc., 89, 1752 (1967).
115. Lewis, I.C. and L.S. Singer, J. Chem. Phys., 43, 2712
(1965).
116. Maki, H. and D.H. Gaske, J. Chem. Phys., 1959, 30, 1356.
117. Billon, J.P., J. Electroanal. Chem., 1960, 1, 486.
118. Billon, J.P., Bull. Soc. Chim. 1962, 863.
119. Private Communication, N. Ise.
120. "Organic Chemistry of Synthetic High Polymers", Robert
W. Leng, Interscience, New York, 1967, p.488.
121. Kennedy, J.P. and R.M. Thomas, J. Polymer Sci., 46 233
(1960).
122. Kushenbaum, I., J.P. Kennedy and R.M. Thomas, J. Polymer
Sci. A-1, 789 (1963).
123. Beard, J.H. and P.H. Plesch, J. Chem. Soc., 1964, 4879.
124. Wawzonek, S. and R.C. Duty, J. Electrochem. Soc. 188,
1135 (1961).
125. Finkelstein, M., R.C. Peterson and S.D. Ross, J. Amer.
Chem. Soc., 81, 2361 (1959).
126. Gray, D.G., Ph.D. Thesis, University of Manitoba (1968).
127. Bhadani, S.N., Ph.D. Thesis, University of Manitoba
(1966).
128. Longworth, W.R., C.J. Panton and P.H. Plesch, J. Chem.
Soc., 1965, 5579.