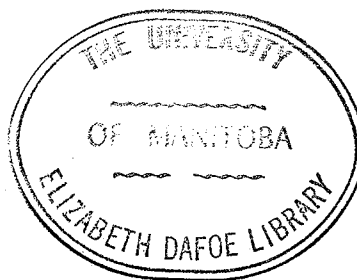


ELECTROLYTICALLY INITIATED LIVING  
ANIONIC POLYMERIZATION

A Thesis  
submitted to  
The Faculty of Graduate Studies and Research  
The University of Manitoba  
in  
Partial Fulfilment  
of  
the Requirement for the Degree  
Doctor of Philosophy

by  
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Winnipeg, Canada  
August, 1966



TO MY PARENTS

## ACKNOWLEDGEMENTS

The author expresses sincere thanks and gratitude to Professor B. L. Funt for his excellent supervision, stimulating discussion and constructive criticism, and for arranging financial assistance.

The author also wishes to thank Dr. D. Richardson for his valuable suggestions and advice.

The staff of both the Science and Technical Laboratory and Physics Department are thanked for the construction of the electrical and mechanical equipment used in the research.

The assistance of Mr. G. Epp and Mr. R. D. Luptak in the construction of glass apparatus is also gratefully acknowledged.

The author is indebted to Dr. A. W. Shaw and Dr. J. G. Balas, Shell Development Company, Emeryville, California for the determination of microstructure of the polyisoprene and to Water Associates Inc., for molecular weight distributions of the poly (alpha-methylstyrene).

The helpful comments of Mr. D. Gray and Mr. T. Blain were greatly appreciated.

## ABSTRACT

Electrolytically initiated polymerizations of unsaturated vinyl compounds were carried out in organic media employing quaternary ammonium and alkali organometallic salts as electrolytes.

Methylmethacrylate was polymerized at 25°C in solutions of dimethylformamide containing quaternary ammonium salts. The course of the reaction was controlled by an electrolytic current passed through the solution. Results over a wide range of initial monomer concentrations at seven selected constant currents served to delineate the dependence of polymer yield on the control parameters. Polymer formation was directly dependent on monomer concentration and on the square root of the impressed current. Different solvents were tested and of these, dimethylacetamide was found to provide the best reaction medium. Molecular weights of approximately 50,000 were obtained. They were independent of salt, current and monomer concentration, but were affected by the type of solvent and the temperature. Inhibitor and copolymerization studies favoured the anionic reaction mechanism.

When tetrahydrofuran solutions of styrene, isoprene and alpha-methylstyrene were electrolysed in the undivided cell polymeric living anions were generated at the cathode,

but were killed by the species formed at the anode. No such termination occurred in the divided cell. Electrolysis of solutions of alpha-methylstyrene in tetrahydrofuran resulted in the formation of the characteristic red color of the living anions in the catholyte while the anolyte was colorless. The red color persisted for a longer period. The ultraviolet absorption spectra of the living anion solutions were measured and the maximum absorbance occurred at 340 m $\mu$ . The increase in absorbance of the solution was strictly proportional to the charge transferred at the electrode, and was independent of the electrolyte for NaAl(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>, NaB(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> and KB(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>. Mixing of the anode and cathode solutions resulted in a destruction of the living ends and a disappearance of the color, which could be regenerated by further electrolysis. Reversal of the polarity of the electrodes produced stoichiometric destruction of the living ends and a decrease in absorbance directly dependent on the charge transferred. The exact stoichiometric dependence furnished a means of estimating impurity levels, living anion concentrations, and optical extinction coefficients based on the number of Faradays passed through the solution.

For solutions of Li(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>B the living anion concentration decreased spontaneously on standing and because of this a linear relationship between absorbance and charge

transferred was not obtained. With tetrabutyl ammonium salts only a transient red color formed at the cathode and the color disappeared immediately in the solution. This was found to be due to interaction between the salt and living anion. Poly (alpha-methylstyrene) formed at  $-80^{\circ}\text{C}$  showed a narrow molecular weight distribution. The substance responsible for the deactivation of the living anions were found to be  $\text{Al}(\text{C}_2\text{H}_5)_3$  and  $\text{B}(\text{C}_6\text{H}_5)_3$  produced by anodic oxidation of the corresponding anions. The possible mechanisms of the formation of living anions and terminating species were discussed.

The living polyisoprene anions in tetrahydrofuran solutions of  $\text{Na}(\text{C}_6\text{H}_5)_4\text{B}$  and  $\text{NaAl}(\text{C}_2\text{H}_5)_4$  were produced electrolytically and the ultraviolet absorption spectra were measured. A spontaneous decrease of absorbance of living anion solutions after the cessation of electrolysis was observed. An electronic device was built which allowed the passage of intermittent electrical current to maintain a constant living anion population. The kinetics of polymerization were studied at constant living anion concentration in the divided cell. The result showed first order decay in monomer. The kinetic studies were also performed dilatometrically in the undivided cell. The polymerization rates were enhanced by increases in

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**CHAPTER I**

**INTRODUCTION**

## PREFACE

Electrolytic techniques, developed in the last few years, have provided a novel method of initiating polymerization which may proceed via anionic, cationic or free radical mechanisms. The work, presented in the thesis, is limited to anionic polymerizations since the previous studies made in this laboratory showed that these proceed at much higher electrical efficiencies and are more suitable for programming and control. The aim of the present research was to demonstrate that polymerization rates, molecular weights and concentration of initiating species could be controlled easily by the electrolytic technique.

In the first part of the thesis, some aspects of anionic polymerization have been discussed and a short review of electrolytically initiated anionic polymerization has been presented. The second chapter describes anionic polymerization of methyl methacrylate initiated electrolytically where polymer chain termination occurred preventing the formation of living polymer. In the third chapter, the electrolytic generation of living polymeric anions where chain termination is absent, has been discussed. Here the effects of anode products and electrolytes on living anions have been also shown.

Finally, in chapter four an electrolytic method of maintaining a constant population of growing polymeric anions is described.

## INTRODUCTION

### ANIONIC ADDITION POLYMERIZATION WITH A TERMINATION

Generally most addition polymerizations consist of three important basic steps, namely:

- (i) An initiation process producing reactive centers from which macromolecules are generated.
- (ii) A propagation or growth process in which monomeric molecules consecutively add to the active centers and eventually yield polymer.
- (iii) Finally the reactivity of the growing centers may be annihilated. This process is known as the termination of polymerization.

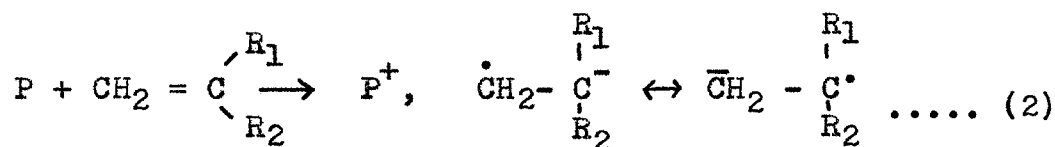
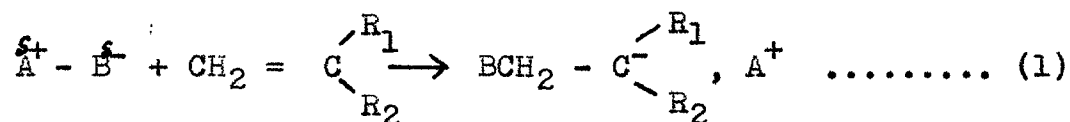
Alternatively the active center of a growing molecule may be transferred to another species. If the product of this transfer reaction is sufficiently reactive to continue the chain reaction, then it is known as a chain transfer process. The reactive centers which initiate the polymerization may be any one of the following species:

- (a) free radicals
- (b) carbanions
- (c) carbonium ions
- (d) co-ordination complexes (Ziegler-Natta type)

Because the present research work is mainly concerned with anionic processes, only anionic polymerization will be

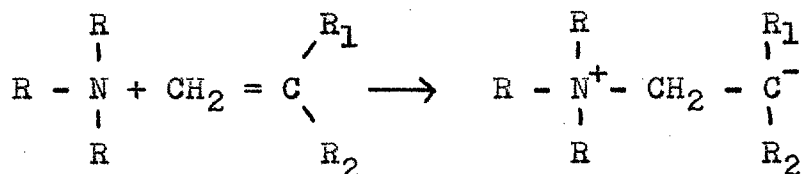
discussed here.

An anionic initiation process may occur in two important ways as represented by equations (1) and (2).



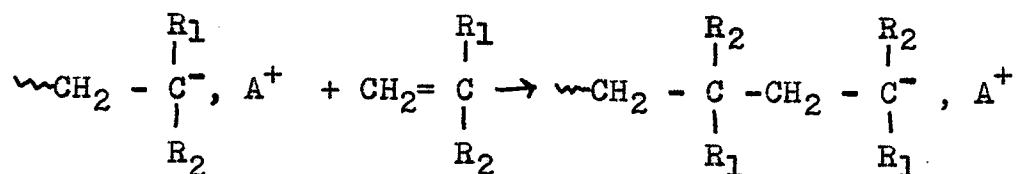
where  $R_1$  and  $R_2$  are electron withdrawing groups such as  $-CN$ ,  $-CO_2R$ ,  $-C_6H_5$  or unsaturated functional groups such as  $-CH=CH_2$  which will stabilize a negative charge by resonance or inductive charge distribution.  $\overset{\delta+}{A} - \overset{\delta-}{B}$  may be a covalent or ionic metal amide, alkoxide, metal alkyl or aryl or hydroxide depending on the nature of the monomer.  $P$  represents an electron transfer reagent such as an alkali metal which may donate an electron to the monomer double bond resulting in the formation of an anion-radical. This ion-radical process will be discussed, in detail, later.

A third type of anionic initiation which does not involve a counter ion seems possible.

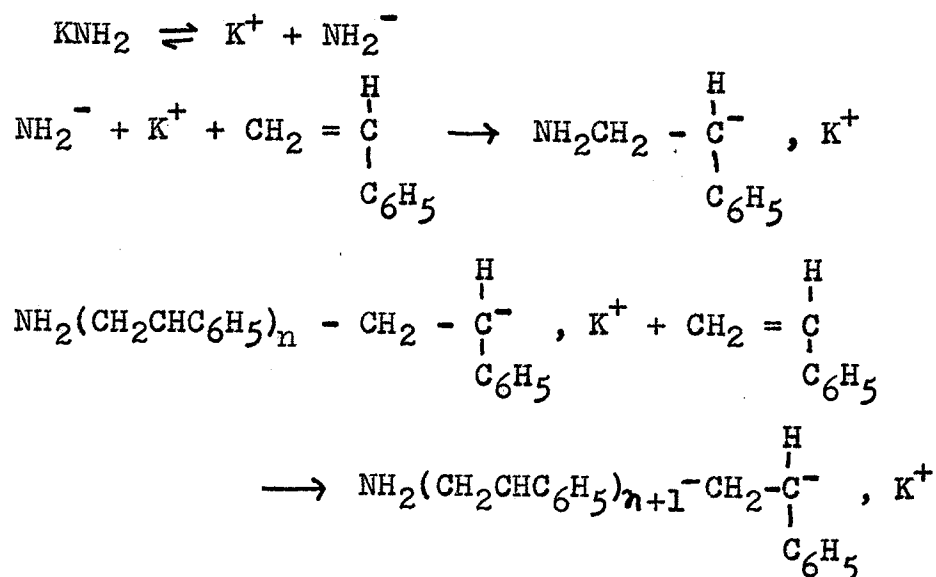


Lewis Base

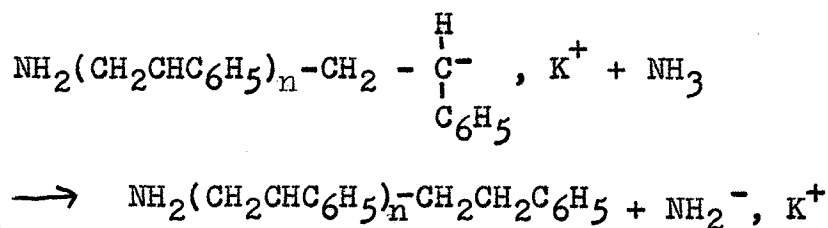
A Lewis base is capable of forming a new bond by means of its unshared electrons. However, this type of reactive center for the initiation of the polymerization is not yet known. The chain growth in an anionic polymerization proceeds classically as follows:



Here the polymerization of styrene by potassium amide in liquid ammonia (1,2) can be given as a specific example,

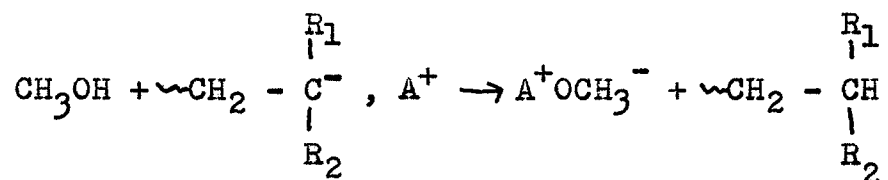
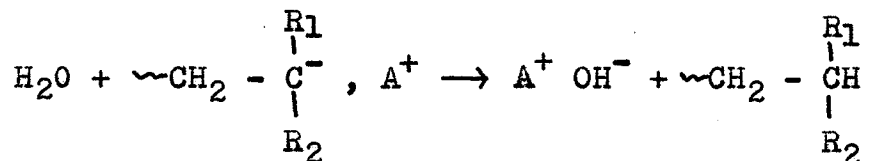


The transfer of a proton is a very common mode of termination in anionic polymerizations.

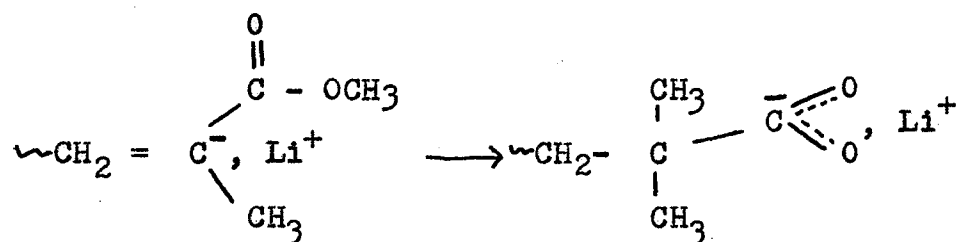


This type of termination reaction in the metal amide initiated polymerization of methyl methacrylate was also suggested (3). Similarly proton donating materials such as water, methanol or acid readily inhibit the growth of anionic polymerization.

The possible reaction takes place as follows (4):



Under certain conditions, termination may also proceed through an isomerization reaction of the carbanion (5).



In the methyl methacrylate polymerization with fluorenyl lithium at  $-60^\circ\text{C}$  in toluene it was proposed that cyclization of growing chains causes the formation of low molecular weight polymers (6,7). Termination or transfer reactions may also occur if the active ends of polymer chains undergo an irreversible reaction with solvent or monomer.



## ELECTROLYTICALLY INITIATED ANIONIC POLYMERIZATION

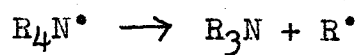
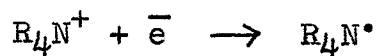
The basic differences among the various initiators which induce polymerization, either by a free radical, anionic or cationic mechanism, lie in their electronic configurations. Therefore, it appears, at least in principle, that a relatively simple way to generate them may be by an electron transfer from an electrode. The cathode can serve as an electron donor whereas the anode acts as an electron acceptor. This method offers an easy way to control formation of the initiating species and consequently the polymerization rate. Recently, therefore, the polymerization by electrochemical means has aroused considerable interest. A brief review of electrolytically initiated anionic polymerization will be presented.

A study of the electrolytic reactions of organic compounds began soon after the discovery of the electrolysis of water by Nicholson et al in 1800. By 1834 Faraday had realized the importance of using electric current to carry out synthesis or degradation of compounds. This method was not used in synthesis until after 1847, when Kolbe discovered that aliphatic hydrocarbons could be prepared by the electrolysis of the salt of aliphatic acids. The field has expanded greatly since that time and it is now possible to carry out synthesis by electrolytic reduction, oxidation, cathodic

coupling, anodic coupling, substitution, polymerization etc.

Although the majority of investigations have been confined to free radical polymerizations a significant number of reports of anionic polymerization by electrochemical means have appeared recently. The first anionic polymerization initiated electrolytically was reported by Yang, McEwen and Kleinberg in 1957 (8). A pyridine solution of NaI and styrene was electrolysed with magnesium electrodes. Polymers formed had a molecular weight of 18,000. The initiation process was believed to be a direct electron transfer to the monomer. In 1961, Murphy and co-workers (9) observed polymer formation during polarographic studies of acrylonitrile in anhydrous dimethyl-formamide. They suggested that the initiating carbanion formed at the cathode is  $\text{CH}_2 = \text{C}^- - \text{CN}$ . This species is also considered to participate in chain transfer during the conventional anionic polymerization of the monomer (10).

In 1960, in a brief note, Breitenbach and his co-workers (11) reported the polymerization of acrylonitrile in anhydrous dimethyl-formamide using quaternary ammonium salts as electrolytes. Breitenbach first suggested that cathodic discharge of a quaternary ammonium ion gives rise to a free-radical initiator and the polymerization mechanism involved the following steps:



Since the tetra alkylammonium ion is discharged at a much more negative cathode potential (cathode, -2.5 versus saturated calomel electrode) than is required for electron uptake by acrylonitrile (cathode -1.9 v) it is unlikely that discharge of this type of cation is involved in the polymerization process. In a note in 1962 (12), Breitenbach published data on the copolymerization of acrylonitrile with methyl methacrylate. The work showed that the compositions of the polymers formed corresponded to an anionic mechanism, and the reaction did not involve free radical initiation. However, Breitenbach could not identify the carbanion in question. He also investigated the polymer formation with different currents. The rate of polymerization showed a pronounced dependence on the presence of very small amounts of water in the medium, and consequently a poor reproducibility of the data was observed. No polymerization occurred with a current below 1 ma. It was assumed that in this system 1 ma was used up by a non-initiating electrode process such as the electrolysis of water. However, high current efficiencies were found because 80 to 400 moles of the monomer were polymerized per electrochemical equivalent.

In 1964, Funt and Williams (13) published in detail the polymerization of acrylonitrile in dimethylformamide using  $\text{NaNO}_3$  as electrolyte. The resulting polymer was yellow. They investigated the rate of polymerization with several currents ranging from 1 to 125 ma and found that the rate of polymer formation was first order with respect to impressed current and monomer concentration. The molecular weights of the resultant polymer were essentially independent of the impressed current and of the monomer concentration. The current efficiencies were extremely high, and ranged to over 3 polymer molecules formed per electron transferred at the electrode. This was attributed to chain transfer to the monomer. The authors also investigated the nature of the chain initiating step by polarographic measurements, which revealed that chain initiation proceeds via direct electron addition to the double bond of the monomer. A close correlation between the tendency to form anionic polymer and the polarographic potential was indicated. A reaction scheme was proposed which fitted all the experimental findings.

In the same year electrolytically initiated anionic polymerization of acrylonitrile was also reported by Lazarov and his co-workers (14). Funt and Laurent (15) investigated the polymerization of styrene using alkali metal nitrates

as electrolytes in dimethyl-formamide. Potassium nitrate was found to be superior to rubidium and caesium nitrate as an electrolyte, while no polymer was obtained with lithium or sodium nitrate. No plausible explanation was offered for the superiority of  $\text{KNO}_3$  to other alkali metal nitrate salts.

The polymerization of styrene with alkali metal salts did not clarify whether the initiation proceeds through a direct electron transfer from the cathode or deposited metals on the electrodes. Therefore, to resolve this ambiguity Funt and Bhadani(16) studied the polymerization of the monomer in anhydrous dimethyl-formamide with quaternary ammonium salts, thus avoiding the possible deposition of active metals. They obtained smooth kinetic curves for the formation of polystyrene at several currents and initial monomer concentrations. An analysis of the kinetic data showed that the rate of polymer formation is first order with respect to the initial monomer concentration and the impressed current. The high electrical efficiencies and molecular weights obtained in this work, contrast sharply with previous fruitless attempts at electrochemical polymerization of this monomer.

The polymer formed exclusively at the cathode. The fact that the polymerization proceeded in the presence of free radical inhibitors and ceased in the presence of water

and methanol, suggests that initiation occurs through a carbanion formed at the cathode since proton donating materials destroy carbanions in contrast to their relative inertness to free radicals. However, the results of copolymerization of this monomer with methyl methacrylate are not compatible with those of a purely anionic polymerization. According to established data for an equimolar mixture of this monomer pair purely anionic copolymerization incorporates less than one percent styrene in copolymer while purely radical copolymerization gives 50 percent styrene (17). In replicate tracer experiments with C<sup>14</sup>-tagged styrene it was found that the initial copolymer contained 36 percent styrene. The experiments were repeated with tagged methyl methacrylate in order to eliminate any systematic error in analysis, but the data showed 64 percent by weight of methyl methacrylate, thus substantiating the previous results. It was suggested that the electrolysis of the reaction mixture might involve some unknown phenomenon that affected the course of the copolymerization.

There is good reason to believe that the polymerization is not initiated by the chloride ion of the salt because the polymer forms solely at the cathode and polymer yields and molecular weights are independent of the anions of the salt.

In 1965 Baizer and Anderson (18,19) reported the

polymerization of acrylonitrile by an electrolytic method. The polymerization under conditions of constant electrode potential was studied. In their first paper the authors reported that polyacrylonitrile was formed as a byproduct during the electrolytic reductive coupling of 8,8-diphenylbenzofulvene with acrylonitrile. The catholyte contained dimethylformamide and tetraethylammonium p-toluene-sulphonate. In order to maintain homogeneity, a small amount of water was added to the catholyte. It was found that polymerization was not inhibited by a free radical inhibitor, and was not initiated in the absence of electric current. The authors, therefore, suggested an anionic mechanism for the initiation process. Owing to the low concentration of water, polymerization was not completely terminated. The polymers were light to dark yellow solids having number average molecular weights in the range of 600-1300.

In a later paper, they published the effects of reaction parameters such as concentration of water, current density, and solvent. It was observed that polymer formation is very sensitive to small quantities of water in the catholyte and that polymerization does not proceed in acetonitrile.

ANIONIC POLYMERIZATION WITHOUT A TERMINATION  
OR TRANSFER PROCESS (I.E. LIVING ANIONIC  
POLYMERIZATION)

Thus far we have been discussing polymerization where the termination reaction is unavoidable. However, under suitable experimental conditions it is possible to eliminate the termination or transfer process in some systems, notably in anionic polymerization. In such systems, growing polymer molecules retain the ability to continue the polymerization if additional monomer is supplied. Therefore, in contrast to dead polymorphic molecules they may be regarded as "living" polymers, as termed by Szwarc (20,21). However, a living polymer does not grow indefinitely nor does its molecular weight become infinite since in every system there is a finite amount of monomer available for polymerization. Also the exclusion of spontaneous termination does not mean immortality. There are reagents which convert a living polymer into an unreactive dead moiety. Treatment of living polymers with such reagents represents, therefore, a "killing process". The difference between normal spontaneous termination and "killing" lies in the unavoidable character of the former polymer reaction, whereas the latter takes place at a time chosen by the experimenter, and may be achieved by a reagent adopted to suit his needs. The mechanisms of various methods of formation of living polymers, their properties and import-



ance will be discussed.

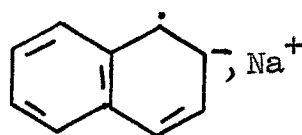
The general methods of initiation of such polymerization fall into two main categories:

- (i) Initiation by electron transfer from a suitable electron donor to a monomer.
- (ii) Initiation by alkali metal alkyls of which the most common probably are ethyl and n-butyl lithium. These initiators generally involve complex initiation processes (22,23,24). Since the present work is mainly concerned with the electron transfer process for the formation of living polymers this process only will be discussed here.

Alkali metals and complexes such as sodium naphthalene, sodium biphenyl etc., are regarded as the best homogeneous electron transfer initiators. The solvents most commonly used are ethers such as tetrahydrofuran (THF) or dioxane, or hydrocarbons such as benzene or hexane. The reaction is carried out under high vacuum. The complete absence of moisture, and other adventitious impurities is of paramount importance for the formation of living polymers.

The early living polymerization work was mainly concerned with the sodium naphthalene complex. In 1936, Scott (25) first prepared a green solution of such a complex by adding sodium to a solution of naphthalene in dimethoxy ethane. He achieved some success in polymerizing 1,2-

dihydronaphthalene with this green solution, and assumed that this complex was composed of the naphthalene disodium adduct  $C_{10}H_8Na_2$ . However, the true nature of the complex was later revealed by Weissman, Paul and Lipkin (26) to be an ion radical of the type:



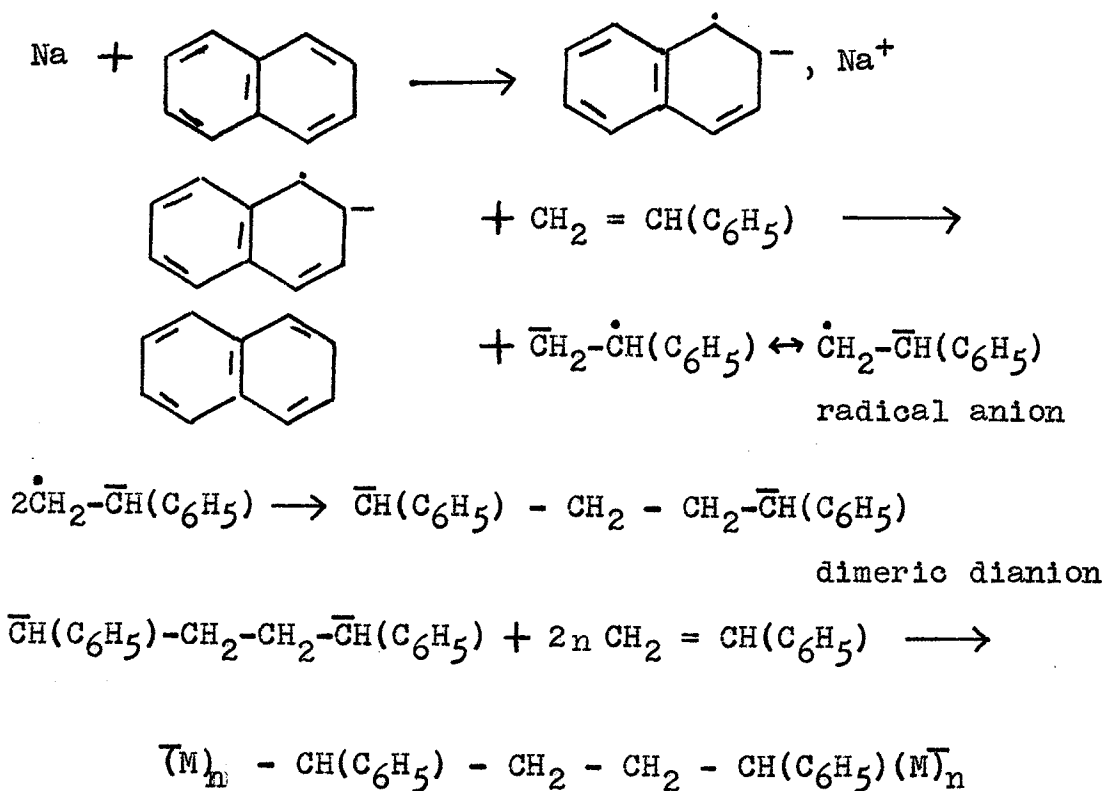
(only one of many possible resonance terms is shown)

Szwarc and his associates (21,27) first extensively studied the system sodium-naphthalene styrene in tetrahydrofuran at  $0^{\circ}$  to  $-78^{\circ}C$ . When the monomer was mixed with the green colored sodium-naphthalene complex, the red color of the styryl carbanion appeared. At 100 percent conversion the molecular weight of the polymer was calculated from the following expression:

$$\text{Mol.wt.} = \frac{\text{monomer (g)}}{\frac{1}{2} \text{ initiator (mole)}}$$

This relationship has also been verified by Leese (28) working with a sodium naphthalene-styrene system. The observed molecular weight of the polymer was in excellent agreement with that calculated. This proves that two sodium atoms are involved with each growing chain. Termination is essentially absent as evidenced by the persistence of the

red color and by the fact that, if more styrene is added, polymerization will continue. Therefore, it is clear that such a system is not propagating by a free radical mechanism because radicals would combine readily and this would eventually cause polymerization to cease. Szwarc suggested the following mechanism for the initiation process:



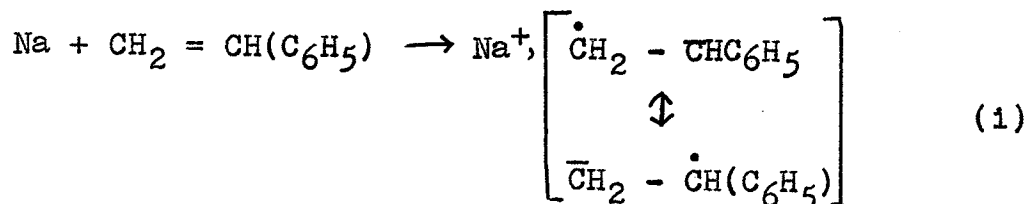
M is monomer unit.

When all the monomer is consumed carbanion ends remain active provided extreme care is taken to avoid adventitious impurities.

In a more general form he proposed the following initiation mechanism (29,30):

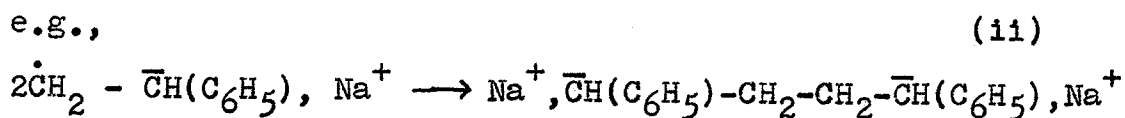
Electron-donor + monomer  $\rightarrow$  monomer $^{\cdot-}$  (radical-anion)

e.g.,



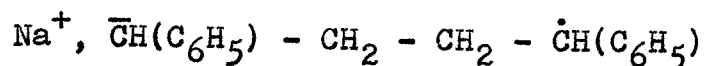
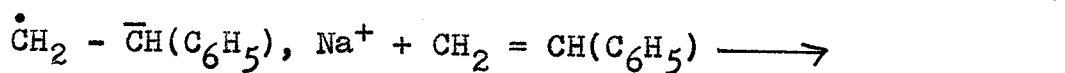
Monomer $^{\cdot-}$  + monomer $^{\cdot-}$   $\rightarrow$  dimeric dianion $^{-2}$

e.g.,



Monomer $^{\cdot-}$  + monomer  $\rightarrow$  dimeric radical-anion $^{\cdot-}$

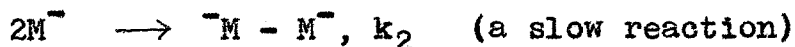
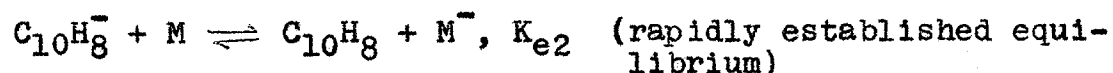
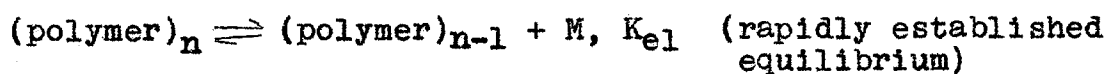
e.g.,



The dimeric species initiates the conventional propagation chain of the polymerization, the growth taking place essentially on the carbanion. The radical ends, if formed by reaction (iii) disappear either through a mutual interaction (combination or disproportionation) or through another electron transfer process, which converts a radical end into a carbanion. However, any initiation process which gives rise to a relatively high concentration of radical ions, e.g. homogeneous initiation by sodium naphthalene, may favor mechanism (ii), the formation of a dicarbanion. On the other

hand, slow heterogeneous initiation by alkali metal mirrors, especially if carried out at high concentrations of the monomer, favours mechanism (iii), with the formation of dimeric radical ions. This type of species is capable of continuing its growth in both directions.

Szwarc and Levy (30) investigated the polymerization using electron spin resonance (ESR) techniques. They observed that living polystyrene, initiated by the sodium or potassium salt of alpha-methylstyrene tetramer, gave no ESR signal and was, therefore, strictly anionic. Sodium-naphthalene initiated polystyrene gave an ESR signal which was found to be due to unreacted initiator. Sodium-biphenyl was found to be more reactive than the naphthalene and anthracene ion-radicals. Therefore, some step of the initiation was slow in comparison to an electron transfer process and had an energy of activation higher than that for propagation. The authors postulated that the dimerization of radical ions and the addition of the first monomer unit to the radical ions were involved in the slow step. They interpreted their findings on the following basis:



The above mechanism led to:

$$-\frac{d C_{10H_8}}{dt} = k_2 (K_{e1} K_{e2}) \left( \frac{C_{10H_8}}{C_{10H_8}} \right)^2$$

which is compatible with experimental findings. Recently, a comprehensive discussion of quantitative studies on the elementary reactions in electron transfer initiations was given by Szwarc (29).

Every living polymer or anion produced from a suitable monomer and initiator has its own characteristic color and also shows a characteristic ultraviolet absorption spectrum. The absorption can be attributed to the reactive living ends on the polymer chains. Once the reactivity is lost by termination the solution becomes colorless. Szwarc, Bywater and their associates (31) measured the spectra of solutions of living polystyrene and living poly (alpha-methylstyrene) formed in THF containing sodium naphthalene, sodium biphenyl, sodium phenanthrene and metallic sodium as electron donors. In each case, they found the absorption spectrum to possess a single peak at 340 m $\mu$  for living polystyrene and at 350 m $\mu$  for poly(alpha-methylstyrene).

While poly(alpha-methylstyrene) solutions were found to be very stable, it was observed that living polystyrene solutions in THF, on standing for a period of a few days, gave a different ultraviolet spectrum than initially. The initial

340  $\mu$  peak decreased with time and a new peak appeared in the 545  $\mu$  region, together with a weaker one at 420-440  $\mu$ . They reported that on addition of further amounts of styrene to this solution no polymerization occurred. It is believed that this is due to some irreversible isomerization of the living polystyrene anions generating new and stable ions which are not capable of initiating polymerization of the monomer. The rapid isomerization of living polyisoprene in THF was also noted by Bywater et al (32)

Recently, Ladacki (33) showed that living alpha-methylstyrene anion retained its vivid red color and reactivity for a period of 7 years. In contrast, the aged Na-naphthalene sample failed to initiate the polymerization. This is due to the conversion of Na-naphthalene into dihydronaphthalene, which is unable to initiate polymerization.

The characteristic colors and absorption maxima of some important living carbanions in THF are summarized in Table 1.

The lack of spontaneous termination in living polymers has many important ramifications, namely,

- (i) It greatly simplifies studies of polymerization kinetics.
- (ii) It permits investigation of the thermodynamics of polymerization processes.
- (iii) It offers methods of synthesising several important kinds of polymers. Each of these will be discussed briefly.

TABLE 1. Absorption maxima and characteristic colors of some living polymeric anions.

Monomer	Counter ion	Color	max. $\mu\mu$		Reference
			Initial	First isomerized	
Styrene	K	Orange red	346	-	32
"	Na	"	343	-	"
"	Li	"	338	-	"
Isoprene	K	Yellow	318	390	"
"	Na	"	300	358 (indistinct)	"
"	Li	"	287	-	"
Butadiene	K	"	312	385	"
"	Li	"	288	-	"
Alpha-methylstyrene	Na	Red	340	-	34
Alpha-phenylstyrene	Na	Brown red	470	-	29
Methyl methacrylate	Li	-	335	-	35

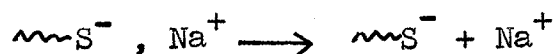


(1) Kinetics

The living polymer can be prepared at the desired concentration and thereafter, mixed with the monomer. The progression of the ensuing reaction may be followed by any suitable technique. Since termination is eliminated, the polymerization is first order with respect to monomer, the concentration  $M_t$  of which is given by the usual equation:

$$M_t = M_0 \exp (k_p [LE] t)$$

where  $k_p$  is the absolute rate constant of propagation,  $[LE]$  the concentration of living ends and  $M_0$  the initial monomer concentration. The method permits, therefore, a direct determination of the absolute rate constant of propagation (36,37,38,39). However, the situation is not quite so simple because it is found that a decrease in  $[LE]$  concentration in THF causes an increase in  $k_p$ . Therefore, it is postulated that the increase of  $k_p$  on dilution may arise from the ionic dissociation of living ion pairs according to:



if a free ion propagates much faster than its ion pair.

$\sim\bar{S}$  denotes living polymeric chain. This means that the observed propagation rate constant is a composite (40,41),

i.e.,

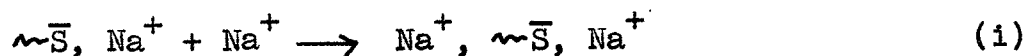
$$k_p = (1-x)k_p(\pm) + x k_p(-) \text{ for fraction } x \text{ of liv-}$$

ing polymers dissociated into ions. The prediction of the existence

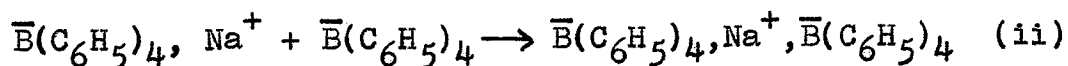
of the ion pair and the free ion in living polymer solutions has been proved true by the following facts:

(a) The solutions show electrical conductivity which increases with increase in the dielectric constant of the medium and decrease of temperature, indicating an increase of ionic dissociation (42, 43, 44).

(b) If  $k_{p(-)} \gg k_{p(\pm)}$ , the addition of a highly ionised sodium salt, e.g.,  $\text{Na}^+(\text{C}_6\text{H}_5)_4\text{B}^-$  should decrease  $k_p$  by depressing the degree of ionic dissociation of  $\sim\text{S}^-, \text{Na}^+$ , according to the mass law. This postulation has been practically confirmed (40, 41, 43). Furthermore, a sufficiently high concentration of the salt may cause the formation of triple ions e.g.,



or



If  $\text{Na}^+$  ions associate more strongly than  $\overline{\text{B}}(\text{C}_6\text{H}_5)_4$  ions, the concentration of  $\text{Na}^+$  may become lower than in the original  $\sim\text{S}, \text{Na}^+$  solution. Consequently a triple ion formation increases ( $\sim\text{S}^-$ ) which in turn, enhances  $k_p$ . Under such conditions one expects that  $k_p$  as a function of the boride concentration may, therefore, pass through a minimum, and then increase. A sufficiently concentrated solution of

$\sim S^-, Na^+$  may produce a similar effect on  $k_p$ . The experimental results are in accordance with the aforesaid postulates.

- (c) The propagation reaction proceeds via the free anion and the ion pair, so called two state polymerization, with two different rate constants  $k_p(-)$  and  $k_p(\pm)$ . In view of this one would expect that the molecular weight distributions should show a remarkable and characteristic deviation from a Poisson distribution, even if a rapid exchange between two different growing centers exists. This deviation may be avoided by addition of the required amount of electrolyte which changes the two-state polymerization into a one-state polymerization. The experimental results are compatible with this assumption (45,46,47).
- (d) On the basis of the concept of the free anion and ion pair Szwarc (43) derived the following expression for the anionic polymerization of styrene in THF:

$$\frac{\text{Rate of propagation}}{[\text{styrene}] [\text{LE}]}$$

$$= k_p(\pm) + K_D^{-\frac{1}{2}} k_p(-) [\text{LE}]^{-\frac{1}{2}}$$

where  $K_D$  is the dissociation constant of the ion pair. A plot of  $k_p$  vs  $[\text{LE}]^{-\frac{1}{2}}$  should be linear with a slope of  $k_p(-) K_D$  and an intercept of  $k_p(\pm)$ . Indeed, such a

plot results in a straight line (43) and, therefore, it substantiates the explanation for the variation of  $k_p$  with living end concentration.

For the polymerization of styrene in THF at 25°C, Szwarc et al (43) found  $k_{p(-)}$  to be 65000 litres/mol.sec, whereas propagation rate constants  $k_{p(\pm)}$  of ion pairs possessing  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  counter ions were 160, 80, 60,

50 and 22 litres/mol.sec. respectively. The dissociation constant of the  $\sim\text{S}^-$ ,  $\text{Na}^+$  ion pair was found to be  $1.5 \times 10^{-7}$  moles/litre, which is in good agreement with that obtained by Worsfold et al (22). Hostalka and Schulz (48) obtained a value of 130,100 litre/mol.sec. for  $k_{p(-)}$  and  $0.4 \times 10^{-7}$  moles/litre for  $K_D$  of the  $\sim\text{S}^-$ ,  $\text{Na}^+$ . These differences between the two sets of results are presumably due to different experimental conditions employed by the authors.

On the basis of experimental results Szwarc showed that among the various alkali metal counter ions the most reactive and most extensively dissociated is  $\sim\text{S}^-$ ,  $\text{Li}^+$ . The reactivity and the dissociation constants are in the order  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ .\* In dioxane (49) he found that the

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\*One end or both ends active living polymers may be prepared, e.g.  $\sim\text{S}^-$ ,  $\text{Cs}^+$  and  $\text{Cs}^+$ ,  $\text{S}^- \sim \text{S}^- \text{Cs}^+$  are referred as one ended and two-ended polymers respectively. For one ended  $\sim\text{S}^-$ ,  $\text{Cs}^+$ , dissociation constant obtained from the conductivity and kinetics data is the same whereas this is not the case with two ended polymer. This difference is discussed thoroughly in the original paper (43).

observed rate constant is independent of the concentration of living ends, and conductivity measurements did not reveal the presence of free ions. Hence, in this solvent only ion pairs propagate polymerization. In contrast to results found in THF, the reactivities of the ion pairs increased along the series  $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$  in dioxane.

These results have been attributed to the influence of the dielectric constant of the medium, and specific effects of the solvent, as well as counter ions. As has been found from conductivity measurements, the apparent radii of the ion increases from  $\text{Cs}^+$  to  $\text{Li}^+$  due to solvation which also increases in this order. Since the ionic dissociation constants of the polystyryl salts are smaller than those of the tetraphenylborons, Szwarc considers polystyryl salts to form intimate ion pairs. Thus the actual carbon-alkali metal distance in the ionic bond is probably greatest for  $\text{Cs}^+$  and smallest for  $\text{Li}^+$ . The ion pairs are solvated in the case of the lighter alkali metal salts, but possibly less so across the series to the caesium salt, which appears to be unsolvated. Under such conditions the driving force or the extra solvation energy of the free cation causes the dissociation of the polystyryl lithium to be the highest of the series and that of polystyryl caesium to be the lowest. This higher dissociation constant of polystyryl lithium, in THF, increases the carbanion concentration which, in turn, enhances the rate of the reaction.

This situation is quite different with dioxane as solvent. Unlike THF it seems that dioxane does not help in separating the ions in the transition state, and thus, the reactivity of the ion pair is determined by the coulombic binding energy of the pair. Therefore, the small and strongly bonded  $\text{Li}^+$  ion gives the least reactive ion pair and the large  $\text{Cs}^+$  yields the most reactive one. Because  $\text{Cs}^+$  is not solvated the reactivity of  $\sim\text{S}^-, \text{Cs}^+$  in both solvents e.g., in THF and dioxane, is almost the same.

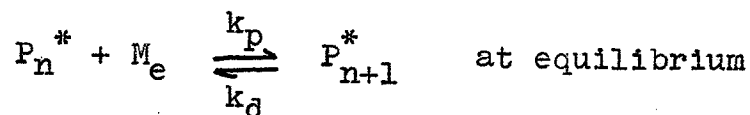
Because of the low dielectric constant of dioxane (2.2 at  $25^\circ$ ) the free polystyryl anion does not exist in this solvent. It is relevant to note that the rate constant  $k_p(-)$  for the free polystyryl anion must be independent of the counter ion but depends on the dielectric constant of the medium, as well as the specific solvation effects of the solvent.

Recently, Russian chemists Korotkov and Podolsky (49) have cast doubts on the free ion and ion pair mechanism, i.e. on the theory of two state polymerization. In place of it they proposed a co-ordination theory. However, the present state of knowledge refutes the co-ordination theory which, in fact, represents a single state polymerization (50). This theory failed to interpret all the experimental findings.

In considering the effect of  $\text{Na}(\text{C}_6\text{H}_5)_4\text{B}$  on the reaction kinetics, the Russian chemists pointed out that this salt reacts with a living polymer. Evidence from kinetic and molecular weight distribution studies done in the presence of this salt, shows that no such reaction exists. However, no direct investigation on the interaction between  $\text{Na}(\text{C}_6\text{H}_5)_4\text{B}$  and the living polymer has been carried out.

(ii) The Thermodynamic Aspect of Living Polymerisation

Because living polymers retain their ability to grow they may also degrade into lower polymers and the monomer. This means, therefore, that a solution of such a polymer must reach equilibrium with its own monomer (51), i.e.,



$$k_p \left( \sum_{n_0}^{\infty} P_n^* \right) [M_e] = k_d \left( \sum_{n_0+1}^{\infty} P_n^* \right)$$

For high molecular weight polymers the following equation applies:

$$\sum_{n_0}^{\infty} P_n^* \approx \sum_{n_0+1}^{\infty} P_n^*$$

Hence in such a system  $[M_e] \approx \frac{k_d}{k_p} = K_e^{-1}$

$P_n^*$  = concentration of the living -mer.

$M_e$  = equilibrium concentration of the monomer

$n_0$  = degree of polymerization of the lowest living polymer (i.e., of that species which may grow but not degrade)

$k_p$  = propagation rate constant

$k_d$  = depropagation rate constant

$K_e$  = equilibrium constant of the propagation step.

The equilibrium constant,  $K_e$ , like any thermodynamic entity is independent of the mechanism of the reaction since

$$\left. \begin{aligned} -RT \ln K_e &= G \\ d \ln K_e / dT &= H \end{aligned} \right\} \text{ for the propagation step.}$$

$G$  denotes the free energy change and  $H$  the enthalpy change. All the thermodynamic functions pertaining to the propagation step are determined by this technique. The method has been used with much success for the system alpha-methylstyrene/poly (alpha-methylstyrene) (51,52,53) and Styrene/polystyrene (54) initiated anionically.

### (iii) Some Important Syntheses

One of the most dominating features of living polymers formation is the synthesis of uniform molecular weight polymers. Under ideal conditions, all polymer chains should grow to the same length and therefore, the polymer should have equal weight average ( $\bar{M}_w$ ) and number average ( $M_n$ ) molecular weights. This means that the ratio  $\bar{M}_w/\bar{M}_n$  must be very close to unity. However, formation of such monodisperse polymers involves considerable practical difficulties, as the



presence of impurities, inefficient rapid mixing of monomer and initiator, poor stirring of the polymerizing solution etc., tend to decrease the monodispersity in the resulting polymer. Despite such difficulties very uniform molecular weight distributions have been prepared by this technique (55,56,57,58,59). One can also prepare block polymers (21,60,61), star-shaped polymers (62,63,64,65), polymers possessing two functional end groups (66,67,68).

#### ELECTROLYTICALLY GENERATED LIVING POLYMERS

Most of the electrolytically initiated anionic polymerizations were performed in highly polar organic solvents such as dimethylformamide where the termination process is unavoidable, at least at room temperature. Hence no living polymerization was ever observed in such systems. Electrolytically produced living polymers were first observed by Yamazaki, Nakahama and Kambara (69). They used THF as solvent and  $\text{NaAl}(\text{C}_2\text{H}_5)_4$  as electrolyte for the polymerization of alpha-methylstyrene. In a brief note, the authors reported that the passage of an electric current through the solution did not immediately yield polymer at room temperature, but rather a deep red solution of the living anion in the cathode region. By cooling the cell to  $-80^\circ\text{C}$  quantitative yields of high molecular weight polymer were obtained. It was postulated that direct electron transfer

from the cathode to the monomer double bond is responsible for the initiation.

Here it is relevant to point out that alpha-methylstyrene does not polymerize at room temperature when its concentration in the solution is low. This is due to its low ceiling temperature (52,53,70) at which rates of polymerization and depolymerization become equal preventing high polymer formation.

Soon after Yamazaki's publication Funt, Richardson and Bhadani (71) reported the electrolytic formation of living polystyrene in THF solutions of  $\text{NaAl}(\text{C}_2\text{H}_5)_4$  and  $\text{Na}(\text{C}_6\text{H}_5)_4\text{B}$ . They found that when naphthalene was added to the solution, the green sodium naphthalene complex was produced by electrolysis. Upon the addition of monomer to this complex, orange red living polystyryl anions were formed instantaneously. These polystyryl anions were also formed in the catholyte by electrolysis. Furthermore, it was found that mixing of the catholyte and anolyte resulted in a decay of living species and decolorization of the orange red solution. The substances responsible are believed to be  $\text{Al}(\text{C}_2\text{H}_5)_3$  and  $\text{B}(\text{C}_6\text{H}_5)_3$  produced by anodic oxidation of the corresponding anions. The authors proposed a probable mechanism of polymerization.

CHAPTER II  
ELECTRICALLY CONTROLLED ANIONIC POLYMERIZATION  
OF METHYLMETHACRYLATE

## PURIFICATION AND PREPARATION OF REAGENTS

### MONOMERS

Styrene and methylmethacrylate (MMA) contain small amounts of inhibitors to prevent polymerization during storage. The inhibitor was removed by passing monomers through a column of chromatographic activated alumina. The inhibitor free monomers were dried over calcium hydride, then distilled under reduced pressure, and middle fractions were collected. The purified monomers were stored under nitrogen in the refrigerator at  $-20^{\circ}\text{C}$  for a period not exceeding more than four days. Just prior to use the monomer was tested to ensure the absence of polymer by adding a sample to methanol.

### SOLVENTS

N,N-dimethylformamide (DMF)(A.R.) was purified by mixing with 10 percent by volume pure benzene, previously dried over calcium hydride. After standing for more than 24 hours, the mixture was fractionally distilled and the fraction boiled at  $150-152^{\circ}\text{C}$ , collected over dried barium oxide, allowed to stand for 24 hours and redistilled at reduced pressure. The middle portion was collected in a flask. N,N-dimethylacetamide (DAM) and dimethylsulfoxide (DMSO) were dried over calcium hydride, and distilled under reduced pressure. Acetonitrile (AR) was dried over anhydrous potassium carbonate, distilled from it, and finally fractionally distilled.

The solvents were stored under nitrogen in the dark, and kept for not more than four days after purification. Some physical properties of the solvents and the monomer employed here are shown in Table 2 (72).

TABLE 2. Some physical properties of solvent and monomer at 25°C.

	bp	$\epsilon$	$\eta$	d
N,N-dimethylformamide (DMF)	153	36.7	0.796	0.9445 0.944*
N,N-dimethylacetamide (DMA)	165	37.8	0.92	0.933
Acetonitrile (AN)	81.6	37.5	0.345	0.7768
Dimethylsulphoxide (DMSO)	189	46.7	1.96	1.096
Tetrahydrofuran (THF)	66	7.4	-	.882*
Methylmethacrylate	100	-	-	.940*
Styrene	146	-	-	.910*

bp - boiling point, °C;  $\epsilon$  - dielectric constant;

$\eta$  - viscosity, CP; d - density, g.cm<sup>-3</sup>;

\* determined in the present work

### SALTS

Tetramethyl ammonium perchlorate was prepared by

mixing an alcoholic solution of tetramethyl ammonium hydroxide with a dilute aqueous perchloric acid solution. The required product precipitated as fine crystals. These were washed several times with methanol until the filtrate was free from acid and chloride. The salt thus obtained was dried in vacuum at 70°C.

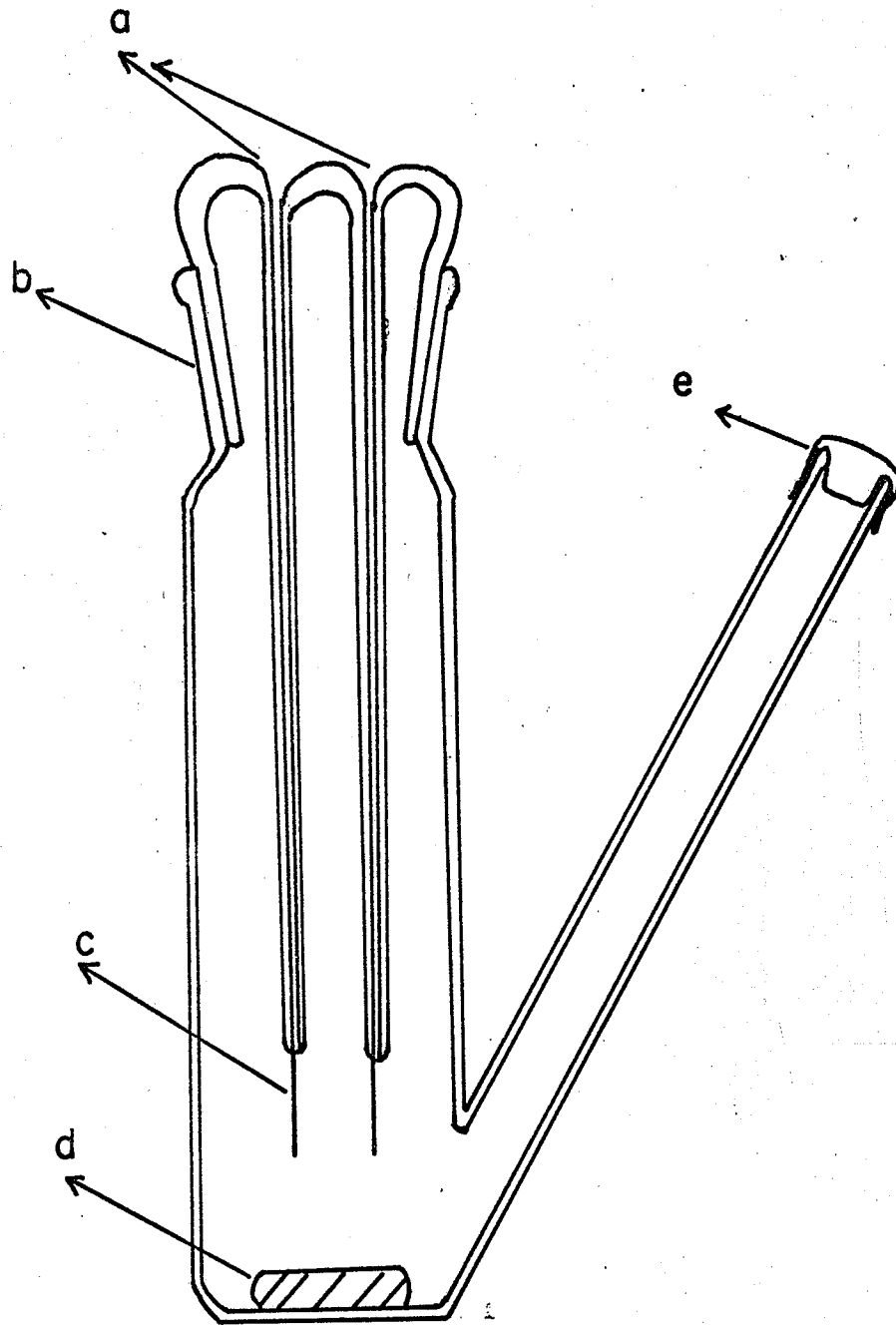
Tetramethyl ammonium borofluoride was prepared by mixing an aqueous solution of tetramethyl ammonium bromide. The precipitate thus formed was washed several times with water until the filtrate was free from acid and bromide. The salt was dried in vacuum at 70°C.

Other quaternary ammonium salts were obtained commercially as polarographic grade, and were used without purification. Prior to use they were dried.

#### POLYMERIZATION PROCEDURE

Polymerizations were carried out in glass cells which were of a basic test tube type as shown in Figure 1. Two platinum electrodes, each of dimensions 1" x 1" and spaced 1 cm apart, were sealed into a 34/45 inner joint and fitted into an outer joint test tube with a side arm. A magnetic stirring bar agitated the solutions during electrolysis. A bank of four such cells could be operated simultaneously in a constant temperature bath at 25°C. One geared motor rotated a series of magnets which provided uniform and

FIGURE 1. Polymerization cell.  
a, mercury contacts.  
b, 34/45 ground glass joint.  
c, platinum electrodes.  
d, stirring bar.  
e, rubber cap.





constant stirring for all cells. Samples were withdrawn with a hypodermic syringe through a serum cap fitted over the side arm of each cell. Prior to use the cells and electrodes were dried and flamed. A constant current supply was used for low currents. A D.C. line of 250 volts was used to pass currents above 15 ma. Both voltage and current were simultaneously measured by means of a recorder and switch gear.

The reaction cell was charged with solutions of monomer, salt and solvent in a dry box under nitrogen atmosphere. In all experiments 1 g. salt was added to 100 ml of a monomer solution in the solvent. This furnished a saturated solution with some excess salt present. Rates of polymerization were determined gravimetrically. During the course of the reaction 2 ml samples were withdrawn periodically, weighed and their polymer content determined by precipitation in cold methanol. After filtration the polymer was washed several times with methanol, dried, and weighed to constant weight. During the polymerization the reaction mixture changed color, first yellow, and gradually became brown at high conversion (over 70%). No such deep color development was observed when polymerization was carried out in DMA.

All polymerizations were performed at 25°C unless otherwise mentioned. The maximum voltage at the highest

current employed was found to be 100 volts. Instead of increasing the applied voltage, necessary to maintain the constant current, decreased slightly during the course of the polymerization.

#### BLANK EXPERIMENT

To ensure that polymerization was initiated electrolytically the reaction mixture containing monomer, solvent and salt was placed in an electrolytic cell, which was thermostated at 25°C and stirred for 24 hours. No current was passed through this solution. In such an experiment, no polymers were isolated. However, when current was passed through the solution, polymer formation occurred. Therefore, under the conditions employed here polymerization is not initiated by the salts or thermally.

#### LOCUS OF POLYMERIZATION

The locus of polymerization was determined to be the cathode by carrying out the electrolysis of the monomer solution in a divided cell. The polymer was formed solely at the cathode, no polymer being obtained at the anode.

#### MOLECULAR WEIGHT DETERMINATION

Viscosity measurements were carried out at 25°C in

a methyl ethyl ketone solution of the polymer using an Ubbelohde dilution viscometer (Fig.2). Molecular weights were calculated by the following expression (73):

$$[\eta] = KM^a$$

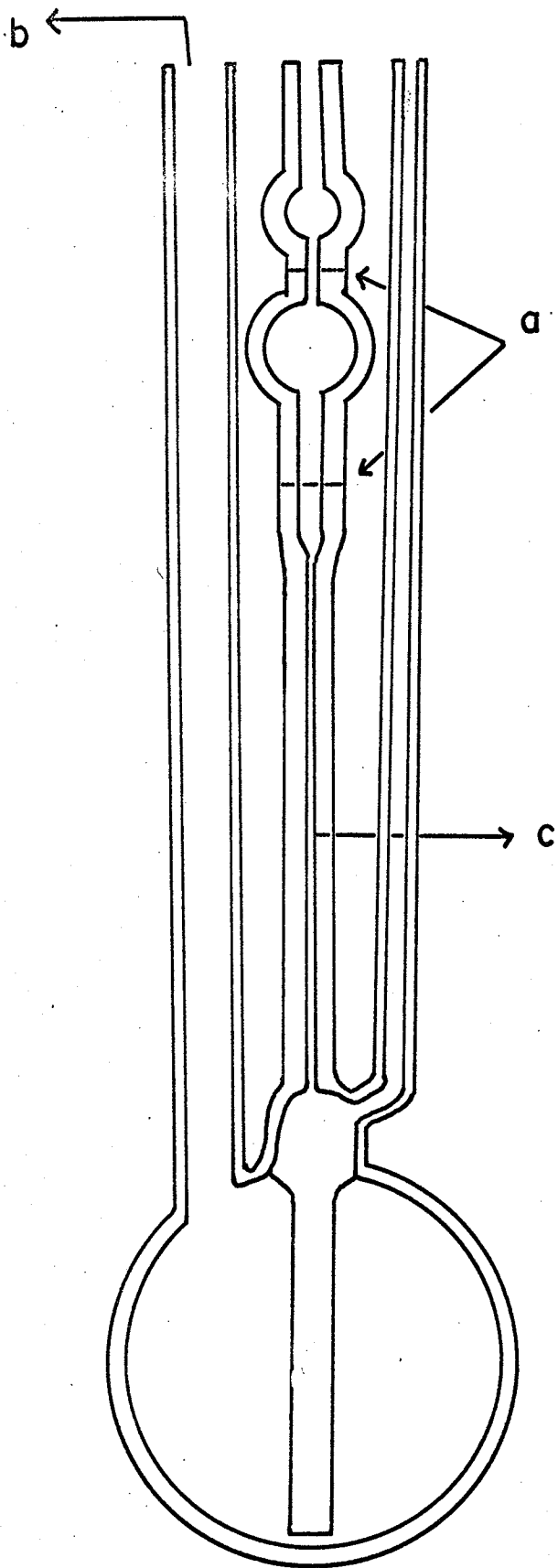
Where  $K = 6.8 \times 10^{-5}$  and  $a = 0.72$ .  $[\eta]$  = limiting viscosity number. The polymer samples, used to determine the limiting viscosity number, were purified by dissolving them in methyl ethyl ketone (MEK). The solution was then filtered and precipitated slowly into cold methanol. The polymer was filtered out, washed several times with methanol, and dried overnight at  $70^\circ\text{C}$ . The reduced viscosities were measured for different concentrations of polymer solution, ranging from 0.25 percent to 1 percent by weight. The limiting viscosity number was calculated by extrapolating results to infinite dilution.

#### COPOLYMER ANALYSIS

The composition of a copolymer was analysed by using one carbon-14 labelled monomer of known  $\beta$  activity. The activity of monomer and copolymer samples was determined by liquid scintillation counting. A liquid scintillator solution, which interacts with the  $\beta$ -particles from the carbon-14 decay to give photon emission, was made by dissolving:

FIGURE 2. Ubbelohde viscometer.

- a, Etched line.
- b, Filling tube.
- c, Capillary tube.



5 g diphenyloxazole (PPO)

0.1 g 1,4 - bis - 2 (4 methyl-5 phenyloxazolyl)-  
benzene (POPOP)

70 g naphthalene

in xylene (A.R.) to give 1 litre of solution. A known amount of radioactive monomer was diluted with inactive monomer. From this active monomer sample, 200  $\mu$  (.2 ml) was added to 20 ml liquid scintillator for the analysis. The activity of the sample was measured by a Tricarb liquid scintillation spectrophotometer which detected the photon emission with photomultiplier tubes and recorded the data automatically. The amount of emission measured on two different energy channels (e.g. channel A and channel B) provides a method of making a correction on counter efficiency. A correction was also made for background counts. The sample count per minute (CPM) was measured at 10 minute intervals over several hours and the reproducibility of count rates was excellent. Knowing the activity of a labelled monomer sample and that of the copolymer, the weight of the radioactive component of the monomer pair in the copolymer could be calculated. Much care was taken to purify the labelled copolymer to remove the contaminated labelled monomer. This was accomplished by the usual solution and reprecipitation techniques. An example of the copolymer formation and the essential steps

involved in calculating its composition is illustrated below. Composition feed:

MMA = 38 ml (35.72 g)

Styrene = 40 ml (36.40 g)

Carbon-14 labelled MMA (.2 ml) was diluted with 38 ml MMA and 0.2 ml of this prepared dilute labelled monomer was mixed with 20 ml liquid scintillator and its activity was determined.

#### COPOLYMER FORMATION

The above mixture of styrene and labelled MMA containing 1 g. tetrabutyl ammonium bromide was electrolysed for 26 minutes at 11 ma. The electrolysed mixture was treated with methanol to precipitate the polymer which was filtered and dried. The degree of conversion was found to be 2.47%. The copolymer thus obtained was purified thoroughly by dissolving it in MEK and precipitating it in methanol. This procedure was repeated three times for the complete removal of uncombined labelled monomer residues in the copolymer.

#### ANALYSIS OF COPOLYMER COMPOSITION

Labelled Monomer	Radioactivity	A/B	Background counting of scintillator	Efficiency of counts
(0.1880 g)	6195	3.11	100	66.5
Active Copolymer				
(0.1695 g)	5561	2.86	119	67.0

Therefore, activity of 0.1 g of labelled MMA = 3747 CPM

Therefore, activity of 0.1 g of labelled copolymer = 3210

Therefore, percentage of MMA in the copolymer = 98.7.

### EXPERIMENTAL RESULTS

A study of the "after effect", i.e. the continuation of polymerization after cessation of electric current, was made using 40 vol. percent monomer in a DMF solution of tetramethyl ammonium chloride at 40 ma. The data obtained are presented in Figure 3 which shows that polymer formation occurs only when current is passing through the solution. The polymerization stops as soon as the current is switched off. Therefore, the system is free from the "after effect" to which frequent references have been made in the literature (74,75,76). The direct control of the polymerization warranted an attempt to determine the order of the reaction with respect to impressed currents and initial monomer concentrations.

The reaction profile as a function of current and time for a 40 volume percent solution of MMA in DMF is shown in Figure 4. The data are summarized in Table 3. A systematic increase of polymer formation with time and with impressed current is evident. The degree of conversion during the experiments ranged up to 50 percent for solutions electrolysed for periods of over five hours at the highest currents



FIGURE 3. Effect of "on and off" passage of electric current of 40 ma on polymer formation for a 40 volume percent of methylmethacrylate in dimethylformamide containing  $(\text{CH}_3)_4\text{NCl}$ .

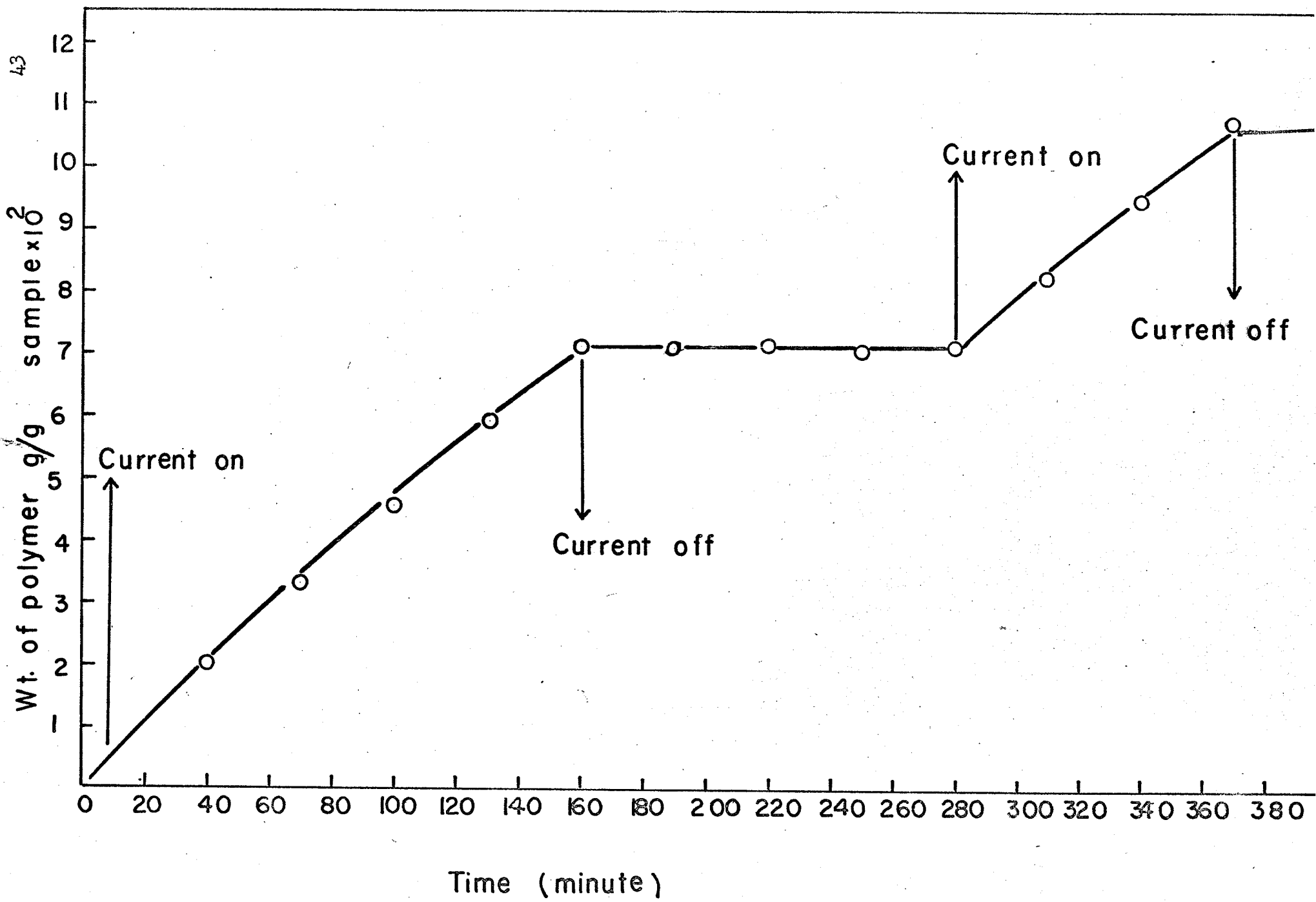


FIGURE 4. Formation of polymer as a function of inscribed current and time for a 40 volume percent of methylmethacrylate in dimethylformamide solutions of  $(\text{CH}_3)_4\text{NCl}$ .

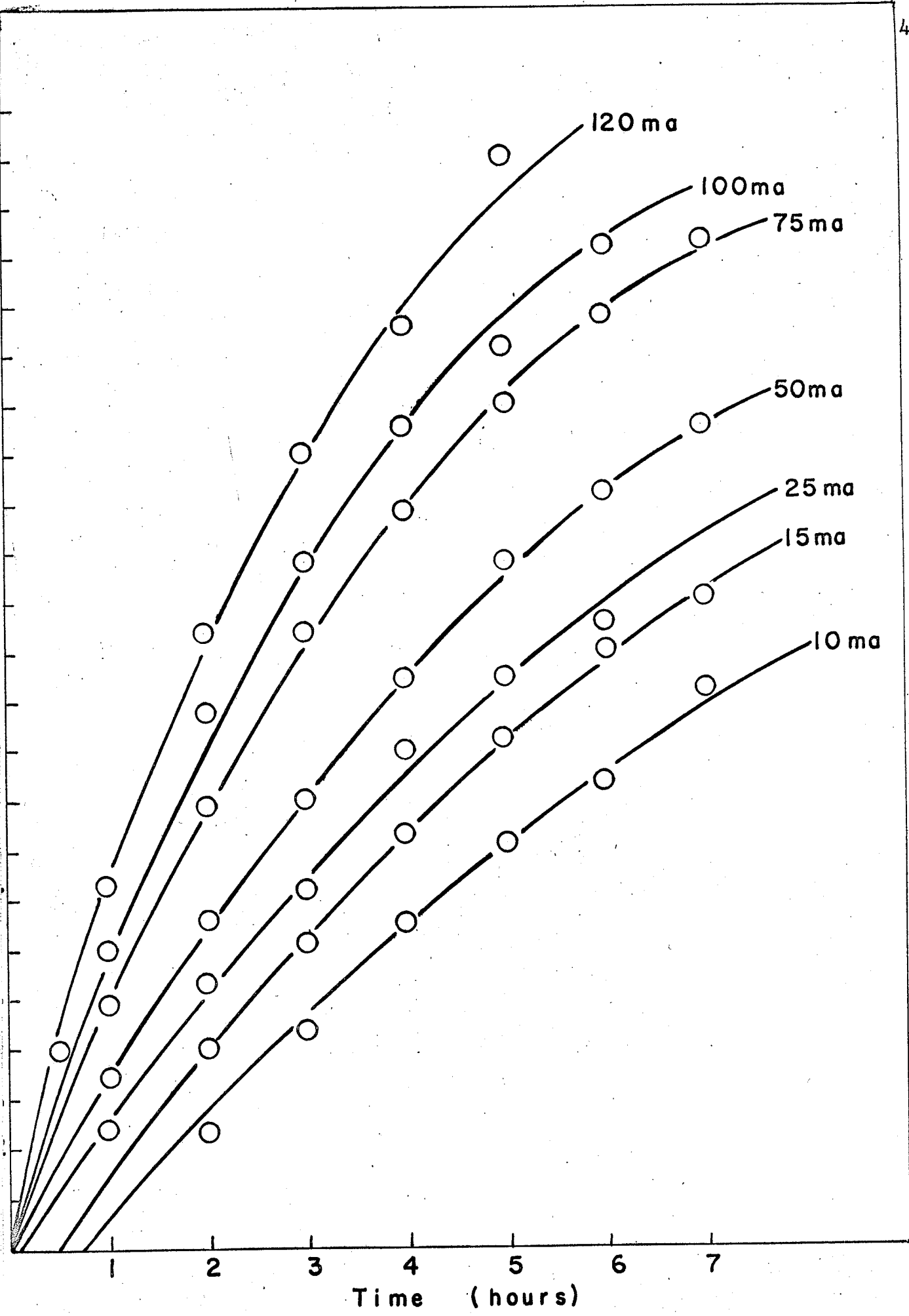


TABLE 3. Polymer formation (g per g sample) in solutions of MMA (40 vol. percent) in dimethylformamide saturated with  $(\text{CH}_3)_4\text{NCl}$  at  $25^\circ\text{C}$ .

Time (hours)	10 ma	15 ma	25 ma	50 ma	75 ma	100 ma	120 ma
1	x	x	.024	.035	.049	.060	.073
2	.024	.040	.053	.066	.089	.108	.124
3	.044	.062	.072	.090	.124	.138	.160
4	.067	.083	.100	.114	.148	.165	.186
5	.081	.102	.114	.138	.171	.181	.220
6	.094	.120	.125	.152	.188	.202	x
7	.112	.131	x	.165	.203	x	x

employed. The data at lower currents show a slight inhibition period which appears to be about 45 minutes at the lowest current of 10 ma. Although this is believed to be due to residual impurities, repeated experiments under more stringent conditions and with particular attention to dryness, did not produce a significant change in this period. However, this work was not planned nor conducted to accommodate the truly vigorous conditions of vacuum transfer as are associated with the later work. It is reasonable to assume that such refinements in technique would have eliminated or reduced the induction period, but the reproducibility of

of the results obtained and the nature of the study did not warrant this type of approach. A correction for the volume change incurred by withdrawal of samples of polymerizing solution, for the analysis of polymer content, did not appreciably alter the data and is not presented here.

A logarithmic plot of the monomer concentration versus time shows a straight line for all impressed currents as shown in Figure 5. The calculation of such a plot is illustrated in Table 4. The results strongly suggest a first order dependence on monomer concentration. The slopes of these curves give rate constants which are dependent on the impressed currents. The intercept shows the initial monomer concentration. The lines did not all meet at a common point and this might be due to the induction period observed at the beginning of the polymerization. A similar and more stringent corroboration of the first order dependence on the monomer concentration is obtained from the data compiled in Table 5, and shown in Figure 6. Here the results collected from various initial monomer concentrations at a fixed current of 15 ma are presented. The logarithmic plot of monomer concentration versus time yields a straight line (Fig.7). The data fit on a series of parallel lines with approximately equal slopes which give the rate constant independent of monomer concentration. The result is in agreement with first order decay of monomer concentration.

FIGURE 5. Logarithmic dependence of monomer concentration on time for a 40 volume percent solution at inscribed currents.

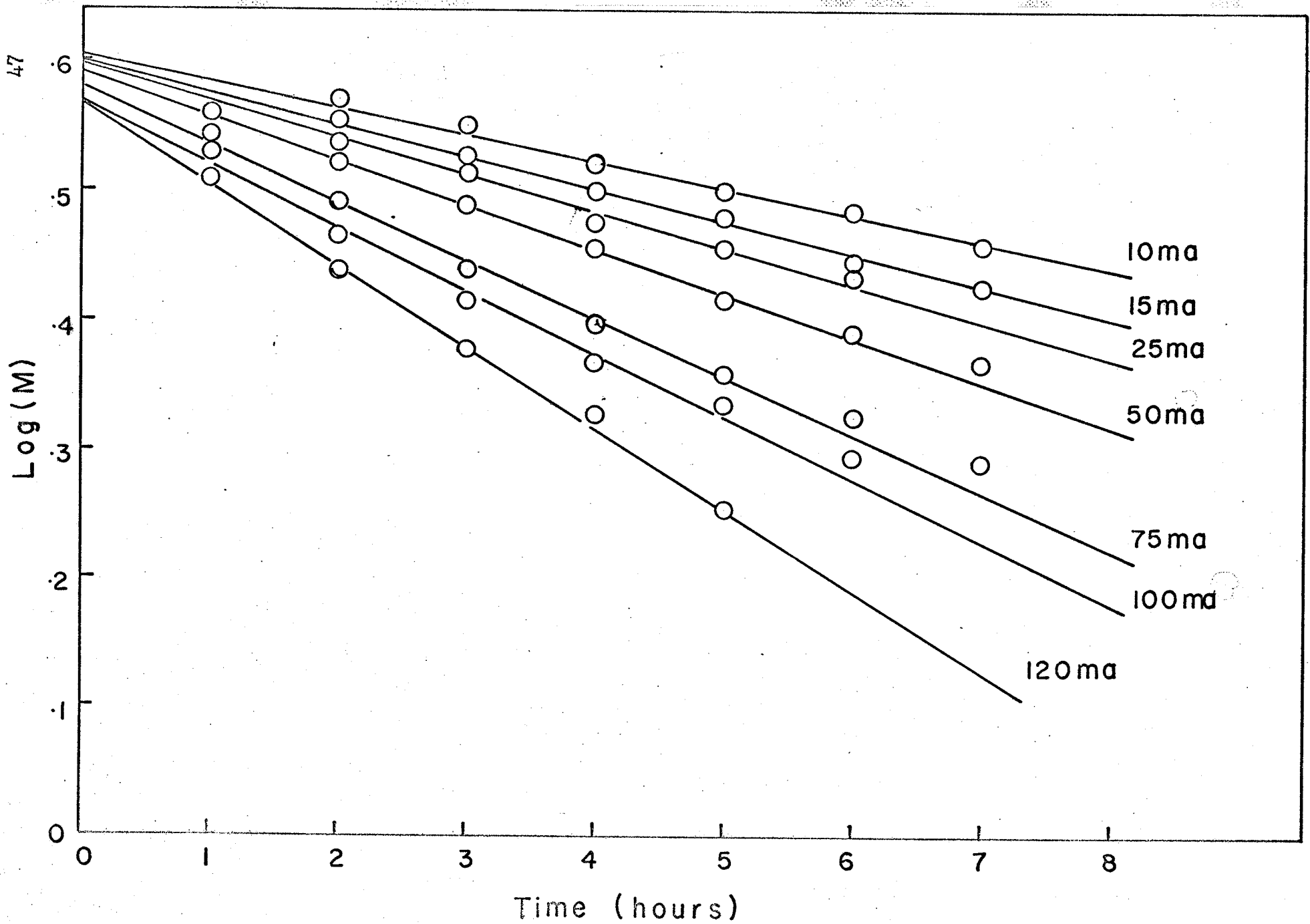




TABLE 4. Polymerization at 50 ma.

Time (hours)	Sample Wt. g.	Wt. Poly- mer in sample g.	Wt. Poly- mer g./g. sample	Monomer mole/1000 g. solution	Unreacted monomer mole/1000 g. solution (M)	log M
1	1.911	0.067	0.035	0.35	3.64	0.561
2	2.140	0.142	0.066	0.66	3.33	0.522
3	2.000	0.180	0.090	0.90	3.09	0.490
4	2.059	0.235	0.114	1.14	2.85	0.455
5	2.090	0.290	0.138	1.38	2.61	0.417
6	2.175	0.330	0.152	1.52	2.47	0.393
7	2.103	0.347	0.165	1.65	2.34	0.370

TABLE 5. Polymer formation (g./g. sample) at  
15 ma in solutions of MMA in dimethyl-  
formamide saturated with  $(\text{CH}_3)_4\text{NCl}$   
at 25°C.

Time (hours)	20 Vol.%	30 Vol.%	40 Vol.%	50 Vol.%	60 Vol.%	70 Vol.%	80 Vol.%
1	x	x	x	.016	.019	.020	.029
2	.037	.032	.040	.042	.047	.053	.066
3	.055	.043	.062	.066	.075	.091	.112
4	.069	.054	.083	.092	.103	.118	.161
5	.081	.062	.102	.110	.123	.146	.201
6	.092	.068	.120	.132	.146	.188	x
7	.100	.077	.131	.152	.119	.228	x
8	.110	.084	x	x	x	x	x

FIGURE 6. Polymer formation at inscribed initial monomer concentrations in dimethylformamide at a current of 15 ma Electrolyte,  $(\text{CH}_3)_4\text{NCl}$ .

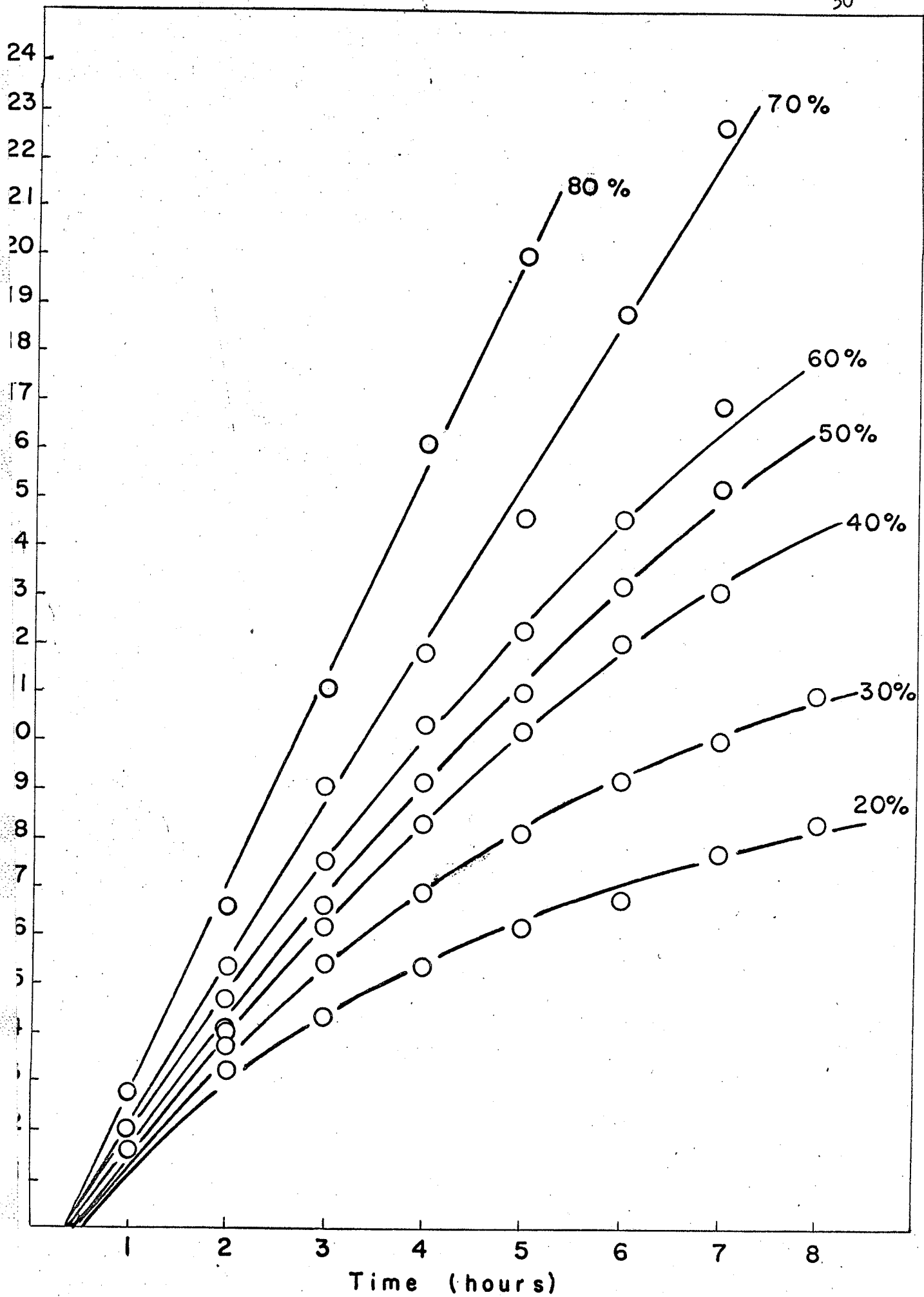
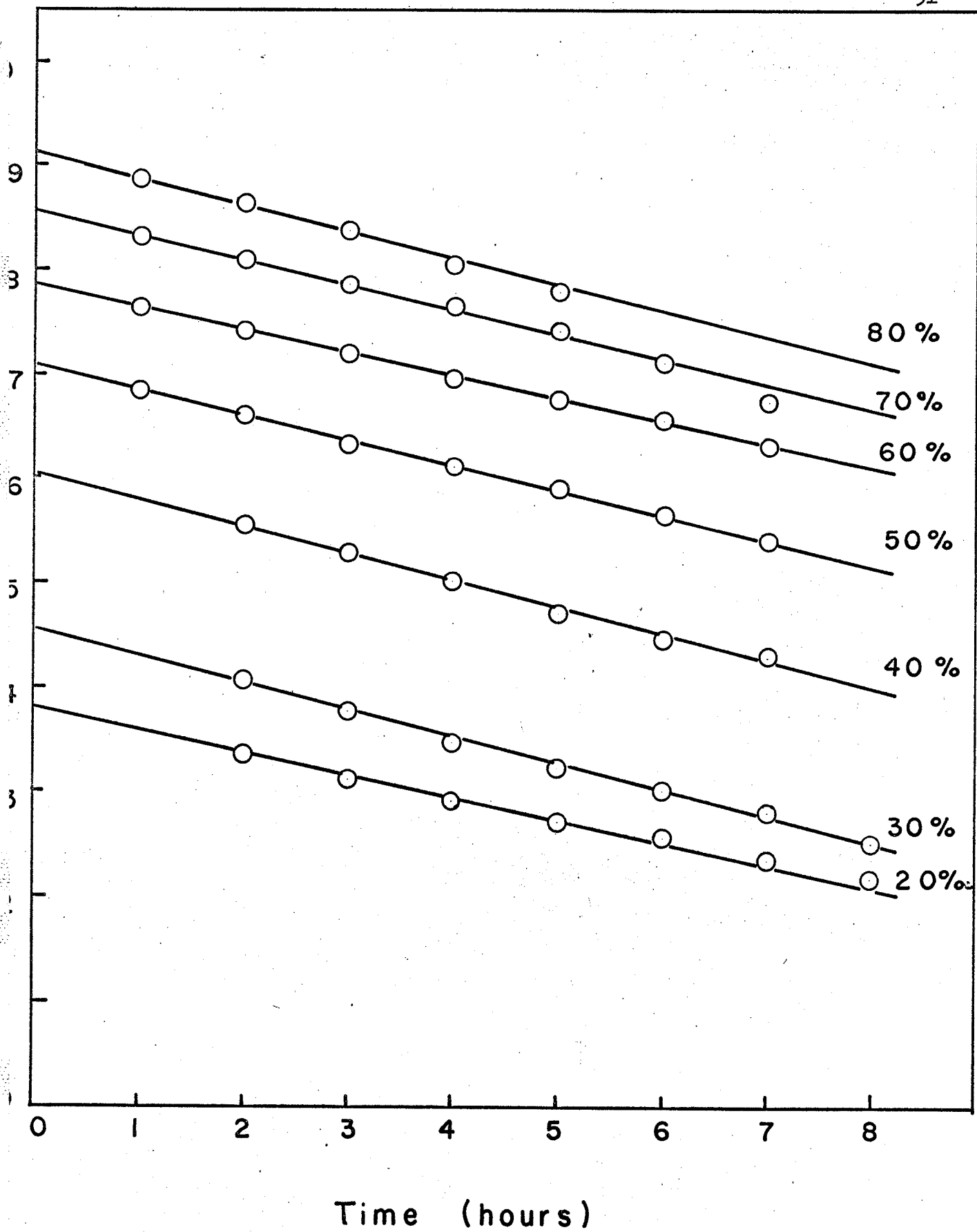


FIGURE 7. Logarithmic dependence at a current of 15 ma and inscribed initial monomer concentrations.



The slopes of each of the lines in the semilogarithmic plots of Figure 5 should be proportional to the rate. A plot of the slopes versus the square root of the current furnishes a linear relation as shown in Figure 8. The presence of an induction period also accounts for this curve not passing directly through the origin. The overall kinetics are believed to be consistent with a rate expression of the forms

$$\text{Rate} = k [M] I^{\frac{1}{2}}$$

#### EFFECT OF TEMPERATURE

Figure 9 shows the variation in the yields of polymer formed at different reaction temperatures and a constant current of 50 ma with time of polymerization. It is evident from the data that the rate of polymerization decreases with decreasing reaction temperature. It was not possible to use much lower temperatures than  $-15^{\circ}\text{C}$  because the applied voltage, to maintain the constant current, increased considerably. From the data the temperature dependence of the rate constants could be calculated. According to the Arrhenius equation the temperature dependence of the rate constant can be expressed by the following equation:

$$\log k = \frac{-E_a}{2.303 R} \frac{1}{T} + A$$

FIGURE 8. Linear dependence of slopes of  
Figure 5 on the square root of the  
current ( $I^1/2$ ).



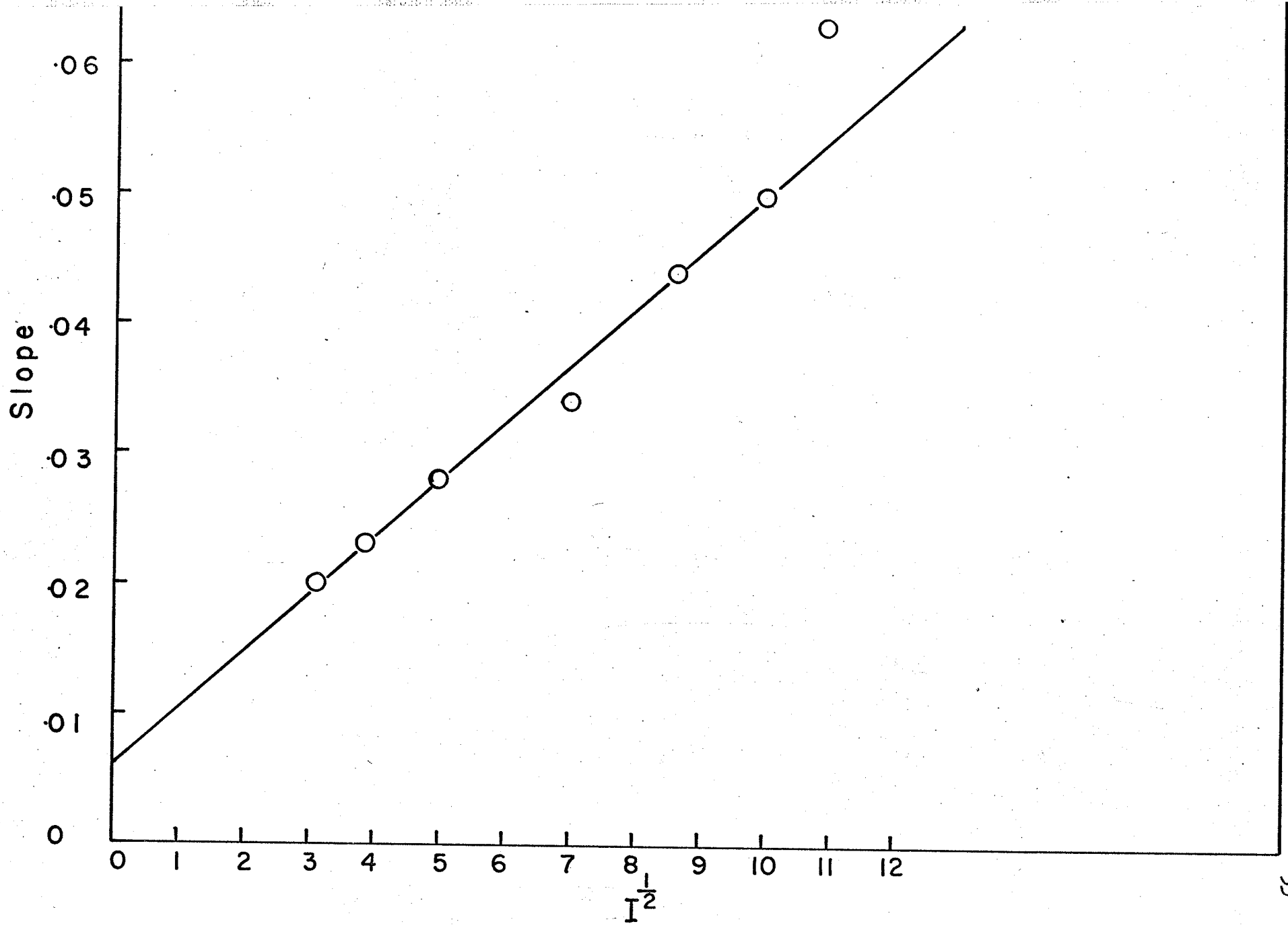
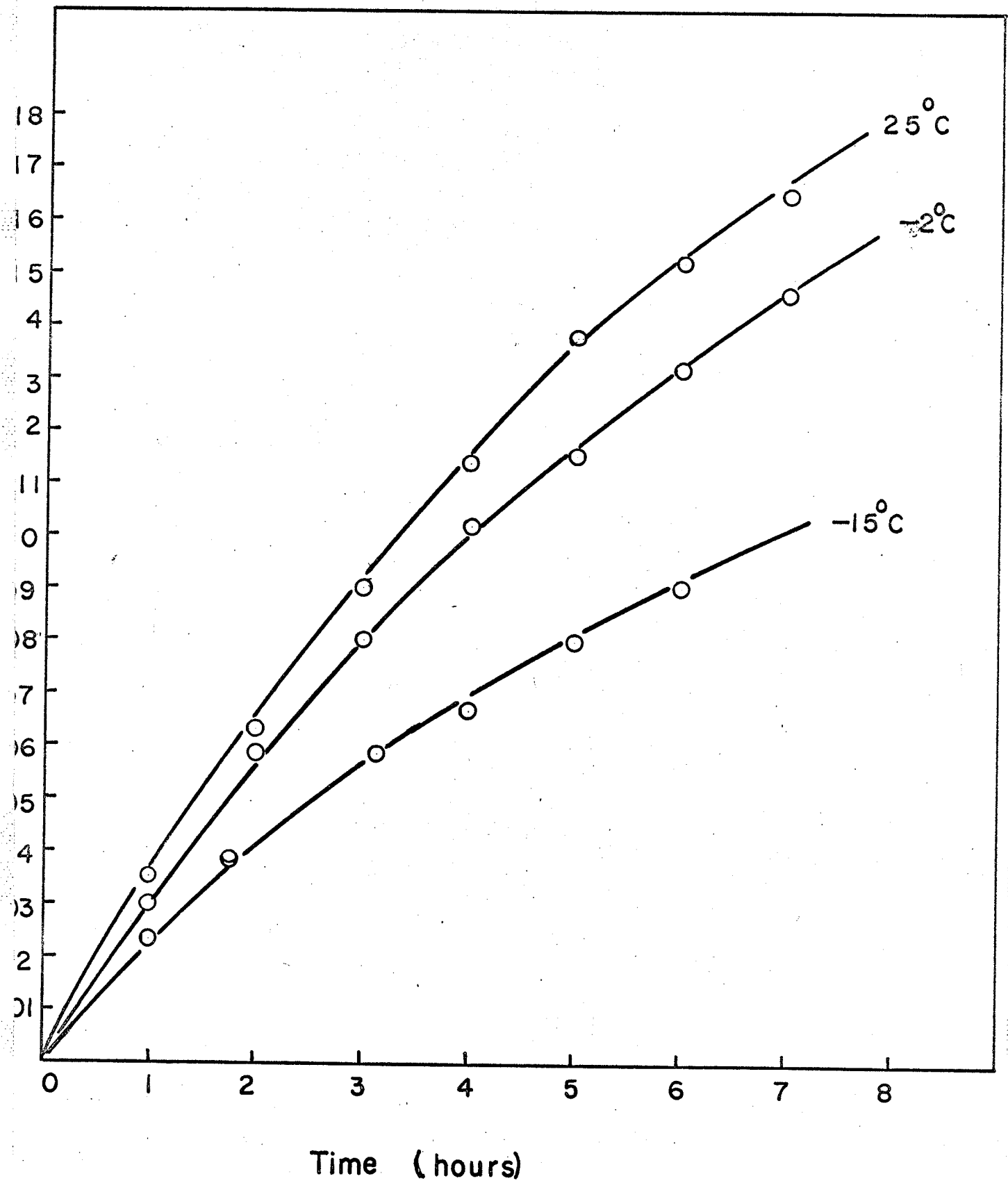


FIGURE 9. Effect of inscribed reaction temperatures on polymerization rates for a 40 volume percent solution of methylmethacrylate in dimethylformamide. Current of 15 ma. Electrolyte,  $(\text{CH}_3)_4\text{NCl}$ .



where  $E_a$  is the activation energy of the reaction,  $R$  the gas constant and  $A$  an integration constant. A plot of  $\log k$  versus  $\frac{1}{T}$  (Fig.10) yields a straight line with a slope of  $\frac{-E_a}{2.303 R}$  from which a value for the activation energy of  $3.6 \pm .5$  Kcal/mol was calculated. However, it must be acknowledged here that the  $E_a$  value is calculated from only a few experimental points over a small temperature range. The value, therefore, is only approximate.

#### EFFECT OF SOLVENT

The choice of solvents is both critical and unfortunately, severely limited. The solvent must be able to dissolve the monomer, salt and polymer, furnish a conducting medium and not interfere with the polymerization process. Results from some of a few candidate solvents are shown in Figure 11. It is seen that DMA is superior to both DMF and DMSO with respect to polymer yield. In acetonitrile, which is a good solvent and furnishes conducting solutions, no polymer formation occurred. It was found that styrene does not polymerize in a DMA solution of tetramethyl ammonium chloride whereas this appears to be a good solvent for its polymerization when potassium acetate is used as electrolyte (77). This monomer also does not polymerize in DMSO and acetonitrile solutions of the quaternary ammonium salt.

The rate of poly (MMA) formation at various initial

1950

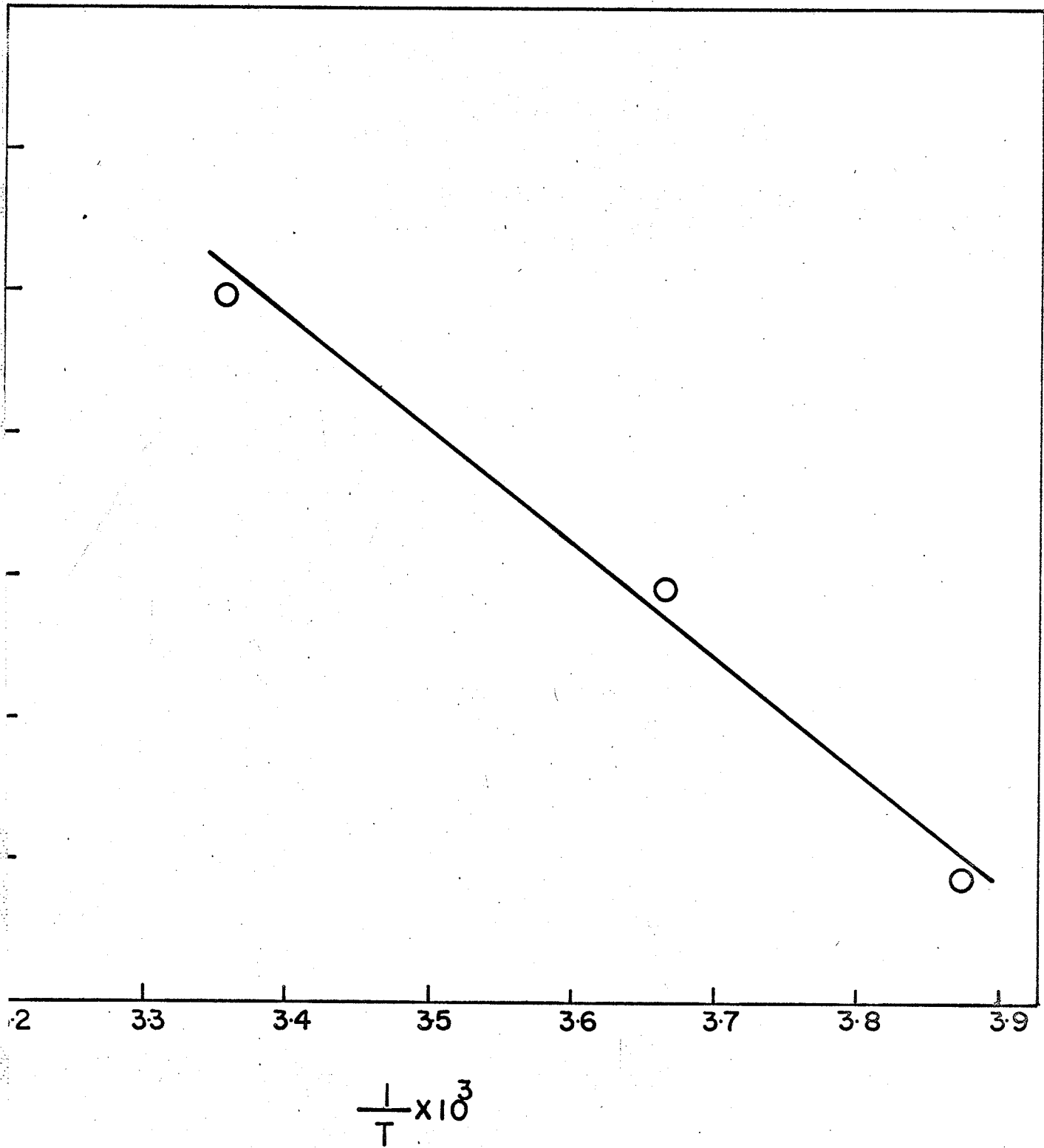


FIGURE 11. Effect of various inscribed solvents on yield of polymer at 50 ma in solutions initially containing 40 volume percent of monomer in

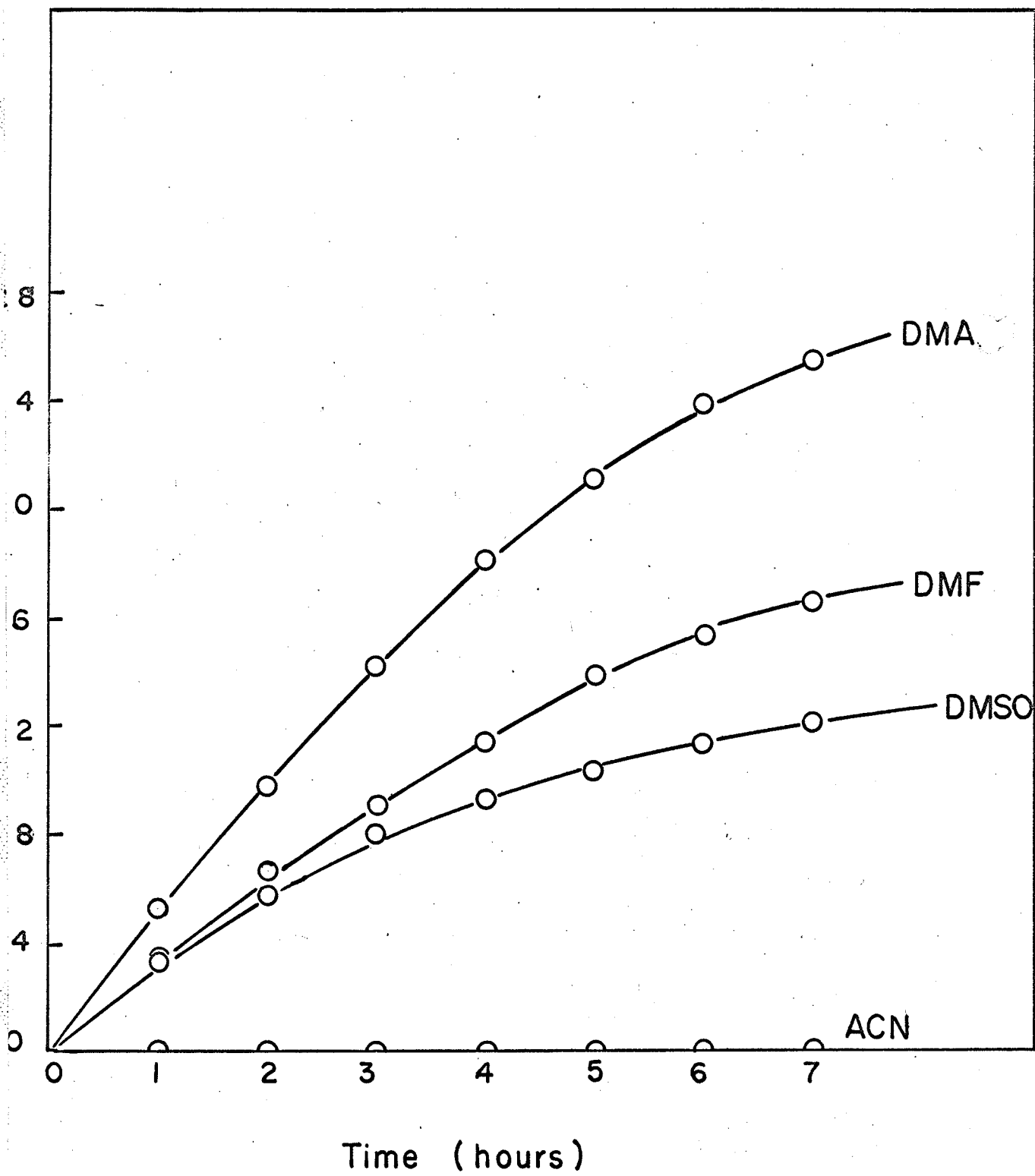
dimethylacetamide (DMA)

dimethylformamide (DMF)

dimethylsulfoxide (DMSO)

acetonitrile (ACN)

Electrolyte,  $(\text{CH}_3)_4\text{NCl}$ .





monomer concentrations in DMA solutions of tetramethyl ammonium chloride at 15 ma are shown in Figure 12. A comparison between Figure 12 and Figure 6 again indicates a higher polymerization rate in DMA.

#### EFFECT OF THE NATURE OF THE SALT

A series of experiments was performed with several salts. In each experiment a 40 vol. percent monomer solution in DMF containing 1 g salt/100 ml was employed. A current of 15 ma was passed through the solution and the weight of polymers formed was determined by precipitation. The salts employed, yields of polymers formed and corresponding molecular weights are shown in Table 6. It is obvious that the nature of the anion has no appreciable effect on the yields and molecular weights, whereas polymer yields are effected considerably by the nature of the cations.

#### EFFECT OF VARIOUS INHIBITORS

Table 7 shows that the polymer yield was essentially unchanged by the addition of a substantial quantity of p-benzoquinone or p-tert-butylcatechol. On the other hand, the addition of proton donating substances, such as methanol or water, greatly decreased the formation of polymer. This suggests the likelihood of an anionic mechanism for the polymerization.

FIGURE 12. Polymer formation at inscribed  
initial monomer concentrations in  
dimethylacetamide at a current of  
15 ma. Electrolyte,  $(\text{CH}_3)_4\text{NCl}$ .

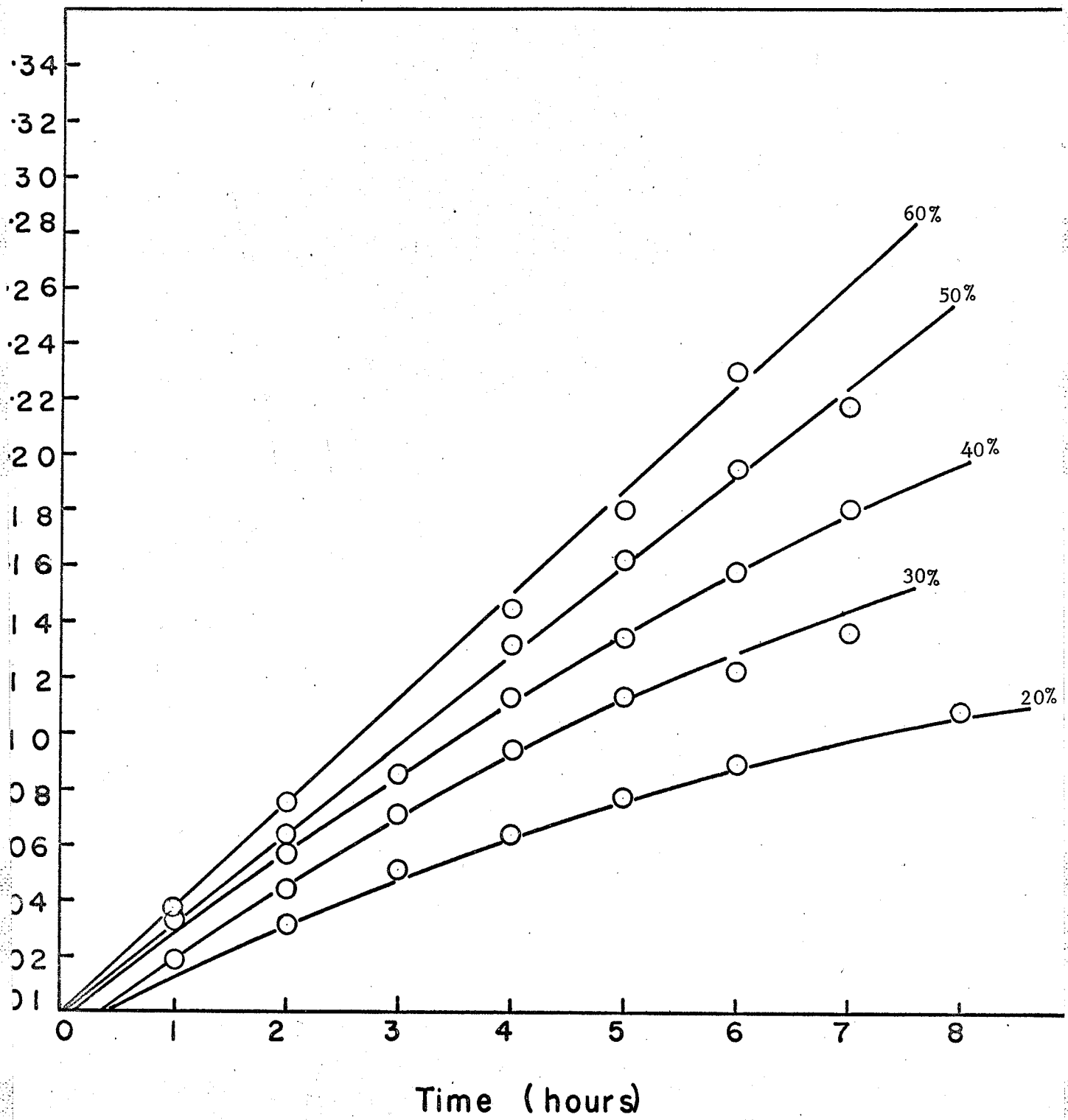


TABLE 6. Polymer formation at 15 ma with various saturated salt solutions (1 g. salt per 100 ml) containing 40 volume percent monomer in dimethylformamide.

Salt	Time of polymerization (hours)	Weight of polymer (g)	Limiting Viscosity Number	Molecular Weight
$(\text{CH}_3)_4\text{NBF}_4$	23	23.66	0.17	53000
$(\text{CH}_3)_4\text{NClO}_4$	23	24.32	0.15	44000
$(\text{CH}_3)_4\text{NCl}$	23	21.50	0.16	45000
$(\text{CH}_3)_4\text{NBr}$	23	21.30	0.15	44000
$(\text{CH}_3)_4\text{NI}$	23	21.00	0.16	48000
$(\text{CH}_3)_4\text{NO}_3$	23	21.63	0.16	48000
$(\text{CH}_3-(\text{CH}_2)_3)_4\text{NBr}$	21.5	28.22	0.19	61000
$\text{NH}_4\text{Cl}$	24	6.00	-	-
$\text{NH}_4\text{NO}_3$	24	Nil	-	-

TABLE 7. Polymer formation in the presence of various inhibitors. Solutions contained  $(\text{CH}_3)_4\text{NCl}$  in dimethylformamide at a current of 15 ma.

Inhibitors	Molar Concentration	Time of polymerization (hours)	Yield of polymer (g)	Molecular weight
p-Benzoquinone	$2.50 \times 10^{-4}$	22.25	18.25	44000
p-t-Butylcatechol	$5.09 \times 10^{-4}$	22.50	21.00	53000
Water	$2.77 \times 10^{-2}$	22.50	1.60	-
Methanol	$1.24 \times 10^{-2}$	22.83	8.50	40000

#### MOLECULAR WEIGHTS

The limiting viscosity numbers were converted to molecular weights; the results show that polymer of gratifyingly high molecular weight (50,000) was obtained. The value of the molecular weight was found to be independent of percent conversion of monomer to polymer. An apparent increase of molecular weight with decrease in temperature and a dependence on the solvent are shown in Table 8. The molecular weight was found to be constant for samples formed from various initial monomer concentration, and the limiting viscosity numbers varied between 0.15 and 0.20 (Table 9). Similarly, for the range of seven currents between 10 and 120 ma, the limiting viscosity numbers were approximately

TABLE 8. Influence of solvent and temperature on molecular weights of polymer formed at a current of 50 ma.

Solvent	Temperature °C	Limiting viscosity number	Mol. Wt.
Dimethylacetamide	25	.22	75000
Dimethylsulfoxide	25	.15	44000
Dimethylformamide	25	.18	57000
Dimethylformamide	46	.11	28000
Dimethylformamide	-2	.19	61000
Dimethylformamide	-15	.20	66000

TABLE 9. Influence of initial monomer concentration on molecular weights of polymer formed at a current of 15 ma.

Monomer concentration volume %	Limiting viscosity number	Mol. wt.
80	0.20	66000
70	0.18	57000
60	0.15	44000
50	0.18	57000
40	0.16	48000
30	0.18	57000
20	0.15	44000

the same (Table 10). The independence of the molecular weight on monomer concentration and impressed current is similar to the behavior observed in the polymerization of styrene.

### ELECTRICAL EFFICIENCIES

The electrical efficiency can be calculated from Faraday's Laws. It varies, however, with impressed current and with concentration. The limiting initial efficiency may be obtained from the initial rates of the reaction or, more conveniently, from the specific rate constants derived from the slopes of Figure 5. If a rate constant which is a function of current is defined, then,

$$\text{Initial Rate} = - \left( \frac{dM}{dt} \right)_{t=0} = kM_0$$

The electrical efficiency can be obtained by dividing this initial rate (mole monomer/unit time) by the impressed current (Faraday's/unit time) to give the initial rate in moles monomer per Faraday. The data are assembled in Table 10. The efficiency decreases with an increase in the impressed currents. On the basis of a molecular weight of approximately 50,000 an electrical efficiency of 46 moles monomer per Faraday represents about 0.1 mole polymer per electrochemical equivalent.

The depletion of monomer near the electrode by its

TABLE 10. Electrical efficiency of polymer formation in solutions containing 40 volume percent monomer.

Current ma.	Slope from Fig.5	Rate Constant (hours <sup>-1</sup> ) k	Moles of Monomer polymerized per Faraday	Limiting Viscosity Number	Mol. Wt.
10	.020	.046	46.3	.17	53000
15	.023	.054	35.9	.16	48000
25	.028	.065	26.2	.17	53000
50	.034	.078	15.7	.18	57000
75	.044	.101	13.6	.15	44000
100	.050	.115	11.6	.16	48000
120	.063	.146	12.3	.15	44000



reaction with growing chains and its electrochemical reduction might be the probable explanation for the lower electrical efficiencies at a high current density.

### COPOLYMERIZATION

The composition of the copolymers of the monomer pair MMA-Styrene, formed in various solvents at a current of 15 ma, was determined by tracer techniques. The data compiled in Table 11 show conclusively that considerable amounts of styrene incorporate in the copolymer formed in DMF and THF. This system was studied in detail by Funt and Gray (78).

### DISCUSSION

Figure 3 shows that when the passage of electric current through the monomer solution is stopped, polymerization ceases. Therefore, this clearly points out that the initiating species dies as soon as the impressed current is shut off; but its formation continues so long as the current flow exists. In the MMA polymerization by cathodic hydrogen in a heterogenous aqueous system, Tsvetkov (75) observed the continuation of polymer formation up to six hours after cessation of the current passage. This after-effect was considered as a non-stationary state involving the decay of radical concentration as soon as the electrolysis was stopped. Undoubtedly, Tsvetkov's observation is

TABLE 11. Copolymer composition from 1:1 molar ratio of styrene and methylmethacrylate polymerized in various solvents at current of 15 ma.

Solvent	Salt	Time of polymerization (minutes)	Percent conversion	Mole percent MMA in Copolymer
dimethylsulfoxide	$(\text{CH}_3)_4\text{NCl}$	230	10.9	100
dimethylacetamide	$(\text{CH}_3)_4\text{NCl}$	120	5.9	90.4
tetrahydrofuran	$(\text{C}_4\text{H}_9)_4\text{NBr}$	85	14.1	62.9
no solvent*	$(\text{C}_4\text{H}_9)_4\text{NBr}$	26	1.8	98.1
dimethylformamide	$(\text{CH}_3)_4\text{NCl}$	-	10.0	64.9

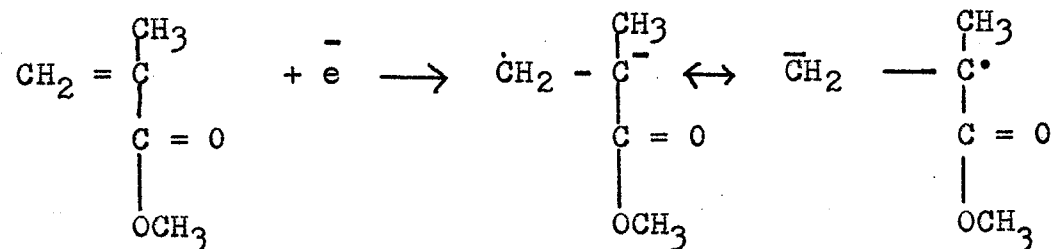
\* current between 11 and 7 ma.

not in harmony with the conventional idea of average life times of free radicals, ordinarily being a few seconds. A similar after-effect was observed by Parravano et al (74) who found that polymer radicals continued to add monomer units over a period of hours after the cessation of electrolysis. This phenomenon was also reported by Kern et al (76). However, none of these workers offered any convincing explanation for the observed after-effect. Contrary to previous works the present system is completely free from such an after-effect and hence it dramatically illustrates the control of the polymerization rate by the impressed current.

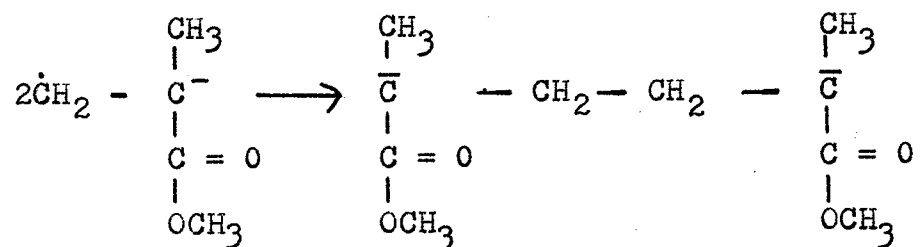
It is confirmed that the polymerization of MMA is not initiated by the anion of the quaternary ammonium salt because the polymer forms solely in the cathode. Furthermore, the yields and molecular weights of the polymers are independent of the nature of the anions of the salt as is evident from Table 6. Similar results were also obtained for the polymerization of styrene in DMF solutions of this salt.

The fact that the polymer yield is very sensitive to proton donor materials such as water or methanol, and is unaffected by the free radical inhibitors (Table 7), indicates that the initiating species is a carbanion rather than a free radical. Furthermore, the copolymerization

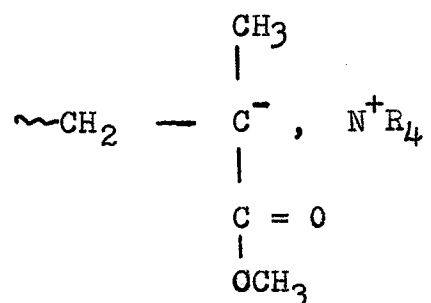
data (Table 11) suggest the anionic character of the reaction. Only with THF and DMF is there any indication of a possible free radical reaction accompanying the anionic propagation. However, it is becoming increasingly evident that it is not safe generally to accept that a copolymer formed from the anionic copolymerization of equimolar mixtures of styrene and MMA will contain less than 1 percent styrene monomer. Such a polymerization is not only a function of the monomer pair but also of initiators, solvents and other experimental conditions. In any event, if free radical polymerization does occur, it can be considered insignificant relative to the occurrence of the anionic reaction path. Possible explanations for the incorporation of styrene in the copolymer formed in DMF solutions were given by Funt *et al* (78). It is plausible to assume that the initiation process occurs through electron transfer from the electrode to the vinyl double bond of the monomer:



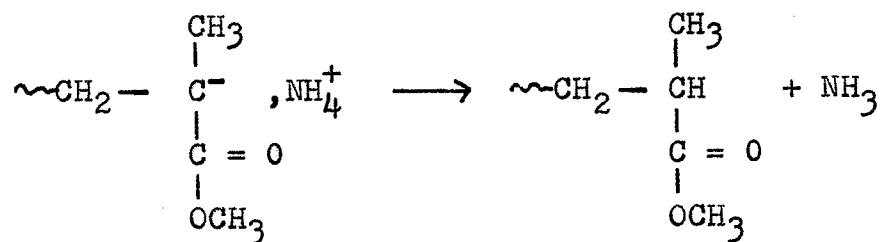
The radical ion may dimerize and give a dianion:



Under such conditions, true anionic polymerization is possible since the dianion takes part in the growth process. The anion is probably associated with the cation of the quaternary ammonium salt.



However, in view of high dielectric constant of the solvent the existence of free anions cannot be ruled out. It is obvious from Table 6 that when  $\text{N}^+\text{R}_4$  is replaced by  $\text{N}^+\text{H}_4$  the yield of the polymer is considerably decreased. It is not surprising since  $\text{N}^+\text{H}_4$  is very much less stable than  $\text{NR}_4^+$ . The  $\text{NH}_4^+$  ion can lose a proton which may cause termination of the polymerization, e.g.,



The reactivity of the growing anions also depends on the nature of the solvent. Figure 11 shows that no polymerization occurs in acetonitrile. Recently it has also been reported that electrolytically initiated anionic polymerization of acrylonitrile does not proceed in acetonitrile (19). This may be due to the fact that acetonitrile can inhibit the polymerization by losing a proton:

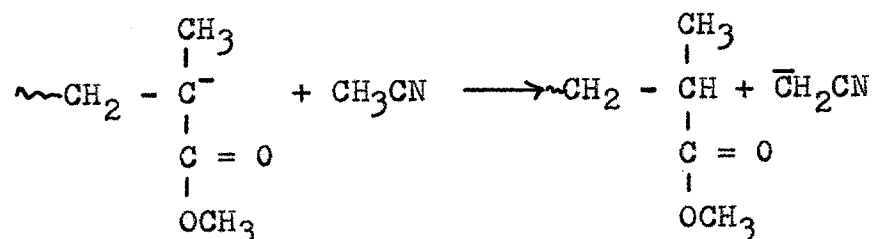
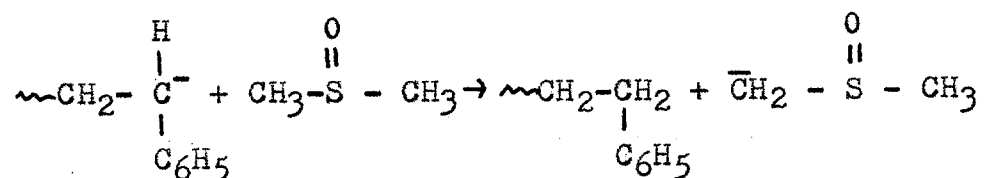
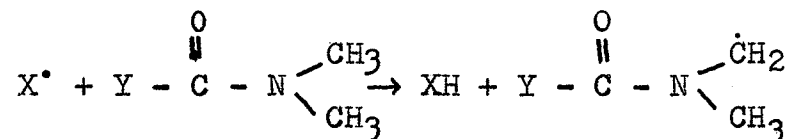


Figure 11 shows that the rates of polymerization of MMA in different solvents are in the order: DMA > DMF > DMSO. On the other hand, no styrene polymer formation occurs in DMA and DMSO when a quaternary ammonium salt is used as electrolyte (77). This monomer also does not polymerize in these solvents through a conventional method (79). The authors believe that the styrene anion presumably abstracts a hydrogen from DMSO:



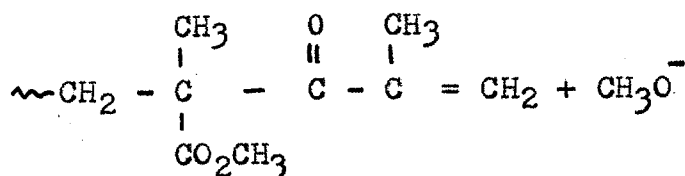
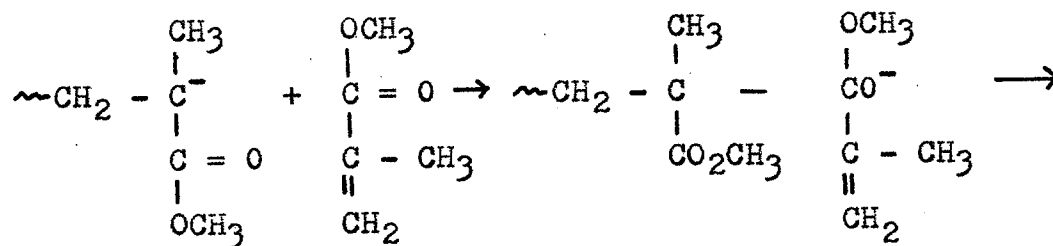
In the free radical polymerization of styrene by 2,2-azobisisobutyronitrile in DMA and DMF (80), the authors assumed a

transfer reaction with the solvents. They suggested that the transfer reaction involves abstraction of a hydrogen atom from a methyl group attached directly to the nitrogen atom:



Where X denotes H in DMF, and CH<sub>3</sub> in DMA, and X<sup>•</sup> represents a polymer radical.

In the present work, it was found that the molecular weight of the polymer is independent of monomer/solvent ratios (Table 9). The constancy of the molecular weights, therefore, rules out any appreciable chain transfer to solvent. However, it may be speculated that the reactivity of the growing polymeric anion is greater in DMA than in DMF and DMSO. The fact that a variation in current density leads to approximately identical molecular weights (Table 10) excludes the possibility of chain transfer to, or termination by, the species produced at the anode during the electrolysis. The constancy of the molecular weight with monomer concentration can be explained if it is assumed that chain termination by the monomer, takes place.



Good et al (3) observed this type of termination reaction in the case of the anionic polymerization of MMA initiated by metal amides in liquid ammonia. By polarographic evidence he showed the presence of isopropenyl ketone in the polymer solution. He discarded the possibility of a transfer reaction with the monomer, involving abstraction of an allylic hydrogen, since no double bonds of the  $\alpha,\beta$ -unsaturated ester type could be detected polarographically. Similar reactions of the ester group of MMA with initiating species and polymeric anions have been confirmed by various workers (81, 82, 83, 84, 85).

If every electron leaving the cathode produces one monomeric radical ion, which on dimerization forms a dimeric anion, then electrical efficiency should be 0.5. The result is not in harmony with this view as the maximum efficiency found was 0.1. Therefore, it seems that a sub-



stantial fraction of the electrons is lost in wasteful side reactions and/or in the formation of very low molecular weight polymers which could not precipitate.

The effect of monomer concentration (Figs. 6 and 7) and reaction temperature (Fig.9) on the reaction rate is the same as obtained in the case of styrene polymerization (16,77). The remarkable difference between the polymerization of styrene and MMA, in solutions of quaternary ammonium salts, arises from the dependence of the initial rate of the reaction on the impressed current and solvent. The polymerization of styrene proceeds as the first power of the impressed current, whereas the polymerization rate of MMA is proportional to the square root of the impressed currents (Fig.8). The rate dependence on the square root of the impressed current is difficult to comprehend.

However, this might be accounted for if it was assumed that the ion pairs composed of quaternary ammonium cations and growing polymer chains associated to form dimer complexes. Because of the reactive carbonyl group, the polymerization reaction of MMA is much more complex than that of unsaturated hydrocarbons.

#### SUMMARY

1. Methylmethacrylate was polymerized in several organic solvents containing quaternary ammonium salts. The

polymerization occurred only by the passage of electric current.

2. Kinetic experiments indicated a first order decay of monomer concentration.
3. The polymerization rate was dependent on the square root of the impressed current.
4. Molecular weights of approximately 50,000 were obtained. They were independent of salt, current density and monomer concentration, but were influenced by the nature of solvents and the reaction temperature.
5. Experimental results such as inhibitor and copolymerization studies indicate an anionic mechanism.

CHAPTER III

ELECTROLYTIC FORMATION AND DESTRUCTION  
OF LIVING ANIONS

## HIGH VACUUM APPARATUS

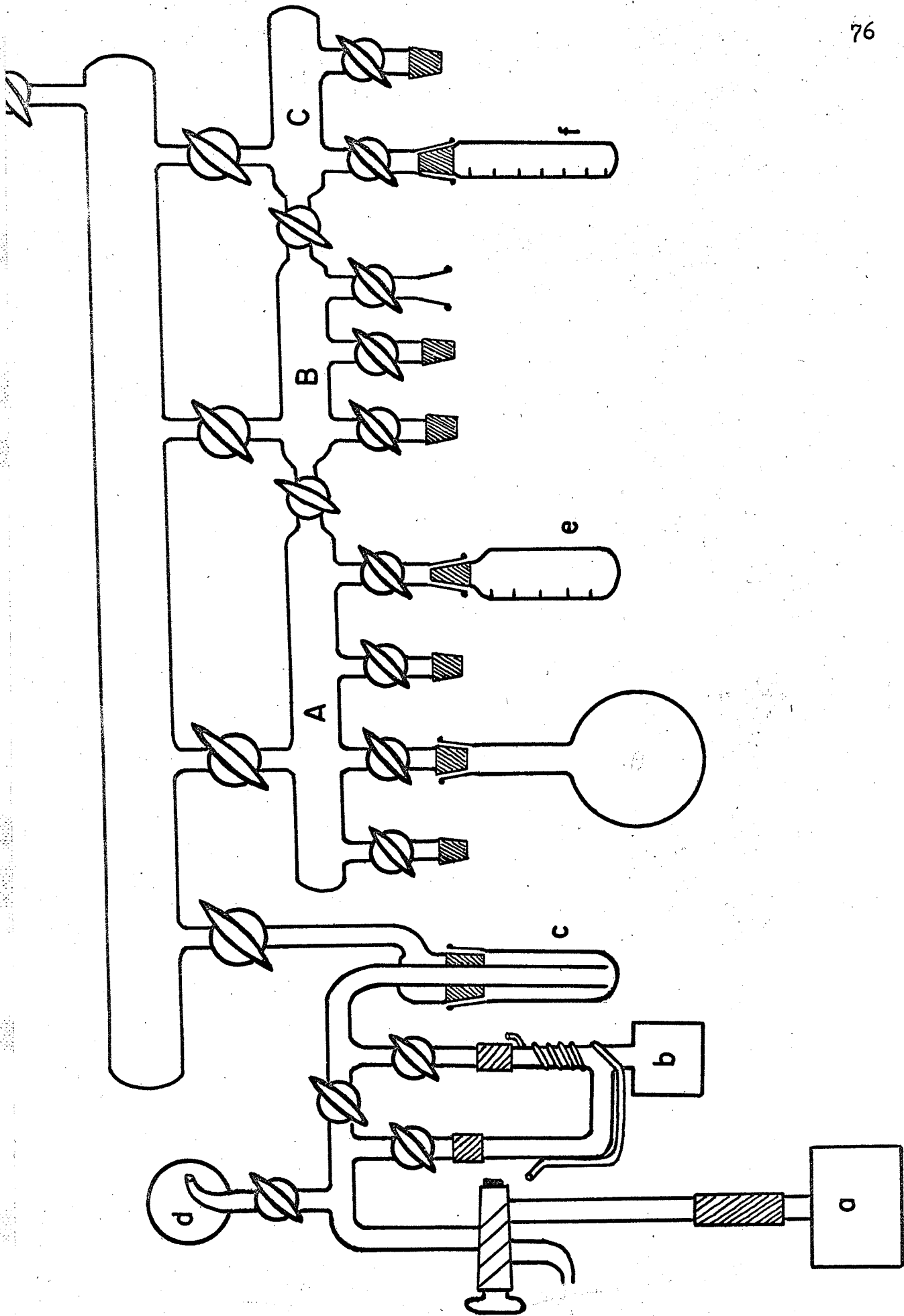
The formation of living polymers requires very rigorous experimental conditions for the exclusion of impurities from the system. Reagents must be purified under vacuum. The type of vacuum manifold employed in the present research work is shown in Figure 13. It primarily consists of a pump "a", capable of producing a vacuum of the order of magnitude of  $10^{-4}$  mm Hg. This pump serves as a fore pump for the oil diffusion pump "b" which reduces the pressure in the system to  $10^{-6}$  mm Hg. Dow corning 702 Silicone Fluid was used in the diffusion pump. A liquid nitrogen cold-trap "c" was used to safeguard the pumps. The pressure in the system was measured by McLeod gauge "d" which could be tilted. The vacuum line was divided into three sections, namely, "A" for purifying solvents, "B" for monomer purification and "C" for drying and filling the electrolytic cell. High vacuum silicone grease was employed to lubricate the vacuum stopcocks.

## PREPARATION OF METALLIC MIRRORS

In the present research sodium mirrors were used extensively as drying agents for the removal of trace amounts of moisture present in the purified solvent and monomer. Such a mirror was prepared by a method described

FIGURE 13. High vacuum apparatus.

- a, vacuum pump.
- b, oil diffusion pump.
- c, liquid nitrogen trap.
- d, McLeod gauge.
- e and f, measuring tube.
- A, B and C three sections for purification of solvent, monomer and filling electrolytic cell respectively.



in the literature (86). Small pieces of the pure sodium metal were placed in the flask to be used in the drying operation and connected to the vacuum line. The flask was pumped under high vacuum for a minimum of two hours. When the pressure fell below  $10^{-5}$  mm Hg, and while still being evacuated, the bottom of the flask was intermittently and gently heated until the sodium metal just began to melt. The sodium vaporized and deposited on the walls of the flask to give a shining mirror. After the mirror formation, evacuation was continued until the flask cooled to room temperature. Then the liquid to be dried was distilled into the flask. A fresh sodium mirror was always used for each subsequent drying operation.

#### DRY BOX

To handle pyrophoric materials such as sodium aluminium tetraethyl a dry box was used extensively. The nitrogen used to purge the dry box was purified by passing it through a liquid nitrogen trap, columns of potassium hydroxide, a further liquid nitrogen trap, a silica gel column, a magnesium perchlorate column and glass wool. Phosphorus pentoxide and magnesium perchlorate were employed as dehydrating agents in the dry box.

#### GAS LIQUID CHROMATOGRAPHY

GLC analyses were performed on a Microtek chromatograph

using a 6 ft. x .25 in. column packed with 20 percent Apiezon L grease deposited on fire brick.

#### SPECTROPHOTOMETER

A Beckman DB equipped with a pen recorder was used for all spectrophotometric measurements. The cell holder of the spectrophotometer was thermostatted at 25°C.

#### PURIFICATION OF SOLVENT AND MONOMER

##### Tetrahydrofuran (THF)

THF (AR) was stirred with calcium hydride for 24 hours and then was fractionally distilled and collected in a flask containing small pieces of sodium metal. It was refluxed with the sodium for several hours and fractionally distilled into a flask containing calcium hydride. This flask was then attached to the vacuum system. The stop cock between the flask and the vacuum was opened momentarily to remove some air from the flask. The THF was flash-distilled into a thoroughly dried and evacuated flask connected to the vacuum line. The solvent was thoroughly degassed by alternate freeze and thaw cycles. Liquid nitrogen was used as a freezing agent. The degassed THF was flash-distilled into a flask freshly coated with a sodium mirror. The flash-distillation was repeated consecutively with three sodium mirrors to ensure complete



dryness. Once again the THF was degassed to remove any hydrogen formed by the reaction of moisture with the sodium mirror. The purified THF was stored in contact with the mirror until it was used; but in any case it was not kept for more than three days.

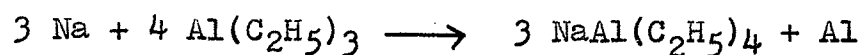
### MONOMERS

Styrene, alpha-methylstyrene and isoprene were dried over calcium hydride. The flask containing the monomer was connected to a vacuum line and its contents frozen and degassed. Then it was flash-distilled into a sodium film coated flask. The monomer was left over the mirror for at least two hours, degassed and distilled into another sodium film coated flask. When the monomer started to polymerize, it was distilled into a flask containing calcium hydride. The distilled monomer was stored over calcium hydride in vacuum.

### ELECTROLYTES

#### Sodium aluminium tetraethyl (Na Al (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>)

The NaAl(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub> was prepared according to the following reaction (87).



The apparatus used for its preparation is shown in Figure 14.

FIGURE 14. Apparatus for preparation of  $\text{NaAl}(\text{C}_2\text{H}_5)_4$ .

A, teflon connector.

B and F, B-24 joints.

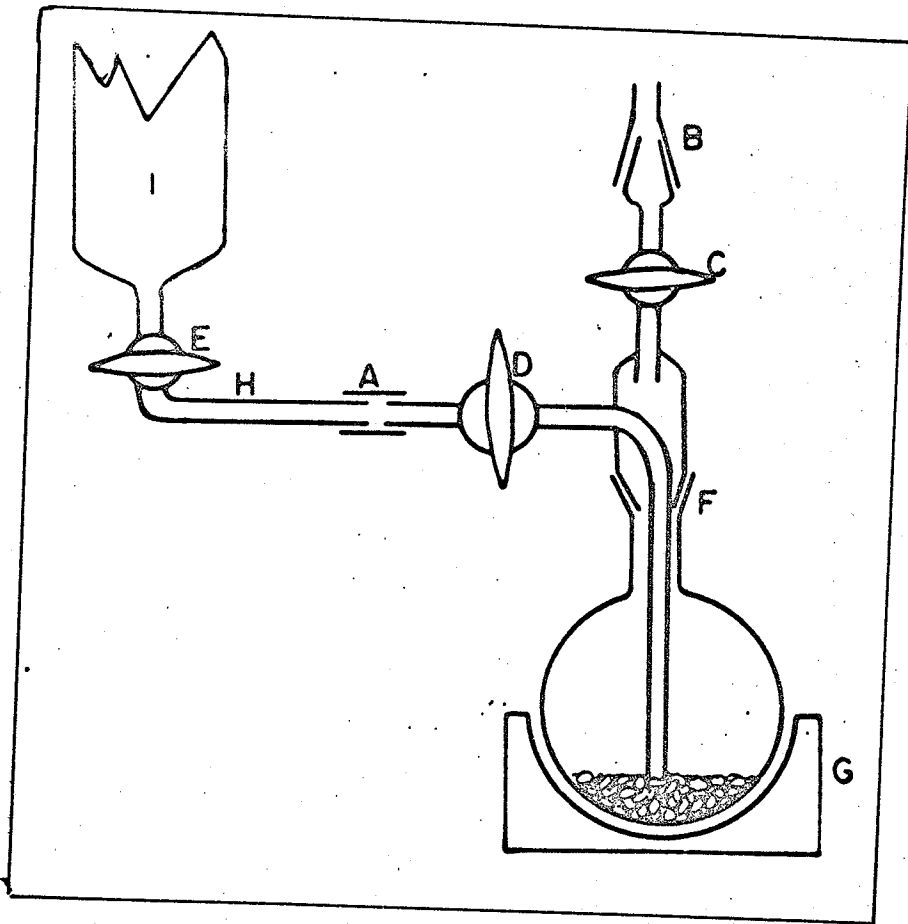
C and D, teflon-plug stopcocks.

E, metal tap

G, heating mantle

H, copper tubing

I, aluminium triethyl cylinder.



An excess of freshly cut sodium was placed in a 500 ml flask which was connected by a teflon joint "A", to the  $\text{Al}(\text{C}_2\text{H}_5)_3$  container "I". Benzene was pumped off the sodium and the tube to the container was evacuated through "B", which was connected to a vacuum pump. When sufficient  $\text{Al}(\text{C}_2\text{H}_5)_3$  had been added E was closed. From time to time the flask was opened to the pump momentarily at C. Eventually the sodium became coated with aluminium and the reaction almost ceased. To reactivate it the temperature of the flask was raised to above  $100^\circ\text{C}$  and further reaction took place in a homogeneous molten phase. At the completion of the reaction the flask and contents were allowed to cool, removed at "A" with "C" and "D", closed and transferred to the dry box. The  $\text{NaAl}(\text{C}_2\text{H}_5)_4$  product was removed by crystallization from freshly distilled benzene. After further recrystallizations the product was pumped on the vacuum line for several hours, yielding white crystals. The storing and all subsequent handling of the salt was performed under a nitrogen atmosphere in the dry box.

#### SODIUM TETRAPHENYL BORON ( $\text{Na}(\text{C}_6\text{H}_5)_4\text{B}$ )

This salt was obtained from Fisher (99.7 percent) and used without further purification as all attempts to recrystallize it from aqueous acetone (3 parts of acetone

by volume and 1 part of water) failed (43).

$K(C_6H_5)_4B$

It was prepared by treating dilute aqueous solutions of sodium tetraphenyl boron with an equivalent amount of potassium chloride (43). The relatively insoluble  $K(C_6H_5)_4B$  precipitated. The filtered and washed product was then purified by repeated crystallization from aqueous acetone (3 parts of acetone by volume and 1 part of water). The salt was dried under vacuum at  $50^\circ C$ .

$Li(C_6H_5)_4B$

The lithium salt was made by mixing a slight excess of a concentrated THF solution of lithium chloride to a concentrated THF solution of  $Na(C_6H_5)_4B$  (43). The relatively insoluble sodium chloride precipitated. The solution was allowed to stand for a few hours to settle down all suspended materials and then the solution was filtered to remove the insoluble sodium chloride. The filtrate containing lithium tetraphenyl boron was slowly evaporated on a steam bath to recover the salt, which was then dissolved in ethylene chloride and insoluble lithium chloride was filtered off. The lithium tetraphenyl boron was precipitated by addition of cyclohexane. This procedure was then repeated at least

five times to ensure the complete removal of lithium chloride. The final product was dried in vacuum at 50° and stored in vacuum.

TETRABUTYLAMMONIUM TETRAPHENYL BORON (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N B (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>

This was prepared by treating sodium tetraphenyl boron with an equivalent amount of tetrabutyl ammonium iodide in aqueous solutions (88,43). The required product precipitated and was purified by repeated recrystallization from aqueous acetone. The salt was dried and stored as before.

Tetrabutyl ammonium bromide and perchlorate were obtained commercially in polarographic grade purity and were used without further purification.

EXPERIMENTAL PROCEDURE

UNDIVIDED CELL

The preliminary exploratory experiments were conducted in a cell shown in Figure 15, referred to as an undivided electrolytic cell, since anode and cathode electrodes were not separated. With reference to the Figure "A" is a teflon enclosed magnetic stirring bar, "BB" are 4.5 x 2 cm platinum electrodes 1 cm. apart. "E" is the filling tube and "C" is the ampoule, a weighed

FIGURE 15. Undivided electrolytic cell.

N and M, constrictions to seal-off.

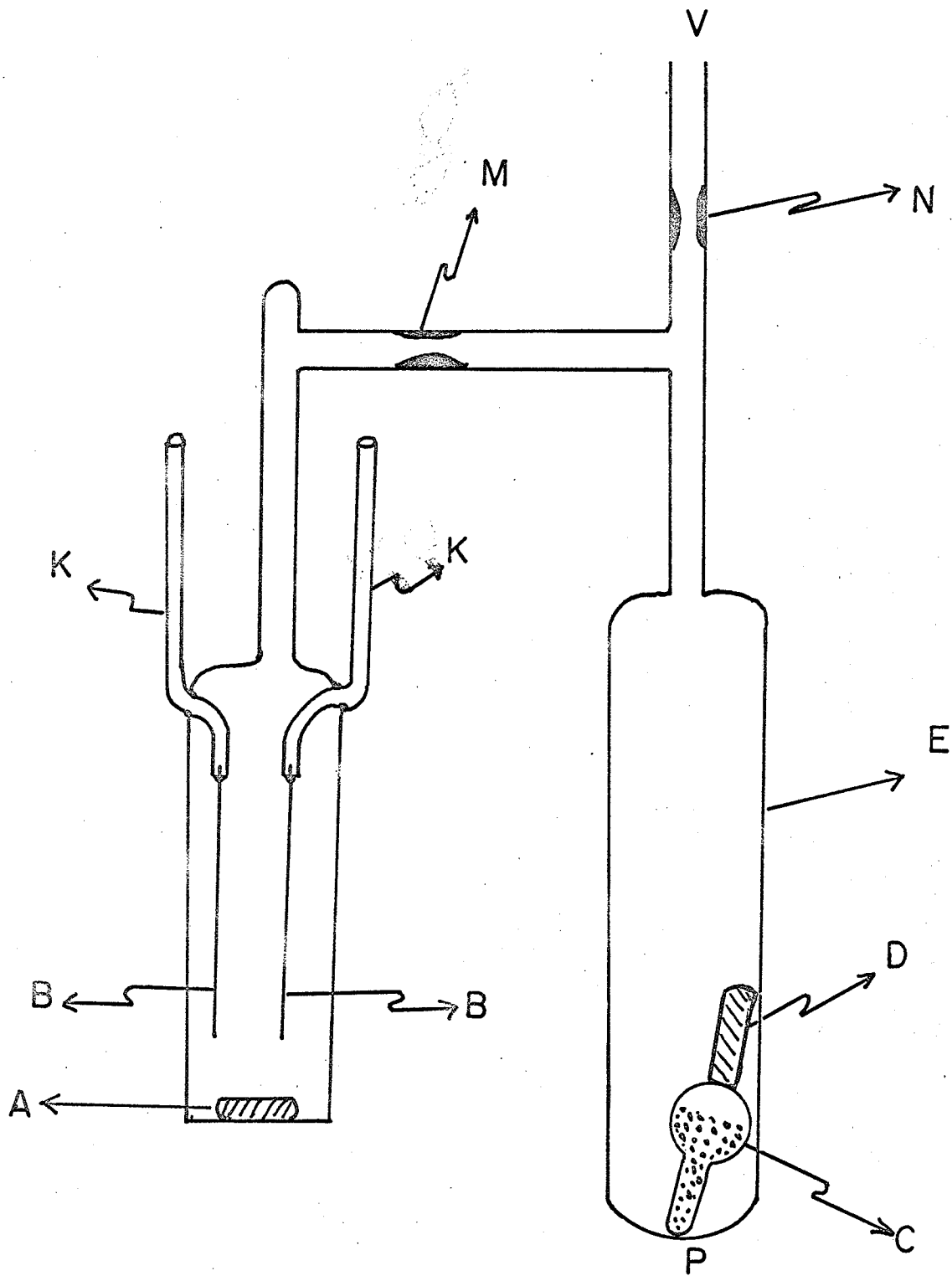
B-B, 4.5 x 2 cm platinum electrodes  
1 cm apart.

K-K, mercury contacts.

D, teflon sealed magnetic bar to  
crash ampoule, C.

E, filling tube.

V, connected to vacuum line.





quantity of  $\text{NaAl}(\text{C}_6\text{H}_5)_4$ , which was prepared in the dry box. The bottom "P" of the filling tube was sealed off after insertion of the ampoule. "D" is a teflon coated magnetic bar. The whole apparatus was connected to the vacuum line through a glass ground joint and subsequently pumped for several hours until the pressure reached below  $10^{-5}$  mm Hg. The ampoule was then crushed and the salt was dried by pumping for several hours.

Measured quantities of solvent and monomer were distilled into the filling tube from graduated tubes. The materials were degassed in the usual manner. The filling tube was removed from the vacuum line by sealing off at the constriction N. The contents were warmed to room temperature and transferred to the electrolytic cell. The empty filling tube was disconnected from the cell by sealing off at the constriction M. The total volume of the solution in the cell was 35 ml at  $25^\circ\text{C}$ ; monomer and salt concentrations being 1 and .042 M respectively. The solution was stirred and thermostated at  $25^\circ\text{C}$  as before.

#### DIVIDED CELL

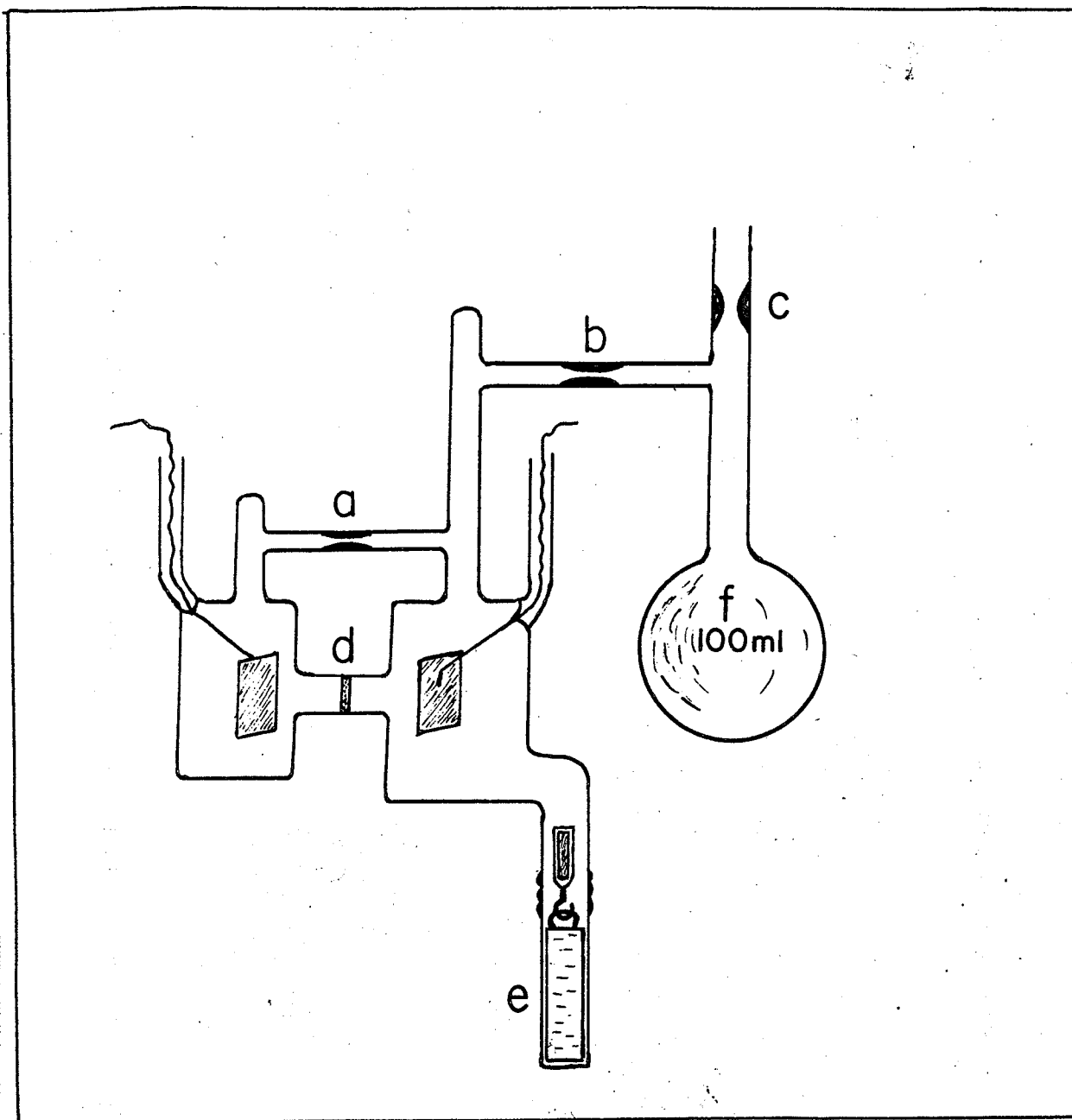
The type of divided cell which was extensively used in the present research is shown in Figure 16. Two platinum electrodes of 1" x 1" area were placed in the divided cell. The electrodes were sealed in the glass with tungsten

FIGURE 16. Divided electrolytic cell.

a, b, c, constrictions for seal-off.

d, sintered disc.

e, 10 mm quartz optical absorption cell  
for DB spectrophotometer and movable  
9 mm quartz.



wire beads which provided a vacuum tight seal and were found to be chemically inert to the reaction components. The electrodes were separated by a fine fritted glass disc "d" of 1 cm diameter, whose maximum pore size was 4.5 to 5 microns. In many cases an ultra-fine fritted disc of maximum pore size 0.9 to 1.4 microns was employed. The disc was rigid enough to withstand applied voltages and was non-corrosive and passive to reaction media. The distance between the two electrodes was approximately 9 cm. The tube "a" between the two compartments was used to fill the anode compartments with the solution and equalize the vapour pressure of the anode and cathode compartments. The appendage "e" to the cathode compartment was a 1 x 1 cm. quartz optical absorption cell and was coupled to the apparatus by a graded seal. A 9 mm quartz spacer attached to a magnet (sealed inside a glass capsule) was inserted into the cell. With the help of this magnet the spacer could be moved to provide a mixing of the contents in the optical cell. A 100 ml glass bulb "f" (termed as a filling bulb) was attached to the electrolytic cell. Alkali metal tetra-phenyl boron, quaternary ammonium tetraphenyl boron and sodium aluminum tetra-ethyl were extensively used as electrolytes for conducting the currents. Generally a weighed quantity of the electrolyte (0.5 g) was dissolved in 10 ml pure THF and the resulting solution was filtered to

remove suspended materials, and was introduced into the filling bulb by a hypodermic syringe. The filling bulb was attached to the vacuum line and its contents were frozen in liquid nitrogen and evacuated. The THF was distilled off and the salt was dried in vacuum at  $10^{-6}$  mm Hg pressure at  $50^{\circ}\text{C}$  for 16-24 hours. Pumping for this period of time ensured the complete removal of moisture and air from the salt and apparatus. In the case of the pyrophoric  $\text{NaAl}(\text{C}_2\text{H}_5)_4$  similar procedure, as had been described in the undivided cell experiment, was adopted. A known volume of rigorously purified alpha-methylstyrene and THF were distilled into the filling bulb. The solution was frozen and degassed for the last time. The vessel was sealed off at the constriction "c" at  $10^{-6}$  mm Hg pressure and removed from the vacuum line. The contents of the filling bulb were brought to  $25^{\circ}\text{C}$  and then thoroughly mixed and transferred to the electrolytic cell to fill the anode and cathode compartments above the level of the electrodes. Ordinarily, the filling bulb was sealed off at the constriction "b" and removed. However, when it was desired to drain back the contents of the cathode compartment to the filling bulb after the experiment, the bulb was not detached from the cell. In such a case, constriction "a" was sealed and, by tilting the apparatus and cooling the

filling bulb, the catholyte was poured back. Now it could be removed from the cell. This procedure prevented mixing the catholyte with the anolyte.

The total volume of solution was 84.8 ml and that of the catholyte  $55.2 \pm 0.5$  ml at  $25^{\circ}\text{C}$ . The monomer concentration in the solution was 0.43 M. In all experiments the same volume of catholyte and monomer and salt concentrations was used unless otherwise stated.

#### RESULTS OF UNDIVIDED CELL EXPERIMENT

##### (a) Styrene Monomer

The passage of 5 ma through styrene solution in THF with  $\text{NaAl}(\text{C}_2\text{H}_5)_4$  resulted in the formation of the characteristic orange-red color of the polystyrene anions at the cathode but it quickly decolorized on stirring. The polymer dropped from the cathode. The solution became very viscous after 15 minutes electrolysis but it did not become red. When the reaction mixture was poured into methanol the solid white polymer precipitated and the yield was quantitative. Such rapid polymerization by electrolytic means was not observed before.

##### (b) Isoprene Monomer

When the solution containing isoprene was electrolysed at 5 ma current and the solution was not stirred, the charac-

teristic yellow color of the polyisoprene anion formed at the cathode and settled at the bottom of the cell. If the solution was stirred the yellow color disappeared immediately. Only when the solution became very viscous did the yellow color persist on stirring but vanished when the mixture was allowed to stand for a few hours. The polymer yield was almost quantitative.

(c) Alpha-methylstyrene

When a monomer solution in THF containing  $\text{NaAl}(\text{C}_2\text{H}_5)_4$  was electrolysed a deep red color formed at the cathode but vanished quickly on stirring. Prolonged electrolysis at 5 ma did not turn the solution red. However, when a current of 40 ma was passed for more than 2 hours, the red color, due to the living anion, persisted even on stirring the solution. Continuous electrolysis yielded a deep red solution which became water clear when it was exposed to air. No polymer was isolated at  $25^\circ$  but it was formed when the red solution was cooled to  $-80^\circ$ . Such a red color formation was also observed when electrolyses were performed with  $\text{Na}(\text{C}_6\text{H}_5)_4\text{B}$  and  $\text{Li}(\text{C}_6\text{H}_5)_4\text{B}$ .

These experimental findings demonstrate that living anions form at the cathode, but are killed by some species generated at the anode. Therefore, it became essential to use a divided cell for separating the anode and cathode

products formed during the electrolysis.

### RESULTS OF DIVIDED CELL EXPERIMENTS

#### ABSORPTION SPECTRA OF LIVING ANIONS OF ALPHA-METHYLSTYRENE AND STYRENE

The passage of an electric current of 5 ma through a solution of alpha-methylstyrene in THF containing  $\text{Na}(\text{C}_6\text{H}_5)_4\text{B}$  resulted in the formation of a red color in the catholyte, while the anolyte remained colorless. Within a few minutes of electrolysis, the catholyte became red. The absorption spectra of the red solution were measured spectrophotometrically; taking pure THF as the reference sample and are shown in Figure 17. It is seen from this figure that maximum absorbance occurs at 340 m $\mu$  and increases with increase in time of electrolysis.

When the catholyte and anolyte were mixed together, the red color disappeared. This implies that the species formed at the anode destroyed the living anions. The spectrum of the resulting mixed solution is shown in the bottom curve of Figure 18. When this solution was again electrolysed at the same current for 16 minutes the original red color reappeared in the catholyte. The spectrum of this re-electrolysed cathode solution is shown in the top curve of Figure 18. The differential spectrum of the resulting solution is also presented. In this case the



FIGURE 17. Absorption spectra of living anion solutions of alpha-methylstyrene after 7, 16 and 22 minutes electrolysis at 5 ma. Electrolyte  $\text{Na}(\text{C}_6\text{H}_5)_4\text{B}$ .

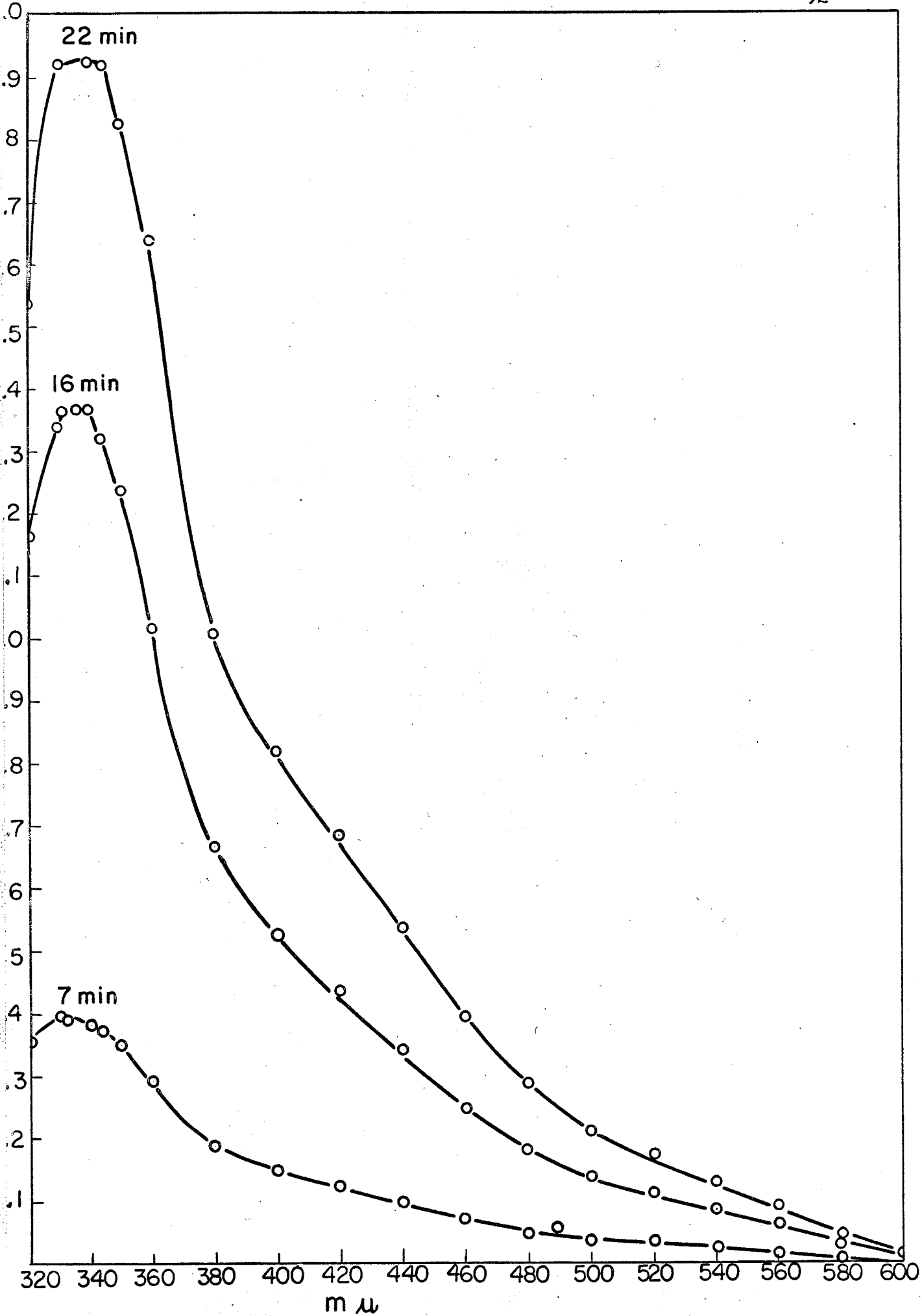
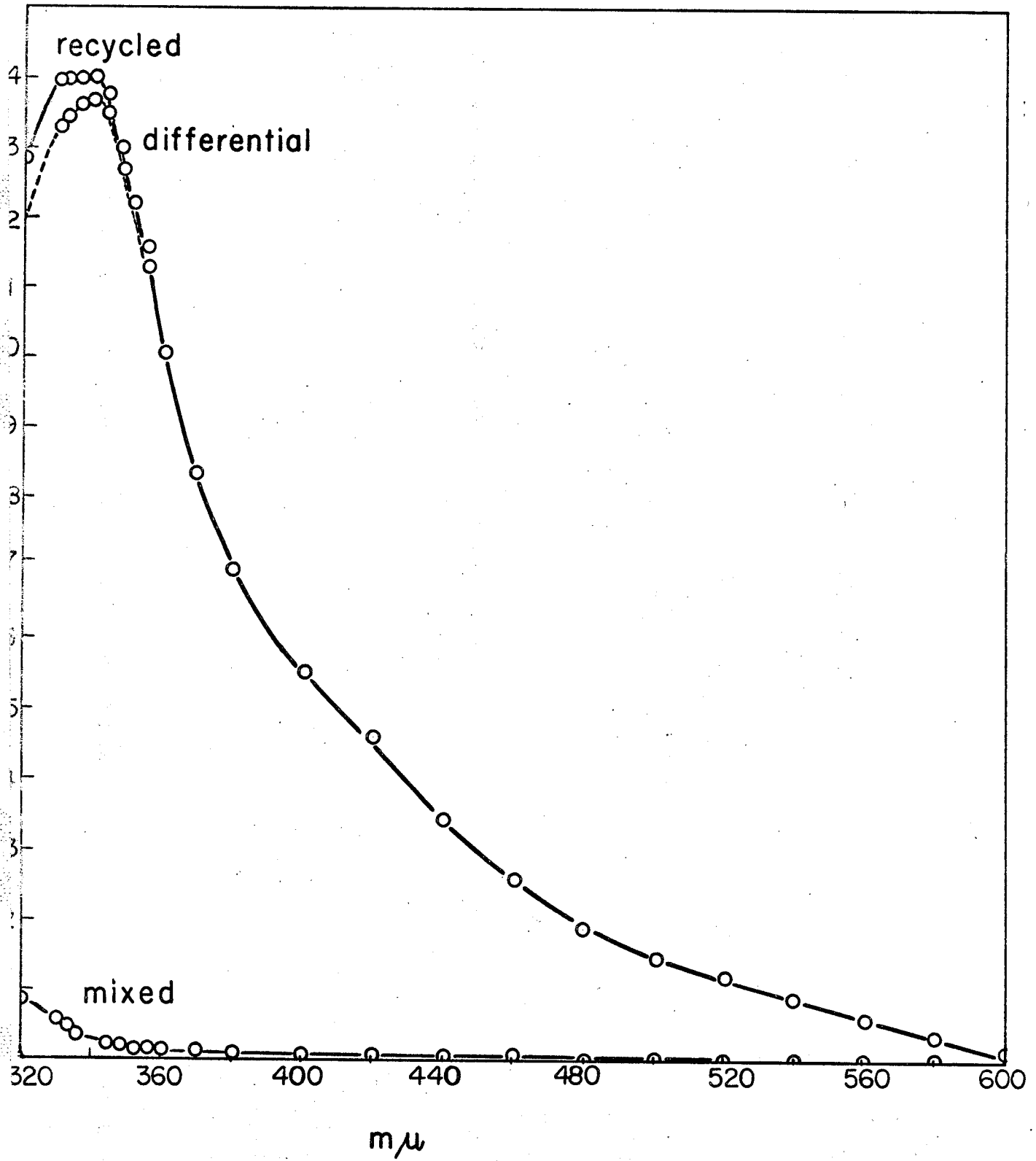


FIGURE 18. Absorption spectra of solution after mixing of anode and cathode solutions of Figure 17 followed by further electrolysis at a current of 5 ma for 16 minutes.



maximum absorbance also occurred essentially at the same position. Similar absorption spectra for the living anions produced electrolytically in the presence of  $K(C_6H_5)_4B$  and  $NaAl(C_6H_5)_4$  are shown in Figures 19 and 20 respectively. When an ampule of styrene was mixed with this red solution, the monomer polymerised immediately. The absorption spectrum of the resulting polymer solution is shown in Figure 21. The absorption maxima of living anions of alpha-methylstyrene and polystyrene are the same as have been described in the literature (34,31,32).

#### STUDY OF DIFFUSION THROUGH THE FRITTED DISC

Before doing a kinetic study on the living anion formation it was believed essential to investigate the possible diffusion through the fritted disc used to separate the anode and the cathode compartments. Therefore, a solution of alpha-methylstyrene in THF containing sodium tetraphenyl boron was electrolysed at 3 ma for 34 minutes. The absorbance of the catholyte after electrolysis was measured at 340 m $\mu$  as a function of time. Data are compiled in Table 12 from which it was concluded that there is no appreciable change in the absorbance for the first 4 hours. After 50 hours there was only a 14 percent change in the absorbance occurred. All of this cannot be considered to be due to diffusion. With  $K(C_6H_5)_4B$  and  $NaAl(C_6H_5)_4$  there was also

FIGURE 19. Absorption spectra of living anion solution of alpha-methylstyrene after 35, 60 and 75 minutes electrolysis at 1.3 ma. Electrolyte,  $K(C_6H_5)_4B$ .

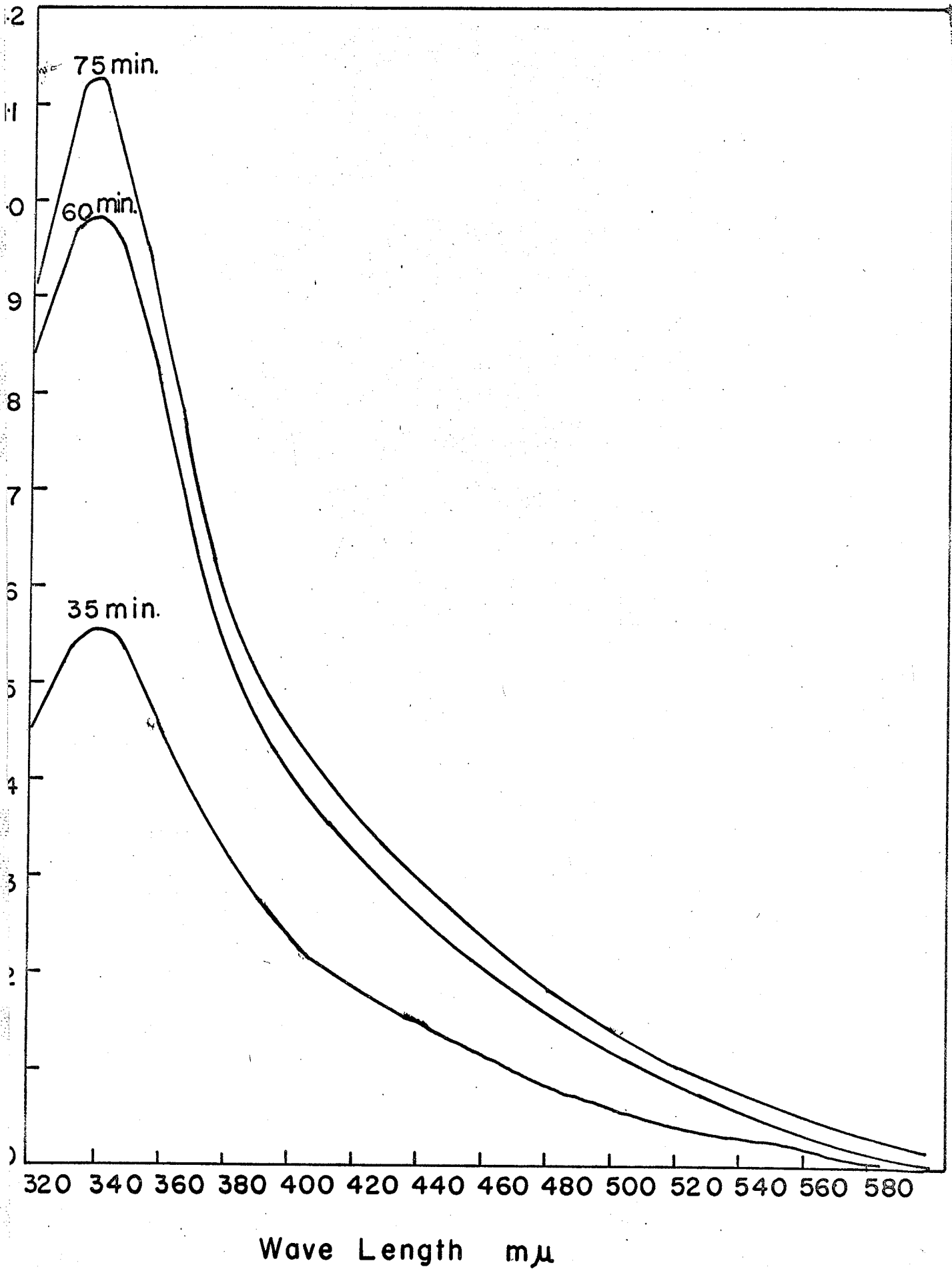
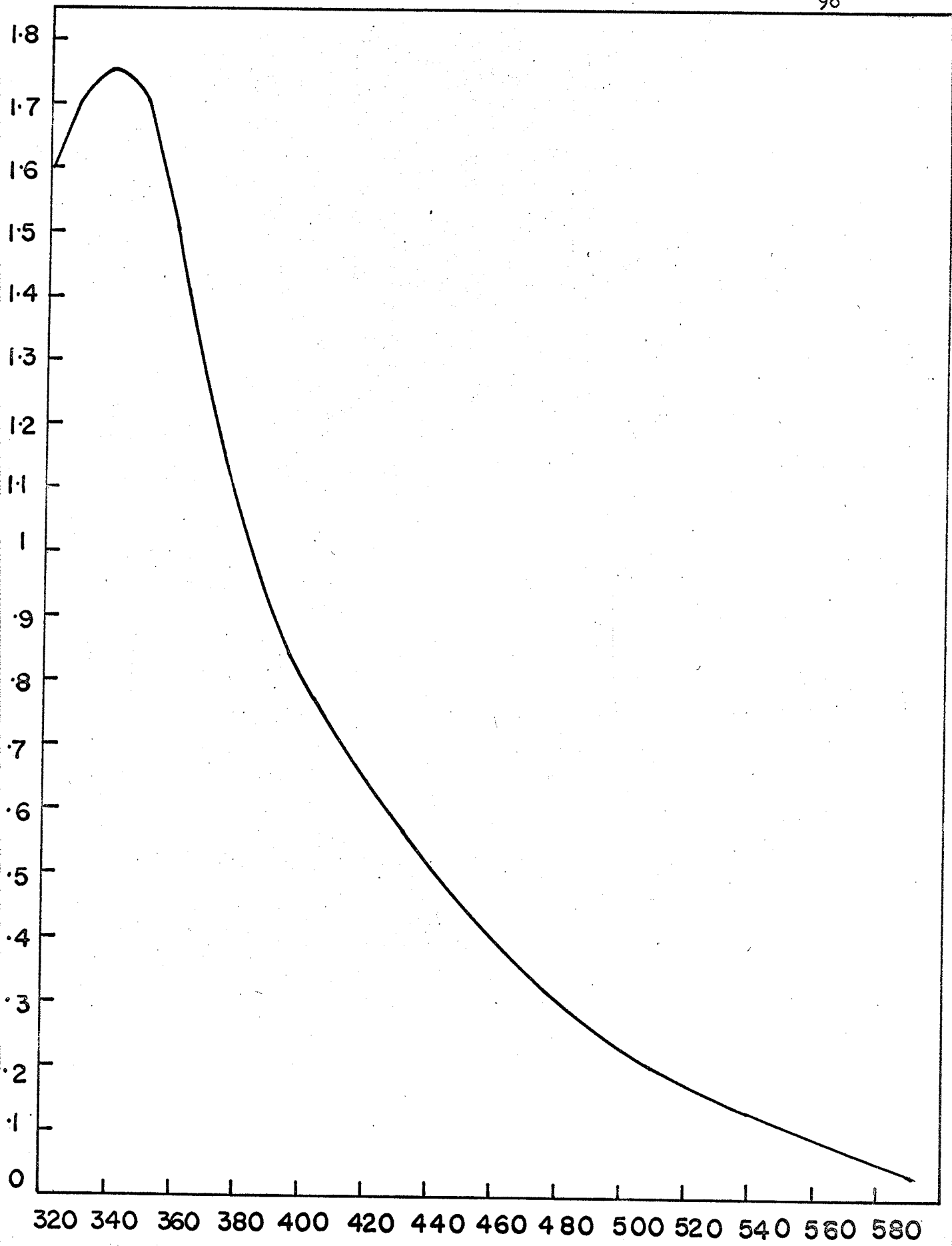


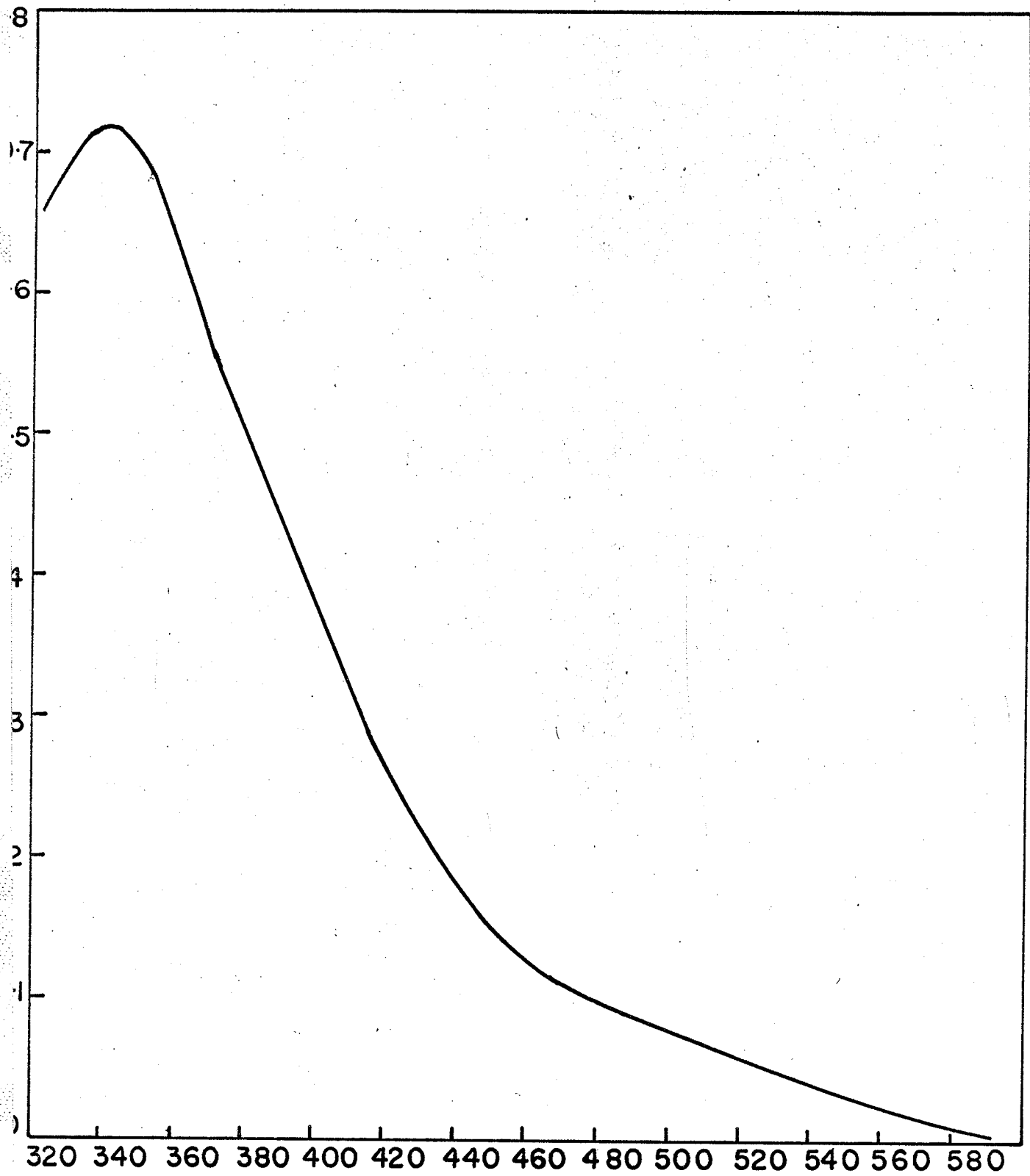
FIGURE 20. Absorption spectrum of living anion solution of alpha-methylstyrene after electrolysis at 2.4 ma for 20 minutes. Electrolyte,  $\text{NaAl}(\text{C}_6\text{H}_5)_4$ .





Wave Length mμ

FIGURE 21. Absorption spectrum of living polystyrene formed by living alpha-methylstyrene anions.



Wave Length mμ

no change in the absorbance in the first 4 hours.

TABLE 12. Change in absorbance of living anion solution after electrolysis.

Time hours	Absorbance (at 340 m $\mu$ ).
0	1.456
1	1.456
2	1.456
3	1.456
4	1.420
5	1.398
6	1.398
7	1.377
8	1.367
9	1.367
50	1.249

QUANTITATIVE RELATIONSHIPS BETWEEN CHARGE TRANSFERRED  
AND THE POPULATION OF LIVING ANIONS

Monomer solutions containing  $\text{Na}(\text{C}_6\text{H}_5)_4\text{B}$ ,  $\text{K}(\text{C}_6\text{H}_5)_4\text{B}$  and  $\text{NaAl}(\text{C}_2\text{H}_5)_4$  were electrolysed at a current of 1.3 ma. The applied voltages necessary for the passage of this constant current with these electrolytes are presented in Table 13. The concentration of living anions in terms of the absorbance at 340 m $\mu$  was measured as a function of electrolysis time. The results are summarized in Table 14 and graphically shown in Figure 22. The charge transferred was calculated by the following equation:

TABLE 13. Applied potential required to maintain a constant current of 1.3 ma with different electrolytes.

Electrolyte	$\text{Na}(\text{C}_6\text{H}_5)_4\text{B}$	$\text{K}(\text{C}_6\text{H}_5)_4\text{B}$	$\text{NaAl}(\text{C}_2\text{H}_5)_4$
Applied voltage (V)	17-17.5	200-210	8

TABLE 14. Increase in absorbance of living anions as a function of electrolysis time at 1.3 ma with different electrolytes.

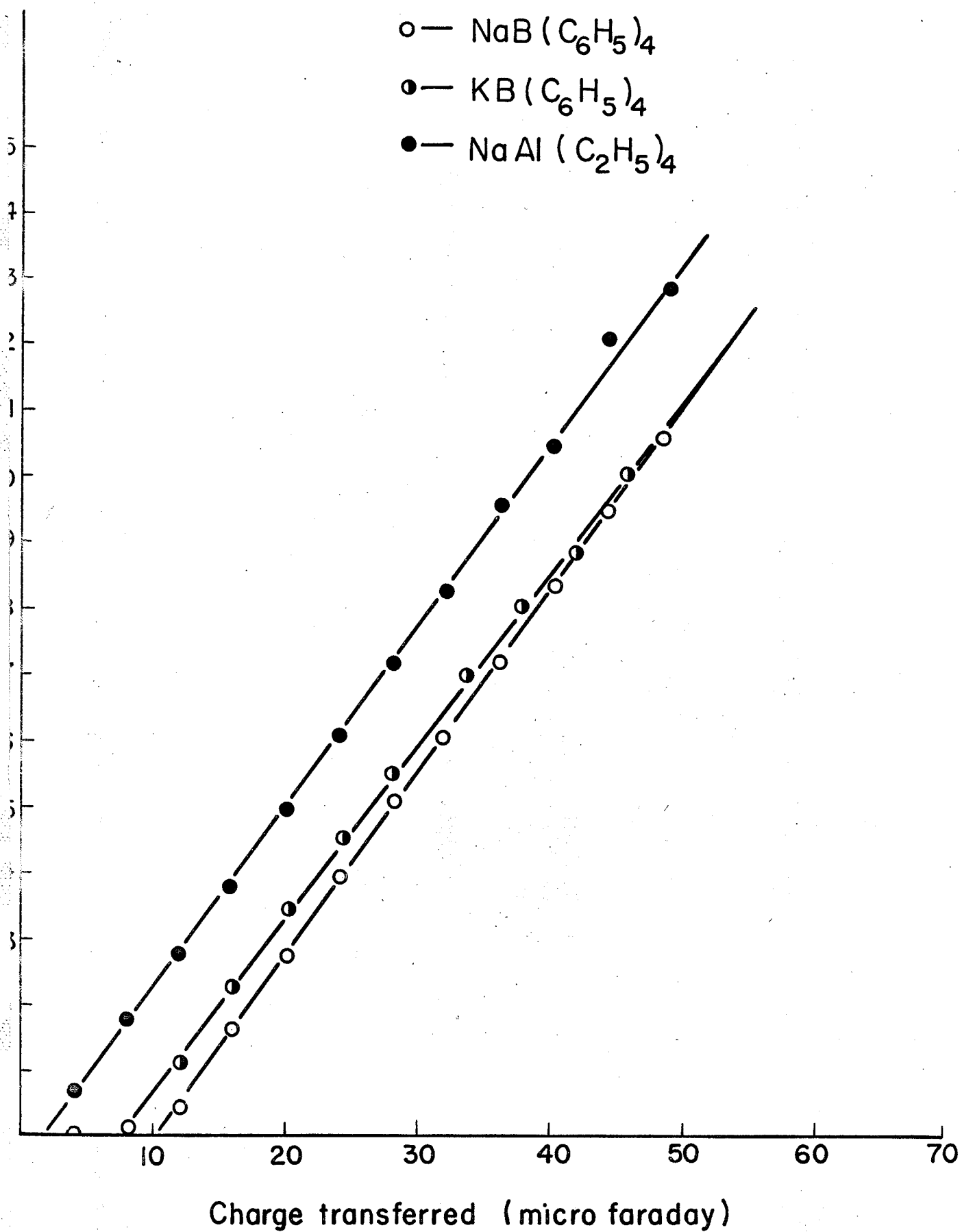
Time of electrolysis minute	Charge transferred $Q \times 10^6$	Absorbance (at 340 $\mu$ )
	$\text{Na}(\text{C}_6\text{H}_5)_4\text{B}$	
0	0	0
5	4.04	.0086
10	8.08	.0153
15	12.12	.0457
20	16.17	.1611
25	20.21	.2758
30	24.25	.3959
35	28.29	.5045
40	32.33	.6109
45	36.37	.7202
50	40.41	.8386
55	44.45	.9508
60	48.50	1.055

continued

TABLE 14 CONTINUED

Time of electrolysis minute	Charge transferred $Q \times 10^6$	Absorbance (at 340 $\mu$ ).
$\text{NaAl}(\text{C}_2\text{H}_5)_4$		
0	0	0
5	4.04	.0781
10	8.08	.1772
15	12.12	.2799
20	16.17	.3786
25	20.21	.4977
30	24.25	.6053
35	28.29	.7152
40	32.33	.8298
45	36.37	.9586
50	40.41	1.047
55	44.45	1.209
60	48.50	1.284
$\text{K}(\text{C}_6\text{H}_5)_4\text{B}$		
0	0	0
5	4.04	0
15	12.12	.1162
20	16.17	.2326
25	20.21	.3516
30	24.25	.4559
35	28.29	.5560
42	33.94	.6990
47	37.99	.7959
52	42.03	.8860
57	46.07	.9967

FIGURE 22. Absorbance increase of living alpha-methylstyrene anions as a function of charge transferred.





$$\text{Charges transferred, } Q = \frac{t \times I}{F}$$

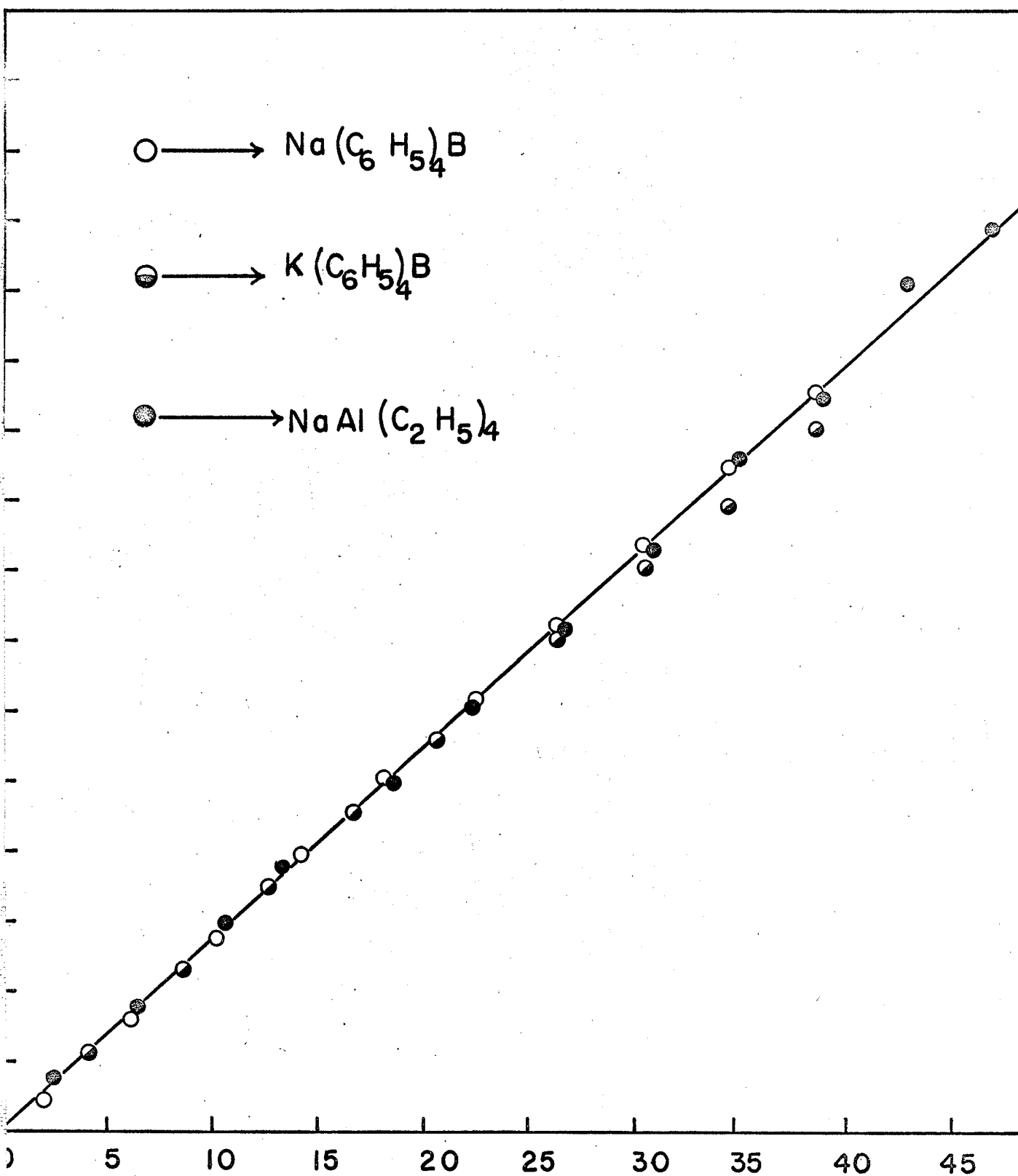
Where I is the current in amperes, t is the electrolysis time in seconds and F is equal to 96,500 coulombs g. equiv.<sup>-1</sup>. Figure 22 shows short induction periods with each salt before the first change in absorbance appeared. Therefore, it seems that some residual impurities such as moisture were present in the reaction mixture. The relatively smaller induction period observed with NaAl(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> is expected because of the high reactivity of the salt with moisture and oxygen. The induction period being equal to 2 to 10 micro Faradays represents 2 to 10 micromoles of the impurity in the reaction solution. This is approximately 4 x 10<sup>-5</sup> M in impurity at the lower limit and is in reasonable agreement with other estimates of impurity levels (23). All the data for the electrolysis of the three salts fall accurately on a single straight line (Fig.23), if the effects of the varying induction periods of Figure 22 are subtracted from the total charge transferred. From Figure 23 it is seen that in the case of K(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>B the last few points are not on the curve. This probably arises from electro-diffusion effects which may occur at relatively high applied voltage (Table 13). At this voltage migration of the catholyte to anolyte was observed. Nevertheless, Figure 23 obviously proves that the living anion formation does not depend on the nature of the salts used as conducting electrolytes.

FIGURE 23. Plot of data shown in Figure 22 after making necessary induction period corrections for total charge transferred.

○ →  $\text{Na}(\text{C}_6\text{H}_5)_4\text{B}$

◐ →  $\text{K}(\text{C}_6\text{H}_5)_4\text{B}$

● →  $\text{NaAl}(\text{C}_2\text{H}_5)_4$



Charge transferred (micro faradays)

DESTRUCTION OF LIVING ANIONS BY A REVERSAL OF THE  
POLARITY OF ELECTRODES

When the direction of current passage was reversed so that the cathode became the anode, the absorbance of the living anions present in the catholyte started decreasing. The results are shown in Figures 24, 25 and 26. It is seen that almost the same quantity of charge is required to decrease the absorbance as is required to increase it initially. However, in the case of  $\text{NaAl}(\text{C}_6\text{H}_5)_4$  the last few points do not lie on the same curve (Fig.25). Furthermore it was observed that at the very instant the red solution in what is now the anode compartment, became colorless, the cathode solution acquired its first trace of the red color. In the case of  $\text{NaAl}(\text{C}_2\text{H}_5)_4$  the catholyte became colored before the anolyte had discharged its red color.

THE EFFECT OF IMPRESSED CURRENTS ON THE  
FORMATION OF LIVING ANIONS

Solutions of the monomer in THF with sodium tetraphenylboron were electrolysed at several currents ranging from 0.62 to 5 ma. The corresponding voltages to maintain the constant currents are compiled in Table 15. The increase of absorbance at 340  $\mu$  with the time of electrolysis for several impressed currents is summarized in Table 16 and after making necessary induction period correc-

FIGURE 24. Absorbance increase of living alpha-methylstyrene anions (rising curve) and its absorbance decrease (falling curve) on reversal of electrode polarity. Absorbance was measured at 340 m $\mu$ . Electrolyte, Na(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>B.

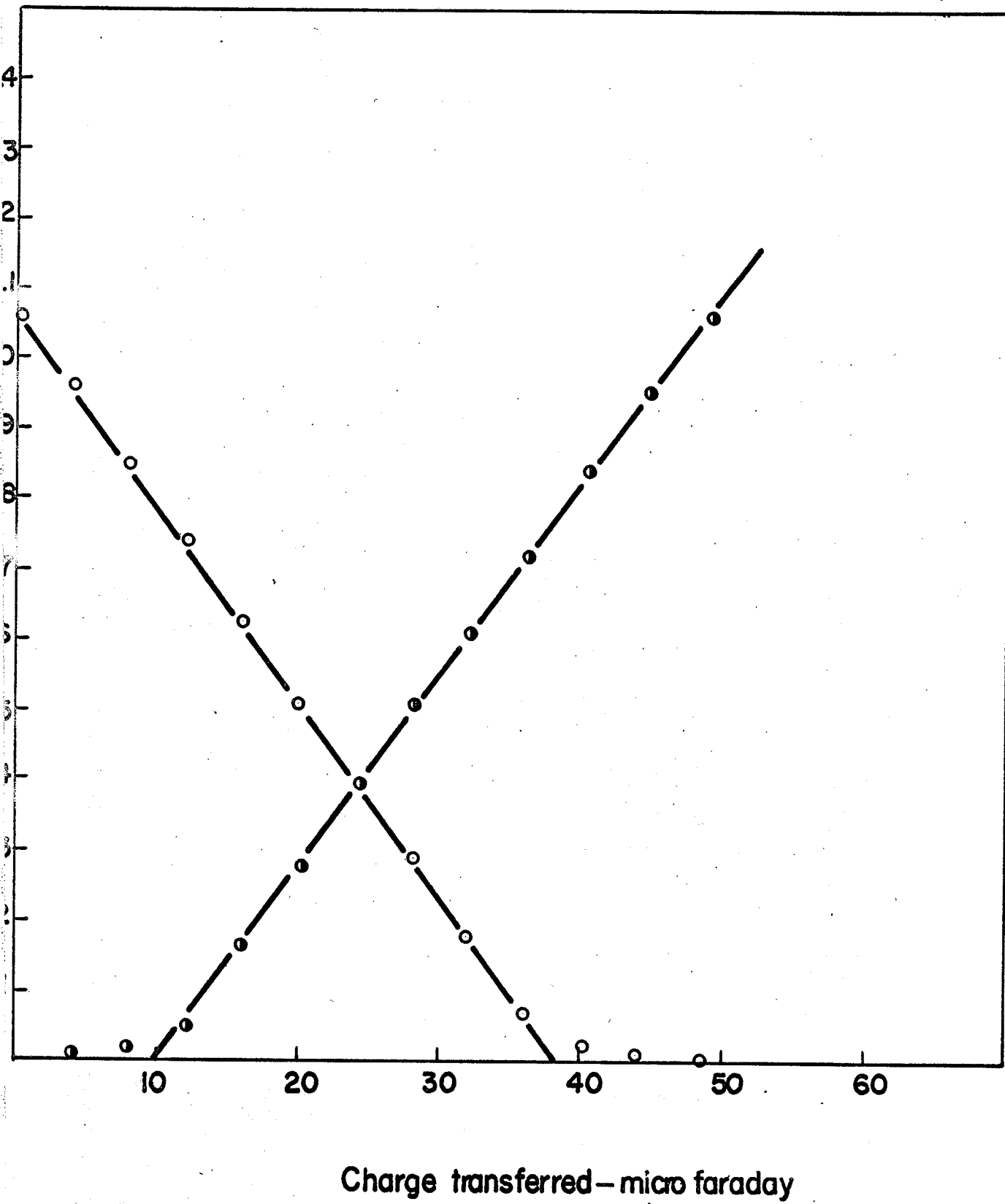
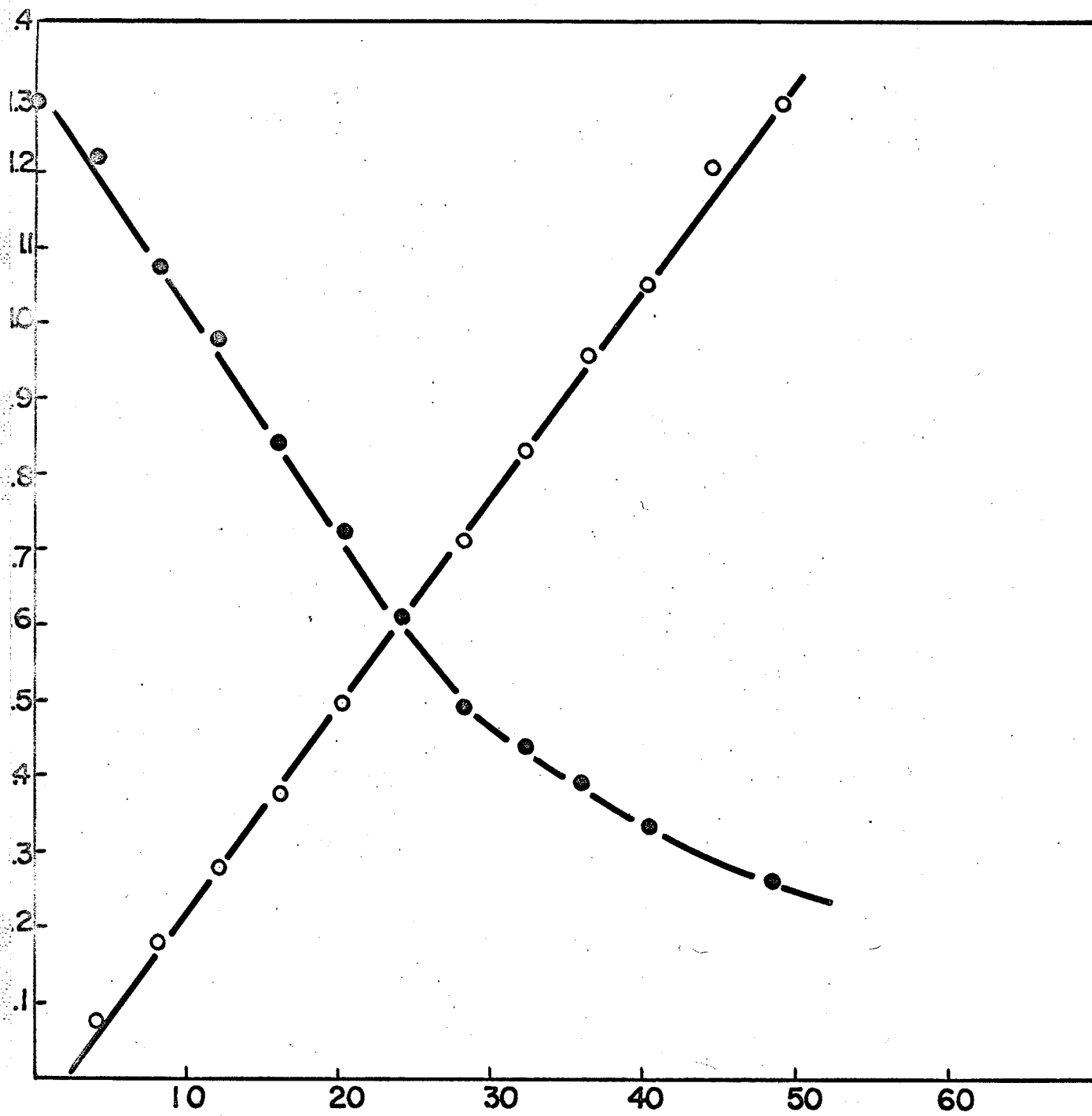


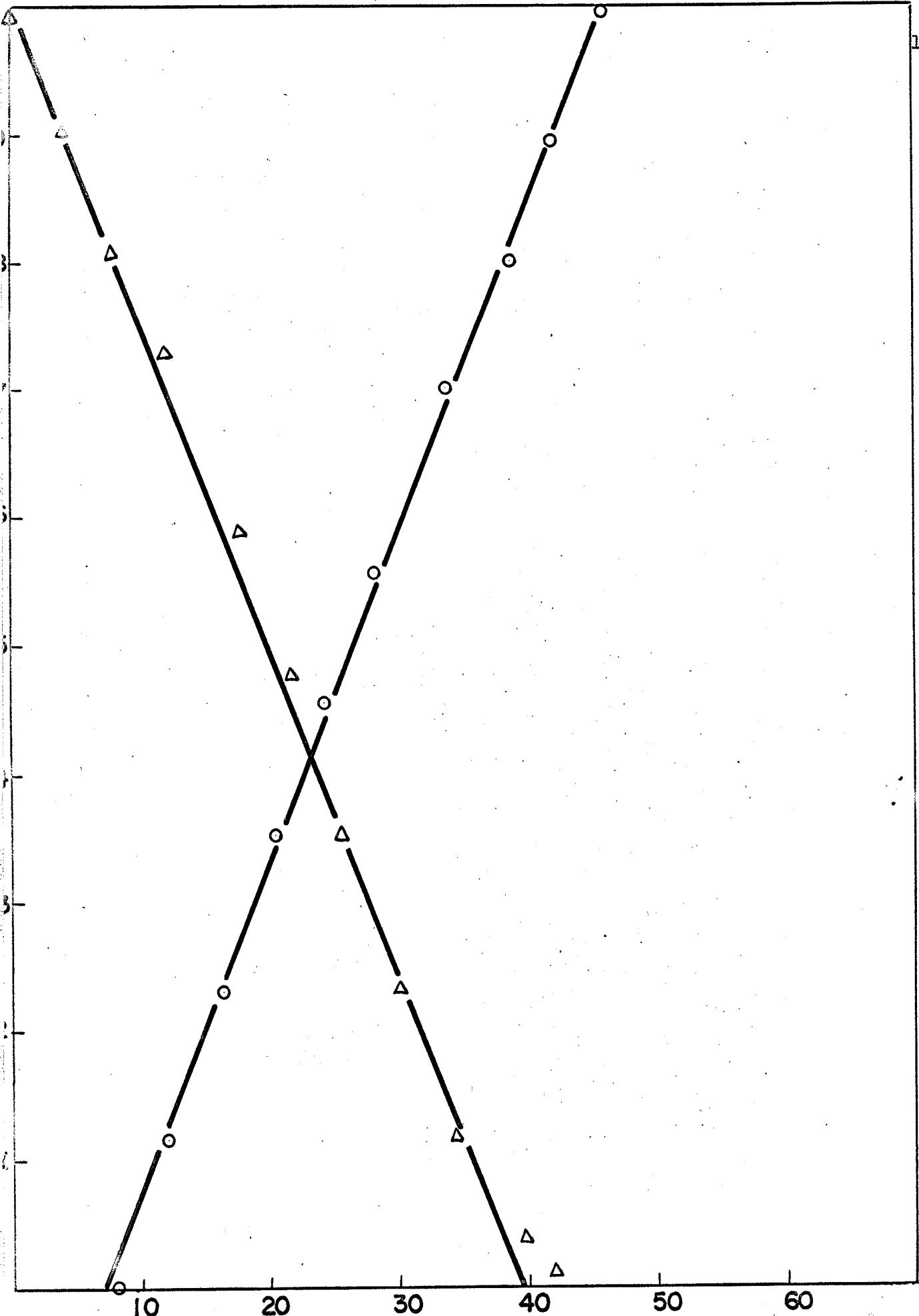
FIGURE 25. Absorbance increase of living alpha-methylstyrene anion and its absorbance decrease (falling curve) on reversal of electrode polarity. Absorbance was measured at 340 mμ. Electrolyte,  $\text{NaAl}(\text{C}_2\text{H}_5)_4$ .



Charge Transferred - micro faradays



FIGURE 26. Absorbance increase of living alpha-methylstyrene anion (rising curve) and absorbance decrease (falling curve) on reversal of electrode polarity. Absorbance was measured at 340 mμ. Electrolyte,  $K(C_6H_5)_4B$ .



Charge transferred - micro faradays

TABLE 15. Applied potential essential to maintain constant currents.

Current (ma)	.62	1.3	2	3	4	5
Voltage (V)	10.5-11	12-17.5	25.5-27	40-42	55-57	65-68

TABLE 16. Increase of the absorbance of living anion solutions as a function of electrolysis time for several impressed currents.

Time of electrolysis (Minute)	Absorbance (at 340 m $\mu$ )
<u>.62 ma</u>	
0	0
21	.0038
27	.0457
33	.0934
39	.1485
45	.2111
51	.2774
57	.3373
63	.4034
69	.4624
75	.5376
81	.6021
87	.6675
93	.7447
<u>2 ma</u>	
0	0
5	0
10	.0705
15	.2350
20	.4057
25	.5850
30	.7695
35	.9509

TABLE 16 CONTINUED

Table of electrolysis (Minute)	Absorbance (at 340 $\mu$ )
40	1.143
45	1.293
<u>3 ma</u>	
0	0
4	.0064
8	.0245
12	.2558
15	.4203
18	.5935
21	.7645
24	.9393
27	1.097
30	1.283
34	1.468
38	1.699
42	1.959
<u>4 ma</u>	
0	0
6	.1320
9	.3510
11.5	.5791
15	.8210
18	1.049
21	1.260
<u>5 ma</u>	
0	0
3	.0692
6	.3863
8	.5777
10	.7939
12	.9858
14	1.191
16	1.375
18	1.612
20	1.778

For 1.3 ma see Table 13.

tions (Table 16) the data are shown in Figure 27.

TABLE 17. Induction periods observed with different impressed currents.

Current (ma)	.62	1.3	2	3	4	5
Induction period (minute)	24	12.5	8.5	7.6	4.5	2.5

An excellent linear relationship between the absorbance and time at each of the currents over a tenfold range is evident. However, for each current there appeared to be an induction period which is shown in Table 17. All the curves shown in Figure 27 can be reduced to a single curve when the absorbance is plotted against the quantity of the charge transferred at the cathode. Figure 28 shows a plot of slopes of lines in Figure 27 as a function of the impressed currents. This offers further clear evidence that the concentration of living anions is equivalent to the number of Faradays passed through the solution, after the induction period. Therefore, the formation of living anions by electrolytic means offers a subtle method for the calculation of the molar extinction coefficient of the solution. The slope of the absorbance versus charge transferred will give directly the molar extinction coefficient which is defined by the following expression:

FIGURE 27. Absorbance increase of living alpha-methylstyrene anions with time of electrolysis at inscribed currents. Absorbance was measured at 340 m $\mu$ .

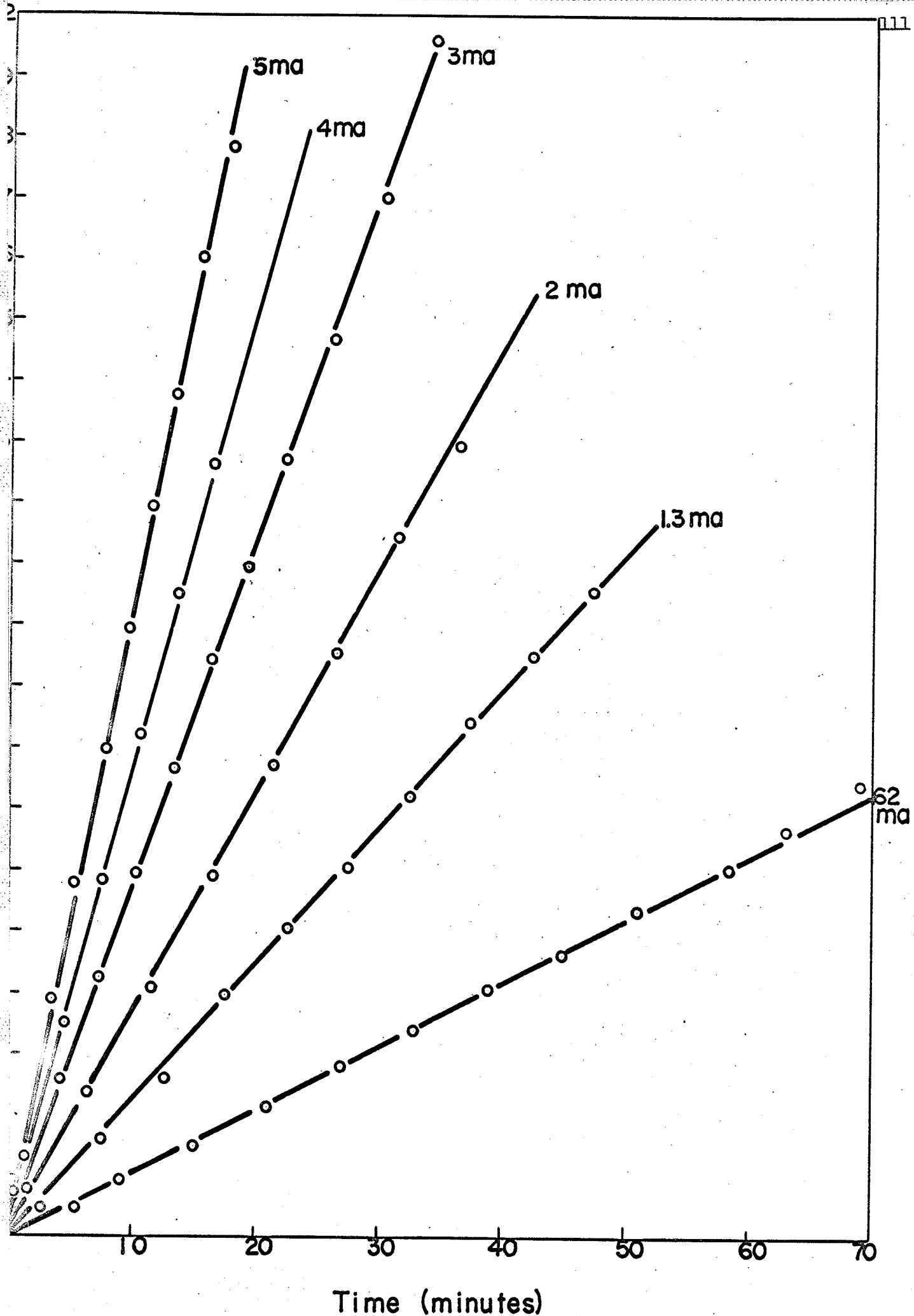
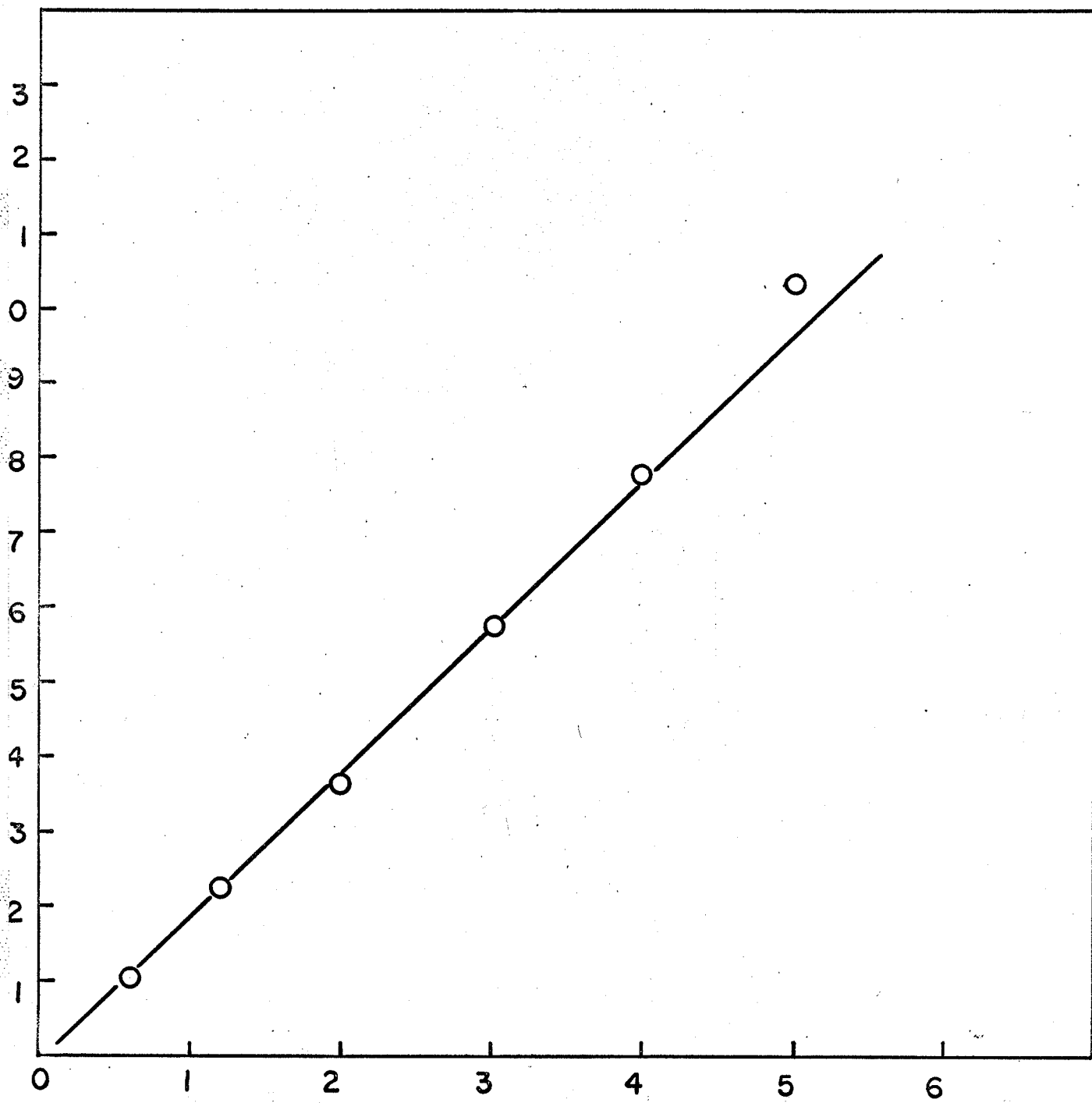


FIGURE 28. Plot of slopes of Figure 27 versus currents.





Current ma

$$\text{Molar extinction coefficient } E = \frac{A}{L \cdot C}$$

Where A is the absorbance of the solution, C is the molar concentration of the absorbing species and L is the path length of the optical cell. In the present work, calculation of E can be illustrated as follows:

For the current of 0.62 ma, the slope is .0103 absorbance/minute (Fig.28), the path length, L is 0.1 cm and the volume of the living anion solution is 55.2 ml at 25°C. The concentration of the living anions showing the absorbance .0103 can be given by the charge transferred at 0.62 ma for 60 seconds, i.e.,

$$\frac{.62 \times 60 \times 10^{-3}}{96,500} = 1.3855 \times 10^{-3} \text{ g. equiv.}^{-1} \text{ or mol.}$$

$$\therefore \text{molar concentration } C = \frac{3.855 \times 10^{-3} \times 1000}{55.2}$$

Substituting values of C, A, L in the expression  $E = \frac{A}{C \cdot L}$  we get  $E = 1.5 \times 10^4 \text{ l. mole}^{-1} \text{ cm}^{-1}$ .

Similarly, values of E for other impressed currents were calculated and are assembled in Table 18. The result indicates a slight variation in E with impressed currents.

The molar extinction coefficient of the living anion solution of alpha-methylstyrene has been given as  $1.4 \times 10^4$  at 350 mμ in the literature (89). Therefore, the value of E obtained is in a good agreement with the literature value.

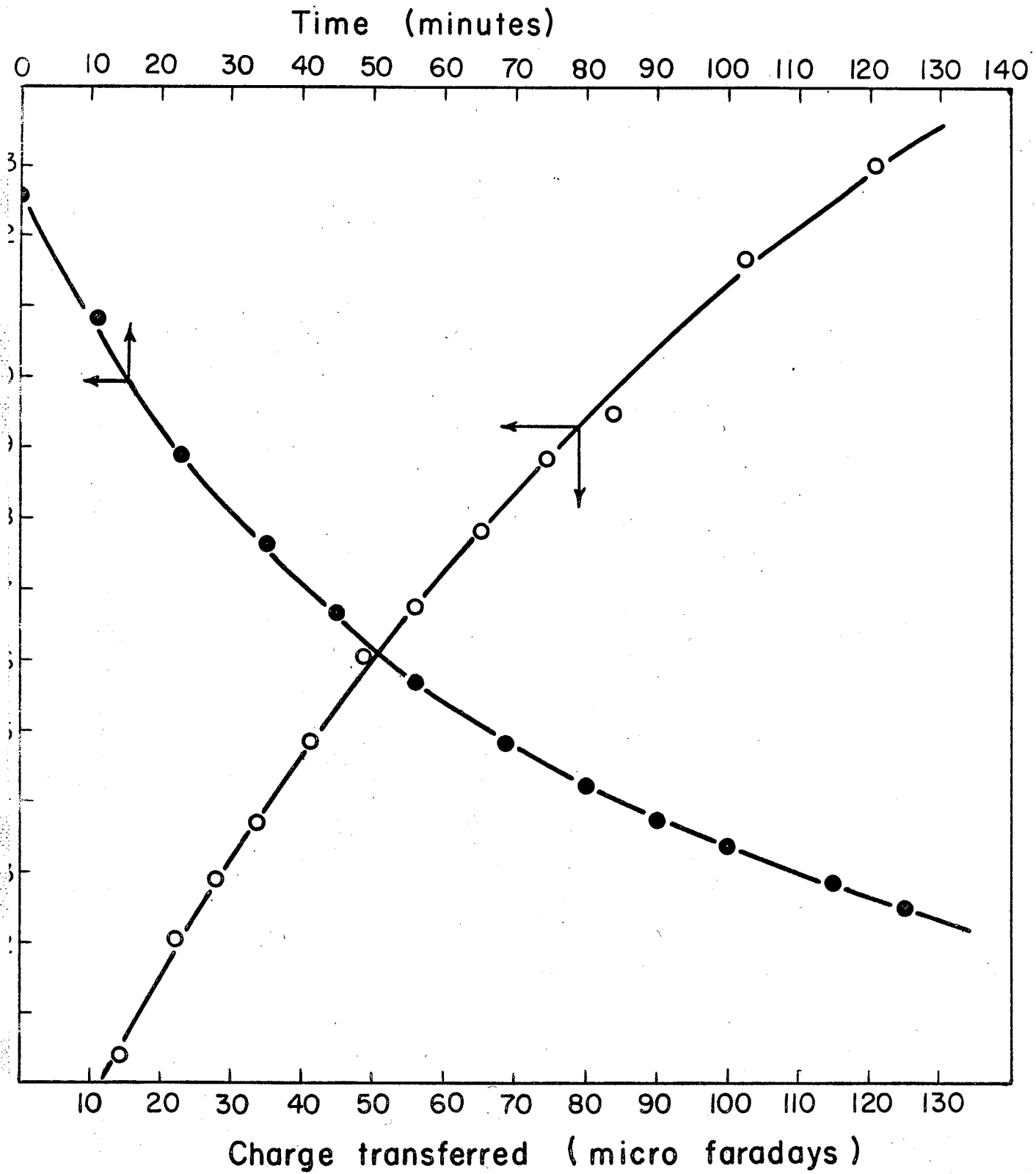
TABLE 18. Molar extinction coefficient of living anion solution of alpha-methylstyrene.

Current (ma)	Slope from Fig. 27 (absorbance/min.) x 10 <sup>2</sup>	Molar extinction coefficient (litre.mole <sup>-1</sup> cm <sup>-1</sup> ) 340 mμ x 10 <sup>-4</sup>
0.62	1.03	1.5
1.3	2.23	1.5
2.0	3.63	1.6
3.0	5.70	1.7
4.0	7.75	1.7
5.0	10.33	1.8

#### LIVING ANION FORMATION WITH Li(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>B

A living anion solution of the monomer with this salt was prepared as usual at a current of 3 ma and an applied voltage of 58 V. Unlike other salts, in this case a plot of the increase of absorbance of the catholyte versus charge transferred did not yield a linear curve as is evident from Figure 29. Furthermore, it was found that after electrolysis the absorbance decreased spontaneously as shown at the left of Figure 29. Repeated experiments with the rigorously purified salt yielded the same results. Therefore, this result suggests that there exists an interaction between the living anions and the salt resulting in a decrease in the absorbance of the solution. However, at -80°C no decrease of the intensity of the red color in 24

FIGURE 29. Living anion formation of alpha-methylstyrene on electrolysis and its spontaneous decay with time in the presence of  $\text{Li}(\text{C}_6\text{H}_5)_4\text{B}$ .



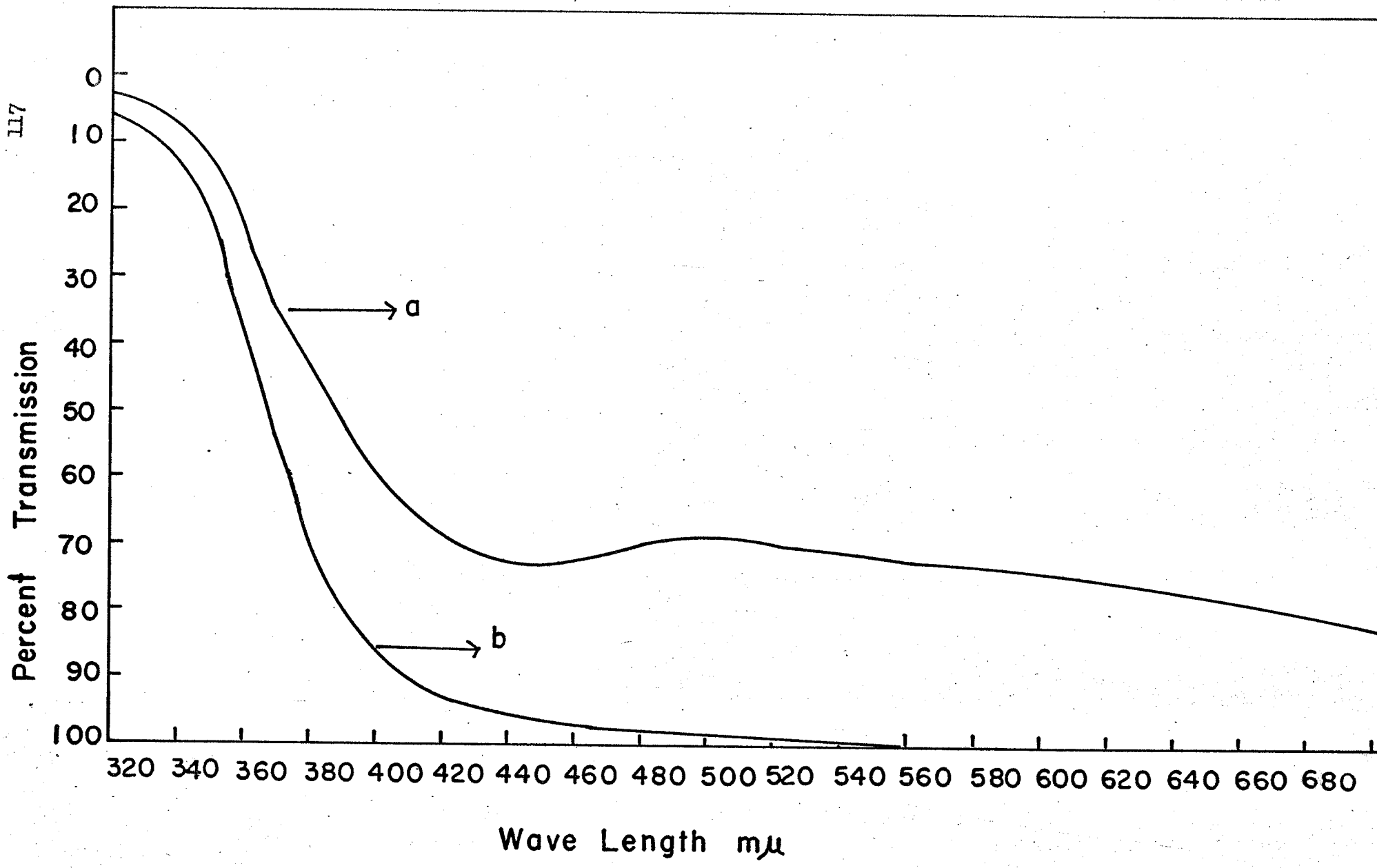
hours was noticed although the actual absorbance could not be measured at this temperature with the apparatus employed.

#### LIVING ANION FORMATION WITH QUATERNARY AMMONIUM SALTS

Under the same experimental conditions as employed earlier, a monomer solution in THF with tetrabutyl ammonium tetraphenyl boron as electrolyte was subjected to electrolysis at 3 ma and 90 V. A red color formed at the cathode but disappeared quickly in the solution. Even 5 hours electrolysis did not result in a persistent red color at the living anions. When passage of the current was continued for more than 8 hours, the applied voltage increased from 90 v to above 500 v and the catholyte became deep purple. The spectrum of this resulting purple colored solution was measured and is shown in Figure 30a. The solution was cooled to  $-80^{\circ}\text{C}$  and allowed to stand overnight and then exposed to air. The solution turned from deep purple to faint yellow. The resulting spectrum of the air-exposed solution is shown in Figure 30b. No polymer precipitated when it was poured into methanol. This experiment could suggest that impurity present in the salt killed the living anions. Therefore, the salt was recrystallised several times and the experiment was repeated, but the same result as before was obtained. The formation of the purple color was also observed when electrolysis was performed in the absence of

FIGURE 30. Absorption spectra.

- a, purple colored solution formed by electrolysis in the presence of  $(C_4H_9)_4N^+ B(C_6H_5)_4^-$
- b, the electrolysed solution exposed to air.





monomer. However, in this case the transient red color did not appear. When a solution of naphthalene, in THF containing tetrabutyl ammonium salt was electrolysed only a transient faint green color formed around the cathode. This green color may be due to naphthalene radical anion. The catholyte did not become green but prolonged electrolysis resulted again in formation of the purple color at high applied voltages.

From these results it seems that there may be a strong interaction between the salt and living anions resulting in their quick destruction. In order to explore this view the following experiment was performed.

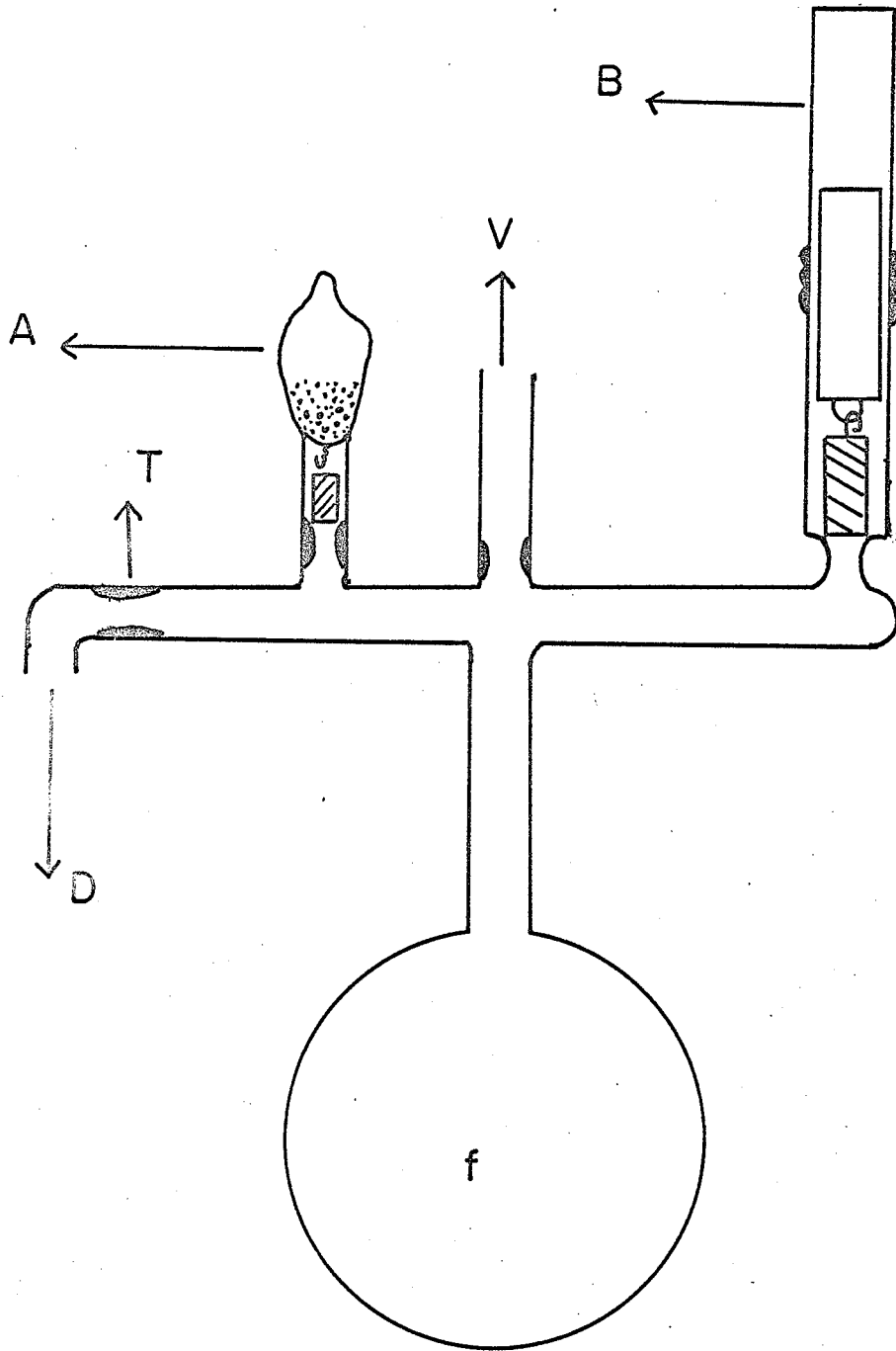
The apparatus used in the experiment is shown in Figure 31. "A" is an ampoule of the pure and thoroughly dried salt, "B" is a quartz optical cell equipped with a 9 mm spacer, which was attached with a glass sealed magnet, and "f" is the filling bulb. This whole apparatus was sealed to the divided cell and the living anions were formed with  $\text{Na}(\text{C}_6\text{H}_5)_4\text{B}$  by the usual procedure. The red catholyte was drained back to the filling bulb and the divided cell was removed by sealing off at the constriction "T". The absorbance of the solution was measured at 340  $\mu$  for twenty minutes and then the ampoule "A" was crushed and the salt was quickly mixed with the living anion solution. The absorbance of the resulting solution was again measured as a function of time. In this case

FIGURE 31. Apparatus used to study the deactivation of living anions.

B, quartz optical cell equipped with 9 mm spacer and magnet.

A, ampoule of tetrabutyl ammonium tetraphenyl boron.

D, sealed to divided cell (Fig.16).



the absorbance was found to decrease rapidly to zero within a few minutes. The deep red solution became a very faint yellow. The result is shown in Figure 32. This observation conclusively proves that the quaternary ammonium salt kills the living anions and thus the red color formed at the cathode does not persist. An attempt was also made to form the living anion using tetrabutyl ammonium perchlorate. Again only a transient red color formed at the cathode and vanished in the solution. But it was found that when the electrolysis was continued for 6 hours at 2 ma, the THF was polymerized. It seems that this salt also reacts with the living anions. However, it is emphasized that the living anion formation in the absence of alkali metals was first observed in this work.

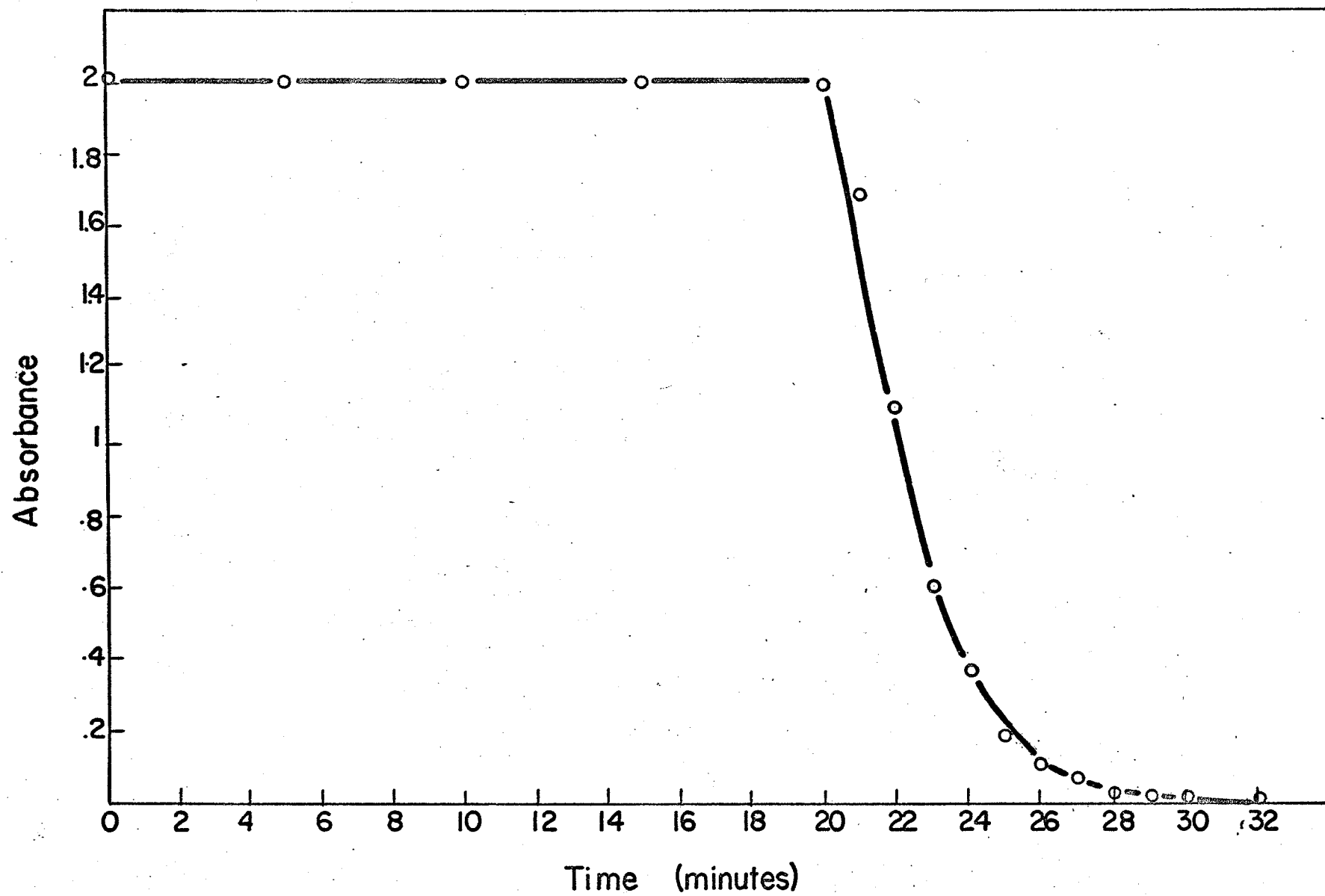
#### DESTRUCTION OF LIVING ANIONS BY $\text{Al}(\text{C}_2\text{H}_5)_3$

When  $\text{Al}(\text{C}_2\text{H}_5)_3$  (<.1 g.) was mixed with living anions, the deep red solution became instantaneously water clear. This proves that  $\text{Al}(\text{C}_2\text{H}_5)_3$  deactivates the living anions.

#### LIVING ANION FORMATION OF ALPHA-PHENYLSTYRENE (1,1 Diphenyl ethylene)

This hydrocarbon resembles styrene and alpha-methylstyrene, but because of the bulkiness of two phenyl groups it does not polymerize at room temperature. However, it also forms living anions via an electron transfer reaction.

FIGURE 32. Deactivation of living anions by tetrabutyl ammonium tetraphenyl boron. After 20 minutes the salt was mixed with the living anion solution.



It was intended here to measure the absorption spectrum and extinction coefficient of the living anion solution of this monomer.

A 2.5 ml monomer sample and 0.25 g.  $\text{Na}(\text{C}_6\text{H}_5)_4\text{B}$  were dissolved in THF to give 86 ml solution (catholyte volume being 55 ml at 25°C) and the resulting solution was electrolysed at a current of 3 ma and a voltage of 35 V. The red color started to drop from the cathode but turned blue in the solution. After half an hour electrolysis the catholyte became blue and exhibited an absorption peak at the region of 660  $\mu$ . It was found that when electrolysis was continued with the polarity of the electrodes reversed, the blue color disappeared completely and the solution became colorless. Once again the polarity was reversed and now the red color which formed at the cathode did not turn blue. The blue color formation might be caused by some impurity present in the monomer. The latter could not be purified under high vacuum because of its high boiling point.

The absorption spectra of the red solution with electrolysis time are shown in Figure 33. The spectrum is broad with a maximum absorption peak at the region of 470  $\mu$  which is in an agreement with the literature value (29). The living anion could be killed by reversing the polarity of the electrodes. In another run, the increase

FIGURE 33. Absorption spectra of living anion solutions of alpha-phenylstyrene after electrolysis at 3 ma for inscribed times. Electrolyte,  $\text{Na}(\text{C}_6\text{H}_5)_4\text{B}$ .



123

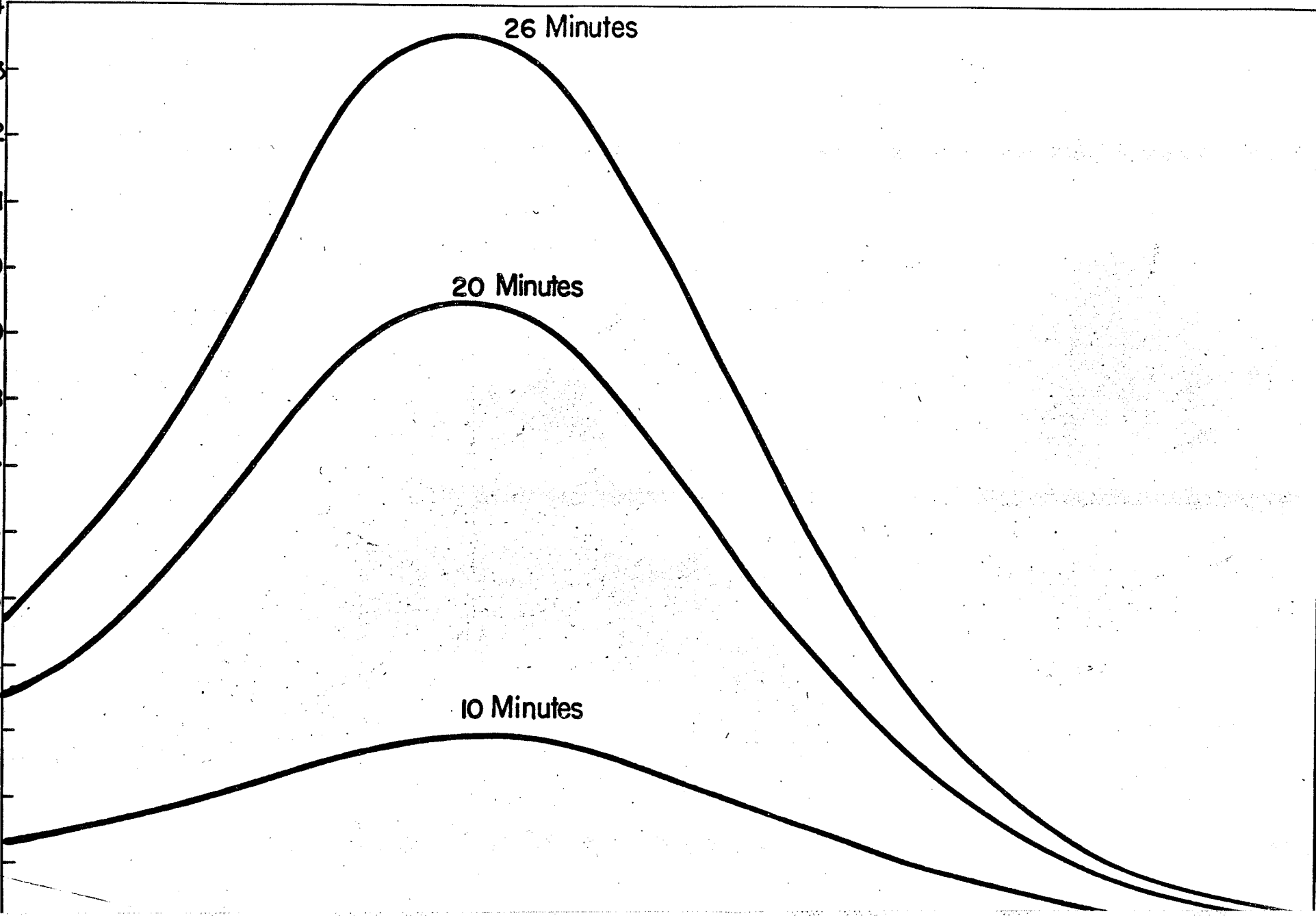
26 Minutes

20 Minutes

10 Minutes

Absorbance

14  
13  
12  
11  
10  
9  
8  
7  
6  
5  
4  
3  
2  
1



of absorbance at 470  $\mu$  was measured and is shown in Figure 34. The molar extinction coefficient was calculated as before and was found to be  $1.6 \times 10^4$  l. mol<sup>-1</sup> cm<sup>-1</sup>. The literature value is  $2.6 \times 10^4$  l. mol<sup>-1</sup> cm<sup>-1</sup> (29).

#### YIELD AND MOLECULAR WEIGHT OF POLY (Alpha-methylstyrene)

When the living anion solution of the monomer was cooled to -80°C in a dry ice-acetone bath, polymerization occurred. After completion of the reaction, living polymers were killed by adding a few drops of methanol. The polymer was isolated by precipitation in methanol, filtered, washed with methanol and then dried in a vacuum desiccator at 50°C for 24 hours. The yields of polymers obtained with Li(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>B and Na(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>B are shown respectively in Tables 19 and 20. No polymer was obtained in the case of quaternary ammonium salts. With lithium salt the yields of polymers were not quantitative because the reaction time was not sufficient. Longer reaction time was not employed because this would increase the chance of living anion destruction. However, the conversion exceeded 92 percent when the reaction was continued for 20 hours (last run Table 19).

The polymers used in the measurement of molecular weights were purified by methanol precipitation from THF solution and dried. Viscosity measurements were done at

FIGURE 34. Increase of absorbance  
(at 470 m $\mu$ ) of living alpha-  
phenylstyrene anions with time  
of electrolysis at 2 ma.

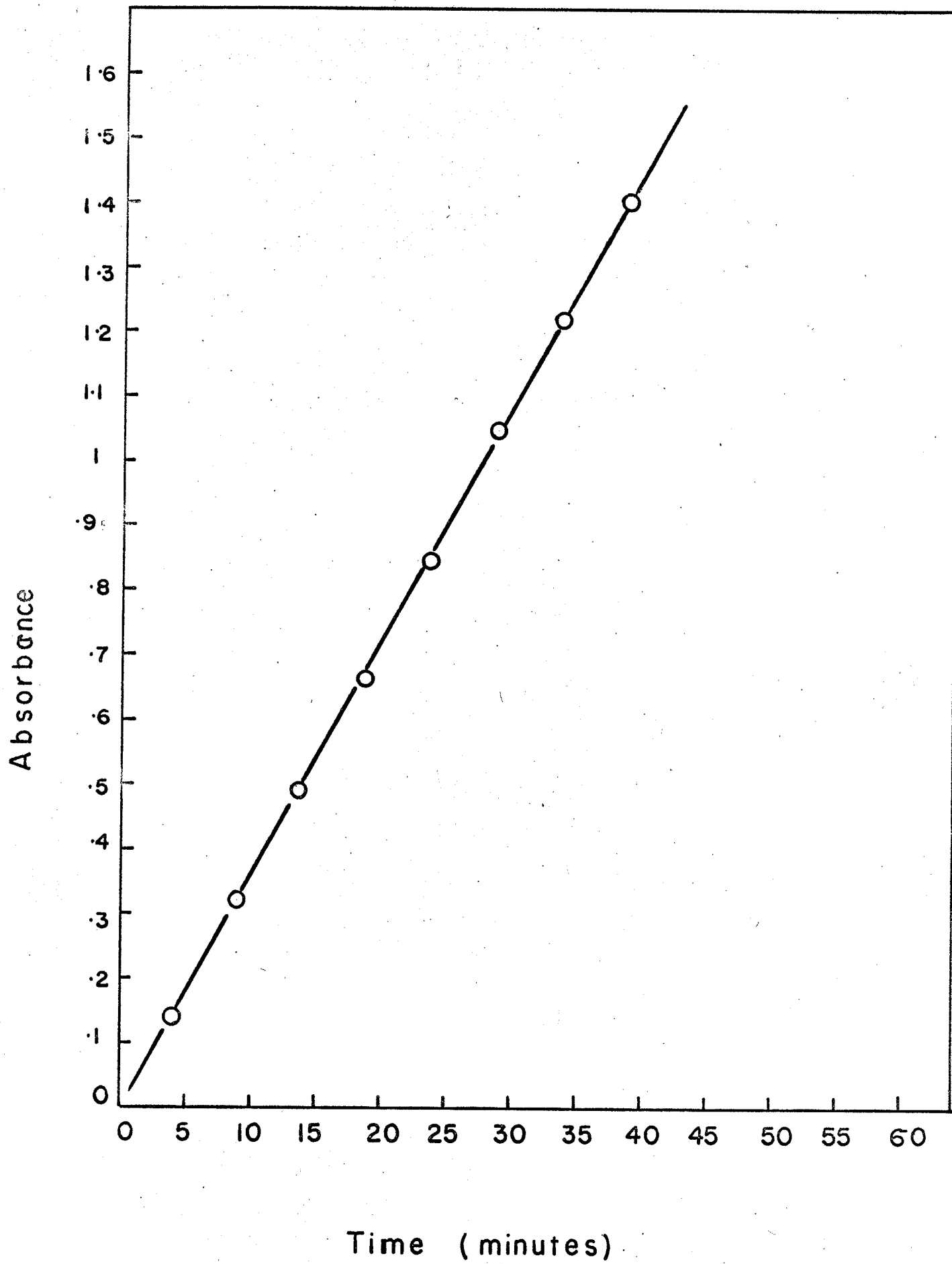


TABLE 19. Yield and molecular weight of poly  
(alpha-methylstyrene) formed at  $-80^{\circ}\text{C}$   
in the presence of  $\text{LiB}(\text{C}_6\text{H}_5)_4$ .

R.N.	Monomer moles/litre	Current (ma)	Time of electrolysis (minute)	Monomer (cathode) g.	Polymer cathode g.	mol.wt. $\times 10^{-4}$	
						observed	calculated
Reaction time 3 hours.							
1.	1.28	2.2	60	4.83	4.40	23.1	10.7
2.	1.28	1.3	90	4.38	3.22	27.4	8.8
3.	1.28	2.0	40	4.77	3.97	31.3	15.9
4.	1.28	1.3	60	4.86	2.17	48.6	8.9
5.	1.26	3.0	30	4.98	3.20	30.3	11.4
6.	0.64	1.3	75	2.98	2.04	21.3	6.7
7.	0.59	1.3	70	2.45	1.86	17.1	6.6
8.	0.51	1.3	60	2.34	1.66	17.6	6.8
9.*	0.51	2.4	60	2.33	2.15	-	4.8

\* Time of polymerization 24 hours.

TABLE 20. The yield and molecular weight of poly (alpha-methylstyrene) formed at  $-80^{\circ}\text{C}$  in the presence of  $\text{Na}(\text{C}_6\text{H}_5)_4\text{B}$

R.N.	Monomer mole/litre	Monomer (cathode) g.	Current (ma)	Time of electrolysis (minute)	Induction period (minute)
Reaction time 24 hours.					
1.	0.419	1.92	2.4	60	8.5
2.	0.403	1.91	2.0	70	9.0
3.	0.872	4.09	2.0	90	9.0
4.	0.613	2.91	2.0	60	9.0
5.	0.613	2.63	3.0	35	7.5
	Charge transferred (Faraday $\times 10^5$ )	Polymer (cathode) g.	Limiting viscosity number	Molecular weight $\times 10^{-4}$	
				observed	calculated
1.	7.68	1.90	.240	5.17	4.95
2.	7.59	1.89	.274	6.23	4.98
3.	10.07	4.05	.323	7.85	8.04
4.	6.34	2.88	.335	8.28	9.09
5.	5.13	2.61	.397	10.5	10.2

30°C in toluene solution using an Ubbelohde viscometer (Fig. 2). Measurements in the concentration range 0.25 - 1 percent by weight were extrapolated to infinite dilution, by means of linear  $\eta_{sp}/C$  (viscosity number) against  $C$  (polymer concentration) plots, to obtain limiting viscosity numbers. Such plots are shown in Figure 35. The molecular weights were calculated from the limiting viscosity number by the following expression (56).

$$(\eta) = 1.08 \times 10^{-4} M^{0.71}$$

The theoretical molecular weight was calculated by the following equation (69).

$$\text{Mol. Wt. } (\bar{M}_n) = \frac{\text{polymer (g)}}{\frac{1}{2} \text{ charge transferred}}$$

Both observed and calculated molecular weights are summarized in Tables 19 and 20.

#### MOLECULAR WEIGHT DISTRIBUTIONS

The molecular size distribution of samples of poly (alpha-methylstyrene) formed in run No.5 (Table 19) and run No.1 (Table 20) were determined by the gel permeation chromatography (GPC) technique. The data are presented in Figures 36 and 37. Plots of the cumulative weight percent versus the chain length of polymer molecules are shown in Figures 38 and 39. It is seen that the polymer produced

FIGURE 35. Plots of  $\eta_{sp}/C$  versus  $C$ .



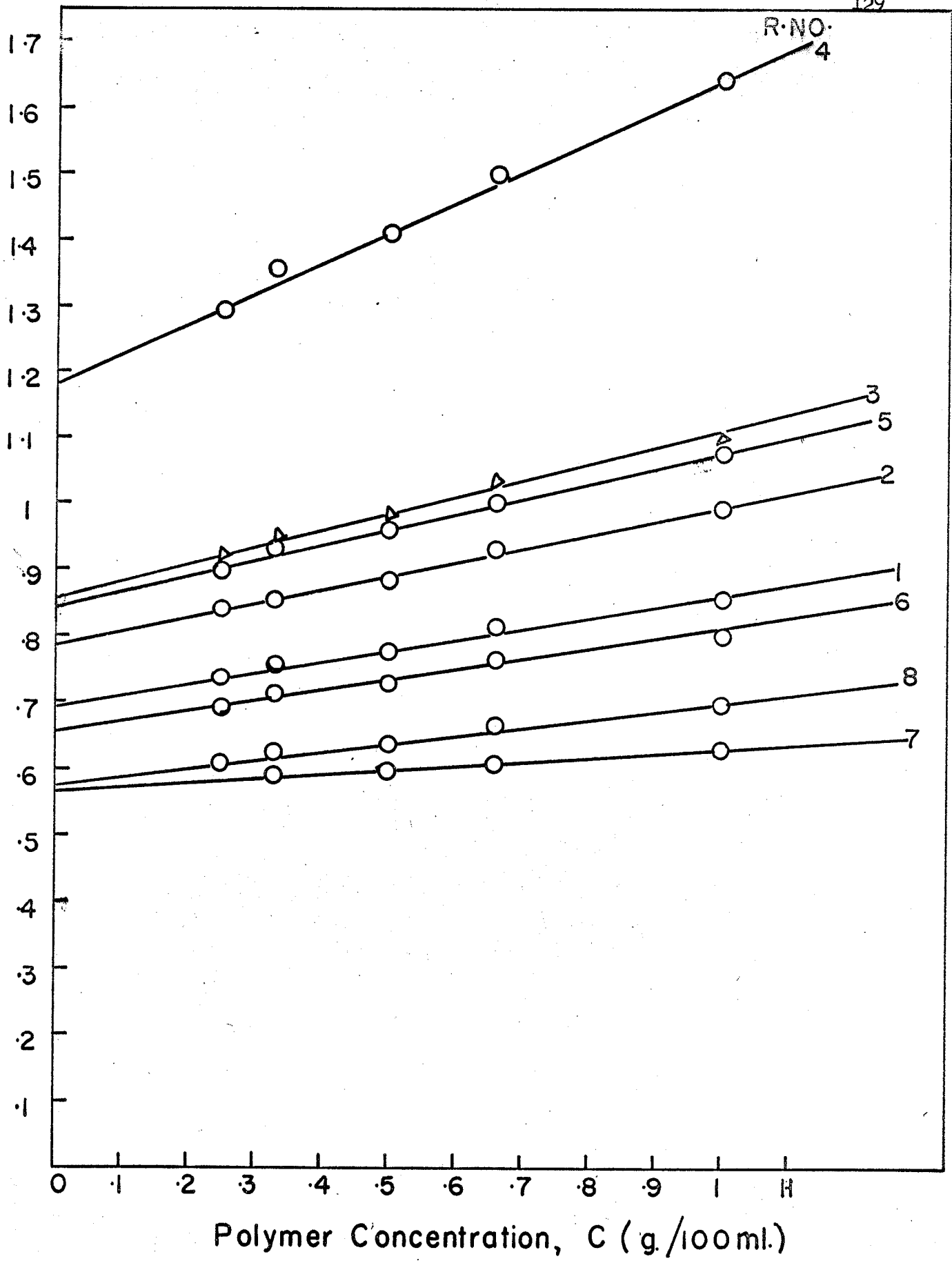
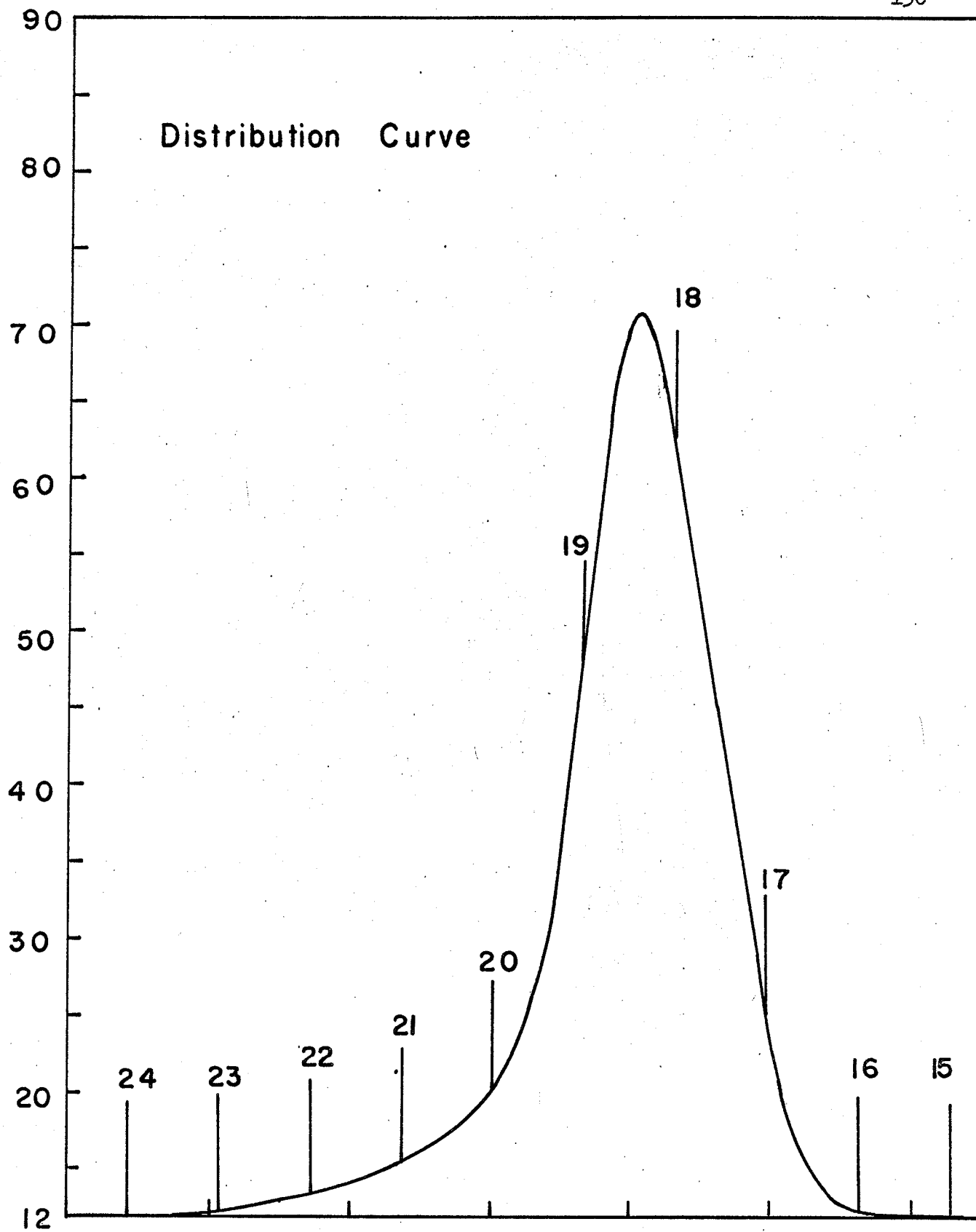
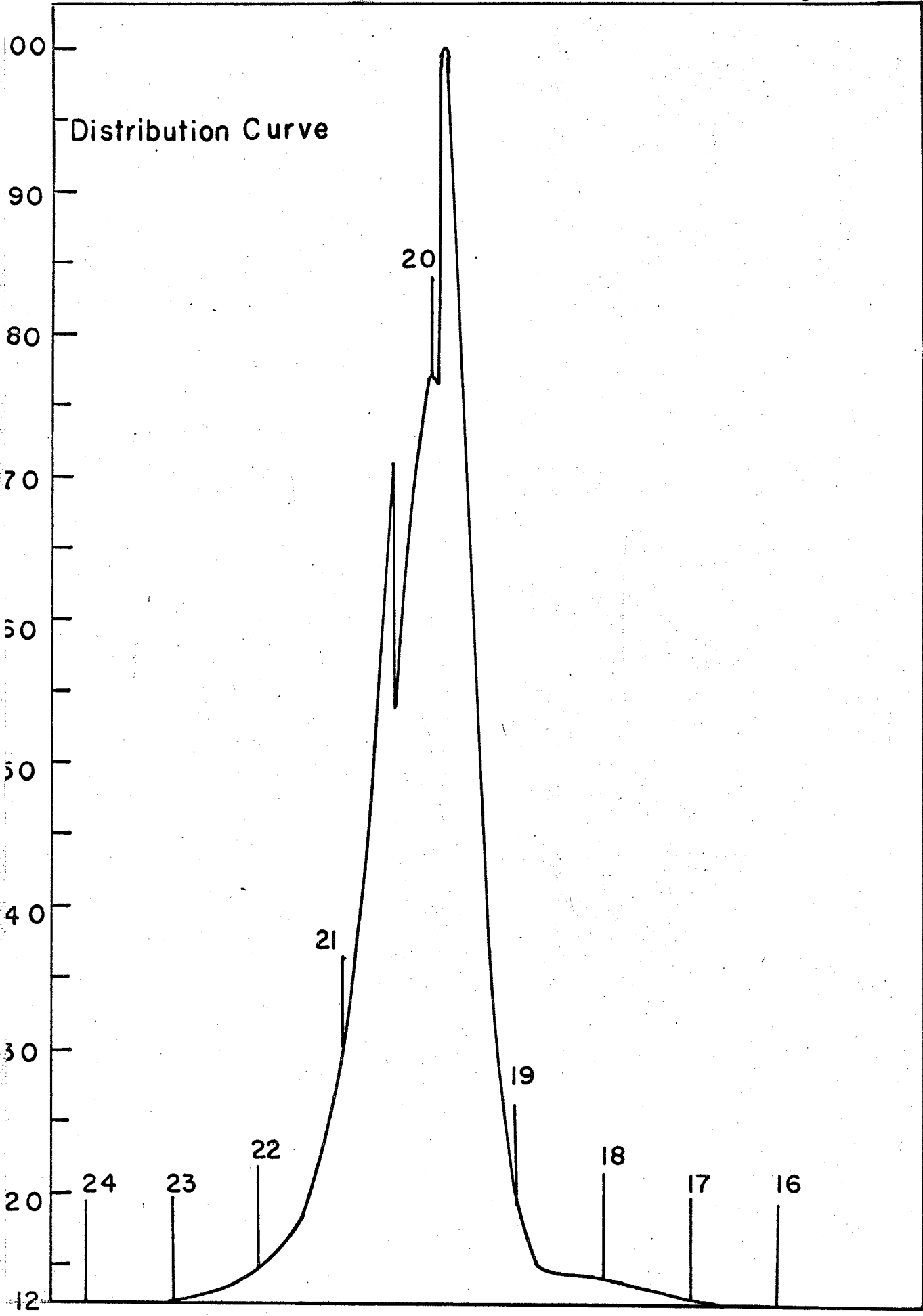


FIGURE 36. Molecular weight distribution curve  
of poly (alpha-methylstyrene) formed  
at  $-80^{\circ}\text{C}$  in the presence of  $\text{Li}(\text{C}_6\text{H}_5)_4\text{B}$ .



GPC Chart Record

FIGURE 37. Molecular weight distribution curve of poly (alpha-methylstyrene) formed at  $-80^{\circ}\text{C}$  in the presence of  $\text{Na}(\text{C}_6\text{H}_5)_4\text{B}$ .



GPC Chart Record

FIGURE 38. Plot of cumulative weight percent  
(calculated from Fig.36) versus  
chain length of polymer molecules.

Weight Percent

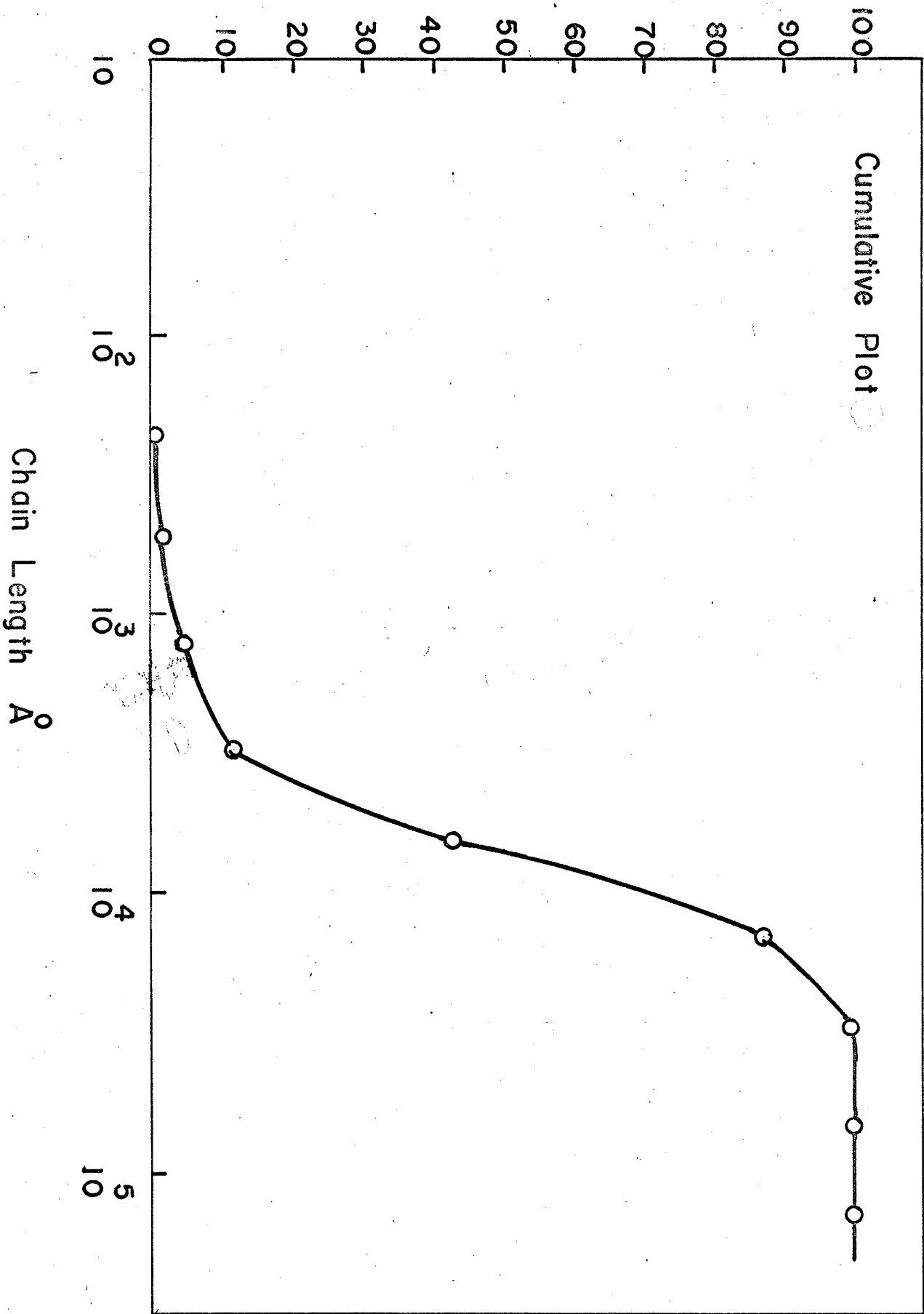
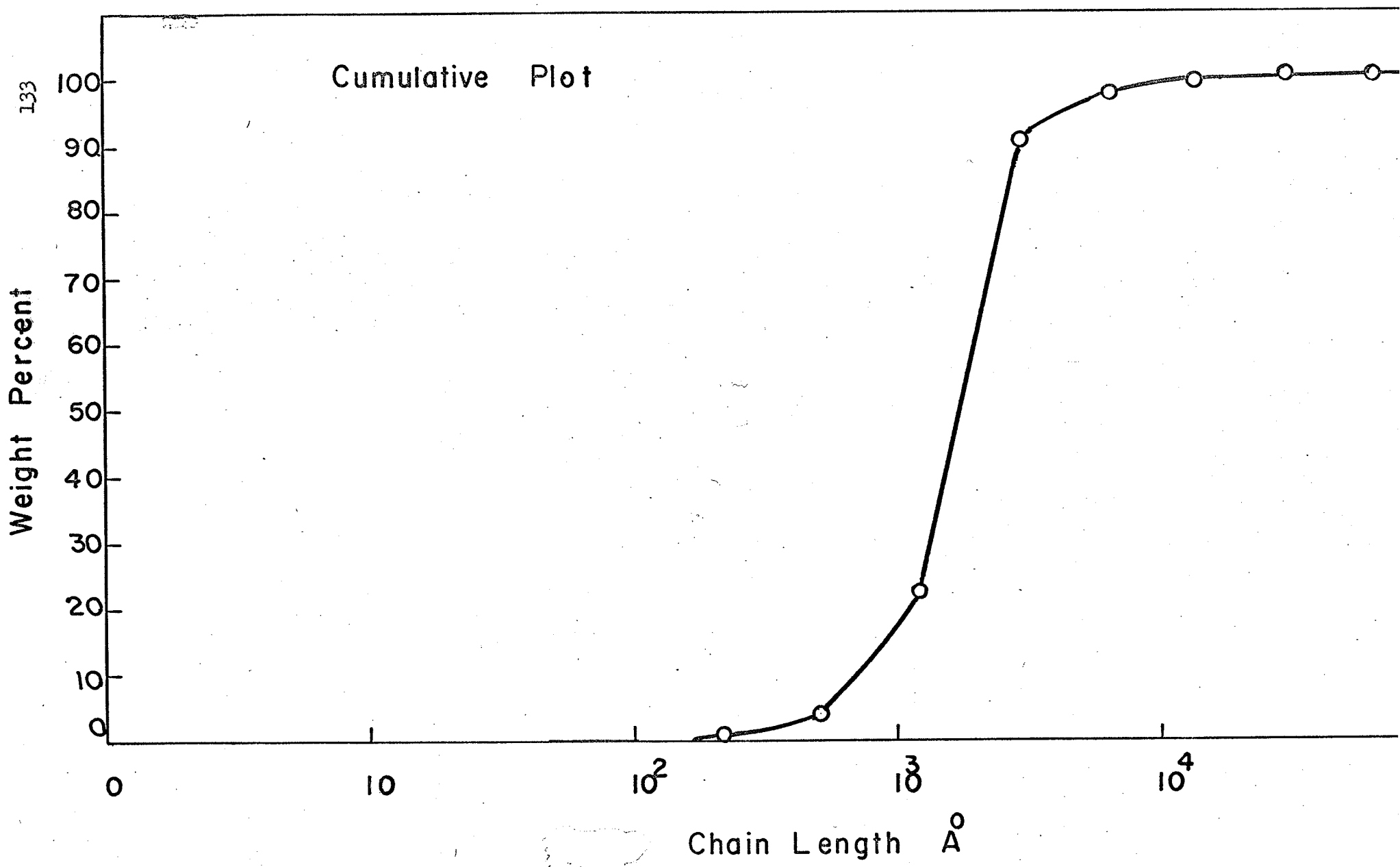


FIGURE 39. Plot of cumulative weight percent  
(calculated from Fig. 37) versus  
chain length of polymer molecules.





in the presence of  $\text{Na}(\text{C}_6\text{H}_5)_4\text{B}$  has a relatively uniform molecular weight distribution.

#### ANALYSIS OF THE ANODE SOLUTION

A current of 2 ma at an applied potential of 25 V. was passed for 70 minutes through a THF solution of alpha-methylstyrene (0.4 M) and sodium tetraphenyl boron (.02 M). After the electrolysis the anode solution was exposed to air and was analysed by a method described by Geske (90). Here the procedure for the analysis had to be modified for removal of the monomer and unused  $\text{Na}(\text{C}_6\text{H}_5)_4\text{B}$ .

A 12 ml anode solution was shaken with 12 ml (1 M) sodium hydroxide solution. This mixed solution was treated with 15 ml cyclohexane and vigorously agitated for half an hour and then allowed to stand until aqueous and non-aqueous layers appeared. They were separated and reserved for analysis.

The aqueous portion was washed several times with cyclohexane until the washings were found to be free from the monomer. The presence of the monomer in the solution was examined spectrophotometrically. The monomer shows a maximum absorption peak at 240  $\mu$ . Now the monomer-free aqueous solution was treated with a saturated solution of KCl which reacted with  $\text{Na}(\text{C}_6\text{H}_5)_4\text{B}$  (present in the

solution) to form relatively insoluble  $K(C_6H_5)_4B$ . The precipitate was filtered off and the solution acidified with acetic acid and shaken for half an hour. This acidified solution was mixed with 10 ml cyclohexane, agitated vigorously and the cyclohexane portion was separated from the aqueous layer.

The cyclohexane sample thus obtained was treated with 8 ml distilled water and the aqueous and cyclohexane portions were again separated. The optical absorption spectrum of the aqueous extract was measured against pure water as a reference sample and an absorption peak appeared at 268  $\mu$ . A spectrum of a known sample of a phenol solution ( $\sim 10^{-5}M$ ) was also measured. Both spectra are shown in Figure 40. A comparison between the two spectra shows that the aqueous extract contained phenol. When the absorption spectrum of the cyclohexane extract was measured, a peak showed at 238  $\mu$  with three shoulder peaks between 260 and 280  $\mu$  presented in Figure 41. When this solution was washed three times with water, filtered and its spectrum measured, a sharp absorption peak appeared at 238  $\mu$  (Fig.42) without the previous tail peaks (Fig.41). This absorption peak is due to diphenyl boronous acid whose maximum absorbance occurs at 238  $\mu$ .

The cyclohexane sample, obtained from the alkaline

FIGURE 40. Absorption spectra in water,  
a, known sample of phenol  
b, sample obtained from analysis  
of anolyte.  
path length = 1 cm.

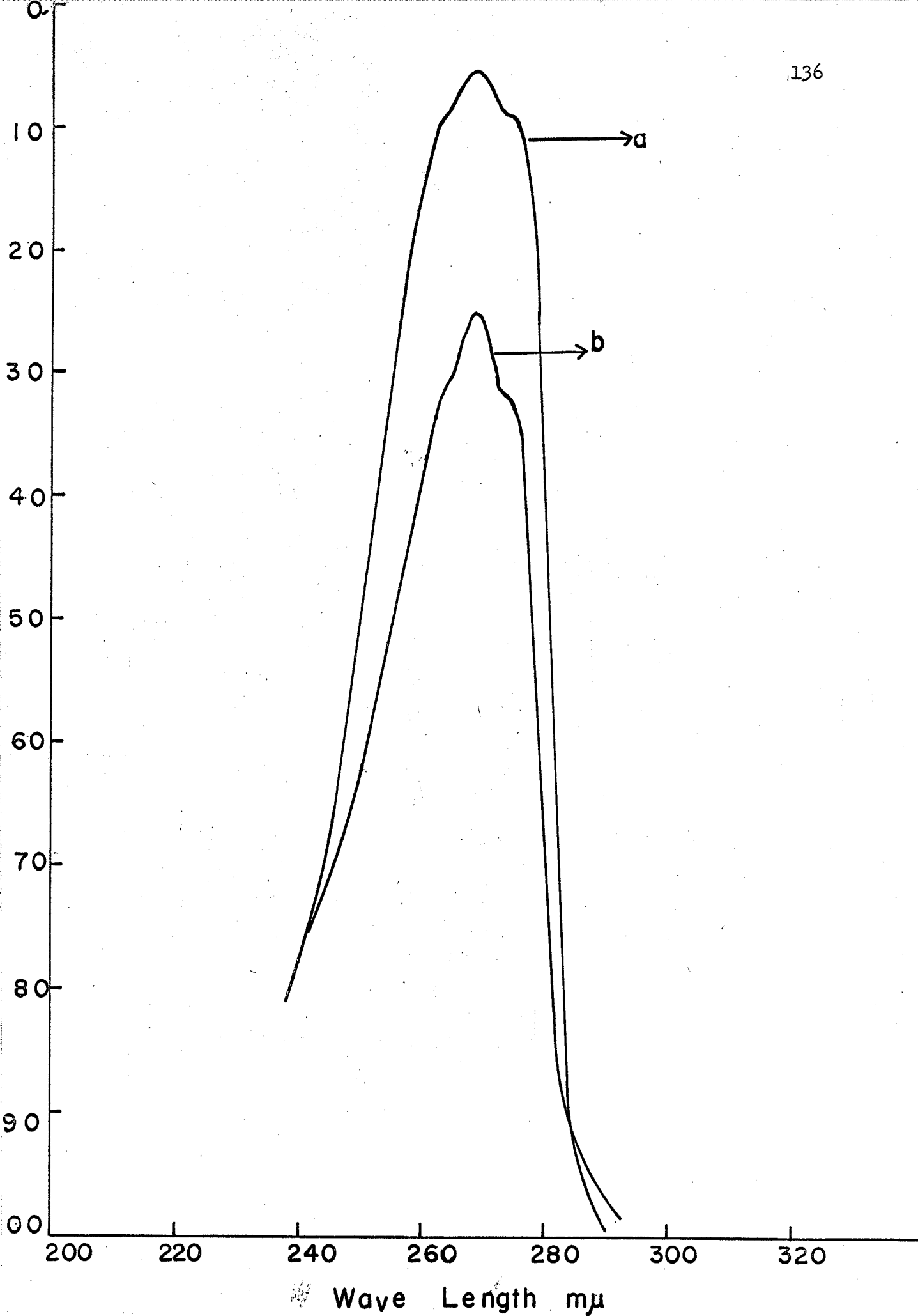
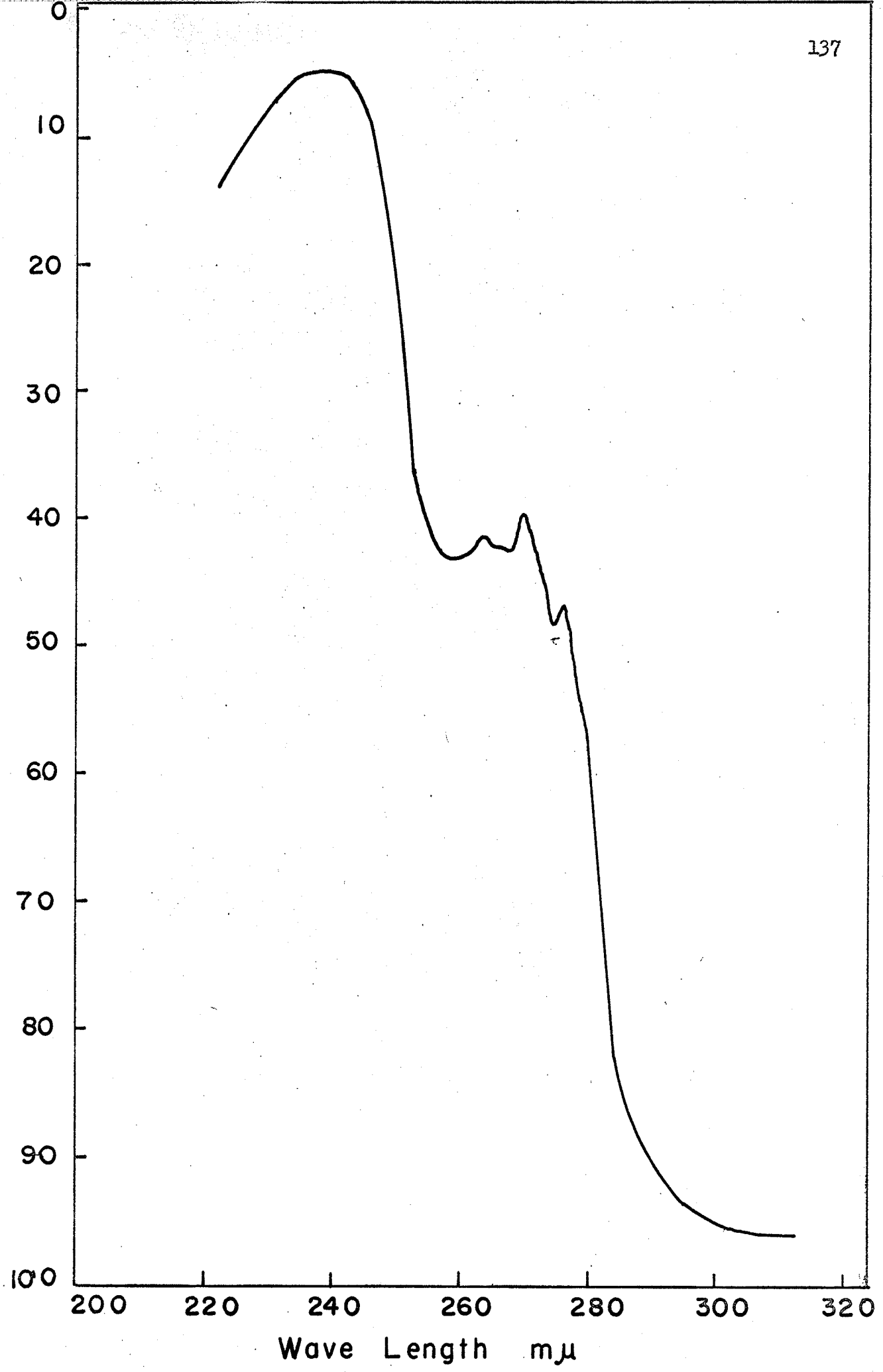


FIGURE 41. Absorption spectrum of cyclohexane  
extract obtained from acidified  
aqueous solution. Path length 1 cm.

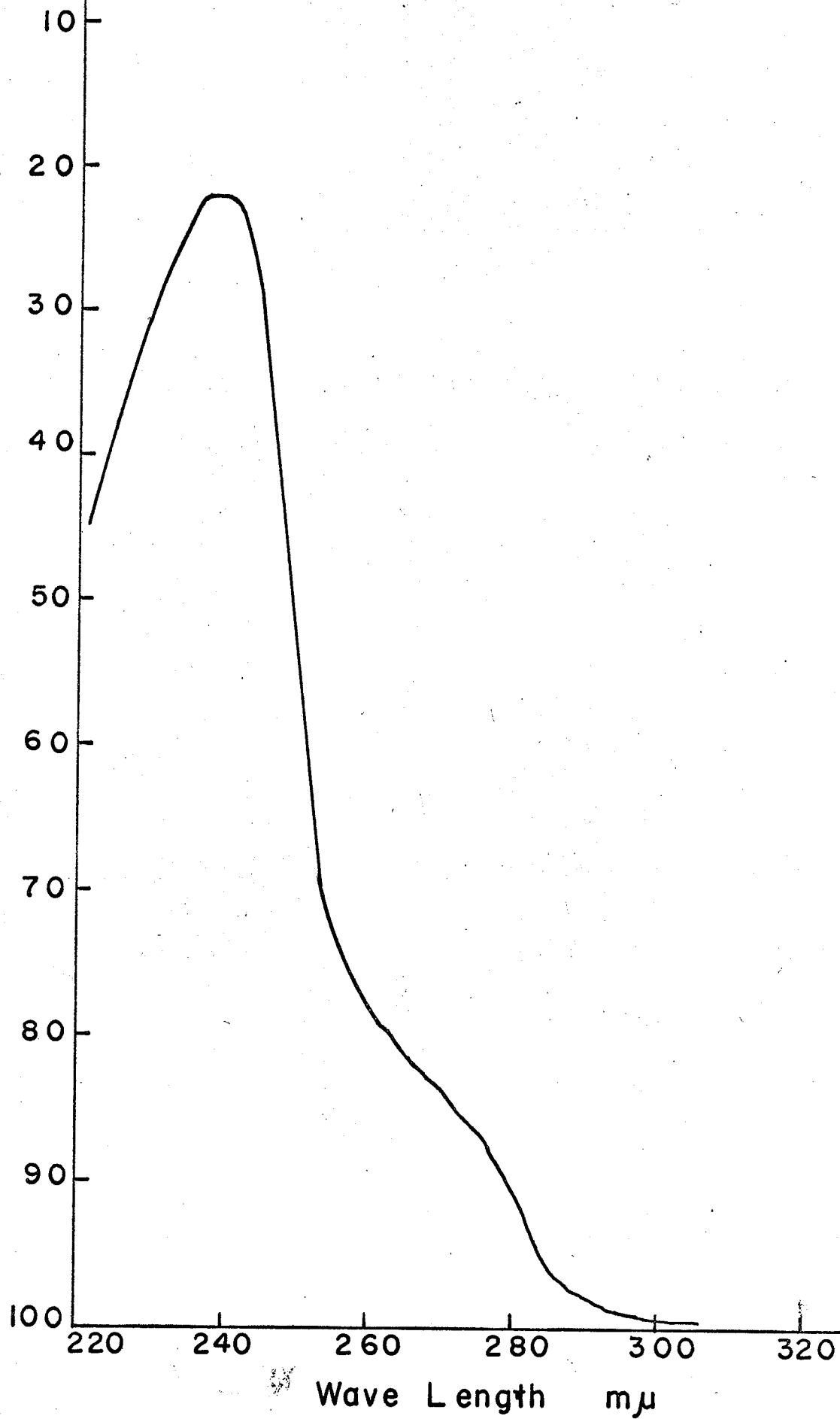
Percent Transmission



Wave Length  $\mu$

FIGURE 42. Absorption spectrum of diphenyl boronous acid,  $(C_6H_5)_2BOH$ , extracted in cyclohexane after washing the solution (Fig.41) with water. Path length 1 cm.





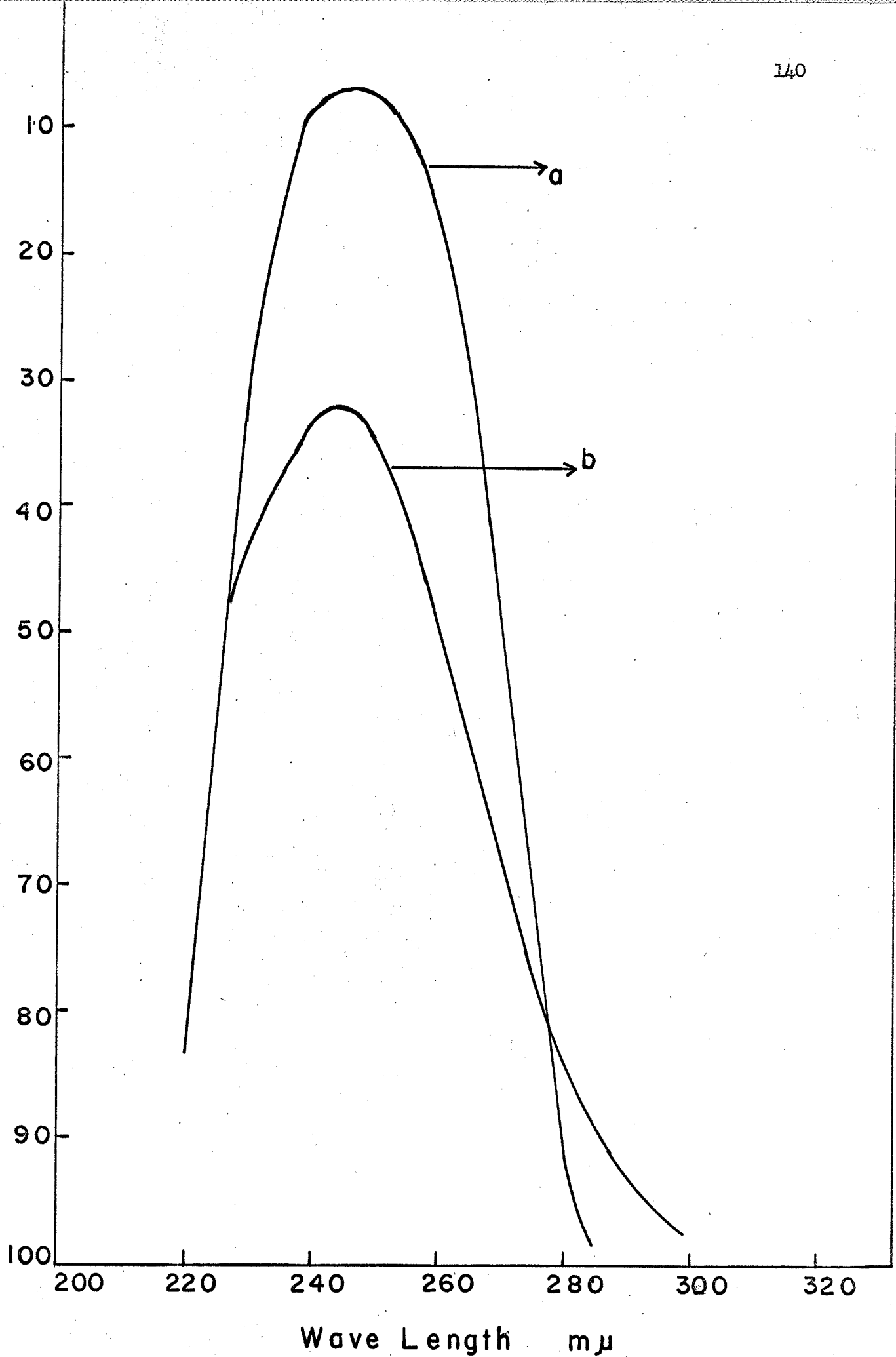
aqueous solution, was washed with water and suspended materials filtered off. The solution was evaporated in vacuum and the residue was pumped for more than two hours. This procedure was followed for removal of the monomer. The residue was dissolved in 15 ml cyclohexane, filtered and the absorbance was measured. The spectrum of this solution and that of a known sample of biphenyl solution ( $\sim 10^{-5}$  M) in cyclohexane are shown in Figure 43. From examination of these spectra it appears that the solution had contained biphenyl. The presence of biphenyl in the solution was also detected by a gas chromatogram. The analysis by the gas chromatogram showed the absence of benzene in the anolyte.

A solution of styrene (0.47 M) and  $\text{NaB}(\text{C}_6\text{H}_5)_4$  (.02 M) in the THF was electrolysed for 2 hours at 2 ma. The anolyte was then exposed to air and analysed by the procedure described above. The results were the same as those obtained in the case of alpha-methylstyrene. The styrene shows a maximum absorbance at 291  $\mu$ .

#### BLANK EXPERIMENT

A THF solution of the same concentrations of salt and alpha-methylstyrene as were used in the previous experiments, was prepared. No current was passed through

FIGURE 43. Absorption spectra in cyclohexane,  
a, known sample of biphenyl  
b, sample obtained from analysis of  
anolyte. Path length 1 cm.

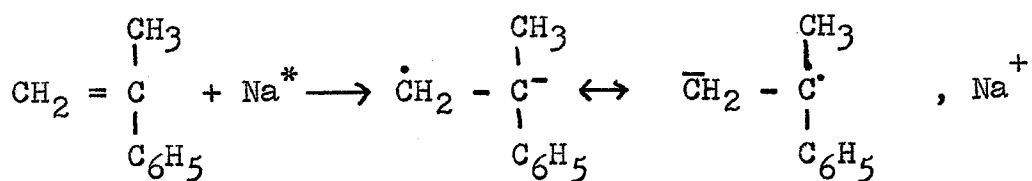


Wave Length mμ

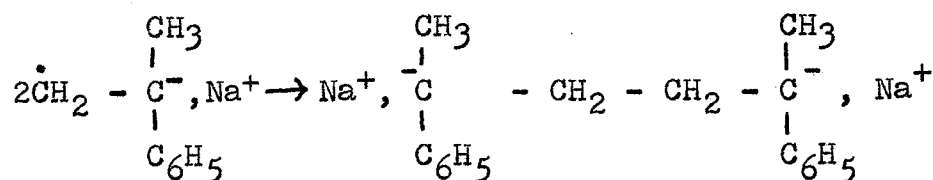
this solution. The unelectrolysed solution was analysed for biphenyl, phenol, benzene and diphenyl boronous acid. None of these compounds was detected in the solution.

### DISCUSSION

The addition of an electron to the double bond of alpha-methylstyrene yields a radical anion which, in turn, forms either a dimeric dianion, a dimeric radical anion or a tetrameric dianion depending on the experimental conditions (34,91,92). The formation and structures of these charged species can be illustrated as follows.

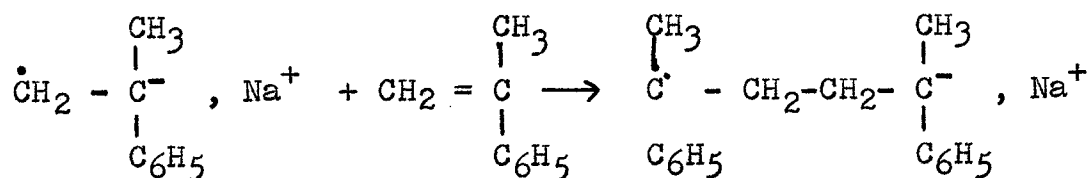


radical anion.....(1)

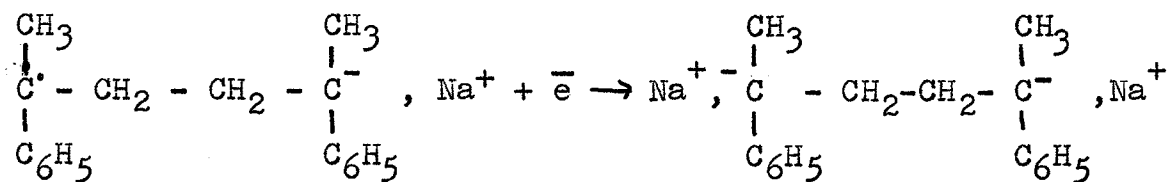


dianion.....(2)

or



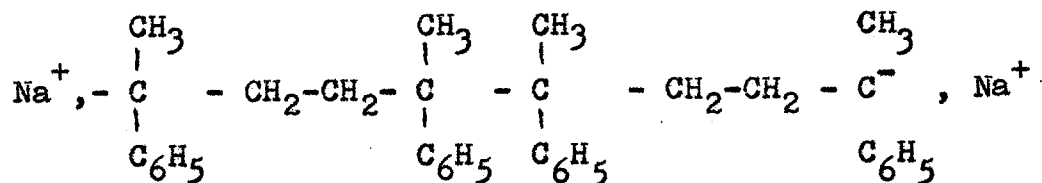
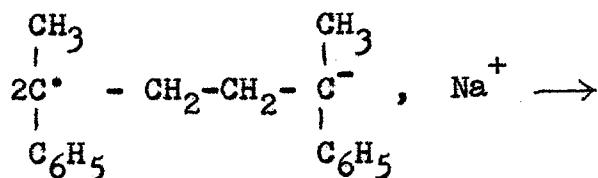
dimeric radical  
anion ..... (3)



dianion..... (4)

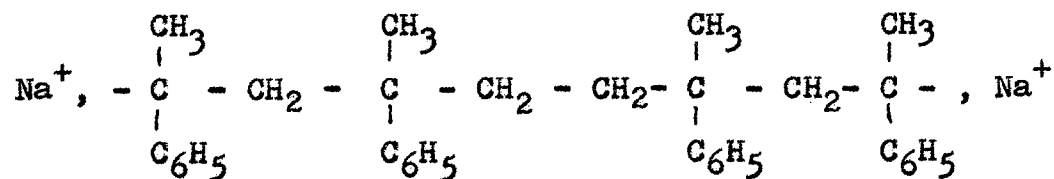
\* Sodium is taken as an electron transfer agent for illustration purposes.

Therefore, the dianion may be formed either by direct dimerization of the radical anion (reaction 2) or through a sequence of reactions yielding, the dimeric radical ion (reaction 3), which acquires an electron (reaction 4), resulting in the formation of the dianion. The electron transferred in reaction 4 may come from the original electron transfer reagent, from the monomeric radical anion, or from the dimeric radical anion. Because of the large difference in the concentration of the monomer and its radical anions, reaction 3 was found much faster than the dimerization of the monomeric radical anions (reaction 2)(34). A similar result was obtained with 1, 1-diphenyl ethylene (alpha-phenylstyrene)(29). The structure of the dimers was proved by their carboxylation to 2,5-diphenyl 2,5 dimethyl adipic acid (93). The dimerization of the dimeric radical anion results in a tetrameric dianion.



Tetrameric dianion...(5)

The tetramer is assigned to the head-to-head central configuration, arising from the coupling of two tail-to-tail radical anion dimers. The tetrameric dianions formed by the addition of two equivalents of the monomer to the dianion has the following tail-to-tail linked structure:



The head-to-head linked tetramer is more reactive than the tail-to-tail. The formation of dimeric radical ions is favored in a system where electrons are not easily available such as a metallic mirror. On the other hand, sodium naphthalene or sodium dispersion which because of their relatively large surface areas provide electrons more readily, yields the dianion through reaction 4. The

tetrameric dianion is not a mixture of oligomers having an average degree of polymerization of 4, but is a very stable single species. Because of thermodynamic restrictions, the chain length of the dianions does not increase (52,53). However, both dianion and tetrameric dianion are efficient and suitable initiators for anionic polymerization and retain their initiating ability for a long time.

In the present system radical anions may be formed by either of two possible processes, namely, (i) by a direct electron transfer from the cathode to the double bond of the monomer, (ii) by electron transfer from the alkali metal formed by the cathodic reduction of the metal ion. In view of the more positive reduction potential of the monomer than that of the  $\text{NaAl}(\text{C}_2\text{H}_5)_4$  in THF the first process was considered to be the more likely (69). Recently, however, on the basis of polarographic results, Yamazaki (94) postulated that the second process might occur preferably. However, the transient living anion formation in the presence of a quaternary ammonium salt can be undoubtedly interpreted by the first process. Nevertheless, both processes result in the formation of the same primary radical anion which, in turn, yield dianions (reactions 2 or 4) or tetrameric dianions (reaction 5). In the present study, however, no attempt



was made to characterise the nature of the charged species, but their absorption spectra (Figs, 17,19, 20), were measured and found to be the same as have been reported in the literature (34). Because two electrons are required to form the charged species, which initiates polymerization, the molecular weights of polymers formed in the absence of termination, can be given by the following equation:

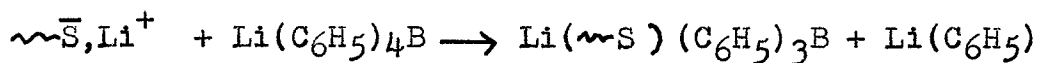
$$\text{Mol.Wt. } (M_n) = \frac{\text{Polymer g.}}{\frac{1}{2} Q}$$

This expression is the same as:

$$\frac{\text{Polymer g.}}{\frac{1}{2} \text{ Mols. of initiator}}$$

used extensively to calculate the molecular weights in the conventional living polymerization.

The observed and calculated molecular weights of polymers obtained with  $\text{Na}(\text{C}_6\text{H}_5)_4\text{B}$  are in a good agreement (Table 20), whereas a discrepancy was found in the molecular weights of the polymers formed with  $\text{Li}(\text{C}_6\text{H}_5)_4\text{B}$  (Table 19). This discrepancy may be attributed to the destruction of the living anion at  $25^\circ\text{C}$  (Fig.29), by the following reaction (49):



where  $\sim\bar{\text{S}}$  is an active chain end.

LiBr and LiOH have also been reported to terminate the living anions of alpha-methylstyrene in the mole ratio of 1:1 in THF (95). The authors believe that this is, presumably, due to a complex formation between the salts and active chain ends. However, they did not reveal the nature of the complex. Some anomalous behaviour with  $\text{Li}(\text{C}_6\text{H}_5)_4\text{B}$  was also observed by Szwarc and his co-workers (43). The uniform molecular weight-distribution of the polymer formed with  $\text{Li}(\text{C}_6\text{H}_5)_4\text{B}$  (Fig.36), and the persistence of the red color for a long time, shows that the deactivation of the living ends is not significant at a temperature of  $-80^\circ\text{C}$ .

From Figure 32 it is seen that the quaternary ammonium salt reacts rapidly with living ends. Again, it appears that the salt forms, either a complex with the active ends resulting in destruction of the red color of the solution, or the following reaction may take place:

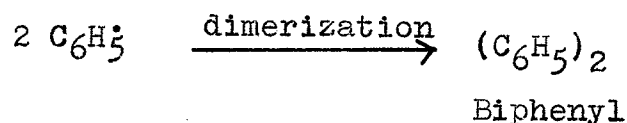
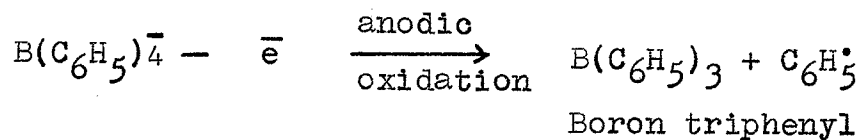
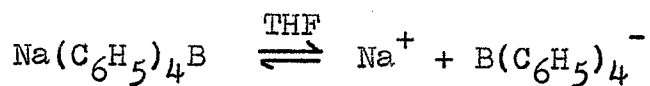


The nature of the purple color formation (Fig.30) during the electrolysis of a THF solution of the quaternary ammonium salt is not clear.

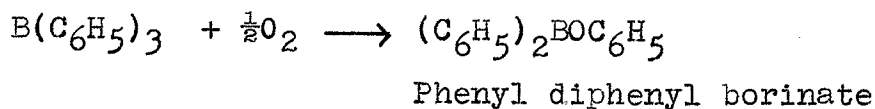
The extraction of biphenyl (Fig.43), diphenyl boronous acid (Fig.41) and phenol (Fig.40) from the anolyte may be explained by one of the two mechanisms

given below:

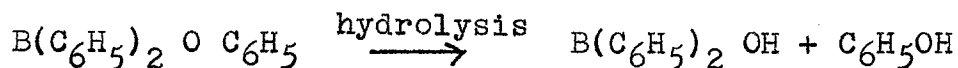
(i) One electron reaction



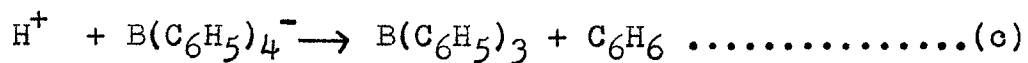
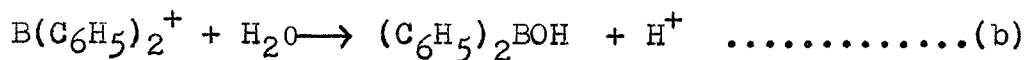
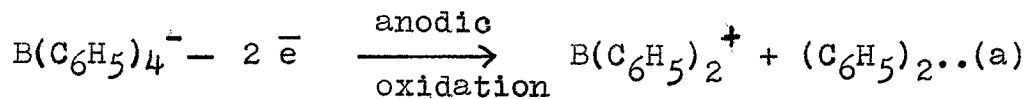
When a boron triphenyl solution is exposed to air (after electrolysis) the following reaction takes place:



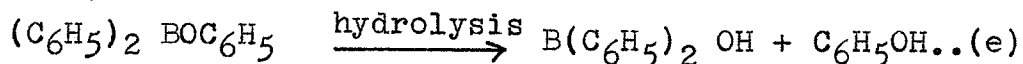
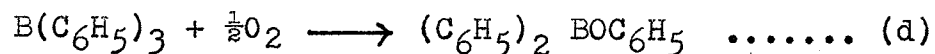
On hydrolysis phenyl diphenyl borinate forms diphenyl boronous acid and phenol.



(ii) Two electron reaction



(after electrolysis)



Geske (90) investigated the anodic oxidation of the tetraphenyl borate ion, electrolysing  $\text{Na}(\text{C}_6\text{H}_5)_4\text{B}$  solution in acetonitrile under conditions of controlled potential. He proposed the two electron reaction mechanisms for the oxidation process. Evidence for the existence of the diphenyl boronium ion,  $\text{B}(\text{C}_6\text{H}_5)_2^+$ , in methyl ethyl ketone and nitrobenzene solutions was also obtained by Davidson and French (96). However, in the present system, the one electron reaction is confirmed by the following experimental facts:

- (1) No benzene was found in the anolyte.
- (2) The terminating species formed at the anode deactivates the living anions in a 1:1 ratio (Fig.24). They are not transient, since the anolyte after standing for a few days still killed the living anions.

Nevertheless, if the two electron reaction occurs, then the terminating species may be either  $\text{B}(\text{C}_6\text{H}_5)_2^+$  which is transient or  $\text{B}(\text{C}_6\text{H}_5)_3$  which is produced in a secondary process (reaction c) in the presence of proton donating substances. The THF and monomer present in the solution

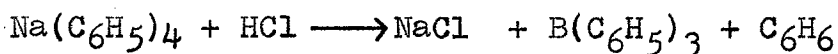
do not lose a proton as readily as acetonitrile does.

Therefore, it seems that  $B(C_6H_5)_3$  is formed directly at the anode by the anodic oxidation of the tetraphenyl borate ion (one electron reaction) and this species causes the destruction of the living ends, probably by a complex formation. The ability of triphenyl boron to react with anions and inhibit the anionic polymerization has also been reported in the literature (97, 98).

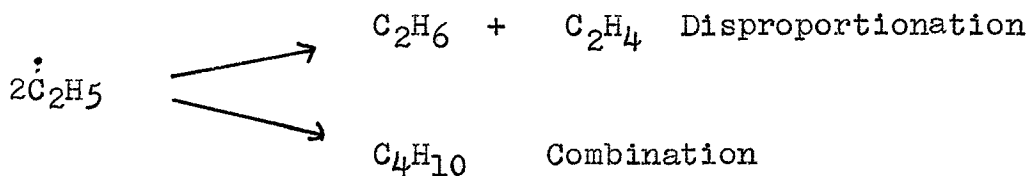
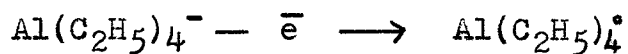
The blank experiment (page 139) offers evidence that the following reaction did not take place during analysis of the anolyte.



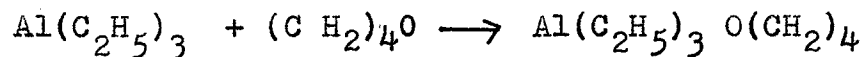
However, when an aqueous solution of the salt is treated with HCl, boron triphenyl is formed (90).



Using  $NaAl(C_2H_5)_4$  the  $Al(C_2H_5)_3$  which kills the living anions may be formed at the anode by the anodic oxidation of  $Al(C_2H_5)_4^-$  ion (87, p. 251).



No gas evolution was observed at the anode. The aluminum triethyl formed may react with THF as follows:



Here it is relevant to point out that when the catholyte, containing living anions produced with  $\text{NaAl}(\text{C}_2\text{H}_5)_4$ , is mixed with the anolyte the complete destruction of the living anion does not occur. Therefore, some  $\text{Al}(\text{C}_2\text{H}_5)_3$  might be consumed by complex formation with the solvent.

The present technique for the production of living anions promises a ready control of the concentration of living ends at any desired level (Figs. 24, 25, 26). The concentration is determined by the number of Faradays passed through the solution. This is further substantiated by the results presented in Figures 27 and 28. The importance of the method lies in the fact that the activation and deactivation of the living ends can be achieved at will. Therefore, such a process can offer several synthetic possibilities such as the formation of polymers of an arbitrarily chosen molecular weight distribution. Furthermore, the transient red color formation in the case of quaternary ammonium salts demonstrates that the generation of living anions is possible even in the absence of alkali metals which are solely used in the conventional method.

SUMMARY

1. The absorption spectra of electrolytically formed living anions of alpha-methylstyrene and alpha-phenylstyrene were measured and found to be the same reported in the literature.
2. The possible mechanisms for such a living anion formation were discussed.
3. The living end concentration was calculated by Faraday's Law. The concentration could be decreased and increased easily at will.
4. At the anode a terminating species was formed in an amount equivalent to the living anions. These species were found to be  $B(C_6H_5)_3$  and  $Al(C_2H_5)_3$  formed by the anodic oxidation of  $B(C_6H_5)_4^-$  and  $Al(C_2H_5)_4^-$  respectively. The mechanism of their formation was given.
5. The transient red color of the living anions was formed at the cathode in the presence of quaternary ammonium salts. The deactivation of living anions with these salts and  $LiB(C_6H_5)_4$  were observed.
6. The alpha-methylstyrene polymers exhibited narrow molecular weight distribution.

CHAPTER IV

ELECTROLYTICALLY INITIATED ANIONIC POLYMERIZATION  
OF ISOPRENE



## EXPERIMENTAL PROCEDURE

### DIVIDED CELL EXPERIMENT

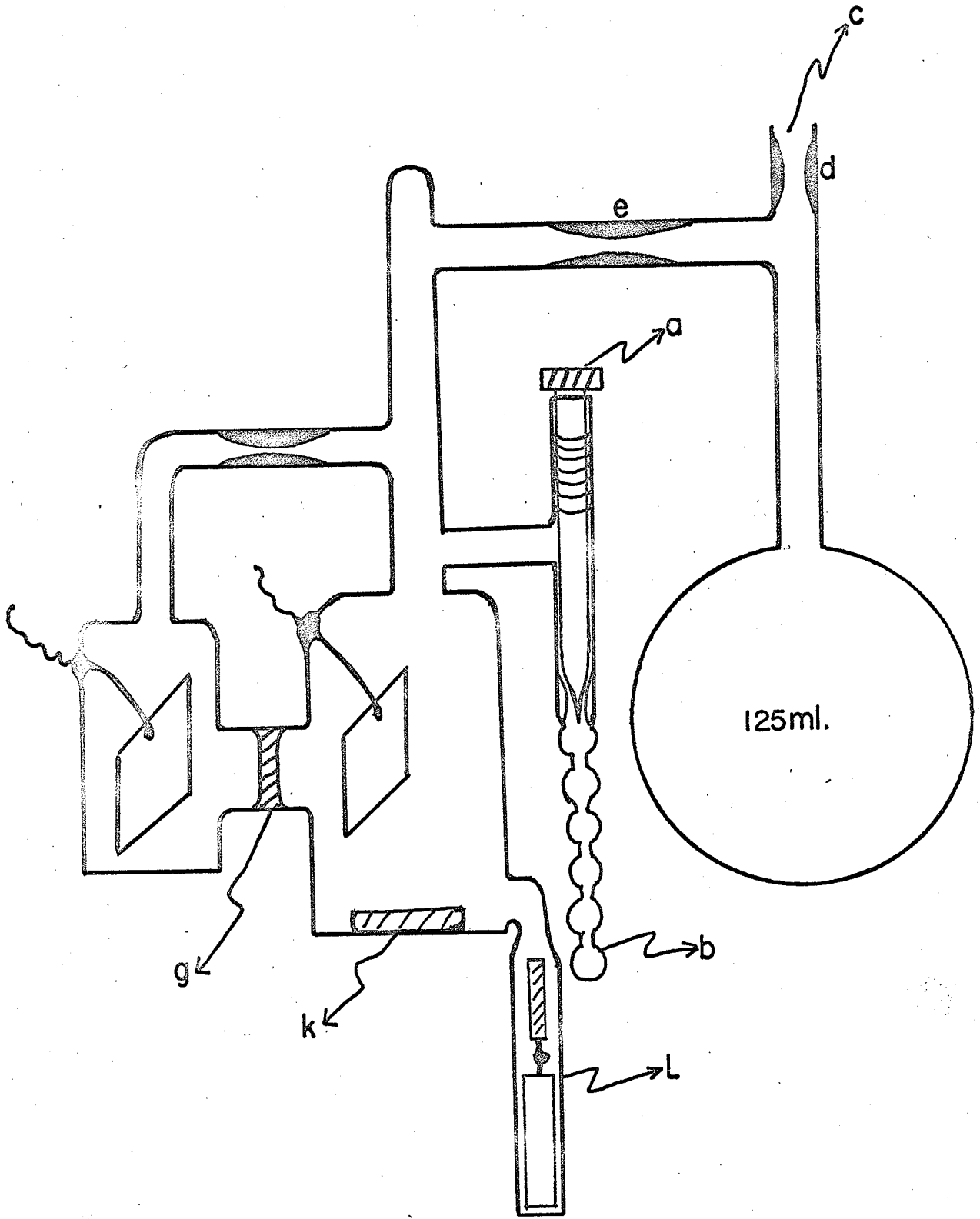
The type of electrolytic cell used in this work is shown in Figure 44. This is quite similar to that described in Figure 16. A few sampling bulbs "b" connected with teflon  $1\frac{1}{2}$  mm needle valve "a" (Fisher and Porter Co.) were attached to the cathode compartment for withdrawal of the reactive mixture. The catholyte was drained into the bulb at certain intervals of the reaction time through opening the needle valve, and the sample was frozen. Then the bulb was sealed off, detached and kept frozen in liquid nitrogen until it was analysed by gas chromatogram. The analysis procedure was as follows:

The helium gas at a flow rate of 40 ml/minute was used as a carrier of the sample to be analysed. The sample of 2 microlitre was injected via a microliter syringe. The column (6 ft. x 25 in.) packed with 20 percent apiezon L grease deposited on fire brick was operated at  $64^{\circ}\text{C}$ . The monomer content in the sample was determined by using solvent internal reference standard technique. A triplicate analysis for each sample was done and reproducibility was about  $\pm 1$  percent.

The total volume of solution was 110.3 ml and that of the catholyte 75.4 ml at  $25^{\circ}\text{C}$ . In each kinetic run the isoprene and sodium tetraphenyl boron concentrations were 0.66 M and  $1.06 \times 10^{-2}\text{M}$  respectively, unless otherwise

FIGURE 44. Divided electrolytic cell.

- a, Teflon-glass needle valve
- b, Sampling bulbs
- g, Sintered glass diaphragm (very fine maximum  
bore size 2 to 2.5 microns)  
9 mm spacer and glass sealed magnet
- k, glass sealed magnet
- d and e, constrictions to seal off.



stated. The apparatus was charged with the solution in vacuum line. The reaction was carried out at room temperature (25°C).

#### DILATOMETER

Polymerization was also carried out in the dilatometer shown in Figure 45, which is identical to that described in Figure 15, "d" is 20 cm long precision bore capillary tube. The procedure for filling the dilatometer was essentially the same as described in the case of undivided cell experiment. The liquid level in the dilatometer was adjusted up to the calibration mark "m" at thermostatted temperature  $25 \pm 0.05^\circ\text{C}$  requiring 31.76 ml solution. The change in volume of the reaction mixture was measured with a precision of  $\pm 0.001$  ml. A cathetometer with a precision of .001 cm was used. All the transfer of chemicals was done in vacuum. The success of using a dilatometer to determine polymerization rate in the present system essentially depends on the fact that no gas evolution should occur during the course of electrolysis. Furthermore, low current at low applied potential must be employed in order to avoid possible heating effect. Sodium aluminum tetraethyl was invariably used as electrolyte because it furnished a relatively highly conducting solution in THF.

FIGURE 45. Dilatometer.

K , ground glass joint

e and L, constrictions to seal off

m, calibration mark

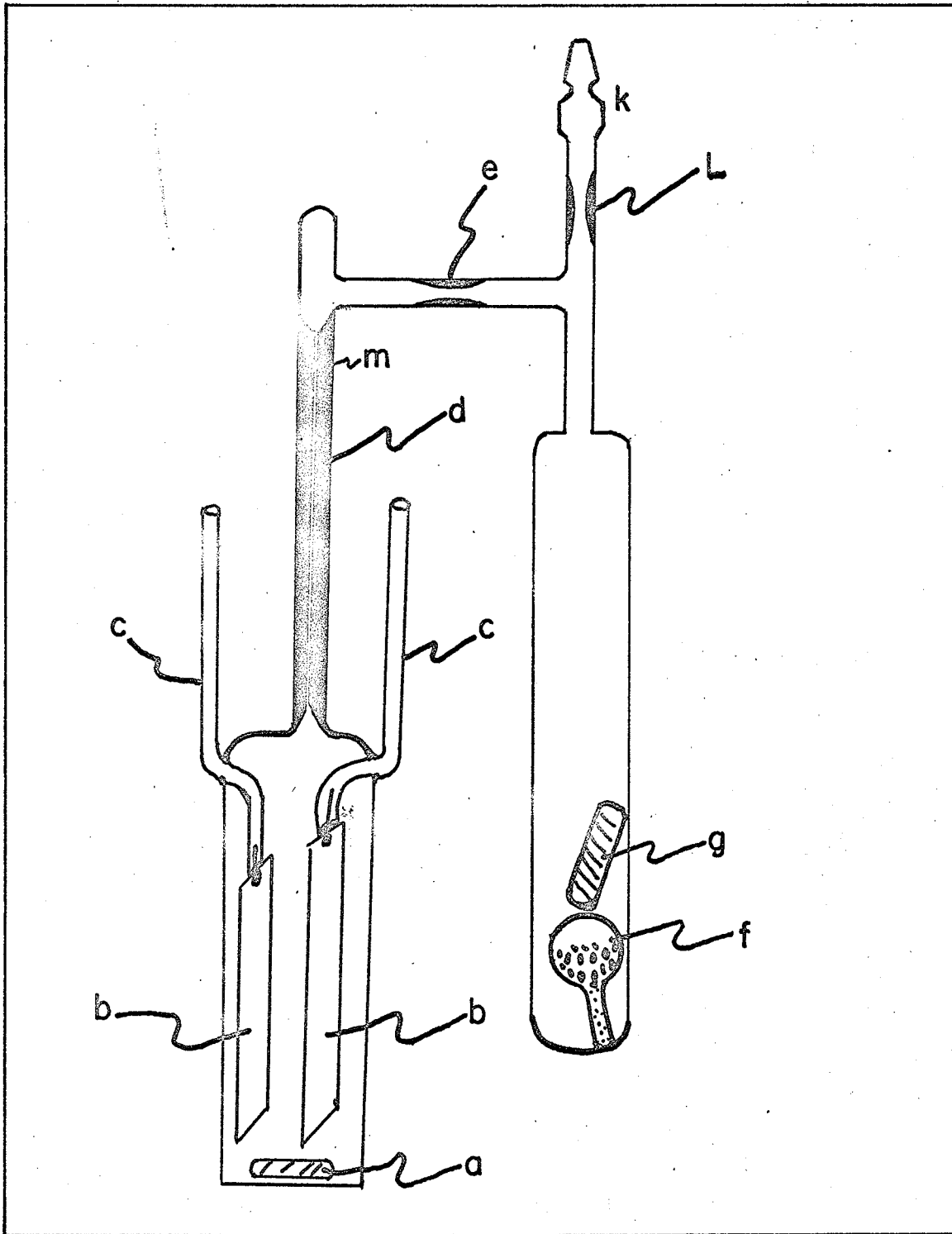
d, 20 cm. long precision capillary tube

C, for mercury contact

b,b 4.5 x 2 cm. platinum electrodes 1 cm. apart

a and g, teflon coated magnetic bars

f,  $\text{NaAl}(\text{C}_2\text{H}_5)_4$  ampoule.



## RESULTS

### ABSORPTION SPECTRA OF LIVING POLY-ISOPRENE

When a current of 5 ma at applied potential of 42 V was passed through the .59M monomer solution in THF containing  $1.06 \times 10^{-2}$ M  $\text{Na}(\text{C}_6\text{H}_5)_4\text{B}$  (catholyte vol. being 55 ml at  $25^\circ\text{C}$ ) the characteristic yellow color due to living anions was formed at the cathode. After a short induction period the catholyte became yellow and its absorption spectra were measured and are shown in Figure 46. After the electrolysis it was found that absorption of the solution started to decrease and the solution eventually turned to faint pink from the deep yellow. The resulting pink colored solution became colorless when it was exposed to air. The decrease in absorbance with time is exhibited in Figure 47. The absorption spectra obtained in the presence of  $\text{NaAl}(\text{C}_2\text{H}_5)_4$  are shown in Figure 48, and the absorbance decrease at 320  $\mu$  is presented in Table 21. The mixing of anolyte and catholyte or reversal of the polarity of electrodes also resulted in destruction of the yellow color. Using  $\text{Na}(\text{C}_6\text{H}_5)_4\text{B}$ , the increase in absorbance of polyisoprenyl anions at 320  $\mu$  was measured as a function of electrolysis time and the result is shown in Figure 49.

FIGURE 46. Absorption spectra of a solution of  
isoprene in THF containing  $\text{Na}(\text{C}_6\text{H}_5)_4\text{B}$   
1. Before electrolysis, (2) after 25 and  
55 minutes electrolysis at 3 ma current.



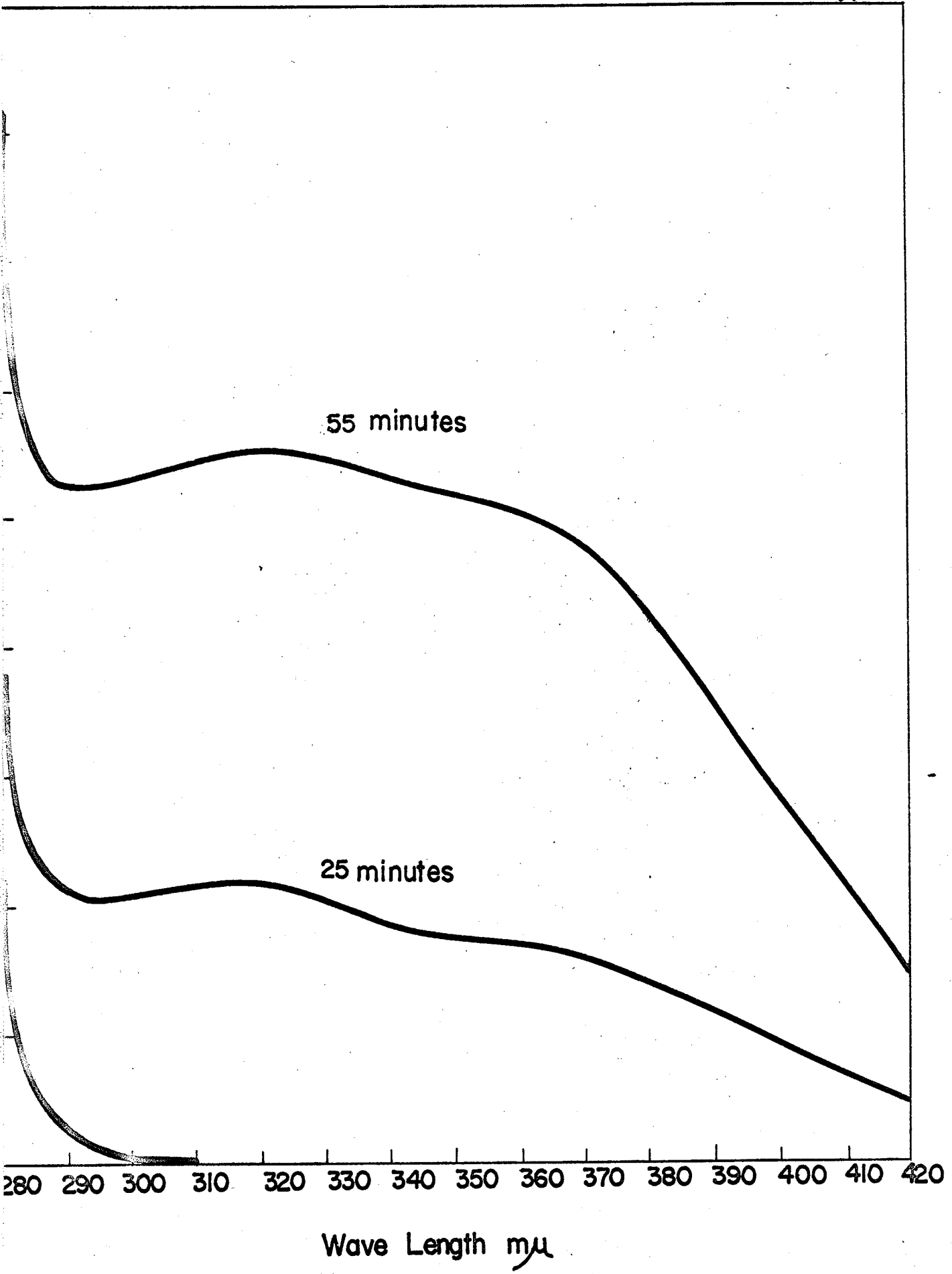


FIGURE 47. Spontaneous decrease of absorbance  
of living polyisoprene anions at inscribed  
times after cessation of electrolysis.

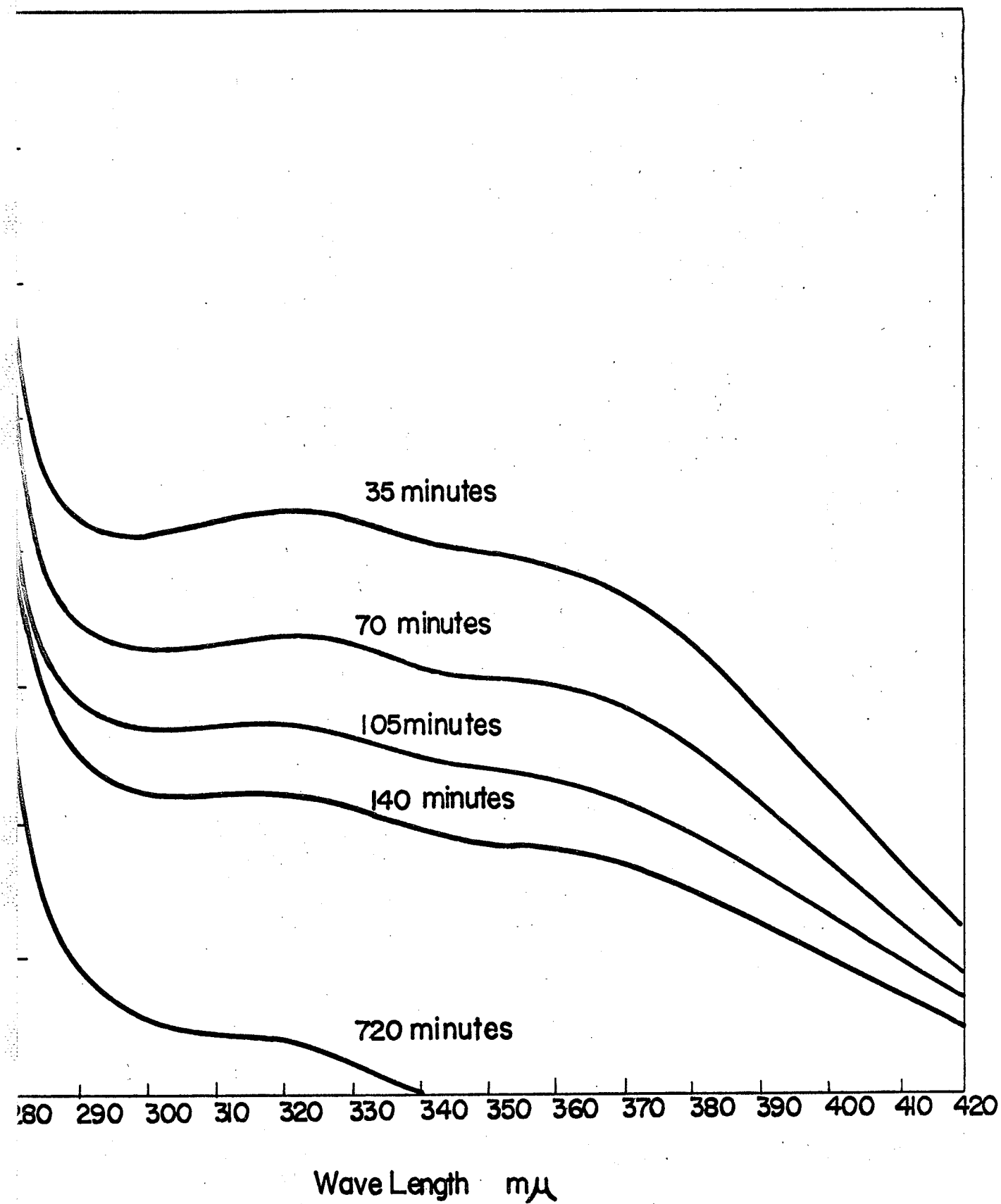


FIGURE 48. Absorption spectra of a solution  
of isoprene in THF containing  
 $\text{NaAl}(\text{C}_2\text{H}_5)_4$ .

a, before electrolysis; b, c and d after  
electrolysis at 3 ma for 14, 30 and 45  
minutes respectively.

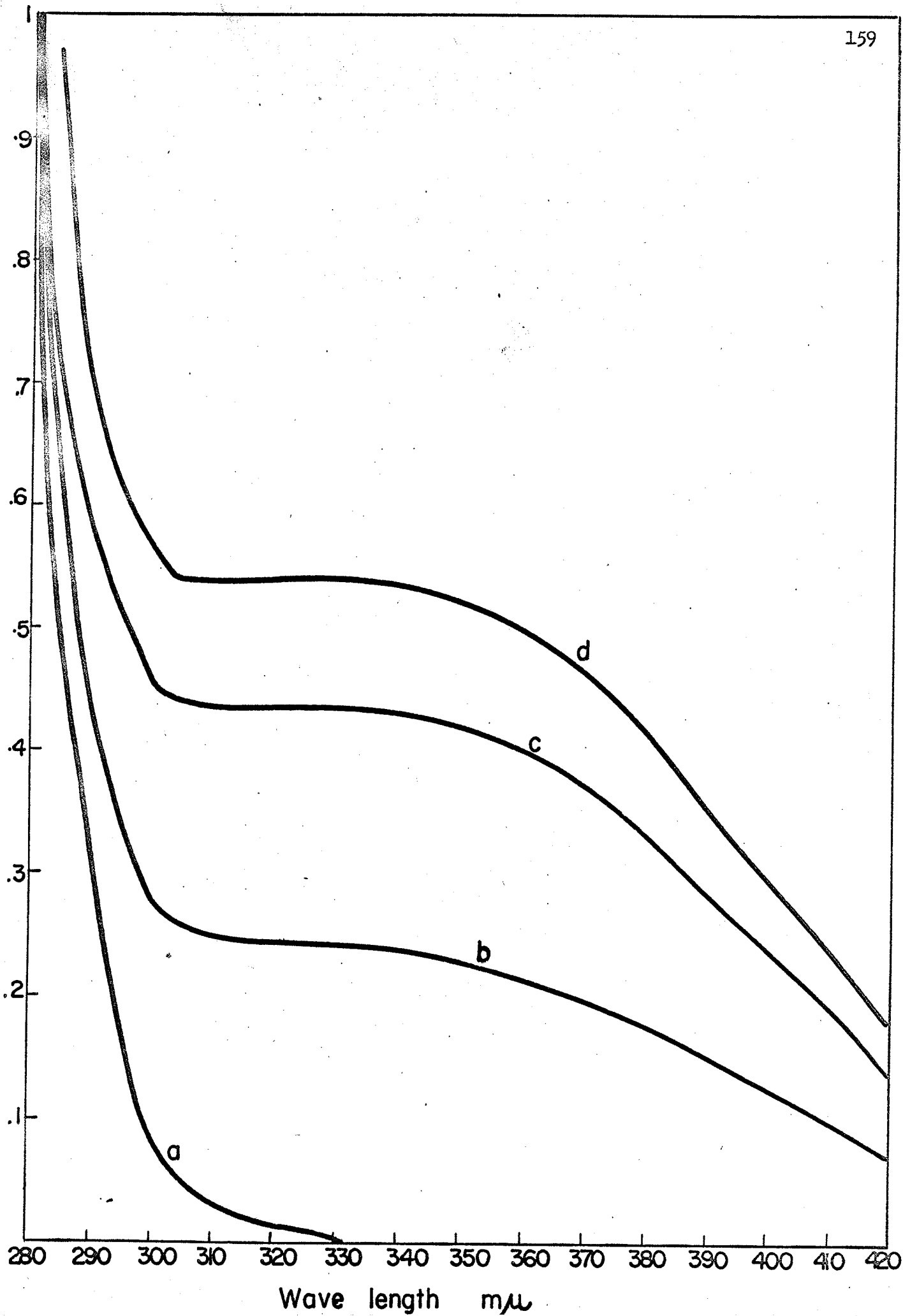


FIGURE 49. Increase of absorbance at 320 m $\mu$  of living polyisoprene anions with electrolysis time current - 3 ma.

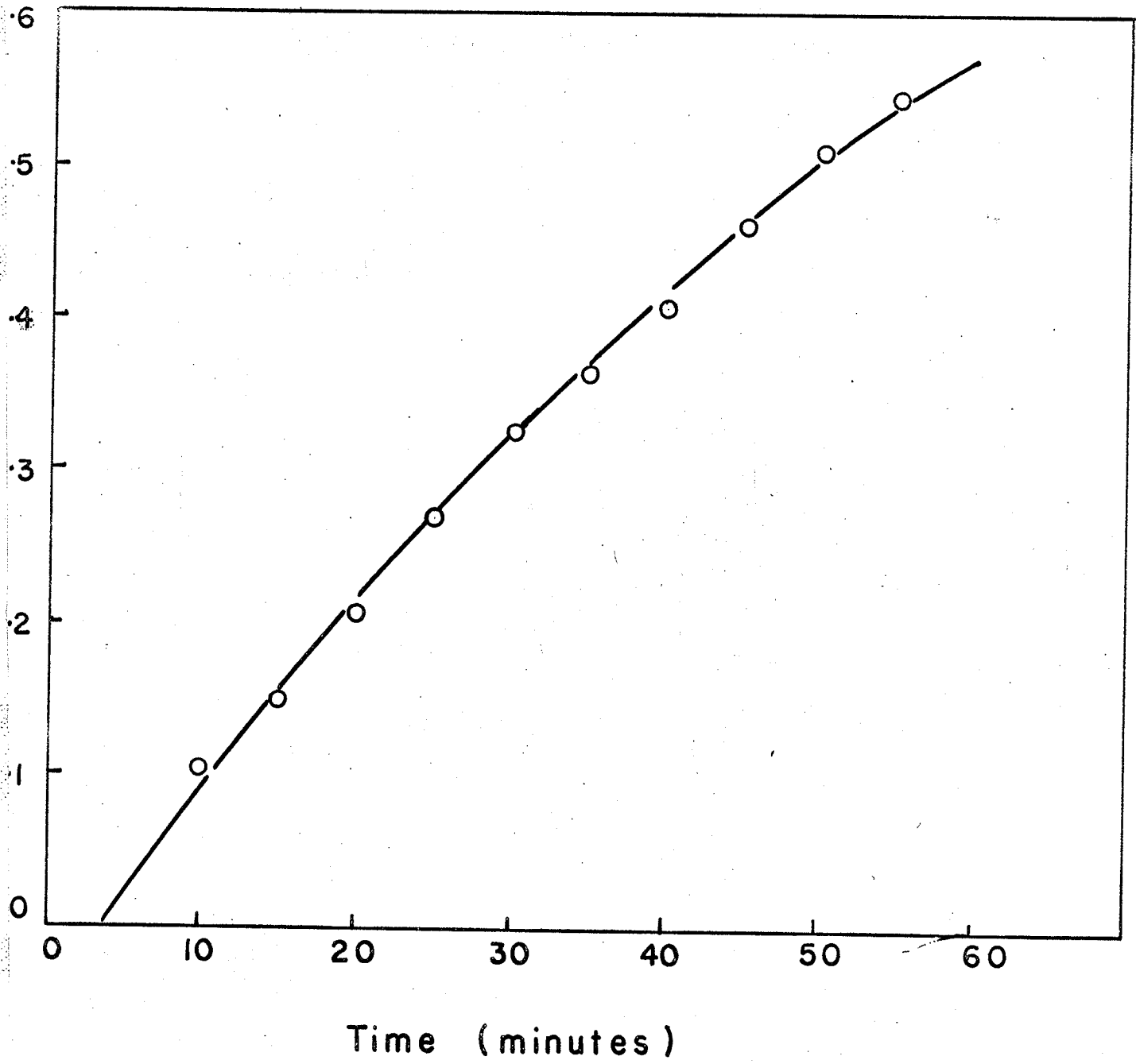


TABLE 21. Decrease in absorbance of polyisoprenyl anions.

Time (minute)	Absorbance at 320 m $\mu$
0	.538
15	.477
30	.450
48	.398
60	.367
77	.328
90	.301
105	.272
120	.250

ATTEMPT TO MAINTAIN CONSTANT LIVING ANION  
CONCENTRATION

It was found possible to keep the intensity of yellow color constant during polymerization and this was achieved by an electronic device (99). The solution was electrolysed to obtain the desired concentration of living anions and then the electronic relay was precisely adjusted to monitor the output signal from the spectrophotometer in which the appendage to the cathode compartment of the cell was placed. On reduction in absorbance of the solution, the relay allowed current to pass through the cell raising the absorbance back to the initial value at which point the flow of current was stopped. This intermittent



passage of the current maintained the absorbance at a constant value. However, the success inherently depended on thorough stirring of the reaction mixture in the electrolytic and optical cells. Therefore, agitation of the catholyte was effected by glass sealed magnetic bars (Fig.44 - "L" and "K"), which were being simultaneously whirled by a water driven magnetic stirrer. From time to time, the spacer was also momentarily moved up and down by means of the magnet. An example of the absorbance constancy is shown in Figure 50. It is seen that so long as the relay to control the current was on, the absorbance remained constant, otherwise it gradually decreased.

#### KINETIC STUDY OF THE POLYMERIZATION

The kinetic data obtained at four different living anion concentrations (Table 22) maintained constant throughout the course of the reaction and are shown in Figure 51. Plots of logarithmic dependence of monomer concentration versus polymerization time are shown in Figure 52. The polymerization time was regarded as beginning after the cessation of the electrolysis necessary to obtain the required living anion concentration. Although the initial monomer concentration for each run was almost the same, all the curves (Fig.52) did not

FIGURE 50. Constancy of polyisoprene anion population by passage of trickle current.

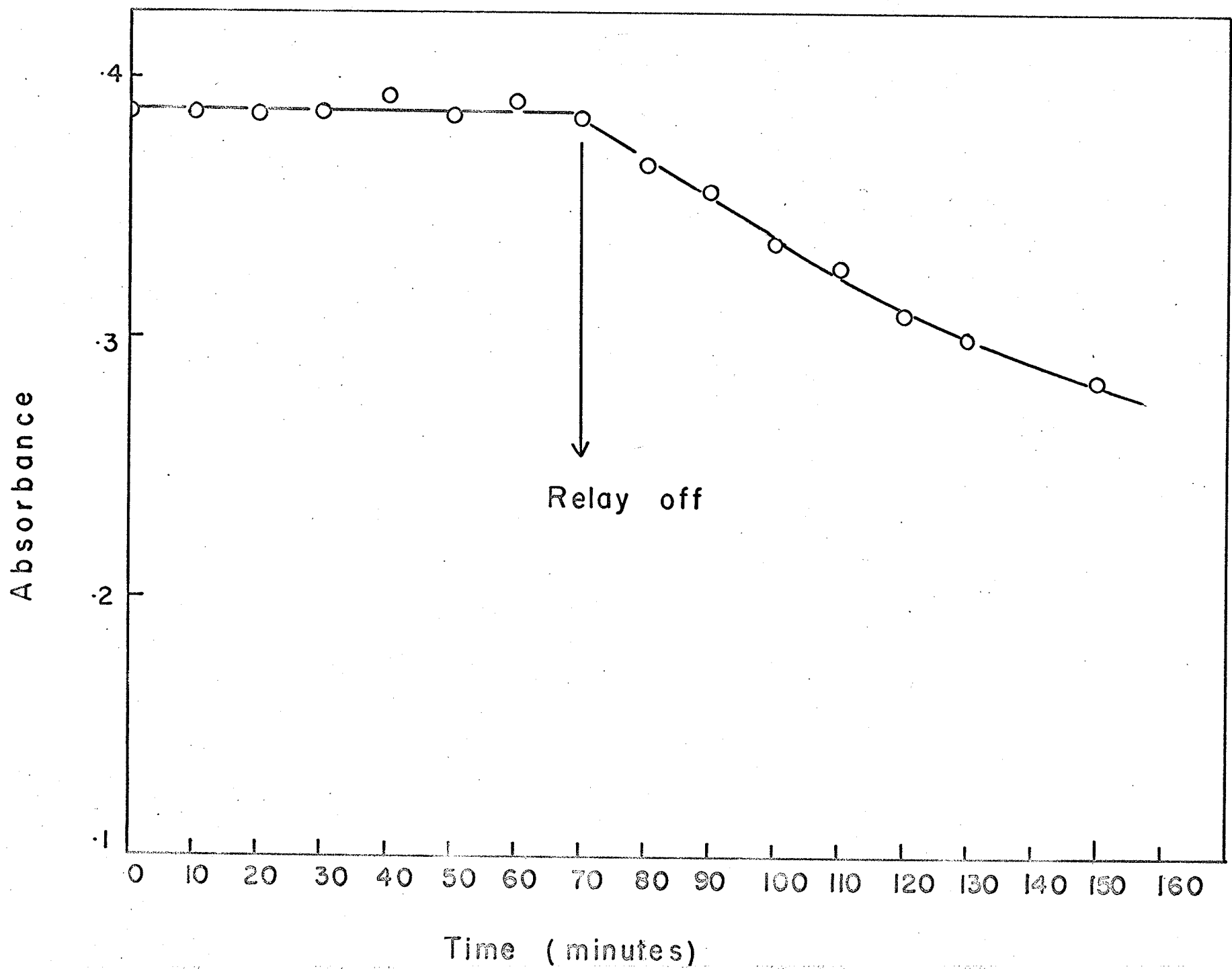


FIGURE 51. Polymerization rate at constant concentration of living ends.

Absorbance at 320 m $\mu$ .

○	-	.08
●	-	.10
◐	-	.18
△	-	.22

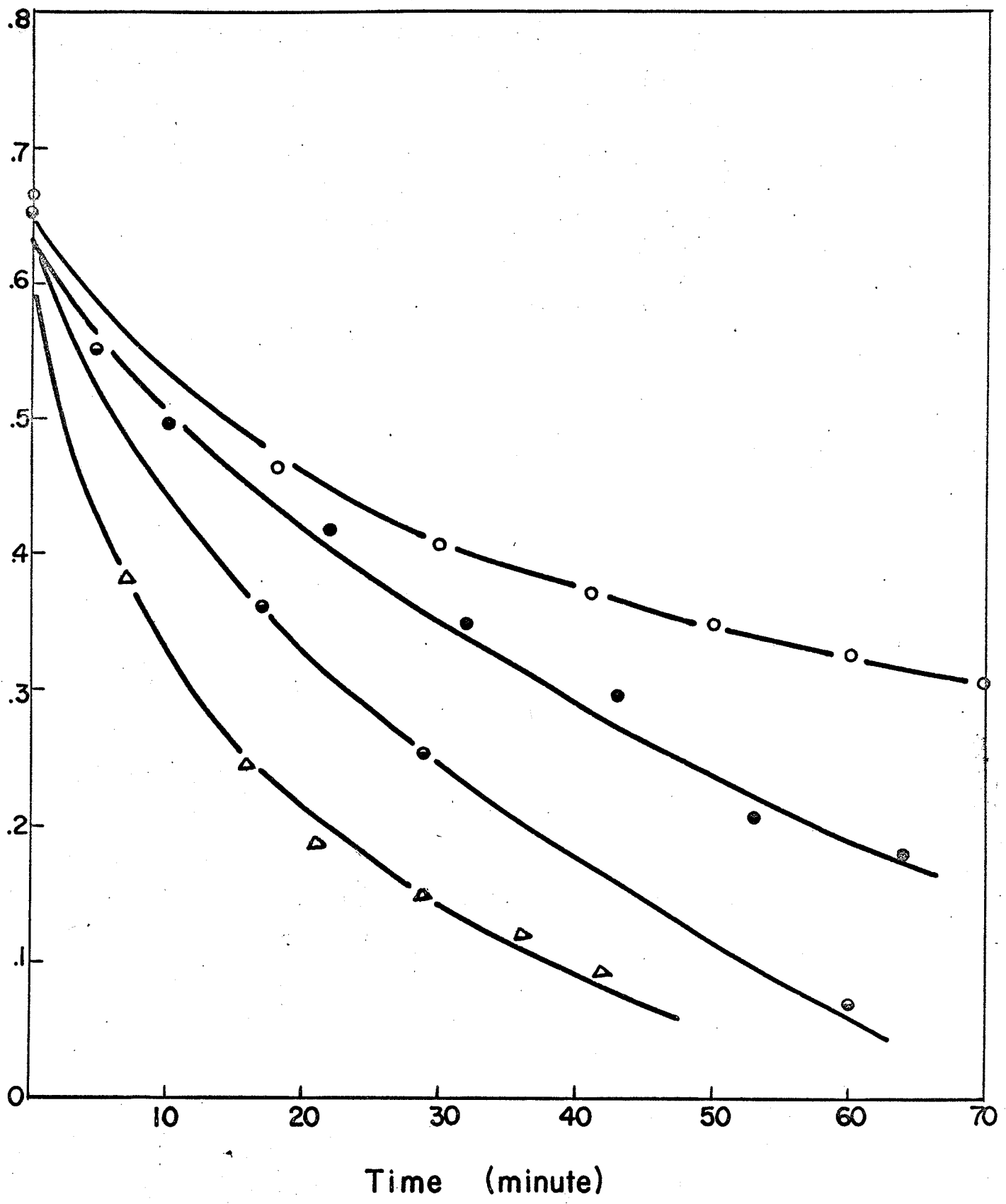
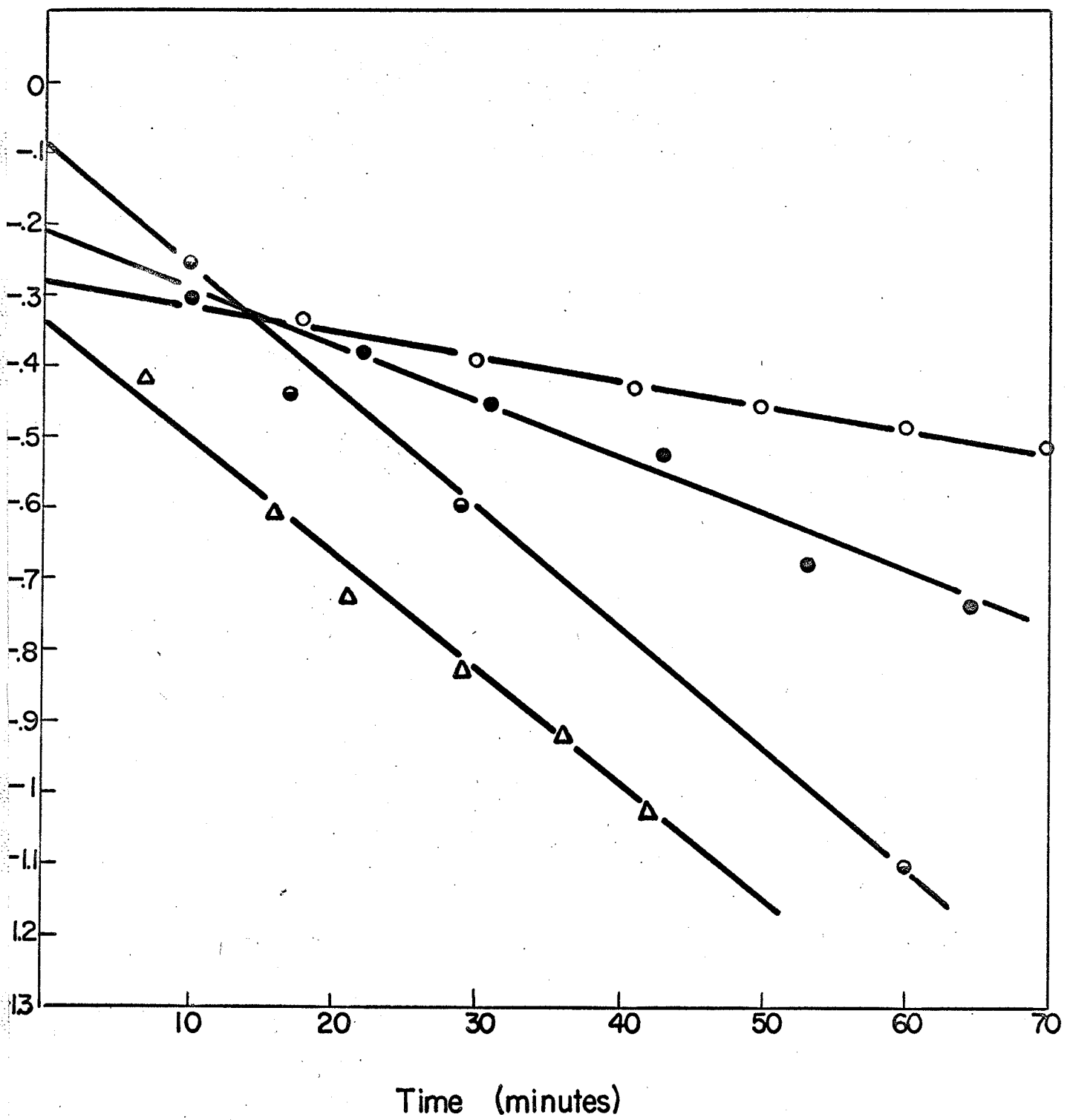


FIGURE 52. First-order plots of data shown in  
Figure 51.



meet at the same point. This may be attributed to a decrease in the monomer concentration during electrolysis. Figure 53 shows the polymerization rate when the living anion concentration was not kept constant.

TABLE 22. Living anion concentration

Time of electrolysis (minute)	Current ma	Absorbance at 320 m $\mu$	Concentration of living anion* (mol/litre) x 10 <sup>4</sup>
5	6	.08	2.1
8	6	.10	2.6
11	6	.18	4.7
9	10	.22	5.8

\*Calculated on the basis of extinction coefficient =  $3.82 \times 10^3$  (litre mol.<sup>-1</sup> cm<sup>-1</sup> at 320 m $\mu$ ) which was determined from the slope of initial linear portion of the curve (Fig.49).

The exploratory experiment showed that although the species generated at the anode killed polyisoprenyl anion, it was nevertheless, possible to form polymers on high yield. Therefore, it was of interest to measure the polymerization rate dilatometrically. The volume change of the reaction mixture on polymerization was calculated from the specific volumes of monomer and polymer. The density of polyisoprene was determined in

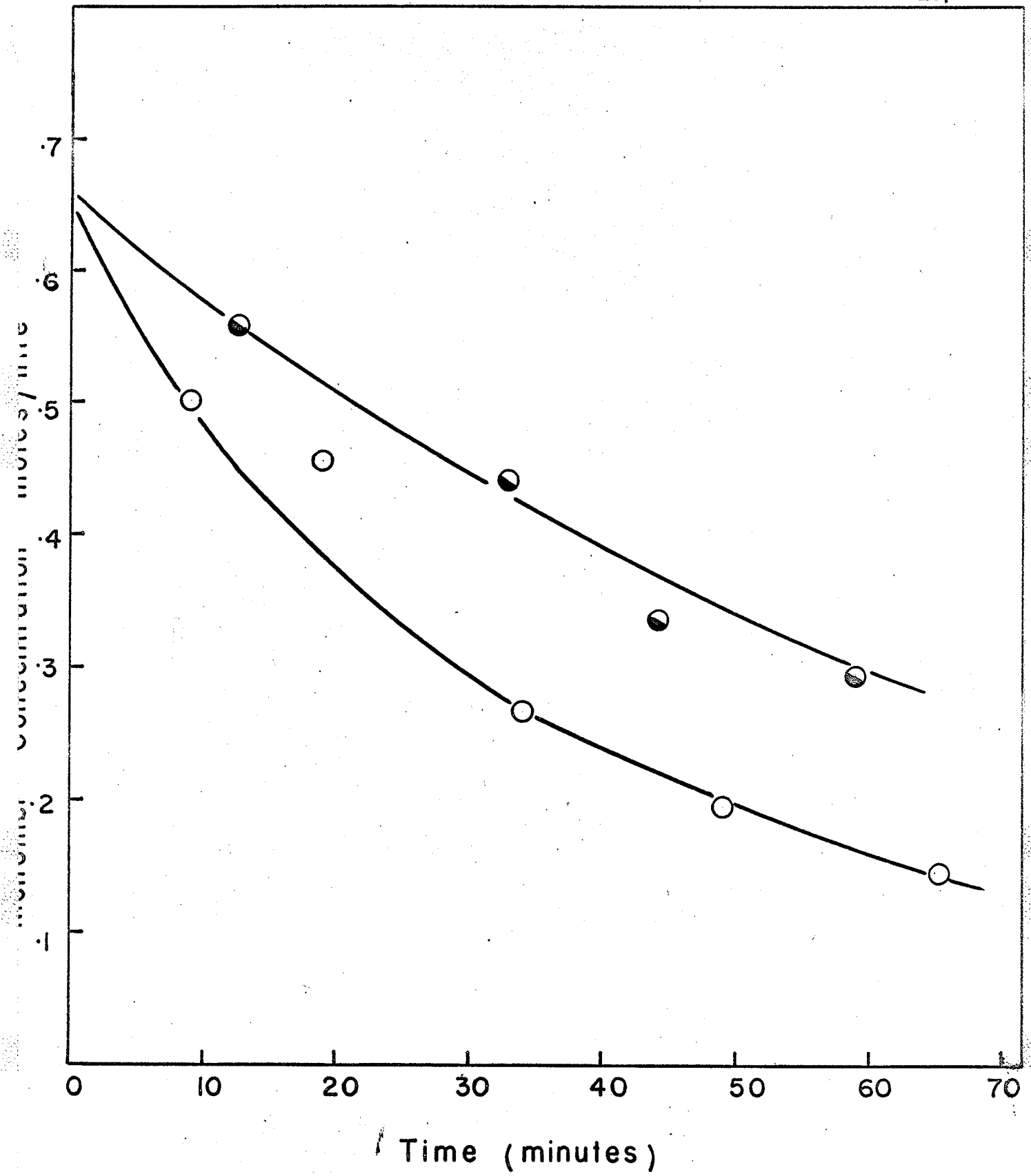


FIGURE 53. Polymerization rate when living end concentration was not kept constant.

Absorbance at 320 m $\mu$ .

○ - .20

● - .18



THF solution at 25°C and was found to be 0.920 g/ml. The monomer density was measured as 0.675 g/ml. Therefore, the specific volumes of monomer and polymer are 1.481 ml/g and 1.087 ml/g respectively. The volume contraction,  $\Delta V$  per gram monomer on polymerization =  $1.481 - 1.087 = 0.394$  ml/g.  $\therefore$  volume contraction  $\Delta V$  per mole,

$$= 68.11 \times .394 = 26.84 \text{ ml/mole.}$$

The literature value is 25 ml/mole (100). The dilatometer was charged with 31.76 ml of THF solution containing 1.46 M monomer and .0425 M  $\text{NaAl}(\text{C}_2\text{H}_5)_4$ . The theoretical volume contraction of 31.76 ml reaction mixture for 100 percent monomer conversion would be equal to,

$$\frac{26.84 \times 1.46}{31.76} = 1.234 \text{ ml}$$

The solution of the above composition was subjected to electrolysis at various impressed currents ranging between 3 to 15 ma and polymerization rate was followed dilatometrically. The results are shown in Figure 54. The corresponding applied potential for different impressed currents is presented in Figure 55. Figure 56 shows the first order plot of monomer concentration versus time. The plots were made only for 30 percent conversion. The initial rates of polymerization were computed from slopes of the Figure 56 and are compiled in Table 23, which indicates that the initial rate is proportional to the impressed current. The polymerization rates at different initial

FIGURE 54. Polymer formation as a function of inscribed currents and time for 1.46 M isoprene in THF containing .0425 M  $\text{NaAl}(\text{C}_2\text{H}_5)_4$ .

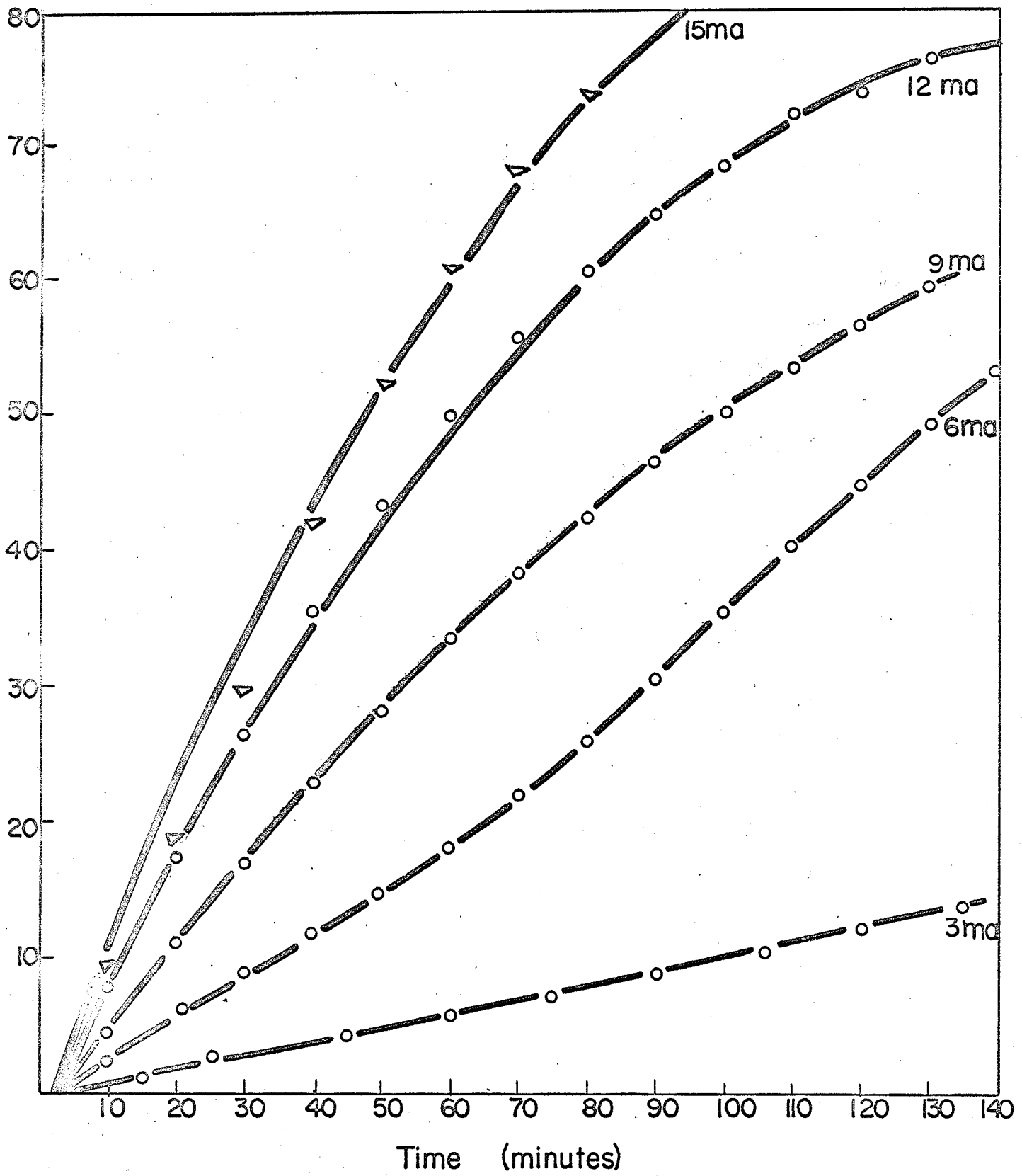


FIGURE 55. Increase in applied potential during course of polymerization.

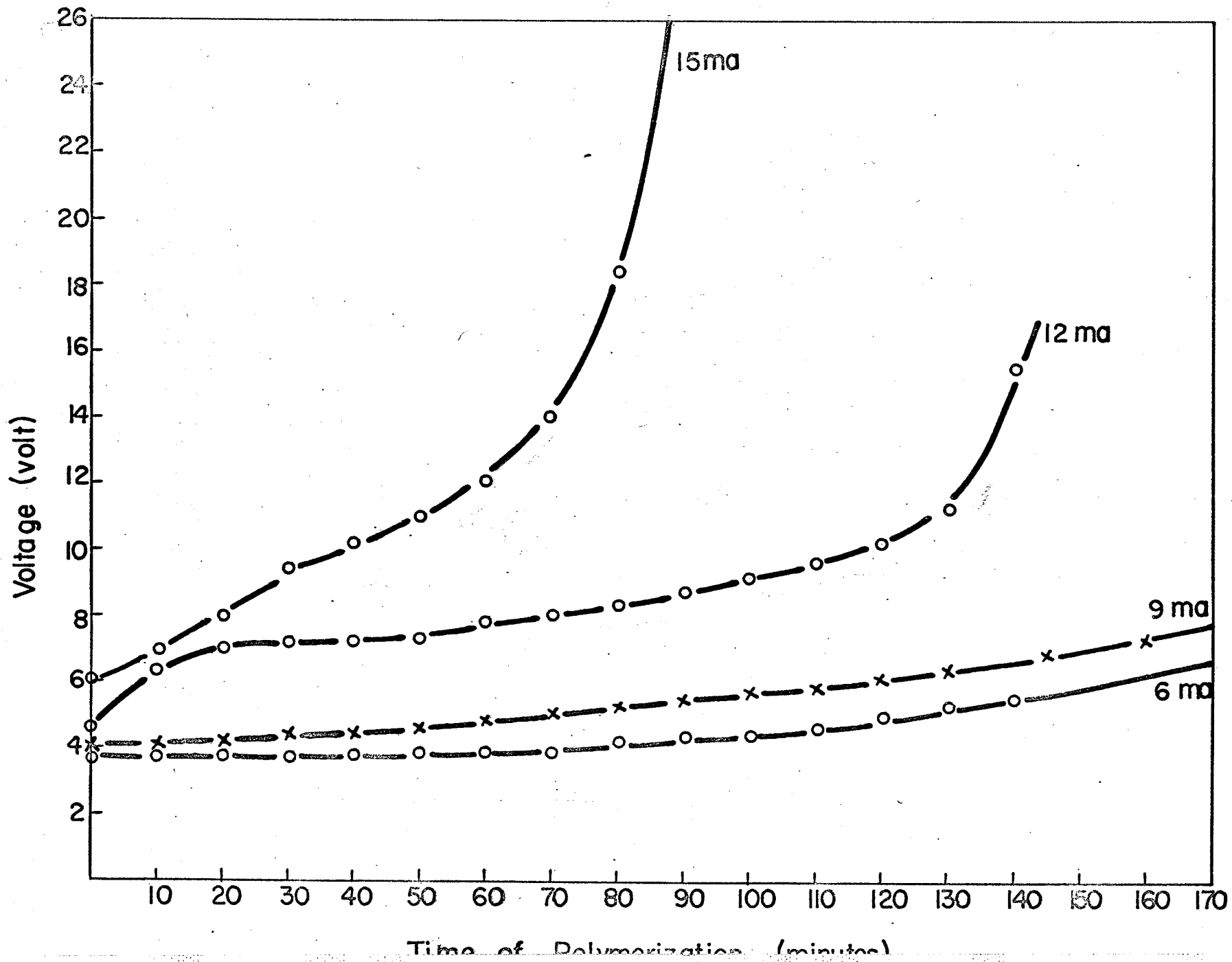
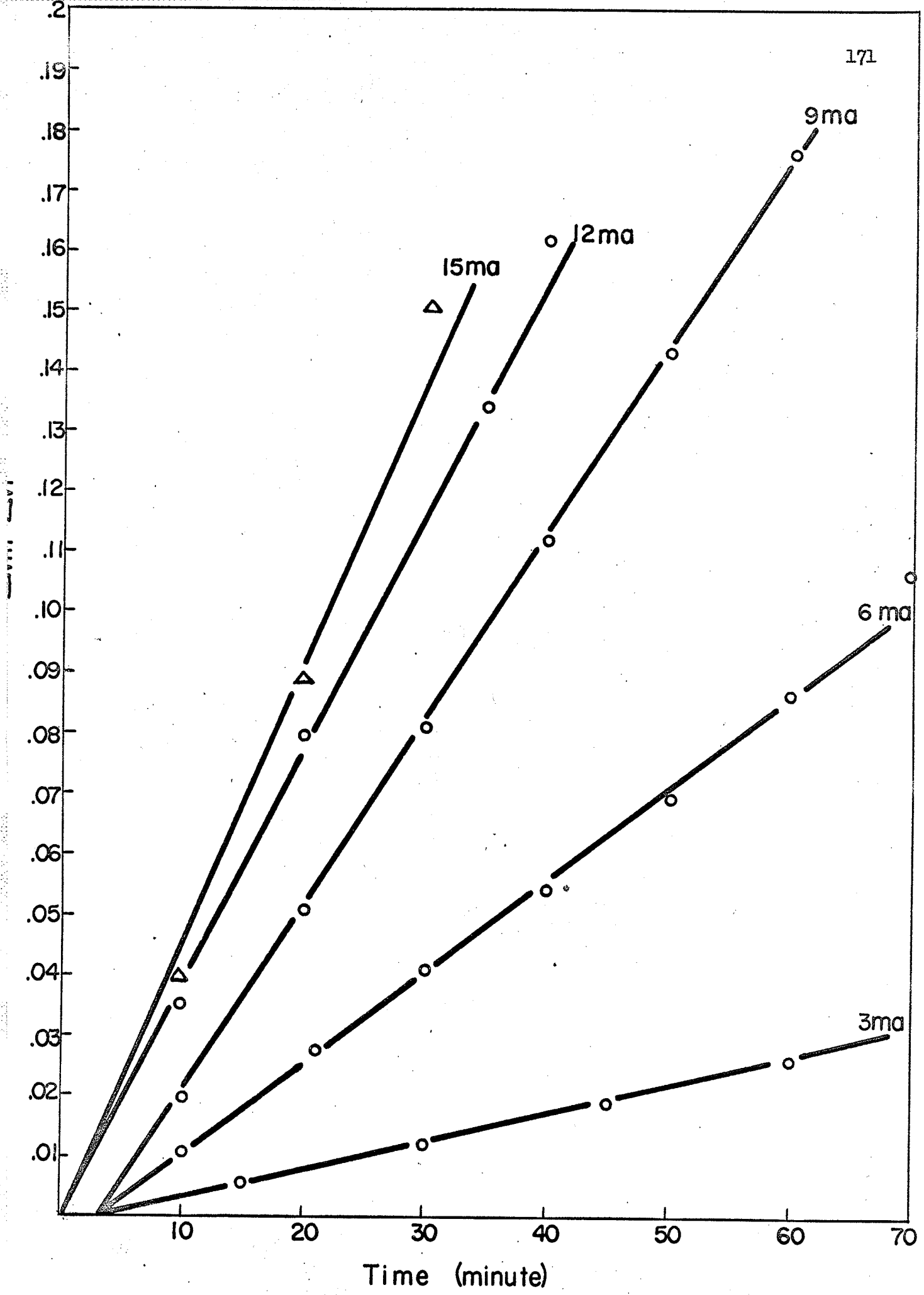


FIGURE 56. First order plots of the propagation reaction at several inscribed currents.

$\Delta V_m$  = maximum volume charge

$\Delta V_t$  = volume charge at time t.





monomer concentrations but a constant current of 5 ma are shown in Figure 57. The effect of stirring on polymerization rate is evident from Figure 58.

TABLE 23. Influence of impressed current on initial rate of polymerization.

Current ma	Rate mole litre <sup>-1</sup> min <sup>-1</sup> x 10 <sup>3</sup>
3	1.51
6	5.14
9	10.4
12	13.0
15	15.5

The microstructure of polymers formed in 2.04 M monomer solution in THF was determined by the infra-red and nuclear magnetic resonance spectroscopy and the data are assembled in Table 24. For the sake of comparison the microstructure of polyisoprene formed in THF with the sodium metal (101,102) are also included in the table. The molecular weights were determined by osmometry (Table 24).

FIGURE 57. Polymer formation at inscribed initial monomer concentrations with a current of 5 ma.

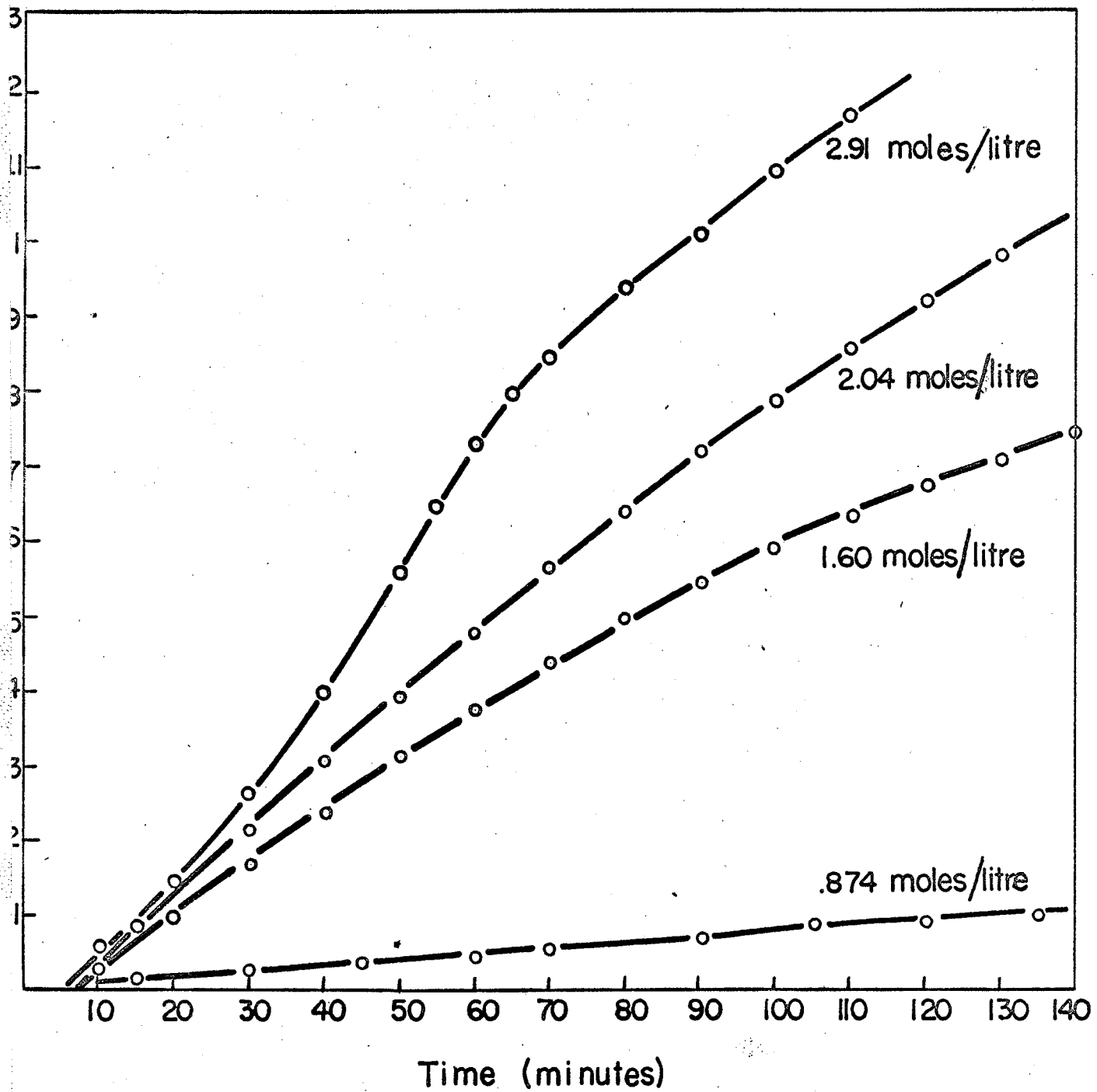


FIGURE 58. Effect of stirring on polymerization rate in undivided cell.

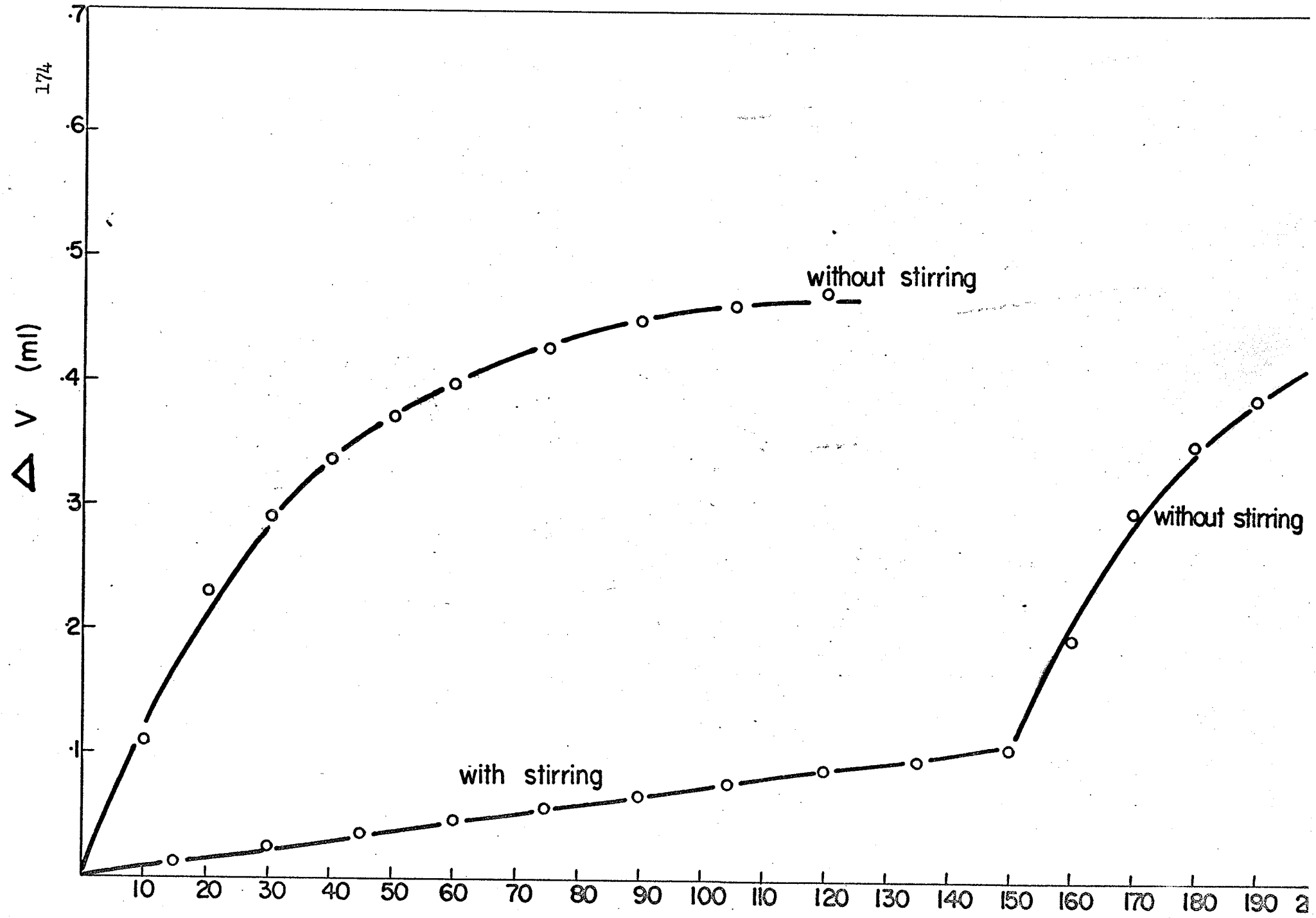
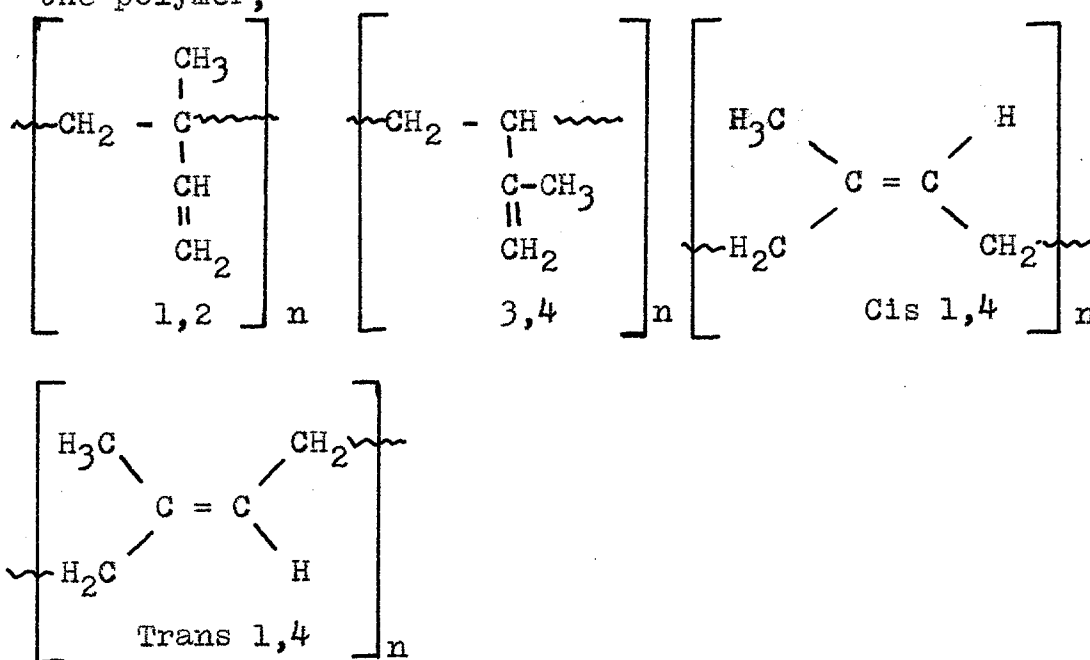


TABLE 24. Polyisoprene microstructure and molecular weight.

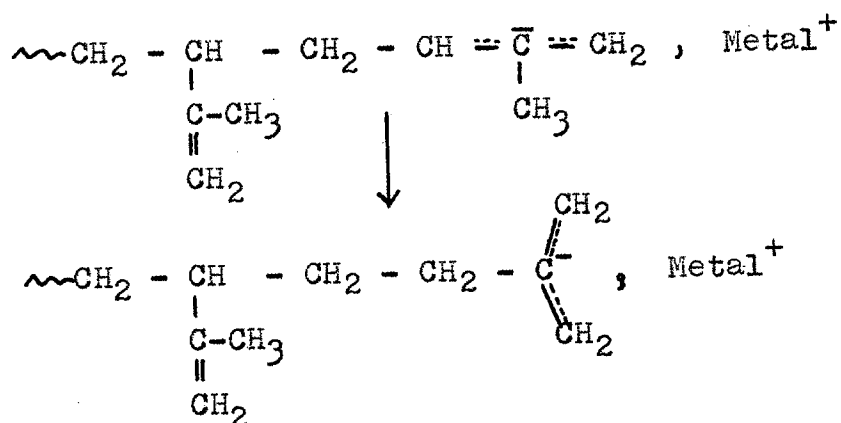
Current	% 3,4	% 1,2	% 1,4 Cis	% 1,4 Trans	$M_n$	Ref.
5 ma	73	15	10	2	40,000	Present work
10 ma	60	35	5 total		23,000	"
Metallic Na	82	18	-	-	-	101
"	51	15		34	-	102

DISCUSSION

Owing to the presence of two double bonds in isoprene, the following structural segments are possible in the polymer,

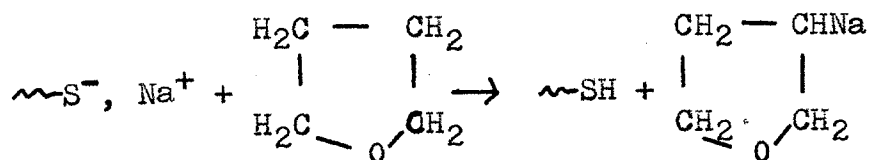


which structural unit will predominate in the propagation reaction depends on experimental conditions. Bywater *et al.*, (32) found that the initial ultraviolet absorption peaks of living polyisoprene anions in THF decayed and shifted rapidly with the formation of new peaks at longer wave lengths. Isomerization of the growing anions were assumed to be responsible for this phenomenon. In the case of 3:4 structure formation the most probable isomerization mechanism was stated as follows:



In the present system, however, it is evident from Figures 46 and 48 that the spectra are broad and no new absorption peaks of polyisoprene anions appear; but the absorbance gradually decays with time (Fig.47, Table 21). The yellow solution eventually becomes faint pink. The decay in absorbance might be attributed to interaction between the THF and living anions (43,59,103) as the following termination reaction may occur.





However, the salt is not responsible for such a decay because the previous work has proved that  $Na(C_6H_5)_4^B$  and  $NaAl(C_2H_5)_4$  do not deactivate the living anions. Figure 49 shows that the increase in the absorbance at 320  $\mu$  is not linear with time and this is caused again by the destruction of the living anions and decrease in monomer concentration during the electrolysis. Such a termination reaction would vitiate the kinetic results obtained in THF (104). However, in the present study the living chain end concentration can be kept constant until the monomer is completely consumed by polymerization (Fig.50). As a demonstration kinetics were done at four different low living anion concentrations kept constant by the passage of a trickle current through the reaction mixture. When the result (Fig.51) is compared with that (Fig.53) obtained without keeping living anion concentration constant, it may be seen that in the former case, the polymerization rate is faster. The results for each of the constant absorbance experiments show a logarithmic dependence on monomer concentration (Fig.52). The method of study at the constant concentration of growing polymorphic

anions offers an interesting new technique for studies of anionic polymerization where the deactivation of active chain ends with the monomer or solvent hinders the kinetic analysis.

Although the anode products kill the polyisoprenyl anions, nevertheless, it was found that high yield polymers formed in the undivided cell. The dilatometric studies clearly prove that the rate of polymer formation increases with increase in impressed currents (Fig.54) and polymerization is in first order in monomer (Fig.56). Figure 57 shows that the polymerization rate at a constant current also increases with increase in monomer concentration. At high monomer concentration the solution becomes very viscous, which causes an increase in the rate (top curve Fig.57). Presumably, at this point the polymerization becomes diffusion controlled giving rise to a slow termination reaction. The polymerization rate is also enhanced when the solution is not stirred (Fig.58). This is because in the absence of stirring the anode and cathode products are not quickly mixed resulting in a decreased termination rate.

The polymer formation in the undivided cell offers evidence that the living anions react faster with monomer molecules than with anode products. Under such conditions

polymer chains grow to their final length and eventually terminate. Because new chains are continually being produced, polymerization does not cease until the monomer is completely depleted. The initiation occurs essentially via electron transfer either from the cathode or sodium metal. The propagating end of the chain may be the ion-pair,  $\sim\text{S}^-$ ,  $\text{Na}^+$  and/or free anion,  $\sim\text{S}^-$ . However, the existence of free propagating anions is less likely because of the presence of the highly ionisable salt which depressed the ion-pair dissociation by the mass law (43).

The effect of impressed currents on polymer structure is evident from Table 24. Although the data are limited, nevertheless, they clearly demonstrate that molecular weights and microstructure may also be controlled by the impressed currents.

### SUMMARY

1. The absorption spectrum of polyisoprene anions in the THF solution was measured. The characteristic yellow color due to the living anions gradually disappeared and this was attributed to the deactivation of living anions with THF.
2. An electronic device was built to keep the living anion concentration constant with polymerization time.
3. Kinetic studies were performed at several constant living anion concentrations. The result obtained shows a first order relation with monomer concentration.
4. The kinetics were also performed dilatometrically and the effects of monomer concentration, impressed current and stirring on the polymerization rates were studied.
5. The molecular weights and microstructure were found to be dependent on current density.

## CONCLUSION

One of the most important features of the electrolytic polymerization is the control over the rates of formation and molecular weights of polymers. The polymerization of MMA has clearly demonstrated that the reactions can be started and stopped at will or increased or decreased in rate by the passage of electric current.

In thermal polymerization one may control the polymerization rate as well as the molecular weights of polymers by controlling the reaction temperatures. However, one does not have the same degree of control over the temperature as over the passage of electric current. The electrochemical polymerization bears a close similarity to photochemical polymerization where external energy source is light.

Furthermore, the electrolytic technique employed for the production of living polymers has several distinct advantages over conventional techniques. The living polymer formation by electrochemical means may be less critically related to the stringent standards of purity of the reactants as a small amount of impurity, present in the solution is purged by passing the electric current. Any desired living anion concentration may be obtained and the concentration is easily determined by the number of electrons transferred at the electrode. The living anion formation of alpha-methylstyrene showed a stoichiometric relationship between the living anion population and charge

CHAPTER V

CONCLUSION

transferred. Moreover, it has been found that the living end concentration can be reduced stoichiometrically by the reversal of electrode polarity. Such processes of activation and deactivation of living anions provide a simple and important tool for the synthesis of tailored polymers. For example, it may be possible to program a desired concentration of living ends by passing a predetermined current for a given time. At the depletion of 50 percent monomer, the current can be reversed to reduce the living end concentration to one tenth of the original value. The remaining 10 percent of the living ends can react with the residual 50 percent of the monomer to produce a polymer of molecular weight ten times of that obtained in the first 50 percent of reaction. This method may be extended to produce polymers of any arbitrary molecular weight distribution. In fact, such a polymer formation has been carried out in this laboratory (105). However, the method may not be suitable for a system in which rates of initiation and propagation are equal.

In many cases, a solvent or a reactive group on the monomer such as carbonyl group on methylmethacrylate deactivates the active growing ends resulting in decreased living anion concentration with time. Such a deactivation process interferes with kinetic studies and polymer synthesis. The electrochemical method offers a suitable way of

maintaining a constant population of the reactive species as has been described in the case of isoprene. It is believed that this process may yield molecular weights with a smaller range of distribution than those formed by direct polymerization. The living anion production in the absence of alkali metals would open the possibility to investigate the effect of a counter ion, other than alkali cations, on the growing polymeric anions.

Since  $\text{Na}(\text{C}_6\text{H}_5)_4\text{B}$  and  $\text{NaAl}(\text{C}_2\text{H}_5)_3$  in THF furnish conducting media at below  $-60^\circ\text{C}$  the present work could be extended to low temperatures. Effects of the current density and electrode material on polyisoprene microstructure may be also investigated. Furthermore, it is feasible to form a stereoregular polymer by electrolytic technique. The initiators or reactants formed by the electrolysis may be adsorbed on the electrode in a regular manner and may result in stereoregularity in the polymer. Under such conditions different electrode materials may have a remarkable influence on the stereospecificity of the polymer.

A clear insight into the reaction mechanisms may be obtained from polarographic and constant potential electrolysis studies. Such studies are underway in this laboratory.



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