ELECTROINITIATED COPOLYMERIZATIONS

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ABSTRACT

Preliminary cyclic voltammetry of the polymerizing systems studied was useful in providing the overall characteristics of these systems and the information necessary for the application of controlled potential electrolysis. However, the use of these techniques to study polymerizations initiated by radical anions met with only limited success.

The styrene - acrylonitrile - zinc bromide system was chosen for a detailed study of a donor acceptor complex polymerization initiated by electrolysis. At the cathode, this system was found to yield high molecular weight alternating copolymers under a wide range of conditions. Large after effects were observed and were shown to be due to a Zn^{O} - Zn^{II} interaction on the electrodeposited zinc metal surface. The 'zinc effect' was found to be operative only in systems which contained zinc metal, a zinc salt and a monomer capable of complexing with the salt. Other metals with a d^{10} electronic structure were also active. A possible initiating mechanism is discussed. This mechanism satisfactorily explains the molecular weight dependence on conversion observed during current reversal studies.

At the anode, a mixture of high molecular weight alternating copolymer and low molecular weight polystyrene is formed. Using tetrabutylammonium perchlorate as supporting electrolyte, only low molecular weight alternating copolymer is produced, under a wide range of conditions. Electrolytic control of the reaction has been shown, and the overall activation energy was found to be 5.3 kcal/mole. Under continuous electrolysis conditions, the low molecular weights are found to be independent of conversion and rate of initiation. However, monitoring the molecular weight as a function of after effect time shows a steady increase. Possible initiation and termination mechanisms are postulated to account for the observations.

TO MY PARENTS

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"Now listen to the rule of the last inch. The realm of the last inch. The job is almost finished, the goal almost attained, everything possible seems to have been achieved, every difficulty overcome - and yet the quality is just not there. The work needs more finish, perhaps further research. In that moment of weariness and self-satisfaction, the temptation is greatest to give up, not to strive for the peak of quality. That's the realm of the last inch - here the work is very,very complex but it's also particularly valuable because it's done with the most perfect means. The rule of the last inch is simply this - not to leave undone. And not to put it off - because otherwise your mind loses touch with that realm. And not to mind how much time you spend on it, because the aim is not to finish the job quickly but to reach perfection."

Alexander Solzhenitsyn
"The First Circle"

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I.1.1. IMPORTANCE OF COPOLYMERIZATION.

A chain polymerization process in which two monomers are simultaneously polymerized is termed a copolymerization and the product is a copolymer. Copolymerization is important from several considerations. Much of our knowledge of the reactivities of monomers, radicals, carbonium ions and carbanions in chain polymerization arise from copolymerization studies. Copolymerization is also very important from the technological viewpoint. It greatly increases the ability of the polymer chemist to tailor-make a product with specifically desired properties by varying the nature and relative amounts of the two monomer units in the copolymer. A good example of the versatility of the copolymerization process is the case of polystyrene. Polystyrene is a brittle plastic with poor impact strength and solvent resistance, limiting its practical use. Copolymerization of styrene with acrylonitrile leads to increase in impact strength and solvent resistance while copolymerization with butadiene leads to elastomeric properties.

I.1.2. TYPES OF COPOLYMERS.

There are four types of copolymers known; random, alternating, block and graft, depending on the structural distribution of the two monomers along the chain. In a random copolymer, the units have a relatively random distribution along the chain:-

∼∼∼∼AABBABBBAABBAABAAABABB∼∼∼∼

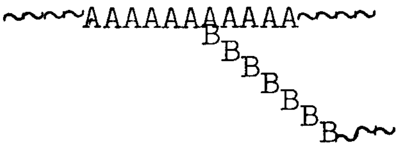
The alternating copolymer contains the two monomer units in equimolar amounts in a regular alternating sequence

∼∼∼∼ABABABABABABABAB∼∼∼∼

The block and graft copolymers differ from random and alternating in that there are long sequences of each monomer in the chain. A block copolymer has a linear structure, with one or more long sequences of each monomer unit,

∼∼∼∼AAAAAAAAAABBBBBBBB∼∼∼∼

while a graft copolymer has a branched structure with a backbone of one monomer to which are attached one or more side chains of another monomer



I.1.3. COPOLYMERIZATION EQUATION.

In most cases the composition of a copolymer is found to be different from the original comonomer feed due to the different tendencies various monomers have in undergoing copolymerization. The relative copolymerization tendencies of monomers bear little resemblance to their rates of homopolymerization (1). Some monomers, such as maleic anhydride, stilbene and fumaric esters, are easily copolymerized whereas they have little or no tendency to homopolymerize.

The copolymerization equation was derived by Mayo and Lewis (2) and Alfrey and Goldfinger (3), assuming that the rate of addition of monomer to a growing chain depends only on the end group on the chain. If monomers M_1 and M_2 yield $M_1{*}$ and $M_2{*}$, then there are four possible propagation steps:

$$\sim M_1{*} \quad + \quad M_1 \quad \xrightarrow{k_{11}} \quad \sim M_1{*}$$
$$\sim M_1{*} \quad + \quad M_2 \quad \xrightarrow{k_{12}} \quad \sim M_2{*}$$
$$\sim M_2{*} \quad + \quad M_1 \quad \xrightarrow{k_{21}} \quad \sim M_1{*}$$
$$\sim M_2{*} \quad + \quad M_2 \quad \xrightarrow{k_{22}} \quad \sim M_2{*}$$

The quantity $d[M_1]/d[M_2]$, the copolymer composition, can then be related to $[M_1]/[M_2]$, the monomer feed composition by the copolymerization equation:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{(r_1[M_1] + [M_2])}{(r_2[M_2] + [M_1])}$$

where $r_1 = \frac{k_{11}}{k_{12}}$ and $r_2 = \frac{k_{22}}{k_{21}}$

The monomer reactivity ratios, r_1 and r_2 are important copolymerization parameters representing the preference of the propagating species to react with its own monomer or the other monomer.

The copolymerization equation has been experimentally verified in many comonomer systems. It is equally applicable to radical, cationic and anionic chain copolymerizations, although the r_1 and r_2 values for any particular comonomer pair can be quite different depending on the mode of initiation.

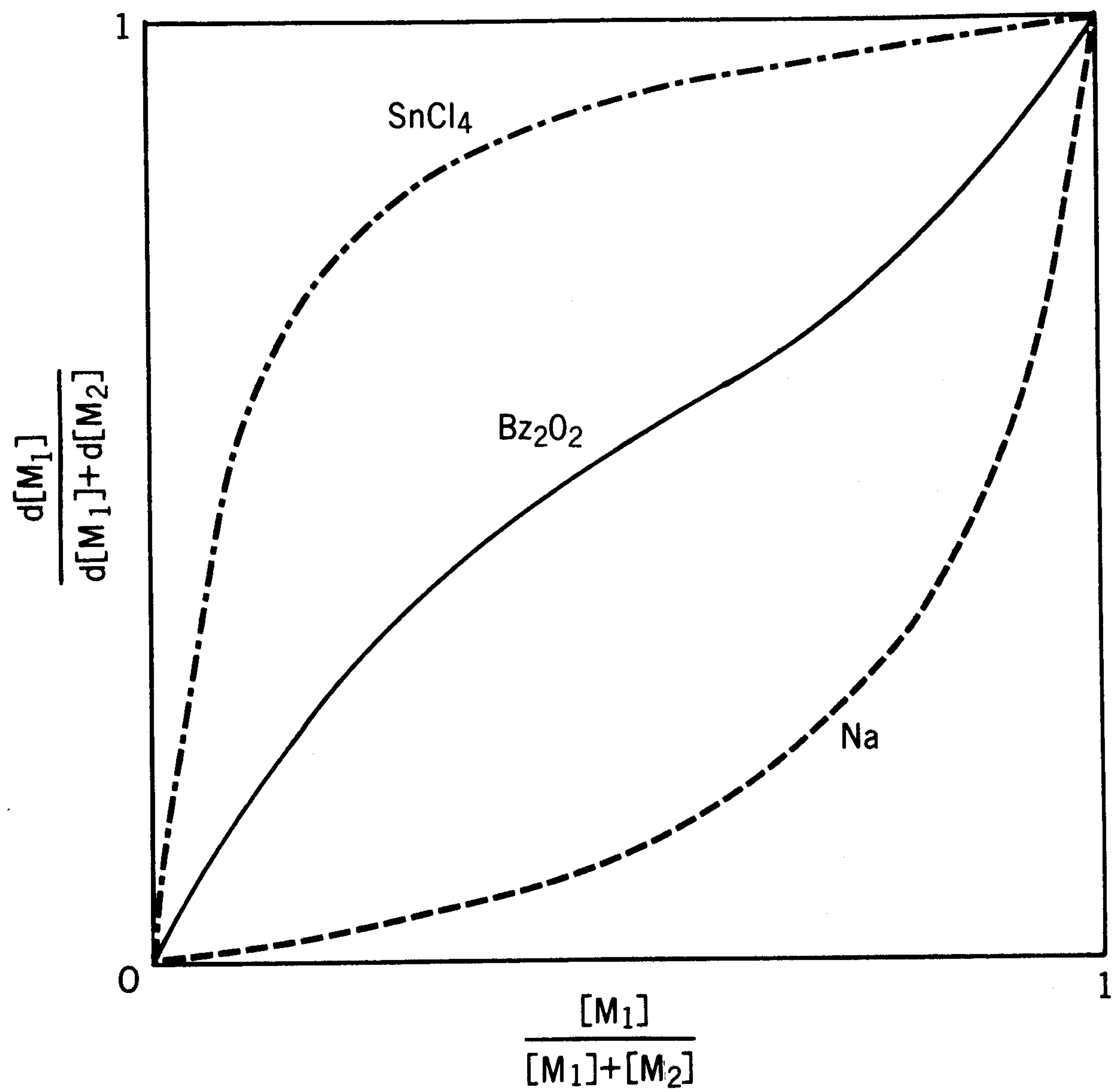
Thus, the r_1 and r_2 values for styrene (M_1) and methyl methacrylate (M_2) are 0.52 and 0.46 in radical copolymerization, 10.5 and 0.1 in cationic and 0.12 and 6.4 in anionic copolymerization (4). Figure 1 shows how the differences in r_1 and r_2 values, which depend on the mode of initiation, affect the copolymer composition.

I.1.4. TYPES OF COPOLYMERIZATION BEHAVIOUR.

Copolymerization can be classified into two main types based on whether the product of the two monomer ratios r_1r_2 is unity or less than unity. When $r_1r_2 = 1$ the copolymerization is termed ideal and this means that the two types of propagating species M_1^* and M_2^* have the same preference for adding one or the other of the two monomers. Most ionic copolymerizations are characterized by this type of behaviour. In the general case, i.e. $r_1>1$ and $r_2<1$ or $r_1<1$ and $r_2>1$, one of the monomers is more reactive than the other towards the propagating species and the copolymer will therefore contain a larger proportion of the more reactive monomer.

An important practical consequence of ideal copolymerizations is that it becomes progressively more difficult to produce copolymers containing appreciable amounts of both monomers as the difference in reactivities of the two monomers increases. This can be seen in Figure 1. Thus copolymerization of an 80:20 methyl methacrylate: styrene feed ratio by $SnCl_4$ would yield a copolymer containing only 20% of methylmethacrylate.

Figure 1. INCREMENTAL COPOLYMER COMPOSITION AS A FUNCTION OF MONOMER FEED COMPOSITION FOR THE STYRENE (M_1)-METHYL METHACRYLATE (M_2) SYSTEM, POLYMERIZED BY CATIONIC ($SnCl_4$), FREE RADICAL (Bz_2O_2) AND ANIONIC (Na) MECHANISMS (5).


1
SnCl4
Bz2O2
Na
0
1
d[M1] / d[M1]+d[M2]
[M1] / [M1]+[M2]

When $r_1 = r_2 = 0$, and $k_{12}, k_{21} \neq 0$, the copolymerization is termed alternating. The two monomers will enter into the copolymer in equimolar amounts in a non-random, alternating arrangement. The two types of propagating species preferentially add the other monomer. Many radical copolymerizations show an alternating tendency.

Most comonomer systems lie between the two extremes of ideal and alternating copolymerization. As the r_1r_2 product decreases from unity towards zero, there is an increase in alternating tendency. The range of behaviour can be seen in Figure 2. Of greater practical significance is the fact that a larger range of feed compositions will yield copolymers containing sizable amounts of both monomers. However when r_1r_2 is very small or zero, the alternating tendency is too great and the range of copolymer compositions which can be obtained is again limited.

I.1.5. Q - e SCHEME.

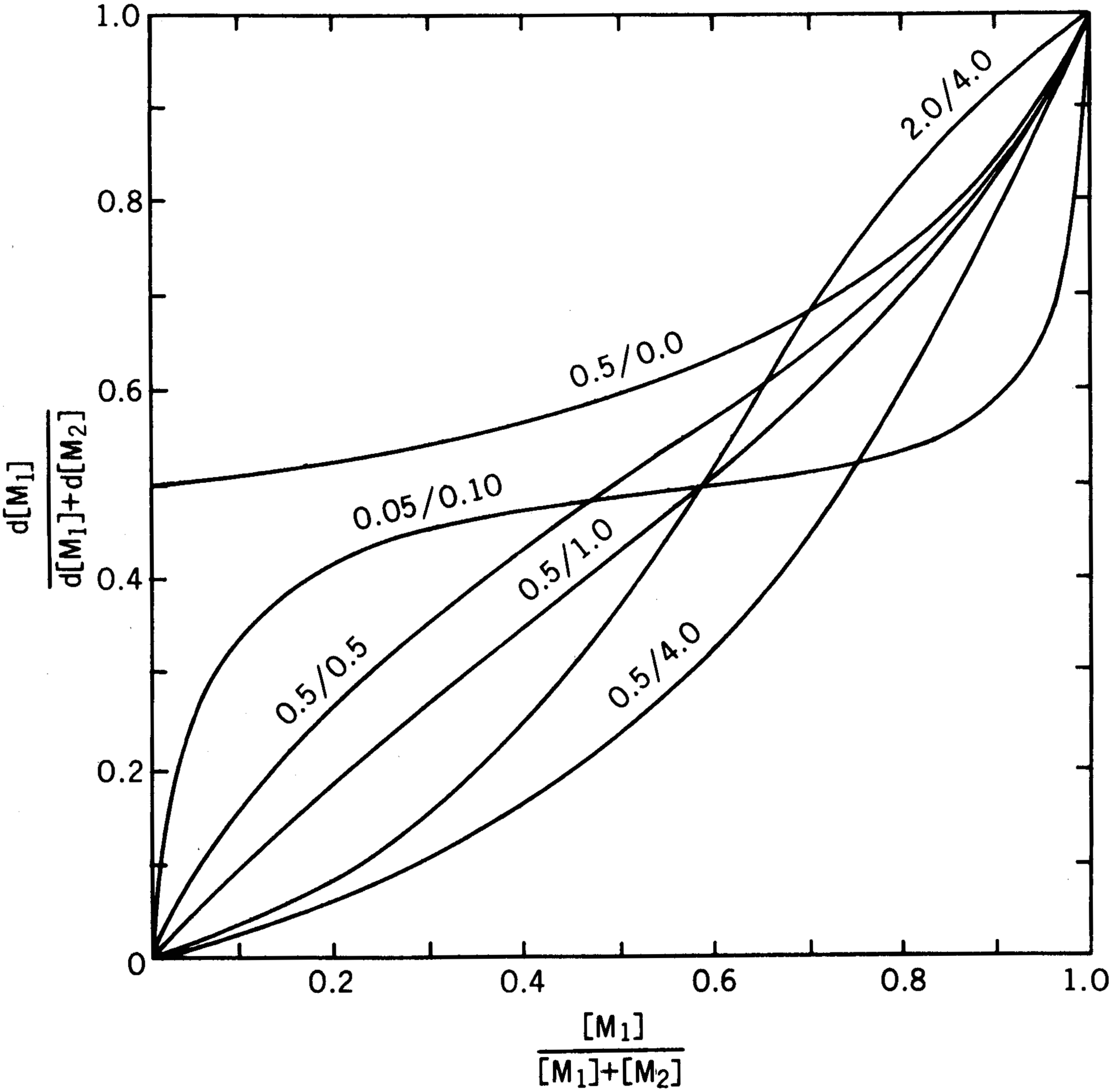
It is generally accepted that a general order of reactivity exists among monomers in copolymerization. Alfrey and Price (7) proposed a method of predicting monomer reactivity in copolymerization on the basis of polar and resonance factors of the monomer.

In their Q-e scheme, Alfrey and Price proposed that the rate constant for a radical-monomer reaction, $M_1{}^*$ with M_2 be written

$$k_{12} = P_1Q_2 \exp(-e_1e_2)$$

where P_1 and Q_2 relate to the reactivities of the radical M_1 and the monomer M_2, respectively, and e_1 and e_2 are measures of the

Figure 2. INCREMENTAL COPOLYMER COMPOSITION AS A FUNCTION OF MONOMER FEED COMPOSITION FOR VARIOUS r_1/r_2 RATIOS (6).


1.0
0.8
0.6
0.4
0.2
0
0.2
0.4
0.6
0.8
1.0
$\frac{d[M_1]}{d[M_1]+d[M_2]}$
$\frac{[M_1]}{[M_1]+[M_2]}$
2.0/4.0
0.5/0.0
0.05/0.10
0.5/1.0
0.5/0.5
0.5/4.0

polarity of radical M_1 and monomer M_2. The P and Q terms primarily define resonance effects in the radical and monomer. By assuming that the same e value applies to both a monomer and its radical, it is possible to write expressions for k_{11}, k_{22} and k_{21} analogous to k_{12} above, and obtain the monomer reactivity ratios in the forms

$$r_1 = \frac{Q_1}{Q_2} \exp(-e_1(e_1 - e_2))$$

$$r_2 = \frac{Q_2}{Q_1} \exp(-e_2(e_2 - e_1))$$

which correlate monomer-radical reactivity with the parameters Q_1, Q_2, e_1 and e_2.

The Q-e scheme has many inherent deficiencies and at the best of times is semi-quantitative. Its main use is its ability to give a general idea of the behaviour to be expected from a comonomer pair which has not been studied.

I.2. ALTERNATING COPOLYMERIZATION.

It has been noted that as the r_1r_2 product for two monomers tends towards zero, there is an increasing tendency towards alternation. One can list monomers in order of their r_1r_2 values with other monomers in such a manner that the further apart two monomers are, the greater is their alternating tendency. This can be seen in Table I. The values in brackets after each monomer is the e value of that monomer. The tendency to alternate is seen to increase as the difference in polarity between two monomers increases. This polar effect thus gives rise to enhanced reactivities in certain monomer pairs and can be illustrated quite dramatically by the ease of copolymerization

Table I. VALUES OF r_1r_2 IN RADICAL COPOLYMERIZATION (8).

	Isobutyl vinyl ether (-1.77)	Butadiene (−1.05)	Styrene(−0.80)	Vinyl acetate(−0.22)	Vinyl chloride(0.20)	Methyl methacrylate(0.40)	Vinylidene chloride(0.36)	Methyl vinyl ketone(0.68)	Acrylonitrile(1.20)	Diethyl fumarate(1.25)	Maleic anhydride (2.25)
Isobutyl vinyl ether (-1.77)											
Butadiene (−1.05)											
Styrene(−0.80)		0.98									
Vinyl acetate(−0.22)			0.55								
Vinyl chloride(0.20)		0.31	0.34	0.39							
Methyl methacrylate(0.40)		0.19	0.24	0.30	1.0						
Vinylidene chloride(0.36)		⟨0.1	0.16	0.6	0.96	0.61					
Methyl vinyl ketone(0.68)			0.10	0.35	0.83		0.99				
Acrylonitrile(1.20)	~ 0	0.0006	0.016	0.21	0.11	0.18	0.34	1.1			
Diethyl fumarate(1.25)	~ 0		0.021	0.0049	0.056		0.56				
Maleic anhydride (2.25)	~ 0		0.006	0.00017	0.0024	0.11					

of monomers which show little or no tendency to homopolymerize. Thus maleic anhydride and diethyl fumarate do not homopolymerize but will readily form alternating copolymers with electron donor monomers such as styrene and isobutyl vinyl ether (9).

The enhancement of reactivity in radical reactions by polar effects has been explained in two ways. Bartlett and Nozaki postulated the formation of a molecular donor acceptor complex to explain the alternating tendency observed in allyl acetate - maleic anhydride copolymerizations (10). However, Walling and his coworkers (11,12) preferred to view the interaction as a transition-state phenomenon. They postulated that the electron donating or accepting properties of the monomer were important during interactions of the growing polymer radical. The selectivity leading to alternation was then based upon reaction of the polymer radical with the monomer which would give the most stable transition state.

Recently there has been a great upsurge of interest both from the practical (13 - 16) and academic viewpoints (17 - 37) by a large number of workers in systems which yield alternating copolymers. Although much has been done, the detailed mechanism of these reactions is the subject of some controversy (45). Many workers believe that the copolymerization involves donor acceptor complexes. The argument centres around whether the donor acceptor complex can act as a unit and essentially homopolymerize (Bartlett and Nozaki) or whether donor acceptor complex formation is only important at the chain end (Walling et al.). The leading proponent of the copolymerization of donor acceptor complex units is Gaylord (17) who has to date published over forty papers in this field. While most workers are in agreement with Gaylord (21,28,30,33,37,39) a few, but of increasing number (18,25-27,40,43,46) prefer the chain end theory favoured by Zubov et al. (38).

I.3. DONOR-ACCEPTOR COMPLEXES IN ALTERNATING COPOLYMERIZATION.

A number of excellent and up-to-date reviews have been written (17,26,38,41-44) by workers active in this field and it is therefore unnecessary to provide a comprehensive review here. In this introduction, the various features and characteristics of donor acceptor complex polymerizations will be briefly outlined.

I.3.1. PREPARATION OF ALTERNATING COPOLYMERS.

Monomers having large e value separations (see Table I) are known to form donor acceptor complexes spontaneously and yield alternating copolymers on polymerization. Thus Tsuchida and Tomono (28) observed an alternating copolymerization between styrene ($e = -0.8$) and maleic anhydride ($e = +2.25$). In this system, donor-acceptor complexes were detected by U.V. and N.M.R. spectroscopy. The existence of donor acceptor complexes in polymerizing systems which yield alternating copolymers has also been shown for many other monomers (36,37,47-51). It has been noted that spontaneous formation of donor acceptor complexes occurs if the e value separation is about 3.0 (52). This value can be correlated with the equilibrium constant K for the formation of donor acceptor complexes (30). Thus the larger the K value the greater the tendency for spontaneous alternating copolymerization. In most co-monomer systems, e is less than three, and this leads to non-equimolar compositions and an increasing random configuration in the copolymer.

The number of possible monomer combinations yielding alternating copolymers has been extended remarkably by the discovery that addition of Lewis acids to the comonomer feed results in a system which yields alternating copolymers. Zinc chloride (18,21,24,32,34,53-67) and aluminum sesquichlorides (16,19,31,53,57,68-81) have been the most frequently studied Lewis acids although others such as zinc bromide (82-87) and various alkyl aluminum chlorides (19,20,35,48,79,81,88-90) have also been found effective.

These Lewis acids complex with the polar group of the acceptor monomer causing the delocalisation of π electrons in the double bond, resulting in increased electrophilic character (64,65,91-93). The overall result is an increase in electron acceptor properties of the monomer, and this is reflected by an increase in the e value of the complexed monomer (18,43,62,65, 94,115,116). The resultant increase in e value separation of the two monomers gives rise to an increase in alternating tendency.

The complex between the acceptor monomer and Lewis acid is usually crystalline and easily isolated. Thus, for example, complexes between acrylonitrile and various transition and non-transition metal salts have been prepared and characterized by IR spectroscopy (92,199). It is characteristically observed that the CN stretching frequency of acrylonitrile is increased on complexation due to the large increase in the force constant upon coordination (92).

Although the complexes between Lewis acids and acceptor monomer are easily isolated and detected, the situation for donor acceptor complexes between two monomers is much different. In favourable cases the charge transfer complex is highly coloured, crystalline and isolatable. However, in most situations, spectroscopic techniques have to be used to detect the presence of a donor acceptor complex between the monomers, and the strength of the interaction (equilibrium constant).

Thus, for example, in the case of furan (donor monomer) and maleic anhydride (acceptor monomer), the spontaneous formation of a donor acceptor complex was shown by U.V. and N.M.R. spectroscopy (37). Thus, when a chloroform solution of maleic anhydride was added to a solution of furan, there appeared in the near-ultraviolet spectrum of the mixture a new and large band at 291mμ whose appearance and position was attributed to the formation of a donor acceptor complex (37). The interpretation of these spectra permitted the determination of the stoichiometric composition using the continuous variation method of Vosberg and Cooper (200).

It was found that the maximum adsorption of the new band appeared at a mole fraction of 0.5 in maleic anhydride, signifying that the donor acceptor complex between maleic anhydride and furan has a stoichiometry of 1:1.

The equilibrium constant of the donor acceptor complex was determined independently by NMR and UV spectroscopy. In the NMR method, the shift of the acceptor protons (singlet of maleic anhydride) was observed while keeping the acceptor concentration constant and varying the donor concentration (with donor in large excess). Analysis of the spectra by the method of Hanna and Ashbaugh (201) yielded the equilibrium constant of complex formation.

In the UV spectroscopy technique, the donor concentration was similarly increased while the acceptor concentration was held constant. The absorbance at 291mμ was recorded and the results analysed using the well known Benesi-Hildebrand method (202). Comparison of the K_{eq} values obtained by these two techniques showed excellent agreement (37).

I.3.2. CHARACTERISTICS OF 1:1 ALTERNATING COPOLYMERIZATIONS.

The addition of a Lewis acid to a comonomer system results in dramatic changes in the characteristics of the copolymerization. These can be listed as follows:

(a) Composition of the Copolymer

The copolymer product tends to have an equimolar alternating structure at all monomer feed ratios (16,17,20,31,34,37,79,95).

The effect of the presence of a complexing agent on the copolymer composition is best illustrated by Figure 3 for the styrene - methylmethacrylate - ethylaluminum sesquichloride system (79). It can be seen that these copolymerizations in the presence of Lewis acids exhibit a high degree of selectivity. This selectivity has been explained as being due to the formation of a donor acceptor complex between the two monomers which then behaves as a single entity or 'new monomer' (17,95). This 'new monomer' then undergoes a homopolymerization which must result in a 1:1 alternating copolymer at all feed ratios:

$$A + Z \xrightleftharpoons{K_1} ZA$$

$$ZA + D \xrightleftharpoons{K_2} \underset{\text{'new monomer'}}{(ZAD)}$$

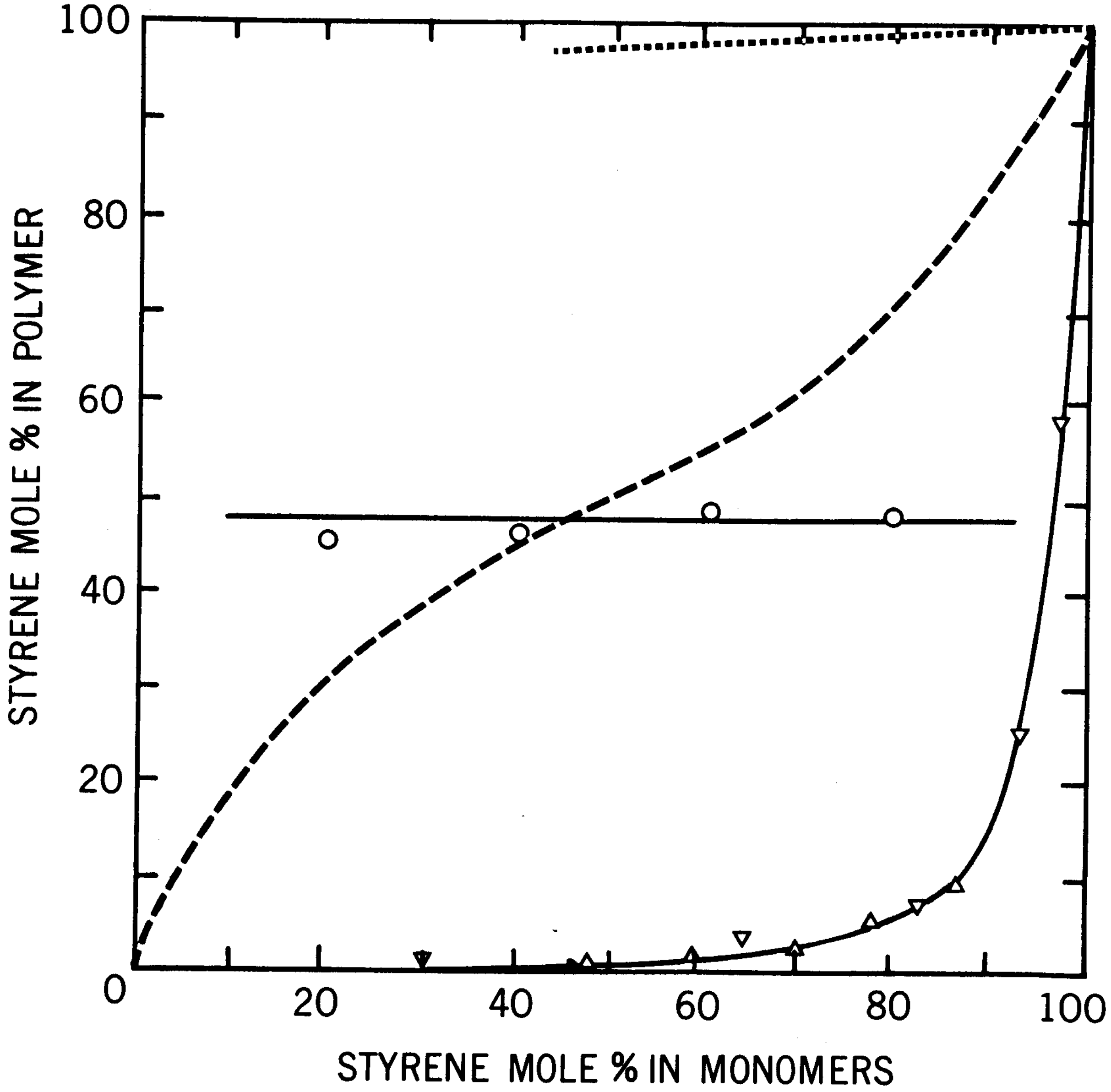
$$(ZAD) + n(ZAD) \xrightarrow{\text{polymerization}} \underset{\text{polymer}}{(ZAD)_{n+1}}$$

Where A and D are the acceptor and donor monomers respectively, and Z is the Lewis acid. It has been argued (43,95) that the propagating chain end is not a conventional radical or ionic species, since it does not add uncomplexed monomer, i.e., monomer in excess of the equimolar composition, although the monomer may be a normally reactive donor such as styrene or acceptor such as acrylonitrile.

The selectivity argument seems to hold for most systems, but Yamashita (48) has found that in the spontaneous alternating copolymerization of p - dioxene and maleic anhydride in the presence of acrylonitrile, acrylonitrile is incorporated

Figure 3. COPOLYMERIZATION OF METHYLMETHACRYLATE AND STYRENE.

(o) with ethylaluminum sesquichloride;
(--) radical;
(.....) cationic;
(Δ) anionic, Na catalyst; (∇) anionic, BuLi catalyst.


100
80
60
40
20
0
20
40
60
80
100
STYRENE MOLE % IN POLYMER
STYRENE MOLE % IN MONOMERS

(forming a terpolymer) despite the fact this monomer is inert to donor acceptor interaction with p - dioxene or maleic anhydride.

(b) Rates of Copolymerization and Molecular Weight of Copolymer

These systems are characterized by increased rates of polymerization as well as the formation of polymers with higher molecular weights than are formed in the absence of metal halides (17,95). Usually, the rate maximum occurs at 1:1 feed ratios corresponding to the maximum concentration of donor acceptor complex (48,49,51,60,76,96-99,105) and in many cases the molecular weights also (48,60,76,96,97,99).

Gaylord (68) has found, in the styrene-methylmethacrylate - ethylaluminum sesquichloride case, that the initial stage of the reaction proceeds very rapidly followed by a second, slower stage. During the initial rapid stage the molecular weight of the 1:1 alternating copolymer increases with conversion and then attains a maximum constant value in the second slower stage. The formation of a matrix or ordered array of complexes has been postulated to account for these observations (68,78). The rapid polymerization in the initial stage is considered to be the result of the formation of a matrix whose size is determined by the initial complex concentration (78,95). When the complex concentration decreases as a result of its conversion to copolymer, the rate of polymerization decreases. The diffusion of monomer molecules to the complexing agent bound to the copolymer chain results in the generation of new complexes on or in the immediate vicinity of the copolymer. The latter then acts as a template in the second stage of the polymerization, the molecular weight being constant and determined by the size of the template.

Gaylord's matrix theory has been subject to some criticism recently (45). Although the existence of matrices or ordered arrays is not an unknown phenomenon, Gaylord has been unable to produce any physical evidence for their existence in his systems (45). In the styrene - methylmethacrylate - ethylaluminum sesquichloride case mentioned above, formation of matrices was postulated to account for the initial rate increase and the steady increase in molecular weight to a constant value. In the styrene - acrylonitrile - ethylaluminum sesquichloride system also studied by Gaylord (76), the rate increases as before, but the molecular weight is found to decrease to a constant value. It would appear difficult to explain both sets of these experimental results by matrices.

(c) Chain Transfer

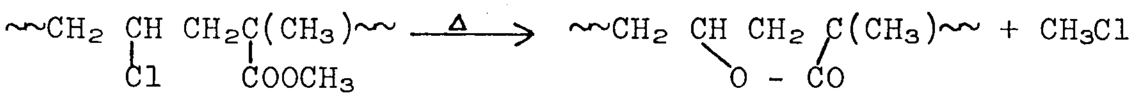
Chain transfer agents active in conventional polymerizations have little or no effect in donor acceptor copolymerizations (28, 43,95,100-102). It has been postulated that since normal chain transfer agents such as carbon tetrachloride have weak electron accepting or donating properties, they are therefore unable to complex with growing radicals (28). Thus it has been shown that addition of stronger donor or acceptor molecules can lead to chain transfer (28,49).

I.3.3. CHARACTERIZATION OF 1:1 ALTERNATING COPOLYMERS.

In general, IR spectra show no characteristics assignable to an alternating structure (42). Elemental analysis merely provides an indication of 1:1 alternating behaviour. That a copolymer is found to have an equimolar composition by elemental analysis is not proof of an alternating structure since a random copolymer can be prepared from a monomer feed of the appropriate composition. However, if the composition of a copolymer is found to be 1:1 regardless of the monomer feed composition, then the alternating effect is the only satisfactory explanation of the phenomenon.

NMR techniques have been used as a method for distinguishing between equimolar random and alternating structures (32,34,35, 60,62,63,79,80,103-108,126). The spectra of copolymers prepared in the presence of Lewis acids in most cases show definite differences from conventionally prepared copolymers of the same composition. Recent work by Schaefer (107) using high resolution pulsed carbon - 13 NMR indicates that this tool would have greater sensitivity to differences between alternating and random structures.

In favourable cases, the presence of substituents on the monomers allows chemical treatment yielding direct evidence of the monomer sequence. For example, vinyl chloride - methylmethacrylate copolymers prepared in the presence of ethyl aluminum dichloride have been shown to have an alternating structure by exploiting thermal cyclization (75,108):



Recently, equimolar alternating copolymers of styrene and methylmethacrylate have been cyclized using polyphosphoric acid (109). The extent of cyclization was found to be 40% compared with only 10% for equimolar copolymers prepared in the absence of complexing agent.

The recent use of thermal techniques (16,102,106) has indicated the possibilities of employing these methods to characterize alternating copolymers.

I.3.4. EVIDENCE FOR PARTICIPATION OF DONOR ACCEPTOR COMPLEXES IN ALTERNATING COPOLYMERIZATIONS.

Although spontaneous formation of donor acceptor complexes is known to occur in a small number of polymerizing systems which yield alternating copolymers (28,36,37,47-51), there is less evidence for their existence in systems which require Lewis acids to give an alternating effect. Ikegami and Hirai (63) reported U.V. evidence for a charge transfer complex in the styrene - acrylonitrile - zinc chloride system. N.M.R. and U.V. evidence shows the presence of a donor acceptor complex between complexed methylmethacrylate and butadiene (110). Similar evidence has been presented for the existence of donor acceptor complexes in the styrene - methylmethacrylate - $SnCl_4$ and styrene - methacrylonitrile - $SnCl_4$ systems (111,112). However, in some systems which yield 1:1 alternating copolymers, no evidence of donor acceptor complexes has been obtained (27, 43,113). Thus Uschold (27), using an extremely sensitive calorimetric technique capable of detecting molecular complexes with formation constants $\geq 10^{-3}$, was unable to detect any interaction between complexed acrylonitrile and 1-hexene. Similarly, Hirooka (43) was unable to detect any complex between styrene and complexed methyl acrylate using U.V. and cryoscopic techniques.

Most comonomer systems yielding alternating copolymers fall into this class of forming weak donor acceptor complexes. Since these complexes are therefore in extremely low concentrations, this would require them to have exceptionally high reactivity. It seems difficult to expect such high reactivity of a monomer complex whose bond is considered to be as weak as a contact charge transfer interaction (25,43). Hence it could be argued that the existence of molecular complexes in a reaction system does not prove that they are intermediates through which the reaction products are formed (25,37,114).

Many authors have cited the observed characteristic properties of Lewis acid catalysed and spontaneous alternating copolymerizations (Section I.3.2.) as being proof that donor acceptor molecular complexes are the polymerizing entity in these systems (21,28,30,33,39,95). However, some systems which yield 1:1 alternating copolymers fail to show those very characteristics. Thus a number of comonomer systems do not yield 1:1 alternating copolymers at all feed ratios (24,28,49, 55,63,70,71,75,76,94,117-120) and some systems do not give the expected rate and molecular weight maximum at 1:1 feed ratios (36,79,121).

The tendency towards formation of non-equimolar copolymers has been explained by Gaylord as being due to the existence of competing reactions or complex dissociation (55,70,71,120). Thus in the polymerization of styrene with acrylonitrile in the presence of zinc chloride, a non-equimolar, high acrylonitrile copolymer accompanies the 1:1 alternating copolymer when the polymerization is carried out at elevated temperatures or high conversions (55).

Gaylord suggests that two kinds of donor - acceptor complexes exist in the solution:

$$\mathrm{ZA} + \mathrm{A} \rightleftharpoons \mathrm{ZAA}$$

$$\mathrm{ZA} + \mathrm{D} \rightleftharpoons \mathrm{ZAD}$$

Copolymerization of ZAA with ZAD would thus result in the formation of a high A content copolymer. If ethylaluminum sesquichloride is used instead of zinc chloride in this system, the non-equimolar copolymer accompanying the alternating copolymer is found to be rich in styrene (70,120). In this case, dissociation of the terminal complex is postulated to occur, this process giving rise to a conventional copolymerization of the donor and acceptor monomers:

$$\sim\!\sim(\mathrm{DA})_n\mathrm{D}^{\overset{+}{\cdot}}\ \ {}^{\cdot}\overset{-}{\mathrm{A}} \ldots \mathrm{Z} \rightleftharpoons \sim\!\sim(\mathrm{DA})_n\mathrm{D}^{\overset{+}{\cdot}} + {}^{\cdot}\overset{-}{\mathrm{A}} \ldots \mathrm{Z}$$

$$\sim\!\sim(\mathrm{DA})_n\mathrm{D}^{\overset{+}{\cdot}} + x\mathrm{D} + y\mathrm{A} \longrightarrow \sim\!\sim(\mathrm{DA})_n\mathrm{D} - \mathrm{D}_x\,\mathrm{A}_y$$

I.3.5. MECHANISM OF DONOR-ACCEPTOR COMPLEX POLYMERIZATION.

The mechanism through which donor acceptor complex polymerizations proceed is the subject of some controversy (45). Most workers favour a propagation reaction involving homopolymerization of donor acceptor complexes (21,28,30,33,37,39, 95), while other workers prefer the chain end theory propounded by Zubov et al. (18,25-27,38,40,46). The initiation and termination mechanisms have received little attention but they are generally considered to proceed along similar lines, irrespective of the propagation mechanism.

Thus, initiation is thought to occur in several possible ways, depending on the conditions e.g. by direct attack of radical initiator fragments (28,38), hydrogen abstraction from the complex (95) or energy transfer from the initiator fragments to the complex or to a monomer and then to the complex (122,123). Creation of excited states by the decomposition of organic peroxides and azo compounds (124,125) could account for the unusual catalytic effect of radical precursors that has been observed (45). The termination step is considered by Gaylord to be either monomolecular or bimolecular involving polymer-polymer or polymer - complex interaction (95).

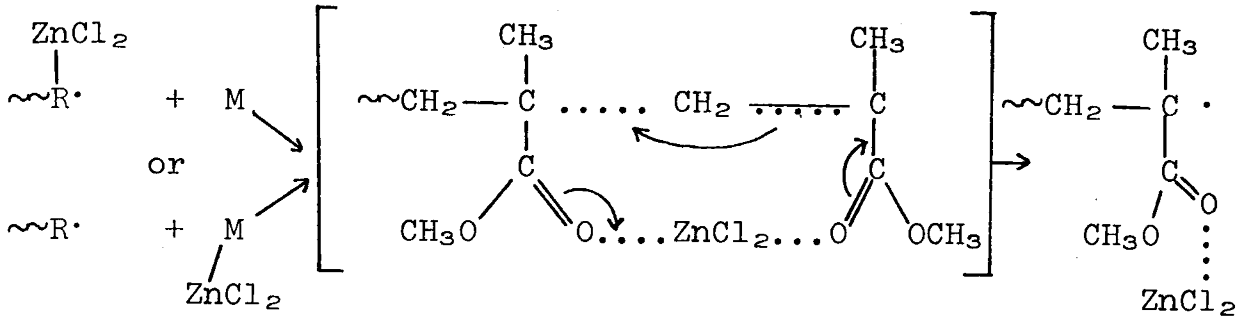
The major differences of opinion in the mechanism of donor acceptor complex polymerization centres around the propagation step. Although it is generally agreed that the propagation reaction is radical in nature, the exact details of the mechanism are not agreed upon. Gaylord and others believe that propagation proceeds through the homopolymerization of donor acceptor molecular complexes (section I.3.2.). The overall scheme for the polymerization reaction is summarized below:

$$\begin{array}{lcl}
D + ZA & \rightleftharpoons & (ZAD) \\
\text{Catalyst} & \longrightarrow & R\cdot \\
R\cdot + (ZAD) & \longrightarrow & R - (ZAD)\cdot \\
R - (ZAD)\cdot + (ZAD)_n & \longrightarrow & R - (ZAD)_{n+1}\cdot \\
2R - (ZAD)_{n+1}\cdot & \longrightarrow & P - P \text{ or } 2P
\end{array}$$

Zubov and other workers feel that the main argument against such a propagation step is the very small concentrations of complexes that are known to exist in these solutions.

Zubov feels that the alternating effect observed in these polymerizations can be explained by means of a mechanism involving the effect of Lewis acids on the propagation rate constants with complexed monomers and radicals (24,38). In a study of the radical copolymerization of methylmethacrylate and various monomers in the presence of various Lewis acids ($ZnCl_2$, $AlCl_3$, $AlBr_3$ and $AlEt_2Cl$), it was found that the copolymerization behaviour could be split into two different types (24).

(a) When the comonomer (methyl acrylate, butyl acrylate) was also able to form complexes with the complexing agent, the reactivity ratios r_1 and r_2 both tended towards unity and the copolymer composition approached the monomer feed composition as the concentration of complexing agent was increased. These results were explained by the following scheme.



Thus the monomer addition occurs by electron transfer through the metal atom in the cyclic transition complex. The efficiency of this process is postulated to be higher than that of ordinary homolytic opening of the double bond. (E.S.R. studies of polymethyl methacrylate radicals complexed with metal halides have been shown to differ from uncomplexed polymethyl methacrylate radicals (64). The difference is due to the fact that the electron density of the unpaired electron on the metal atom is not zero.) If the propagation occurs by this mechanism then the differences in the relative activities of the double bonds of the two monomers may disappear, and thus the copolymerization becomes ideal in nature.

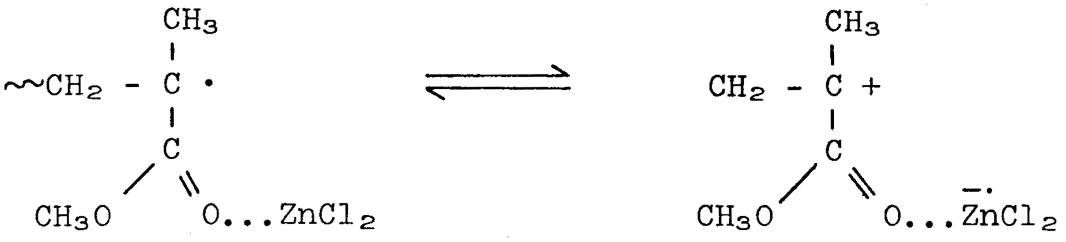
(b) When the comonomer (vinylidene chloride, 2,6 - dichlorostyrene, p - chlorostyrene, styrene) was unable to form a complex with the complexing agent, the value of r_1 either increased and passed through a maximum, or decreased throughout (depending on the comonomer and/or the complexing agent) as the concentration of the Lewis acid was increased. The value of r_2 was found to decrease in all cases.

It has been found that Lewis acids are more strongly bound to growing radicals than to the corresponding monomers (64).

Thus variations in r_1 values are direct measures of the reactivities of the complexed radicals with comonomers. An increase in r_1 signifies that the reactivity of a complexed radical is less than the corresponding uncomplexed radical. This behaviour was observed when comonomers of low donor strength (e.g. vinylidene chloride) or less strong Lewis acids (e.g. $ZnCl_2$) were used. With stronger donor molecules (e.g. styrene) or stronger complexing agents (e.g. $AlCl_3$),r_1 tends to decrease with increasing concentration of Lewis acid, signifying that the complexed radical is more reactive than the uncomplexed radical. The steady decrease in r_2 values as the concentration of Lewis acid increases, signifies that the reactivity of complexed monomer increases compared to pure monomer.

Thus the copolymerization behaviour of comonomer systems having a wide range of e values can be satisfactorily explained by considering the effect of Lewis acids on the propagation rate constants.

The increase in reactivity of the complexed over the uncomplexed radical is explained as being due to the greater delocalisation of the unpaired electron, which thus decreases its ideal radical activity (64). At the same time, the radical attains some cationic character that may enhance its reactivity to the other monomer due to polar effects. This polar interaction can be viewed as a formation of a donor acceptor complex at the chain end.



I.3.6. SUMMARY.

It can be seen from this review that despite the fact that a large amount of work has been done in the field of donor acceptor complex polymerizations, a great deal of conflicting evidence exists. In any particular system, there exists a delicate balance between factors such as e value separation, complexing ability of the Lewis acid, temperature, solvent, and it is difficult to make generalizations.

During a recent panel discussion on a paper presented by Zubov (45), the state of the field was excellently summed up by Bamford:- "....... we're dealing with a wide variety of systems .... there may well be many different reactions and we shall get ourselves into a terrible tangle, I think, if we try to push everything into one mechanism."

I.4. ELECTROINITIATED POLYMERIZATIONS.

Polymerization reactions are initiated by reactive species such as free radicals, carbanions or carbonium ions. These can be generated via suitable chemical processes or by electrolysis. The field of electroinitiated polymerizations is fairly new and has been reviewed by a number of workers

(127-132). In this introduction, a brief survey of electro-initiated polymerizations will be given together with a description of the techniques used in this thesis.

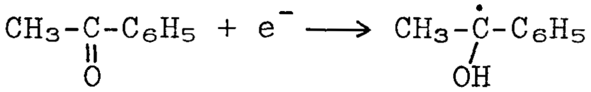
I.4.1. ELECTRODE REACTIONS.

There is a great number of possible reactions that can occur at an electrode. A superficially simple overall reaction may require a complex series of individual steps at the electrode. Such factors as overpotential at an electrode surface, interactions on the electrode material and diffusion from the electrode all can play important roles in the determination of the particular products of an electrochemical transformation. Yamazaki (129) has classified electrode reactions into two major types: cathodic and anodic. The cathodic reactions are classified as follows:

A: Generation of free radicals

i) $H^+ + e^- \longrightarrow H\cdot$

ii)



$CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}C_6H_5 + e^- \longrightarrow CH_3\text{-}\overset{\bullet}{\underset{\underset{OH}{/}}{C}}\text{-}C_6H_5$

iii) Reduction of oxidizing agents (peroxides)

$H_2O_2 + e^- \longrightarrow OH^- + OH\cdot$

$ROOR + e^- \longrightarrow RO^- + RO\cdot$

B: Generation of radical-anions

i) Indirect electron transfer to monomer

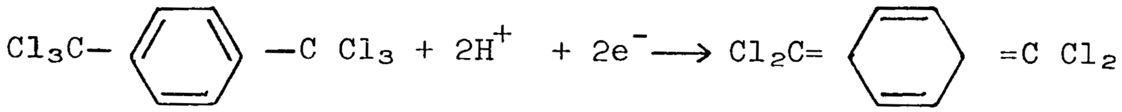
$Na^+ + e^- \longrightarrow Na$

$Na + M \longrightarrow Na^+ + M^{\overline{\cdot}}$

ii) Direct electron transfer to monomer

$M + e^- \longrightarrow M^{\overline{\cdot}}$

C: Formation of unstable monomer



D: Formation of an active catalyst

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

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

The anodic reactions, on the other hand, give rise to oxidation products and are classified as follows:

E: Formation of free radicals by the Kolbe reaction

$R\text{-}COO^- \longrightarrow R\text{-}COO\cdot + e^- \longrightarrow R\cdot + CO_2 + e^-$

F: Formation of radical-cations

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

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

ii) $M \longrightarrow M^{\overset{+}{\cdot}} + e^-$

G: Ring opening polymerization arising from F (i) above.

H: Oxidative condensation polymerization

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

$F\cdot + C_6H_6 \longrightarrow FH + C_6H_5\cdot$

$2\ C_6H_5\cdot \longrightarrow C_6H_5\text{-}C_6H_5$

Electrolytic initiation often implies a significant degree of control over the rate of the initiation reaction. This can be demonstrated by the example of a reduction-oxidation initiator system, such as described by D i). The hydroxyl radicals produced by the reaction of hydrogen peroxide with ferrous ion initiate the polymerization of a vinyl monomer. Taking advantage of electrolysis, one may start with an inactive system composed of Fe^{3+} ions and H_2O_2 and produce the required amount of active Fe^{2+} ions by the electrolytic reduction.

From this point of view, the electrolytic method possesses a great degree of flexibility as to the instantaneous control of initiator concentration.

It is important to note, that in most electrochemical polymerizations it is only the initiating step that can be affected by the variation of electrochemical parameters. Under a given set of conditions, a radical polymerization of styrene will proceed by the same mechanism regardless of whether it was initiated by electrolysis or by a chemical initiator, provided that diffusion from the surface of the electrode is fast enough and absorption effects are negligible. However, if the two electrodes are not separated and the solution can move freely from one electrode to the other, products formed at the counter electrode may react with the initiating species or with the growing chains (133-135). Such reactions may cause termination or chain transfer.

The choice of experimental conditions for electro-initiated polymerizations is frequently difficult due to contravening demands of the electrolytic process on one hand and the polymerization reaction on the other. Specifically, as the majority of useful polymers are insoluble in aqueous systems, it is necessary to employ non-aqueous solvents for polymerization reactions. This places constraints on electrochemical techniques. Also, the viscosity changes encountered during a polymerization are far greater than those encountered in organic synthesis. The resultant effect upon the diffusion, migration and other transport phenomena is often ill-defined, and is a feature of electrochemical polymerization.

I.4.2. TYPES OF ELECTROINITIATED STUDIES.

Polymerization by electrochemical techniques may be studied from a variety of different standpoints:

(a) the rate of the reaction may be controlled by programming the current-time profile. Thus Funt and Yu (189) studied the homopolymerization of methylmethacrylate and found a linear dependence of the rate of polymerization on the impressed current. Similar studies on the electroinitiated anionic polymerizations of methylmethacrylate (136), acrylonitrile (137), isoprene (138) and styrene (139) showed similar relationships between rate and applied current. Although electroinitiated cationic polymerizations have received far less attention, direct current control of those reactions that have been studied is also evident (140-144).

(b) the molecular weight distributions can be controlled through variation of the impressed current. This control is possible only in 'living' systems, the pioneering work in which was done by Szwarc (145). In these systems, the growing chain ends referred to as "living ends" (LE) will not terminate with one another in a pure medium, and therefore retain their reactivity indefinately. The molecular weight in such polymerizations is simply given by

$$\overline{DP} = n[M]/[LE]$$

where n is the number of living ends per polymer molecule.

Funt and his co-workers have applied electrochemical techniques to produce polymers with controlled molecular weight distributions (135,146). This is achieved by producing a specified concentration of living ends and conducting the polymerization until a predetermined quantity of monomer has been polymerized. Current reversal then produces a stoichiometric destruction of growing ends until the living end concentration reaches a new and lower value. The polymerization is then allowed to proceed until a second portion of monomer is consumed.

A cycling technique has also been applied to produce polymer of high degree of monodispersity as well as controlled molecular weight distributions (147).

(c) the initiation step can be controlled by selective potential control. This will be mentioned in the section dealing with controlled potential electrolysis.

I.4.3. CYCLIC VOLTAMMETRY AND CONTROLLED POTENTIAL ELECTROLYSIS.

In order to bring about electrolytic reactions, a dc voltage, sufficient to cause a current to pass, is applied to a cell consisting of two electrodes in contact with a solution of electroactive and ionic species. Electrons flow through the external circuit from the anode to the cathode. At the cathode surface, electrons are transferred to some electroactive substance in solution, which is thereby reduced. The reverse occurs at the anode.

The total impressed voltage, V, across the electrolysis cell may be divided in the following manner:-

$$V = E_a + E_c + iR$$

where E_a and E_c are the potentials of the anode and cathode referred to some reference electrode, R is the resistance of the solution, and i is the current flowing through the cell. In simple electrolyses, either the applied voltage V, or the current i remains constant for the duration of the experiment. However, because the electroactive substances are removed by electrolysis, the solution resistance and the potentials of the anode and cathode may alter with time. To avoid this, electrolysis may be performed at a controlled electrode potential.

Consider the electrolytic reduction of a given electroactive substance present in the solution at the cathode. It may be determined, using voltammetric techniques such as cyclic voltammetry, that the required reduction takes place when the cathode is at some optimum potential, E_c. The essential feature of electrolysis at controlled potential is that the electrode potential is maintained at E_c, despite changes in the solution composition and resistance.

By this means, the reaction at the cathode may be restricted to the reduction occurring at potential E_c, even in the presence of other species in solution which are reduced at more cathodic potentials. Thus, this process is much more selective than electrolysis at constant current or constant voltage.

In order to apply controlled potential electrolysis effectively, it is necessary to determine the current-potential relationship for the system under study. Polarography at the dropping mercury electrode is the best-known technique for finding this information, but the use of this system in organic solutions of high resistance under conditions similar to those necessary for anionic polymerizations raises severe experimental problems. Of the possible electrochemical methods for examining organic reactions, cyclic voltammetry at a platinum microelectrode seems the most promising.

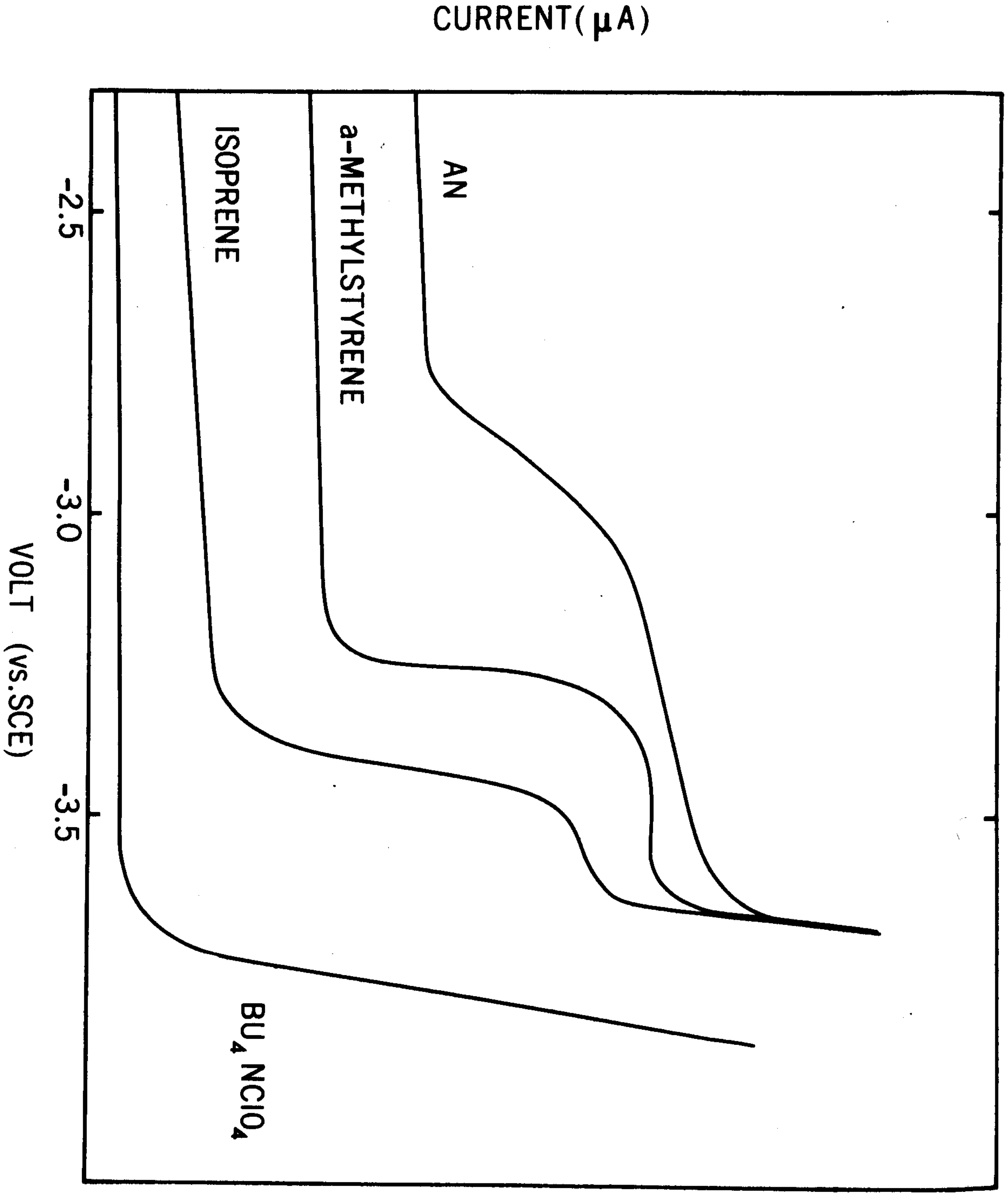
Cyclic voltammetry, which is basically cyclic polarography in an unstirred solution, gives not only the reduction potential characteristics of the system under study, but also gives information into the possible fate of the reduced species (148). In unstirred solution, the products reduced during the forward sweep can be re-oxidised during the reverse sweep. For a reversible process, a symmetrical wave is obtained with a separation between positive and negative peaks of approximately 59 millivolts. However, when a rapid chemical reaction such as polymerization follows the reduction cycle, the corresponding reverse peak disappears. Thus by variation of the sweep rate, the kinetics of secondary electrochemical reactions can be studied.

Thus a cyclic voltammetry study of phenyl substituted ethylenes has shown that protonation and polymerization are competitive under certain conditions (149). Diphenylpicrylhydrazyl, a substance of particular interest as an inhibitor in free radical polymerizations, has been studied by cyclic voltammetry (150). This substance shows four reversible electron transfer steps in tetrahydrofuran. The potential dangers of using such inhibitors, which are themselves electroactive, in determining the propagating species in electro-initiated polymerizations, was indicated from this study.

Although the application of cyclic voltammetry in electropolymerization studies has received little attention, the advantages of controlled potential electrolysis has been recognized. Thus Yamazaki et al. (190) conducted an excellent study of some ten monomers using polarography and controlled potential electrolysis. These workers obtained the reduction potentials of the ten monomers by polarographic means using dimethoxyethane as solvent and tetrabutylammonium perchlorate as electrolyte. Results for three monomers are shown in Figure 4. Having found the reduction potentials, the polymerization of each monomer was then conducted at the appropriate cathodic potential at which monomer alone could be reduced and the electrolyte not affected. This then enabled the authors to postulate direct electron transfer to the monomer as the initiation step. Similar mechanistic interpretations have been made by other workers (137, 151-154).

The potentialities of the combined application of controlled potential and polarographic techniques has been shown in a number of recent papers by Mengoli et al. (155-161). In these studies, radical anions or cations have been generated electrochemically by controlled potential electrolysis and their decay followed by polarographic techniques. The decay reaction involves either direct electron transfer to or from a monomer

Figure 4. POLAROGRAMS OF ACRYLONITRILE, α-METHYLSTYRENE AND ISOPRENE. (190)


CURRENT(μA)
AN
a-METHYLSTYRENE
ISOPRENE
BU$_4$NClO$_4$
-2.5
-3.0
-3.5
VOLT (vs.SCE)

(156,158,160) or by hydrogen transfer (155,157) with subsequent ionic polymerization of the monomer. Initiation of anionic polymerization by radical anions produced chemically is well known (145). However the electrochemical methods permit direct control of the concentration of active species and the ability to continuously determine these species by polarographic techniques without altering the system during the reaction.

I.4.4. ELECTROINITIATED COPOLYMERIZATION REACTIONS.

Electroinitiated copolymerization reactions have received very little attention. In fact, copolymerization has been almost exclusively studied only as a diagnostic technique for the determination of propagation mechanisms (133,134,136, 137,152). In the only electroinitiated copolymerization study done until recently, the anionic copolymerization of styrene and methylmethacrylate was carried out (162). Recently, there has been some interest in the electroinitiation of donor acceptor complex copolymerizations (83,84,86,87,163). Thus Phillips et al. (84-87) studied the styrene - diethylfumarate (DEF) - zinc bromide system by electrolysis. They found that alternating copolymers were obtained in the cathode compartment under a wide range of conditions. The studies were carried out using very high currents, and no effort was made to control the potential. Under these conditions it is extremely difficult to make any sensible conclusions regarding the initiation mechanism.

Comparison of photoinitiation and electroinitiation in this system showed definite correlations between product yield and cumulative energy input. On the basis of this and other observations, the authors postulated that in both electroinitiation and photoinitiation, the first step involved the formation of the donor acceptor complex between St and DEF.

The system studied by Phillips et al. is similar to the St-AN-zinc bromide system studied in this thesis. However, there are some very important differences which makes direct comparison extremely misleading. This will be seen later in the thesis.

II. EXPERIMENTAL METHODS.

II.1. CHEMICALS AND THEIR PURIFICATION.

II.1.1. MONOMERS.

Acrylonitrile (Matheson), styrene (Eastman) and methylmethacrylate (Matheson) were dried for several days over calcium hydride, eluted through an alumina column and distilled at reduced pressure on a spinning band column of high efficiency, the centre cut being used in all experiments.

II.1.2. SALTS AND ELECTROLYTES.

Zinc chloride (Allied Chemical) and zinc bromide (Fisher) were dried for twenty-four hours at 100°C in a vacuum oven before use.

Tetrabutylammonium perchlorate (Eastman) was dried at 80°C in a vacuum oven. Other reagent grade electrolytes were similarly treated.

II.1.3. SOLVENTS.

1,2 - dichloroethane (Fisher Certified) was dried over P_2O_5 for a week before distillation. The 70% centre cut was used throughout.

Tetrahydrofuran (Fisher, Histological Grade) was dried over CaH_2 for several days and distilled onto a sodium mirror. Repeated distillations were carried out until the sodium mirror remained intact.

Acetonitrile (Fisher) was dried over $CaSO_4$ for several days, distilled and stored over molecular sieve #4A.

t-Butyl chloride (Eastman) was distilled prior to use.

All other chemicals employed in this work were reagent grade, and used without further purification.

II.2. ELECTRONIC EQUIPMENT.

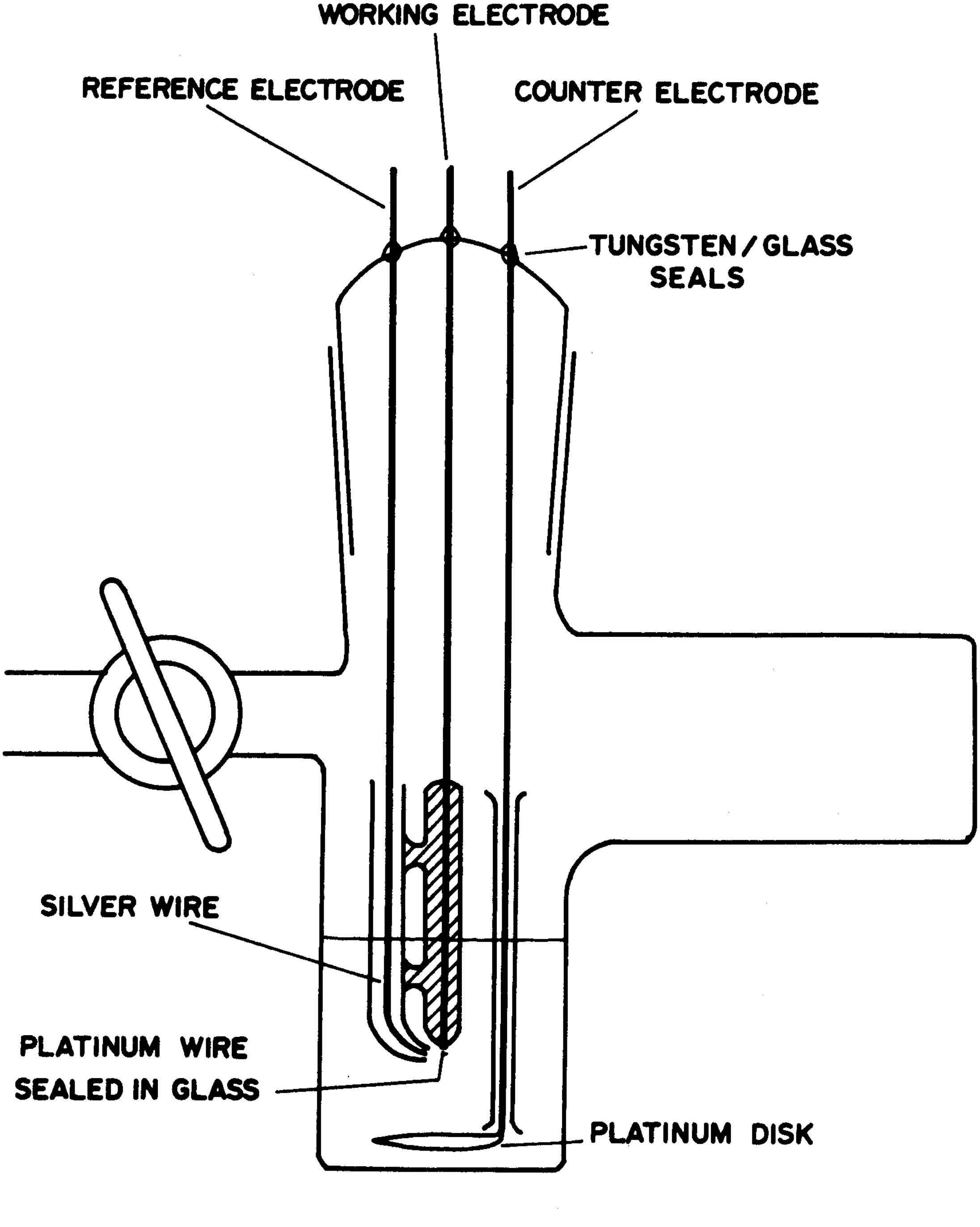
Electrochemical work was carried out using a Princeton Applied Research #170 Electrochemistry System (PAR). This instrument was capable of providing up to 5 amps, and the maximum voltage output of 90V between the working and counter electrodes was sufficient for work in the high resistance non-aqueous solvents used here. Some of the initial cyclic voltammetry and controlled potential work was done using a Wenking RH potentiostat in conjunction with a Hewlett-Packard 3300A function generator which provided square, triangular, sine and sawtooth signals with a frequency range from 0.01 Hz to 10k Hz.

Current reversal experiments were carried out using the PAR set for constant current. The signal generator supplied a square wave signal of the required frequency and also activated an electronic relay which reversed the direction of the current through the cell.

II.3. ELECTROLYSIS CELLS.

The cell used for cyclic voltammetry is shown in Figure 5. The working electrode consisted of the cross-section of a 1/16 inch diameter platinum wire sealed in glass. A simple silver wire sheathed in a glass capillary proved

Figure 5. CELL USED FOR CYCLIC VOLTAMMETRY.


WORKING ELECTRODE
REFERENCE ELECTRODE
COUNTER ELECTRODE
TUNGSTEN / GLASS SEALS
SILVER WIRE
PLATINUM WIRE SEALED IN GLASS
PLATINUM DISK

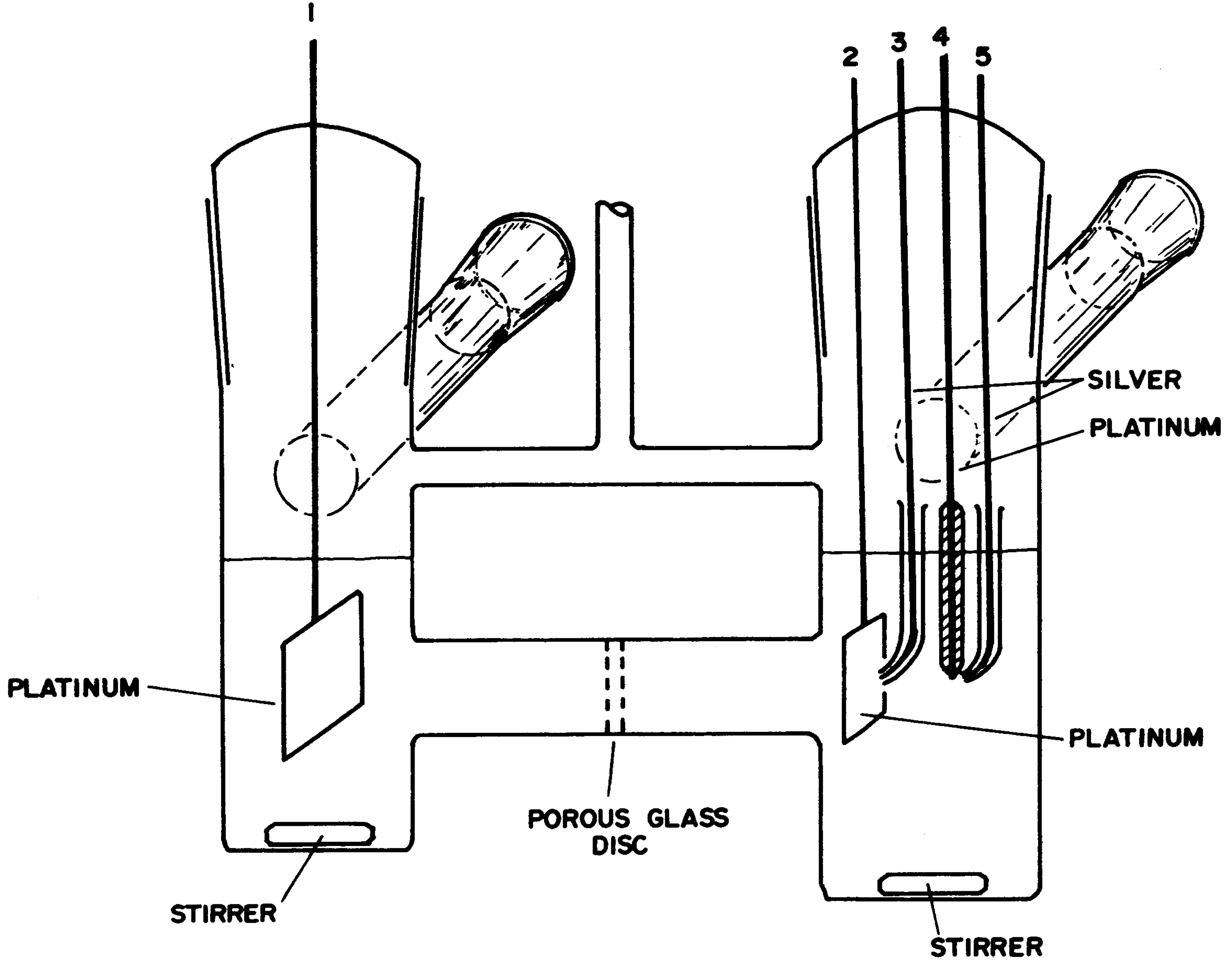
adequate as a reference electrode (164,165). A divided cell which could be used for cyclic voltammetry and controlled potential studies of the same solution is shown in Figure 6. Cyclic voltammetry work could be carried out before and during a polymerization by employing electrodes 2 (counter), 4 (working) and 5 (reference). Polymerization under controlled potential electrolysis was effected using electrodes 1 (counter), 2 (working) and 3 (reference). In the donor acceptor experiments, the set-up was less complicated. Only electrodes 1,2 and 3 were utilized with electrodes 4 and 5 being completely absent. The reference electrode 3 was either a silver or platinum wire or alternatively a demountable Ag/Ag^+ reference electrode (166). The side arm arrangement provided ease in handling solutions as well as an entry port for the Ag/Ag^+ reference electrode when used. The undivided cell used in some experiments is shown in Figure 7. The two electrodes are 1" square platinum (as is the case for electrodes 1 and 2 in Figure 6) separated by ½".

II.4. POLYMERIZATION PROCEDURE.

The initial cyclic voltammetry and controlled potential electrolysis experiments were carried out under high vacuum techniques. Thus, for example, background electrolyte and stilbene were evacuated overnight before introduction of solvent (and monomer when required) by distillation.

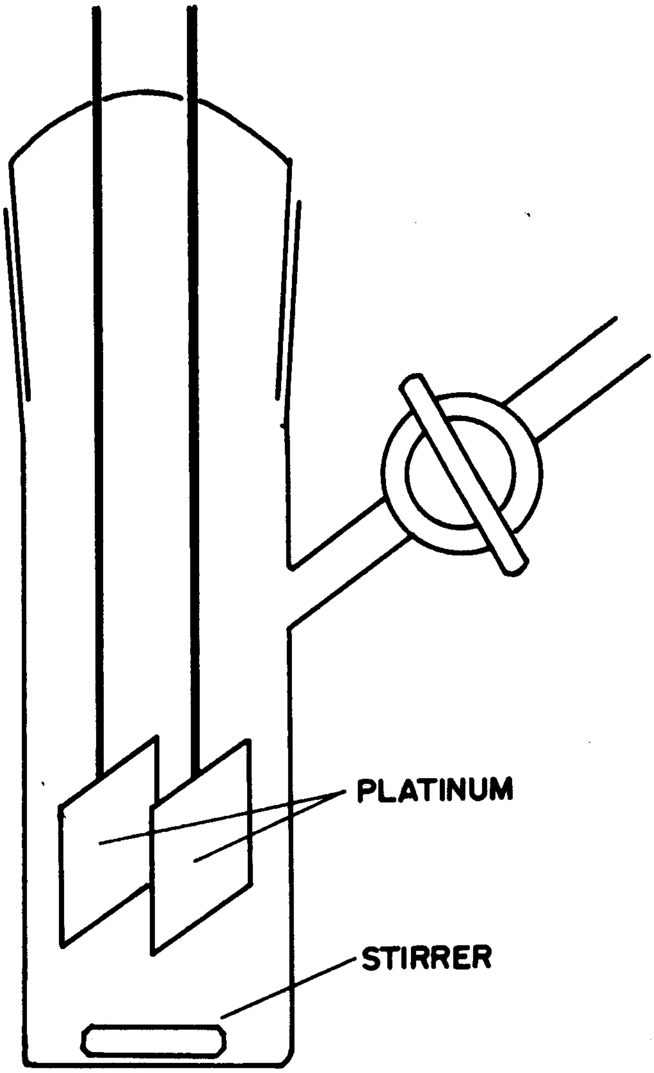
In the donor acceptor work, degassing techniques were employed. Thus, for example, the required quantities of acrylonitrile (AN) or methylmethacrylate (MMA) were mixed with dichloroethane (DCE) in a flask.

Figure 6. CELL USED FOR CYCLIC VOLTAMMETRY AND CONTROLLED POTENTIAL ELECTROLYSIS.

1
2
3
4
5
SILVER
PLATINUM
PLATINUM
PLATINUM
POROUS GLASS DISC
STIRRER
STIRRER

[illegible]

Figure 7. UNDIVIDED CELL.



PLATINUM
STIRRER

Previously weighed zinc bromide was then completely dissolved in this mixture and styrene (St) added. The resulting solution was transferred to an electrolysis cell and degassed twice before placing in a controlled temperature bath. After electrolysis, the contents of the cell were poured into a large volume of methanol. The polymer was collected, washed with an ammoniacal solution of methanol, dried at room temperature in a vacuum oven, then weighed.

Polymerizations under U.V. irradiation at 2537Å were carried out in quartz tubes using a circular "Rayonet" Srinivasan-Griffith Photochemical reactor. Prior to polymerization nitrogen was flushed through the system for three minutes.

II.5. POLYMER CHARACTERIZATION.

II.5.1. ELEMENTAL ANALYSIS.

Elemental Analysis of the copolymers for carbon, hydrogen and nitrogen was carried out on a Perkin-Elmer Elemental Analyser M240. The copolymer composition was calculated from the nitrogen content.

II.5.2. IR SPECTROSCOPY.

IR spectroscopic analysis of the copolymers was carried out on a Perkin-Elmer 457 Infrared Spectrophotometer employing the KBr pressed disc technique. A typical IR spectrum of a 50:50 copolymer of styrene - acrylonitrile prepared in the presence and absence of a Lewis acid, is seen in Figure 8. A rapid method for obtaining the copolymer composition of a sample from its IR spectrum was devised. The method, similar to that employed by Tazuke and Okamura (29), involved measuring the area under peaks characteristic of both monomers. For styrene, this was the 1600 cm^{-1} band whereas for acrylonitrile, the 2240 cm^{-1} absorption was used. It was found that greater accuracy was obtained by cutting out these bands and weighing them gravimetrically. A number of St-AN copolymers of different composition were prepared using a free radical initiator in the absence of zinc halide. A plot of the logarithm of the weight ratios of the two characteristic bands against the copolymer composition determined by Elemental Analysis was found to be a linear and is shown in Figure 9. Comparison of results obtained by the two methods of copolymer analysis showed that the IR method was within 1% of the results obtained by elemental analysis.

II.5.3. NMR SPECTROSCOPY.

NMR spectroscopy of the copolymers was performed at room temperature in deuterated chloroform solutions. The 60 MHz spectra were recorded on a Varian A-56/60A instrument, the 100 MHz spectra being obtained on a Varian XL-100 NMR Spectrometer. The observed NMR spectra of the copolymers were compared with a series of calibration spectra of alternating and non-alternating copolymers. The calibration spectra for the St-AN copolymers are shown in Figures 10 and 11.

Figure 8. IR SPECTRUM OF STYRENE - ACRYLONITRILE COPOLYMER. Prepared in the presence or absence of $ZnBr_2$.

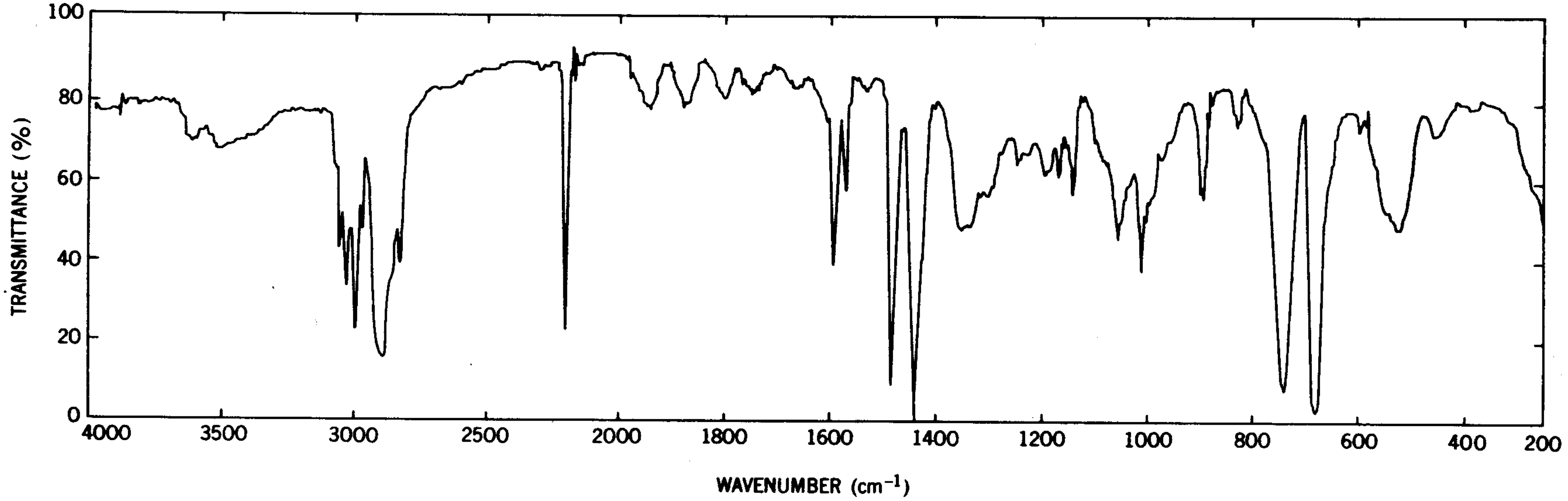

TRANSMITTANCE (%)
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
WAVENUMBER (cm⁻¹)

Figure 9. CALIBRATION CURVE FOR OBTAINING COPOLYMER COMPOSITION FROM IR SPECTRA.

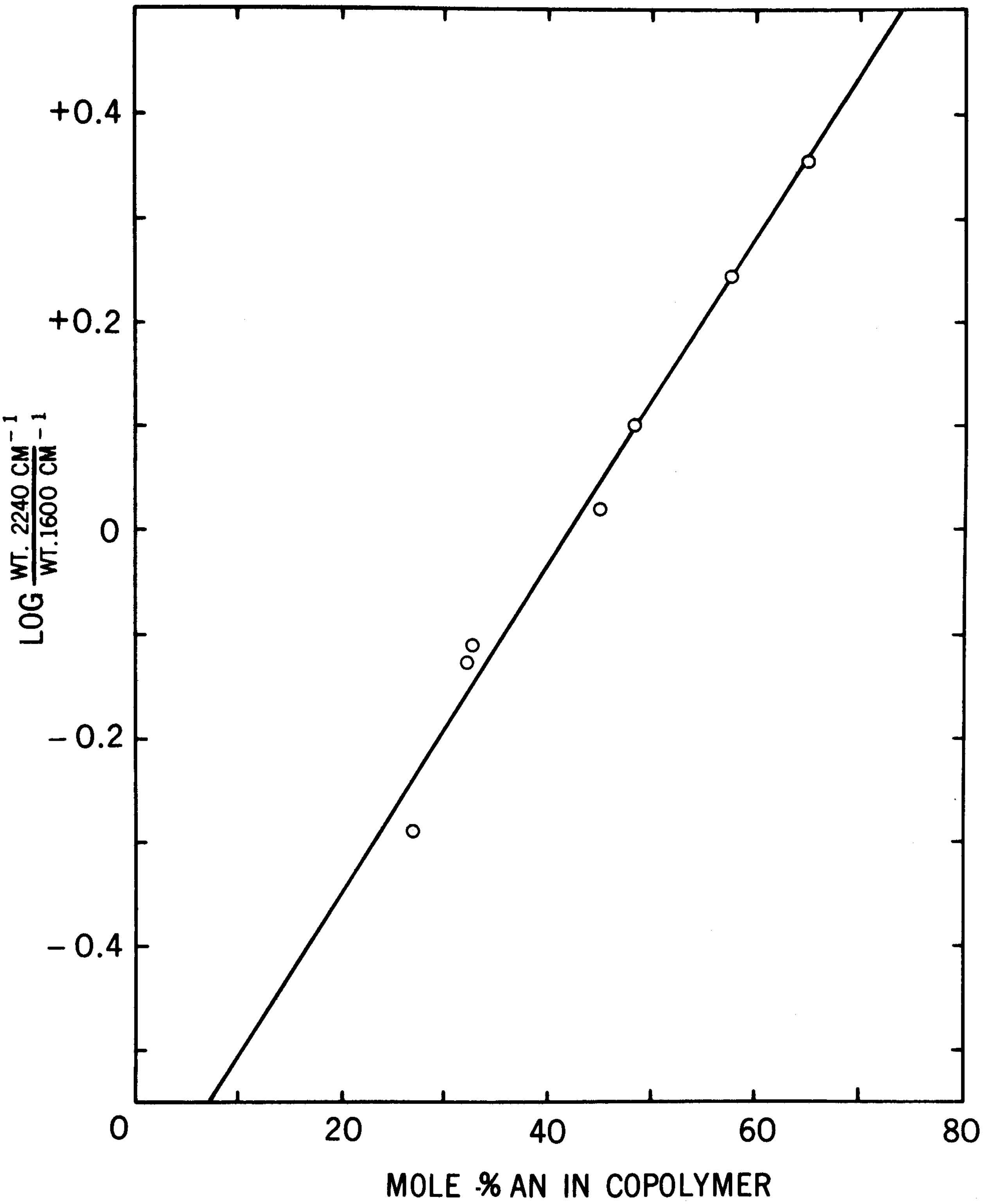

+0.4
+0.2
0
−0.2
−0.4
LOG $\frac{\text{WT. } 2240 \text{ CM}^{-1}}{\text{WT. } 1600 \text{ CM}^{-1}}$
0
20
40
60
80
MOLE -% AN IN COPOLYMER

Figure 10. NMR SPECTRA OF STYRENE - ACRYLONITRILE COPOLYMERS PREPARED WITH FREE-RADICAL CATALYST (126). Copolymer composition of St/AN copolymer (mole ratio): (A) 71/29; (B) 65/35; (C) 45/55; (D) 30/70.

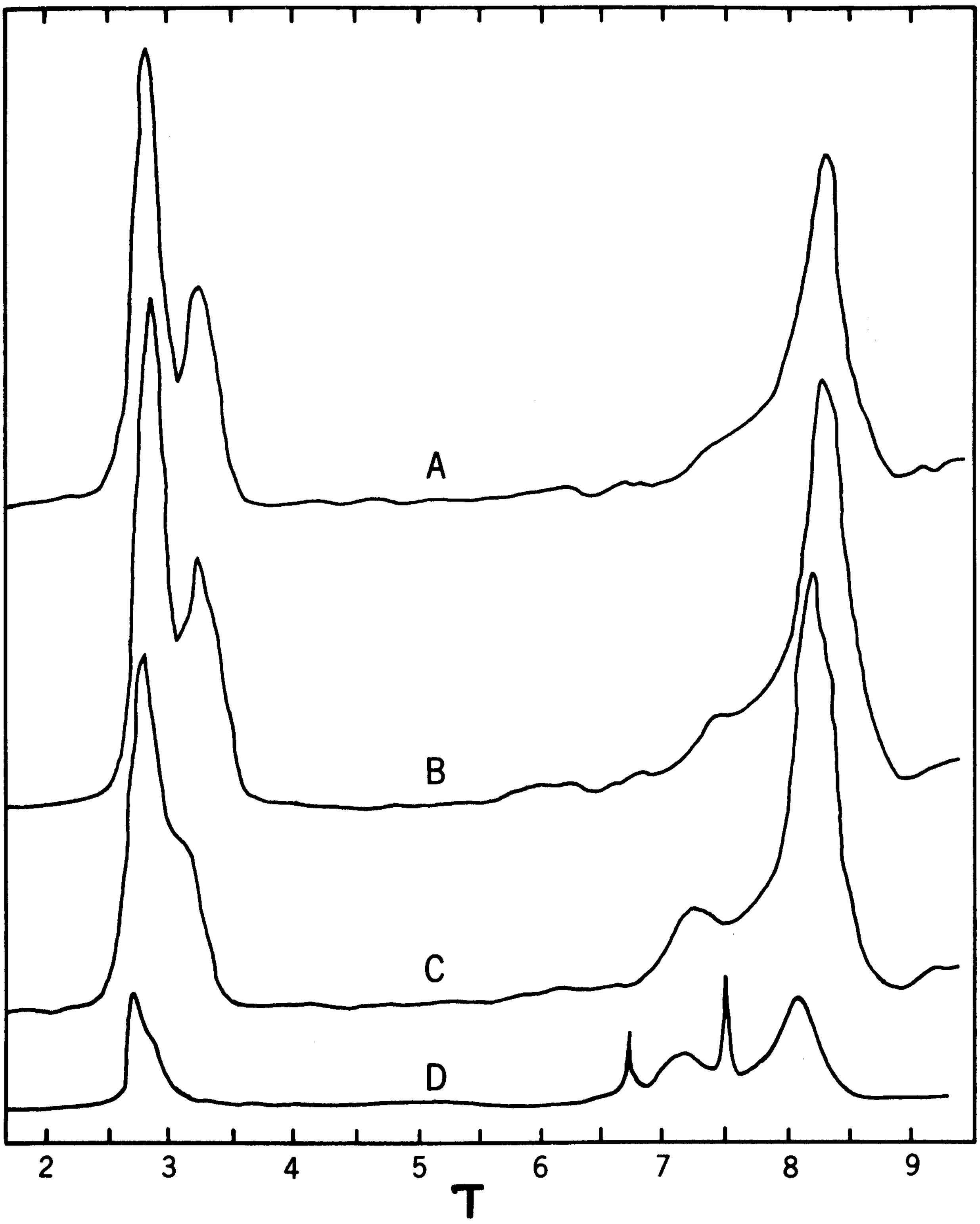
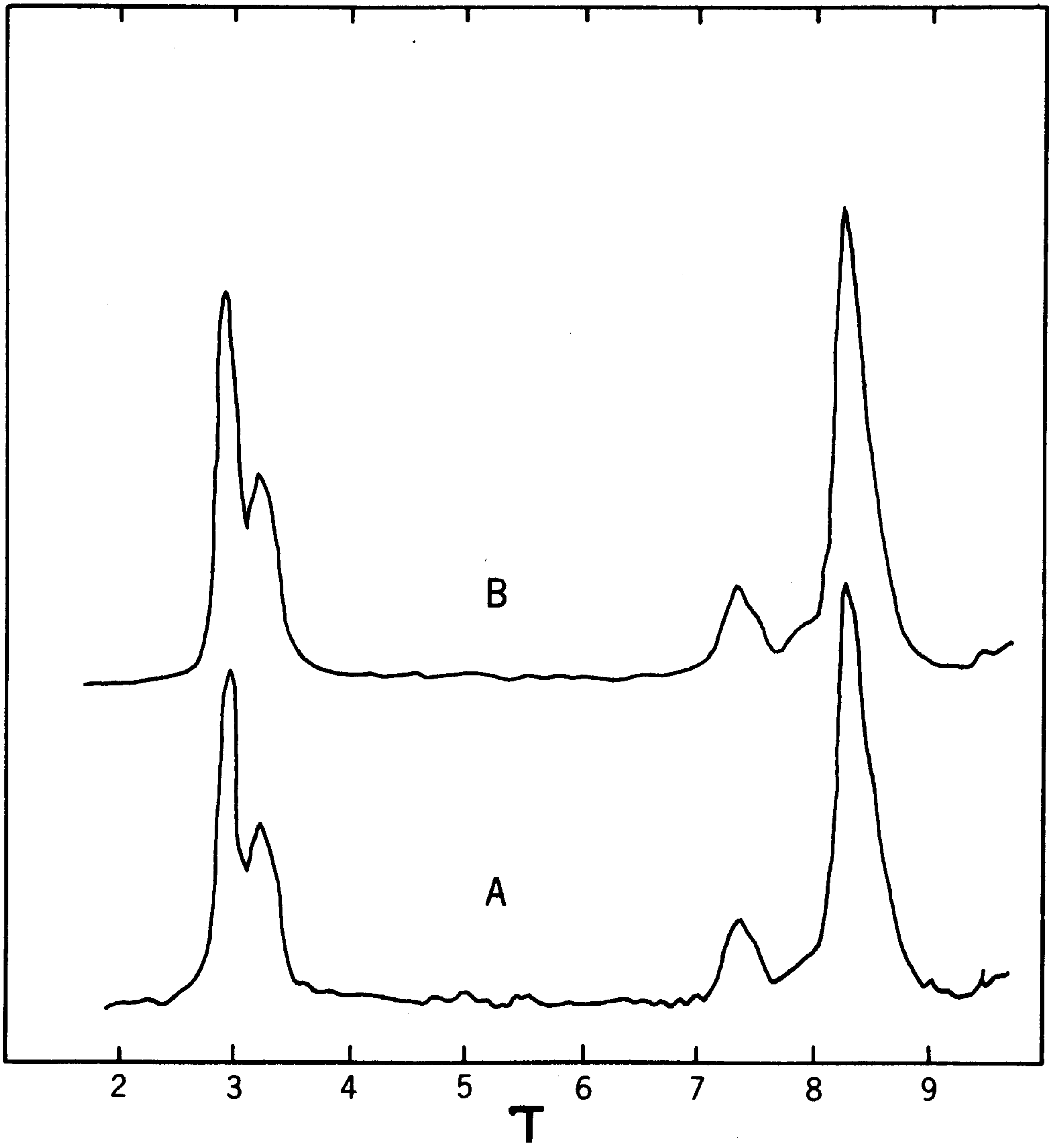

A
B
C
D
2
3
4
5
6
7
8
9
τ

Figure 11. NMR SPECTRA OF ALTERNATING STYRENE - ACRYLONITRILE COPOLYMER PREPARED WITH $ZnCl_2$ (126).

(A) Spontaneous; (B) Benzoyl peroxide catalysed.


B
A
2
3
4
5
6
7
8
9
τ

It should be mentioned here that NMR does not provide definitive evidence for alternation in St - AN copolymers. From the r_1 and r_2 values for these monomers, it is obvious that 50:50 free radical copolymers (prepared in the absence of Lewis acids) are strongly alternating. The NMR spectra in Figures 10 and 11 indicate that 50:50 copolymers prepared with Lewis acids have a similar structure to 50:50 free radical copolymers. Hence NMR provides only an indication of alternation, and by no means a definite proof.

II.5.4. GEL PERMEATION CHROMATOGRAPHY.

Molecular weights and molecular weight distributions were measured on a Waters Associates Model 301A Chromatograph. The styragel columns were calibrated by a series of narrow molecular weight distribution polystyrene samples, supplied by Waters Associates. Samples containing approximately 0.25g of polymer per 100 ml of THF were used for the analysis. All solutions were filtered under pressure to remove impurities and undissolved polymer particles. Two millilitres of the sample solution was then used for the M.Wt. determination. A typical chromatogram of a St-AN copolymer prepared in the presence of $ZnBr_2$ is shown later in this thesis (Figure 22). Comparison with a standard polystyrene sample demonstrates the typically high molecular weights and broad distributions of these alternating copolymers.

III. RESULTS AND DISCUSSION.

III.1. GENERAL STUDIES.

III.1.1. CYCLIC VOLTAMMETRY AND CONTROLLED POTENTIAL ELECTROLYSIS.

One of the initial aims of this thesis was to explore the possibilities of using cyclic voltammetry to follow some aspects of electropolymerization. Radical anions formed chemically are known to initiate anionic polymerizations reactions (145). It was thought advantageous to produce these radical anions electrochemically due to the ease by which their concentrations could be controlled and the possibilities of monitoring their reactions by cyclic voltammetry. From a large number of candidate compounds, nitrobenzene and trans stilbene were chosen for this study since both were found to undergo one electron reductions to form their corresponding radical anions and also, their reduction potentials seemed sufficiently separated from those of most monomers to allow a cyclic voltammetry study in the presence of these monomers.

The cyclic voltammograms of stilbene and nitrobenzene in tetrabutylammonium perchlorate - THF solution are shown in Figures 12 and 13. For the nitrobenzene wave and the first stilbene wave the separation between positive and negative peak potentials is 60mV. Also, a plot of the peak current height against the square root of the scan rate for these waves is

Figure 12. CYCLIC VOLTAMMOGRAM OF STILBENE.

Stilbene (1.0mM) in 0.1M Bu_4NClO_4 - THF solution. Pt wire reference.

Scan rates 10,8,6,4,2,1 V/sec.

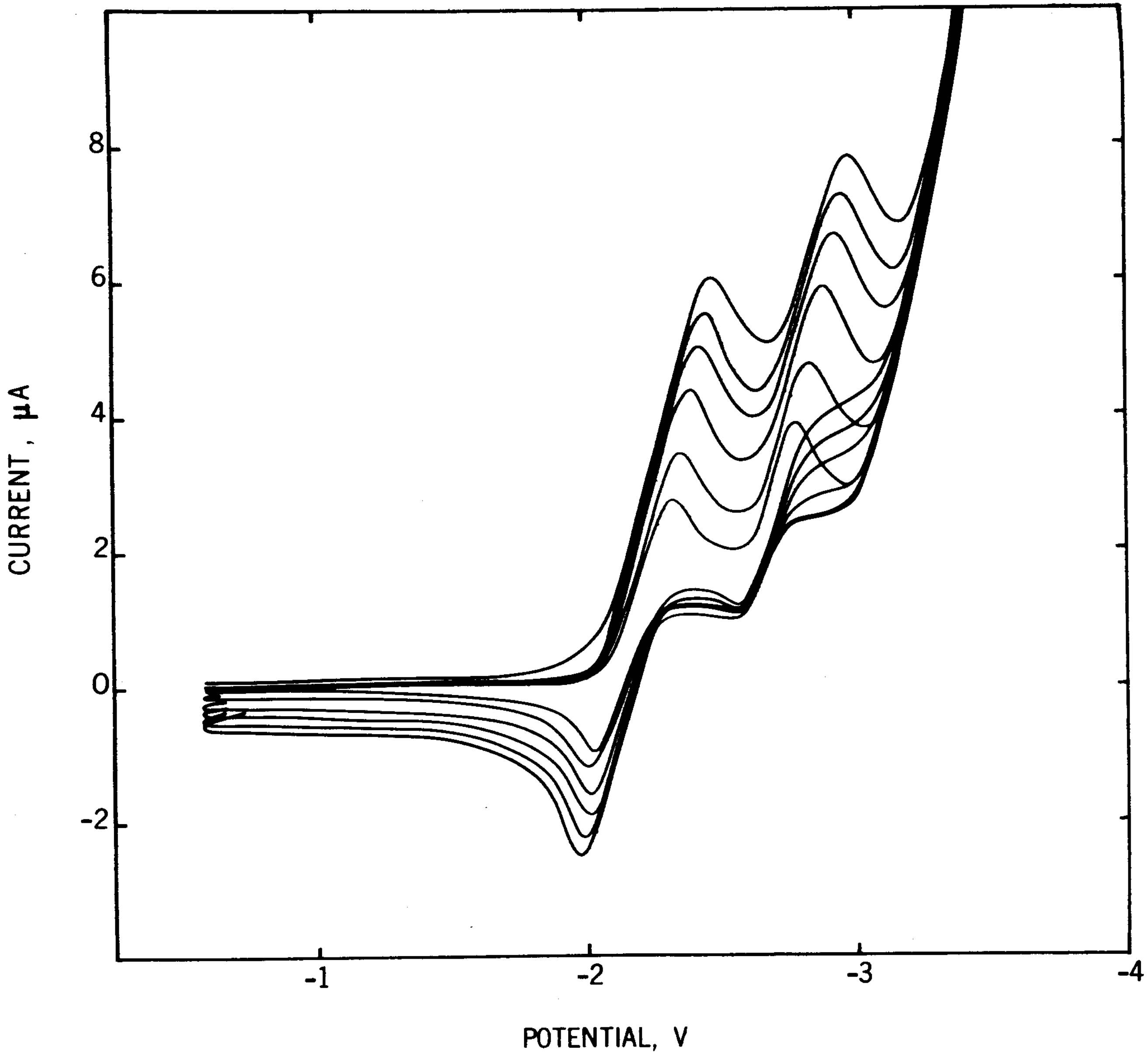
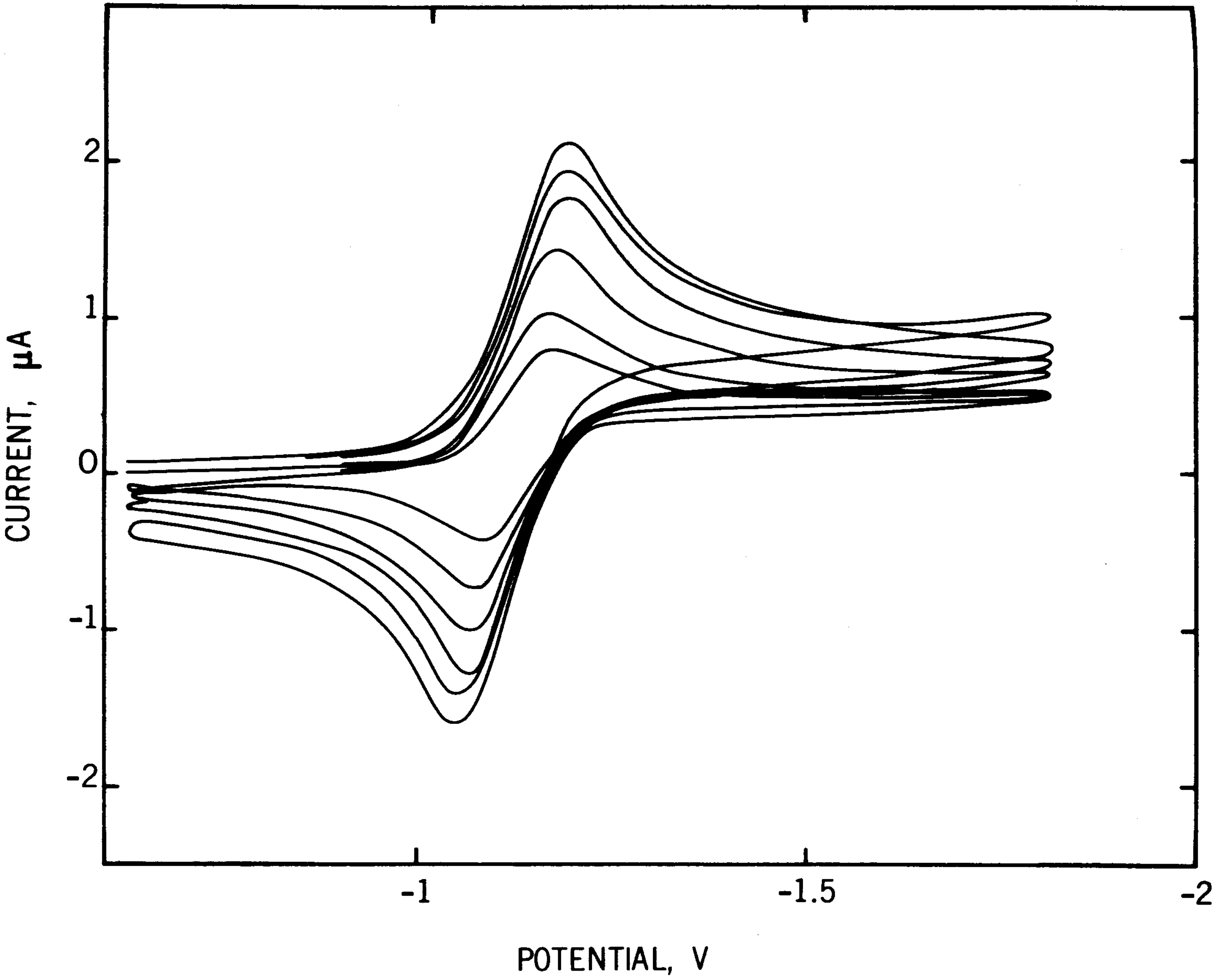

CURRENT, μA
8
6
4
2
0
-2
-1
-2
-3
-4
POTENTIAL, V

Figure 13. CYCLIC VOLTAMMOGRAM OF NITROBENZENE.

Nitrobenzene (0.6mM) in 0.1M Bu_4NClO_4 - THF solution. Pt wire reference.

Scan rates 10,8,6,4,2,1 V/sec.


CURRENT, μA
2
1
0
-1
-2
-1
-1.5
-2
POTENTIAL, V

linear (Figure 14). Both these observations confirm that stilbene and nitrobenzene undergo a reversible one electron reduction to form their corresponding radical anions (148). It should be noted that the second reduction wave of stilbene, corresponding to the formation of the dianion, has no re-oxidation wave. This signifies that the second reduction step is irreversible in the time scale of the sweep.

The cyclic voltammograms of the two monomers methylmethacrylate (MMA) and styrene (St) in tetrabutylammonium perchlorate - THF solution are shown in Figures 15 and 16. In both cases, the voltammograms show that the reductions of the two monomers proceed irreversibly, since no re-oxidation peak appears on the reverse scan. This has been explained as being due to protonation or polymerization reactions, depending on the conditions (149).

In order to determine whether the radical anions of stilbene and nitrobenzene were capable of initiating the polymerizations of some monomers, solutions containing stilbene (or nitrobenzene) were electrolysed at -2.2V (or -1.2V), with respect to Pt wire reference, the reduction potentials of these compounds as determined by their cyclic voltammograms, in the presence of a monomer.

In the case of stilbene, the monomers St and MMA were investigated. Electrolysis in the presence of St produced the characteristic green colour of the stilbene radical anion, but no polystyrene was isolated on precipitation in methanol.

Figure 14. VARIATION OF PEAK CURRENT WITH THE SQUARE ROOT OF THE SCAN RATE.

A - stilbene (first wave)
B - nitrobenzene

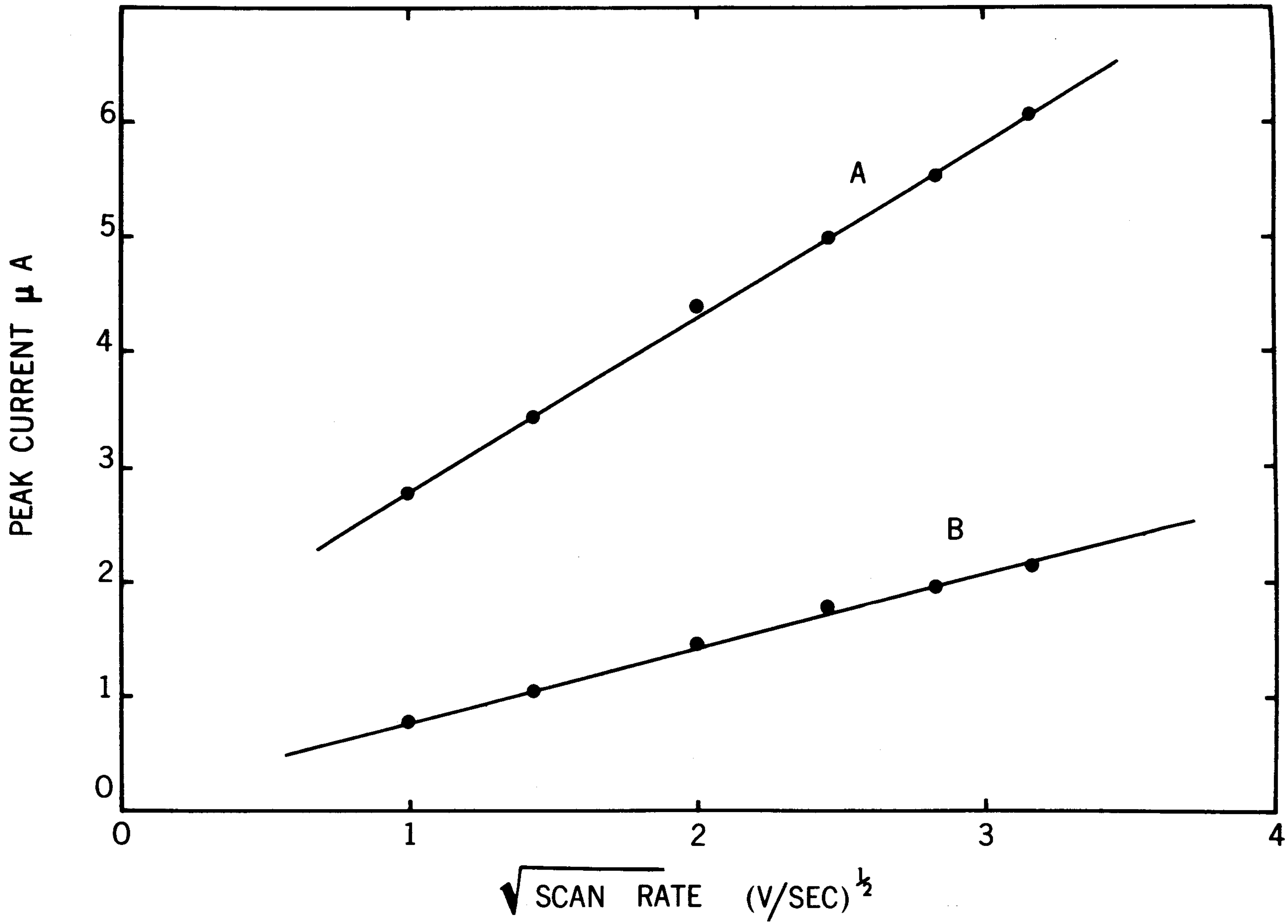

PEAK CURRENT μ A
0
1
2
3
4
5
6
A
B
0
1
2
3
4
√SCAN RATE (V/SEC)½

Figure 15. CYCLIC VOLTAMMOGRAM OF METHYLMETHACRYLATE.

MMA (1mM) in 0.1 M Bu_4NClO_4 - THF solution.
Pt wire reference.

Scan rates 10,8,6,4,3,2,1.5,1 V/sec.

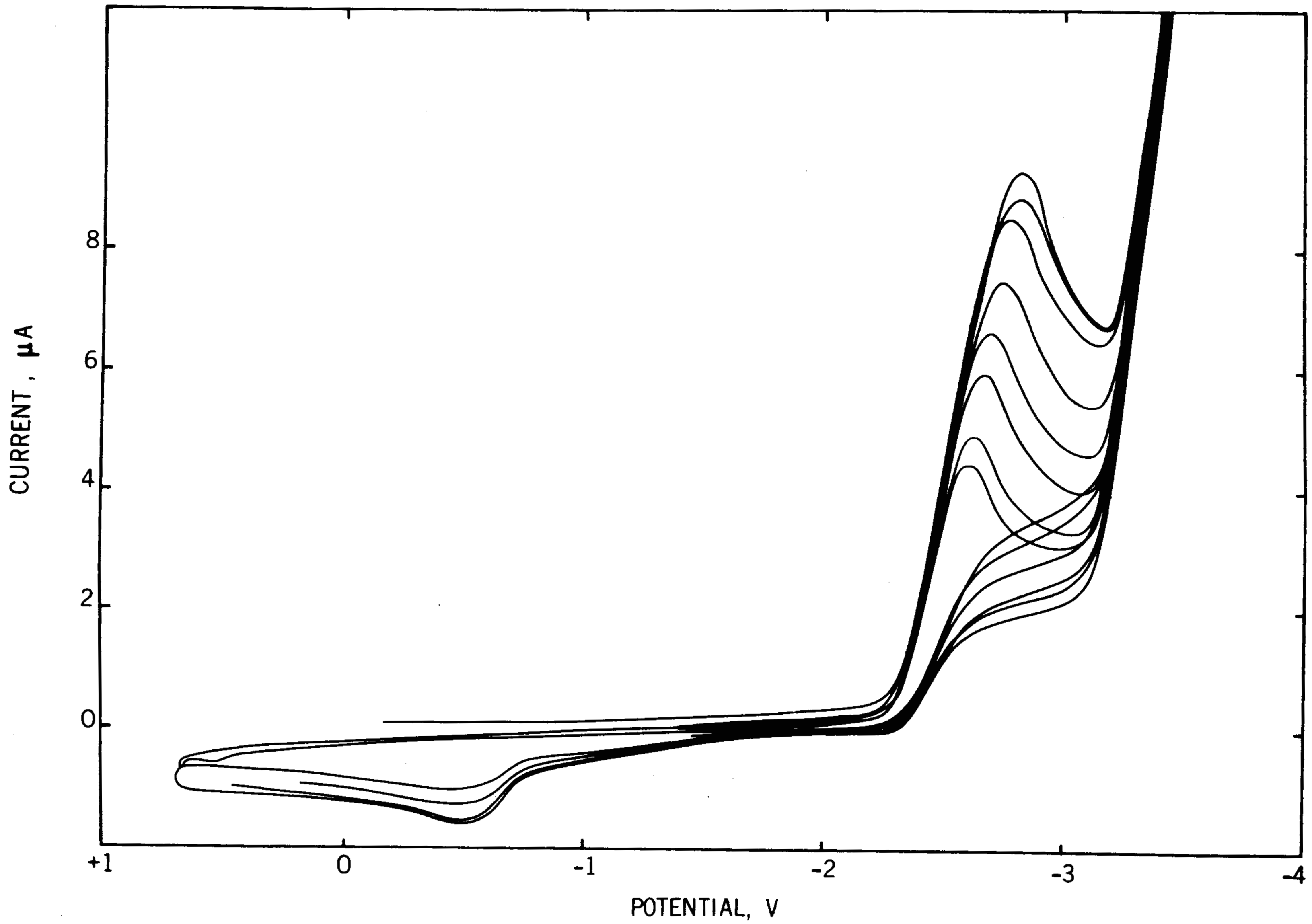
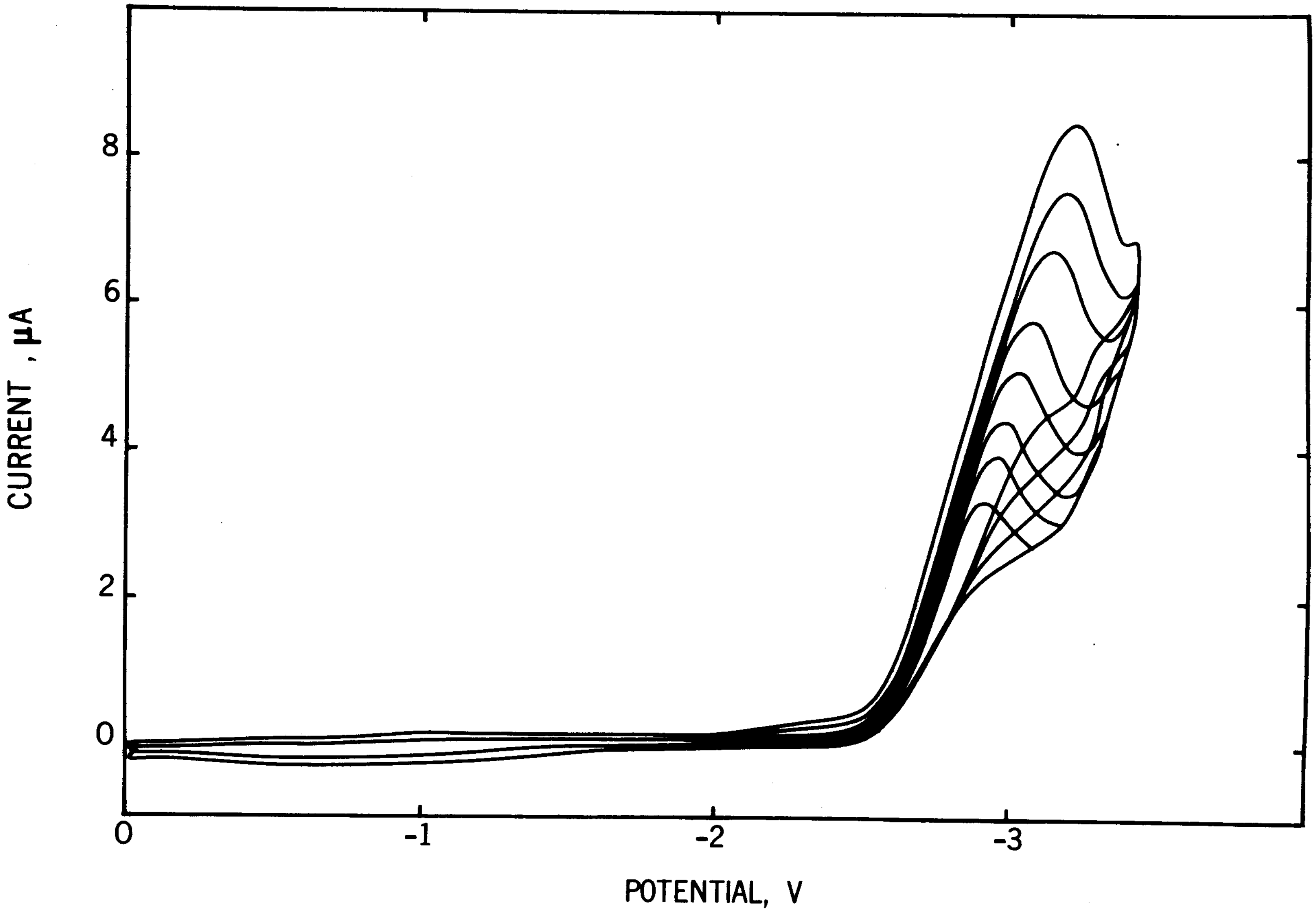

CURRENT , μA
8
6
4
2
0
+1
0
-1
-2
-3
-4
POTENTIAL, V

Figure 16. CYCLIC VOLTAMMOGRAM OF STYRENE.

St (1mM) in 0.1 M Bu_4NClO_4 - THF solution.
Pt wire reference.

Scan rates 10,8,6,4,3,2,1.5,1 V/sec.


CURRENT , µA
8
6
4
2
0
0
-1
-2
-3
POTENTIAL, V

This is in accord with previous results (149), and is attributed to proton abstraction from the background electrolyte to the radical anion. Although the use of sodium tetraphenylboron as background electrolyte resulted in the formation of polystyrene, this salt was unsuitable for cyclic voltammetry work due to its electroactivity in the region of interest.

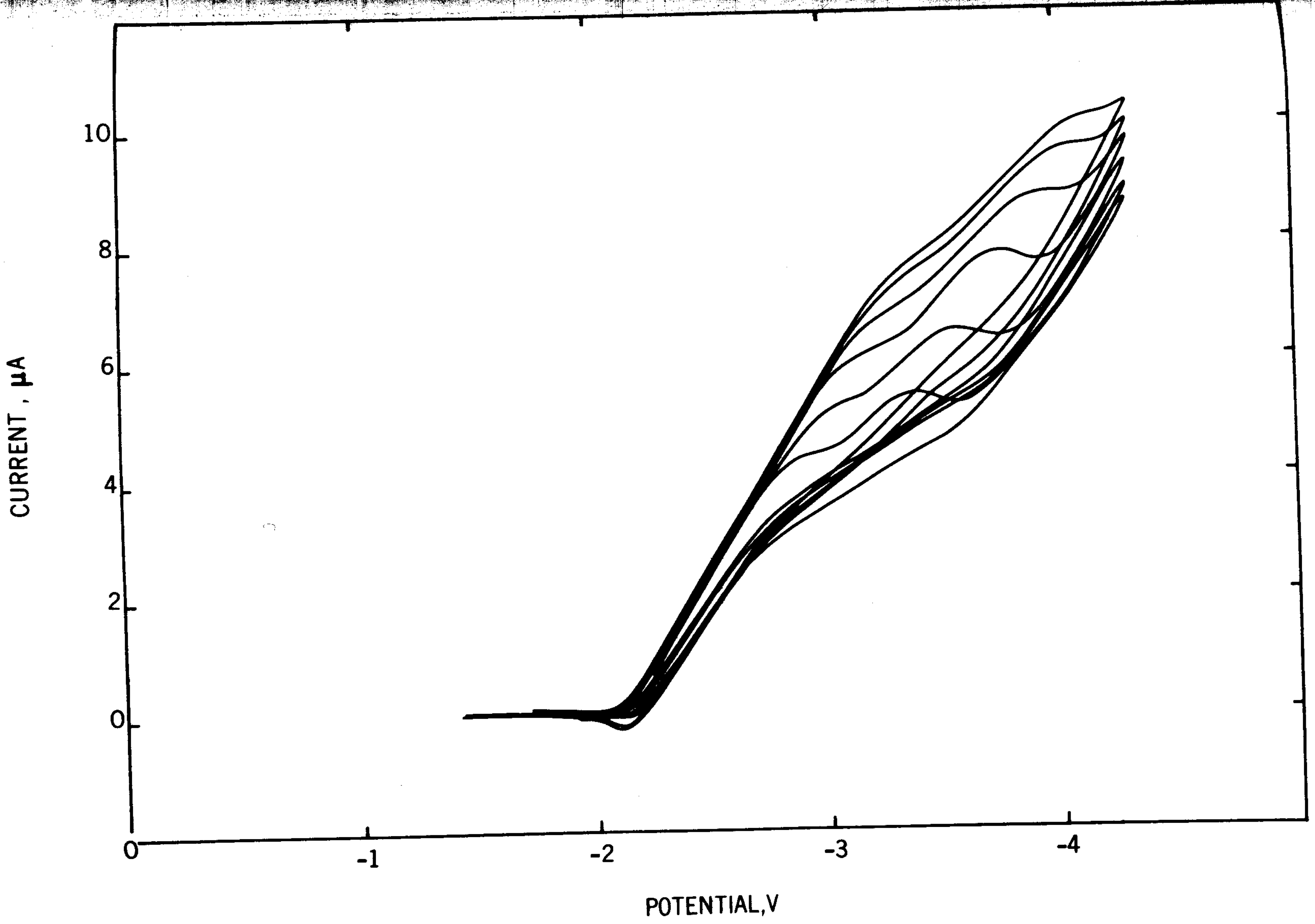
Electrolysis of stilbene in the presence of MMA again produced the characteristic green colour of the radical anion, and precipitation in methanal gave poly methylmethacrylate. No evidence for the incorporation of stilbene into the polymer was obtained, even at 2:1 MMA: stilbene feed ratios. This is the first reported polymerization of MMA initiated by the stilbene radical anion created electrochemically. A detailed cyclic voltammetry study was again thwarted due to interference by the methylmethacrylate reduction wave. This can be seen in Figure 17. Although the two waves of stilbene can be clearly distinguished, their sharpness has been lost due to overlap with the MMA wave. The most interesting observation that can be made from this voltammogram is the almost complete disappearance of the re-oxidation wave of stilbene. This signifies that the stilbene radical anion has reacted with MMA in the time scale of the sweep so that no radical anion is available for re-oxidation during the reverse cycle.

It should be mentioned at this stage that during the cyclic voltammetric study of the stilbene - MMA system, potential drift problems were encountered. Thus if voltammograms were taken during a polymerization, peak potentials

Figure 17. CYCLIC VOLTAMMOGRAM OF STILBENE IN THE PRESENCE OF METHYLMETHACRYLATE.

Stilbene (1mM) and MMA (1mM) in 0.1M Bu_4NClO_4 - THF solution. Pt wire reference.

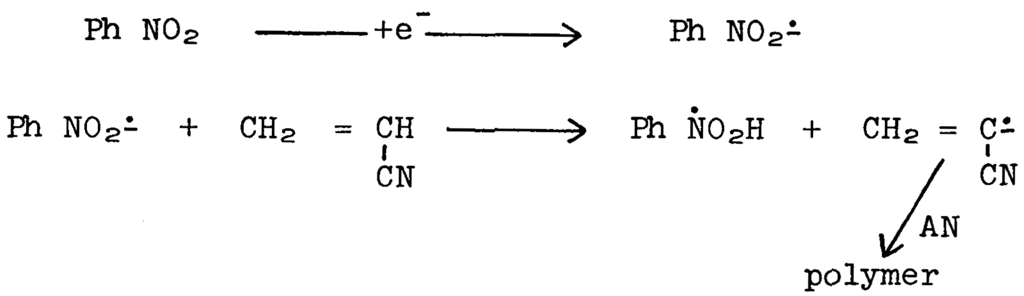
Scan rates 10,8,6,4,2,1 V/sec.


CURRENT , μA
10
8
6
4
2
0
0
-1
-2
-3
-4
POTENTIAL,V

were found to drift anodically with time, thus precluding the use of this technique during a polymerization reaction. Although this drift was not investigated further, the problem most likely originates in the unpoised nature of the reference electrode (168).

In the case of nitrobenzene, the monomers St, MMA and acrylonitrile (AN) were investigated. Electrolysis in the presence of St and MMA gave rise to the characteristic yellow-brown colour of the nitrobenzene radical anion (167), but no polymers were isolated in either case. Cyclic voltammetry studies of both these systems showed that the nitrobenzene wave was unaffected by the presence of either monomer, i.e. the voltammograms were merely superpositions of the nitrobenzene and monomer waves, signifying no interaction between the nitrobenzene radical anion and the monomers. This is in direct contrast to the stilbene - methylmethacrylate case.

Electrolysis of nitrobenzene in the presence of AN gave rise to the production of small quantities of polyacrylonitrile. No cyclic voltammetric study was carried out in this system. Coincident with these preliminary studies, Mengoli et al. (155) published work on the initiation of the anionic polymerization of acrylonitrile by nitrobenzene radical anions. Mengoli, who also found no interaction between nitrobenzene radical anions and St or MMA, used an amperometric technique to follow the decay of the radical anion and concluded from his work that the initiation proceeded by hydrogen abstraction from acrylonitrile:



$$\mathrm{Ph\ NO_2} \xrightarrow{+e^-} \mathrm{Ph\ NO_2^{\dot{-}}}$$

$$\mathrm{Ph\ NO_2^{\dot{-}}} + \mathrm{CH_2} = \underset{\mathrm{CN}}{\mathrm{CH}} \longrightarrow \mathrm{Ph\ \dot{N}O_2H} + \mathrm{CH_2} = \underset{\mathrm{CN}}{\mathrm{C^{\dot{-}}}} \xrightarrow{\mathrm{AN}} \text{polymer}$$

The same set of workers have carried out similar studies using radical anions such as benzophenone (156), naphthalene (158) and nitroaniline (159) as initiators in vinyl polymerizations. Their studies have shown the great potentialities of using electrochemical techniques in the study of some polymerization processes.

In summary, the following observations have been made:

1) cyclic voltammetry is a useful tool in the preliminary investigation of the characteristics of a system.

2) polymerization of monomers can be effected at potentials below the reduction potentials of the monomers by formation of a radical anion at this lower potential which is capable of initiating the polymerization.

3) in the polymerization of MMA initiated by the stilbene radical anion, no evidence for the incorporation of stilbene into the polymer was found even for an initial M_1 to M_2 feed ratio of 2:1 MMA : stilbene. This signifies that if this is considered in terms of a copolymerization, r_1 is extremely large while r_2 is the expected zero.

In the copolymerization of styrene (M_1) with stilbene (M_2), the r_1 value was found to be 2.3 in the THF (169). The above results indicate that when M_1 is methylmethacrylate, the r_1 value is much larger than this.

III. 1.2. PRELIMINARY STUDIES ON DONOR ACCEPTOR COMPLEX POLYMERIZATIONS.

The main objective of this thesis was to study some donor acceptor (DA) complex polymerizations using electrochemical techniques. Initially, several different monomer combinations were selected as possible candidates for a more detailed study. These are listed in Table II, together with the conditions used and the preliminary results obtained upon electrolysis.

TABLE II.

Monomer Combinations Tried and Initial Results Obtained.

Donor	Acceptor	Lewis Acid	Solvent	Current	Polymer obtained
stilbene	MMA	$ZnBr_2$	with or without	15mA	poly MMA
stilbene	AN	$ZnBr_2$	"	15mA	small amount of poly AN
stilbene	maleic anhydride	with or without	with	15mA	no polymer
St	MMA	$ZnCl_2$	with or without	15mA	copolymer
St	AN	$ZnBr_2$	"	15mA	copolymer

The results with stilbene and maleic anhydride were disappointing in that no polymer was produced on electrolysis. Of the five systems studied, this monomer combination was the only one to give rise to a coloured solution on mixing. The presence of such coloured solutions is usually an indication of charge transfer complex formation (170). Thus the presence of a yellow colour was a strong indication that a copolymerization of stilbene and maleic anhydride would proceed on suitable initiation to form an alternating copolymer in a similar way to other reported 'spontaneous' systems (37).

Despite numerous attempts to electrochemically initiate this system using various combinations of solvents and supporting electrolytes, no polymer was ever obtained. In double cells (anode and cathode compartments separated), the initial yellow solution underwent dramatic colour changes, ranging from green to red, depending on the conditions and the electrode compartment. Presumably a wide variety of side reactions were occurring in this system.

Styrene - Methylmethacrylate System.

Initial experiments were carried out in single cells (anode and cathode compartment not separated) using different electrode systems. The results are summarized in Table III.

TABLE III.

Copolymerization of Styrene and Methylmethacrylate in the Presence of $ZnCl_2$.

Sample	Yield in 90 mins	Anode/cathode material	Products obtained
SM 18	0.43g	Al/Al	copolymer only
SM 19	0.71g	Pt/Pt	copolymer + large amount of polystyrene

Conditions: MMA:St = 63:37; MMA:$ZnCl_2$ = 5:1; 0°C, bulk, 15 mA.

Using a cell in which the electrode compartments were divided by a sintered glass disc, the locus of the polymerization was found to be exclusively at the anode for times up to three hours. For longer time periods, pure copolymer in the cathode compartment accompanied the polymer formed in the anode.

It can be seen from Table III that the nature of the anode exerts a profound effect on the type of product obtained. Thus, using a platinum anode, copolymer together with large amounts of polystyrene is formed (low molecular weight, approximately 5000), whereas with an aluminum anode only pure copolymer is obtained (although small amounts of polystyrene is observed at higher degrees of conversion).

Gel permeation chromatographs of SM 18 and SM 19 clearly demonstrate the effect of electrode material on the product distribution (Figure 18). The high molecular weight copolymer, in the million region, is in direct contrast to the much lower molecular weights obtained in the absence of Lewis acids.

The reason for the differences between Pt and Al anodes in this system is not understood. Further work in this system was limited to using aluminum electrodes.

Experiments were carried out to determine the degree of electrolytic control, if any. The results, shown in Figure 19, demonstrate the linear dependence of copolymer yield on the amount of current passed. All samples were shaken in cyclohexane to dissolve any extraneous polystyrene produced.

Figure 18. GEL PERMEATION CHROMATOGRAM.

--- SM 18

___ SM 19

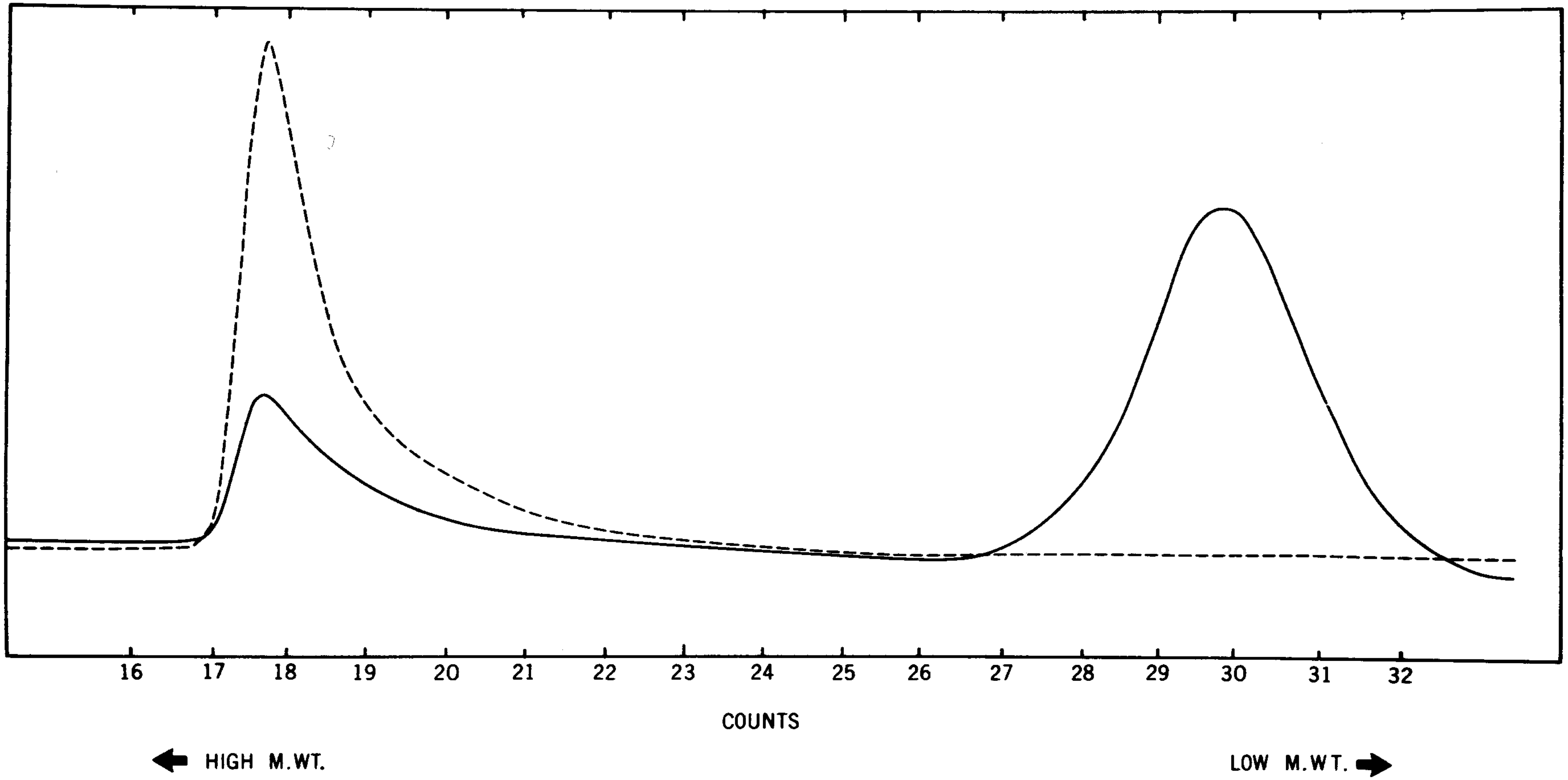
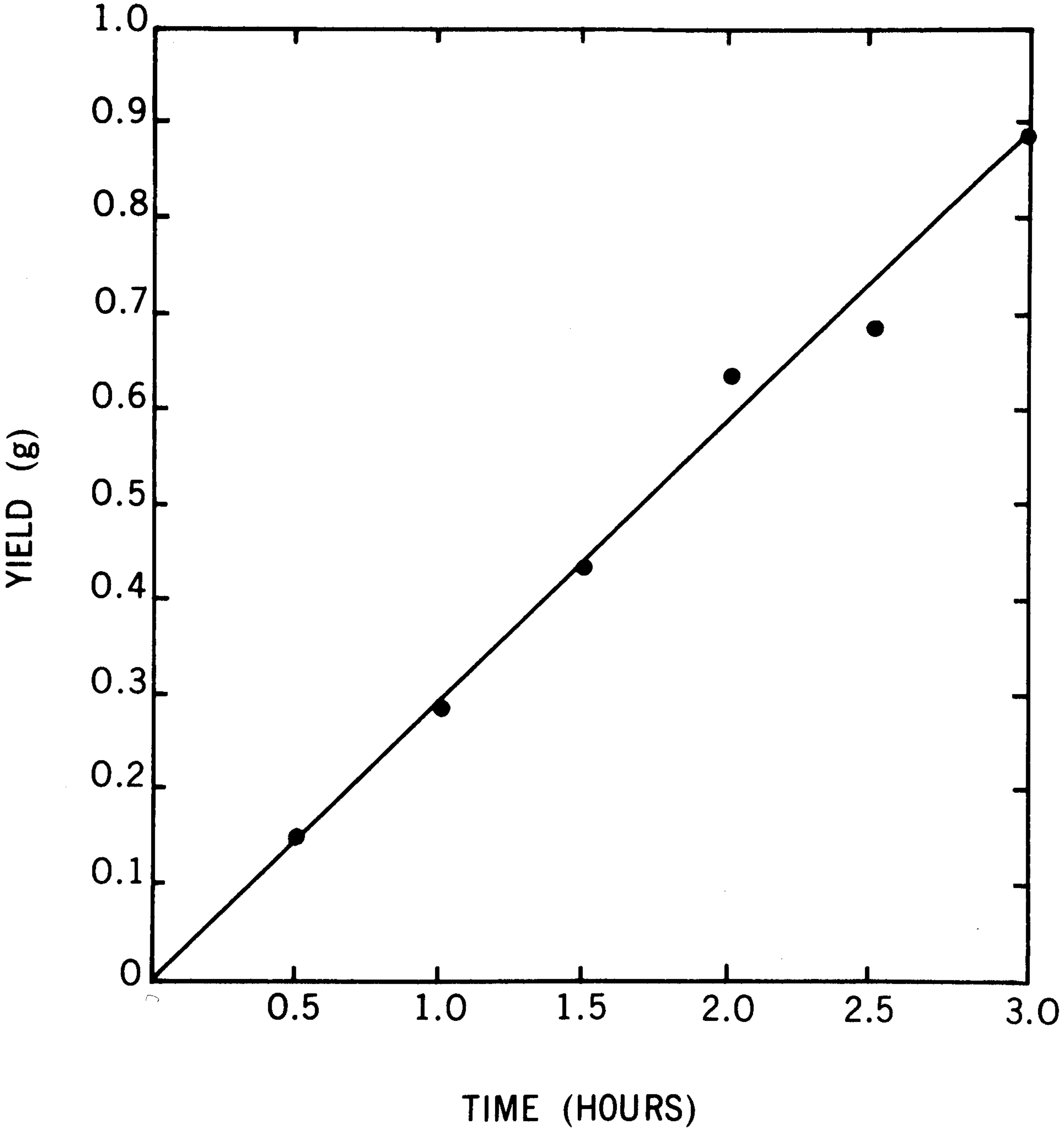

16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
COUNTS
HIGH M.WT.
LOW M.WT.

Figure 19. INFLUENCE OF ELECTROLYSIS TIME ON COPOLYMER YIELD. 0°C, 15mA.



YIELD (g)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.5
1.0
1.5
2.0
2.5
3.0
TIME (HOURS)

IR spectra of the copolymers showed the presence of both monomers in the copolymer, but demonstrated no differences from copolymers prepared in the absence of Lewis Acids. Elemental analyses indicated that these copolymers were high in MMA content, containing approximately 60% of this monomer. A typical NMR spectrum, shown in Figure 20, is similar to that obtained by Ikegami and Hirai (63) for a copolymer containing 67% MMA prepared in the presence of $ZnCl_2$, but differs from the spectrum obtained by Hirooka (79) for a 50:50 copolymer prepared in the presence of $AlEt_{1.5}Cl_{1.5}$.

Styrene - Acrylonitrile system.

Using cells in which the electrode compartments were separated, it was found that polymer was formed in both compartments. The cathode yield was far in excess of the anode yield, in direct contrast with the styrene - methylmethacrylate case. This can be seen in Table IV. The extremely low current efficiencies obtained in these systems is also evident from the data.

TABLE IV.

Comparison of Cathode and Anode Copolymer Yields.

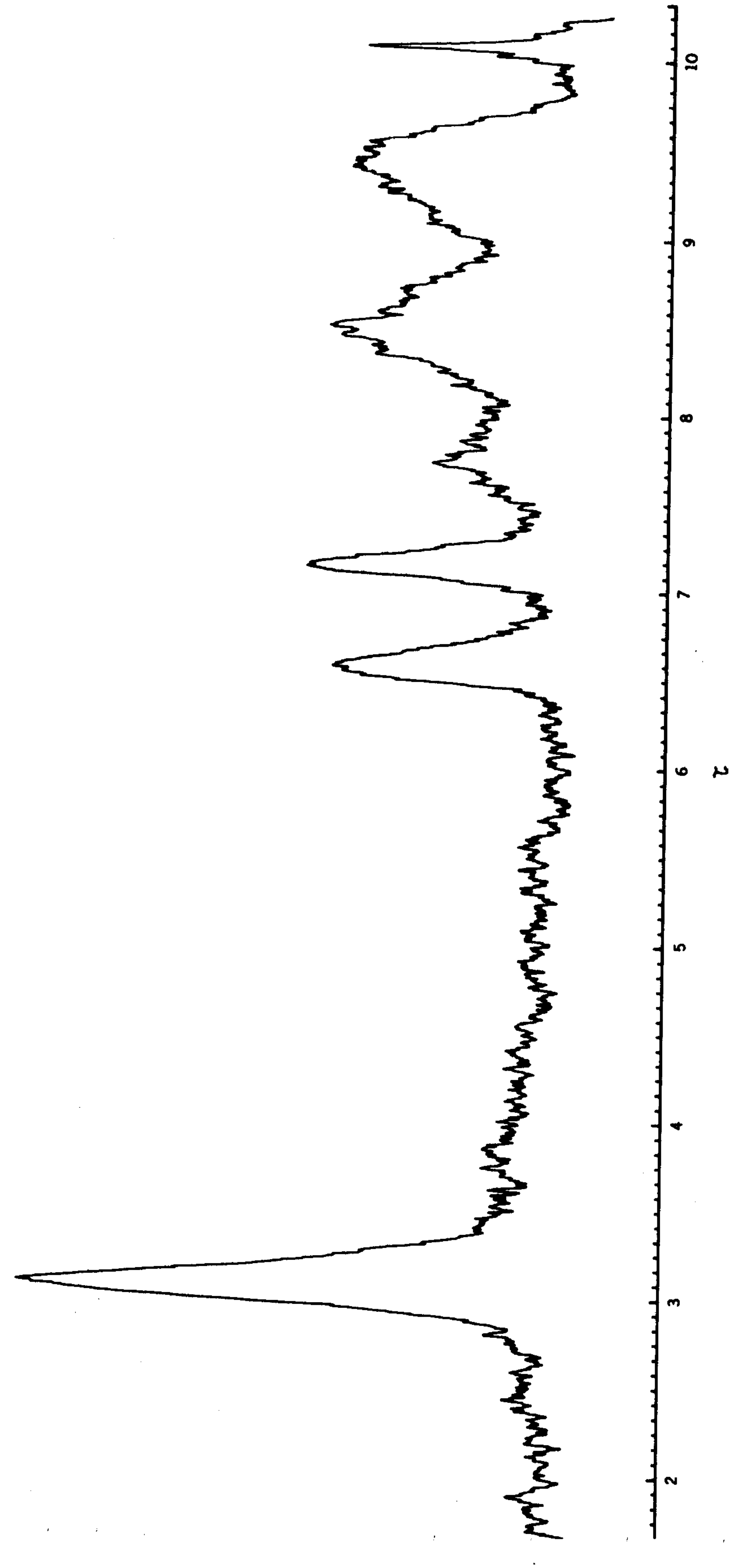
Electrode Compartment	No F.passed x 10^3	% conversion[a]	Faradaic Yield[b] x 10^4
cathode	2.4	8.5	2.92
anode	2.4	0.5	0.17

Conditions: 0.26 moles AN, 0.053 moles St, 0.019 moles $ZnBr_2$, 25 ml DCE; 0°C, Pt electrodes.

a based on St

b assuming a molecular weight of 1×10^6.

Figure 20. 60 MHz NMR SPECTRUM OF THE PRODUCT.


2
3
4
5
6
7
8
9
10
τ

At the cathode, only pure copolymer was obtained whereas copolymer and polystyrene was obtained at the anode, similar to the styrene - methylmethacrylate system. The effect of anode electrode material was investigated and the results are shown in Table V.

TABLE V.

Effect of Anode Electrode Material on Composition of the Product in the Styrene - Acrylonitrile System.

Anode material	Products obtained	polystyrene/ copolymer	%AN in copolymer
Al	polystyrene + copolymer	~4:1	51.0
Pt	polystyrene + copolymer	~4:1	50.0

Conditions: 0.26 moles AN, 0.053 moles St; An: $ZnBr_2$ = 14:1; 25 ml DCE, 15 mA for 2 hours.

It can be seen that the product composition is similar irrespective of the nature of the anode material. This is again in contrast to the styrene - methylmethacrylate system.

Elemental analyses of cathode copolymers revealed that their compositions were 50:50. This was also found for the copolymer fractions in the anode products.

The three major differences between the St - MMA system and the St - AN system can be summarized as follows:-

(a) yield of cathode copolymer in St - AN case $\gg$ yield of cathode copolymer in St - MMA case.

(b) change from Pt to Al anode causes change in relative product composition in St - MMA case but not in St - AN case.

(c) cathode and anode copolymers have a 1:1 composition in the St - AN case, but have high MMA content in the St - MMA case.

From these results the styrene - acrylonitrile system at the cathode seemed the most attractive for further detailed studies.

III.2. STYRENE - ACRYLONITRILE SYSTEM.

III.2.1. GENERAL CHARACTERISTICS.

Introduction

The central purpose of this thesis was to investigate the feasibility of electrochemical initiation of donor acceptor complex polymerizations and to compare the results with those obtained by conventional initiation techniques. Since electro-initiation provides a means of varying the initiation rate at a constant temperature, the technique may be particularly useful in donor acceptor systems since any delicate temperature - equilibrium balance can remain undisturbed.

Controlled potential electrolysis was employed during this study, more reproducibility being obtained relative to controlled current experiments. A possible reason for this irreproducibility will be given later. In all experiments, except where noted, the anode and cathode compartments were separated by sintered discs.

Results and Discussion

The experiments summarized in Table VI demonstrate that 1:1 copolymers are produced over a wide range of initial feed ratios.

TABLE VI.

Effect of Monomer Feed Ratio on Copolymer Composition.

AN/St in feed	%AN in copolymer
83 : 17	50.8
50 : 50[a]	52.2
35 : 65[a]	51.0

Conditions: St + AN = 0.31 moles, $ZnBr_2$ = 0.019 moles
DCE = 25 ml; 0°C, 0.72 x 10^{-3}F.
a - polymer insoluble in reaction solution.

The alternating character of the polymer was identified by the following procedures:

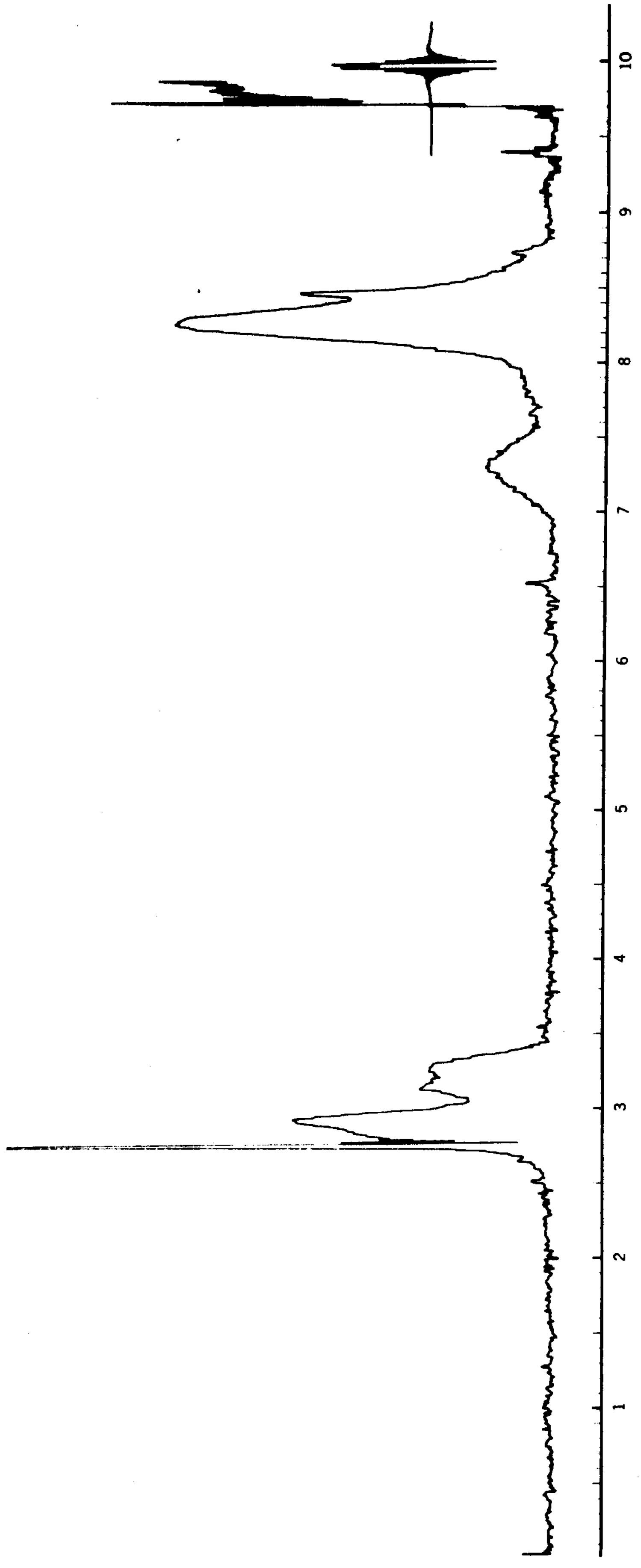
(a) Elemental and IR analyses showed a 1:1 mole ratio of St to AN in the copolymers.

(b) The IR spectra of the copolymers, identical to the spectrum of Figure 8, showed the presence of both St and AN units in copolymer.

(c) The NMR spectrum (Figure 21) confirms the presence of the copolymer and comparison with the calibration spectra (Figures 10 and 11), indicates an alternating sequence of AN and St units.

Due to the completely homogeneous nature of the polymerizations carried out at 83:17 AN:St feeds, all further work was carried

Figure 21. 100 MHz NMR SPECTRUM OF THE COPOLYMER.


1
2
3
4
5
6
7
8
9
10
τ

out at this feed ratio.

Table VII shows the effect of the degree of conversion on the copolymer composition and limiting viscosity.

TABLE VII.

Effect of Degree of Conversion on Composition and Limiting Viscosity.

Yield (g)	Time (min.)	No. Faradays x 10^3	% Conversion[a]	%AN in copolymer	$(\eta)^b$ dl/g
0.20	60	0.52	2.43	48.5	2.52
0.36	90	0.90	4.37	51.0	3.24
0.77	165	1.35	9.24	50.0	2.43
1.00	210	2.12	12.13	48.5	2.63
1.34	390	2.93	16.25	51.0	3.32

Conditions: 0.26 moles AN, 0.053 moles St, 0.019 moles $ZnBr_2$,
25 ml DCE; 25°C, controlled potential.
a - based on St.
b - THF, 30°C.

The composition is essentially invariant with conversion and there is no correlation between the limiting viscosity and extent of the reaction.

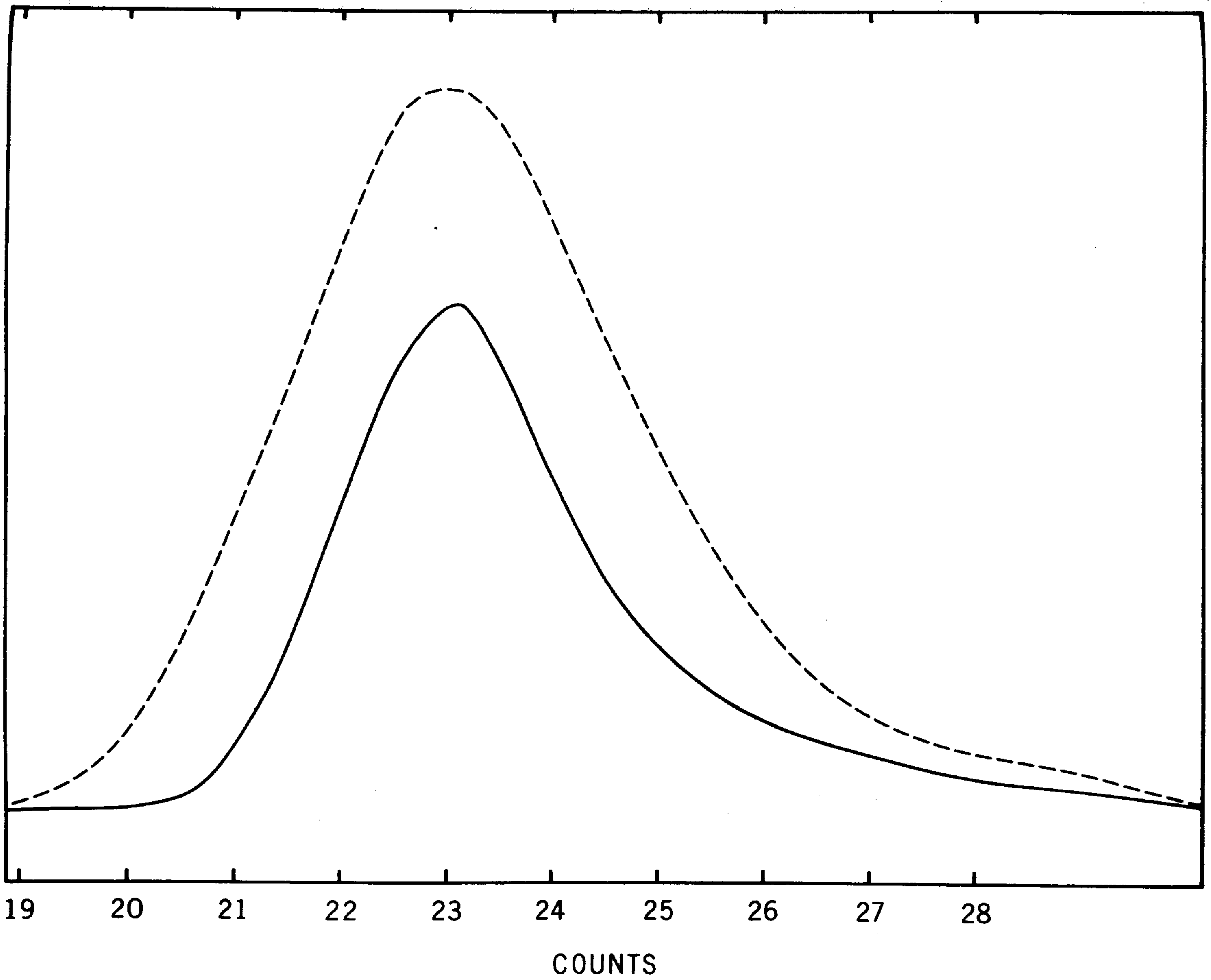
The high limiting viscosities are characteristic of these donor acceptor complex systems. The gel permeation chromatograms (G.P.C.) of these polymers exhibited very broad molecular weight distributions, as can be seen in Figure 22. In many cases it was not possible to obtain accurate peak molecular weights of these copolymers since the upper limits of their distributions fell significantly above the highest standard

Figure 22. GPC MOLECULAR WEIGHT DISTRIBUTION OF THE COPOLYMER.

--- St - AN copolymer

—— Styrene standard #61970

Mw 2.145×10^6 ; Mn 1.78×10^6


19
20
21
22
23
24
25
26
27
28
COUNTS

[illegible]

sample of polystyrene (Waters #61970, peak molecular weight 1,987,000) available to us, calculation of molecular weight being quite sensitive to calibration in this region.

It was observed during these and other experiments that the viscosity of the reaction medium became unusually high at fairly low conversions (of the order of 8%), and the solutions took on a 'pearly blue' appearance. These observations may be indicative of intermolecular association which is known to exist in zinc chloride - methylmethacrylate solutions (171).

Table VIII demonstrates that the copolymer composition is also invariant with change in $ZnBr_2$ concentration for high AN:$ZnBr_2$ mole ratios.

TABLE VIII.

Copolymer Composition as a Function of AN/$ZnBr_2$ Mole Ratio.

AN/$ZnBr_2$ mole/mole	%AN in copolymer
10:1	50.5
20:1	49.0
40:1	50.3

Conditions: 0.26 moles AN, 0.053 moles St, 25ml DCE; 25°C, controlled potential electrolysis. All samples correspond to approx. 6% conversion w.r.t. St.

The variation of copolymer composition as a function of rate of initiation was investigated by applying different currents (controlled current experiments), the total amount of charge passed being the same in each experiment. The results are given in Table IX.

TABLE IX.

Copolymer Composition as a Function of Rate of Initiation.

Current (mA)	%AN in copolymer
7	51.2
15	50.6
30	49.6

Conditions: 0.26 moles AN, 0.053 moles St, 0.019 moles $ZnBr_2$, 25 ml DCE; 25°C, 0.72×10^{-3}F passed.

It can be seen that the rate of initiation does not affect the copolymer composition.

The reaction profile of a typical run at controlled potential is given in Figure 23 (data from Table VII). Use of an Ag/Ag^+ reference electrode yielded identical results to a Pt wire reference, thereby justifying the latter's use in these systems. Blank solutions yielded negligible polymer under these conditions. Thus the polymer yield is a function of the number of Faradays passed through the solution. Replotting the data in Figure 23 as a function of the square root of the amount of Faradays passed yields Figure 24.

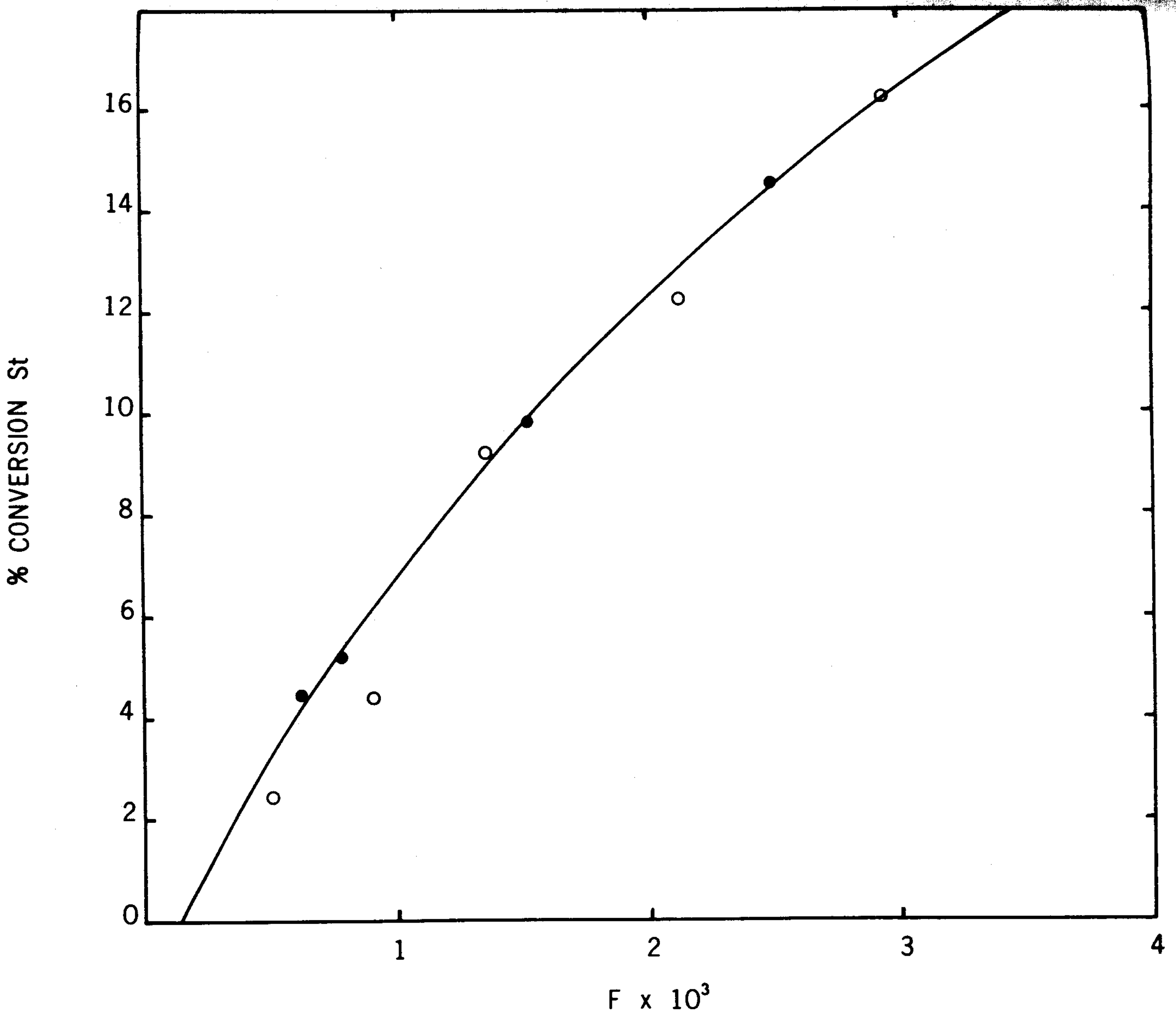
Cyclic Voltammetry Studies.

It has already been shown that cyclic voltammetry is a useful technique in the preliminary investigation of the characteristics of a system. Coupled with the methods of controlled potential electrolysis, cyclic voltammetry enables

Figure 23. COPOLYMER FORMATION AS A FUNCTION OF THE NUMBER OF FARADAYS PASSED.

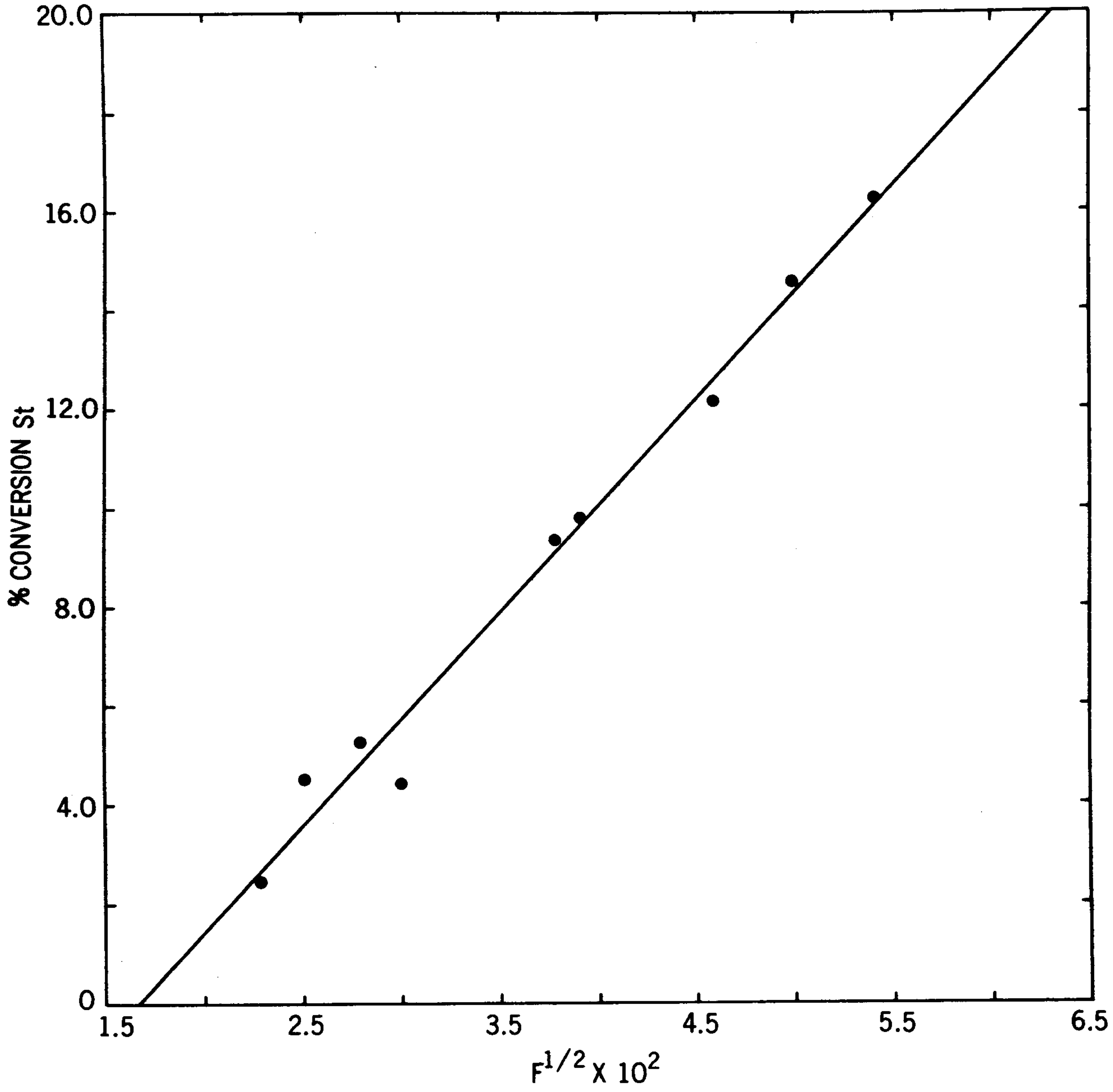
● Pt wire reference (from Table VII)

o Ag/Ag$^+$ reference


% CONVERSION St
0
2
4
6
8
10
12
14
16
1
2
3
4
F x 10^3

[illegible]

Figure 24. DEPENDENCE OF RATE OF POLYMERIZATION ON THE SQUARE ROOT OF THE CHARGE PASSED.


20.0
16.0
12.0
8.0
4.0
0
% CONVERSION St
1.5
2.5
3.5
4.5
5.5
6.5
$F^{1/2} \times 10^2$

the polymer chemist to decide the most likely initiation step in a polymerization reaction (190).

Figure 25 shows a cyclic voltammogram of the AN - $ZnBr_2$ system in dichloroethane solvent using TBAP as supporting electrolyte. The background curve shows the same system in the absence of $ZnBr_2$. It can be seen that the addition of $ZnBr_2$ gives rise to a fairly complex voltammogram. Since controlled potential electrolysis was employed in this thesis, only the first reduction wave is of interest here. Thus a cyclic voltammogram of the first wave only (Figure 26) shows that the re-oxidation peak B is associated with reduction peak A. A voltammogram of this system in the absence of AN is seen in Figure 27. Comparison with Figure 26 conclusively shows that the first wave in this system is associated with the reduction of Zn(II) to Zn(0). Formation of zinc metal on the working electrode is a possible explanation for the very large oxidation wave B compared to reduction wave A. Asymmetric peaks due to adsorption or film effects on the electrode surface are quite common in voltammetry studies, but are not clearly understood (148).

It should be noted that all controlled potential work was carried out at potentials corresponding to this first reduction wave.

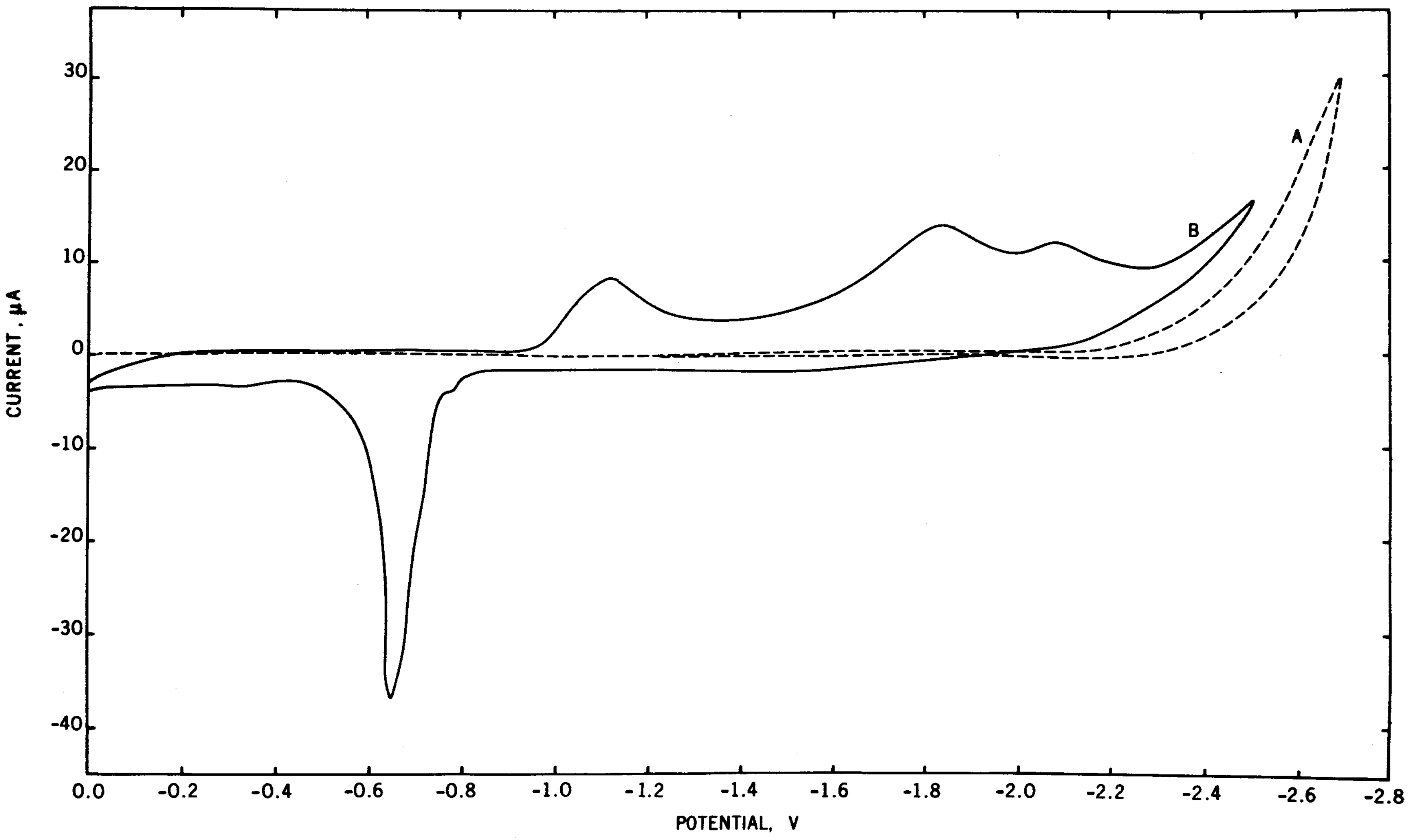
Conclusions.

The styrene - acrylonitrile - zinc bromide system has been found to yield an alternating copolymer under various

Figure 25. CYCLIC VOLTAMMOGRAM OF THE AN - $ZnBr_2$ SYSTEM.

A AN(1mM) in 0.1M Bu_4NClO_4 - DCE.
B AN(1mM) + $ZnBr_2$ (1mM) in 0.1M Bu_4NClO_4 - DCE.

Scan rate 100 mV/sec.



CURRENT, µA
30
20
10
0
-10
-20
-30
-40
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
-1.6
-1.8
-2.0
-2.2
-2.4
-2.6
-2.8
POTENTIAL, V
A
B

Figure 26. CYCLIC VOLTAMMOGRAM OF THE FIRST REDUCTION STEP IN THE AN - $ZnBr_2$ SYSTEM.

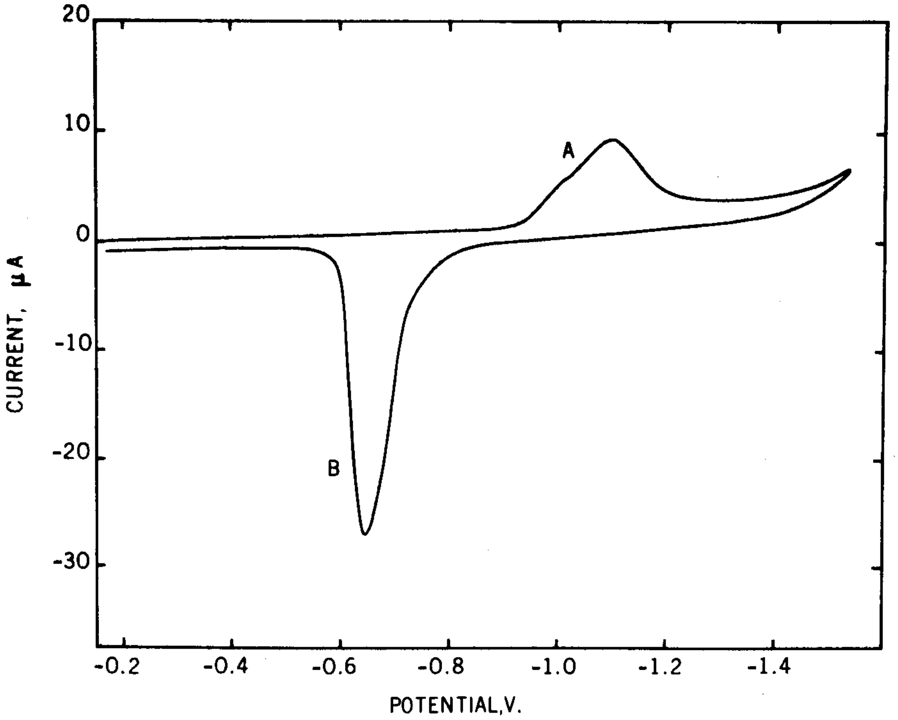
AN (1mM) + $ZnBr_2$(1mM) in 0.1M Bu_4NClO_4 - DCE.

Scan rate 100 mV/sec.

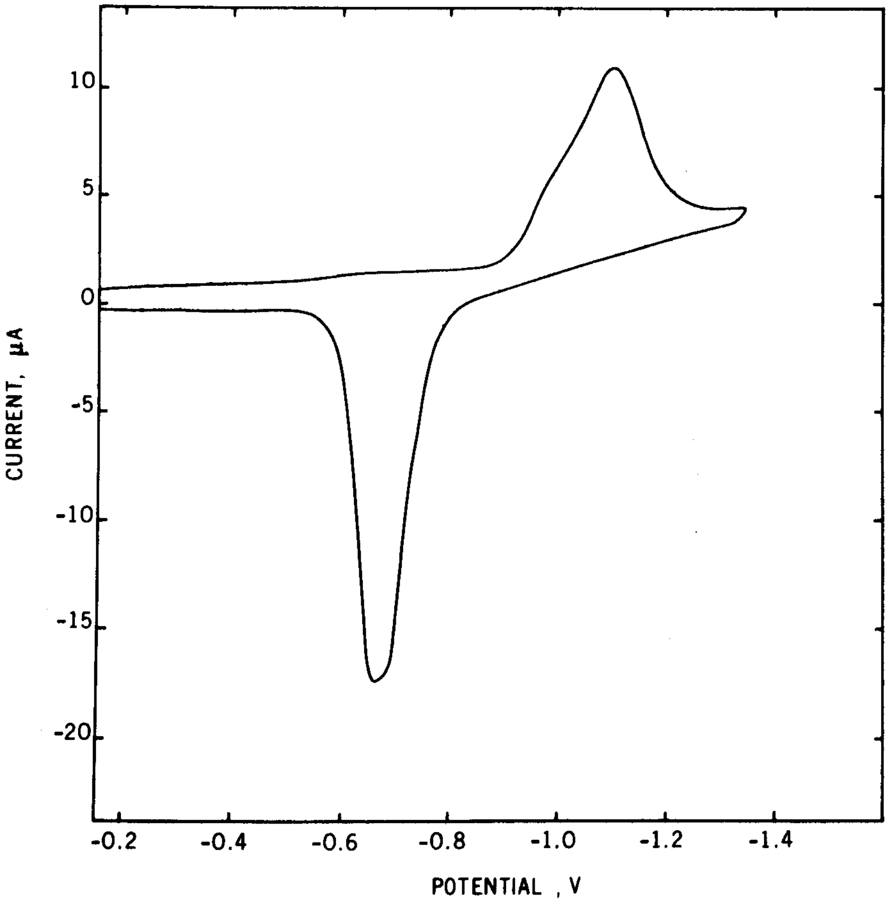
Figure 27. CYCLIC VOLTAMMOGRAM OF $ZnBr_2$.

Saturated solution of $ZnBr_2$ in 0.1M Bu_4NClO_4 - DCE.

Scan rate 100 mV/sec.



20
10
0
-10
-20
-30
CURRENT, μA
A
B
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
POTENTIAL,V.



10
5
0
-5
-10
-15
-20
CURRENT, μA
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
POTENTIAL , V

reaction conditions. Thus elemental and IR analyses show that the copolymers contain 50% of each monomer irrespective of degree of conversion, zinc bromide concentration and rate of initiation. Although NMR spectra only indicate an alternating structure, proof is obtained from the independence of copolymer composition on the comonomer feed ratio.

The polymerization apparently proceeds at a rate dependent on the square root of the amount of charge passed, compatible with a process of second order termination and first order initiation. However, the Faradaic dependence is made more complex by the observation of "after effects" in this system.

III.2.2. AFTER EFFECT.

Introduction.

Free radical polymerizations conducted under the influence of electrolytic current usually stop on the cessation of current and resume when current is passed again (189). However, some workers have observed after effects in free radical polymerizations manifested by continued rates of copolymerization after the current has been stopped (172-174). The system presently under study was investigated for the appearance of such after effects.

Results.

Figure 28 shows the very large after effects that are obtained in this system in the presence or absence of a solvent. Thus 5.0×10^{-4} Faradays were passed in 90 minutes, the current switched off, and the post polymerization followed as a function

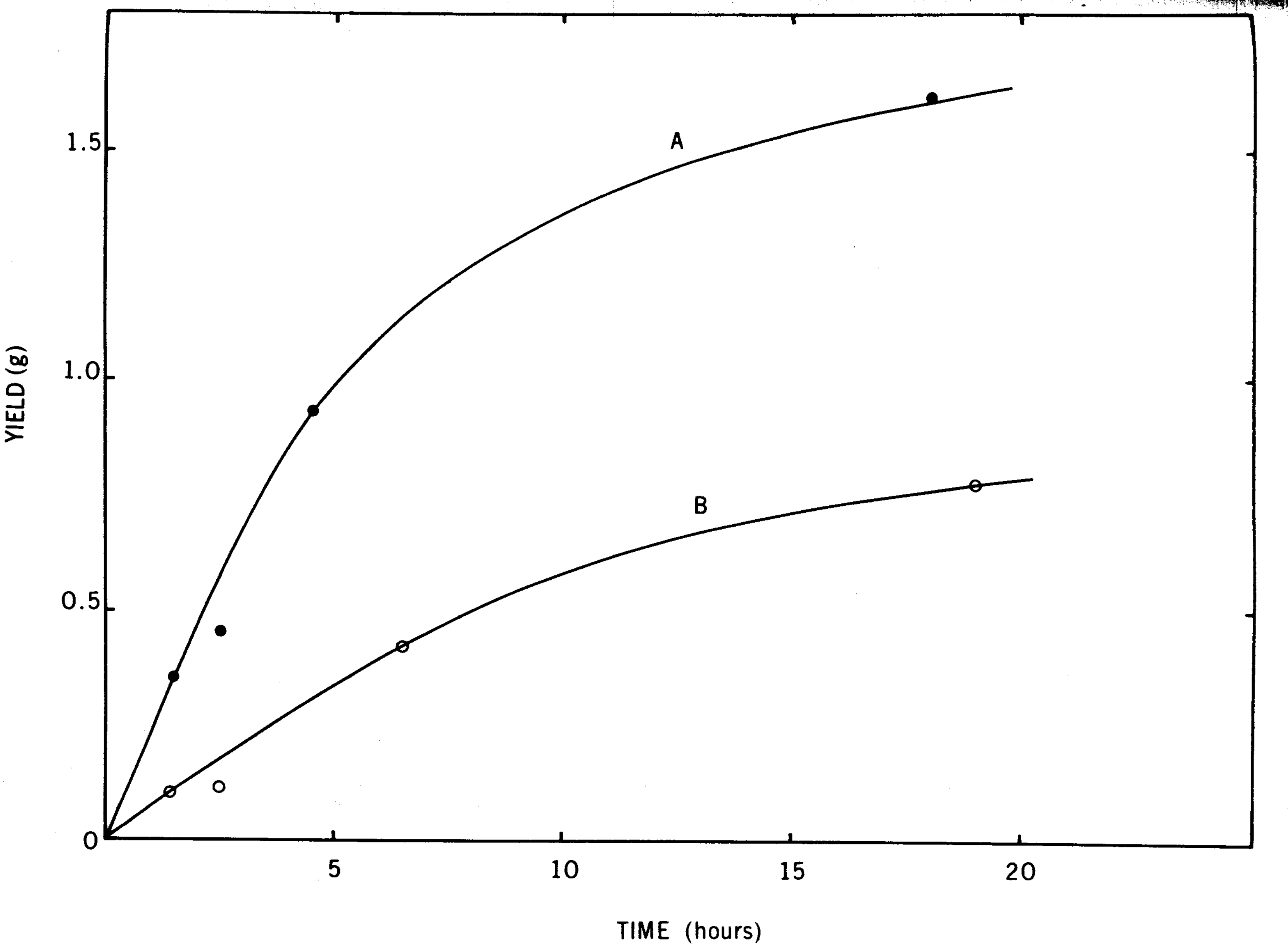
Figure 28. AFTER EFFECT IN BULK AND IN SOLVENT.

Conditions:

Curve A 0.52 moles AN, 0.106 moles St, 0.038 moles $ZnBr_2$.

Curve B 0.26 moles AN, 0.053 moles St, 0.019 moles $ZnBr_2$, 25 ml DCE.

0°C, 5.0×10^{-4}F passed in 90 minutes at controlled potential.


YIELD (g)
1.5
1.0
0.5
0
5
10
15
20
TIME (hours)
A
B

of time. The magnitude of the after effect can be seen on comparing its reaction profile to that of a reaction carried out under the same conditions but with continuous electrolysis. This is shown in Figure 29.

It can again be seen that the after effect is quite large and not much different from experiments employing continuous electrolysis. It should be pointed out that at 0°C, no polymer was formed after 40 hours in the absence of electrolysis.

The fact that the after effect is not lowered in the single cell may signify that the propagating species in the anode and cathode compartments are of a similar nature. This further suggests that the entity must be radical in nature since anions and cations created at the cathode and anode, respectively, would annhiliate each other, as has been observed in some instances (133,135). The validity of this proposal will be investigated later.

The effects of various initial passages of current followed by polymerization for 5 hours are shown in Figure 30. The minimum pulse for detectable post-polymerization was found to be 5 x 10^{-5}F. An important observation was made during these experiments in that no trace of zinc metal was seen on the cathode when the pulse was 2.5 x 10^{-5}F. All other runs in this experiment gave varying amounts of zinc on the cathode depending on the magnitude of the pulse. The importance of this observation will become obvious later.

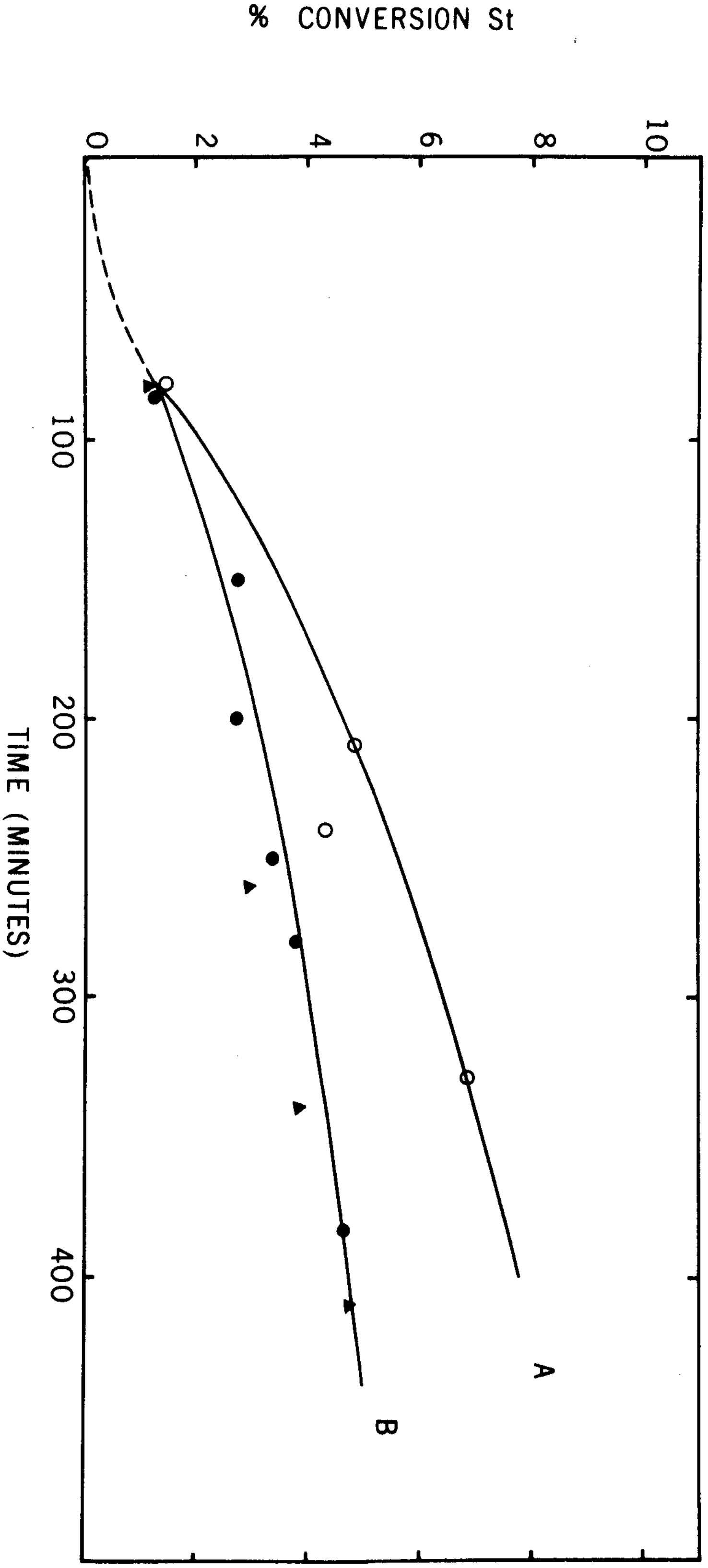
Figure 29. COMPARISON OF AFTER EFFECT AND CONTINUOUS ELECTROLYSIS.

o Continuous electrolysis.

● Electrolysis stopped after 80 mins.

▲ After effect in an undivided cell, electrolysis stopped after 80 mins.

0°C, controlled potential, conditions identical to those for curve B, Figure 28.



% CONVERSION St
0
2
4
6
8
10
TIME (MINUTES)
100
200
300
400
A
B

Figure 30. EFFECT OF INITIAL PASSAGES OF CURRENT.

○ 4.0×10^{-4}F

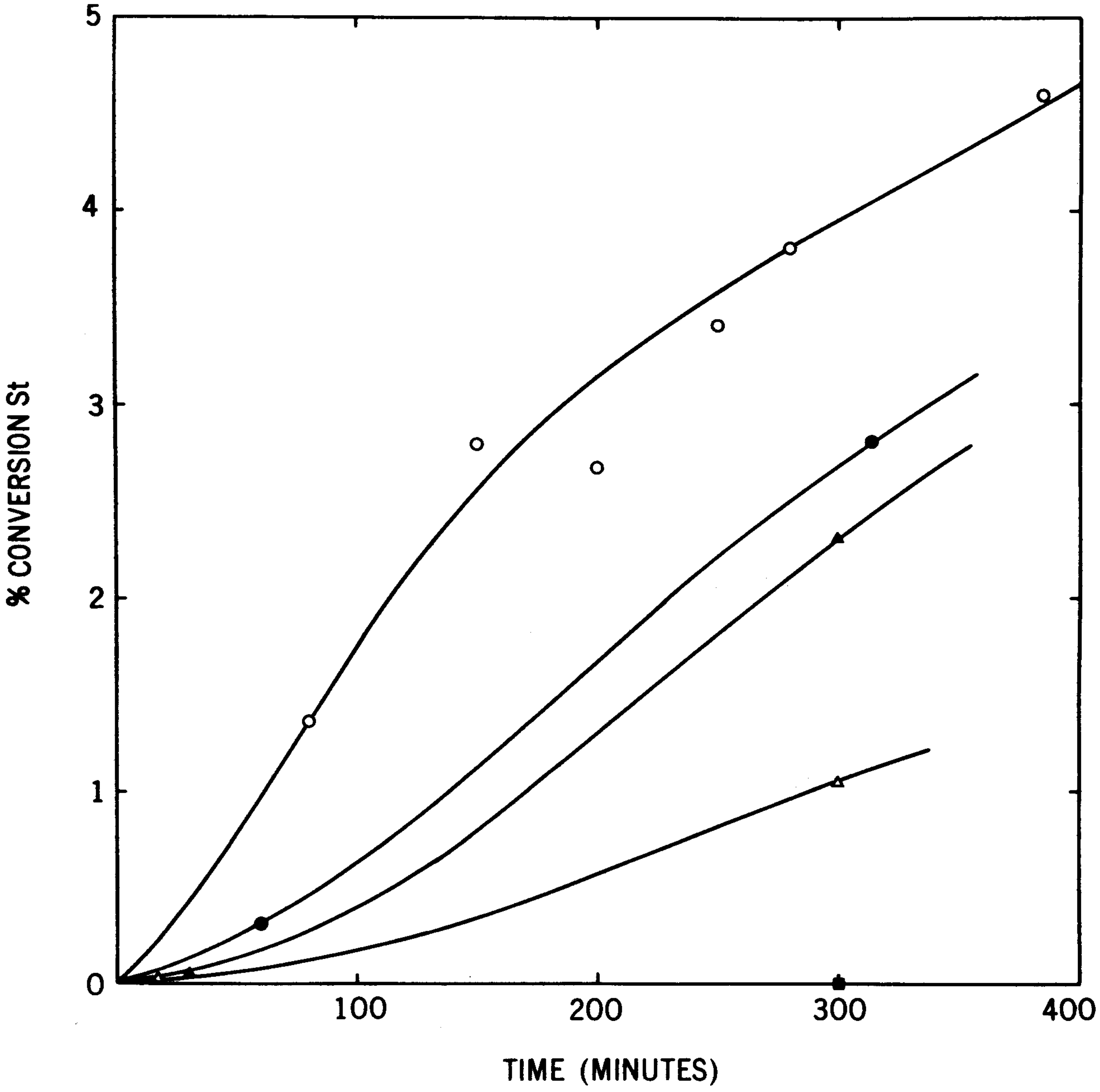
● 2.0×10^{-4}F

▲ 1.0×10^{-4}F

△ 0.5×10^{-4}F

■ 0.25×10^{-4}F

Conditions same as for Figure 29.


% CONVERSION St
0
1
2
3
4
5
100
200
300
400
TIME (MINUTES)

For the sake of comparison, this system was investigated for the presence of a U.V. after effect. The solution was subjected to 2537 Å light for three minutes, the lamp switched off and the yield determined as a function of time as before. The results are plotted in Figure 31. It is clear that the after effect observed in the electrochemical situation has no counterpart in the U.V. case.

Discussion.

An after effect, or post polymerization, manifests itself in continued rates of polymerization after initiation has ceased. It has been observed in a number of systems both photochemical (191) and electrochemical (141).

Electrochemical initiation may produce an active compound or an activated monomer which can continue to polymerize without the additional passage of current. Such is the case in the 'living' polymerizations conducted under anionic conditions (135,152,192). Alternatively, the passage of current can generate an initiator or catalyst which is stable in the reaction medium. This is postulated to occur in some cationic systems (133,141). A third possibility is the existence of a type of gel effect which effectively reduces the rate of termination. Gel effects are caused by an increase in viscosity of the medium and also by the existance of trapped polyradicals (5). In these cases the radicals can be considered to be 'protected' since their effective lifetimes are increased considerably (193).

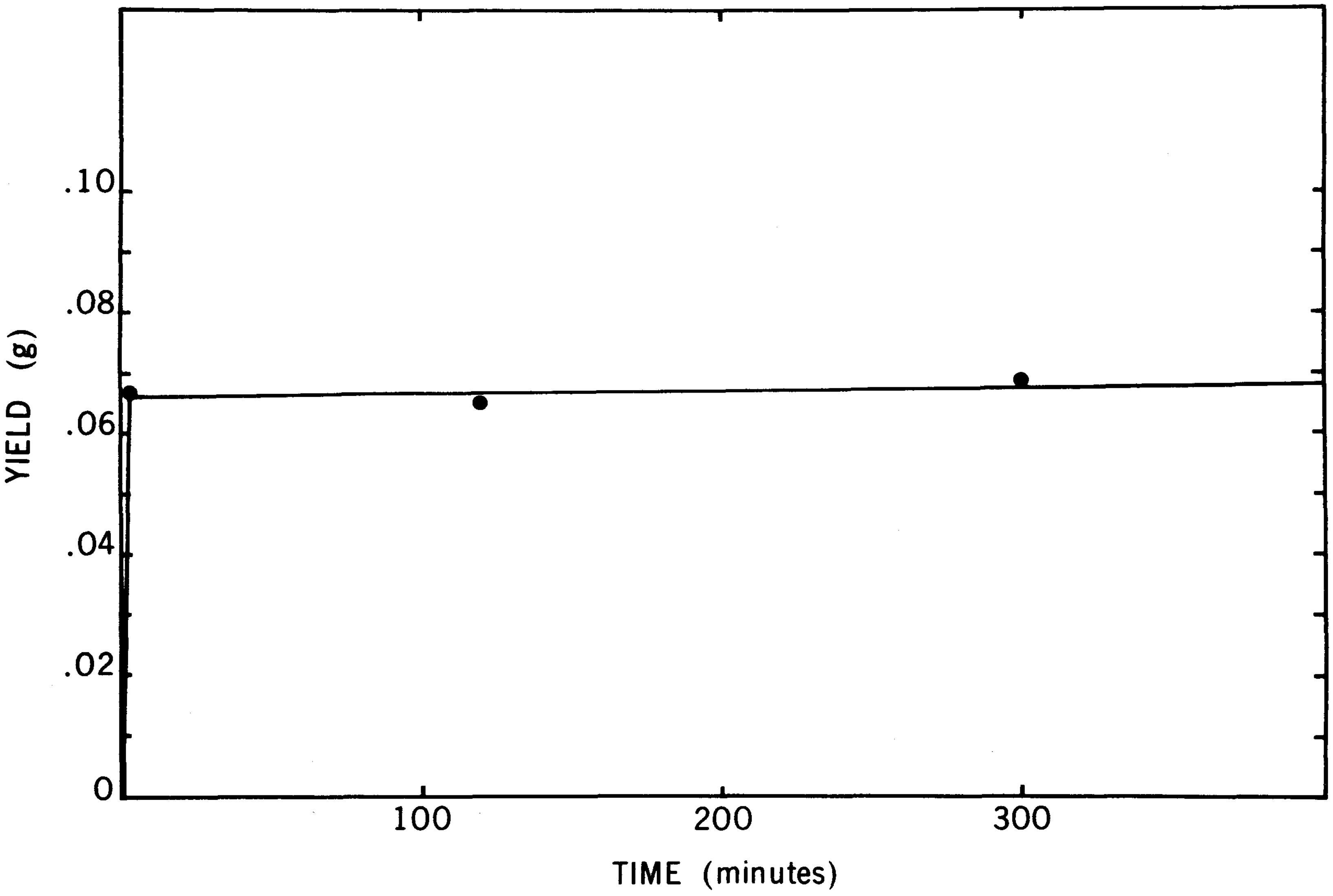
In the present system protected radicals could arise from delocalization of the electrons in the AN moiety by the

Figure 31. U.V. AFTER EFFECT.

Conditions;

0.52 moles AN, 0.106 moles St, 0.038 moles $ZnBr_2$, 50 ml DCE. 25°C, U.V. lamp on for 3 minutes.

U.V. LAMP SWITCHED OFF AFTER 3 MINUTES



associated $ZnBr_2$ (24). However, these protected radicals should give rise to an after effect irrespective of their mode of formation. The absence of a U.V. after effect is evidence against such an explanation.

It has already been noted that these polymerizing solutions have abnormally high viscosities at fairly low conversions. This and the 'pearly blue' colour observed may be indicative of microgel particles similar to those found by Zubov (194) for the polymerization of allyl acetate in the presence of $ZnCl_2$. Trapped polyradicals in such a microgel is thought to give rise to the observed after effect in the anodic polymerization of methylmethacrylate (174). However, this argument does not account for the after effect in the present situation since polymerization under U.V. conditions also gives rise to highly viscous and pearly blue solutions at low conversions, and no after effect is found in this case.

The possibility of existence of 'living' anionic species in the present situation is highly unlikely. Rigorous purification techniques are needed to observe this type of polymerization, the living anions being extremely sensitive to impurities such as water. In the system under study these purification techniques were not employed and indeed, polymerization has been found to occur with essential undiminished rates in the presence of added water (175).

The most likely explanation of the after effect is the electrochemical generation of an initiator or catalyst which is stable in the reaction medium but which cannot be formed photolytically. This unit or catalyst is then capable of initiating the polymerization in some way. The present situation is similar to the cationic polymerization of isobutyl vinyl ether (141) in which very small current pulses (of the order of μF) were used to initiate an extremely fast polymerization. In this case cyclic voltammetry studies indicated that an initiating substance was being generated at the electrode surface. This initiating substance was postulated to arise from the oxidation of the supporting electrolyte (sodium tetraphenylboride) in one of two possible ways:

$$\text{(i)} \quad BF_4^- \quad -e^- \longrightarrow BF_4\cdot$$

$$\text{(ii)} \quad SH + BF_4\cdot \longrightarrow S\cdot + HF + BF_3$$

It was considered likely that either $BF_4\cdot$ or the HF/BF_3 catalyst/cocatalyst pair could initiate the cationic polymerization.

In the styrene - acrylonitrile - $ZnBr_2$ case considered here, a similar type of process must be occurring. Cyclic voltammetry measurements have shown that at the potentials employed in the electrolysis of these solutions, the only process that can occur is the reduction of Zn^{2+} to zinc metal. This and the observation that polymer is produced only when zinc is deposited on the cathode suggests that zinc metal in some way causes the after effect.

Two exploratory experiments were carried out to confirm this postulation. The first involved the use of a cell normally used for cyclic voltammetry (Figure 5), two 1" square platinum electrodes replacing the three electrode set-up. The solution was electrolysed for a short period of time after which the current was switched off and the cell tipped so that the electrodes no longer made contact with the solution. The results were compared with those in which the cell was not tipped, and are given in Table X.

TABLE X. Effect of Cell Tipping.

		Cell Tipped	Cell Not Tipped
Yield polymer (g)	(1)	0.21g	0.39g
	(2)	0.20g	0.41g

Conditions: 0.26 moles AN, 0.053 moles St, 0.019 moles $ZnBr_2$
25 ml DCE.
4 x 10^{-4}F passed then left for 5½ hours at 0°C.

It can be seen that the after effect yield is markedly reduced on removing the electrodes from the solution after electrolysis.

A second experiment involved plating out zinc metal from an acetonitrile/$ZnBr_2$ solution. The zinc coated electrode was then removed, washed with DCE and finally placed into a solution of AN,St,$ZnBr_2$ in DCE (usual proportions) and left after degassing, at 0°C for 5 hours. Precipitation of polymer after this time period signified the presence of a true'zinc effect'. As a final confirmation of the existence of this effect, experiments were performed in the absence of electrolysis but with zinc dust added. The effect of different amounts of added zinc on the yield of copolymer produced is seen in Figure 32. It can be seen that the polymer yield increases with the amount of zinc dust added, up to a limiting amount. The polymers obtained were examined in the usual way (I.R., N.M.R., G.P.C.) and found to be identical in every way to the polymers formed under electrolysis conditions in the cathode.

Thus it has been conclusively shown that zinc metal is involved in producing the large after effects observed in the St-AN system. Even more surprising is the fact that zinc dust can initiate or catalyse the polymerization. This 'zinc effect' is totally unexpected and constitutes a novel but extremely interesting catalytic or initiating system deserving further study.

III.2.3. ZINC EFFECT.

Introduction.

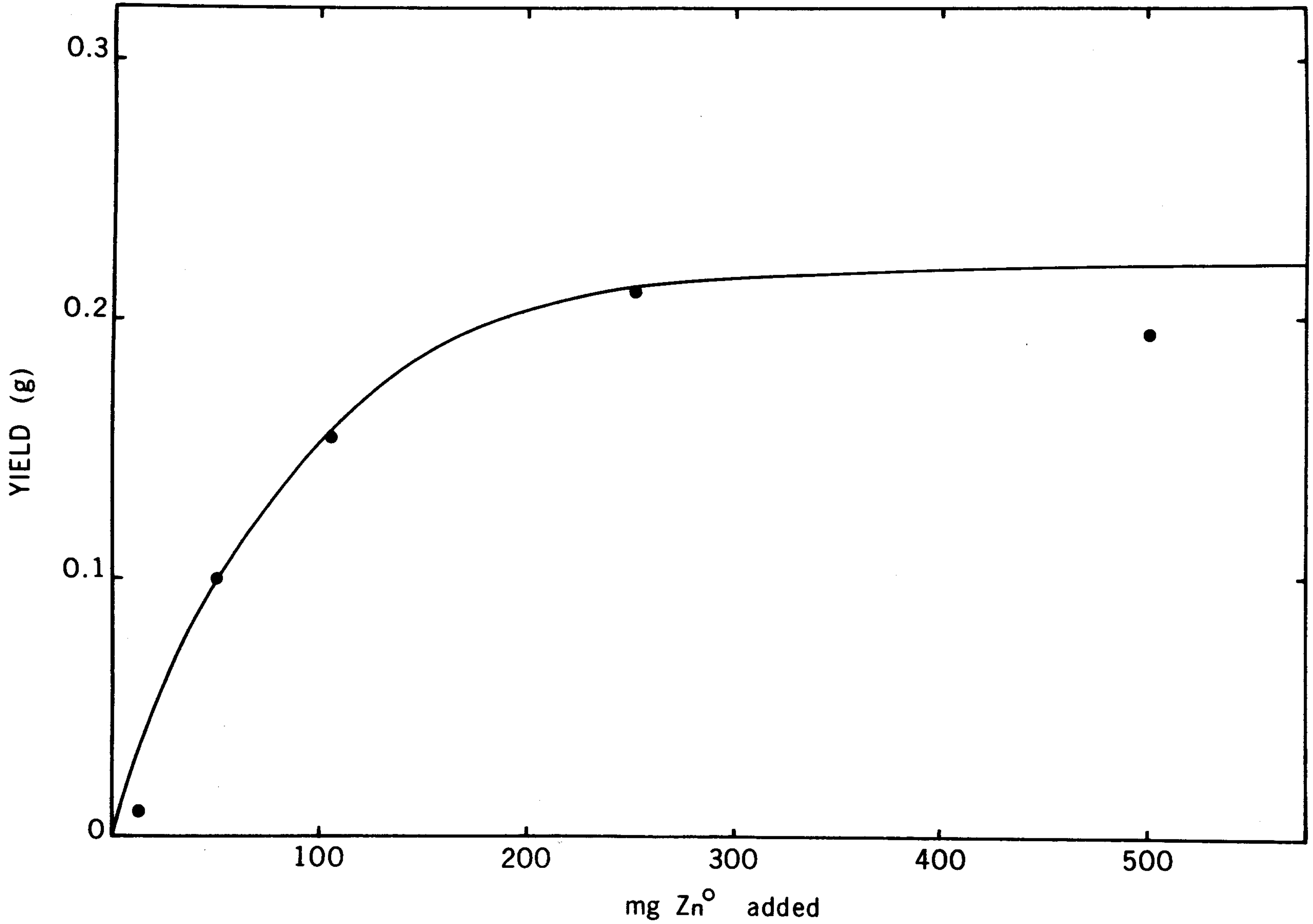
Metals are known to catalyse various chemical reactions, including polymerizations (176). However zinc metal is regarded as being fairly inert and an extensive literature survey has revealed that very little if any work has been done using this metal as a catalytic surface. Only two reports of polymerizations in the presence of zinc metal have been found (177,178). The observation of a polymerization in the presence of zinc dust is therefore of great synthetic interest.

As far as this thesis is concerned the main question is whether the polymerization is a heterogeneous surface reaction and whether zinc is acting as an initiator in some fashion. A second question concerns whether this process is specific to

Figure 32. EFFECT OF ZINC DUST.

Conditions:

0.26 moles AN, 0.053 moles St, 0.019 moles $ZnBr_2$, 25 ml DCE; 0°C, $5\frac{1}{2}$ hours.



YIELD (g)
0.3
0.2
0.1
0
100
200
300
400
500
mg Zn^{o} added

donor acceptor type systems or whether it is of more general applicability. A series of experiments were designed in an attempt to answer these and other important questions.

Results and Discussion.

The amount of zinc deposited on the cathode during a controlled potential run was compared with the total number of Faradays passed. The results obtained are shown in Table XI.

TABLE XI. Comparison of Amount of Zinc Deposited and the Number of Faradays Passed.

# F passed x 10^3	Wt. Zn deposited (mg)	Theoretical max. Wt. of Zn(mg)
0.4	12.0	13.1
0.8	23.6	26.2
1.6	51.6	52.4

Conditions: 0.26 moles AN, 0.053 moles St, 0.019 moles $ZnBr_2$, 25 ml DCE; 0°C.

It can be seen that the amount of zinc deposited is slightly less than the amount of Faradays passed. Electrolysis of impurities may account for the observed differences. Thus almost the entire Faradaic process involves the deposition of zinc metal, a conclusion already reached from the cyclic voltammetry work.

A rough comparison between the effects of electrodeposited zinc and added zinc dust was made. Thus 12 mg zinc metal was deposited by passing 4×10^{-4}F of electricity. The amount of polymer obtained after standing at 0°C for 5½ hours was compared with that obtained for the addition of 13 mg Zn dust to an identical solution. The results are shown in Table XII.

TABLE XII. Copolymer Yield as a Function of Type of Zinc Metal.

Type of Zinc	Weight Zinc (mg)	Yield copolymer(g)*
Electrodeposited	12	0.39
Zn dust	13	0.01

* Data from Table X and Figure 32.

Hence electrodeposited zinc gives a much larger effect than a similar quantity of zinc dust. The reasons for this will be discussed later.

The effect of addition of polymerization inhibitors such as diphenylpicrylhydrazyl (DPPH) and Hydroquinone (HQ) to polymerizations using zinc dust was studied. The results are given in Table XIII.

TABLE XIII. Effect of DPPH and HQ.

DPPH/AN (mole ratio)	HQ/AN (mole ratio)	Yield copolymer(g)
1.5×10^{-5}	-	trace
1.5×10^{-5}	-	0.01
-	2.3×10^{-2}	no polymer
-	2.3×10^{-2}	no polymer
-	-	0.47
-	-	0.44

Conditions: 0.26 moles AN, 0.053 moles St, 0.019 moles $ZnBr_2$, 25 ml DCE, 250 mg zinc dust; 25°C for 3 hours.

It is obvious from these results that the polymerization reaction in the presence of zinc dust proceeds by a radical mechanism. It can be inferred from this that in the electrodeposited zinc case, the propagation is similarly radical in nature. This conclusion is in accord with the earlier postulation, based on after effect results obtained in a single cell, that a radical propagation is the most likely possibility for both compartments (Figure 29).

Other Metals.

A number of other metals were studied to determine whether the 'zinc effect' was specific to zinc or whether it was a more general phenomenon. The metals used were in the form of powders or filings. The results obtained are given in Table XIV.

TABLE XIV. Effect of Other Metals.

Metal	Polymerization Yes	 No	Yield (g)
Zn	*		0.21
Cd	*		0.03
Hg	*		0.02
Cu	*		0.02
Ag	*		0.008
Au	*		0.005
Fe		*	
Co		*	
Ni		*	
Al		*	
Ga		*	

Conditions: 0.26 moles AN, 0.053 moles St, 0.019 moles $ZnBr_2$, 25 ml DCE, 250 mg metal; 0°C, $5\frac{1}{2}$ hours.

It is obvious that the effect is not restricted to zinc although this metal gives by far the largest effect. What is more surprising is that metals known for their catalytic properties (e.g. Co,Ni) exert absolutely no effect in this system under the conditions used. It should also be noted that the metals which do give the effect all have d^{10} electronic structures.

Other Monomer Systems.

In an attempt to ascertain the generality of the zinc effect, a number of monomers and comonomer pairs were studied under a variety of experimental conditions. The results are given in Tables XV and XVI.

TABLE XV. Other Comonomer Pairs.

System (moles-moles)	$ZnBr_2$ (moles)	Zn° (mg)	Yield Copolymer (g)
St - AN	0.019	250	0.21
(0.053 - 0.26)	-	250	-
	0.019	-	-
	-	-	-
St - MMA	0.045	250	0.116[a]
(0.053 - 0.21)	0.045	-	0.016[b]
	-	250	-
Stilbene-maleic	0.019	250	-
anhydride[c]	0.019	-	-
(0.1 - 0.4)	-	250	-
St - diethylfumarate[d]	0.016	250	0.15
(0.082 - 0.082)	0.016	-	-
	-	250	-

Conditions: 50 ml total volume of solution, DCE solvent; 0°C for 5½ hours.

[a] mixture of copolymer (0.095g) and polystyrene (0.021g).

[b] polystyrene only.

[c] 45°C for 5½ hours.

[d] 25°C for 2 hours; solution made up to 30 ml with absolute MeOH (no DCE present).

TABLE XVI. Use of One Monomer at 40°C.

Monomer (moles)	$ZnBr_2$ (moles)	Zn° (mg)	DCE (ml)	CH_3CN (ml)	Time (hours)	Polymer Yield (g)
AN (0.26)	0.019	250	30	-	5	0.07
	-	250	30	-	5	-
	0.019	-	30	-	5	-
AN (0.45)	0.032	250	-	-	1	0.26
	-	250	-	-	1	-
	0.032	-	-	-	1	-
Methacrylonitrile (0.20)	0.015	250	30	-	1	0.06
	-	250	30	-	1	-
	0.015	-	30	-	1	-
MMA (0.20)	0.025	250	-	-	18	0.19
	-	250	-	-	18	-
	0.025	-	-	-	18	-
St (0.13)	0.019	250	30	-	5	0.04
	-	250	30	-	5	-
	0.019	-	30	-	5	0.03
St (0.13)	0.005	250	-	30	24	-
	-	250	-	30	24	-
	0.005	-	-	30	24	-

The important results contained in these two Tables can be summarized as follows:

(a) When copolymerization occurs, it occurs only when both Zn° and $ZnBr_2$ are present. In the stilbene - maleic anhydride case, no polymer is formed under all conditions. However, $ZnBr_2$ is only sparingly soluble in this system.

(b) The zinc effect is not specific to donor acceptor systems. This is evident from the homopolymerization data in Table XVI. However, it is again noted that homopolymerization occurs only when zinc and zinc halide is present. In the styrene case, the polystyrene observed in DCE probably arises from a cationic contribution due to $ZnBr_2$ (179). Thus changing from a good cationic solvent (DCE) to a poor one (acetonitrile) eliminates the formation of polystyrene. It is also important to note that no polystyrene was formed using acetonitrile despite the fact that Zn^{2+} ions are present in the solution. In other words, only systems in which a monomer can complex with a zinc salt are capable of exhibiting the zinc effect.

It could be argued in the copolymerization cases, that the reason copolymer formation is observed only in the presence of $ZnBr_2$ is simply due to the large rate accelerations that are observed on the addition of zinc halides. In other words, $ZnBr_2$ may not be necessary for the zinc effect. This argument can be settled by studying the styrene - acrylonitrile system at a higher temperature in the absence of $ZnBr_2$. In this situation, there is no rate acceleration due to $ZnBr_2$ and use of higher temperatures should increase the propagation rate sufficiently enough to observe polymer formation in the time scale of the experiment. The results obtained are given in Table XVII.

TABLE XVII. Zinc Effect in the Absence of Zinc Bromide.

Styrene (moles)	Acrylonitrile (moles)	Zn° (mg)	DCE (ml)	Copolymer Yield
0.053	0.26	1000	25	trace
0.053	0.26	-	25	trace
0.053	0.26	1000	-	trace
0.053	0.26	-	-	trace

Conditions: 40°C for 4 hours.

The fact that traces of polymer are obtained indicates that polymer formation is proceeding. It can be seen that the addition of zinc metal alone has no effect in this system. These results prove conclusively that $ZnBr_2$ is necessary for the observation of the 'zinc effect'. It should be mentioned at this point that other zinc halides - zinc chloride and zinc fluoride - were also used in this study with similar results, signifying that the type of halide is not important.

The results of Furukawa and Fueno (177) should be mentioned. These workers observed the homopolymerization of a number of monomers in a heterogeneous mixture of various metals and organic chlorides. For methyl methacrylate

(a) The metals Mg, Fe, Zn, Al and Sb were used in conjunction with various organic halides such as t-butylchloride, α-chloromethylnaphthalene, chloroform. When Se, Pb, Cu, Ti, Bi or Cr was used as a component of the catalyst mixture, no polymer was obtained. It was found that zinc metal in the presence of t-butyl chloride gave the optimum yield of polymer. The polymer yield was found to increase with increase in the amount of zinc added up to a limiting quantity, similar to the results obtained in the present study (Figure 32).

(b) Molecular weights of the polymers were low and independent of conversion except in the case of Mg, for which the molecular weight was found to increase with time. Hydroquinone was found to have no effect on the reaction.

For styrene, Fe and Ti in the presence of various organic halides were found to be the most effective metals. However, only very low molecular weight products were obtained with this monomer. Other monomers used in this study, methyl acrylate, acrylonitrile and vinyl acetate were found to polymerize only in the presence of zinc metal and various halides.

Furukawa explains these observations by postulating the in situ formation of Grignard type compounds capable of initiating polymerization. Thus the metal is considered to interact with the organic halide to produce a Grignard compound which then adds monomer by an anionic mechanism:

$$RX + M \longrightarrow \bar{R}\cdots\overset{+}{M}X$$

$$\bar{R}\cdots\overset{+}{M}X \xrightarrow{CH_2CHY} RCH_2\bar{C}HY\cdots\overset{+}{M}X$$

$$RCH_2\bar{C}HY\cdots MX \xrightarrow{CH_2CHY} RCH_2CHYCH_2CH\bar{Y}\cdots\overset{+}{M}X \longrightarrow \text{polymer}$$

The experimental conditions used by Furukawa are similar to those used in the present study, the only difference being that $ZnBr_2$ was not used by the Japanese workers. However dichloroethane was employed for much of the work reported here and there is a possibility that this solvent could interact with zinc to produce an initiator similar to those proposed by Furukawa. This possibility was investigated by a series of experiments.

The use of t-butyl chloride instead of DCE in the St-AN system gave the results shown in Table XVIII.

TABLE XVIII. Use of t-Butyl Chloride.

$ZnBr_2$ (moles)	Zn° (mg)	Copolymer Yield (g)
0.019	250	~ 0.1[a]
0.019	-	0.0[b]
-	250	0.0[b]

Conditions: 0.26 moles AN, 0.053 moles St, 25 ml t-butyl chloride;

a 25°C, not degassed. Reaction over in a few seconds.

b 0°C for 5½ hours, degassed.

The polymerization in the presence of Zn and $ZnBr_2$ proceeded very rapidly. Addition of Zn dust to a non-degassed solution containing AN, St and $ZnBr_2$ caused immediate coagulation of the dust, and the resulting sticky mass sank to the bottom of the reaction vessel. Extraction of the polymer using THF gave a copolymer which analysed as 1:1 alternating, but which had a low molecular weight (around 50,000). This is in contrast to the extremely high molecular weights that are normally observed in these systems.

The results in Table XVIII again indicate the necessity of both Zn and $ZnBr_2$ for the observation of the effect, under the conditions employed in the work reported in this thesis. It should be noted that Furukawa employed temperatures of 60°C for very long time periods (between 5 and 45 hours). Under these conditions, polymerization in the present system may occur in the absence of $ZnBr_2$. The important conclusion, however, is that a mechanism similar to that postulated by Furukawa is not operative here, and is not the cause of the after effect. This conclusion has been confirmed by the previously reported observations of an after effect in the absence of solvent (Figure 28) and polymerization in the presence of Zn dust in the absence of solvent (Table XVI).

Conclusions

The results reported to date on the zinc effect can be summarized as follows:

(a) electrodeposition of zinc constitutes the entire Faradaic process at the controlled potentials used in this study.

(b) electrodeposited zinc is much more efficient than zinc dust in the polymerization reaction.

(c) propagation in the presence of zinc metal proceeds by a radical mechanism.

(d) other metals having a d^{10} electronic structure are capable of giving the effect.

(e) the effect is restricted to systems which contain a monomer capable of forming a complex with a zinc halide.

(f) the effect occurs only when both zinc and a zinc halide are present.

(g) the effect is not caused by a zinc-organic halide interaction.

From the point of view of this thesis, the most significant observation is the necessity for both Zn and $ZnBr_2$ to give the 'zinc effect'. This indicates that the polymerization is not a simple catalytic effect on the zinc surface, but rather an initiation involving the Zn(0) - Zn(II) couple. If such an interaction occurs, then a possible initiating species would be a Zn^{I} cation formed in the electron exchange reaction

$$Zn^{II}\,Br_2 \;+\; Zn^{\circ} \;\rightleftarrows\; Zn^{I}\,Br_2^{-} \;+\; Zn^{I}$$

the ions perhaps being held at the zinc surface by an ionic bond (180). Since such electron exchange reactions are most likely to occur at surface defects, this would explain the much higher efficiency of electrodeposited zinc over zinc dust, the former containing a much larger concentration of surface defects. Also, zinc dust is more likely to contain impurities such as oxide layers, whereas electrodeposited zinc is uncontaminated.

Although Zn^{I} species have been shown to exist in fused melts (181), their existence would be difficult to prove in the present system. However the postulation of their existence is not without some merit. Recent work by Matlack and Breslow (182) has shown that ethylene can be polymerized by a combination of titanium and titanium trichloride. These workers postulate the in situ formation of Ti(II) since neither component is active alone. The formation of polyethylene in the presence of titanium dichloride lends support for this hypothesis. Thus the formation of Zn(I) from Zn(o) and Zn(II) could be occurring in a similar way to the formation of Ti(II) from Ti(I) and Ti(III). Also, results from current reversal experiments to be reported later in this thesis are consistent with the postulated formation of a Zn(I) species.

Although the formation of alkyl zinc compounds similar to those postulated by Furukawa (177) is likely to occur, their participation in the present system under the conditions employed has been shown to be negligible.

Thus zinc, present as zinc dust or formed electrochemically, interacts with a zinc halide to produce a polymerization initiating system. The effect is general, and is operative in all systems which satisfy the criteria summarized above. It is postulated that the initiating species may be a Zn^{I} cation formed by an electron exchange reaction between Zn^{o} and Zn^{II}. A proposed mechanism for the donor acceptor complex copolymerization of styrene and acrylonitrile in terms of the zinc effect will be given in a later section.

III.2.4. RELATED STUDIES.

Current Reversal Experiments.

Donor acceptor complex polymerizations are characterized by the formation of very high molecular weight copolymers even in the presence of conventional chain transfer agents. It has been mentioned previously that the use of electrochemical techniques (specifically current reversal) has met with a great deal of success in controlling the M.Wt. distribution (135,146, 147). Thus experiments employing current reversal techniques were attempted in the styrene - acrylonitrile system to test the feasibility of using such techniques to control the molecular weight of copolymers produced in donor acceptor type systems.

Pilot experiments revealed that M.Wt. control was possible if current reversal was carried out within a well defined time range. Thus if the period of the square wave was varied between approximately 0.1 seconds and 3 seconds, molecular weight reduction was observed. Current reversal outside this range either gave no polymer (<0.1 sec.) or normal high M.Wt. copolymer (>3 sec.).

Several experiments were carried out employing different periods for various times of polymerization. The copolymers obtained were all found to have 1:1 alternating structures by elemental and N.M.R. analysis. The peak molecular weights were measured by gel permeation chromatography and were found to increase with conversion as shown in Figure 33. This is an extremely surprising and totally unexpected result. From Table XIX it is evident that there is no relationship between peak molecular weight and period.

TABLE XIX. Dependence of Molecular Weight on Period.

Period(sec)	Peak M.Wt.x 10^{-5}	%Conversion(St)
0.25	2.3	1.0
0.50	2.3	1.2
1.0	2.45	1.3

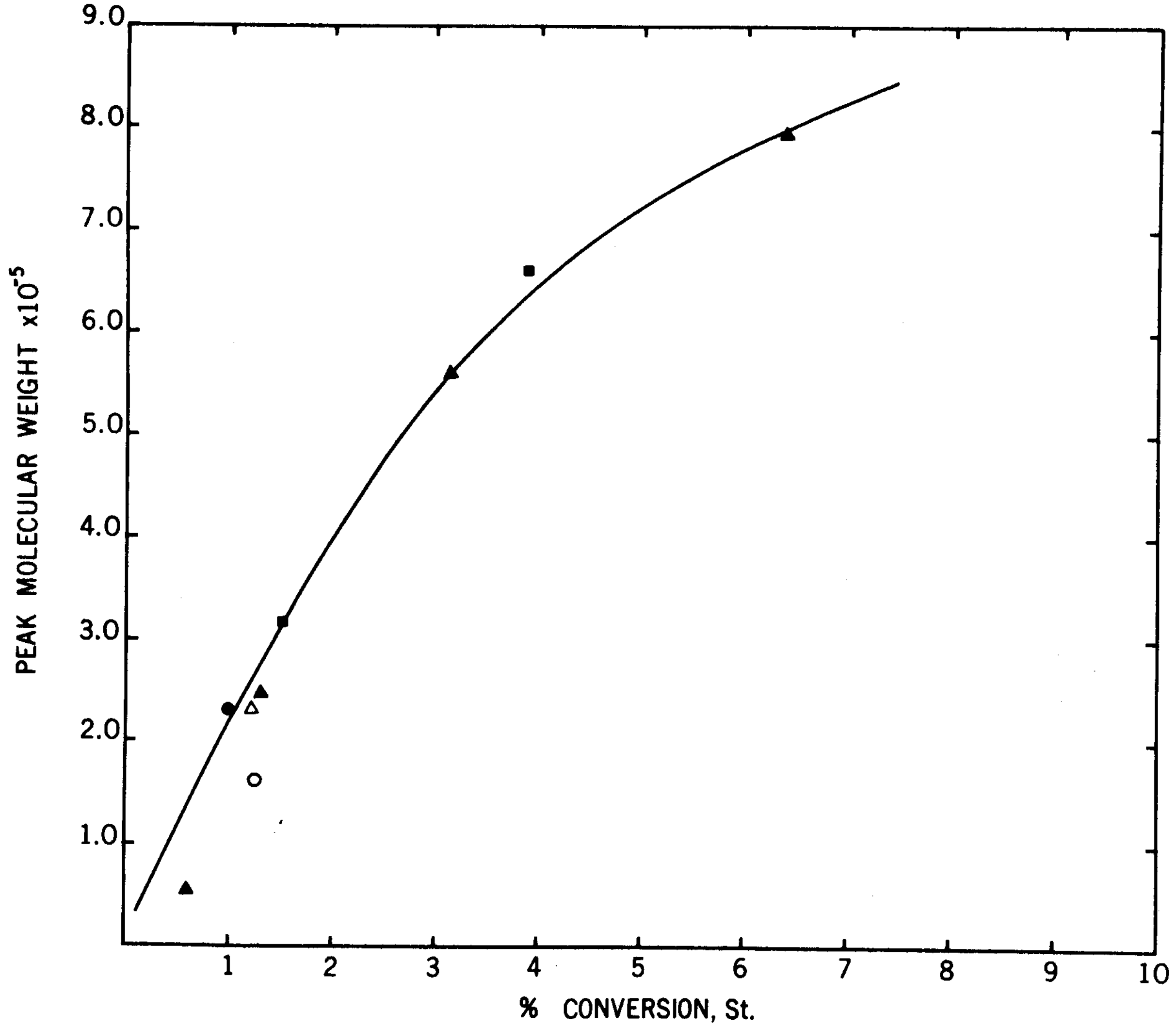
Data from Figure 33.

The explanation of such a molecular weight profile is very difficult. An increase in molecular weight with conversion usually signifies the presence of a long lived radical or a living system. Both these possibilities have been ruled out previously when attempting to explain the after effect. The conclusion reached at that time, which was subsequently shown to be correct, was that zinc metal was responsible for the after effect. It is therefore quite probable that zinc is also giving rise to these unexpected observations in some way. It should be noted that at the end of each experiment, a small amount of zinc metal was observed on both electrodes. This would not be expected if oxidation and reduction of zinc were

Figure 33. DEPENDENCE OF MOLECULAR WEIGHT ON CONVERSION.

Conditions: 0.26 moles AN, 0.053 moles St, 0.019 moles $ZnBr_2$, 25ml DCE, 25°C.

Period:
■ 2.0 sec.
○ 1.5 sec.
▲ 1.0 sec.
△ 0.5 sec.
● 0.25 sec.


9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
PEAK MOLECULAR WEIGHT x10^{-5}
1
2
3
4
5
6
7
8
9
10
% CONVERSION, St.

the only electrochemical process occurring.

An attempt at rationalizing the above observations in terms of the zinc effect will be discussed later in this thesis.

Polymerization in the Absence of Zinc Metal.

The work reported thus far in this thesis concerns the initiation of an alternating copolymerization by a Zn(0) - Zn (II) couple at the cathode. Although initiation of polymerization by metals created electrochemically is not new, the metals in question (e.g. sodium) are unstable in the reaction medium, and react immediately with monomer (137,192). The present system involves a completely different situation in which the metal formed is quite stable in the reacting medium. It would be of interest to ascertain whether donor acceptor systems were susceptible to more 'conventional' electroinitiation reactions at the cathode. Thus the copolymerization of styrene and acrylonitrile was attempted electrochemically in situations where zinc metal would not be formed. The Lewis acids used, $AlCl_3$ and $CoCl_2$, were chosen so that even if the corresponding metals were plated out during electrolysis, they would have no effect on the polymerization (Table XIV). Electrolysis of monomer solutions containing these salts were found to yield copolymers which were extremely high in acrylonitrile content, in both cases. The reason for these results is not fully understood. It is generally believed that there exists an optimium acidity of metal halide for the observation of an alternating copolymerization and that Lewis acids can be too strong or too weak in some cases (43). This may be the case in the present situation. The use of other salts to further this investigation met with little success due to the poor solubility and complexing ability of these salts.

A second possibility of removing the effect of zinc metal while retaining the same reaction conditions was to use a mercury cathode in place of platinum. Any zinc plated out from $ZnBr_2$ would dissolve in the mercury thereby hopefully removing it from the electrode surface. The results obtained in this study are shown in Figure 34. The results show the failure of this method in eliminating the zinc effect. The blank runs are high, presumably due to the effect of mercury metal itself in this system. The after effect is again not much different from continuous electrolysis suggesting the participation of zinc. It was found that the yield of polymer was not affected by the amount of mercury used for the cathode, signifying that again a surface reaction is occurring. Thus the presence of small quantities of zinc at the mercury surface (i.e. a zinc amalgam) is sufficient to give the large after effect observed. Although these experiments did not produce the results hoped for, they do provide further evidence for the existance of the zinc effect.

Phillips et al. (84-87) are the only other group to publish work on electroinitiated donor acceptor studies. The styrene - diethylfumarate (DEF) - zinc bromide system was studied by these workers. Copolymer was found exclusively at the cathode and the copolymer composition was invariant with the degree of conversion, electroinitiation rate and monomer feed ratio.

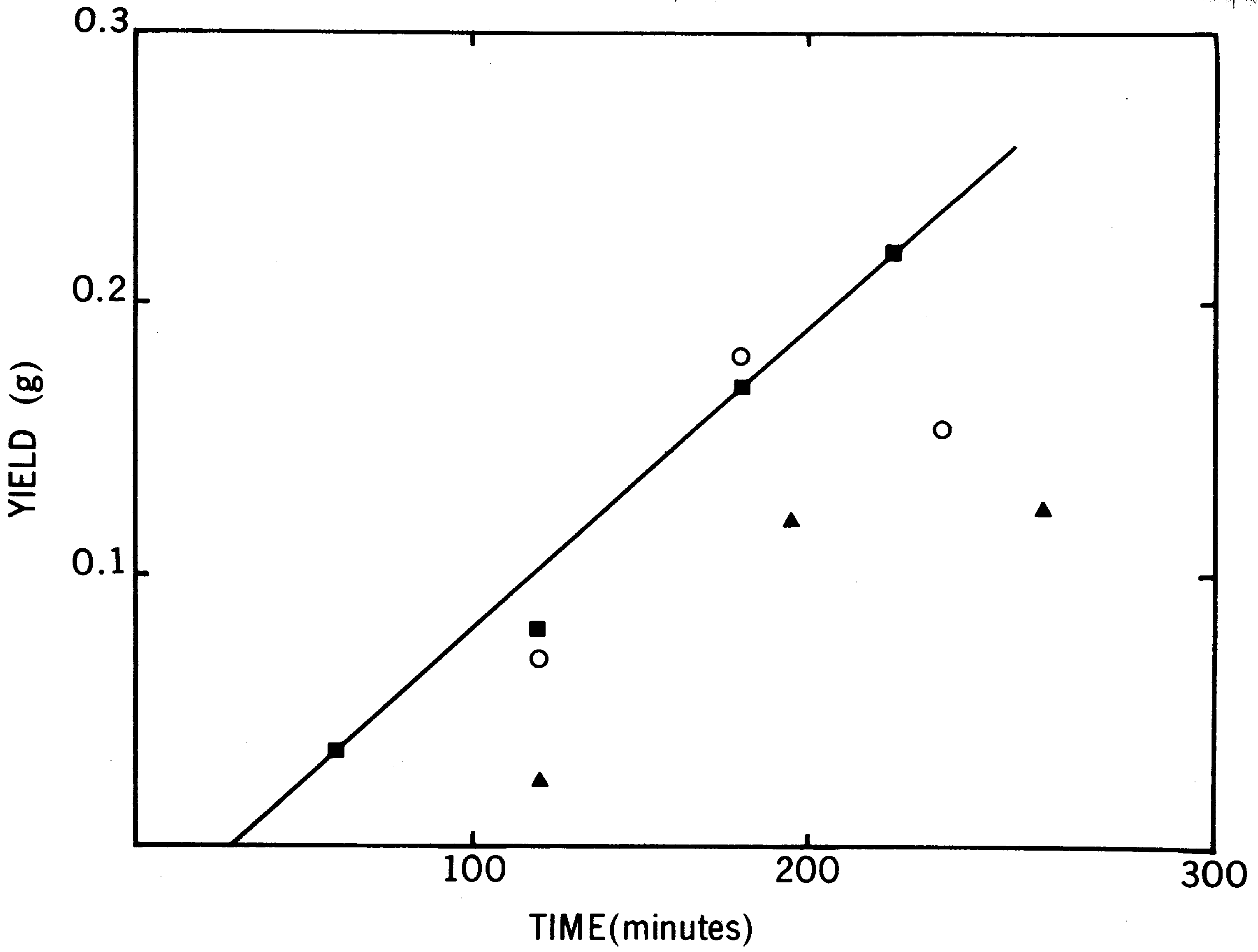
Figure 34. REACTION PROFILE USING Hg CATHODE.

Conditions: 0.26 moles AN, 0.053 moles St, 0.019 moles $ZnBr_2$, 25 ml DCE. 25°C, constant current.

■ constant current, 20 mA

○ after effect, current switched off after 60 min.

▲ blank


0.3
0.2
0.1
YIELD (g)
100
200
300
TIME(minutes)

However no work was done to examine the possible effects of zinc metal on this system. Since the present study has shown that an alternating copolymer between St and DEF is produced in the presence of added zinc dust (Table XV), this might suggest the participation of zinc metal in the electroinitiation case also. An experiment was carried out under Phillips's conditions using an applied current of 25 mA. After twenty hours of electrolysis a small amount of polymer was precipitated. Also, it was noted that very little zinc metal was electrodeposited on the cathode, in sharp contrast to the St-AN case reported here. However, it should be remembered that in the St-AN case only a small amount of electrodeposited zinc was required to give polymer formation. Hence the fact that only small amounts to zinc are deposited is not an argument against the absence of a 'zinc effect' here.

The very low current efficiencies observed coupled with the high current densities employed in Phillips's studies suggest that other electrode reactions are occurring which give rise to transient species incapable of initiating polymerization. It is quite possible that zinc plays no part in this reaction. The reproducibility of the kinetic results obtained (84,86,87) and the definite parallels shown between the photochemical and electrochemical initiated systems (87) seem to indicate the non-participation of zinc in this system. If this is so, then it constitutes the first 'real' electroinitiated donor acceptor complex polymerization at the cathode. However the observation of an after effect in this system (86), which was reported and subsequently ignored, together with the effect of zinc metal on the polymerization (reported in this thesis), suggests the need for further work to determine the exact role, if any, of zinc in the St-DEF copolymerization.

III.3. POLYMERIZATION AT THE ANODE.

Introduction.

Initiation of alternating copolymerizations at the cathode has been shown to be due to the presence of zinc metal. Attempts to electroinitiate the donor acceptor copolymerization of styrene - acrylonitrile by more direct methods have so far failed. Studies of this system show that polymer is also obtained at the anode. It was found that the yields were much less than the cathode case, and the resulting polymer was a mixture of 1:1 alternating copolymer and polystyrene. However the fact that no zinc metal is present in these anode solutions would indicate that a more direct electroinitiation reaction is occurring.

Also, work has shown that the polymerization characteristics are considerably altered in the presence of the supporting electrolyte tetrabutylammonium perchlorate (TBAP) in the following manner:

(a) the total yield of polymer is greatly increased.

(b) only pure copolymer is obtained i.e. there is no polystyrene present.

(c) the molecular weights of the copolymers are low.

On the basis of the above observations, it was decided to make a brief study of the copolymerization reaction in the presence of TBAP, at the anode.

Results.

On electrolysing these TBAP solutions, the anode compartment was found to develop a yellow colour while the cathode remained colourless.

The reaction profile under different applied currents is seen in Figure 35. Electrolytic control of the polymerization is evident from these results.

The polymers obtained from the above series of experiments were analysed with the following results:

(a) I.R. spectra of the yellowish polymers revealed the presence of both St and AN groups, as well as a new band at 1670 cm^{-1}.

(b) I.R. and elemental analyses indicated a 50:50 copolymer composition.

(c) N.M.R. spectra indicated the alternating character of the copolymers.

(d) gel permeation chromatograms revealed that the molecular weights of these polymers were substantially lower than those obtained at the anode in the absence of TBAP. The distributions were wide with peak molecular weights being in the 50,000 region.

(e) the molecular weights were independent of conversion and rate of initiation.

Table XX shows that the copolymer composition is 50:50 irrespective of the initial comonomer feed ratio.

Figure 35. INFLUENCE OF CURRENT ON POLYMER FORMATION.

Conditions: 0.26 moles AN, 0.053 moles St, 0.019 moles $ZnBr_2$, 0.005 moles TBAP, 25 ml DCE, 0°C.

● 20 mA

○ 15 mA

▲ 10 mA

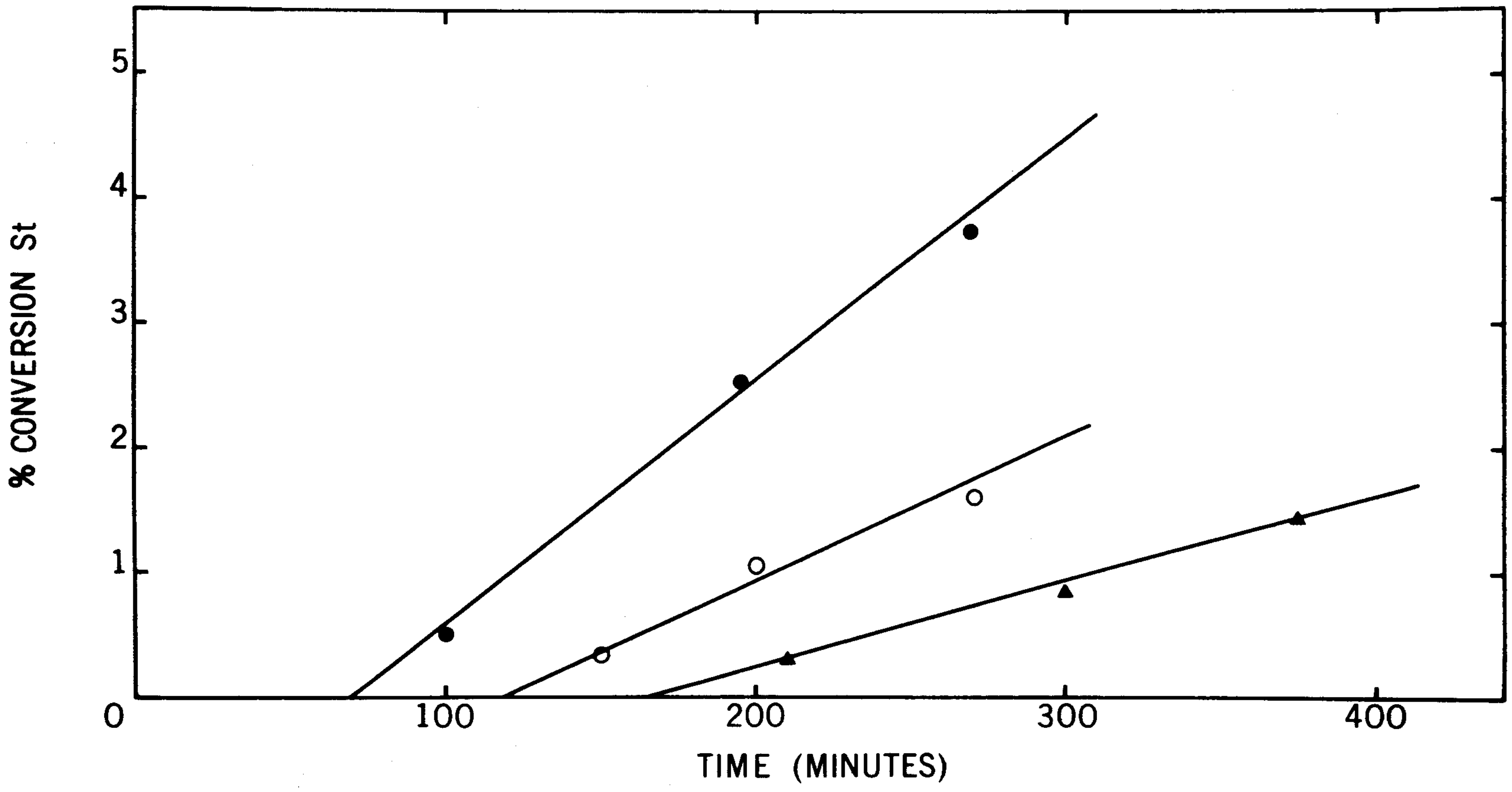

% CONVERSION St
0
1
2
3
4
5
100
200
300
400
TIME (MINUTES)

TABLE XX. Copolymer Composition as a Function of Initial Feed Ratio.

AN:St in feed	% AN in copolymer
83:17	50.0
50:50[a]	46.5
35:65[a]	49.0

Conditions: AN + St = 0.31 moles, $ZnBr_2$ = 0.019 moles, 0.005 moles TBAP, 25 ml DCE; 0°C, 10mA for 30 minutes.

[a] polymer insoluble in reaction solution.

The results of varying the temperature at a constant applied current are shown in Figure 36.

An Arrhenius plot, shown in Figure 37, is obtained if the slopes of the lines in Figure 36 are plotted against the reciprocal of the temperature. From this graph, the overall activation energy for the polymerization, E_a, is found to be 5.3 kcal/mole.

Table XXI demonstrates the existence of an after effect in this system.

TABLE XXI. After Effect in the Presence of TBAP.

Sample	After effect time (minutes)	Yield anode (g)
SAN 123a	0	trace
SAN 126a	120	0.11
SAN 127a	180	0.13
SAN 125a	240	0.16

Conditions: 0.26 moles AN, 0.053 moles St, 0.019 moles $ZnBr_2$, 0.005 moles TBAP, 25 ml DCE, 0°C, 20mA for 40 mins.

Figure 36. EFFECT OF TEMPERATURE AT A CONSTANT APPLIED CURRENT.

Conditions: 0.26 moles AN, 0.053 moles St, 0.019 moles $ZnBr_2$, 0.005 moles TBAP, 25 ml DCE, 20mA.

▲ 25°C
○ 15°C
● 0°C

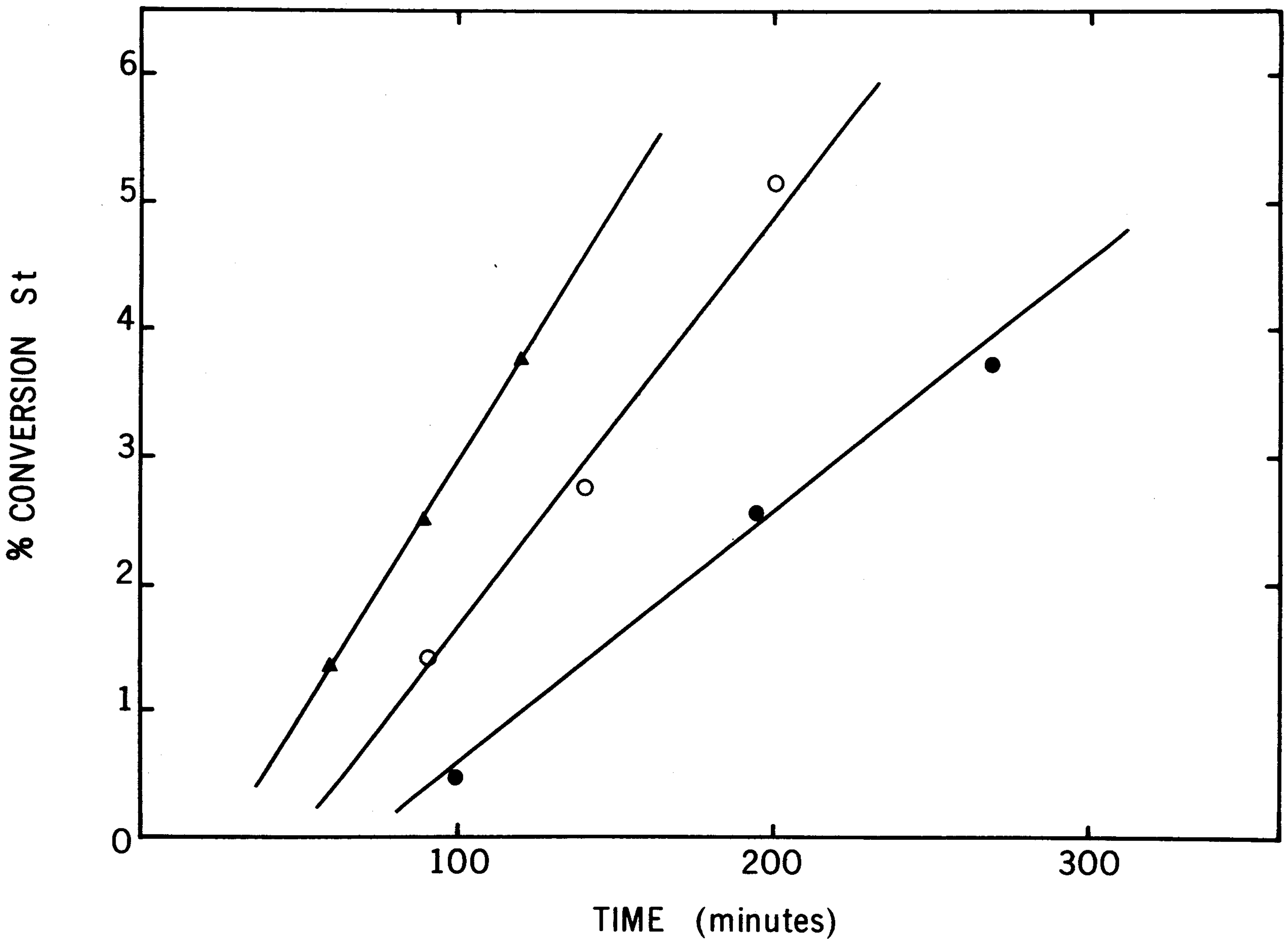
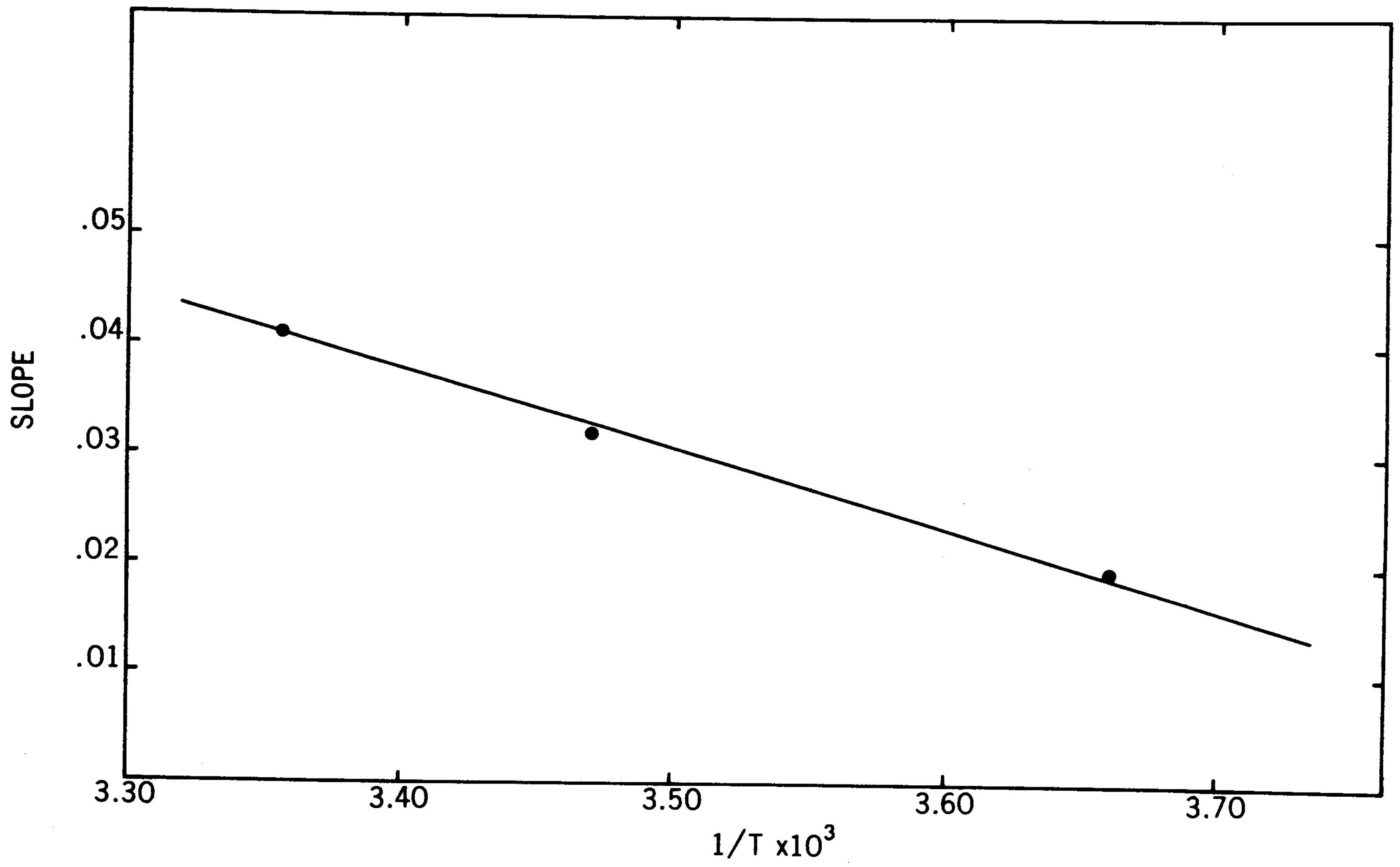

% CONVERSION St
0
1
2
3
4
5
6
100
200
300
TIME (minutes)

Figure 37. ARRHENIUS PLOT.


SLOPE
.05
.04
.03
.02
.01
3.30
3.40
3.50
3.60
3.70
1/T x10^3

During the after effect, it was observed that the yellow colour initially present in the anode disappeared with time.

It is obvious that the characteristics of the present system is very similar to the cathode situation previously studied. The existence of an after effect is again indicative of the generation of an active species which subsequently interacts with monomer. In this case there is no zinc present and the situation closely resembles other anodic polymerizations in which TBAP is involved, and which give rise to after effects (140-142,195,196). The most important difference between the copolymers produced here and those obtained in the cathode, is the low molecular weights in the present study. This aspect was studied further in an attempt at elucidating the nature of the active species responsible for the initiation of the polymerization.

Molecular Weight Studies.

The molecular weights of copolymers produced in the cathode compartment remain unchanged when the polymerization is carried out in the presence of TBAP. The molecular weights of copolymers formed in the anode are invariant to change in the nature of the cation of the perchlorate salt. These observations signify that neither the anion ClO_4^- nor the nature of the cation R_4N^+ is responsible for the lowering of the molecular weight of the copolymers produced in the anode compartment. Since this electrolyte is the only new addition to the system, it suggests that the oxidation product of ClO_4^- is in some way responsible for the molecular weight reduction. The increased yields that are obtained when this salt is used also suggests that this same species initiates the polymerization.

The molecular weights of the polymers produced as a function of time in the after effect were studied. The results can be seen in Figure 38.

SAN 120a shows the M.Wt. distribution of a typical polymer produced under continuous electrolysis. It can be seen that as the after effect time increases, the M.Wt. approaches the values obtained on electrolysing in the absence of TBAP.

Although the M.Wt. of anode copolymers are low, high M.Wt. polymers are obtained in the cathode in the presence or absence of TBAP. The effect of conducting the polymerization in a single cell (anode and cathode compartments not separated) was investigated. The results are shown in Figure 39. The peak molecular weight is 35,000. It is apparent that very little high M.Wt. copolymer is produced under these circumstances. This implies that the species responsible for terminating the anode polymerization is also effective in doing so for the cathode polymer (the polymer yield is greater than that expected for an anode process occurring to the exclusion of a cathode process and vice versa). This observation again lends support to the postulation that the cathode and anode propagating species are similar in nature.

Several other supporting electrolytes primarily of the form TBAX were used to investigate the effect of different anions.

Figure 38. MOLECULAR WEIGHT OF AFTER EFFECT COPOLYMERS.[a]

———— SAN 120a

······· SAN 126a

-.-.-.-. SAN 127a

------- SAN 125a

a refer to Table XXI.

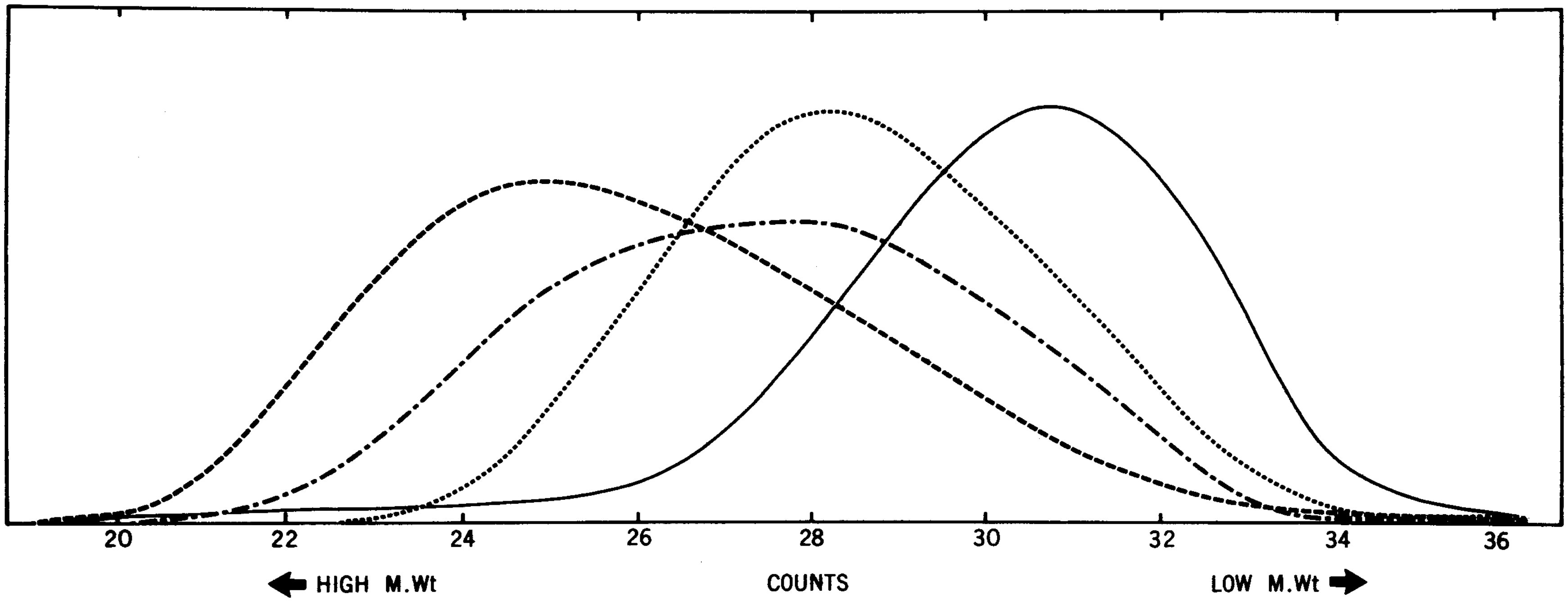
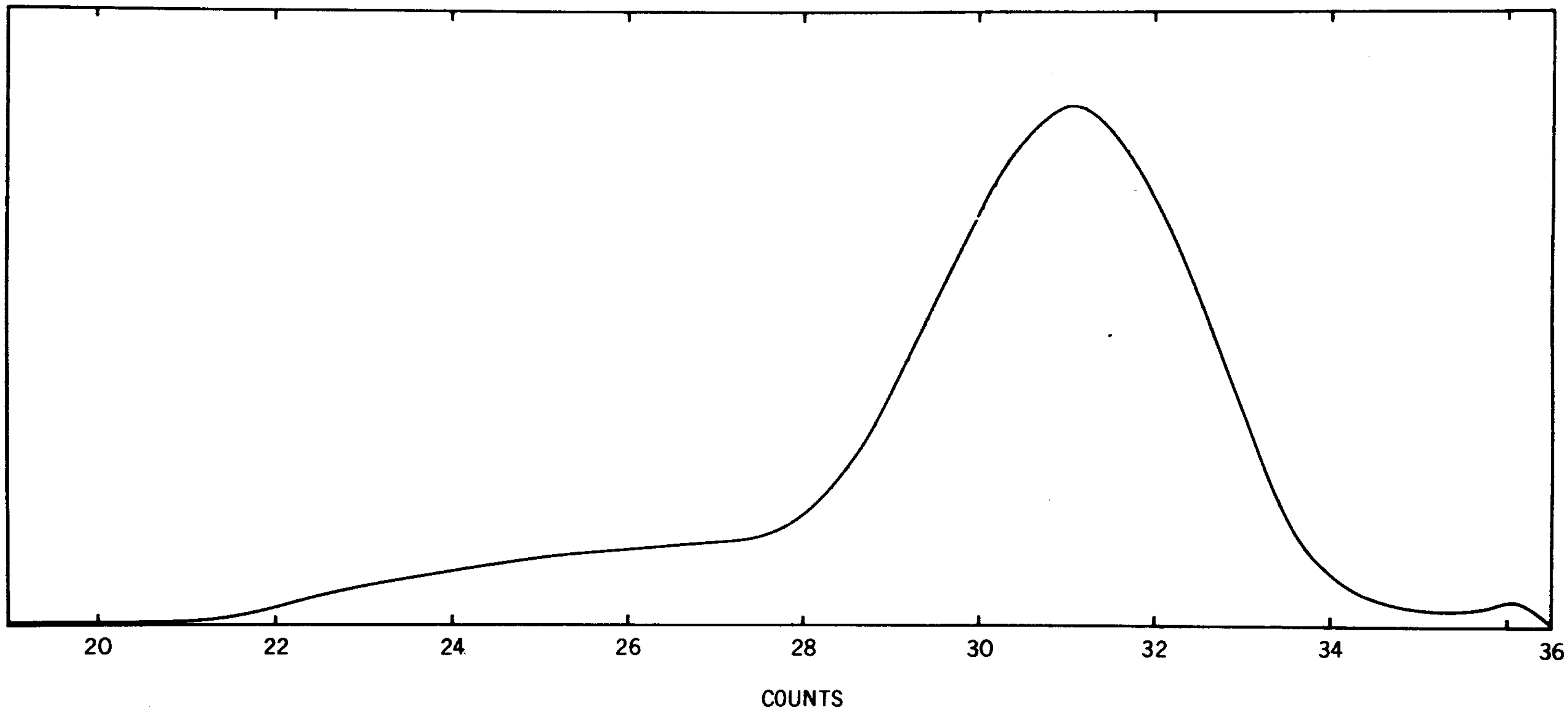

20
22
24
26
28
30
32
34
36
HIGH M.Wt
COUNTS
LOW M.Wt

Figure 39. GPC OF POLYMER PRODUCED IN SINGLE CELL.


20
22
24
26
28
30
32
34
36
COUNTS

If oxidation of the perchlorate anion generates the initiating and terminating species, then one would expect large differences in M.Wt. and polymerization behaviour on changing the anion of the background electrolyte. The results obtained are given in Table XXII.

TABLE XXII. Use of Other Supporting Electrolytes.

Electrolyte	Polymer Formation	M.Wt.
TBA bromide	trace	-
TBA iodide	-	-
TBA tetrafluoroborate	-	-
Na tetraphenylboron	yes	$>1.0 \times 10^6$

Conditions: 0.26 moles AN, 0.053 moles St, 0.019 moles $ZnBr_2$, 0.005 moles electrolyte, 25 ml DCE; 0°C, 15 mA for 5 hours.

It is obvious that lowering of the molecular weight is a property specific to perchlorate. These results will be discussed more fully later in this thesis.

III.4. MECHANISTIC ASPECTS.

The propagation mechanism of donor-acceptor complex polymerizations has been the subject of many publications. Although much controversy exists over the exact details of such a mechanism, it is generally accepted that these reactions proceed through radical intermediates in most cases. The existence of donor acceptor complexes in many of these systems is beyond question. However, proof of their participation in alternating copolymerization reactions is not at all conclusive.

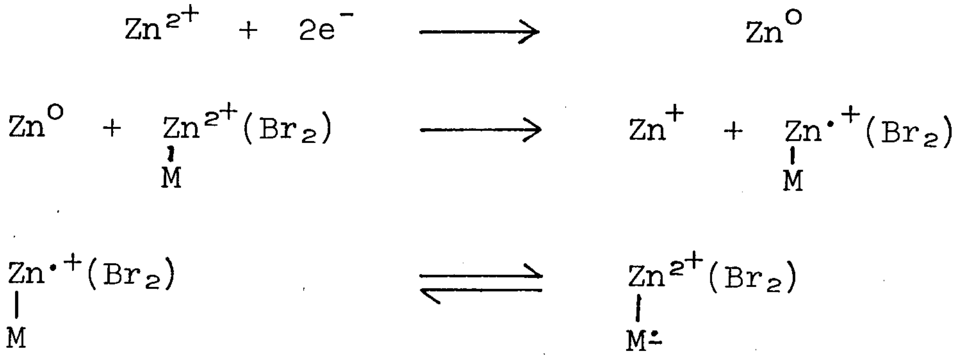
Initiation and termination reactions in these systems have received little attention. Thus, for example, the exact role of free radical initiators such as AIBN is not fully understood at this time. In this section of the thesis, possible initiation and termination mechanisms for the polymerizations conducted under electrolysis will be discussed.

Cathode.

It has been conclusively shown that polymerization at the cathode involves zinc metal. The observation that (a) the copolymer yield is increased with amount of zinc added and (b) a small amount of electrodeposited zinc gives a large effect indicates that the controlling factor in this effect is surface area. In the electrodeposited case, the active surface area is much larger than in the zinc dust case. If the amount of surface is important then a kinetic study of this effect during continuous electrolysis becomes impossible for the following reasons.

Initially a monolayer of zinc is deposited which can interact with complexed monomer. Simultaneously, more zinc is deposited forming jagged microcrystallites which grow outwards into the solution, ensuring a continuous fresh supply of new surface. However some of the zinc surface will be 'poisoned' by polymer, and this 'poisoning' will become more severe as the solution viscosity increases. Polymer will tend to envelop the active zinc surface so that the polymerization becomes diffusion controlled. It is evident that this situation is radically different from cases involving electrochemical generation of an active species which is consumed instantaneously by reaction with monomer. These systems are well documented and have been analysed kinetically (140-142).

A possible scheme for the initiation reaction in the presence of zinc can be written as follows:-



$$Zn^{2+} + 2e^- \longrightarrow Zn^0$$

$$Zn^0 + \underset{\substack{| \\ M}}{Zn^{2+}}(Br_2) \longrightarrow Zn^+ + \underset{\substack{| \\ M}}{Zn^{\cdot +}}(Br_2)$$

$$\underset{\substack{| \\ M}}{Zn^{\cdot +}}(Br_2) \rightleftharpoons \underset{\substack{| \\ M^{\cdot -}}}{Zn^{2+}}(Br_2)$$

Thus zinc metal interacts with zinc bromide (complexed to acrylonitrile) to form a monopositive zinc species. Conjugation of M through the zinc halide facilitates the formation of a radical anion monomer entity which then propagates through the radical end (inhibitor studies). Whether the propagation involves participation of donor acceptor complexes or merely consecutive addition of monomer units, has not been elucidated from the present work.

The results obtained from the current reversal experiments can also be explained in terms of the above mechanism. Although a scheme can be worked out to generate a biradical propagating species ·M· which could possibly account for the increase in molecular weight with conversion, it is difficult to see why a biradical entity would initially give rise to a low molecular weight polymer whereas a very high M.Wt. product is obtained immediately for the monoradical polymerization case.

If we consider that the observed M.Wt. dependence is a manifestation of the zinc effect, then it is possible to explain the phenomenon in terms of the mechanism already postulated. A stepwise process is envisaged and is outlined in Figure 40. Since the polymer chain, X units long at the end of Step 2, is still in the electrode vicinity (and possibly bonded to the zinc surface), Step 3 can involve this same chain so that, at the end of Step 4, the polymer chain is now 2X units in length. This scheme would therefore account for the observed increase in M.Wt. with conversion.

The whole mechanistic argument hinges on the electron transfer step between Zn^{o} and Zn^{II}. Whether this actually occurs or not is a matter of some conjecture. However, the Zn^{o} - Zn^{II} interaction in these systems is beyond question, and electron transfer reactions from electroplated zinc, containing a large amount of defects, to a Zn^{II} entity, is a very likely possibility (180).

Anode.

In the absence of supporting electrolyte, small amounts of alternating copolymer together with pure low molecular weight polystyrene areformed at the anode. Hence the following initiation mechanisms are possible:

1. Direct electron transfer from monomer to the electrode

$$M \quad -e^- \longrightarrow M^{+}\cdot$$

2. Indirect electron transfer via Br^-

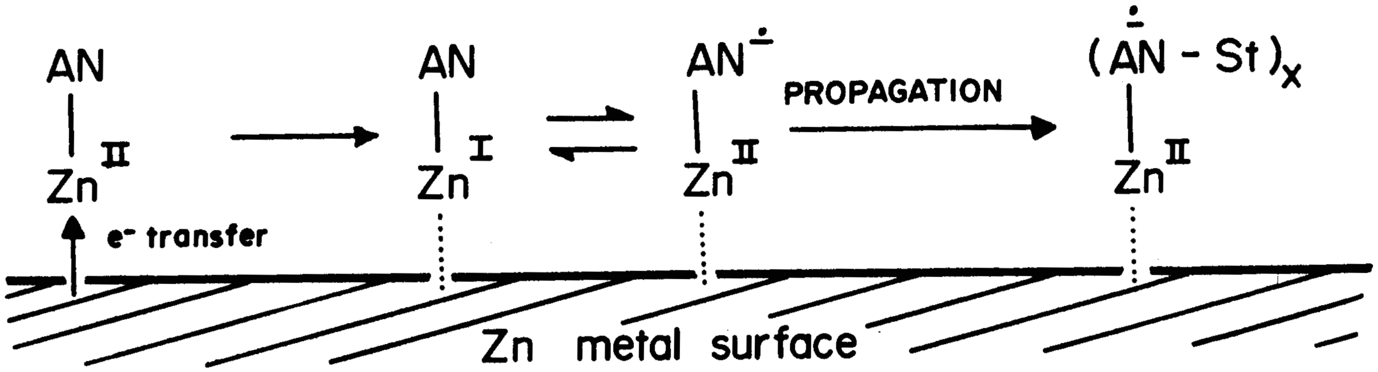
$$Br^- \quad -e^- \longrightarrow Br\cdot$$

$$Br^- \quad + M \longrightarrow Br - M\cdot \text{ or } HBr + M\cdot$$

Figure 40. POSTULATED MECHANISM TO ACCOUNT FOR CURRENT REVERSAL RESULTS.

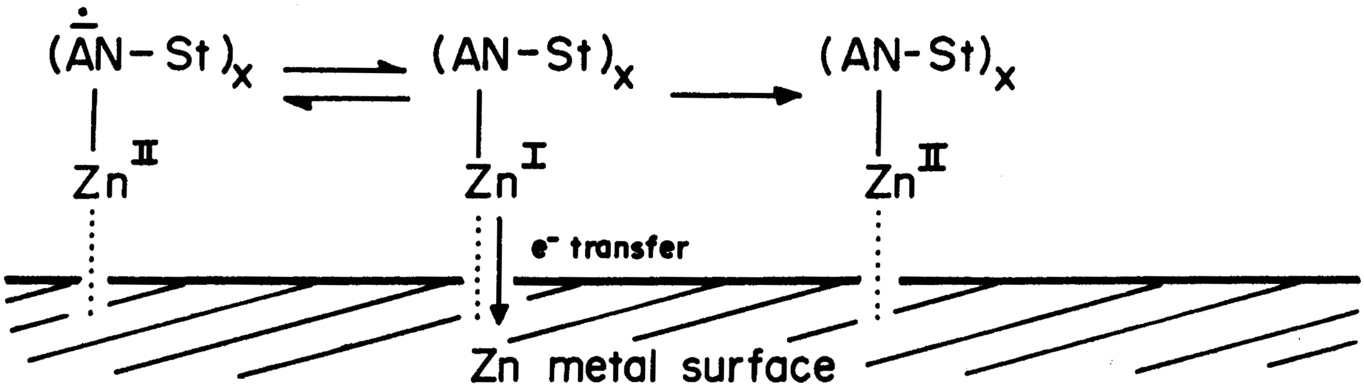
STEP 1 Cathodic Cycle

Zinc is deposited on cathode

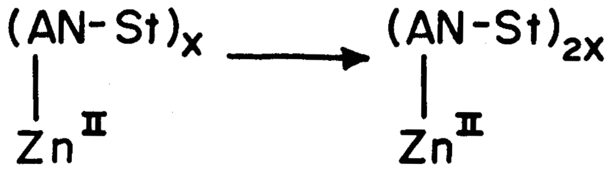


STEP 2 Anodic Cycle

Cathode now becomes anode



STEP 3+4 Repeat of Steps 1+2



3. Direct or indirect electron transfer from styrene

$$\mathrm{St}\ -e^{-} \longrightarrow \mathrm{St}^{\dot{+}}$$

$$\mathrm{Br}^{-} + \mathrm{St} \longrightarrow \mathrm{Br-St}\cdot \text{ or } \mathrm{HBr} + \mathrm{St}\cdot$$

4. Lewis acid catalysed cationic polymerization of styrene.

The presence of $ZnBr_2$ in a cationic supporting medium such as DCE suggests that mechanism 4 is the most likely to account for the presence of polystyrene at the anode. Since work on this particular system was carried out at controlled cathodic potentials, it is difficult to differentiate between mechanisms 1 and 2 for the initiation of the copolymerization reaction. Unfortunately, cyclic voltammograms observed during anodic sweeps were fairly featureless and difficult to interpret, and therefore did not aid in this differentiation. It should be commented here that a similar situation is believed to exist in the anodic polymerization of styrene and methylmethacrylate.

It has been mentioned previously that it is unlikely that the copolymerization in either the anode or cathode proceeds ionically, due to the conditions employed in this study. Furthermore, single cell experiments have indicated that the propagating species in the anode and cathode compartments are identical.

Since the cathode reaction is known to propagate radically, we may postulate that the polymerization proceeds similarly in the anode. Again, this work makes no conclusions regarding the participation of donor acceptor complexes in the propagation step. Similarly, it is difficult to make any definite conclusions concerning the termination mechanism.

In the presence of TBAP, no polystyrene is obtained and the molecular weight of the copolymer formed is found to be low. It is not obvious at this time why the polymerization of styrene is inhibited by the presence of TBAP. In fact, the electrolysis products of the perchlorate ion is thought to initiate the cationic polymerization of styrene (140). The complete absence of polymerization would seem to indicate the existence of considerable transfer processes.

Polymerizations occurring in the anode compartment in the presence of TBAP have been postulated to occur either by direct oxidation of the monomers to radical cations or indirectly through the formation of $ClO_4\cdot$ radicals (140,142,196). In the present situation the latter possibility seems most likely due to the complete change in characteristics of the polymerization in the presence of TBAP.

Although $ClO_4\cdot$ radicals have been postulated by most workers as being possible initiating species, there is now evidence that in fact lower oxides of chlorine, such as chlorine dioxide ClO_2, are responsible for the initiation. The E.S.R. spectrum of radicals formed during the electrochemical oxidation of perchlorates was first assigned to the $ClO_4\cdot$ radical by Maki and Geske (183). Subsequent work has revealed that the spectrum actually corresponds to an extremely long lived ClO_2 radical (184,185). The yellow colour obtained on electrolysis of these TBAP solutions has also been attributed to the formation of ClO_2 and possibly other decomposition products of the unstable perchlorate radical (184,186,187).

Thus in the present system, the initiation reaction is envisaged as follows:-

$$\begin{array}{lll} ClO_4^- \quad -e^- & \longrightarrow & ClO_4\cdot \\ ClO_4\cdot & \longrightarrow & ClO_2\cdot \; + O_2 \\ ClO_2\cdot \; + M & \longrightarrow & ClO_2 - M\cdot \qquad \text{or} \\ & & HClO_2 + M\cdot \end{array}$$

The propagation reaction is thought to proceed in a fashion similar to that in the absence of TBAP. The main difference between the present situation and the former (absence of TBAP) is the low molecular weights that are obtained, signifying an extremely efficient termination reaction. Although transfer to supporting electrolyte is the most likely possibility, it is not operative here due to (a) the high M.Wt. products that are obtained in the cathode in the presence of electrolyte and (b) the observation of an increase in M.Wt. with time during the after effect. As far as the latter observation is concerned, one would not expect an increase in M.Wt. if transfer to electrolyte were occurring, due to the large excess of this salt in the system. Also, the fact that only low M.Wt. polymer is obtained when TBAP is used in a single cell, instead of the expected high and low M.Wt. products, indicates that the products of the anode oxidation also interact with the cathode propagating species.

It is possible that acids such as $HClO_4$ and $HClO_2$, produced from $ClO_4\cdot$ and $ClO_2\cdot$ by hydrogen abstraction, give rise to cationic polymerizations as has been postulated in some cases

(140,142,196-198). Although a cationic process could account for the increase in M.Wt. with time in the after effect (197), it would not explain why the M.Wt. is low and invariant with time under continuous electrolysis.

The results obtained in the presence of TBAP can be explained if it is postulated that the products responsible for the initiation reaction are also involved in the termination in some way. Let us assume that the ClO_2 radical initiates and terminates the polymerization. Under continuous electrolysis enough radicals exist in solution to terminate the polymerization and give rise to low M.Wt. polymer. When the current is switched off during the after effect experiments, initiation occurs as previously. However, termination now becomes less frequent due to consumption of ClO_2. The polymer is therefore allowed to grow to higher and higher molecular weights before termination and eventually the stage is reached when the polymer has a molecular weight comparable to those polymers obtained in the absence of TBAP. This qualitative picture is borne out by the after effect results obtained and shown in Figure 38.

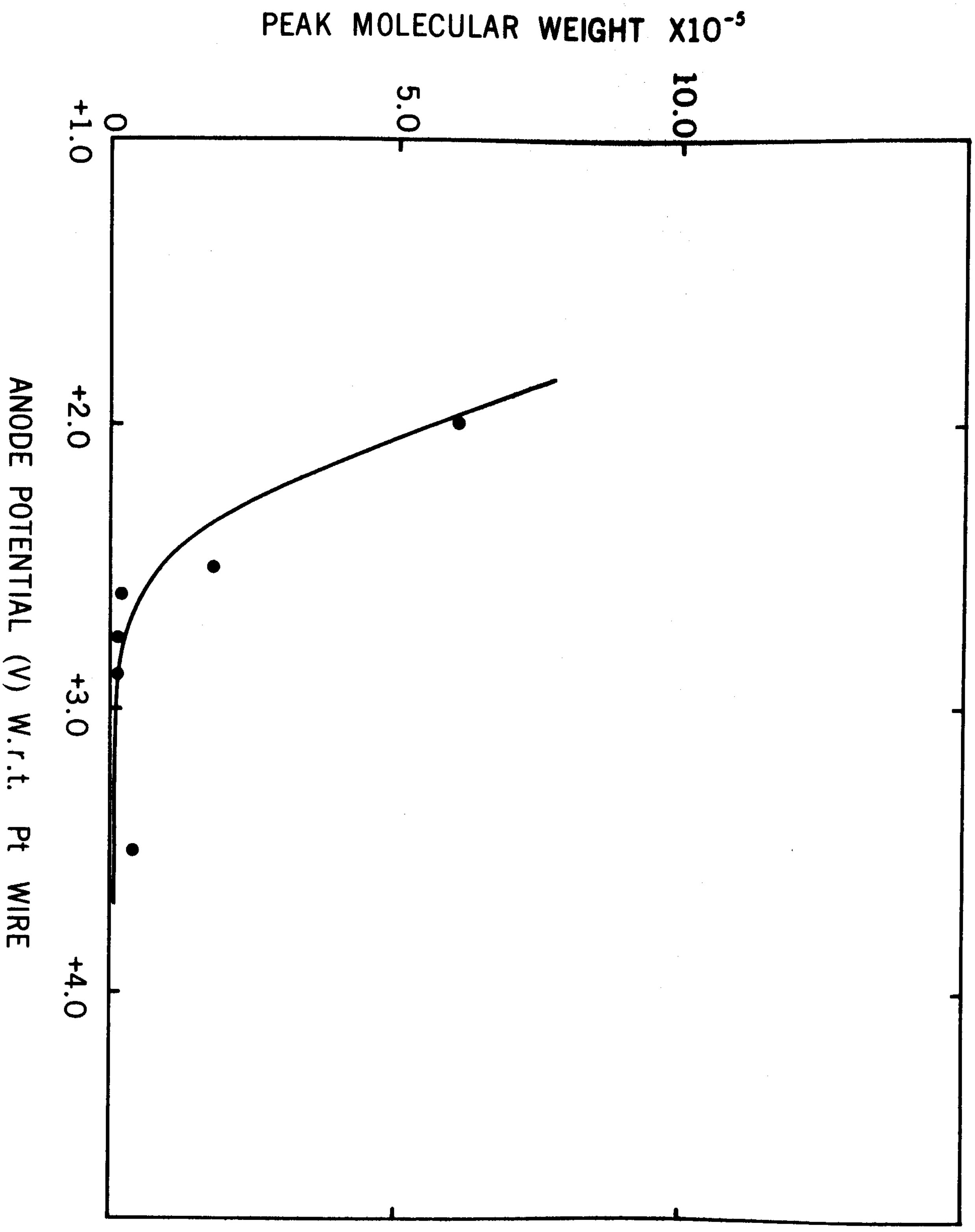
An experiment was attempted to test the validity of the above postulation. Since all experiments previously reported in this thesis were carried out at controlled cathode potential, no control over the anode electrode process was maintained. Hence a number of possible initiation mechanisms are possible at the anode e.g. direct electron transfer from monomer, oxidation of ClO_4^- etc.. In the presence of TBAP, the results reported show that the oxidation of perchlorate is the most important step. This is not to say that other processes, which occur in the absence of TBAP, are not occurring simultaneously. If now the anode potential is controlled, it might be possible to observe the potential region in which there is a change in the predominating mechanism. Thus at low anode potentials, in which little or no ClO_4^- is oxidised, one would expect the polymerization to occur by a mechanism similar to that in the absence of TBAP, yielding a high M.Wt. polymer. As the anode potential is gradually increased positively, ClO_4^- ions begin to be oxidised. On the basis of the above postulation, one would expect a decrease in M.Wt. with increase in anode potential.

The results of a controlled anode experiment are shown in Figure 41. Although it is difficult to make definite conclusions from the limited data shown in Figure 41, the M.Wt. decrease does provide some evidence in favour of the proposed mechanism.

It is perhaps not necessary to invoke a change in initiation mechanism. In fact, the above results are explicable merely by postulating the electrochemical generation of a transfer agent at the anode. Thus initiation can proceed in a similar way to the situation in the absence of TBAP. A decomposition product (or products) of ClO_4^- would then act as a transfer agent, and give rise to the observed M.Wt. behaviour. It is obvious that more work, at controlled anode potentials, needs to be done in this system.

The exact details of the termination mechanism are not understood. The presence of a new band at 1670 cm^{-1} may be

Figure 41. MOLECULAR WEIGHT AS A FUNCTION OF ANODE POTENTIAL.


PEAK MOLECULAR WEIGHT X10^{-5}
10.0
5.0
0
+1.0
+2.0
+3.0
+4.0
ANODE POTENTIAL (V) W.r.t. Pt WIRE

indicative of a >C=N- group (137,188). The observation that the intensity of this band decreases with increase in after effect time implies that this group arises only from a termination reaction. A mechanism similar to that proposed by Grassie (188) may be operative in the present situation.

The lack of polymer formation on using other tetrabutylammonium salts indicate that the primary radicals formed are incapable of initiation due to predominant side reactions such as dimerization and hydrogen abstraction. The use of sodium tetraphenylboride yielded high M.Wt. copolymers at the anode. If the tetrafluoroborate anion is oxidised at the anode thus,

$$Ph_4B^- - e^- \longrightarrow Ph_3B + Ph\cdot$$

it is unlikely that either of the oxidation products would be capable of initiation. Hence, since the anode potential is not controlled, polymerization will occur by a mechanism similar to that occurring in the absence of this electrolyte.

IV. SUMMARY.

The work discussed in this thesis deals with the application of electrochemical techniques to the study of some polymerization processes. The use of cyclic voltammetry has been shown to give the overall characteristics of a number of systems and has provided the information needed for controlled potential studies.

The application of electrochemical techniques to donor acceptor systems provided some interesting and unexpected results. At the cathode, a novel zinc - zinc halide initiating system was generated on the electrodeposition of zinc. The same effect was obtained on using zinc dust, and showed that this cathodic process was identical to a non-electrochemical situation. The generality of this 'zinc effect' and the simplicity of the experimental set-up indicates possible industrial applications.

Current reversal experiments demonstrated the inherent advantages of using electrochemical techniques to control molecular weight. The closest parallel to this in conventional polymerizations is the addition of a chain transfer agent, which can act as an additional complicating feature in donor acceptor systems.

The anodic polymerizations in the presence of TBAP were shown to be similar to previously reported reactions in the presence of this salt. The molecular weight behaviour observed during the after effect was found to be the only anomolous feature in this study.

It is obvious from this work that before detailed kinetic and other electrochemical studies can be carried out on donor acceptor systems at the cathode, a method of eliminating the zinc effect must be found. A more extensive study of alternative Lewis Acids or the use of more favourable solvents would seem to be a logical starting point. Alternatively, the cathode can be ignored and attention focused on the anode. From the preliminary results reported here, the anode compartment seems less complex than the cathode. The similarity to previously reported anodic polymerizations in the presence of TBAP indicates that further detailed studies would be relatively straightforward and fruitful.

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