KINETICS OF
DONOR-ACCEPTOR COMPLEX POLYMERIZATION

by

JAROSLAV RYBICKY

R.N.Dr., J.E. Purkyne University,
Brno, Czechoslovakia, 1968

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Name: Jaroslav Rybicky

Degree: Doctor of Philosophy

Title of Thesis: The Kinetics of Donor - Acceptor Complex Polymerization

Examining Committee:

D. Sutton
Chairman

B.L. Funt
Senior Supervisor

J.M. D'Auria
Examining Committee

T.N. Bell
Examining Committee

I. Gay
Examining Committee

K.F. O'Driscoll
External Examiner
Professor
The University of Waterloo
Waterloo, Ontario

Date Approved: Sept 21, 1972

ABSTRACT

The butadiene-acrylonitrile-$ZnCl_2$ system was chosen for study of donor-acceptor complex polymerization. It was demonstrated that this system yields an alternating copolymer in a broad region of reaction and concentration conditions, irrespective of the means of initiation. The rate of reaction was found to be maximum when the concentration of the complex formed between the components was also a maximum. This observation is consistent with the theory of the production of copolymer via complexes formed "in situ" prior to the polymerization process.

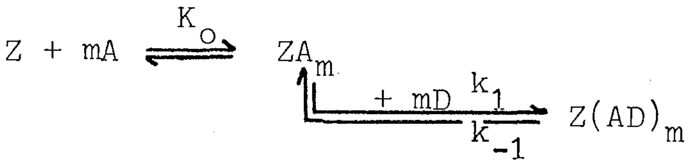
Kinetic equations linking the copolymer yield with time were derived and tested. The following reaction scheme was used as a basis for the derivations.

$$\begin{tikzcd} Z + mA \arrow[r, shift left, "K_o"] & ZA_m \arrow[l, shift left] \arrow[dr, shift left, "+\,mD\quad k_1"] & & & \\ & & Z(AD)_m \arrow[ul, shift left, "k_{-1}"] \arrow[r, "k_p"] & P_mZ \arrow[r, "k_r"] & mP + Z \arrow[d] \\ & & & & \text{recycled} \end{tikzcd}$$

It was necessary to assume steady state conditions and a low concentration of one of the components to achieve this aim. The kinetic equation describing the system with a low concentration of the complexing salt was derived for all stoichiometric ratios between the salt and the monomer pair and for zero and first order reactions of the complex. Zero order was experimentally disproved. Several examples of the initiation, propagation and termination mechanisms leading to first order reactions are discussed. When a low concentration of either monomer was presupposed the kinetics could be derived only for the stoichiometric factor equal to unity.

As the kinetic equations derived carry the assumptions of a steady state of the complex and of a constancy of concentration of two of the components, the effect of these approximations on the exactness of the final equations was tested. The approximate equations were compared with the exact solutions found by the Runge-Kutta numerical method. A good agreement was obtained.

The overall reaction scheme on which the derivations are based was experimentally supported. The formation of the complex



$$Z + mA \overset{K_o}{\rightleftharpoons} ZA_m \xrightleftharpoons[k_{-1}]{+\ mD\quad k_1} Z(AD)_m$$

prior to the polymerization step was indicated by a limit in the rate of polymerization. When the rate of electrochemical initiation was increased, the amount of polymer in a given time increased, reached a maximum and remained unchanged with further increase of current passage through the solution. The regeneration step was evidenced by the distribution of the complexing salt. The amount of the salt associated with the copolymer was found to increase and attain a constant value. This plateau was reached at the same time as the attainment of the constant rate of polymerization.

The kinetics was applied to polymerization experiments and kinetic parameters were evaluated.

TO MY PARENTS

PUBLICATIONS FROM THIS THESIS

1. "Electroinitiated Copolymerization Reactions with Donor-Acceptor Complexes. III. Copolymerization of Butadiene and Acrylonitrile with $ZnCl_2$ as Catalyst", with B.L. Funt in J. Polymer Sci., A1, 9, 1441-1449, (1971).
2. "The Kinetics of Donor-Acceptor Complex Polymerization. I. Introduction and Theory", with J. Tanner and B.L. Funt in J. Macromol. Sci., A6, 223-239, (1972).
3. "The Kinetics of Donor-Acceptor Complex Polymerization. II. Applications of the Kinetic Equations", with J.Tanner and B.L. Funt in J. Macromol. Sci., A6, 241-257, (1972).
4. "The Kinetics of Donor-Acceptor Complex Polymerization. III. Assesment of Some Approximations in the Kinetics", with J. Tanner and B.L. Funt in J. Polymer . Sci., A, (in press).
5. "The Kinetics of Donor-Acceptor Complex Polymerization. IV. Limiting Yield in the Butadiene-Acrylonitrile Copolymerization", with J. Tanner and B.L. Funt in J. Polymer Sci., (in press).

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LIST OF CONTENTS

page

I. THEORETICAL PART 1
- I.1. Introduction 1
  - I.1.1. Basic Concepts of Copolymerization 1
    - I.1.1.1. The Copolymer Composition Equation 1
    - I.1.1.2. General Relationship among Monomers in Copolymerization 5
  - I.1.2. Alternating Effect in Copolymerization 8
- I.2. Donor-Acceptor Molecular Complexes in Alternating Copolymerization 15
  - I.2.1. Spontaneous Formation of the Complex 15
  - I.2.2. Enhanced Formation of the Complex 21
- I.3. Proof of the Alternating Structure of a Copolymer 27
- I.4. Mechanism of the Donor-Acceptor Complex Polymerization 29
  - I.4.1. Studies Related to the Donor-Acceptor Complex Polymerization 29
  - I.4.2. Mechanism of the Donor-Acceptor Complex Polymerization 32
- I.5. Deviation from the Alternating Structure 39
- I.6. Kinetics of Donor-Acceptor Complex Polymerization 42

II. CHEMICALS AND TECHNIQUES USED 47
- II.1. Chemicals and Their Purification 47
  - II.1.1. Monomers 47
  - II.1.2. Complexing Agent 47
  - II.1.3. Solvents 47
- II.2. Polymerization Procedure 48
  - II.2.1. Electrochemical Polymerization 48
  - II.2.2. Spontaneous Polymerization 51

page

II.2.3. Isolation of Polymer 51
II.3. Characterization of Polymer 52
II.3.1. Elemental Analysis 52
II.3.2. NMR Spectroscopy 52
II.3.3. IR Spectroscopy 52
II.3.4. Viscosity Measurements 57
II.4. Determination of $ZnCl_2$ on Polymer 57
III. EXPERIMENTAL AND THEORETICAL RESULTS 59
III.1. General Studies 59
III.1.1. Preliminary Experiments 59
III.1.2. Concentration Effects 69
III.1.3. Solvent Effect 74
III.2. Kinetic Studies 76
III.2.1. Polymerization at Low Concentration of Complexing Agent 76
III.2.2. Derivation of Kinetics of Donor-Acceptor Complex Polymerization 79
Derivation of Kinetic Equations 79
Further Considerations 87
Discussion of the Significance of the Kinetic Equations 90
Appraisal of the Kinetic Equations 91
Outline of Methods of Extracting Kinetic Parameters from Experimental Data 97
III.2.3. Assesment of the Approximations in the Kinetics 101
Concentration Variations 103
Assumption of Steady State Conditions 108
III.2.4. Application of the Kinetics. Limiting Rate in the Butadiene-Acrylonitrile Copolymerization 113

page

III.2.5. Application of the Kinetics. Determination of Zinc Chloride Distribution and Evaluation of Kinetic Parameters in the Styrene-Acrylonitrile-$ZnCl_2$ in Dichloroethane System 116

III.2.6. Application of the Kinetics. Evaluation of Kinetic Parameters for the Butadiene-Acrylonitrile-$ZnCl_2$ in Dichloroethane System 121

IV. SUMMARY AND DISCUSSION 125

Appendix I. Systems Reported to Yield Alternating Copolymers 132

Appendix II. Solutions of Some Integrals 135

Appendix III. Error Calculations 136

List of References 145

LIST OF TABLES

		page
Table I.	Arrangement of Monomers in Order of Their Increasing Tendency to Alternate with Styrene	13
Table II.	Summary of Experimental Facts which Favour Donor-Acceptor Complex Polymerization Theory	19
Table III.	Copolymer Formation in the Presence of $ZnCl_2$	60
Table IV.	Effect of Degree of Conversion on Composition of the Product	61
Table V.	Copolymer Composition as a Function of $ZnCl_2$/AN Mole Ratio	64
Table VI.	Copolymer Composition as a Function of BD/AN Mole Ratio	64
Table VII.	Copolymer Composition as a Function of Rate of Initiation	65
Table VIII.	Polymerization in Solvents	75
Table IX.	Conditions for Which a Kinetic Equation is Derived	87
Table X.	Effect of Conversion Under Case I Conditions of Low Complexing Agent Concentration	106
Table XI.	Effect of Conversion Under Case II Conditions of Low Donor Monomer Concentration	106
Table XII.	Effect of Ratio $[Z]_o/[A]_o$	107
Table XIII.	Effect of Ratio $[D]_o/[A]_o$	107
Table XIV.	Kinetic Parameters at Various Temperatures	123

LIST OF FIGURES

page

Figure 1. Incremental Copolymer Composition as a Function of Monomer Feed Composition for Various r_1/r_2 Ratios 3

Figure 2. Plot of Logarithm of Relative Reactivity toward the Styrene Radical versus Hammett σ Value of Substituent for Various Substituted Styrenes 9

Figure 3. Plot of Logarithm of Relative reactivity toward the Methyl Methacrylate Radical versus Hammett σ Value of Substituent for Various Substituted Styrenes 10

Figure 4. Incremental Copolymer Composition as a Function of Monomer Feed Composition for the System Styrene and Methyl Methacrylate Polymerized by Cationic, Free Radical and Anionic Mechanisms 11

Figure 5. Copolymerization of Methyl Methacrylate and Styrene 25

Figure 6. Copolymerization of Methyl Acrylate and Styrene 26

Figure 7. The Electropolymerization Cell 49

Figure 8. Apparatus for Introducing Gaseous Monomer 50

Figure 9. NMR Spectra of Butadiene-Acrylonitrile Copolymers 53

Figure 10. NMR Spectra of Styrene-Acrylonitrile Copolymers Prepared with Free Radical Catalyst 54

Figure 11. NMR Spectra of Alternating Styrene-Acrylonitrile Copolymer Prepared with $ZnCl_2$ 55

Figure 12. Infrared Spectra of Polybutadienes 56

page

Figure 13. Infrared Spectra of the Products 62

Figure 14. NMR Spectrum of the Product 63

Figure 15. Copolymer Formation as a Function of Time 66

Figure 16. Copolymer Formation as a Function of Charge Transfered 67

Figure 17. "Spontaneous" Copolymer Formation as a Function of Time 68

Figure 18. Rate of Polymerization as a Function of Butadiene Concentration. Spontaneous Reaction 71

Figure 19. Rate of Polymerization as a Function of Butadiene Concentration. Electroinitiated Reaction 72

Figure 20. Rate of Polymerization as a Function of $ZnCl_2$ Concentration 73

Figure 21. Polymerization at Low Concentration of $ZnCl_2$ 78

Figure 22. Demonstration of the k_p/k_r Variation. Case I 93

Figure 23. Demonstration of the k_p/k_r Variation. Case I 94

Figure 24. Demonstration of the m Variation. Case I 95

Figure 25. Demonstration of the k_p Variation. Case II 96

Figure 26. Analysis of the Curve $[P_t]=Et+F(1-\exp(-C_2t))$ when $k_p \gg k_r$ 99

Figure 27. Validity Test. Effect of Conversion and Component Concentrations. Case I 104

Figure 28. Validity Test. Effect of Conversion and Component Concentrations. Case II 105

Figure 29. Validity Test. Effect of Relative Magnitudes of k_1, k_{-1} and k_p 110

Figure 30. Validity Test. Effect of Relative Magnitudes of k_1, k_{-1} and k_p 111

page

Figure 31. Validity Test. Effect of Relative Magnitudes of k_1, k_{-1} and k_p 112
Figure 32. Copolymer Yield as a Function of Applied Current 115
Figure 33. NMR Spectrum of the Product 117
Figure 34. $[P_mZ]$ and $[P_t]$ as Functions of Time 118
Figure 35. Copolymer Yield as a Function of Time at Various Temperatures 122

I. THEORETICAL PART.

I.1. INTRODUCTION.

I.1.1. BASIC CONCEPTS OF COPOLYMERIZATION.

Although the polymerization of organic compounds has been known for over one hundred years, the simultaneous polymerization of two monomers - copolymerization - was not investigated until about 1911. It was found that copolymerization sometimes enabled one to employ monomers which do not homopolymerize, but which can be built into a copolymer with another monomer. In many cases the mechanical and chemical properties of a copolymer are more desirable than those of the homopolymers. Thus the discovery of copolymerization extended the range of preparation and application of the plastic materials and copolymerization became a subject of concerted study.

I.1.1.1. The Copolymer Composition Equation.

In 1936 Dostal (1) made the first attempt to elucidate the mechanism of copolymerization. He assumed that the rate of addition of monomer to a growing free radical depends only on the end group on the radical chain. If monomers M_1 and M_2 yield radicals $M_1\cdot$ and $M_2\cdot$, there are four possible propagation reactions :

$$\begin{aligned}
\sim M_1\cdot \ + \ M_1 &\xrightarrow{k_{11}} \sim M_1\cdot \\
\sim M_1\cdot \ + \ M_2 &\xrightarrow{k_{12}} \sim M_2\cdot \\
\sim M_2\cdot \ + \ M_1 &\xrightarrow{k_{21}} \sim M_1\cdot \\
\sim M_2\cdot \ + \ M_2 &\xrightarrow{k_{22}} \sim M_2\cdot
\end{aligned} \qquad (1)$$

Later, Mayo and Lewis (2) and Alfrey and Goldfinger (3) elaborated upon the scheme and derived the copolymerization equation which links the copolymer composition, $d[M_1]/d[M_2]$, the monomer feed composition, $[M_1]/[M_2]$, and the rate constants of the four simple propagation steps.

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \; \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \qquad (2)$$

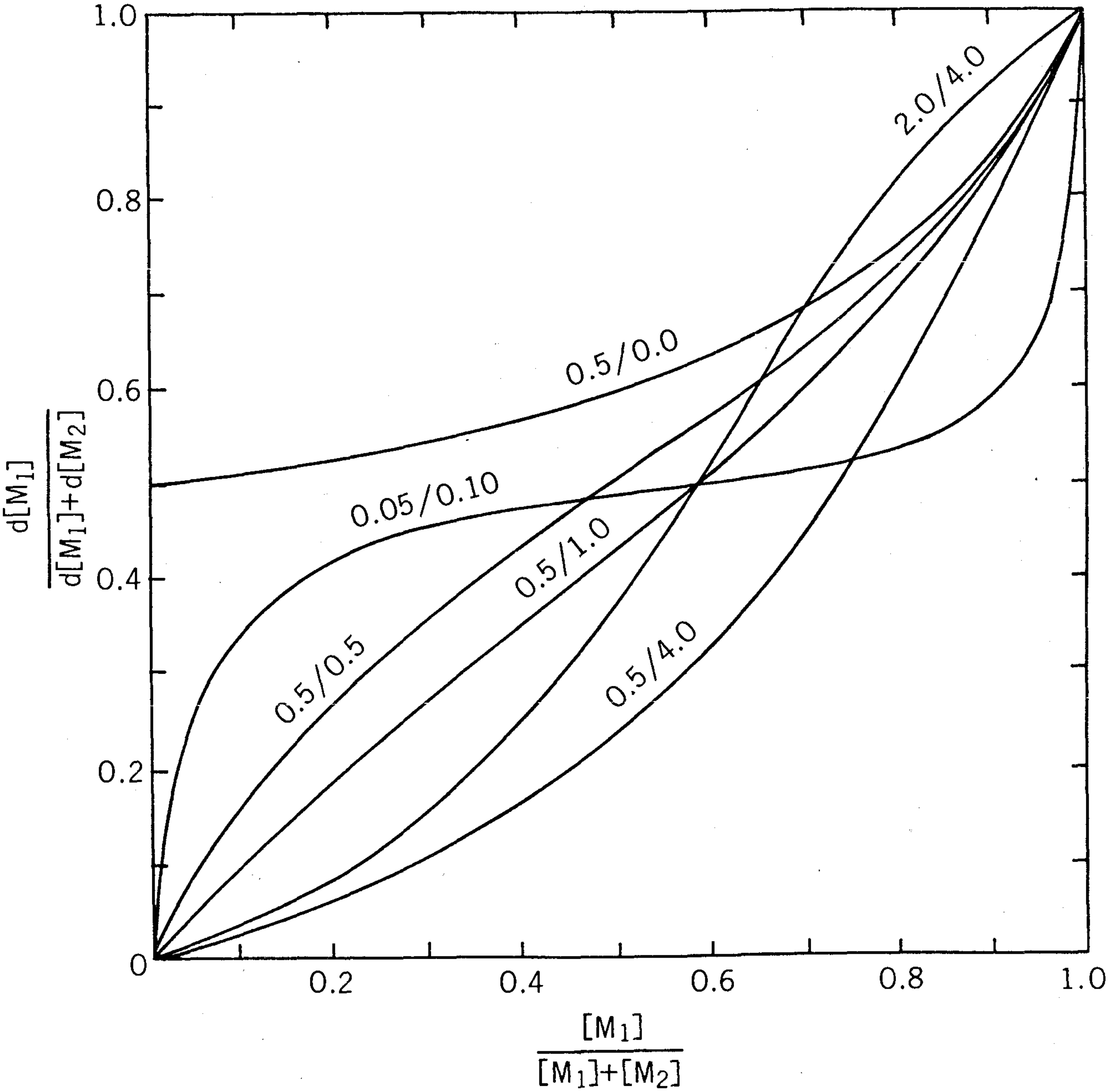
$$\text{where} \qquad r_1 = \frac{k_{11}}{k_{12}} \qquad\qquad r_2 = \frac{k_{22}}{k_{21}} \qquad (3)$$

The monomer reactivity ratios, r_1 and r_2, are important copolymerization parameters representing the preference of a radical to react with its own monomer over its reaction with the other monomer.

The quantity $d[M_1]/d[M_2]$, which represents the ratio of the two monomers in the increment of the polymer formed when the ratio of unreacted monomers is $[M_1]/[M_2]$, generally changes continually as the polymerization proceeds. Wall (4) first called attention to the close analogy between the copolymer-monomer mixture composition relationships and vapour-liquid equilibria in binary systems. The values of r_1 and r_2 determine the composition of the copolymer instantaneously formed at a given monomer mixture composition. Several examples of copolymerization curves are shown in Figure 1.

In 1946 Merz et al. (6) proposed that there might be instances where the penultimate unit might influence the addition of monomers to a growing free radical. Eight propagating steps were envisioned as follows.

Figure 1. INCREMENTAL COPOLYMER COMPOSITION AS A FUNCTION OF MONOMER FEED COMPOSITION FOR VARIOUS r_1/r_2 RATIOS (5).


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

$$\begin{array}{llll}
\sim M_1\text{-}M_1\cdot & + \; M_1 & \xrightarrow{k_{111}} & \sim M_1\text{-}M_1\text{-}M_1\cdot \\
\sim M_1\text{-}M_1\cdot & + \; M_2 & \xrightarrow{k_{112}} & \sim M_1\text{-}M_1\text{-}M_2\cdot \\
\sim M_2\text{-}M_2\cdot & + \; M_2 & \xrightarrow{k_{222}} & \sim M_2\text{-}M_2\text{-}M_2\cdot \\
\sim M_2\text{-}M_2\cdot & + \; M_1 & \xrightarrow{k_{221}} & \sim M_2\text{-}M_2\text{-}M_1\cdot \\
\sim M_2\text{-}M_1\cdot & + \; M_1 & \xrightarrow{k_{211}} & \sim M_2\text{-}M_1\text{-}M_1\cdot \\
\sim M_2\text{-}M_1\cdot & + \; M_2 & \xrightarrow{k_{212}} & \sim M_2\text{-}M_1\text{-}M_2\cdot \\
\sim M_1\text{-}M_2\cdot & + \; M_2 & \xrightarrow{k_{122}} & \sim M_1\text{-}M_2\text{-}M_2\cdot \\
\sim M_1\text{-}M_2\cdot & + \; M_1 & \xrightarrow{k_{121}} & \sim M_1\text{-}M_2\text{-}M_1\cdot
\end{array} \qquad (4)$$

If $r_1 = \dfrac{k_{111}}{k_{112}}$, $r_2 = \dfrac{k_{222}}{k_{221}}$, $r_1' = \dfrac{k_{211}}{k_{212}}$, $r_2' = \dfrac{k_{122}}{k_{121}}$, (5)

the extended copolymer composition equation may be written in the following form.

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \; \frac{r_2'[M_2]+[M_1]}{r_1'[M_1]+[M_2]} \; \frac{[M_2]^2 + r_1'[M_1](2[M_2]+ r_1[M_1])}{[M_1]^2 + r_2'[M_2](2[M_1]+ r_2[M_2])} \qquad (6)$$

The problem of the copolymer composition can alternatively be treated in terms of probabilities (7). In this way, the conventional copolymerization equation (2) and the penultimate equation (6) can be derived without the qualifying assumptions of steady state and constancy of the monomer reactivity ratios. The equations thus obtained appear to be far more general. Also, it has been shown that if the penultimate units affect the selectivity of the radical end, then the monomer reactivity ratios, r_1 and r_2 , given by equation (3), may be observed to vary with the monomer feed composition, as they become functions of the rate constants of reactions (4) and the $[M_1]/[M_2]$ ratio.

The multicomponent polymerizations are readily approached through application of the concepts and techniques employed in two component systems. The Alfrey-Goldfinger treatment of terpolymerization (8,9) is based on the assumption that in terpolymerization of three monomers, M_1, M_2, and M_3, three different types of active growing chain-ends must be considered, $M_1\cdot$, $M_2\cdot$, and $M_3\cdot$. Each of these can react with any of the three monomers of the system, and hence there are nine different elementary chain propagation reactions. The subsequent treatment is similar to that of copolymerization and the derivations are complicated only by the large number of equations.

I.1.1.2. General Relationships among Monomers in Copolymerization.

Today it is widely recognized that a general order of reactivity exists among monomers in copolymerization. Alfrey and Price (10) offered a means of predicting monomer reactivity in copolymerization on the basis of resonance and polar factors. Their Q-e scheme is an attempt to combine, in at least a semiquantitative fashion, the recognized effects of resonance stabilization and polarity on the relative reactivities of monomers with free radicals. The central assumption of the Q-e scheme is that the rate constant, k_{ij}, for the attack of radical i upon monomer j is given by

$$k_{ij} = P_i Q_j \exp(-e_i e_j) \qquad (7)$$

Here P_i characterizes the reactivity of radical i, Q_j characterizes reactivity of monomer j, and e_i and e_j are measures of the polarity of the radical and monomer, respectively. The derivation of the equation was based on the hypothesis that the rate constant for the addition of the monomer of type j to a free radical of type i can be given to a good approximation by the following expression :

$$k_{ij} = A_{ij} \exp(-(p_i + q_j + e_i e_j)) \qquad (7a)$$

In this expression for the propagation step, A_{ij} represents the probability factor, p_i is an activation factor related to the general reactivity of the polymer end-group, q_j is a similar factor related to the general monomer reactivity, and e_i and e_j are the two electrical factors. The general reactivities here are the geometric means of the relative reactivities of a given radical end-group with several monomers and of a given monomer with several radical end types, respectively. When the factor A_{ij} was assumed to be essentially constant, equation (7a) yielded equation (7). The same polarity factor, e, is used for a monomer and its radical. Thus, if the Q and e values of two comonomers are known the copolymerization parameter, r , may be estimated :

$$r_i = \frac{k_{ij}}{k_{ik}} = \frac{Q_j}{Q_k} \exp(-e_i(e_j-e_k)) \qquad (8)$$

In particular, the two reactivity ratios, r_1 and r_2, in a binary system can be written as follows.

$$r_1 = \frac{k_{11}}{k_{12}} = \frac{Q_1}{Q_2} \exp(-e_1(e_1-e_2)) \qquad (9)$$

$$r_2 = \frac{k_{22}}{k_{21}} = \frac{Q_2}{Q_1} \exp(-e_2(e_2-e_1)) \qquad (10)$$

The orders of monomer reactivities in cationic and anionic copolymerizations are quite different from those in free radical copolymerization and from each other. However, the reactivities seem to correspond to the anticipated effect of substituents upon the reactivity of double bonds toward electrophilic or nucleophilic reagents (11).

According to Price (12), when monomers carrying polar substituents copolymerize the selectivity of the radical end is determined by the polarities of both the double bond of the monomer and the radical end. The polarity of the radical end might be expressed in the language of the Linear Free Energy Relationship in terms of Taft substituent constants, σ^* . These may be used in a relation entirely analogous to the Hammett expression originally developed for aromatic systems (13), and relate the polar effect of a substituent on an aliphatic chain to the rate constant of the reaction (14).

$$\log(k/k_0) = \rho^*\sigma^*$$

That a Linear Free Energy Relationship could be applied to the radical polymerizations was demonstrated by Walling, Mayo et al.(15). They performed a series of copolymerization experiments employing styrene as the first monomer and substituted styrenes as the second monomer. The reciprocal of the monomer reactivity ratio for the styrene radical expressed the relative reactivity of the substituted styrene with the styrene radical. When the logarithm of the relative reactivity was plotted against Hammett's σ values for each substituent, a striking linearity was observed (Figure 2). Thus, if the σ values are interpreted as measures of the electron density at the reaction site, this result suggests that polar interactions between reactants, as suggested by Price, may be of primary importance in determining the selectivity of the radical end.

Similar studies of systems of methyl methacrylate with substituted styrenes did not show a simple linear relation. This author emphasises that the deviation from linearity was observed for the monomer pairs with the strongest tendency to produce alternating copolymers. The application of Hammett's treatment presupposed a reaction of two components, the polymer free radical and a monomer , which is true when copolymerization proceeds by the conventional mechanism described by scheme (1). Such systems yield random copolymers. However, when an alternating copolymer is formed the reaction can presumably proceed via a molecular complex of the two monomers. Figure 3 shows that a satisfactory linear relation could have been found if the first two, alternating copolymerizations had been omitted.

The polarity, which appears to be the factor determining selectivity in radical polymerizations, cannot affect the monomer competition for the propagating ion in ionic copolymerizations (16). The three methods of copolymer preparation are contrasted in Figure 4. The instantaneous composition of the copolymer styrene-methyl methacrylate was followed as a function of the monomer feed composition when three different initiators were used corresponding to radical, cationic and anionic polymerizations.

For commercial use it is often desirable to produce a copolymer which is homogeneous in composition. This can be done by maintaining a constant composition of the monomer feed during the polymerization process by replenishing the more reactive monomer as the polymerization proceeds, or, in the case of an azeotropic copolymerization, by stopping the reaction before complete conversion.

Another method is to employ a system in which the reactivity ratios, r_1 and r_2 , are much less than one, preferably zero, in which case an alternating copolymer is formed regardless of the composition of the monomer feed.

I.1.2. ALTERNATING EFFECT IN COPOLYMERIZATION.

The preference of each radical to react exclusively with the other monomer is reflected in zero or very low values of the monomer reactivity ratios, r_1 and r_2 . The tendency to alternate is usually expressed by the product $r_1 r_2$; the lower the value of the product, the greater the tendency to alternate.

By examining the tendency for alternation it is possible to tabulate monomers in a series arranged so that the

Figure 2. PLOT OF LOGARITHM OF RELATIVE REACTIVITY TOWARD THE STYRENE RADICAL VERSUS HAMMETT σ VALUE OF SUBSTITUENT FOR VARIOUS SUBSTITUTED STYRENES (15).

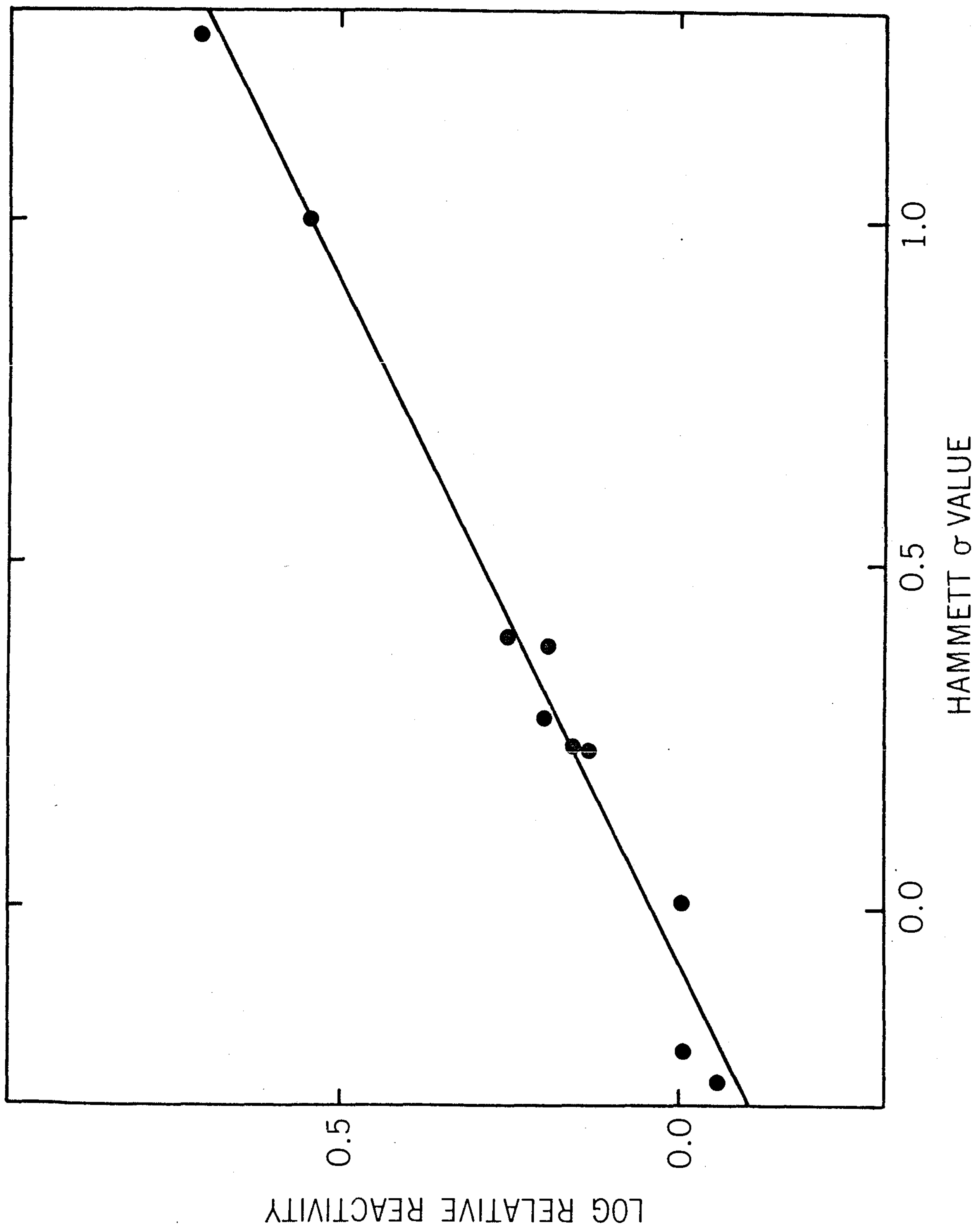

LOG RELATIVE REACTIVITY
0.0
0.5
HAMMETT σ VALUE
0.0
0.5
1.0

Figure 3. PLOT OF LOGARITHM OF RELATIVE REACTIVITY TOWARD THE METHYL METHACRYLATE RADICAL VERSUS HAMMETT σ VALUE OF SUBSTITUENT FOR VARIOUS SUBSTITUTED STYRENES (15). The solid line was added by this author.

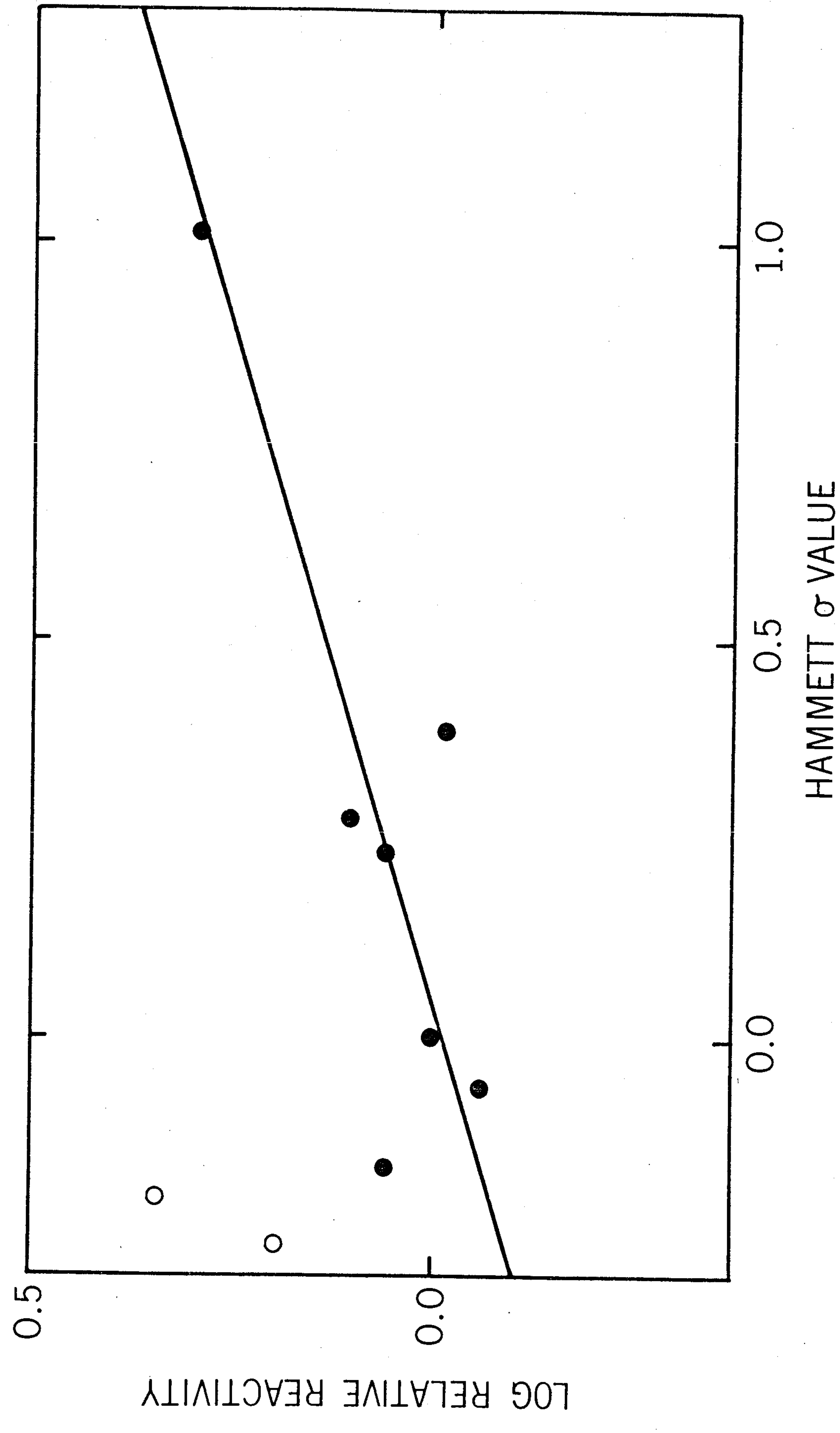
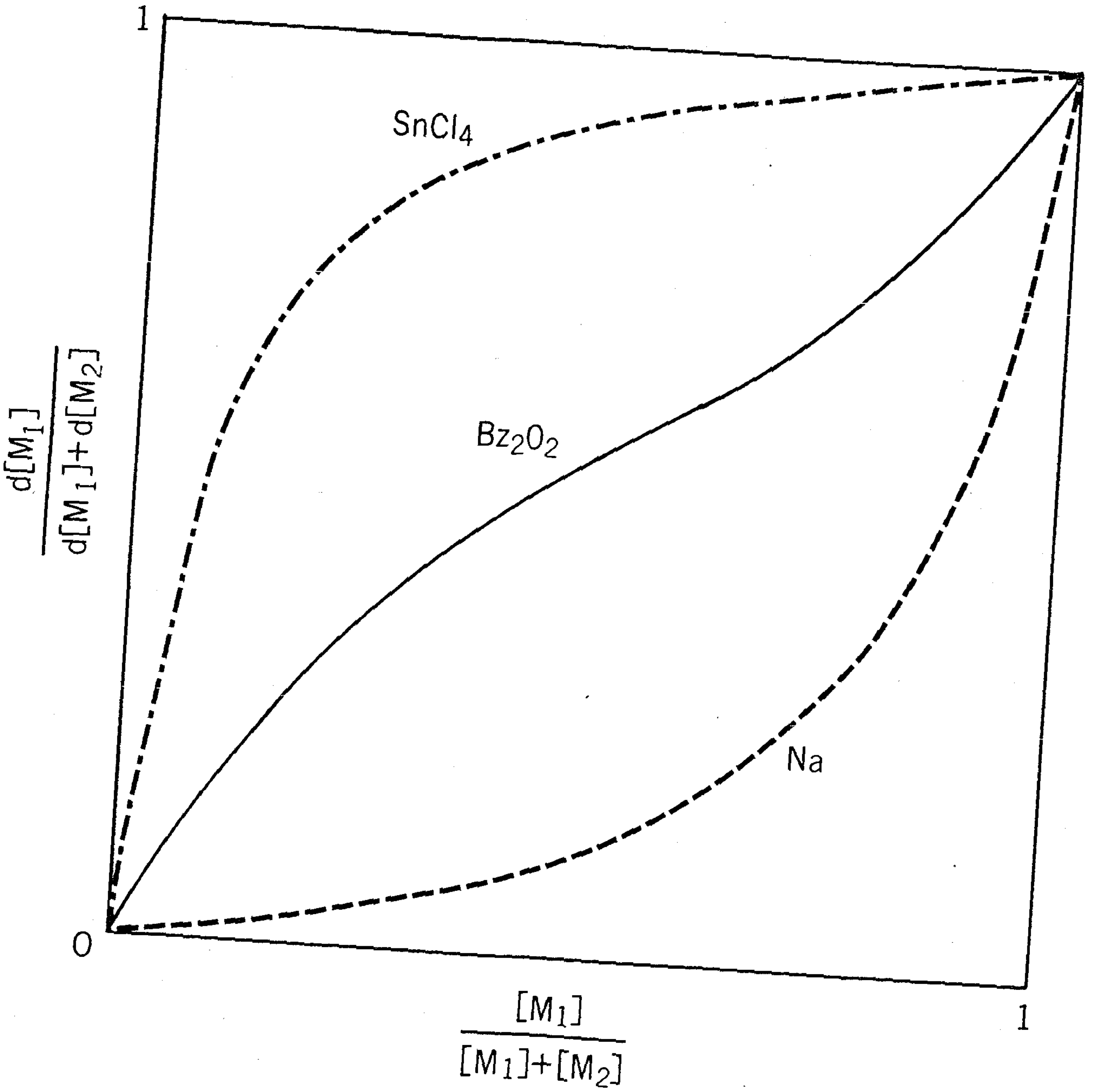
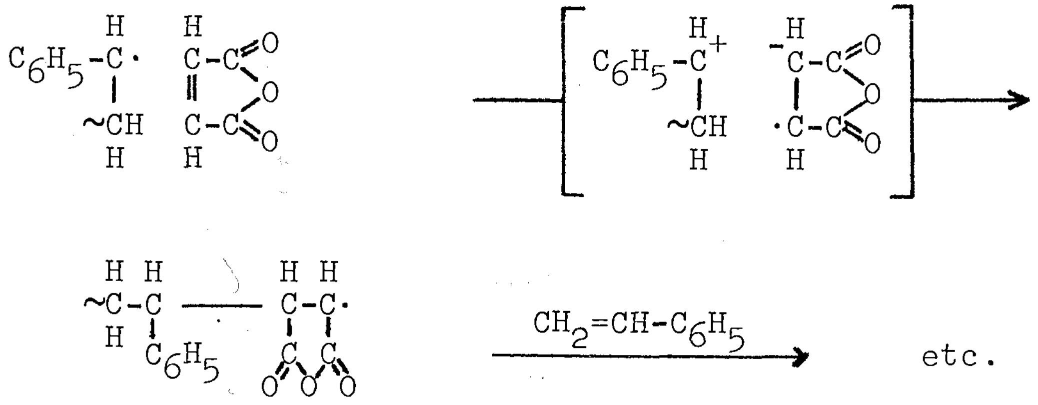

LOG RELATIVE REACTIVITY
0.5
0.0
HAMMETT σ VALUE
0.0
0.5
1.0

Figure 4. INCREMENTAL COPOLYMER COMPOSITION AS A FUNCTION OF MONOMER FEED COMPOSITION FOR THE SYSTEM STYRENE (M_1) AND METHYL METHACRYLATE (M_2) POLYMERIZED BY CATIONIC ($SnCl_4$), FREE RADICAL (Bz_2O_2) AND ANIONIC (Na) MECHANISMS (17).


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

monomer pair with the greater separation in the series has the greater tendency to alternate. A tabulation of monomers in order of their increasing tendency to alternate with styrene was presented by Mayo, Lewis and Walling (18) and is shown in Table I. The order of the monomers in the table closely parallels the order of the tendency of substituents around the double bond to donate electrons to the bond (hydrocarbon, acetoxy) or to withdraw them (carbonyl, cyano). Monomers with electron-releasing substituents occur at the top and those with electron-withdrawing substituents at the foot of the table. This suggests that the alternating tendency is primarily due to the polarity of the double bond in the monomer.

Mayo, Walling and co-workers (15,19) discussed the alternating effect in the context of monomer-radical interactions. The alternation of the monomers in a copolymer was ascribed to an interaction between a negative double bond and a positive radical, or vice versa, in the transition state of the propagation step. For example,



Recently, Hirooka (20) has suggested that the initially formed complex between the chain-end radical and a comonomer might be stable enough to come in contact with another monomer before the propagation proceeds. A double complex is formed between the radical chain-end, the donor-monomer and the acceptor-monomer, through a donor-acceptor interaction.

Table I. Arrangement of Monomers in Order of Their Increasing Tendency to Alternate with Styrene, as Measured by the Decreasing Product of Their Monomer Reactivity Ratios (18).

	Vinyl acetate	Butadiene	Styrene	Allyl acetate	Vinyl chloride	Methyl methacrylate	Vinylidene chloride	Methyl acrylate	Methyl vinyl ketone	β-Chloroethyl acrylate
Vinyl acetate										
Butadiene										
Styrene		1.08								
Allyl acetate	0.3									
Vinyl chloride	0.39		0.34							
Methyl methacrylate	<0.3	0.19	0.26							
Vinylidene chloride	<0.1		0.16			0.61				
Methyl acrylate			0.14							
Methyl vinyl ketone			0.10							
β-Chloroethyl acrylate			0.054	0.3				0.8		
Methacrylonitrile			0.05			0.43				
Acrylonitrile	0.25		0.02		0.07	0.24	0.34		1.1	
Diethyl fumarate	0.004		0.02		0.06		0.56			

$$\sim P\cdot \; + \; M_1 \; \xrightleftharpoons{K_1} \; \sim P\overset{\cdot}{-}--M_1$$

(radical complex)

(a) If the radical complex is unstable,

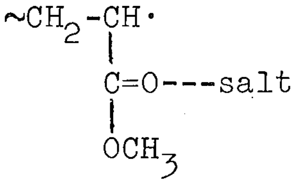
$$\sim P\overset{\cdot}{-}--M_1 \; \xrightarrow{k_p} \; \sim PM_1^{\cdot}$$

(b) If the radical complex is stable,

$$\sim P\overset{\cdot}{-}--M_1 \; + \; M_2 \; \xrightleftharpoons{K_2} \; \sim P\overset{\cdot}{-}-M_1--M_2 \; \xrightarrow{k_p'} \; \sim PM_1M_2^{\cdot}$$

(double complex)

He supported his view with the fact that only the methyl methacrylate radical was detected (21) in the irradiated styrene, methyl methacrylate and aluminum halide system. The key role in this mechanism was attributed to complexing salt which stabilizes the growing radical, e.g.,



$$\begin{array}{l}\sim CH_2-CH\cdot \\ \qquad\qquad | \\ \qquad\qquad C{=}O---salt \\ \qquad\qquad | \\ \qquad\qquad OCH_3\end{array}$$

as well as the radical complex. When a double complex has been formed, the complexing salt may be released and the radical localized. Propagation could then proceed through the two monomers via a concerted reaction.

A fundamentally different explanation of the alternation in copolymerization is based on monomer-monomer interactions. The different polarities of the double bonds of two monomers enhance the formation of a molecular complex which then undergoes homopolymerization. This complex is described as a donor-acceptor molecular complex or a charge transfer complex resulting from the one-electron transfer from the electron-donor monomer to the electron-acceptor monomer.

I.2. DONOR-ACCEPTOR MOLECULAR COMPLEXES IN ALTERNATING COPOLYMERIZATION.

One way to prepare an equimolar copolymer is to maintain a constant monomer feed which can be found in the copolymer composition diagrams, as they are shown in Figures 1 and 4. Copolymers prepared in this manner have a random sequence of monomers. A basically different method of preparing an equimolar copolymer employs a monomer pair which yields an equimolar copolymer regardless of the monomer feed. In this case, the monomer units are found to alternate in the polymer chains. The structural difference of random and alternating copolymers is reflected in their different properties. For example, when random and alternating equimolar acrylonitrile-styrene copolymers were examined and compared (22) the latter were characterized by higher resistance to alkalies and temperature.

It has already been mentioned that an alternating copolymer is formed when the two monomers are far apart in the Mayo-Walling series. If the separation is small a non-alternating copolymer is formed. A difference in the polarities of the double bonds of the two comonomers thus appears to be essential for a system to yield an alternating copolymer.

Spectroscopic studies of such systems have revealed new absorption bands which are attributed to a molecular complex of the two monomers (23-29).

I.2.1. SPONTANEOUS FORMATION OF THE COMPLEX.

The concept of a molecular complex as an intermediate in polymerization reactions was first introduced in 1946 in order to explain the alternating tendency in allyl acetate - maleic anhydride copolymerization (30). Barb later obtained spectroscopic evidence for the existence of a charge transfer complex in a system of two monomers, maleic anhydride and styrene (23). By this time, however , Walling's elucidation of the selectivity (15,19), based upon reaction of the copolymer radical with the monomer, was generally accepted.

In 1965, Iwatsuki and Yamashita (24) presented a detailed study of the copolymerization of p-dioxene and maleic anhydride and discussed their experimental observations in terms of the formation of a charge transfer complex between the two monomers. It was found that p-dioxene and maleic anhydride could easily copolymerize with a radical initiator to form an alternating copolymer regardless of the monomer feed composition, although neither monomer could homopolymerize. In this alternating copolymerization, both the rate of copolymerization and the viscosity of the copolymer depended on the monomer feed ratio, and had their maxima at a monomer ratio of 1:1. In terpolymerization with acrylonitrile, the ratio of p-dioxene and maleic anhydride in the terpolymer was always found to be unity, regardless of the monomer feed ratio or amount of acrylonitrile included in the terpolymer. The latter result in particular was not compatible with the usual theory of terpolymerization and led to the consideration of an interaction between p-dioxene and maleic anhydride. Supplementary studies showed that a yellow color appeared when the two monomers were mixed with each other and spectroscopic analysis of the solution by a continuous variation method detected the 1:1 complex formation between p-dioxene and maleic anhydride. It was concluded that the interaction was an electron transfer between the two monomers and that the charge transfer complex might be the polymerizing species.

The results of a study of the terpolymerization of dodecyl vinyl ether, fumaronitrile and β-chloroethyl acrylate were found to be at variance with the usual theoretical treatment of terpolymerization (31). The monomer reactivity ratios depended upon the monomer feed ratios and the calculated composition did not agree with experiments at extreme monomer feed ratios. From the fact that the composition ratios of donor-type monomer units and acceptor-type monomer units in terpolymers were always constant and equal to unity regardless of the monomer feed ratios, it was assumed that an interaction between the donor-monomer and the acceptor-monomer might result in the formation of a donor-acceptor molecular complex which then undergoes copolymerization with the third monomer. The terpolymerization was treated as a copolymerization of β-chloroethyl acrylate with the molecular complex formed between fumaronitrile and dodecyl vinyl ether. Employing the equilibrium between fumaronitrile, dodecyl vinyl ether and the molecular complex,

$$\mathrm{FN} + \mathrm{DVE} \xrightleftharpoons{K} \text{complex} \quad ,$$

the concentration of the complex may be written as a product of the equilibrium constant, K, and the concentrations of the two components. The expression for the complex concentration was substituted into the Mayo and Lewis's equation for copolymer composition (eq.2) and the subsequent treatment was analogous to that of copolymerization. A good agreement was found between the theoretically predicted composition curve and the experimental values.

Similar contradictions between experimental results and theory were found when the conventional analysis of a ternary system was applied to the system of β-acrolein, α-methyl styrene and methyl acrylate (25). Spectroscopic studies indicated the formation of a 1:1 molecular complex between β-cyanoacrolein and α-methyl styrene and copolymerization of the two monomers was shown to yield an alternating copolymer.

Terpolymerization of anethole, maleic anhydride and one of β-chloroethyl methacrylate, methacrylonitrile or acrylonitrile produced polymers in which the molar ratio of anethole and maleic anhydride was always unity (32). An application of the conventional treatment of terpolymerization failed to give results consistent with a mechanism employing the three components as single reactants. Agreement of the experimental values with theory was much better when the polymerization was treated as a copolymerization of the molecular complex with the third component.

Ywatsuki and Yamashita (33) investigated the dilution and solvent effects in radical terpolymerizations. The compositions of the terpolymers obtained from feeds of the same monomer ratios were found to be changed beyond the limit of error for the various dilutions and solvents. In other words, the apparent monomer reactivity ratios changed remarkably with dilution and with the nature of the solvent. While two of the monomers invariably entered the polymer in equimolar amounts, the proportion of the third monomer in the terpolymers increased, reached a maximum, then decreased, as the amount of solvent increased. The change in copolymer composition was not compatible with conventional radical terpolymerization. It was suggested that the effect was due to the formation of a molecular complex between the donor-type and acceptor-type monomers. From the relationship determining the concentration of the complex,

$$[\text{complex}] = K[\text{donor}][\text{acceptor}] ,$$

it is clear that, with dilution, the complex concentration changes non-linearly while the third monomer concentration changes linearly. Since the complex and the third monomer may be considered to copolymerize randomly with each other, a change of the molar ratio of the complex to the third monomer is expected to result in a change in the composition of the product.

Characterization of the charge transfer complex between furan and maleic anhydride was presented by Butler and co-workers (26) using NMR and UV spectroscopy. Although neither of the two monomers underwent homopolymerization, the mixture of them yielded the alternating copolymer, suggesting that the polymerization proceeded via a molecular complex of the two components.

A donor-acceptor complex of 1:1 composition has also been detected in systems of maleic anhydride and each of the following donor-monomers : n-butyl vinyl ether, iso-butyl vinyl ether, tert-butyl vinyl ether (27), 2-chloroethyl vinyl ether, styrene, and 2,5-dihydrofuran (138). The composition of the resulting copolymers is always 1:1 regardless of the monomer feed ratio. The rate of polymerization increases with the increasing complex formation constant and is a maximum at a monomer feed ratio of 1:1 at which the concentration of the molecular complex is highest. These findings are consistent with the participation of the molecular complex as the active species in the polymerization process.

Further studies have been made of the styrene-maleic anhydride(28) and the divinyl ether-chloromaleic anhydride(29) systems. Charge transfer complexes of 1:1 molar compositions were detected in these binary systems which yielded, when polymerized, the alternating copolymers. When another donor-monomer was added to the styrene-maleic anhydride system, the polymerization could be treated as a copolymerization of two complexes, styrene/maleic anhydride and donor/maleic anhydride, with participation of free maleic anhydride in the propagation steps.

These and further experimental observations consistent with and/or favoring the theory of donor-acceptor complex polymerization are summarized in Table II.

Table II. Summary of Experimental Facts which Favor Donor-Acceptor Complex Polymerization Theory.

Subject investigated	Observation	Refr.
Copolymer structure	The copolymer is always equimolar and alternating regardless of the monomer feed composition	26-30 34-41
Polymerization rate	The rate is maximum at a 1:1 monomer feed composition	24,27 40-43 37,138
Chain transfer	Chlorine is not incorporated in the copolymer when CCl_4 or $CHCl_3$ is used as a solvent. Strong electron-acceptor or donor molecules act as chain transfer agents	28,33 44

Subject investigated	Observation	Refr.
Species present	Spectroscopic experiments reveal the presence of donor-acceptor complexes	23-29
Initiation	$\cdot CCl_3$ radicals(resulting from the solvent-initiator interaction) do not participate in the initiation step (no chlorine is found in the copolymer	28,33
Molecular weight of copolymer	In the initial stages of polymerization the molecular weight increases continuously with conversion	28,45
Effect of inhibitors	p-Benzoquinone increases the rate of polymerization	42
Solvent effect	Solvents bearing a labile hydrogen induce the polymerization, while solvents which are stable to hydrogen abstraction are ineffective	46
Solvent effect	In terpolymerization experiments, the dilution and the nature of the solvent affect the product composition	33,25
Composition of terpolymers	Terpolymerization of an acceptor-monomer (A), donor-monomer (B) and a monomer (C) which forms no complexes with either A or B yields a polymer of composition $(AB)_xC_y$	24 31-33
Kinetics of terpolymerization	The conventional kinetics treatment fails. A good agreement is obtained when the reaction is treated as a copolymerization of a complex between the donor-monomer and the acceptor-monomer with the third monomer	31,32 130
Sensitivity to light	The polymerizations are accelerated by light, exclusion of light lowering the yield correspondingly. This is explained by the photosensitivity of the charge transfer complexes	47-49
Hammett's relation	Despite a good fit of Hammett's relationship in a series of copolymerization pairs, a sharp deviation is observed for systems yielding alternating copolymers	15

The above experimental work leaves no doubt about the existence of charge transfer complexes in polymerization systems which yield alternating copolymers. Another question involves the extent that these complexes participate in the polymerization process. It has been argued (50) that the existence of molecular complexes in a reaction system does not prove that they are the intermediates through which the reaction products are formed. However, the relation of the polymerization rate to the concentration of monomers is evidence that the polymerization does proceed via molecular complexes. The rate has been found to increase with increasing complex formation constants (27) and the maximum rate of polymerization occurs at a monomer feed ratio of 1:1 at which the concentration of the molecular complex is also at a maximum (27,37,40,42,43). The conventional copolymerization kinetic equation predicts a rate minimum in systems that tend to alternate and in which both monomers are capable of homopolymerization. The terpolymerization experiments (24,31-33) and the deviation from the Hammett's relationship of systems which yield alternating copolymers (15) provide further indication of the direct participation of the monomer complexes as the active species in the polymerization process. Some other observations supporting this view are described in the chapter on kinetics.

I.2.2. ENHANCED FORMATION OF THE COMPLEX.

The number of possible monomer combinations yielding the molecular donor-acceptor complex and the alternating copolymer has been extended remarkably by the finding that a system of two monomers which do not satisfy the requirement of separation in the Mayo-Walling series, can nevertheless be modified by a third component and then polymerized to yield an alternating copolymer. The third component is an inorganic salt or an organometallic compound. The most effective modifiers have been found to be zinc chloride (35,38,40,43,48,51-57) and aluminum sesquichlorides (38,39,42,45,47,54,57-70). Similar compounds such as zinc bromide (71-73), aluminum chloride (74), magnesium chloride(34), nickel chloride (34) and various alkyl aluminum chlorides (39,58,61,64,75-77) and bromides (69,58), and triethylaluminum (78) have also been found effective in the preparation of alternating copolymers, although their effectiveness is sometimes specific to certain systems.

The modifiers are in all cases complexing agent acting as Lewis acids. The enhanced formation of a donor-acceptor complex can be attributed to a greater separation of the donor monomer and the acceptor monomer in the Mayo-Walling series. The formation of the complex between the polar group of the acceptor monomer and the complexing agent results in the delocalization of the electrons in the double bond of the monomer, and thus in its enhanced electrophilic character (79-88). Farona and Tompkin described the complex by the following resonance structures (83), postulated on the basis of the observed partial double bond character of the metal-nitrogen bond.

$$\mathrm{CH_2{=}CH{-}C{\equiv}N\overset{+}{-}M^{-}} \longleftrightarrow \mathrm{C^{+}H_2{-}CH{=}C{=}N{=}M^{=}}$$

$$\mathrm{CH_2{=}CH{-}C{\equiv}N\overset{+}{-}M^{-}} \longleftrightarrow \mathrm{C^{-}H_2{-}CH{=}C{=}N\overset{+}{=}M}$$

(The first two canonical forms arise from the interaction of filled p orbitals on nitrogen with empty d or p orbitals on the metal, the other two canonical forms express the back donation).

The composition of the complexing salt-acceptor monomer complex is generally 1:1 or 1:2. Complexes of both types have been isolated (79,84) or determined by cryoscopy (85,87). Complexation of a higher degree is also possible. A 1:3 composition was found for the chromium trichloride-acrylonitrile complex (83). By analogy with the species present in an aqueous solution, $\mathrm{Zn(H_2O)_6^{++}}$ (89), and a methanolic solution, $\mathrm{ZnCl_2Me_4}$ (90), the number of complexed monomer molecules per $\mathrm{ZnCl_2}$ molecule might be as high as six.

An acceptor monomer complexed with a salt via the polar group on the monomer double bond has a remarkably increased tendency to form a donor-acceptor molecular complex with a donor monomer. This is reflected primarily in the detection of a charge transfer complex band in UV spectra of such systems and in changes in chemical shifts in the NMR spectra. For example, a significant interaction between butadiene and methyl methacrylate was not detected in the absence of a complexing agent. However, in the presence of ethylaluminum dichloride a new band appeared in the UV spectrum. Continuous variation curves for the change in the chemical shifts of α-methyl and methoxy protons of methyl methacrylate afforded maximum values at a 1:1 molar ratio of butadiene and methyl methacrylate (85). (An observed chemical shift value ($\tau_c + \Delta\tau$ in ppm) of the acceptor monomer is equal to the weighted average of the chemical shift value due to the salt-complexed acceptor monomer and the chemical shift value due to the molecular complex. Therefore, the stoichiometry coefficients of the complex can be determined by a continuous variation method of plotting $f\Delta\tau_c$ against f, keeping (c_a+c_d) constant, where f is the mole fraction of the acceptor monomer, and c_a and c_d are concentrations of the acceptor monomer and the donor monomer, respectively (91).)

Similar evidence for molecular complexes of various compositions has been reported, and the equilibrium constants determined, for polymerization systems of styrene (donor monomer), acrylonitrile, methacrylonitrile, or methyl methacrylonitrile (acceptor monomers), and $ZnCl_2$ or $SnCl_4$ (complexing agents) (52,91,92).

The formation of the donor-acceptor molecular complexes in two-monomer systems modified with a complexing agent results in an extraordinary change in the composition of the polymer product. For example, when isoprene or 1,3-butadiene and acrylonitrile are polymerized in the conventional radical manner the composition of the instantaneously formed product increment ranges from 0 to 100% diene depending on the monomer feed. When a complexing agent, such as zinc chloride or an aluminum sesquichloride, is added to the system the product has an alternating structure independent of the monomer feed, even when the concentration of the complexing agent is as low as one hundredth of the concentration of the monomers (38).

The effect of the presence of a complexing agent on the copolymer composition is best illustrated by Figures 5 and 6 for the systems methyl methacrylate-styrene-ethylaluminum sesquichloride and methyl acrylate-styrene-ethylaluminum sesquichloride.

Several studies have been made to determine the amount of complexing agent necessary for the system to yield an alternating copolymer. In addition to the diene-acrylonitrile-aluminum sesquichloride systems which yielded alternating copolymers at an AN/Al ratio of 100/1 (38) a very low concentration of the complexing agent has been found sufficient for the polymerization systems of isoprene, acrylonitrile and zinc chloride (the ratio acceptor monomer/complexing agent equalled 20/1) (38), 1,3-butadiene,acrylonitrile and zinc chloride (20/1) (38), and styrene, acrylonitrile and ethylaluminum sesquichloride (50/1) (57,65). These ratios are not limiting values determining the complexing agent concentration; presumably, a lower concentration of the agent could still be sufficient. In some cases a low concentration of complexing agent appears to be necessary for the polymerization system to yield an alternating copolymer as the only product. In the copolymerization of styrene and acrylonitrile in the presence of zinc chloride, the alternating copolymer was accompanied by an acrylonitrile-rich copolymer when the acrylonitrile/$ZnCl_2$ molar ratio was 1/1, whereas at 2/1 ratio the only product was the alternating copolymer (51). The same observation was reported for the system of isoprene, acrylonitrile and zinc chloride in aqueous medium (34).

Copolymerization initiated by a Ziegler-Natta type catalyst may also produce an alternating copolymer (61,93-96). (This catalytic system consists, by definition, of two compo-

Figure 5. COPOLYMERIZATION OF METHYL METHACRYLATE AND STYRENE (39).

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

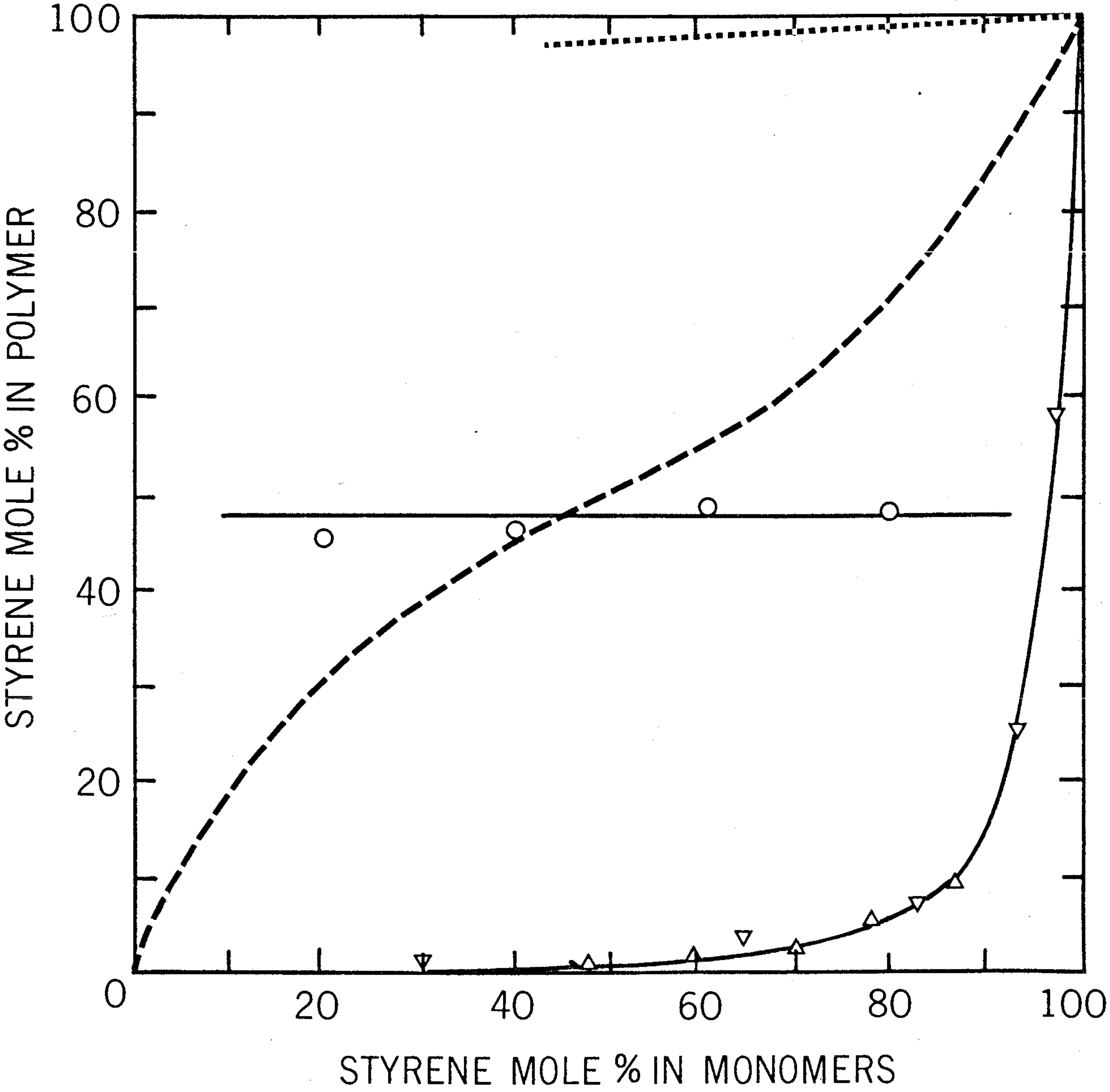
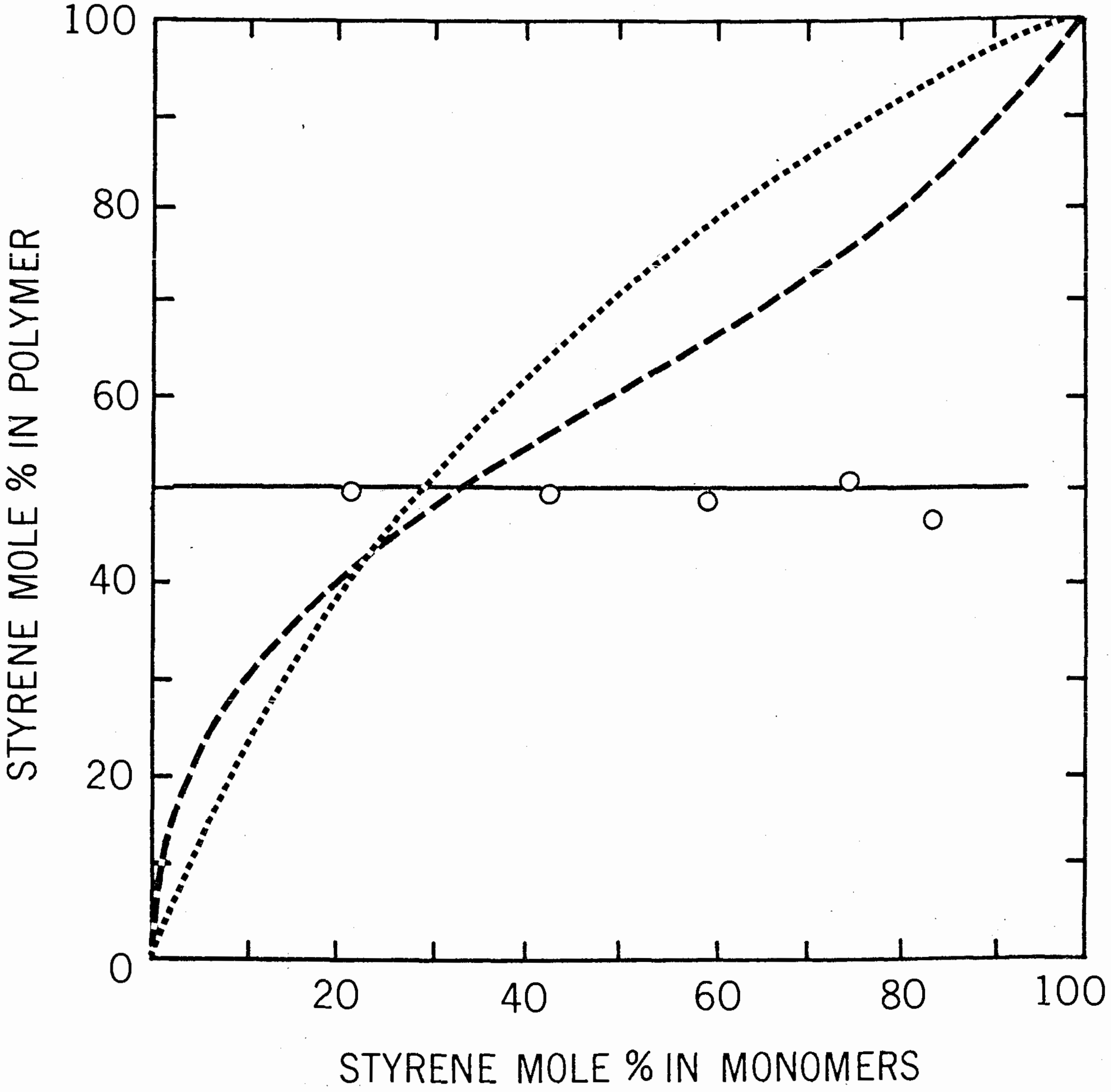

100
80
60
40
20
0
20
40
60
80
100
STYRENE MOLE % IN POLYMER
STYRENE MOLE % IN MONOMERS

Figure 6. COPOLYMERIZATION OF METHYL ACRYLATE AND STYRENE (39).

(o)with ethylaluminum sesquichloride;
(--)radical; (...)cationic.


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

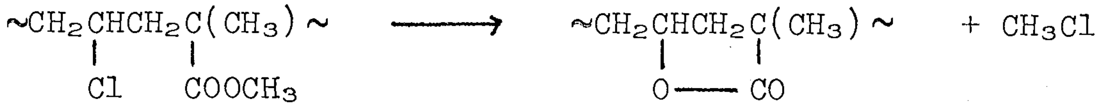
nents: (1) a metal alkyl, a metal halide alkyl, or a metal hydride of groups I-III; (2) a salt of a transition metal of groups IV-VIII). This is not suprizing when one realizes that one of the components of the Z-N catalytic system is an organometal, most frequently an alkylaluminum chloride. For example, alternating copolymers were formed when butadiene and acrylonitrile (94,95) and butadiene and methyl methacrylate(96) were copolymerized with $AlEtCl_2/VOCl_3$ as a catalyst. Copolymerization of acrylonitrile with vinyl chloride catalyzed by $EtAlCl_2/VOCl_3$ yielded an alternating copolymer in the presence of an equimolar or greater amount of the organometal (61). The role of the vanadium compound in the reported systems has been suggested to be in the recycling of the aluminum compound which is complexed on the polymer chain. However, the presence of the Z-N catalyst classifies these polymerizations as the Z-N type and accordingly, must involve all the problems encountered in this class of polymerizations.

The donor-acceptor polymerization systems yielding alternating copolymers reported to date are listed in Appendix I.

I.3. PROOF OF THE ALTERNATING STRUCTURE OF A COPOLYMER.

An elemental analysis of the copolymers yields an indication of the alternating structure. However, the 1:1 molar ratio of comonomers in a copolymer does not prove that the structure is alternating. When a conventional system of two monomers is polymerized, an equimolar copolymer can be prepared from a monomer feed of the appropriate composition. Although the structure of the copolymer would be non-alternating, random in this case, elemental analysis would indicate the equimolarity of monomer units in the product. However, if the composition of a copolymer is found to be 1:1 regardless of monomer feed composition,then the alternating effect is the only satisfactory explanation of the phenomenon. In fact, the elemental analysis and NMR spectra of random copolymers of various compositions, together with the spectra of the corresponding homopolymers and alternating copolymer, have provided a basis for the determination by NMR spectroanalysis of copolymer compositions. When the assignments of the resonances to the monomer unit sequences have been made, the intensities of the peaks for copolymers of different compositions and the alternating copolymer are compared. (Owing to the low resolution the peaks may also shift as a result of the intensity change of unresolved peaks which could only be distinguished at a very high resolution). Such a set of NMR spectra then provides features discriminating between the alternating and random copolymers (39,60,69,70,97,98) and may be later used to identify alternating structures. (The ^{1}H NMR spectra of copolymers can usually be interpreted in terms of triads of monomer units in the chain. The relative chemical shifts of the protons of a unit in the chain depend on the identity of the two nearest neighbor monomer-units. Only rarely are sizable effects of more distant units in the chain observed. For a given central unit these triad shifts are generally small, amounting to only a fraction of a p.p.m. This makes interpretation of the spectra rather difficult, especially if the resonances show the dipolar broadening characteristic of proton NMR polymer spectra (98). In addition, the proton NMR spectra of most copolymers are complicated by spin-spin coupling which does not itself contain any sequence information. However, recent work by Schaefer (98) using high resolution pulsed carbon-13 NMR makes NMR analysis of copolymers atractive enough to overcome the disadvantage of low sensitivity).

Sometimes the presence of substituents on the monomers allows treatments yielding direct evidence of the monomer sequence. For example, vinyl chloride-methyl methacrylate copolymer was shown to have the alternating structure by exploiting thermal cyclization (93), as is shown in the following equation.



$$\sim CH_2\underset{Cl}{\underset{|}{CH}}CH_2\underset{COOCH_3}{\underset{|}{C}}(CH_3)\sim \longrightarrow \sim CH_2\underset{O}{\underset{|}{CH}}CH_2\underset{CO}{\underset{|}{C}}(CH_3)\sim + CH_3Cl$$

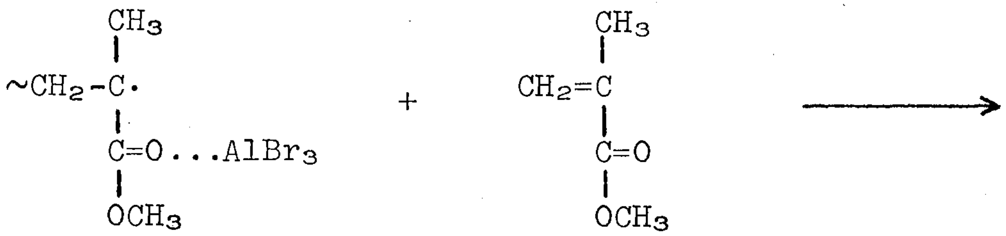
A statistical treatment was used to calculate the extent of cyclization expected when the completely alternating copolymer underwent random cyclization (99). The experimental results were in excellent agreement, the discrepancy being less than two per cent.

I.4. MECHANISM OF THE DONOR-ACCEPTOR COMPLEX POLYMERIZATION.

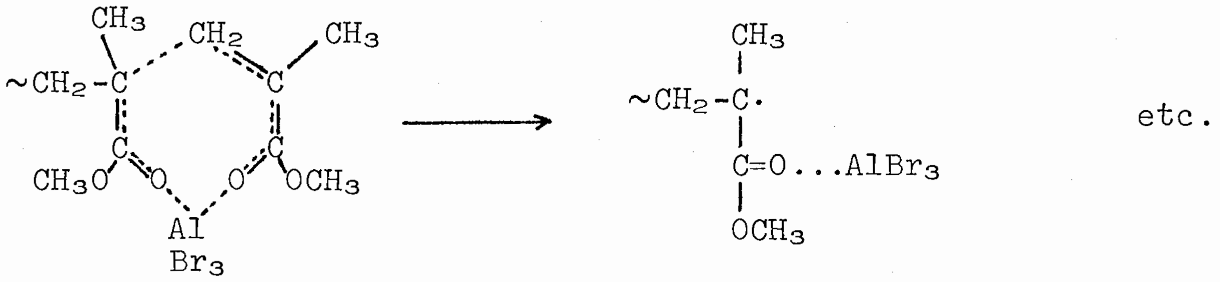
I.4.1. STUDIES RELATED TO THE DONOR-ACCEPTOR COMPLEX POLYMERIZATION.

The presence of Lewis acids, such as $ZnCl_2$, $AlCl_3$, etc., in the free-radical initiated polymerization of a polar monomer containing a pendant nitrile or carbonyl group is characterized by an increased rate of polymerization (81,84,86, 100-103). It has been proved that (86) the presence of $ZnCl_2$ does not affect the rate of decomposition of the free-radical initiator and the enhanced reactivity is attributed to the formation of a complex between the pendant group and the Lewis acid (86,104,105). The salt simultaneously acts as a chain transfer agent (86,104).

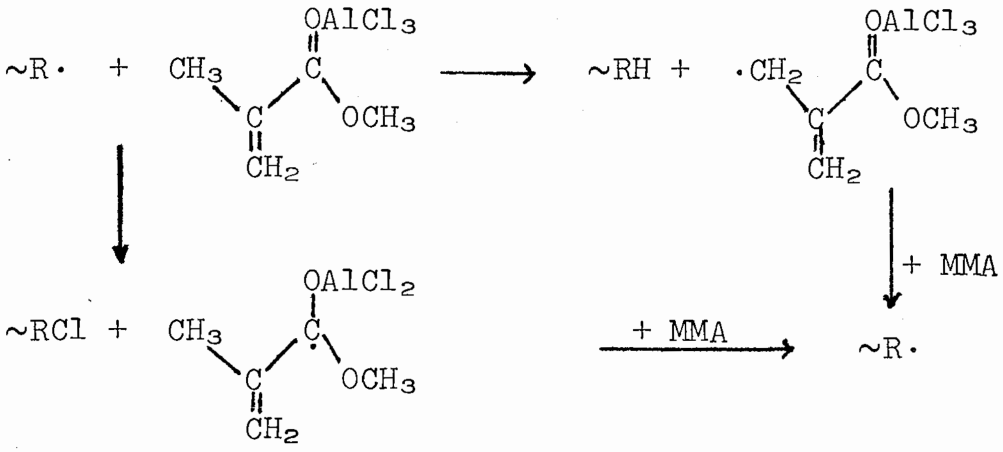
Zubov et al. (136) proposed the following propagation mechanism for the radical-initiated polymerization of methyl methacrylate in the presence of $AlBr_3$.



$$\sim CH_2-\overset{CH_3}{\underset{\underset{OCH_3}{C=O\ldots AlBr_3}}{C\cdot}} + CH_2=\overset{CH_3}{\underset{\underset{OCH_3}{C=O}}{C}} \longrightarrow$$



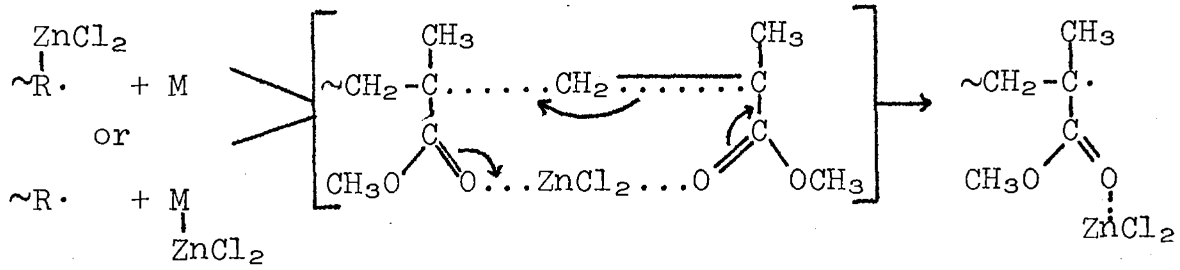
Bamford et al. (101) found an enhanced importance of transfer reactions in the presence of aluminum chloride and suggested that the transfer agent was a complex between methyl methacrylate and aluminum chloride.



This scheme also explained the observed retardation, if it was assumed that the radicals formed by the transfer reaction were more stable than those formed by hydrogen abstraction from the pure monomers.

The enhanced reactivity of the complexed monomer extends to copolymerization with monomers which are readily responsive to free radical polymerization (106-108). This effect is accompanied by a shift in the copolymer composition toward a 1:1 monomer ratio. The significance of the monomer reactivity ratios in the presence of a salt in a conventional non-alternating copolymerization has been elucidated (43). When M_1, M_2 and M_3 represent the free acceptor monomer, the acceptor monomer complexed with the salt, and the donor monomer, respectively, there are nine possible chain-propagation reactions between M_1, M_2, M_3 and all their radicals. The final copolymer composition equation is identical in form with the Mayo-Lewis equation (eq.2), only r_1 and r_2 being different. In this way it was shown that a conventional copolymerization in the presence of a salt might be treated, as far as the relation between the copolymer composition and the monomer reactivity ratios is concerned, as a salt-free copolymerization.

Russian workers (108) have studied the radical copolymerization of methyl methacrylate and various comonomers in the presence of complexing agents: $ZnCl_2$, $AlCl_3$, $AlBr_3$, and $AlEt_2Cl$. When the comonomer (methyl acrylate, butyl acrylate) was able to form complexes with the complexing agent the copolymer composition approached the monomer feed composition as the concentration of the complexing agent increased, and became practically equal to it at the mole ratio (complexing agent $/M_1+M_2) \geq 0.2-0.3$. In other words, the apparent monomer reactivity ratios became equal to unity and remained unchanged for further increases of the complexing agent concentration. These results were explained by the following scheme.

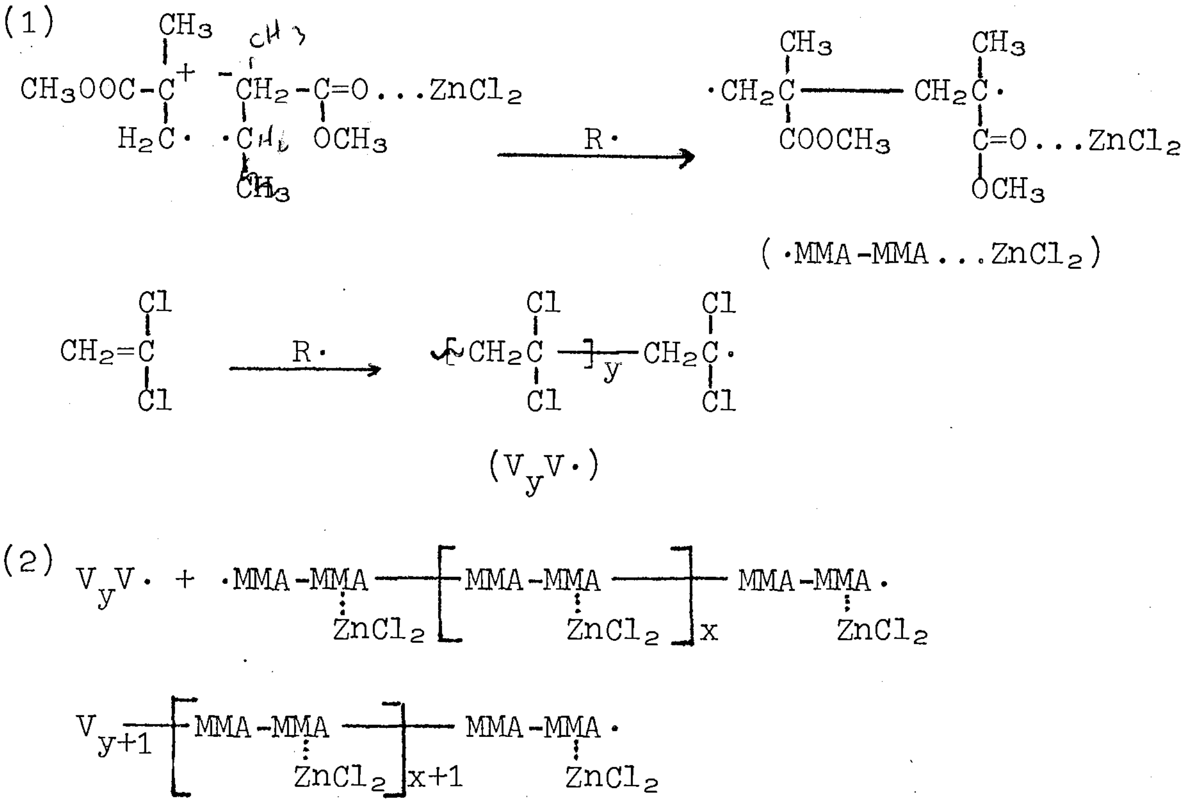


If the propagation occurs through the transition state as shown in the scheme, the differences in the relative activities of the double bonds may disappear, and thus the copolymer composition becomes equal to the composition of the monomer mixture, and the values of r_1 and r_2 approach unity.

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.

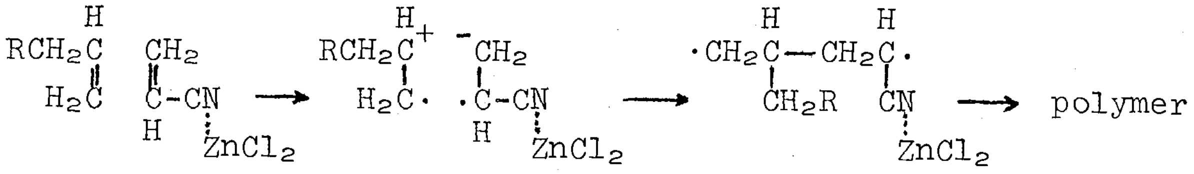
The value of r_2 decreased in all cases. Although the sence of the changes in the copolymer composition was not the same (positive or negative) the methyl methacrylate content always reached a limit (between 50 and 90 per cent) at a relatively low concentration of complexing agent.

For the type of copolymerizations in which only one monomer forms a complex, Gaylord and Takahashi (109) suggested a scheme which involved (1)homopolymerization of a molecular complex of the form MMA-MMA-$ZnCl_2$, and (2)coupling of this polymerized complex with growing vinyl chloride homopolymer. This proposal is consistent with the postulated formation of molecular complexes in the presence of zinc chloride.

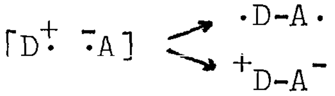


I.4.2. MECHANISM OF THE DONOR-ACCEPTOR COMPLEX POLYMERIZATION.

The first rationalization of alternating copolymerization involved a diradical mechanism (55,109) and was demonstrated by the following scheme.



Later (45), it was postulated that the charge transfer complex might undergo intramolecular coupling of either the ionic centers to produce a diradical species, or the radical centers to produce a zwitterion or dipolar species.



$$[D^{\dot{+}}\ {}^{\dot{-}}A] \rightarrow \cdot D\text{-}A\cdot \quad ; \quad [D^{\dot{+}}\ {}^{\dot{-}}A] \rightarrow {}^{+}D\text{-}A^{-}$$

The bifunctional nature of the proposed intermediates raised the possibility that non-terminating or "living" species are present in these reactions. This view was supported by the finding (45) that the intrinsic viscosity increased with increasing conversion, contrary to the constancy of the molecular weight irrespective of conversion in conventional free radical polymerization. The fact that the copolymerizations in the presence of chloroform and carbon tetrachloride proceeded faster than in toluene and no chlorine was incorporated in the copolymer suggested that serious consideration must be given to a polar intermediate.

Further progress in the investigation revealed that the molecular weight of the copolymer increased with conversion in the initial stage and then appeared to remain constant (63, 68,110). This leveling off is, of course, inconsistent with a living mechanism.

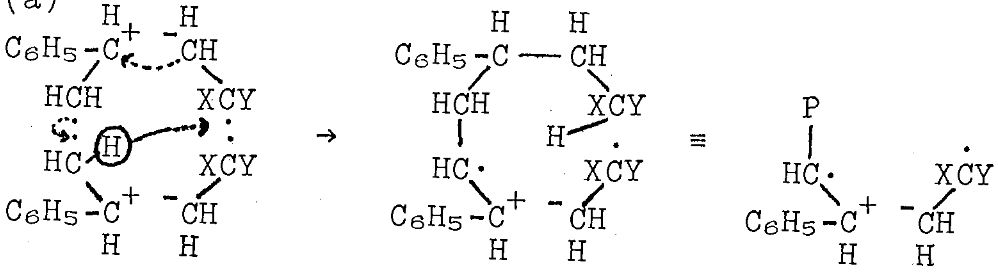
Tsuchida and Tomono (28) tried to establish the mechanism of the alternating copolymerization of styrene and maleic anhydride in terms of the initiating species, the propagation step and chain-transfer reactions. Using different media, they followed radical initiator fragments contained in the copolymer by radioactive tracer techniques and concluded that the polymerization was induced by the direct attack of the initiator radical on the monomer or the comonomer complex. However, the amount of initiator fragments contained in the copolymer was very small, being only 1/30 to 1/90 of the number of macromolecules. They explained this by a violent chain transfer to the acceptor monomer and/or the complex. The chain transfer to carbon tetrachloride, a typical chain transfer agent for conventional radical polymerizations, was negligible. The molecular weight of the product was essentially constant with increasing conversion, and the square root dependence of the polymerization rate on the initiator concentration was attributed to a bimolecular termination. They also showed that only strong donor or acceptor molecules, such as maleic anhydride, N,N-dimethyl aniline or naphthalene , could act as chain transfer agents in a copolymerization of this type. The radical mechanism suggested was analogous to the conventional radical mechanism in which the comonomer complex played the role of a polymerizing monomer.

Gaylord (44) has proposed a mechanism of polymerization of charge transfer complexes which involves hydrogen abstraction from the complex. He supports his view by the finding that the donor-acceptor complex polymerization was accelerated in the presence of $\cdot CCl_3$ radicals from chloroform and carbon tetrachloride (resulting from the solvent-initiator interaction) and that no chlorine was incorporated in the copolymer. Another argument was the absence of catalyst moieties in the copolymer formed. The scheme suggested is illustrated using styrene as the donor monomer and $CH_2=CXY$ as the acceptor monomer, where X represents hydrogen or an alkyl and Y represents the complexed polar group, e.g., CN...salt .

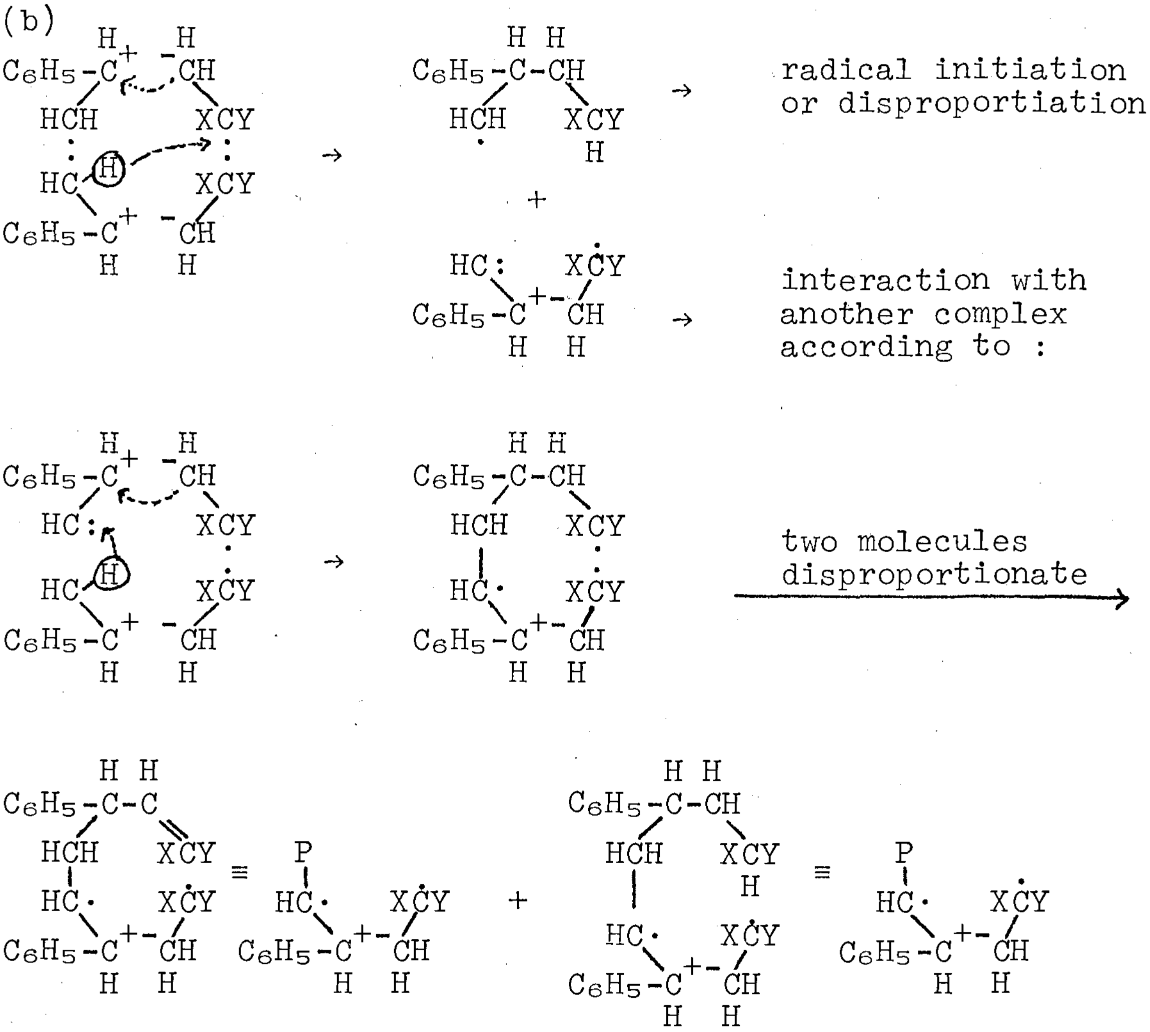
Initiation.

1. Spontaneous initiation.

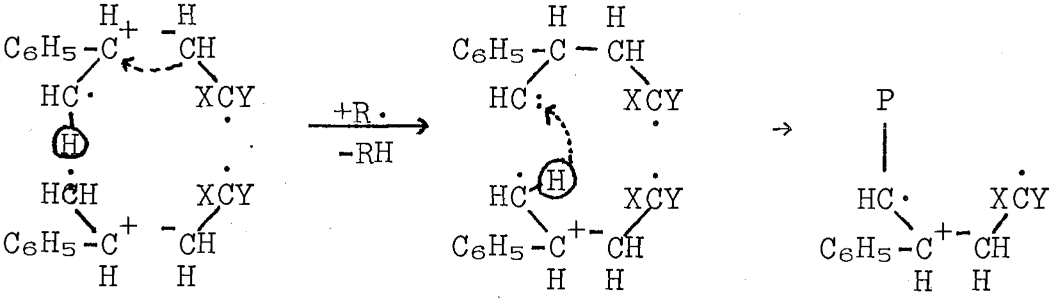
(a)



(b)



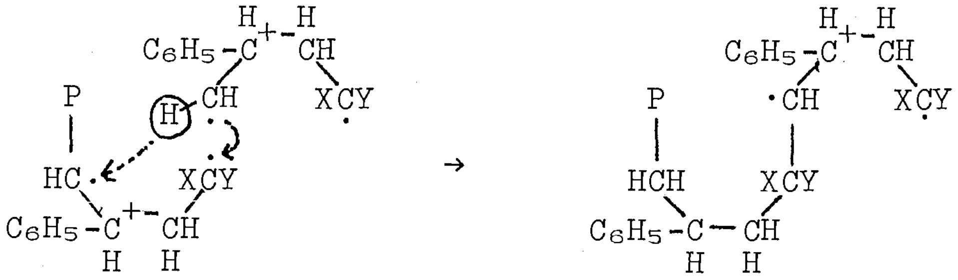
2. Radical-catalysed initiation.



The results of the initiation step is the formation of a chain end which has a structure similar to that of the donor-acceptor complex and has analogous properties. The driving force for the reaction is, according to Gaylord, the arrangement of the complexes in a matrix.

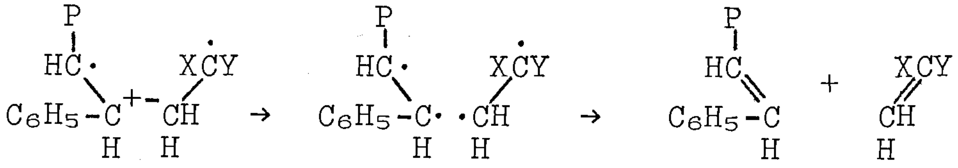
Propagation.

While the initiation is a head-to-head reaction, the propagation step is a head-to-tail reaction. Hydrogen abstraction through a six-membered cyclic transition state regenerates the complex chain end.



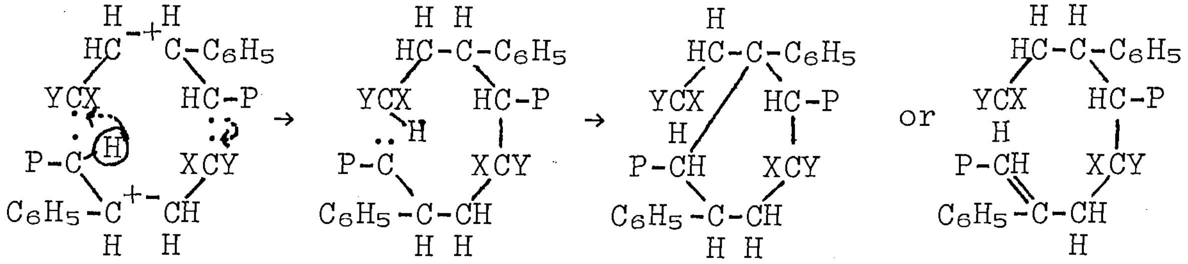
Termination.

1. Monomolecular termination.

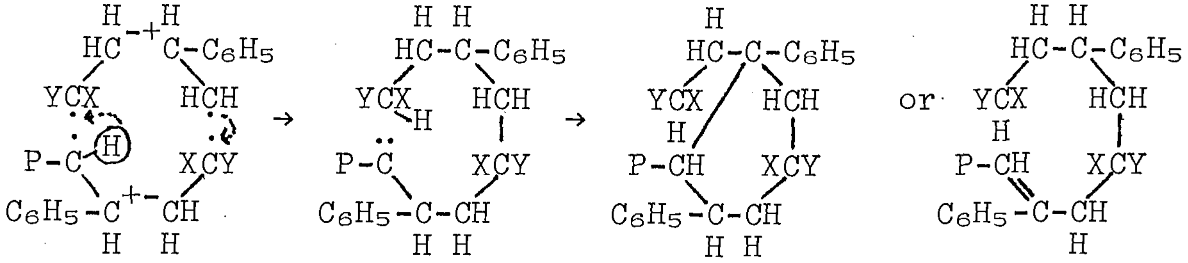


2. Bimolecular termination.

(a) By polymer-polymer interaction.



(b) By polymer-complex interaction.



An important feature of the scheme presented is the bimolecular termination by polymer complex interaction which has no analogy in either of the conventional mechanisms. It should be pointed out that in some aspects the scheme is speculative, showing all the possible interactions without experimental evidence of their occurence.

One can notice that the radical mechanism proposal was based on the presence of the initiator fragments in the resulting copolymer while the hydrogen transfer proposal originated from the absence of such fragments in the copolymer. This discrepancy could be explained by the observations of Bartlett and Nozaki (30) who followed the rate of decomposition of benzoyl peroxide in different monomer media. The rate of the decomposition was found to be 196 times greater in a mixture of allyl acetate and maleic anhydride than the decomposition rate in pure allyl acetate and 76 times greater than in pure maleic anhydride. Since the rate of decomposition of benzoyl peroxide had not been found to vary more than about fourfold in a number of the common solvents, they concluded that the factors 196 and 76 were due largely to chain decomposition of benzoyl peroxide induced by the growing polymer. Therefore, it can not be a chain-initiating step, but a process of chain transfer which incorporates the initiator fragments into the copolymer. In the light of the fact that in Tsuchida and Tomono's work (28) only one initiator fragment was found per 30 or 90 macromolecules, this explanation sounds reasonable.

On the other hand, Gaylord and Maiti (49) showed that the rate of decomposition of azobisisobutyronitrile (AIBN) was not accelerated in a donor-acceptor monomer system. They followed the rate of decomposition in toluene in the presence of ethylaluminum sesquichloride, styrene and methyl methacrylate, in the presence of the organometal and either styrene or methyl methacrylate, in the presence of the organometal alone, and in the absence of all three components, and concluded that the rate of decomposition of AIBN was accelerated by the free, uncomplexed organometallic component, but that it was not affected by either monomer.

An explanation of the discrepancy between the conclusions of Gaylord and Maiti (49) and Bartlett and Nozaki (30) could be offered by the observations of the rate of decomposition of radical initiators in various solvents. While the decomposition of AIBN is basically invariant from solvent to solvent (the rates of decomposition of AIBN in xylene, acetic acid, n-butanol, cyclohexanone, nitrobutane, and isobutanol at 82°C do not differ by more than a factor of 1.16, (111)), the rate of decomposition of benzoyl peroxide is much more sensitive to the nature of the solvent in which the reaction takes place (the rates of decomposition of benzoyl peroxide in benzene, carbon tetrachloride, diphenylmethane, dibutylphthalate, 1,2,4-trimethyl benzene, acetone, acetic acid, and ethyl acetate at 75°C do not differ by more than a factor of 7.5,(112)) and can differ by as much as two orders (the rate of decomposition of benzoyl peroxide in dibutyl ether is two orders greater than in benzene at 60°C, (113)). The latter fact would , of course, detract from the conclusion of Bartlett and Nozaki that the radical initiator fragments had been introduced into the copolymer predominantly by a chain transfer reaction.

Very recently, the nature of the initiation process has been discussed from the point of view of the energy transfer from the initiator fragments to the complex or to a monomer and then to the complex (114,115). These proposals are based on the discovery that exited states are generated in the decomposition of organic peroxides and azo compounds (116-119). The excitation of the ground state complex to the excited charge transfer complex results in the formation of the copolymer by the hydrogen transfer mechanism. The theory of charge transfer complexes suggests that the ground state is stabilized by some contribution (in resonance language) from the excited state.

$$D,A \longleftrightarrow D^+,A^-$$

Although there remains considerable uncertainty about the extent of charge transfer in the ground state, the experimental results overwhelmingly support the existence of only a small contribution of the charge transfer to the ground state (120). Presumably, these non-ionic species are not able to undergo polymerization. In the excited charge transfer complex the contribution from the ionic form is much larger and may be estimated at 90% or even more (114,121). These species then could yield a copolymer and the increase of the polymerization rate with an increase of a radical initiator concentration could be understood as a result of the increased concentration of the excited, polymerizable charge transfer complexes.

I.5. DEVIATIONS FROM THE ALTERNATING STRUCTURE.

Basically, there are three different deviations from the expected 1:1 composition of the total polymer yield.

(1) The total polymer yield is a mixture of an alternating copolymer and a homopolymer.

(2) The total polymer yield is a mixture of an alternating copolymer and a non-alternating copolymer.

(3) The total polymer yield is a non-alternating copolymer.

The apparent explanation for case 1 is that the polymerization of the molecular complex of the monomers is accompanied by homopolymerization of either of the two monomers. Gaylord et al.(59) polymerized α-methylstyrene and acrylonitrile in the presence of ethylaluminum sesquichloride and found that the equimolar alternating copolymer was accompanied by and could be separated from poly(α-methylstyrene). First considerations might lead to the conclusion that the formation of poly(α-methylstyrene) through cationic polymerization is the expected consequence of the presence of the sesquichloride in the reaction mixture. However, the relative increase of the amount of the homopolymer with a decrease of the sesquichloride concentration, and the increase of the amount of the homopolymer when a radical initiator was present argue against this conclusion. Gaylord et al.(59,122) have suggested that a cationic polymerization of the donor monomer, D, is induced by a cationic radical which is formed as a result of the dissociation of the terminal complex, DA, at high dilution.

$$\sim(DA)_xD^{\overset{+}{\cdot}}\overset{-}{\cdot}A\ldots MX \quad \rightleftarrows \quad \sim(DA)_xD^{\overset{+}{\cdot}} \; + \; \overset{-}{\cdot}A\ldots MX$$

$$\sim(DA)_xD^{\overset{+}{\cdot}} \; + \; D \quad \rightarrow \quad \sim(DA)_xDD^{\overset{+}{\cdot}}$$

The initiation of cationic polymerization by the polymerizing charge transfer complex is, therefore, responsible for the formation of homopolymer in the system.

The formation of a non-alternating copolymer together with an alternating copolymer has been reported when a diene and acrylonitrile were polymerized in the presence of zinc chloride at high temperatures and/or high conversions and a radical initiator was employed (38,54). When the polymerization was allowed to proceed spontaneously (thermally), an alternating copolymer was the only product. On the other hand, when the dienes were replaced by styrene or α-methylstyrene, the alternating copolymer was accompanied by a non-alternating copolymer even in the absence of a radical initiator (51,123). To explain these observations, Gaylord and co-workers(51,123) proposed a set of competing reactions in the systems. When styrene, S, acrylonitrile, A, and zinc chloride, Z, are employed, two kinds of donor-acceptor complexes can be formed in the solution.

$$\begin{array}{lcccl} Z & + & A & \rightleftarrows & ZA \\ ZA & + & A & \rightleftarrows & ZAA \\ ZA & + & S & \rightleftarrows & ZAS \end{array}$$

These species are present in concentrations which depend upon the initial concentrations of the components and the equilibria relationships. In addition, the ZAA complex interacts with styrene to generate a ZAS complex and uncomplexed acrylonitrile.

$$\mathrm{ZAA} + \mathrm{S} \rightleftarrows \mathrm{ZAS} + \mathrm{A}$$

Under suitable activation these species may participate in homopolymerization or copolymerization reactions to yield an acrylonitrile-rich copolymer.

$$a\ \mathrm{ZAS} \rightarrow (\mathrm{ZAS})_a \rightarrow (\mathrm{AS})_a + a\ \mathrm{Z}$$

$$b\ \mathrm{ZAS} + c\ \mathrm{ZAA} \rightarrow (\mathrm{ZAS})_b(\mathrm{ZAA})_c \rightarrow (\mathrm{AS})_b(\mathrm{AA})_c + (b+c)\ \mathrm{Z}$$

An alternative rationalization employes the dissociation of the terminal complex. This process can give rise to a conventional copolymerization of the donor monomer, D, and the acceptor monomer, A, (123).

$$\sim(\mathrm{DA})_x\mathrm{D}^{+\cdot}\,{}^{-\cdot}\mathrm{A}\ldots\mathrm{MX} \rightleftarrows \sim(\mathrm{DA})_x\mathrm{D}^{+\cdot} + {}^{-\cdot}\mathrm{A}\ldots\mathrm{MX}$$

$$\sim(\mathrm{DA})_x\mathrm{D}^{+\cdot} + y\ \mathrm{D} + z\ \mathrm{A} \rightarrow \sim(\mathrm{DA})_x\mathrm{D}\text{-}\mathrm{D}_y\mathrm{A}_z$$

The initiation of cationic polymerization in the styrene copolymerizations might involve radical coupling of two terminal cation-radicals to form a polymeric dication. The cationic chain-ends propagate by the addition of styrene or a mixture of styrene and acrylonitrile to yield a styrene-rich copolymer.

Sometimes a non-alternating copolymer becomes the only product at higher temperatures, while at lower temperatures the polymerization system yields a pure alternating copolymer. It was suggested (109) that a block segment of a homopolymer reacted with an alternating copolymer segment, the homopolymerization being initiated by a radical initiator. At a lower temperature where the initiator is not particularly effective the product has a 1:1 composition whereas at higher temperatures a radical homopolymerization is initiated, the growing segments of the homopolymer then interact with the growing end of the alternating copolymer, and the final product contains an excess of one of the monomers. This was demonstrated with styrene, S, and maleic anhydride, M.

$$R\cdot \quad + \quad S \quad \rightarrow \quad S_{x-1}S\cdot$$
$$S \quad + \quad M \quad \xrightarrow{R\cdot} \quad \cdot SM\text{-}(SM)_{\bar{y}}SM\cdot$$
$$S_xS\cdot \quad + \quad \cdot SM\text{-}(SM)_{\bar{y}}SM\cdot \quad \rightarrow \quad S_xS\text{-}SM\text{-}(SM)_{\bar{y}}SM\cdot$$

I.6. KINETICS OF DONOR-ACCEPTOR COMPLEX POLYMERIZATION.

Although there is widespread interest in donor-acceptor complex polymerizations there has been little study of the kinetics of the polymerization. No attempt to determine relevant kinetic parameters has been presented. The complexity of the donor-acceptor complex polymerization system is apparently caused by the many equilibria in the overall reaction process which are not present in the conventional polymerization or copolymerization. These are chiefly the complexation of the acceptor monomer with the complexing agent and the formation of the molecular complex undergoing the polymerization.

$$Z \quad + \quad A \quad \rightleftarrows \quad ZA$$
$$ZA \quad + \quad D \quad \rightleftarrows \quad ZAD$$

Another process present in the scheme must be the regeneration of the complexing agent after polymerization of the complex.

$$x\ ZAD \quad \rightleftarrows \quad \sim(AD)_{\tilde{x}} \quad + \quad x\ Z$$

The direct consequence of the presence of the equilibria is the difficulty in expressing the "monomer" concentration, hampering any further kinetic studies. (Several reports have been published (43,108) giving the monomer reactivity ratios, r_1 and r_2, of the systems in question, determined on the basis of conventional copolymerization kinetics. As this approach ignores the theory of the homopolymerization of molecular complexes, the evaluation of the copolymerization parameters does not contribute to the determination of the kinetics of donor-acceptor complex polymerization.)

Nevertheless, some kinetic observations have been presented. On their basis it seems reasonable to say that copolymerizations of a donor monomer with an acceptor monomer complexed with a complexing agent have the following characteristics.

First, when the monomers are present in excess of the complexing agent the conversion curves (copolymer yield versus time) have two distinct regions, the first being curved, the second linear. Gaylord studied (63,68) the styrene-methyl methacrylate-ethylaluminum sesquichloride system using a threefold excess of methyl methacrylate over the organometal. He was not aware of the possible linearity of the later portion of the conversion curves and looked for a reaction order with respect to the donor-acceptor complex by the conventional method assuming that the initial concentration of the complex was equal to the concentration of the complexing agent. This kinetic treatment, ignoring totally the above equilibria in the system, did not give satisfactory results distinguishing unequivocally between a first and second order of reaction. Nor did a dependence of the type $R_p=kM^{\alpha}$, where R_p is polymerization rate, α is any positive number, k is a constant, and M is monomer concentration, describe the experimental data. On the basis of his failure to find any reaction order fitting the data in the whole range of observation Gaylord concluded that the reaction order depended upon the concentration of the components, and probably varied between one and two.

Kinetic studies of the concentration effects can be summarized as follows. When the rate of polymerization of a donor monomer and an acceptor monomer with or without a complexing agent is followed as a function of the monomer feed composition the rate is found to be a maximum at the equimolar point (27,37,40-43,62). The existence of the maximum and the limiting value of the polymerization rate can be readily explained by the assumption that none of the reaction components enters the polymerization as a single particle and that all of them form a complex which behaves as a monomer molecule. From this point of view an excess of either monomer brings about a decrease of the donor-acceptor complex concentration by dilution.

When the molecular weight of the styrene-methyl methacrylate copolymer prepared in the presence of ethylaluminum sesquichloride was followed as a function of conversion the intrinsic viscosity was found to increase with conversion (68). It was rationalized by the existence of a non-steady state in the polymerization system. The discovery that a constant molecular weight was attained after an initial period of increasing molecular weight (110) called for another explanation. It was proposed (34,110,124) that the comonomer charge transfer complexes are arranged in matrices or ordered arrays whose size is determined by the initial complex concentration. The molecular weight of the copolymer formed in the first stage is determined by the size of the matrices, i.e. the complex concentration. The diffusion of monomer molecules to the complexing agent affixed to the copolymer chain results in the generation of new complexes on or in the immediate vicinity of the copolymer. The latter was postulated to act as a template in the proceeding polymerization, the molecular weight thus being constant and determined by the size of the template. This process would be repeated untill full conversion is attained. However, when acrylonitrile was used instead of methyl methacrylate (62) the molecular weight either remained unchanged with conversion or decreased to a limiting value. The effect observed depended on the concentration of the ethylaluminum sesquichloride. This is in contrast to the above styrene-methyl methacrylate system.

The copolymerization of styrene and methyl methacrylate in the presence of ethylaluminum sesquichloride (66,68), with the organometal concentration lower than the concentration of either monomer, proceeded through an initial stage of rapid polymerization, followed by a second slower stage which continued to full conversion (68). The two stages were related to the formation of matrices of the donor-acceptor complexes. The slower second stage of polymerization has been proposed to be a result of the diffusion of the unpolymerized monomers to the complexing agent affixed to the copolymer chain, and the rate of polymerization being a function of the time necessary for the formation of a void-free array of complexes (110).

The hypothesis of the presence of matrices in the polymerization of donor-acceptor complexes is supported by the results of the multistage addition of an equimolar monomer mixture to a polymerizing system after full conversion (110). When an equimolar styrene-methyl methacrylate mixture in an amount twice that originally present was added to a styrene-methyl methacrylate-ethylaluminum sesquichloride system which had attained full conversion, the added monomer yielded a copolymer of the same intrinsic viscosity as the original copolymer at two different conversions of the new monomers. When additional monomer mixture was added in an amount equal to that already present the intrinsic viscosity of the isolated copolymer, composed of a mixture of the products from each of the addition stages, remained unchanged, independent of conversion.

The unconventional nature of the donor-acceptor complex polymerization has been demonstrated by the effect of p-benzoquinone on the polymerization of styrene with methyl methacrylate complexed with aluminum sesquichlorides (42). At a low benzoquinone concentration the rate of polymerization decreased, as expected. However, as the amount of benzoquinone was increased the polymerization rate increased even above the rate attained in the absence of the quinone. After passing through a maximum at a quinone/Al mole ratio of 1/2, corresponding to an equimolar carbonyl-aluminum mixture, it again decreased. On the other hand, the alternating copolymerization of styrene and acrylonitrile in the presence of zinc chloride was reported (43) to be inhibited by the addition of hydroquinone. However, Gaylord argued (125) that the reported concentrations (HQ/AN/$ZnCl_2$ mole ratio was 2/100/10) had represented a 40% reduction in the concentration of available $ZnCl_2$ as a result of the interaction of one mole of zinc chloride per phenolic hydroxyl group, and he presumed that inhibition of the spontaneous polymerization might have been due to the reduction in the activator concentration.

Conductivity measurements in the styrene-methyl methacrylate-ethylaluminum sesquichloride system showed (42) a slight increase of the specific conductivity of the organometal upon the addition of the acceptor monomer and a further slight increase upon the addition of the donor monomer. Although the conductivity measurements showed that the absolute concentration of ions must have been very low, their presence was undoubtly indicated.

Taking into account that there is a certain concentration of free cations in the systems, as indicated by the conductivity measurements, but that these cations fail to induce the cationic polymerization of styrene, and that benzoquinone, when present in a suitable concentration, not only does not retard the polymerization, but on the contrary accelerates it, it seems reasonable to conclude that the active species in the polymerization are neither conventional radicals nor cations.

II. CHEMICALS AND TECHNIQUES USED.

II.1. CHEMICALS AND THEIR PURIFICATION.

II.1.1. MONOMERS.

ACRYLONITRILE, Matheson Coleman & Bell, b.p. 75.5 to 77.5°C, was dried for several days over calcium hydride and eluted through an alumina column prior to distillation at reduced pressure on a spinning band column of high efficiency. A 60% centre-cut was used in the experiments.

BUTADIENE-1,3, Matheson, Instrument Grade, 99.6% , was used without further purification. Before joining butadiene cylinders to the polymerization apparatus,a fraction of the content was bled off to purge any light gaseous fraction.

STYRENE, Eastman, b.p. 33-35°C/8mm, stabilized with tert-butylpyrocatechol, was dried for several days over CaH_2 and then fractionated at reduced pressure on a high efficiency spinning band column. The 20% cuts at the beginning and the end of the distillation were rejected, and only the center-cut was used.

II.1.2. COMPLEXING AGENT.

ZINC CHLORIDE, Allied Chemical Canada, Reagent A.C.S., was dried for fifty hours in a vacuum oven at 150°C before use.

II.1.3. SOLVENTS.

1,2-DICHLOROETHANE, Fisher Sci., Fisher Certified, b.p. 83.5-83.8°C, was kept over P_2O_5 for a week and distilled through a column filled with glass rings. The 70% center-cut was used in the experiments.

BENZENE, Fisher Sci., Certified A.C.S., thiophene free, was kept over sodium wires for several days and distilled from sodium under an argon atmosphere through a glass-circles-filled column.

CHLOROBENZENE, Matheson Coleman & Bell, Reagent, b.p. 130-132°C, was kept for several days over molecular sieve of type 4A and distilled under an argon atmosphere.

TETRAHYDROFURAN, Fisher Sci., Histological Grade, was used for molecular weight determinations without further purification.

All the liquid components used in the polymerization experiments and the complexing salt were stored under argon. The liquid components were manipulated with hypodermic syringes to prevent their contact with air.

II.2. POLYMERIZATION PROCEDURE.

II.2.1. ELECTROCHEMICAL POLYMERIZATION.

Polymerizations initiated by electric current passing through solution were performed in a single cell for electropolymerization shown in Figure 7. The cell was fitted with a side tube for dosing liquid components and provided with two identical platinum electrodes, each 2.5x2.5 cm, separated by 1.0 cm.

The cell containing a weighed portion of $ZnCl_2$ was connected through a ball joint to the apparatus shown in Figure 8. After evacuation and the introduction of argon, the cell was charged with the required volume of acrylonitrile, cooled in a dry ice-methanol bath and evacuated again. The system was then isolated from the pump and brought to the reaction temperature. The introduction of the gaseous monomer to the solution was performed as follows. Container B was filled with gaseous butadiene from cylinder A (liquid) and isolated from it. The desired pressure of butadiene in the apparatus was set and maintained by means of manometer D and regulator E. A drop of

Figure 7. THE ELECTROPOLYMERIZATION CELL.

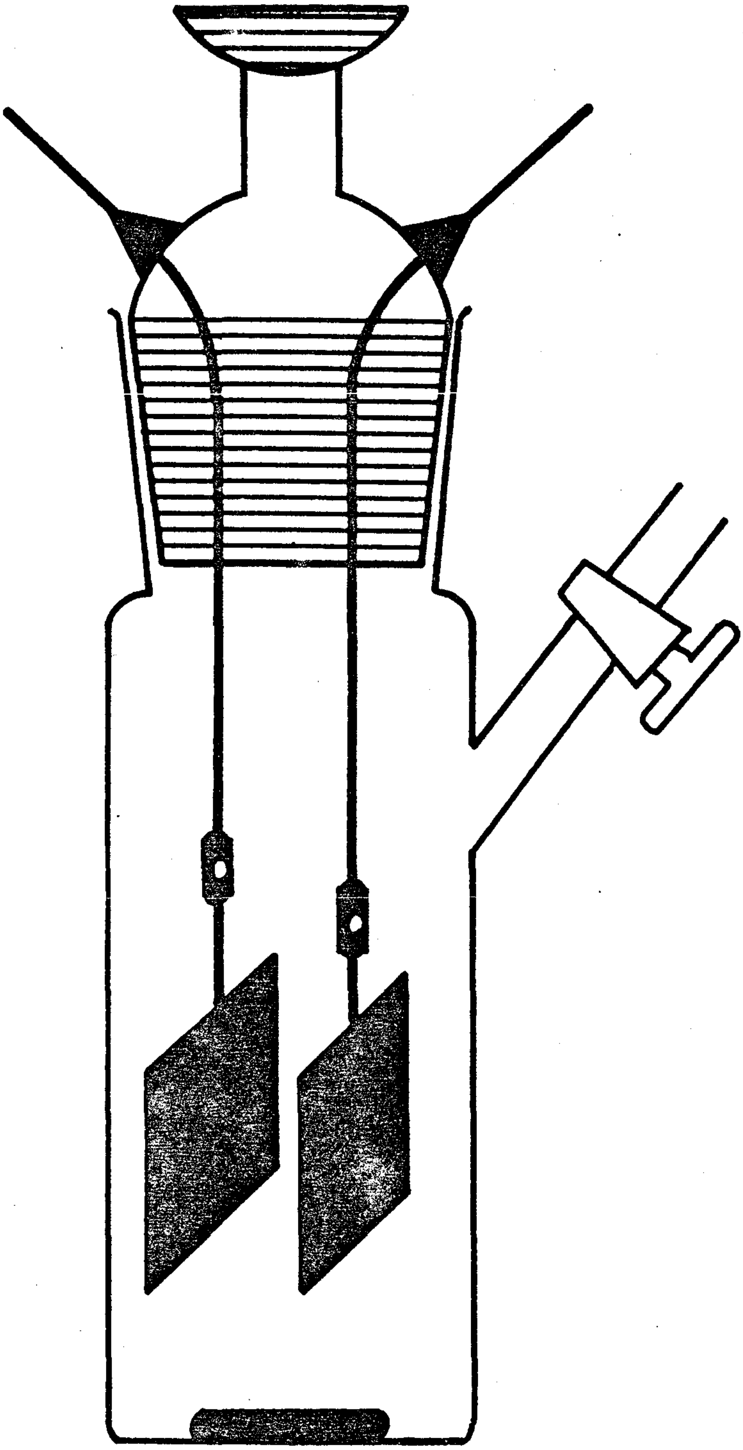
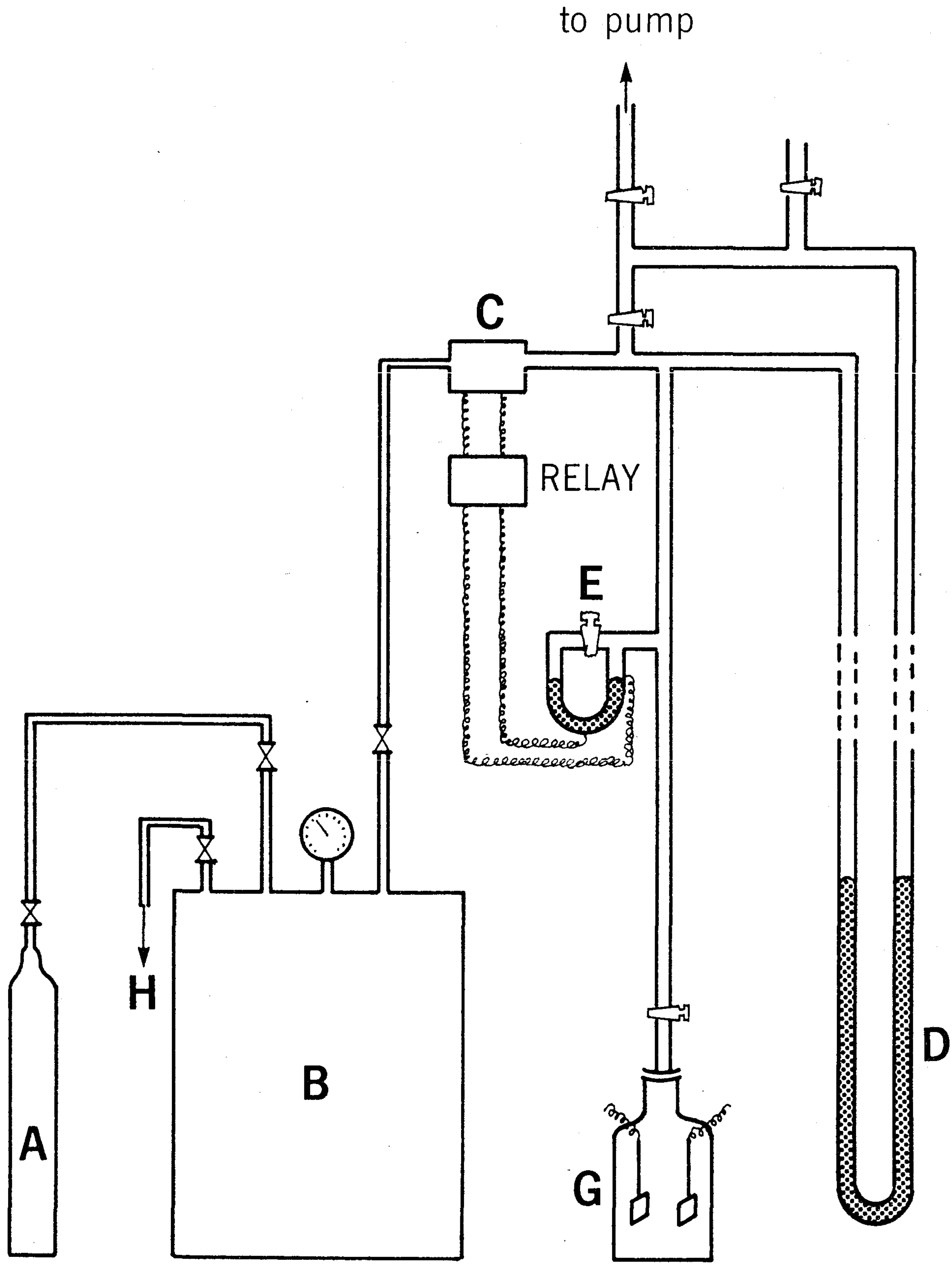


Figure 8. APPARATUS FOR INTRODUCING GASEOUS MONOMER.


to pump
C
RELAY
E
A
B
H
G
D

the Hg-level at the open end of E interrupts the circuit controlling the solenoid valve C, causing the latter to close. Hence, when the stopcock on E is closed a constant pressure of butadiene is maintained, and may be read on manometer D. The stopcock above the cell was opened briefly to bring the pressure to the set value and the reading on manometer H was recorded. The stopcock on the cell was then left open until saturation of butadiene in the system was indicated by no further introduction of butadiene from container B. At this point the solution was ready for polymerization.

A KEPCO ABC 1000 or a Transistorized Power Supply M 4005 (Power Designs Inc.) was used as a constant current supply for currents of less or more than 25 mA, respectively.

II.2.2. SPONTANEOUS POLYMERIZATION.

Essentially the same apparatus and procedures were used as before. The electrodes had been removed, and the reactions were not carried out under a constant pressure of butadiene. Instead, the solution was saturated at 0°C, then isolated from the system for the duration of the experiment. About two minutes after the polymerization temperature was attained the solution became turbid, this time being taken as the onset of polymerization. When styrene was used instead of butadiene it was introduced by syringe before degassing.

II.2.3. ISOLATION OF POLYMER.

At the end of polymerization, performed either in bulk or in solution, the content of the cell was poured into a large excess of methanol. Aqueous ammonia was added to bind the salt present in the system, thus allowing a salt free polymer to be filtered off. The polymer was washed with an ammoniacal solution of methanol, dried at the room temperature under vacuum in the dark for several hours, then weighed.

When the salt content of the polymer was followed the polymerization was stopped by contacting the solution with air. The polymer was isolated by filtrating the solid phase off the solution.

II.3. CHARACTERIZATION OF POLYMER.

II.3.1. ELEMENTAL ANALYSIS.

Elemental analysis of the copolymers for carbon, hydrogen and nitrogen was carried out on a Perkin-Elmer Elemental Analyser M240. As the nitrogen content is the most sensitive to a composition change, the composition of the copolymer was calculated on this basis. By repeated analyses of the same sample it was found that the acrylonitrile content uncertainty was ±2%.

II.3.2. NMR SPECTROSCOPY.

NMR spectroscopy analysis of the copolymers was performed at room temperature in deuterated chloroform solutions using an analytical NMR Spectrometer A-56/60A. Observed NMR spectra of the acrylonitrile copolymers with butadiene and styrene were compared with a series of spectra for the alternating copolymers and non-alternating copolymers.

The calibration spectra for the butadiene-acrylonitrile copolymers are shown in Figure 9, and for styrene-acrylonitrile copolymers in Figures 10 and 11.

II.3.3. IR SPECTROSCOPY.

IR spectroscopic analysis of the acrylonitrile-butadiene copolymers was carried out on a Perkin-Elmer Grating Infrared Spectrophotometer 457 employing the KBr pressed disc technique.

The calibration spectra of polybutadienes with high trans-1,4, cis-1,4 and 1,2 (vinyl) microstructures are shown in Figure 12.

Figure 9. NMR SPECTRA OF BUTADIENE-ACRYLONITRILE COPOLYMERS (97).

(A,B,D) Prepared with free radical catalyst;

(C) Prepared in the presence of $ZnCl_2$ or ethylaluminum sesquichloride.

Copolymer composition BD/AN (mole ratio) :

(A) 78/22; (B) 54/46; (C) 50/50; (D) 43/57.

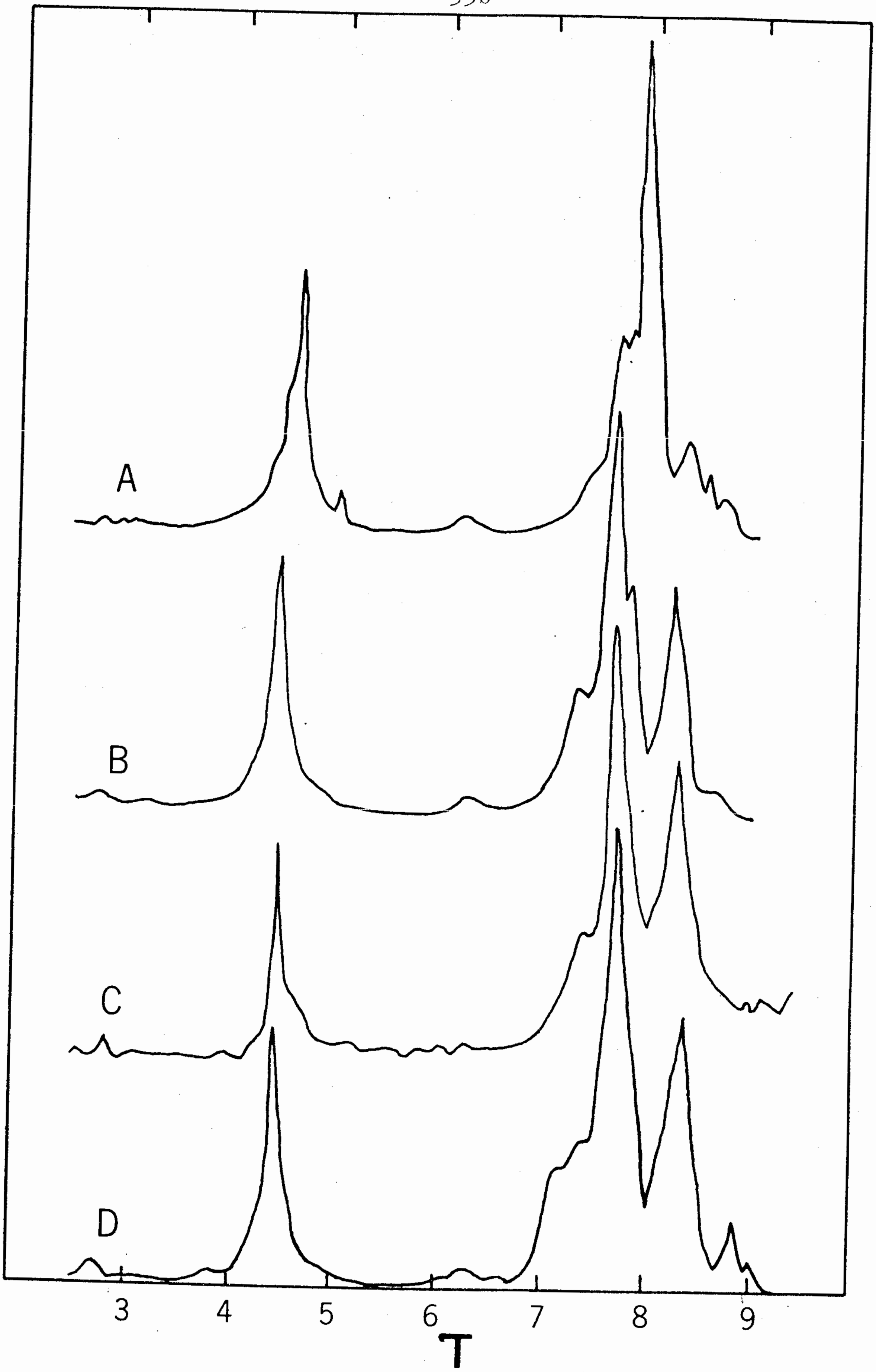

A
B
C
D
3
4
5
6
7
8
9
T

Figure 10. NMR SPECTRA OF STYRENE-ACRYLONITRILE COPOLYMERS PREPARED WITH FREE RADICAL CATALYST.(97). Copolymer composition S/AN (mole ratio) : (A) 71/29; (B) 65/35; (C) 45/55; (D) 30/70.

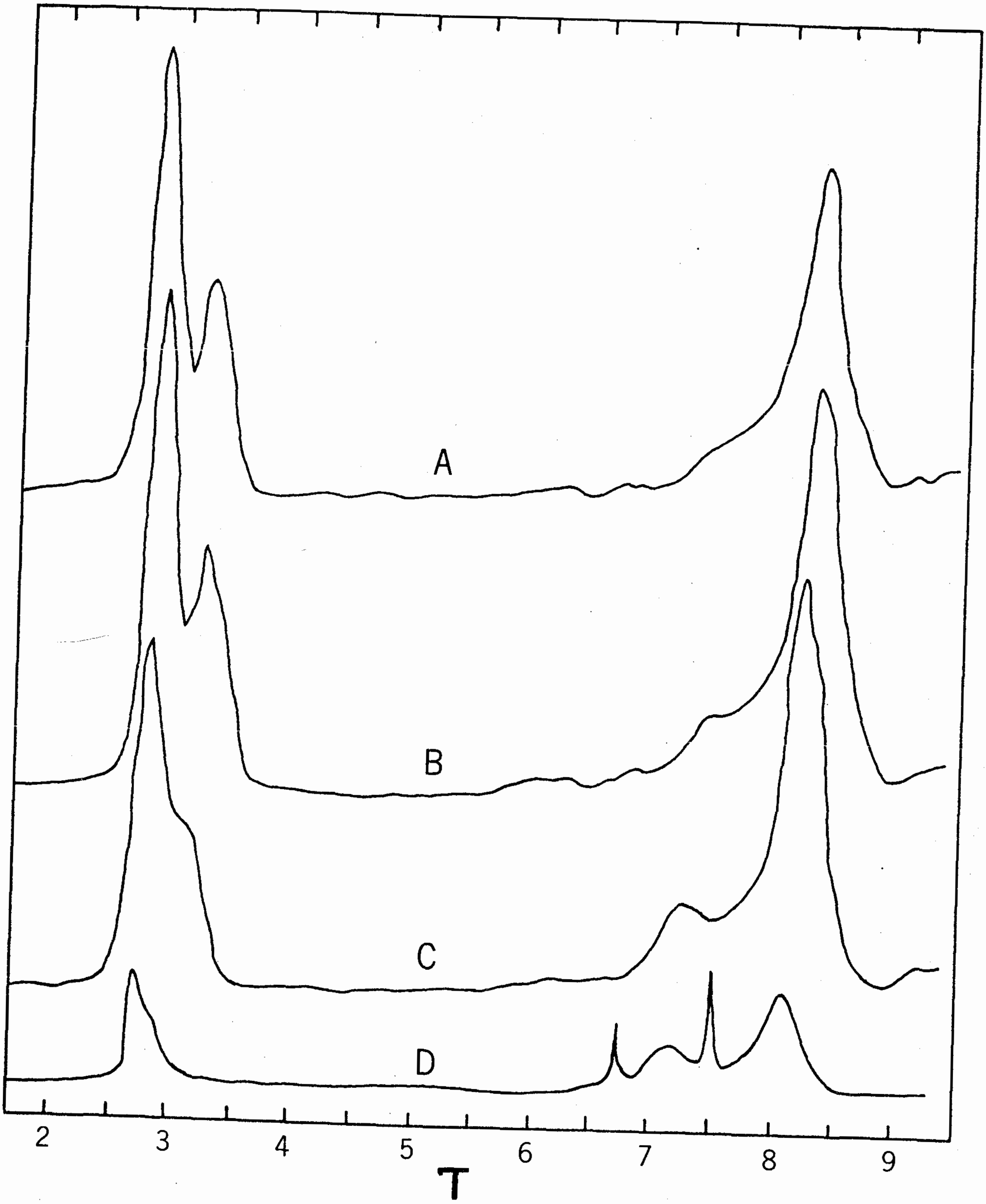

A
B
C
D
2
3
4
5
6
7
8
9
τ

Figure 11. NMR SPECTRA OF ALTERNATING STYRENE-ACRYLONITRILE COPOLYMER PREPARED WITH $ZnCl_2$. (97).
(A) Spontaneous; (B) Benzoyl peroxide catalysis.

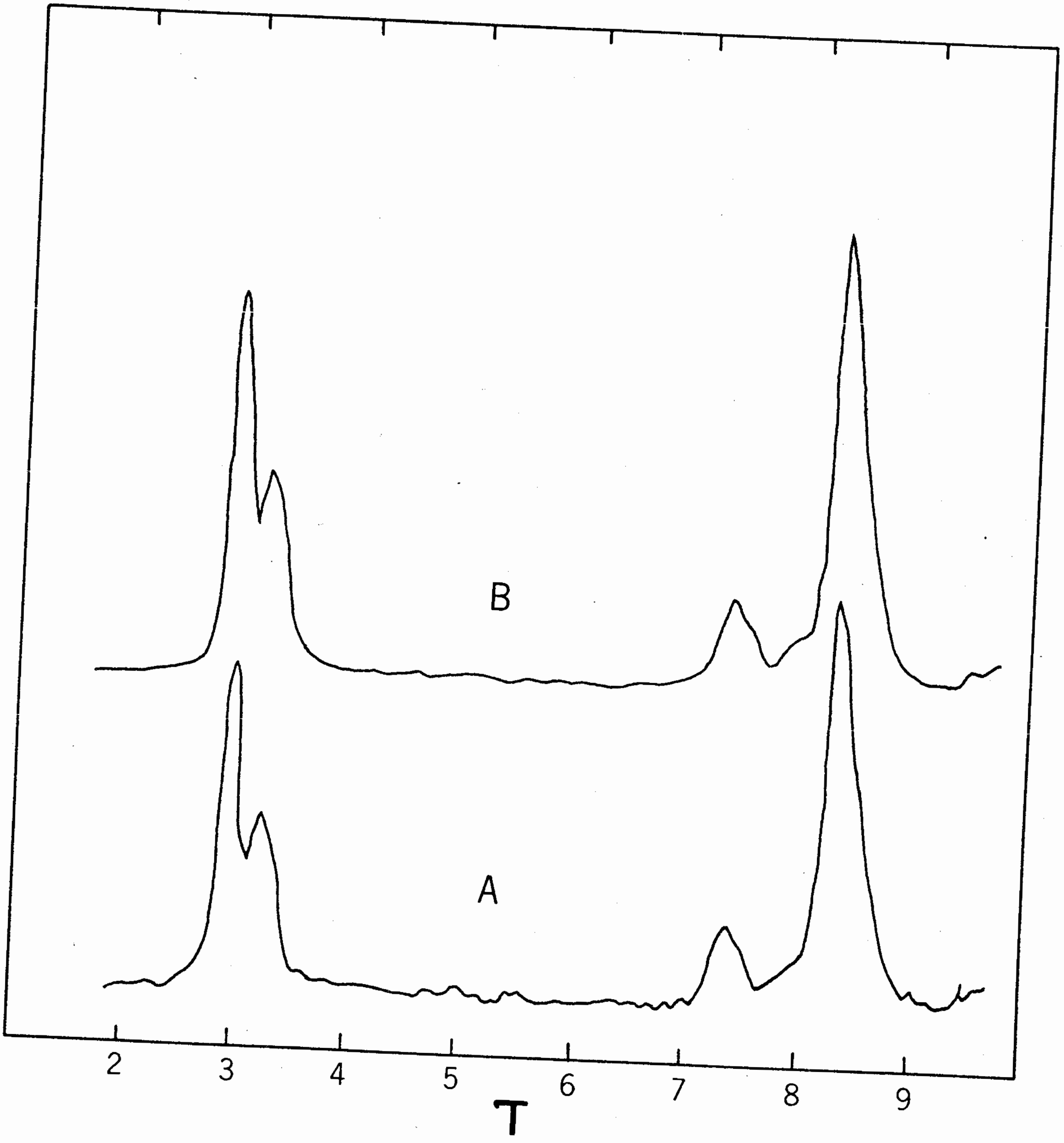
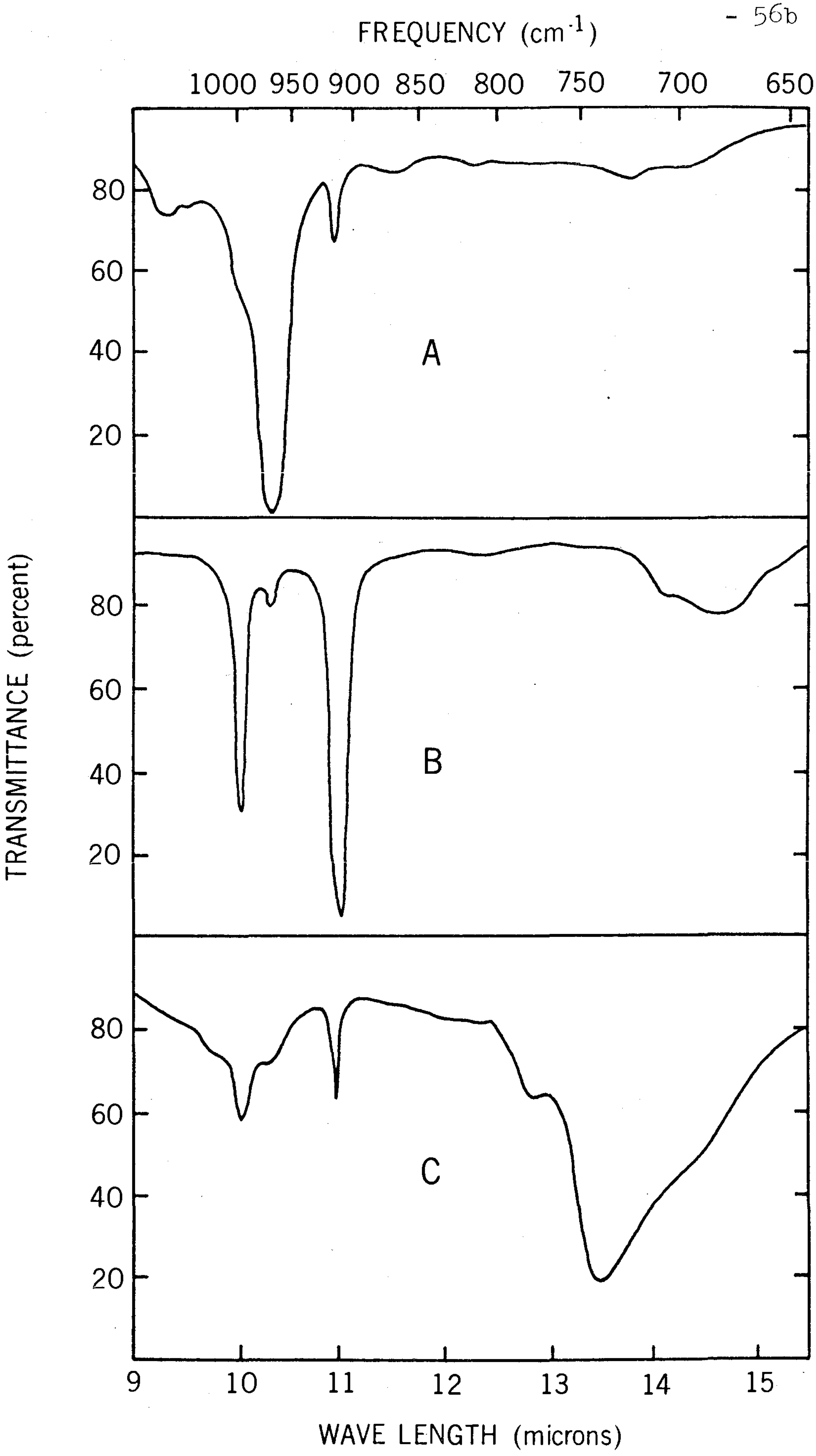

B
A
2
3
4
5
6
7
8
9
τ

Figure 12. INFRARED SPECTRA OF POLYBUTADIENES (127).
(A) High trans-1,4 addition.
(B) High 1,2 (vinyl) addition.
(C) High cis-1,4 addition.


FREQUENCY (cm^{-1})
1000
950
900
850
800
750
700
650
A
B
C
80
60
40
20
TRANSMITTANCE (percent)
9
10
11
12
13
14
15
WAVE LENGTH (microns)

II.3.4. VISCOSITY MEASUREMENTS.

Approximately 0.2 to 0.3 grams of copolymer were treated in less than 25 ml of tetrahydrofuran. After 24 hours of agitation the heterogeneous mixture of polymer solution and undissolved polymer was filtered and the volume of the homogeneous solution of polymer was brought to 25 ml. A 10 ml portion of the solution was used to determine the concentration of polymer in the solution by evaporating the solvent and weighing the remainder. Another 10 ml portion was used to determine the viscosity of the solution. The viscosimetry measurements were carried out in an Ubbelohde dilution viscometer allowing measurements at a series of concentrations by successive dilutions of the solution. The flow times were measured at four concentrations and the intrinsic viscosity (limiting viscosity number) was determined by the graphical method plotting the specific viscosity against the concentration of solution, as developed by Huggins (126).

$$\frac{\eta_{sp}}{c} = [\eta] + k\,[\eta]^2 c$$

where $[\eta]$ is the intrinsic viscosity, c is the concentration of polymer, η_{sp} is the specific viscosity given by the

$$\eta_{sp} = \frac{\eta - \eta o}{\eta o}$$

where η is the viscosity of polymer solution and ηo is the viscosity of pure solvent.

As the flow time is linearly proportional to the viscosity, viscosities η and ηo can be replaced by flow times t and t_o, respectively, so that the specific viscosity is simply calculated according to

$$\eta_{sp} = \frac{t - t_o}{t_o}$$

II.4. DETERMINATION OF $ZnCl_2$ ON POLYMER.

Zinc chloride was determined by the titration with

0.1M EDTA (disodium ethylenediamine tetraacetate) using Eriochrome Black T as an indicator (128).

When the solid phase had been isolated by the filtration from the liquid portion of the mixture the analysis of the latter determined the zinc chloride uncomplexed on polymer. The solid phase was then washed with a methanol-ammonia solution and the resulting liquid phase was analysed. The polymer was dried and weighed. Then it was dissolved in tetrahydrofuran and the resulting solution was again analysed. The last two analyses, when summed, determined the amount of zinc chloride attached to the polymer. The total amount of zinc chloride ($ZnCl_2$ on copolymer plus $ZnCl_2$ in solution) was always found very close to the expected theoretical value given by the concentration of zinc chloride employed in the experiment.

III. EXPERIMENTAL AND THEORETICAL RESULTS.

III.1. GENERAL STUDIES.

III.1.1. PRELIMINARY EXPERIMENTS.

Purpose.

The purpose of the preliminary experiments was to prepare an alternating copolymer, determine the microstructure, and show that the alternating effect is a general characteristic of the butadiene-acrylonitrile-zinc chloride polymerization system.

Results.

Several features of the acrylonitrile-butadiene monomer pair made it suitable for these experiments. The gaseous state of butadiene enables one to maintain a constant concentration of this monomer during the polymerization process. The apparatus described in the experimental section was developed for this purpose, and effectively eliminates the introduction of impurities during the addition of increments of a gaseous monomer. Also, it was interesting to determine the microstructure of butadiene units in a product obtained via the donor-acceptor molecular complex polymerization mechanism.

Acrylonitrile was selected as the other member of the monomer pair because it appeared to be one of the best representatives of the class of acceptor monomers. The same reasoning led to the choice of zinc chloride as the complexing agent.

Electrochemical initiation was attractive in that it made possible the variation of the rate of initiation without altering the temperature, and thus without shifting the equilibria present in the many-component system. Whereas an increase in temperature enhances the reactivity of the donor-acceptor complex, it would also lead to a decrease in its concentration (91,92,129), and thus reduce the rate of overall reaction. These effects can be investigated separately when electropolymerization techniques are employed.

The experiments summarized in Table III demonstrate that it is possible, using electropolymerization techniques, to prepare a pure alternating copolymer from the butadiene-acrylonitrile-zinc chloride system.

Table III. Copolymer Formation in the Presence of $ZnCl_2$.

Feed (g)			Current (mA)	Polymer formation
PrN	AN[a]	BD[b]		
-	20.0	1.3	0	None
-	20.0	1.3	25	Alternating copolymer
-	20.0	-	25	Polyacrylonitrile
20.0	-	1.3	25	None

(a)Initial feed; (b)Concentration of butadiene was constant.
AN (acrylonitrile); PrN (propionitrile); BD (butadiene-1,3).
Conditions: 3.66 g $ZnCl_2$, 0.36 g $Zn(OAc)_2$, 45°C, 60 minutes.

No detectable polymer was formed without electrochemical initiation. When current flowed through the solution a white rubbery product was formed. The substitution of propionitrile for acrylonitrile resulted in the absence of any polymer formation. When acrylonitrile was the only monomer in the system, the product was a white powdery polymer. The alternating copolymer was identified by the following procedures.

(a) Elemental analysis showed a 1:1 mole ratio of acrylonitrile to butadiene units in the copolymer.

(b) A comparison of the infrared spectra of polyacrylonitrile and the copolymer (Fig. 13) clearly indicates the presence of butadiene units in the polymer. The spectra themselves do not confirm that the butadiene units are actually in a copolymer. A mixture of polyacrylonitrile and polybutadiene would presumably yield a similar spectrum as that ascribed to the copolymer (spectrum I). However, the fact that butadiene does not homopolymerize in the presence of propionitrile excludes its homopolymerization in acrylonitrile and leaves the formation of a copolymer as the only explanation of the presence of butadiene units in the product. The peak at 966 cm^{-1} indicates the predominating 1,4-trans microstructure of butadiene units. (Calibration spectra of polybutadienes have been shown in Figure 12).

(c) The NMR spectrum (Fig. 14) confirms the presence of a copolymer and indicates an alternating sequence of acrylonitrile and butadiene units in the copolymer chains. According to the calibration spectra (Fig. 9) for acrylonitrile-butadiene copolymers, the peak at 7.7 τ corresponds to a butadiene-acrylonitrile unit sequence. There is no peak at 7.9 τ corresponding to a butadiene-butadiene sequence.

Table IV shows the effect of the degree of conversion on the composition of the copolymer and on the molecular weight. The composition is essentially invariant in the conversion range followed. The limiting viscosity numbers increase with conversion.

Table IV. Effect of Degree of Conversion on Composition of the Product.

Yield (g)	Composition (mole-% AN)	[η] (dl/g)
0.073	48.8	-
0.135	50.6	4.14
0.203	-	4.48
0.221	50.1	5.30
0.290	-	5.74

Conditions: 8.40 g $ZnCl_2$, 20.0 g AN, 1.3 g BD, 45°C, 25 mA. Concentration of BD was kept constant.

Table V demonstrates that the copolymer composition

Figure 13. INFRARED SPECTRA OF THE PRODUCTS.

(I)Copolymer, (II)Polyacrylonitrile formed under same conditions.

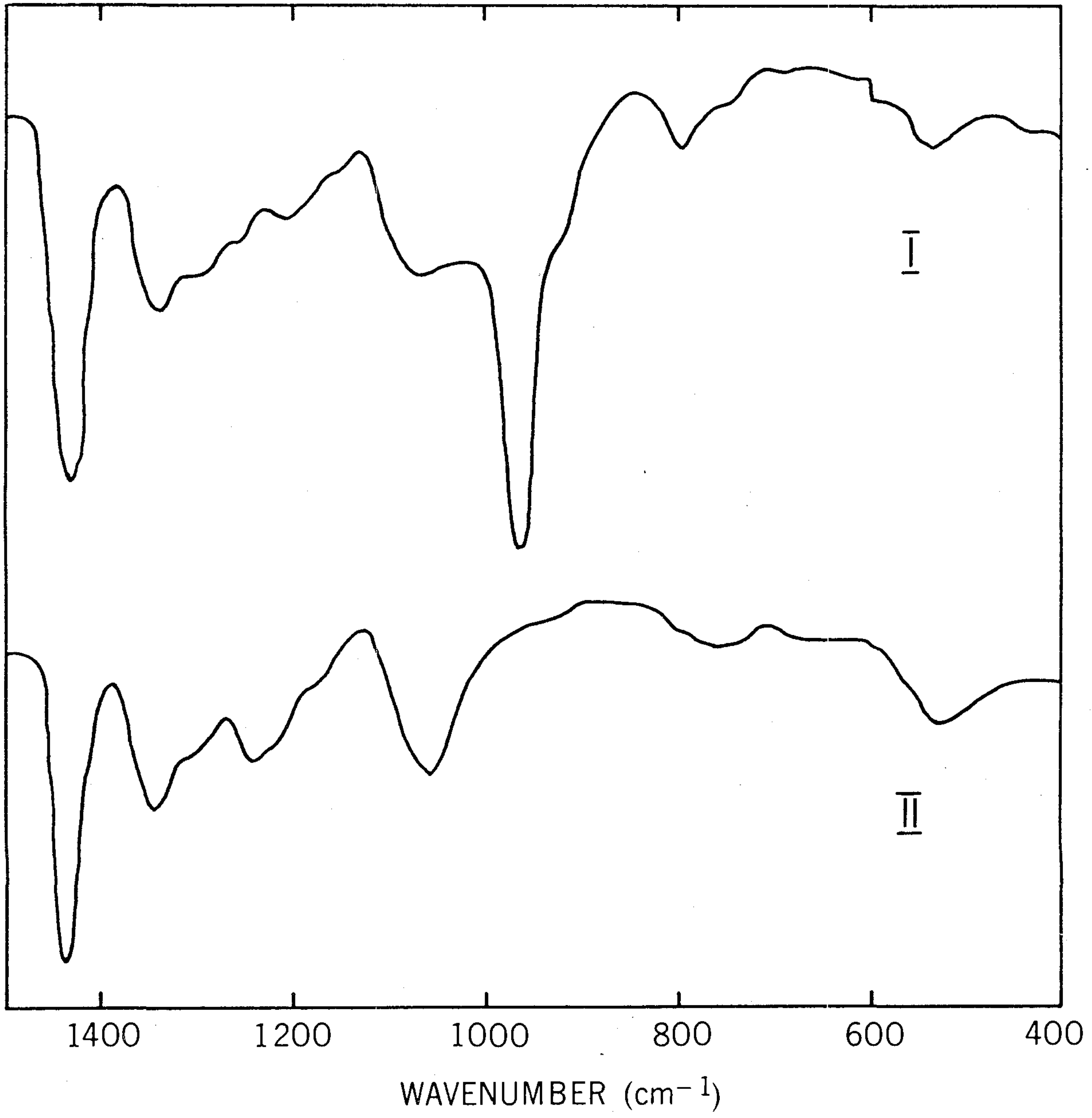
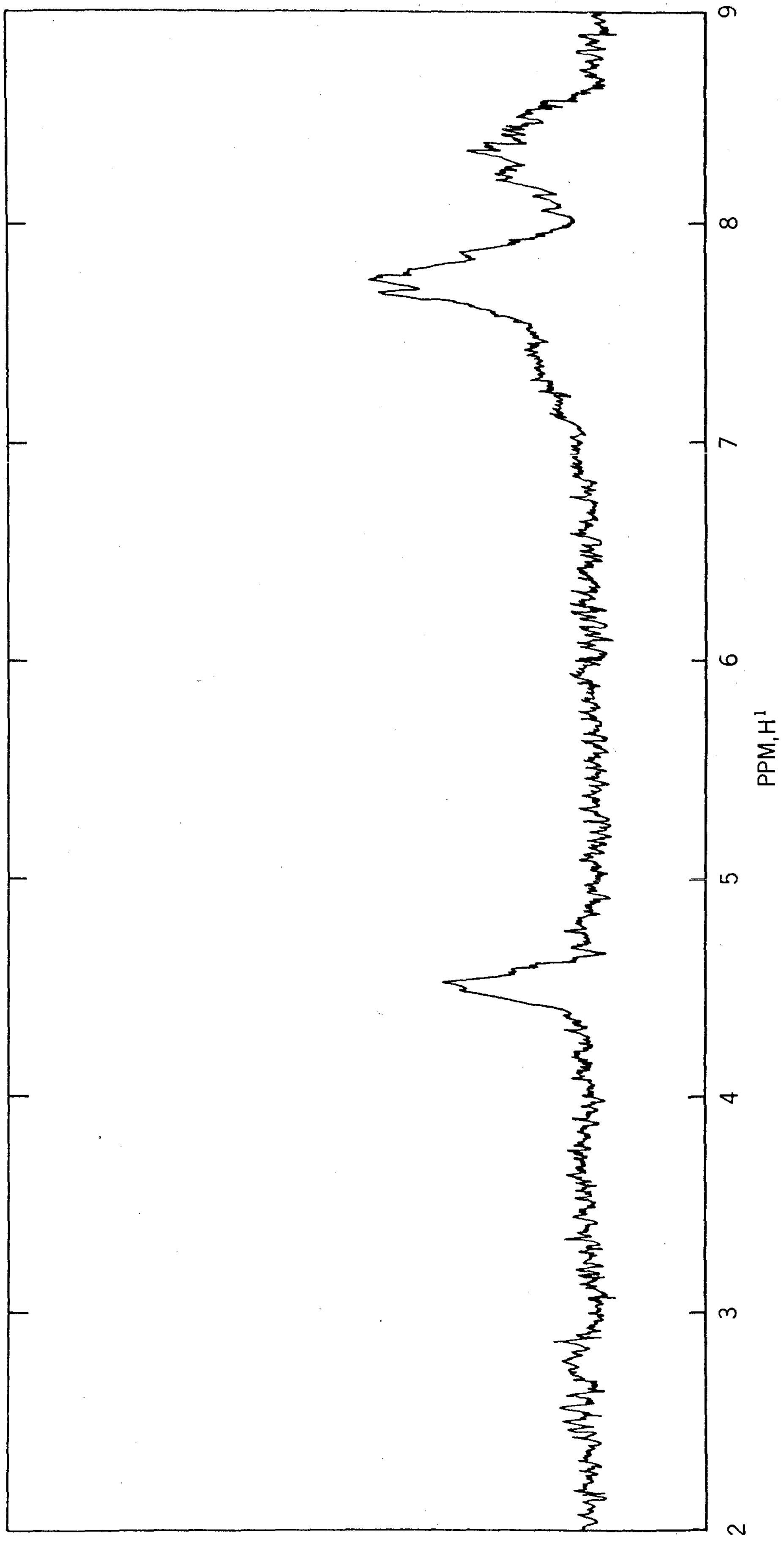

I
II
1400
1200
1000
800
600
400
WAVENUMBER (cm⁻¹)

Figure 14. NMR SPECTRUM OF THE PRODUCT.


2
3
4
5
6
7
8
9
PPM,H^1

is also essentially invariant with the change of the $ZnCl_2$ concentration. The slight deviation from 50% AN is within the range of the experimental error of the elemental analysis.

Table V. Copolymer Composition as a Function of $ZnCl_2$/AN Mole Ratio.

$ZnCl_2$/AN (mole/mole)	BD in feed (g)	Composition (mole-% AN)
0.05	1.33	47.2
0.08	1.28	47.8
0.14	1.19	48.3
0.19	1.23	51.3
0.34	0.69	50.9

Conditions: 20.0 g AN, 0.15 g $Zn(OAc)_2$, 25 mA, 45°C, 60 minutes. Concentration of BD was kept constant.

The effect of the concentration of butadiene is summarized in Table VI.

Table VI. Copolymer Composition as a Function of BD/AN Mole Ratio.

BD/AN (mole/mole)	Reaction time (minutes)	Composition (mole-% AN)	Conditions
0.013	30	62.6	a
0.033	30	56.1	a
0.063	30	50.1	a
0.119	30	50.1	a
0.013	60	83.6	b
0.064	50	57.6	b
0.105	90	51.5	b
0.160	90	51.5	b
0.231	30	51.2	b

Conditions: (a) 8.40 g $ZnCl_2$, 20.0 g AN, 45°C, 25 mA.
(b) 5.00 g $ZnCl_2$, 12.0 g AN, 12.6 g 1,2-dichloroethane, 8.8 g benzene, 45°C.

In Table VI, the concentration of butadiene was again kept constant. It is possible to conclude that the system acrylonitrile, butadiene and zinc chloride yields an alternating copolymer at low ratios of butadiene to acrylonitrile such as 0.063 (in bulk) or 0.105 (in solution). Further decrease of the butadiene concentration results in the formation of a nonequimolar product.

The reaction profile of the electropolymerization is shown in Figure 15. With an excess of acrylonitrile and zinc chloride and constant concentration of butadiene, the rate of polymerization is essentially constant in the investigated range of conversion. When electropolymerization experiments were carried out at different rates of initiation (by applying different currents) and for different periods of polymerization, and the yield of polymerization was plotted against the calculated total charge transfered through the solution, the graph (Fig. 16) indicated that the total number of faradays determines the polymer yield. However, the rate of initiation has no effect on the copolymer composition, as is shown in Table VII.

Table VII. Copolymer Composition as a Function of Rate of Initiation.

Current (mA)	Composition (mole-% AN)
8	49.1
25	50.6
35	49.0
45	50.4

Conditions: 8.40 g $ZnCl_2$, 20.0 g AN, 1.3 g BD, 45°C. Polymer yield was about 0.13 grams in all experiments. Concentration of BD was kept constant.

The reaction profile of the thermal polymerization carried out with excess acrylonitrile and zinc chloride

Figure 15. COPOLYMER FORMATION AS A FUNCTION OF TIME.

Conditions: 8.40 g $ZnCl_2$, 20.0 g AN, 1.3 g BD, 45°C, 25 mA.

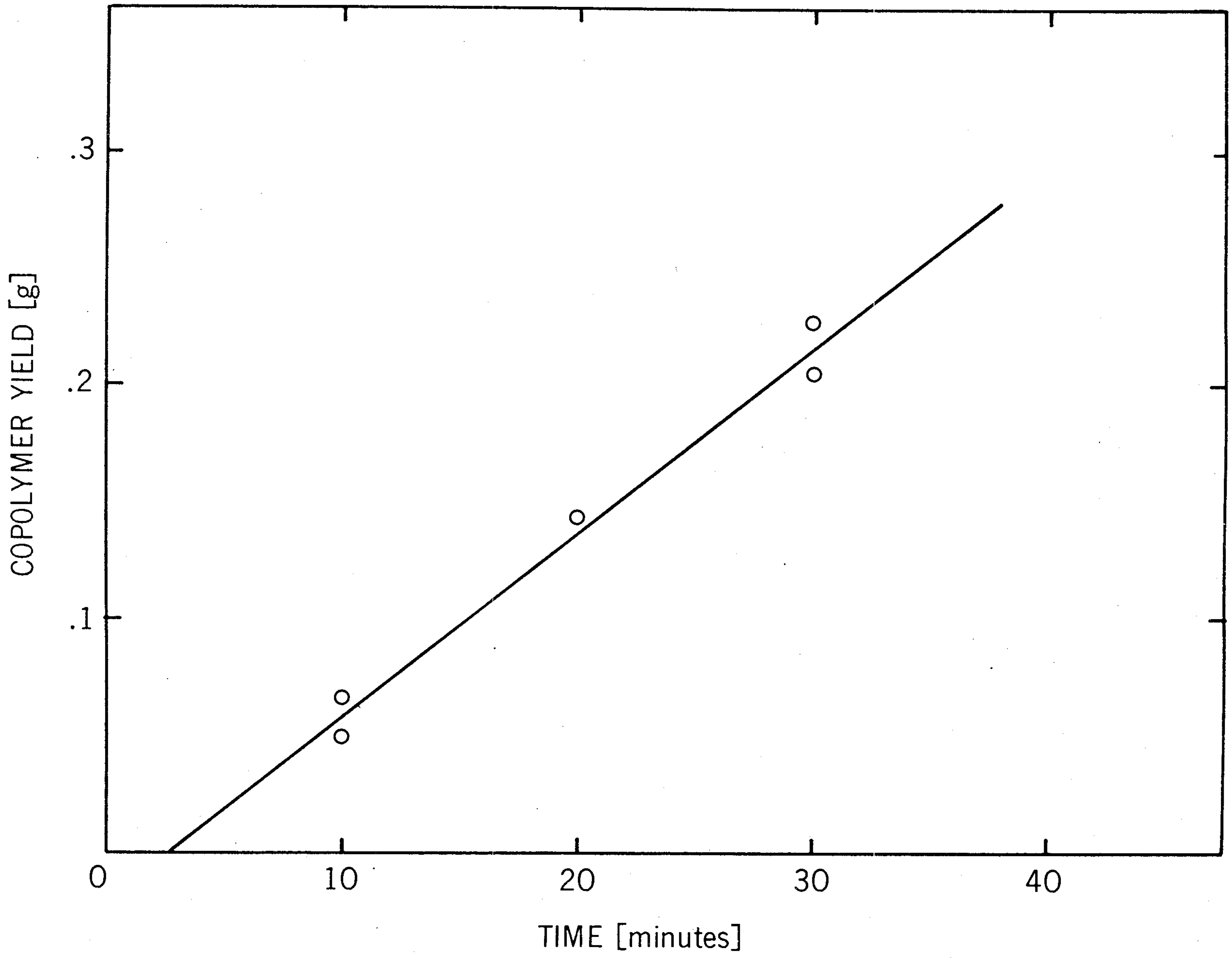

COPOLYMER YIELD [g]
.3
.2
.1
0
10
20
30
40
TIME [minutes]

Figure 16. COPOLYMER FORMATION AS A FUNCTION OF CHARGE TRANSFERED.

Conditions: 8.40 g $ZnCl_2$, 20.0 g AN, 1.3 g BD, 45°C, various currents and conversions.

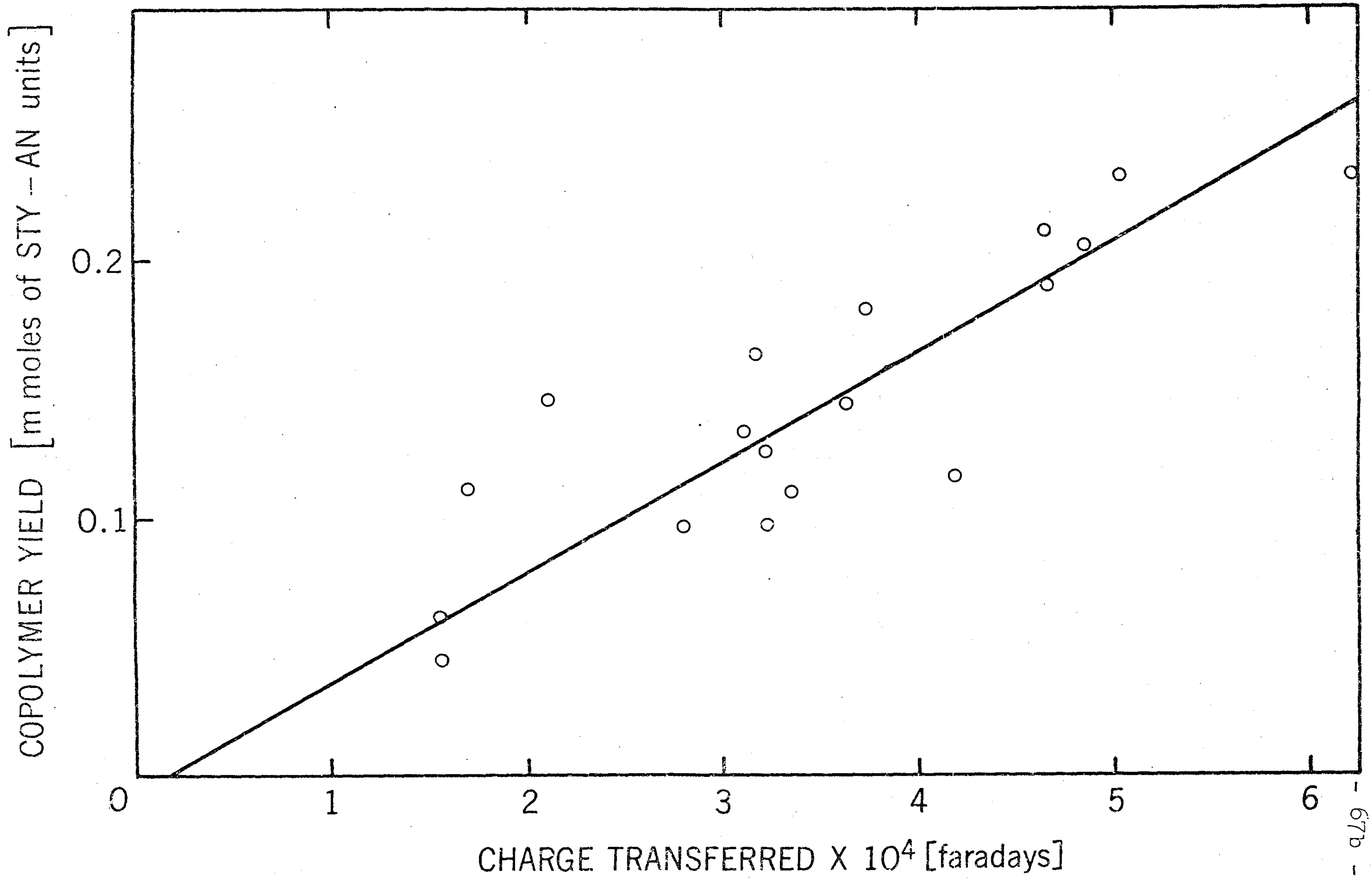
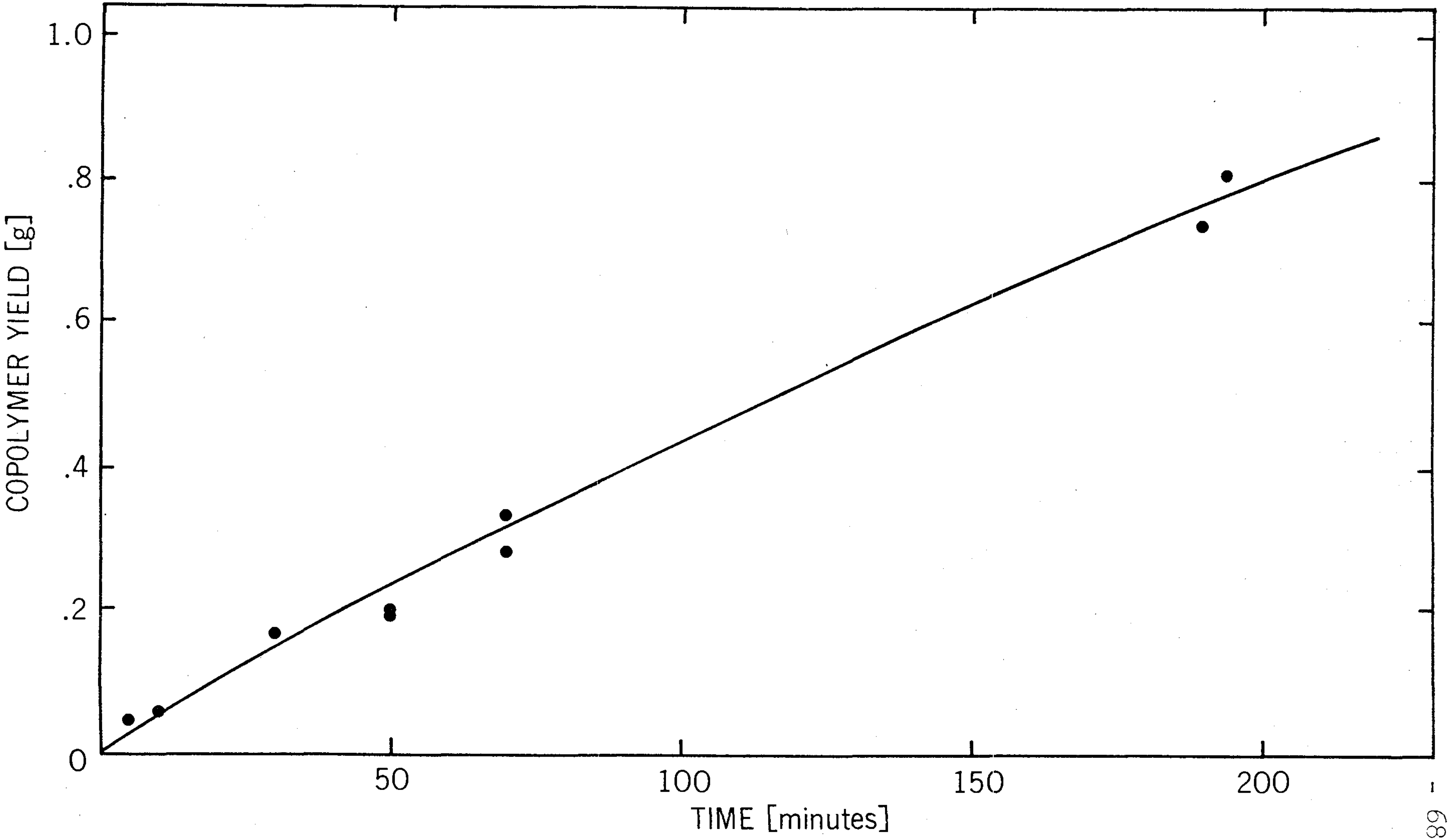

COPOLYMER YIELD [m moles of STY – AN units]
0.2
0.1
0
1
2
3
4
5
6
CHARGE TRANSFERRED X 10^4 [faradays]

Figure 17. "THE THERMAL" COPOLYMER FORMATION AS A FUNCTION OF TIME.

Conditions: 5.00 g $ZnCl_2$, 12.0 g AN, 1.4 g BD,
12.5 g 1,2-dichloroethane, 45°C.


COPOLYMER YIELD [g]
1.0
.8
.6
.4
.2
0
50
100
150
200
TIME [minutes]

is presented in Figure 17. In these experiments the concentration of butadiene was not kept constant. The slight curvature of the line is presumably a result of the consumption of butadiene during the reaction. (It was followed to 30% conversion of butadiene).

Conclusion.

The acrylonitrile-butadiene-zinc chloride system has been found to yield an alternating copolymer under various reaction conditions and means of initiation. Elemental analysis shows that the mole ratio of acrylonitrile to butadiene units in the polymer product is always 1:1 irrespective of zinc chloride concentration, the rate of initiation and the degree of conversion in the range covered by the experiments.

The IF spectrum indicates unequivocally the presence of both acrylonitrile and butadiene units in the polymer product. When this result is considered together with the fact that no polybutadiene is formed in propionitrile under the conditions employed, one may conclude that acrylonitrile and butadiene are built together in a copolymer.

The NMR spectral analysis of the copolymer indicates an alternating structure in the polymer chains. The presence of the acrylonitrile-butadiene sequences, the absence of the butadiene-butadiene sequences and the equimolar composition leave an alternating structure as the only logical conclusion.

The butadiene in the product is predominantly the 1,4-trans isomer.

The control of the yield of polymerization by the number of faradays passed through the solution demonstrates that electrochemical techniques can be employed to vary the rate of reaction by varying the rate of initiation.

III.1.2. CONCENTRATION EFFECTS.

Purpose.

When a molecular complex between two monomers is the polymerizing entity, the rate of polymerization is expected to reach a maximum at the highest concentration of the complex. Thus, the effect of varying the concentrations of the monomers may indicate that the polymerization proceeds via molecular complexes.

Results.

The spontaneous polymerization in 1,2-dichloroethane yielded the rate versus butadiene concentration curve in Figure 18. There is a definite limit to the increase in the rate of polymerization. The maximum rate is achieved when the butadiene concentration/zinc chloride concentration ratio is greater than unity. Since only the salt-complexed acrylonitrile can form molecular complexes with butadiene, the maximum of the curve lies in the region of the highest concentration of the butadiene-acrylonitrile molecular complexes. The fact that the product formed at very low concentrations of butadiene was not a pure alternating copolymer does not alter these conclusions.

The curve constructed from the electroinitiated polymerizations (Fig. 19) also indicates that the rate of polymerization is limited and increases with increasing complex concentration.

When the rate of polymerization was followed as a function of the zinc chloride concentration the curve shown in Figure 20 was observed. The region of observation was restricted by the solubility of the salt in acrylonitrile. The rate increases rapidly at low concentrations of zinc chloride.

In the concentration effect experiments, the rates of polymerization are values averaged for the times of the reactions. The reaction profiles of the electroinitiated (Fig. 15) and spontaneous (Fig. 17) polymerizations have justified this treatment.

Conclusion.

The polymerization experiments with various amounts

Figure 18. RATE OF POLYMERIZATION AS A FUNCTION OF BUTADIENE CONCENTRATION. SPONTANEOUS REACTION.

(oo)Calculated from total yield.

(●●)Calculated from portion corresponding to 1:1 copolymer.

Conditions: 5.00 g $ZnCl_2$, 12.0 g AN, 12.6 g DCE, 8.8 g benzene, 45°C.
(37 mmoles $ZnCl_2$, 226 mmoles AN).

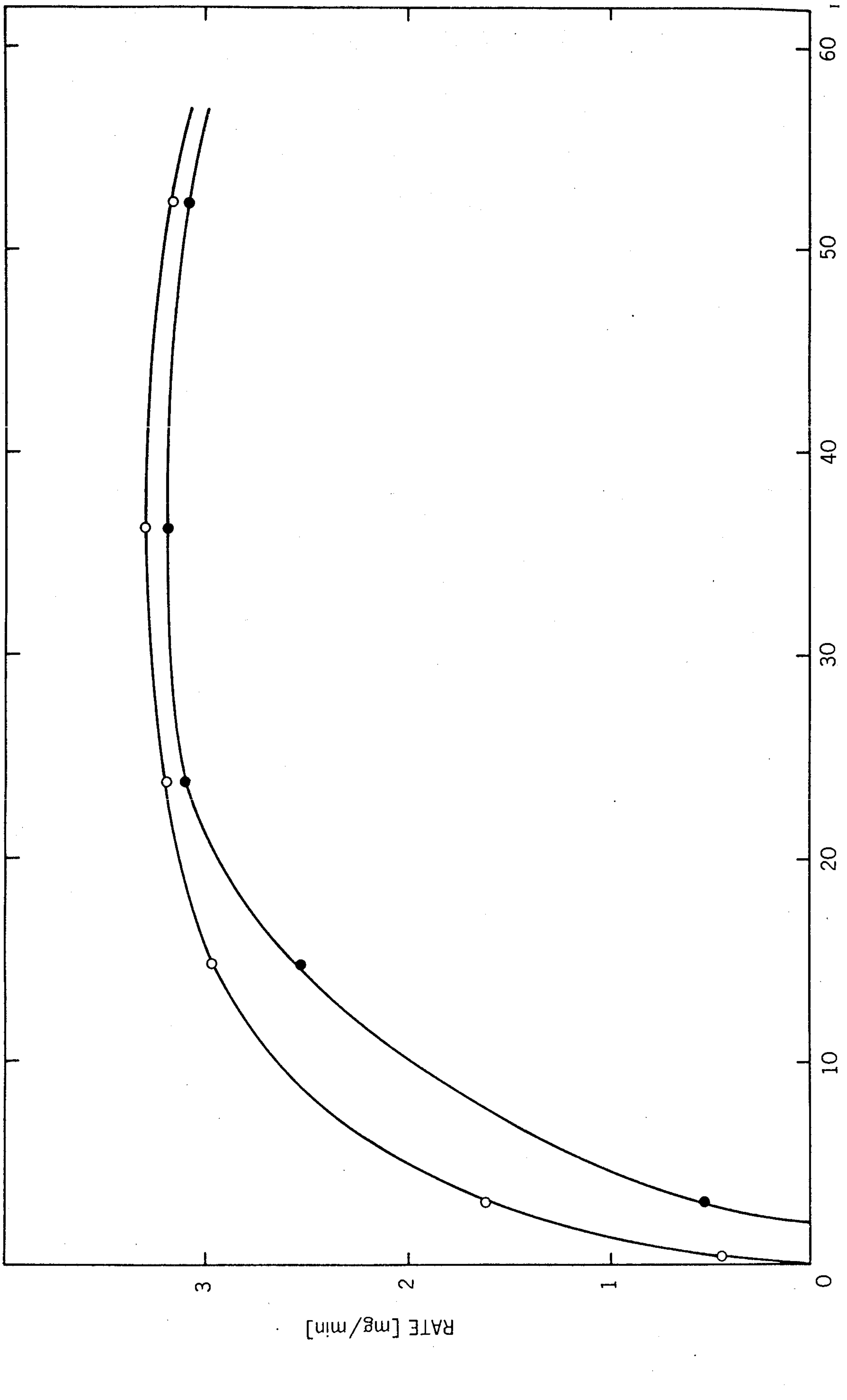

RATE [mg/min]
0
1
2
3
BD [mmoles]
0
10
20
30
40
50
60

Figure 19. RATE OF POLYMERIZATION AS A FUNCTION OF BUTADIENE CONCENTRATION. ELECTROINITIATED REACTION.

(△)Calculated from total yield.

(▲)Calculated from portion corresponding to 1:1 copolymer.

Conditions: 8.40 g $ZnCl_2$, 20.0 g AN, 45°C, 25 mA.
(62 mmoles $ZnCl_2$, 377 mmoles AN).

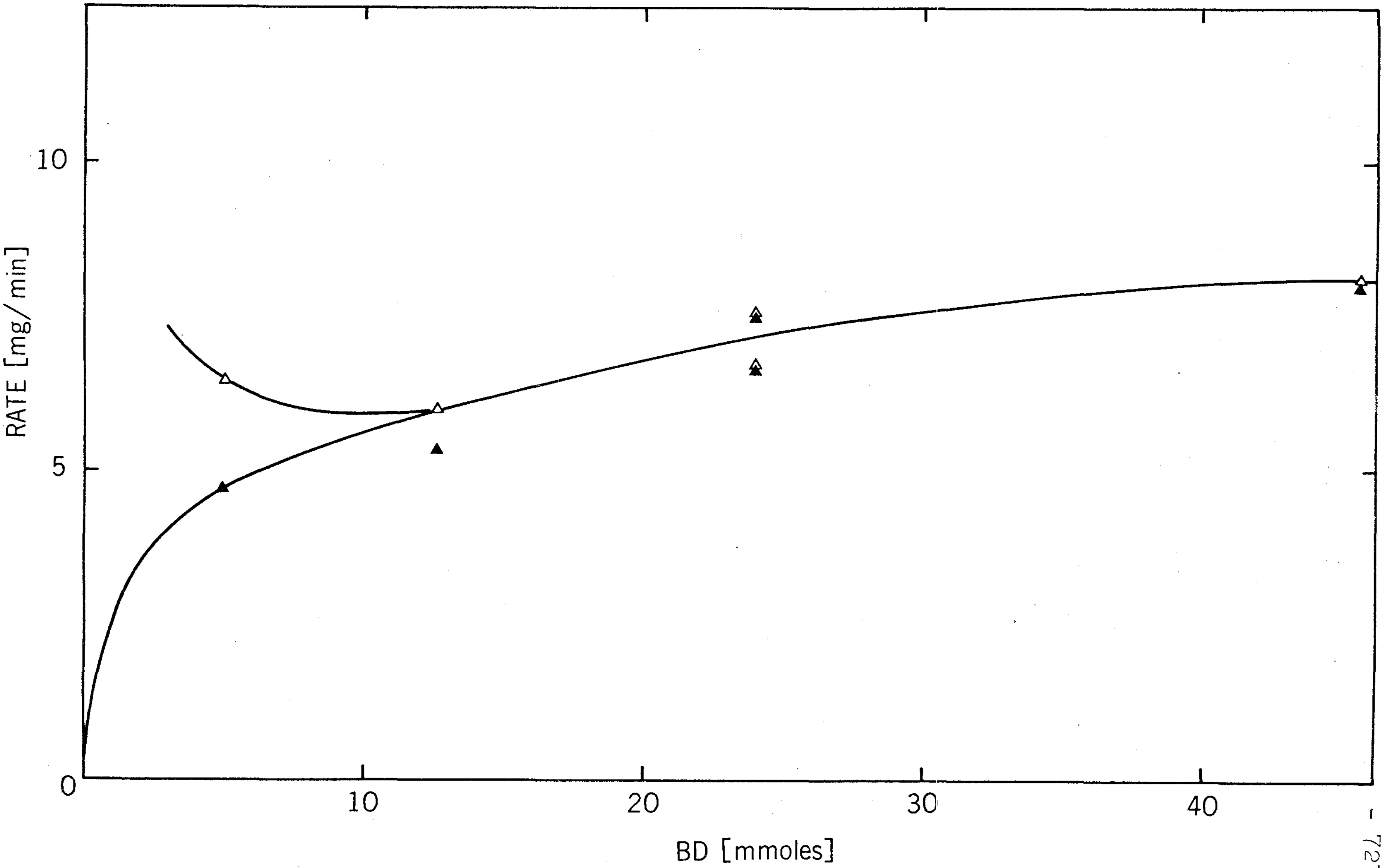
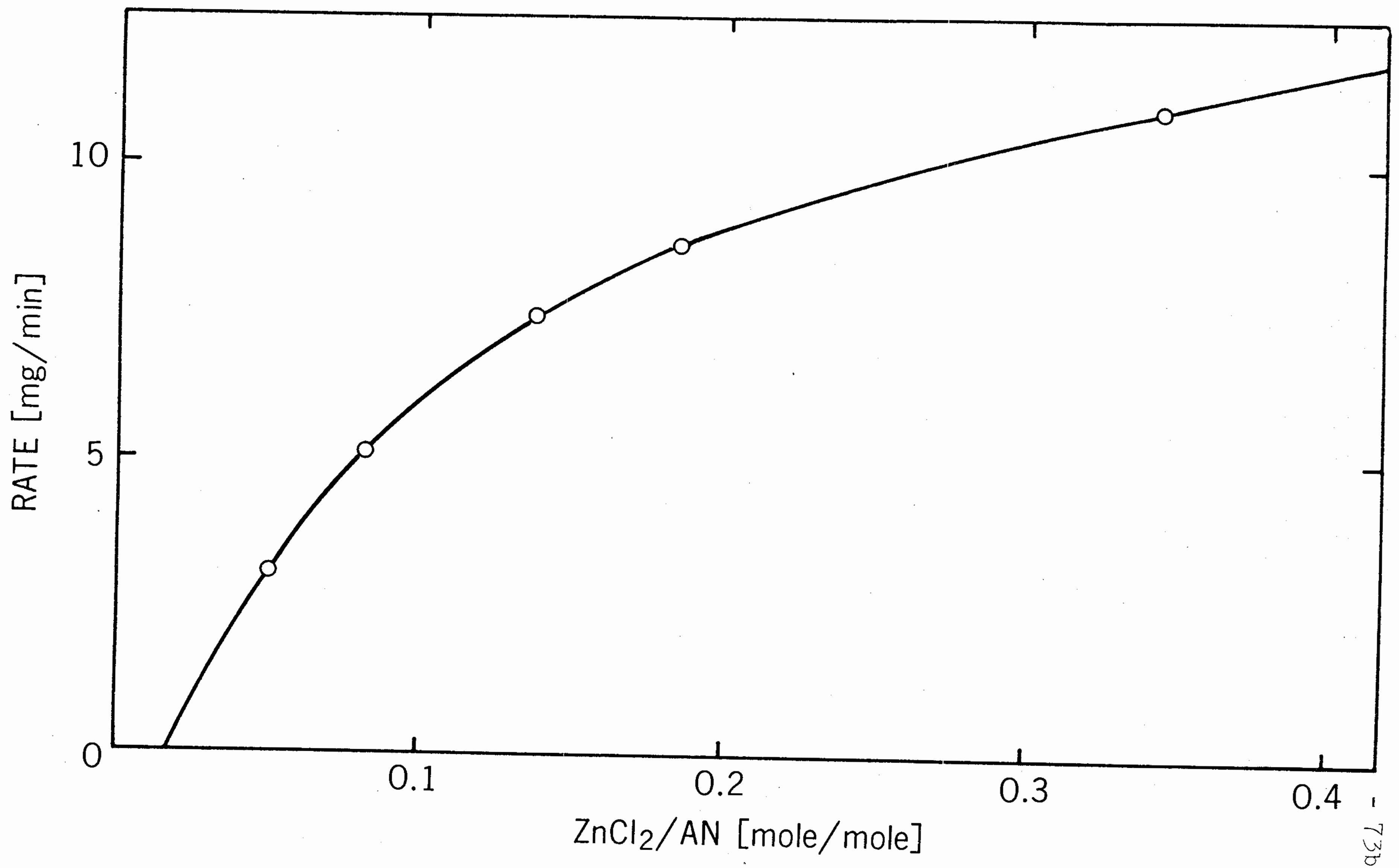

RATE [mg/min]
10
5
0
10
20
30
40
BD [mmoles]

Figure 20. RATE OF POLYMERIZATION AS A FUNCTION OF $ZnCl_2$ CONCENTRATION.

Conditions: 20.0 g AN, 1.3 g BD, 0.15 g $Zn(OAc)_2$, 45°C, 25 mA.
(377 mmoles AN, 24 mmoles BD).


RATE [mg/min]
10
5
0
0.1
0.2
0.3
0.4
$ZnCl_2$/AN [mole/mole]

of butadiene have shown that the rate of polymerization increases initially with an increase of butadiene and levels off. This observation is consistent with the concept of the formation of a complex between the monomers and subsequent homopolymerization. The rate of polymerization is also determined by the amount of zinc chloride available for the complex formation and by the complex concentration.

III.1.3. SOLVENT EFFECT.

Purpose.

When the polymerization systems were prepared in the absence of solvent no product was formed unless the reaction was initiated by an electric current. The author found that addition of 1,2-dichloroethane to the acrylonitrile-butadiene-zinc chloride system results in a spontaneous (or thermal) formation of the copolymer. It appeared technically feasible to follow the production of the copolymer as a function of the nature and amount of solvent.

Results.

The results of spontaneous and electroinitiated polymerizations performed in bulk, 1,2-dichloroethane, benzene and chlorobenzene are summarized in Table VIII. Although no polymer was formed spontaneously when the reaction was carried out in bulk, the addition of a small amount of 1,2-dichloroethane resulted in a rapid spontaneous polymerization. The rate of the copolymer formation increased with a dilution of the polymerization system. The same accelerating effect was observed when the polymerization process was initiated by passing electric current through the system. Elemental and NMR analyses showed no difference in the copolymer composition (49-51% AN) when compared with the polymerization without solvent. NMR spectra indicated an alternating structure in every case.

On the other hand, when benzene was used as a solvent no change in the polymerization rate was observed. Three dif-

Table VIII. Polymerization in Solvents.

Solvent	Solvent volume (ml)	Acrylonitrile volume (ml)	Current (mA)	Yield/Time (g/min)	Rate (mg/min)	
None	0	25	0	0/300		0
DCE	5	20	0	0.354/140		2.5
DCE	10	15	0	0.160/62		2.6
DCE	20	5	0	0.169/19		6.9
Bz	5	20	0	0/90		0
Cl-Bz	18	7	0	0/90		0
None	0	25	25	0.282/60	4.7	4.8
				0.338/75	4.5	
				0.232/45	5.1	
DCE	5	20	25	0.270/34		4.9*
DCE	10	15	25	0.410/37		8.2*
DCE	20	5	25	0.435/17		15.5*
Bz	10	15	25	0.158/30	5.3	4.9
				0.103/20	5.1	
				0.043/10	4.3	
Bz	7.5	17.5	25	0.167/35	4.8	4.6
				0.156/35	4.5	
				0.087/20	4.4	
Bz	5	20	25	0.140/28	5.0	4.7
				0.086/18	4.8	
				0.045/10	4.5	
				0.044/10	4.4	
Cl-Bz	15	10	25	0.143/30		4.8

(*)Rate of spontaneous polymerization has been subtracted.

Conditions: 5.00 g $ZnCl_2$, 1.3 g BD, 45°C.

(DCE)1,2-dichloroethane, (Bz)benzene, (Cl-Bz)chlorobenzene.

ferent concentrations of benzene were tried. The content of acrylonitrile in the copolymer was found to be in range 49-54%, and NMR spectra indicated the alternating structure. Exploratory experiments were performed with chlorobenzene. No spontaneous formation of polymer was observed and the rate of electroinitiated polymerization was not affected by the presence of the solvent.

Conclusion.

The yield of the alternating copolymer in either spontaneous or initiated reaction is increased remarkably when an alkyl chloride is used as the reaction medium. Comparison of the experimental results obtained with dichloroethane and benzene indicates that the change in the polarity of the reaction medium is not responsible for the change in the polymerization rate. This is also concluded from the experiments with benzene. The same polymerization rates were found for various acrylonitrile/benzene volume ratios. The presence of a chlorine atom on solvent molecules is not sufficient for a solvent to induce the polymerization, as may be seen from the ineffectiveness of chlorobenzene. The chloro derivatives of aliphatic hydrocarbons seem to be specific in this matter. No attempt to rationalize the observed acceleration of the reaction is made in this work.

III.2. KINETIC STUDIES.

III.2.1. POLYMERIZATION AT LOW CONCENTRATION OF COMPLEXING AGENT.

Purpose.

A low concentration of one component in a reaction generally simplifies the kinetics describing the process. The presence of many equilibria in the donor-acceptor complex polymerization hinders any attempt to derive a rate equation of the copolymer production. The employment of a low concentration of one of the monomers or the complexing agent is expected to reduce the difficulty. The reaction profile of a donor-acceptor complex polymerization, carried out under this condition, thus appears to be of interest.

Results.

Theoretically, any of the three reaction components can be used at a low concentration. In practise, the limited solubility of zinc chloride in acrylonitrile makes a low concentration of the salt with an excess of the monomers the best and most easily attained case.

Figure 21 shows the yield of copolymer as a function of time when the mole ratios of acrylonitrile and butadiene to zinc chloride were 51 and 19, respectively.

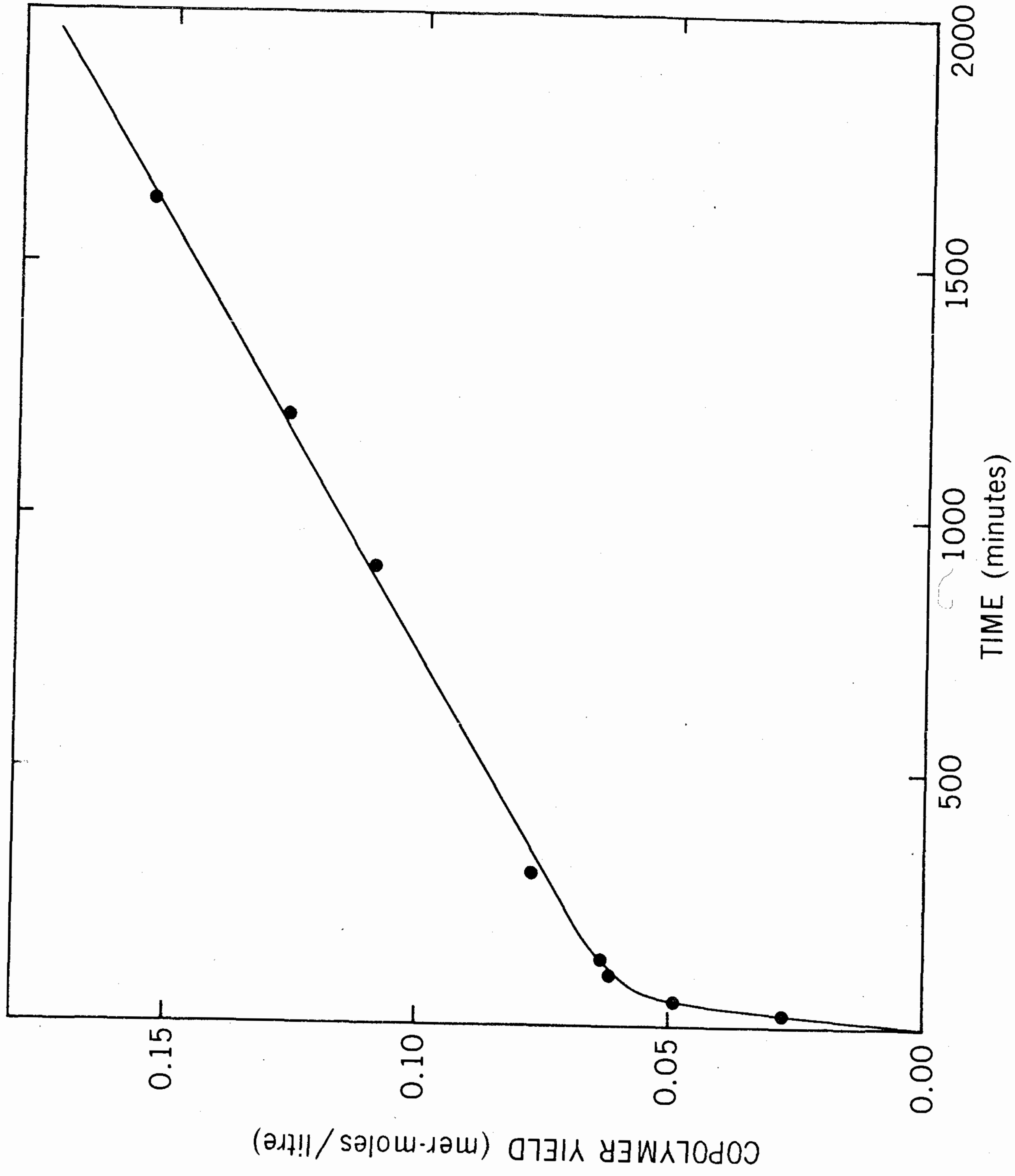
Elemental analysis of the products showed 49-52% acrylonitrile units through out the polymerization, and NMR spectroscopy indicated the alternating structure.

Similar reaction profiles have been observed at various temperatures and conditions, and will be shown in the appropriate parts of this work.

Conclusion.

When a low concentration of zinc chloride is employed the polymerization curve is characterized by a high rate at the beginning of polymer production, followed by a much slower, constant rate of polymerization. This observation suggests that the rate of polymerization is determined by the amount of zinc chloride available for the formation of the complex between the salt and the monomers. At the initial stage of polymerization the complex is being depleted and the rate decreases. Finally, the original complexes are consumed and new ones are formed from zinc chloride molecules regenerated from the copolymer chains. At this time, the rate of regeneration of zinc chloride becomes a rate determining step and the rate of

Figure 21. POLYMERIZATION AT LOW CONCENTRATION OF $ZnCl_2$.
Conditions: 3.87×10^{-2} mole/l $ZnCl_2$, 1.98 mole/l AN, 0.74 mole/l BD, 37 g DCE, 60°C.


COPOLYMER YIELD (mer-moles/litre)
0.00
0.05
0.10
0.15
TIME (minutes)
500
1000
1500
2000

polymerization is constant, the monomers being in excess.

When a reaction scheme involving complex formation and the complexing agent regeneration is employed and the concentration of one component is low, the resulting curve can be described by a kinetic equation which relates the copolymer yield to time. The derivation of such an equation is the subject of the next chapters.

III.2.2. DERIVATION OF KINETICS OF DONOR-ACCEPTOR COMPLEX POLYMERIZATION.

Purpose.

The kinetic studies of donor-acceptor complex polymerization published so far has been focused mainly on the effects of concentration on the polymerization rate and are described in chapter I.6. The copolymer composition has been treated kinetically in the cases when the product is not strictly an alternating copolymer (43,108,139). However, there is a complete lack of kinetic formulation linking the polymer yield with time or for describing the polymerization curves in terms of kinetic parameters.

Derivation of Kinetic Equations

The derivation of the kinetics is based on a scheme which includes the experimentally verified equilibria between the complexing salt and monomers, and a salt regeneration step. This scheme can be written symbolically as follows.

$$Z + mA \overset{K_o}{\rightleftharpoons} ZA_m \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}{\scriptstyle +mD}\; Z(AD)_m \xrightarrow{k_p} P_mZ \xrightarrow{k_r} mP + \underset{\text{recycled}}{\underset{\downarrow}{Z}}$$

The following is a description of the symbols used.

Z The free catalyst salt.

A The acceptor monomer.

D The donor monomer.

ZA_m	The adduct formed between the acceptor monomer, A, and the catalyst salt, Z, of variable stoichiometry, m.
$Z(AD)_m$	The donor-acceptor complex of the salt and both monomers of variable stoichiometry, m.
P_mZ	The catalyst-containing macromolecular product formed from the polymerization of $Z(AD)_m$.
P	The macromolecular product formed after the regeneration of the catalyst from P_mZ .
P_t	The macromolecular product regardless of the presence of the catalyst.
K_o	Equilibrium constant defined as

$$K_o = \frac{[ZA_m]}{[Z][A]^m} \qquad (11)$$

k_1, k_{-1}	The forward and backward rate constants for the complex formation $ZA_m + mD \rightleftarrows Z(AD)_m$.
k_p, k_r	Rate constants for the propagation and regeneration reactions, $Z(AD)_m \rightarrow P_mZ$ and $P_mZ \rightarrow mP+Z$, respectively.
$[P_mZ]$	The concentration of $Z(AD)_m$ units existing as polymer.
[P]	The concentration of catalyst-free AD units existing as polymer.

The total concentration of AD units existing as polymer, regardless of the presence of catalyst Z, is defined as

$$[P_t] = m[P_mZ] + [P] \qquad (12)$$

It should be noted here that the rate constant, k_p, is a composite of the true propagation constant and the rate constant of the initiation and termination reactions. It could also be a function of the catalyst (e.g., AIBN) concentration, or the number of photons passed in UV initiation or the number of faradays passed in electrolytic initiation. The use of such an apparent rate constant, k_p, serves to describe the actual monomer-consuming step at this stage and its internal complexity does not detract from the validity of the scheme.

The initial concentrations of the components are, at any time, defined by the following conservation equations.

$$[Z]_o = [Z] + [ZA_m] + [Z(AD)_m] + [P_mZ] \quad (13)$$

$$[D]_o = [D] + m[Z(AD)_m] + m[P_mZ] + [P] \quad (14)$$

$$[A]_o = [A] + m[ZA_m] + m[Z(AD)_m] + m[P_mZ] + [P] \quad (15)$$

In order to solve this problem it is necessary to assume a steady state concentration of $Z(AD)_m$ in the system. For first order consumption of $Z(AD)_m$ it is

$$\frac{d[Z(AD)_m]}{dt} = k_1[D]^m[ZA_m] - (k_{-1}+k_p)[Z(AD)_m] = 0 \quad (16)$$

This yields the following expression for the concentration of the complex.

$$[Z(AD)_m] = \frac{k_1}{k_{-1}+k_p}[D]^m[ZA_m] \quad (17)$$

Three different extremes of reactant concentration make it possible to evaluate integrals of the rate expression in subsequent treatment. They are as follows.

Case I $\quad [D]_o \gg [Z]_o \quad [A]_o \gg [Z]_o$;
then $\quad [D] \simeq [D]_o \quad [A] \simeq [A]_o$

Case II $\quad [Z]_o \gg [D]_o \quad [A]_o \gg [D]_o$;
then $\quad [ZA_m] \simeq [ZA_m]_o$

Case III $\quad [D]_o \gg [A]_o \quad [Z]_o \gg [A]_o$;
then $\quad [D] \simeq [D]_o \quad [Z] \simeq [Z]_o$

It is now possible to take each case (I,II,III) in turn, perform the necessary substitutions and evaluate the integral involved to find the total polymer yield, P_t, as a function of time, t.

The zero order case is soluble for each of Cases I, II and III to give the same answer:

$$\frac{d[P_t]}{dt} = mk_p[Z(AD)_m]^o \tag{18}$$

$$[P_t] = mk_p t \tag{19}$$

This equation does not match the reaction profile in Figure 21. The first order case is solved for each of the concentration extremes in the next steps.

CASE I.

In this system (low concentration of Z relative to A and D) the combination of equations (11) and (13) yields the following.

$$[Z]_o = \frac{[ZA_m]}{K_o[A]_o^m} + [ZA_m] + [Z(AD)_m] + [P_mZ] \tag{20}$$

$$[ZA_m] = \frac{K_o[A]_o^m[Z]_o - K_o[A]_o^m[Z(AD)_m] - K_o[A]_o^m[P_mZ]}{1 + K_o[A]_o^m} \tag{21}$$

Equation (17) becomes

$$[Z(AD)_m] = Q[ZA_m] \tag{22}$$

where

$$Q = \frac{k_1[D]_o^m}{k_{-1}+k_p} \tag{23}$$

The combination of equations (21) and (22) and rearrangement yield equation (24).

$$[Z(AD)_m] = \frac{QK_o[A]_o^m}{(1 + K_o[A]_o^m)\left(1+ \dfrac{QK_o[A]_o^m}{1+K_o[A]_o^m}\right)}([Z]_o - [P_mZ]) \tag{24}$$

which can be expressed as

$$[Z(AD)_m] = R([Z]_o - [P_mZ]) \tag{25}$$

where
$$R = \frac{QK_o[A]_o^m}{(1 + K_o[A]_o^m)\left(1 + \dfrac{QK_o[A]_o^m}{1+K_o[A]_o^m}\right)} \tag{26}$$

In order to find $[Z(AD)_m]$ as a function of only one variable (time) it is necessary to determine $[P_mZ]$ as a function of time. The rate of formation of P_mZ is

$$\frac{d[P_mZ]}{dt} = k_p[Z(AD)_m] - k_r[P_mZ] \tag{27}$$

The substitution of $[Z(AD)_m]$ in equation (27) by the right hand side of equation (25) yields

$$\frac{d[P_mZ]}{dt} = k_pR[Z]_o - (k_pR + k_r)[P_mZ] \tag{28}$$

Equation (28) may be integrated (see Appendix II) to give equation (29).

$$[P_mZ] = \frac{C_1}{C_2}(1 - \exp(-C_2t)) \tag{29}$$

where
$$C_1 = k_pR[Z]_o \tag{30}$$
$$C_2 = k_pR + k_r \tag{31}$$

Equation (25) thus becomes

$$[Z(AD)_m] = R[Z]_o - R\frac{C_1}{C_2} + R\frac{C_1}{C_2}\exp(-C_2t) \tag{32}$$

Now, taking into account equation (12), the rate of polymer formation can be written as

$$\frac{d[P_t]}{dt} = \frac{m\ d[P_mZ]}{dt} + \frac{d[P]}{dt} \tag{33}$$

The substitution for $d[P_mZ]/dt$ and $d[P]/dt$ according to

$$\frac{d[P_mZ]}{dt} = k_p[Z(AD)_m] - k_r[P_mZ] \qquad (27)$$

$$\frac{d[P]}{dt} = k_r[P_mZ] \qquad (34)$$

yields equation (35).

$$\frac{d[P_t]}{dt} = mk_p[Z(AD)_m] \qquad (35)$$

The combination of equations (32) and (35) and separation of variables result in the following expression.

$$d[P_t] = m(k_pR[Z]o - k_pR\frac{C_1}{C_2})dt + mk_pR\frac{C_1}{C_2}\exp(-C_2t)dt \qquad (36)$$

This may be integrated (see Appendix II) to

$$[P_t] = Et + F(1-\exp(-C_2t)) \qquad (37)$$

where the boundary condition is that $[P_t] = 0$ when $t = 0$ and where

$$E = mk_pR([Z]o - \frac{C_1}{C_2}) \qquad (38)$$

$$F = \frac{mk_pRC_1}{C_2^2} \qquad (39)$$

CASE II.

In this case (the donor monomer, D, is in low concentration relative to the acceptor monomer, A, and the complexing agent, Z) equation (17) becomes

$$[Z(AD)_m] = S[D]^m \qquad (40)$$

where $$S = \frac{k_1}{k_{-1} + k_p}[ZA_m]o \qquad (41)$$

The substitution of equation (40) into equation (14) yields

$$[Z(AD)_m] = \frac{1}{m}[D]_o - \frac{1}{m}\left(\frac{[Z(AD)_m]}{S}\right)^{1/m} - [P_mZ] - \frac{1}{m}[P] \tag{42}$$

or, with respect to equation (12),

$$[Z(AD)_m] = \frac{1}{m}[D]_o - \frac{1}{m}\left(\frac{[Z(AD)_m]}{S}\right)^{1/m} - \frac{1}{m}[P_t] \tag{43}$$

This can be solved when the stoichiometric constant is unity, such that

$$[ZAD] = [D]_o - \frac{[ZAD]}{S} - [P_t] \tag{44}$$

or, in the explicit form,

$$[ZAD] = \frac{S([D]_o - [P_t])}{1 + S} \tag{45}$$

When this expression for the concentration of ZAD is substituted into rate equation (35) the following differential equation is obtained.

$$\frac{d[P_t]}{dt} = \frac{k_pS[D]_o}{1 + S} - \frac{k_pS}{1+S}P_t \tag{46}$$

This may be rewritten as

$$\frac{d[P_t]}{dt} = C_3 - C_4[P_t] \tag{47}$$

where $C_3 = \dfrac{k_pS[D]_o}{1 + S}$ (48)

$$C_4 = \frac{C_3}{[D]_o} \tag{49}$$

Equation (47) may be integrated (see Appendix II) (using the boundary condition that $[P_t] = 0$ when $t = 0$) to give

$$[P_t] = [D]_o\ (1 - \exp(-C_4 t)) \tag{50}$$

CASE III.

In this case (the acceptor monomer, A, is in low concentration relative to the donor monomer, D, and the complexing agent, Z), the combination of conservation equation (15) and equilibrium equation (11) yields

$$[ZA_m] = \frac{1}{m}[A]_o - \frac{1}{m}\left(\frac{[ZA_m]}{K_o[Z]_o}\right)^{1/m} - \frac{1}{m}[P_t] - [Z(AD)_m] \tag{51}$$

Equation (51) becomes useful for further derivation only when m is unity. Then

$$[ZA] = \frac{[A]_o - [P_t] - [ZAD]}{1 + \dfrac{1}{K_o[Z]_o}} \tag{52}$$

In combination with equation (22) this yields

$$[ZAD] = \frac{Q}{1+\dfrac{1}{K_o[Z]_o} + Q}\ ([A]_o - [P_t]) \tag{53}$$

The substitution of equation (53) into rate equation (35) gives the following differential equation.

$$\frac{d[P_t]}{dt} = \frac{k_p Q[A]_o}{1+\dfrac{1}{K_o[Z]_o} + Q} - \frac{k_p Q}{1+\dfrac{1}{K_o[Z]_o} + Q}\,[P_t] \tag{54}$$

This may be written as

$$\frac{d[P_t]}{dt} = C_5 - C_6[P_t] \tag{55}$$

where $$C_5 = \frac{k_p Q[A]_o}{1 + \frac{1}{K_o[Z]_o} + Q} \qquad (56)$$

$$C_6 = \frac{C_5}{[A]_o} \qquad (57)$$

Equation (55) may be integrated (see Appendix II) (when the boundary condition $[P_t] = 0$ when $t = 0$ applies) to give

$$[P_t] = [A]_o \,(1 - \exp(-C_6 t)) \qquad (58)$$

(This equation is analogous to equation (50) for Case II).

The following table summarizes the various combinations of reaction conditions, stoichiometric constants and reaction orders which have proved amenable to direct solution at this stage.

Table IX. Conditions for which a Kinetic Equation is Derived.

Conditions	$[P_t] = f(t)$ when	
I $[A]_o \gg [Z]_o$ $[D]_o \gg [Z]_o$	Reaction order = 1,0	m = m
II $[A]_o \gg [D]_o$ $[Z]_o \gg [D]_o$	Reaction order = 1,0	m = 1
III $[D]_o \gg [A]_o$ $[Z]_o \gg [A]_o$	Reaction order = 1,0	m = 1

Further Considerations.

The presupposition of a steady state of $[Z(AD)_m]$, which can be attained, e.g., when

$$(k_p + k_{-1}) \gg k_1 \tag{59}$$

allows the imposition of a further set of restrictions on the k_p and k_{-1} relation without destroying the stationary state concentration of $Z(AD)_m$. These are that

$$k_p \gg k_{-1} \tag{60}$$

$$k_p \ll k_{-1} \tag{61}$$

It is instructive to test the effect of these restrictions on the previously derived equations for the time dependence of P_t concentration.

Firstly, when relationships (59) and (60) are considered, (and when it is assumed that $K_o \gg 1$, i.e. $K_o[A]_o^m \gg 1$ when $[A]_o$ is not too small), in Case I equation (37) can be supplied with new expressions for constants E, F and C_2. These are derived from equation (23), which is now simplified into

$$Q = \frac{k_1[D]_o^m}{k_p} \tag{62}$$

and equations (26), (31), (38) and (39). Their final forms are:

$$E = mk_1[D]_o^m[Z]_o \frac{k_r}{k_1[D]_o^m + k_r} \tag{63}$$

$$F = m[Z]_o \left(\frac{k_1[D]_o^m}{k_1[D]_o^m + k_r}\right)^2 \tag{64}$$

$$C_2 = k_1[D]_o^m + k_r \tag{65}$$

Similarly, in Cases II and III equations (49) and (57) are simplified to

$$C_4 = k_1[ZA]_o \tag{66}$$

$$C_6 = k_1[D]_o \tag{67}$$

An important feature of the new constants is that they are independent of k_p.

Secondly, when relationships (59) and (61) are considered (and when it is assumed that $K_o \gg 1$, i.e. $K_o[A]_o^m \gg 1$ when $[A]_o$ is not too small) then for Case I the new values of E, F and C_2 become

$$E = mk_pK_1[D]_o^m[Z]_o \frac{k_r}{k_pK_1[D]_o^m + k_r} \tag{68}$$

$$F = m[Z]_o \left(\frac{k_pK_1[D]_o^m}{k_pK_1[D]_o^m + k_r}\right)^2 \tag{69}$$

$$C_2 = k_pK_1[D]_o^m + k_r \tag{70}$$

where $K_1 = \dfrac{k_1}{k_{-1}}$

For Cases II and III, the constants C_4 and C_6 become

$$C_4 = k_pK_1[ZA]_o \tag{71}$$

$$C_6 = k_pK_1[D]_o \tag{72}$$

An important feature of the new constants is that they depend on equilibrium constant K_1.

To complete the kinetic considerations, if a system exists where the two monomers, A and D, are sufficiently reactive to form a donor-acceptor complex without the benefit of a catalyst, then the foregoing scheme may be modified to take this into account.

$$A + D \rightleftarrows (AD) \xrightarrow{k_p} P$$

Similar procedures may be used to derive the yield-time relationships which will themselves be greatly simplified.

Discussion of the Significance of the Kinetic Equations.

(1) The kinetics cannot be solved for all cases. Fortunately, Case I , developed for any value of m, is the most interesting system and may be solved for a first order reaction in "monomer".

(2) The desire to generalize the kinetic scheme made necessary the introduction of variable stoichiometry, m, in the original preequilibrium

$$Z + mA \xrightleftharpoons{K_0} ZA_m$$

Certain Lewis bases, acrylonitrile for example, interact with catalyst salts, such as zinc halides and alkylaluminum halides, to form adducts of variable composition. These adducts equilibrate, each contributing to the overall value of m, which can then be interpreted as the weighted average of the integral values for the descrete complexes.

(3) For those cases which can be solved, two main divisions occur, between Case I and Cases II and III together. This is a consequence of the regeneration of the complexing salt.

(4) The necessary qualification of the solution of the integration steps, that a pair of the reactants had to be in excess over the third reactant, appears at first to be an insurmountable drawback to the analysis. However, because of problems in dissolving the reactants it is frequently advisable to have this excess, and in practice the qualification does not become limiting. At this point the particular interest inherent in Case I becomes apparent. For donor-acceptor complex polymerizations using halides as catalysts, low $[Z]_0$ is an easily attainable and desirable condition. Thus, the integration condition is a realistic goal. A glance at the final kinetic equations themselves will also indicate that Case I is the only one which has the polymer yield as a function of k_r , the catalyst regeneration constant.

(5) One admitted drawback in this overall analysis is the fact

that the differential equations were not solved for cases other than where the reaction order was unity (or zero). In the steady-state treatment discussed here it is, of course, quite possible to envisage polymer systems where the reaction order is unity.

(6) In the case where $k_p \gg k_{-1}$, it was deduced that, in each Case (I,II and III), the yield of polymer as a function of time was independent of k_p, the apparent rate constant of propagation.

It must be stressed that k_p in the foregoing treatment is a function, not only of the true rate constant of propagation, but also of the initiation and termination steps.

Whereas the previous treatment was intended solely for the development of the rate equations, next chapters deal with the subject from a more practical standpoint. This may be summarized as follows. (A)An appraisal of the equations themselves, particularly with respect to the effect of changes in the kinetic rate parameters on the Yield/Time relationships. (B)An outline of methods of extracting useful kinetic parameters from experimental data.

Appraisal of the Kinetic Equations.

The various possible combinations of reactant concentrations (Cases I,II and III) will now be considered in sequence and the effects of the rate parameters on the Yield/Time relationship will be discussed.

Case I.

The polymer yield as a function of time relationship can be written in general as

$$[P_t] = Et + F(1 - \exp(-C_2 t)) \qquad (37)$$

The yield of polymer is therefore determined by two time-dependent terms, a linear term and an exponential term. The relative contributions of these terms appear to be governed by the ratio of k_p, the apparent propagation constant, to k_r, the catalyst regeneration constant. This is shown in Figure 22. Curves 1,2 and 3 correspond to $k_r \gg k_p$, $k_r \approx k_p$ and $k_r \ll k_p$, respectively. The shapes of the curves are independent of the relative values of k_p and k_{-1} except for the special case when $k_p \gg k_{-1}$. In this case, k_p is not rate controlling and the behaviour of the system is determined by the relative magnitudes of k_r and k_1.

In Figure 23, curves 1 through 3 have been constructed for increasing ratios of k_p to k_r ($k_p > k_r$ in all cases). It should also be noted that as k_r decreases, the intercept of the extrapolated linear portion increases to a limiting value (curve 3). This value is in fact $m[Z]_o$.

Figure 24, again when $k_p \gg k_r$, demonstrates the effect of varying m, the stoichiometric constant, without altering k_p/k_r. Curves 1,2 and 3 have values of m equal to 2.0, 1.5 and 1.0, respectively. The intercepts are approximately proportional to the m values.

Cases II and III.

Because of their similarity, these cases are treated together. The catalyst and one of the monomers are in concentration excess over the other monomer. The direct results of this condition is that the final kinetic equations (equations 50 and 58) are independent of k_r , the catalyst regeneration constant.

$$[P_t] = [D]_o(1 - \exp(-C_4t)) \qquad \text{(Case II)} \qquad (50)$$

$$[P_t] = [A]_o(1 - \exp(-C_6t)) \qquad \text{(Case III)} \qquad (58)$$

A plot of yield of polymer against time gives a smooth curve with a change in rate depending on the starting concentrations and the rate constant k_p. (However, when $k_p \gg k_{-1}$ the rate becomes independent of k_p and depends primarily upon k_1). This behaviour is shown in Figure 25. Curves 1 through 3 have

Figure 22. DEMONSTRATION OF THE k_p/k_r VARIATION. CASE I.

Curve 1 $k_r \gg k_p$

Curve 2 $k_r \approx k_p$

Curve 3 $k_r \ll k_p$

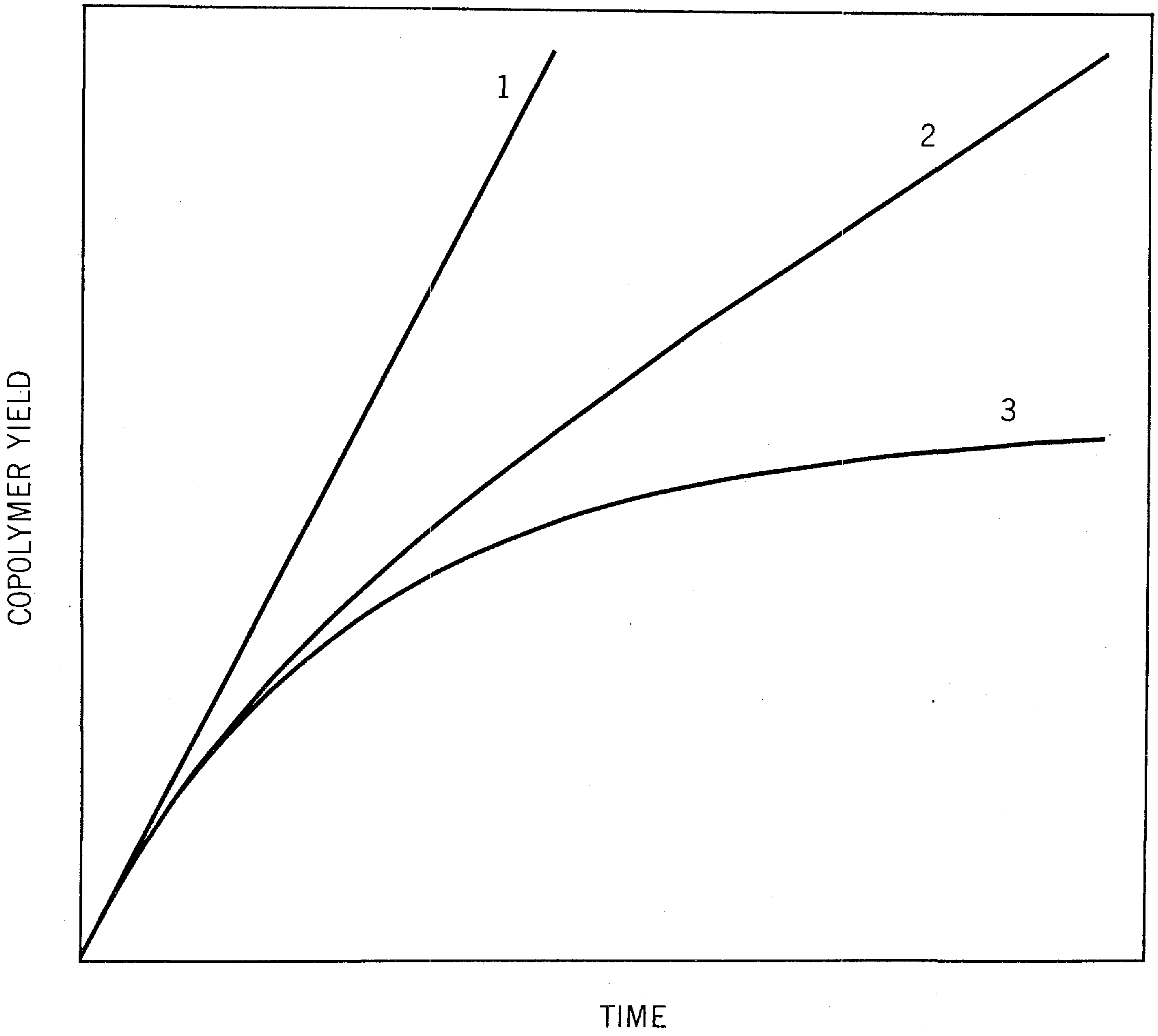

1
2
3
COPOLYMER YIELD
TIME

Figure 23. DEMONSTRATION OF THE k_p/k_r VARIATION. CASE I.

Curve 1	$k_r < k_p$
Curve 2	$k_r \ll k_p$
Curve 3	$k_r \lll k_p$

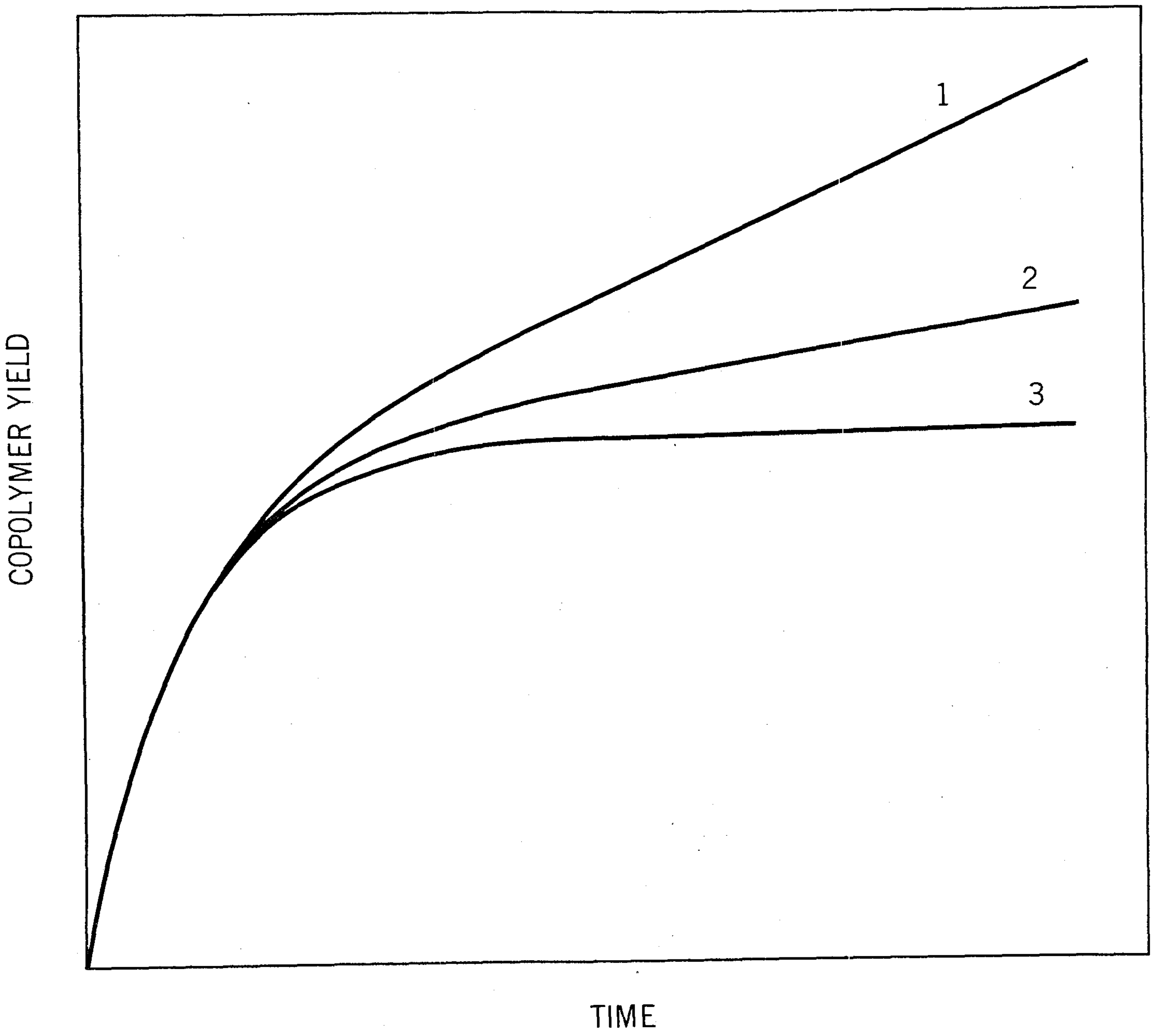

COPOLYMER YIELD
TIME
1
2
3

Figure 24. DEMONSTRATION OF THE m VARIATION. CASE I.

Curve 1 m = 2.0
Curve 2 m = 1.5
Curve 3 m = 1.0

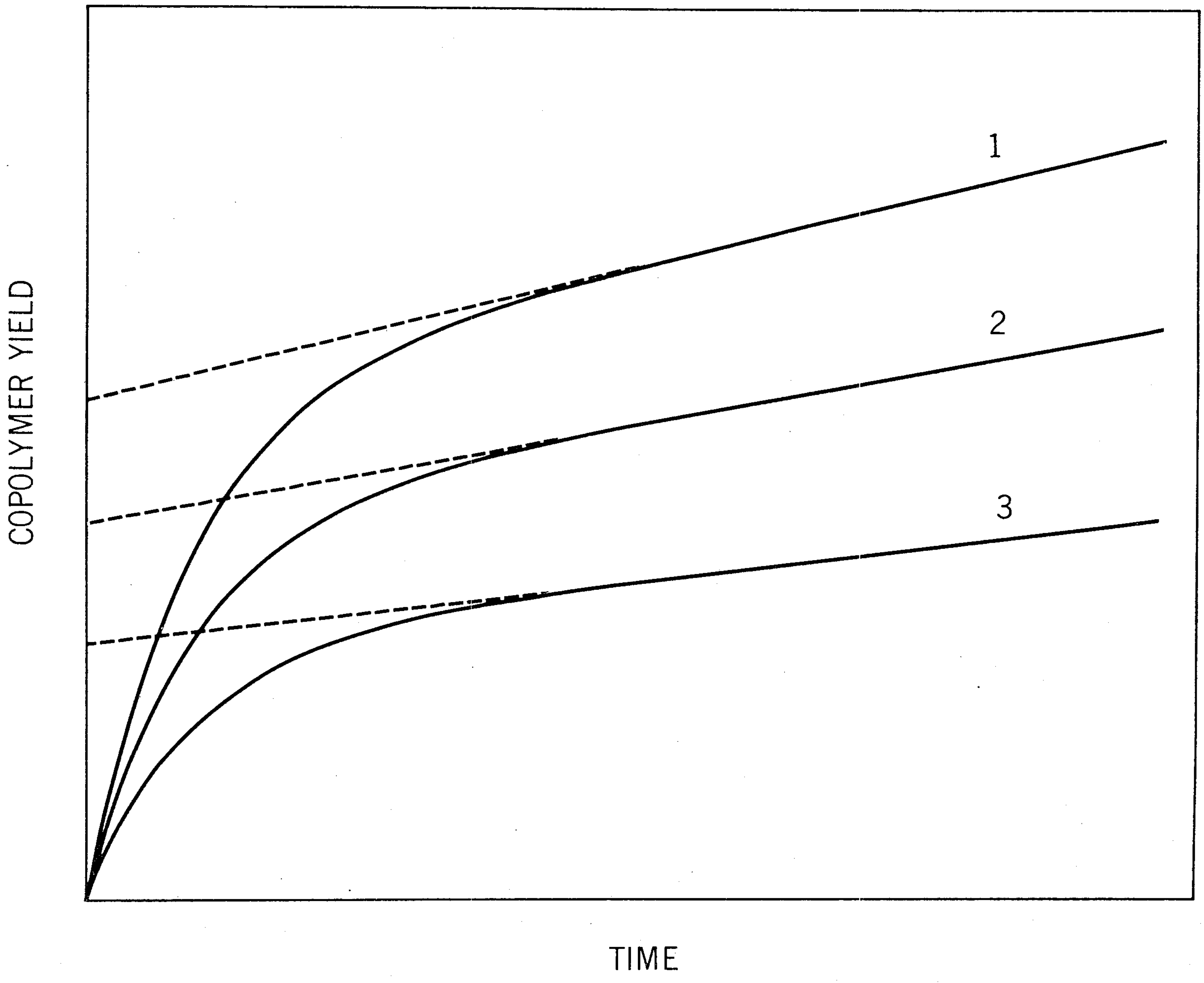
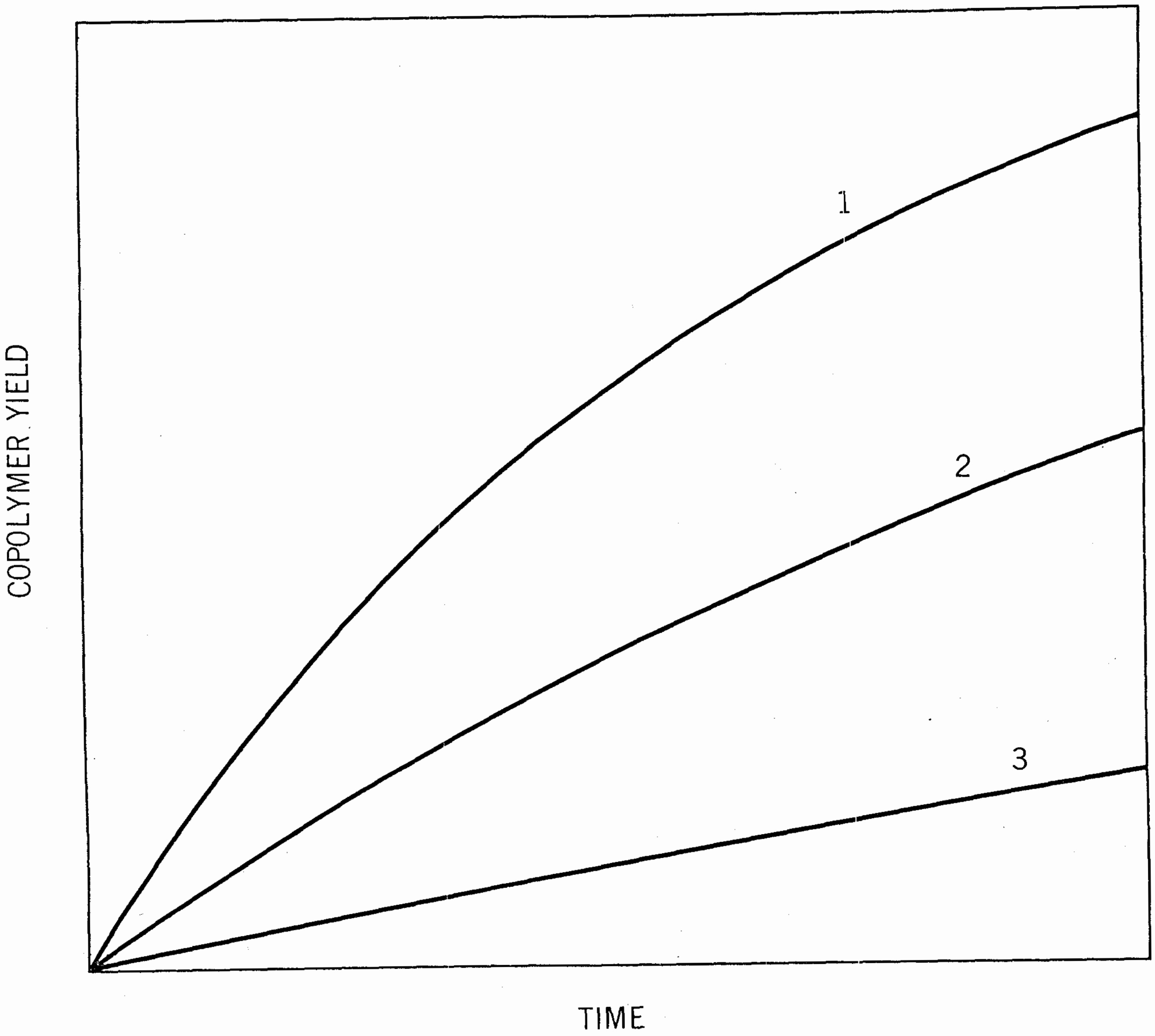

1
2
3
COPOLYMER YIELD
TIME

Figure 25. DEMONSTRATION OF THE k_p VARIATION. CASE II.

Curve 1	$k_p(1)$
Curve 2	$k_p(2)$
Curve 3	$k_p(3)$

$k_p(1) > k_p(2) > k_p(3)$


1
2
3
COPOLYMER YIELD
TIME

been constructed for decreasing values of k_p. The curves tend, at infinite time, to a limiting value of polymer conversion, corresponding to $[D]_o$ in Case II, and $[A]_o$ in Case III. (This is not shown, as such a high conversion does not uphold the condition presupposed for integration of the rate equations). A further point to note here is the possibility, in an experimental situation, of misinterpreting results. When k_p is low (curve 3) the curvature is very slight and analysis might suggest, erroneously, a straight line fit.

It is again stressed that, from an experimental point of view, Case I (low $[Z]_o$) is the most desirable and attainable situation, particularly when inorganic salt catalysts(e.g., zinc halides) are being used. This is due to their limited solubility in the systems used and the very rapid, almost uncontrolable, reactions in the presence of a high concentration of the complexing agent. It might also be noted that at high $[Z]_o$ the solutions rapidly become very viscous, presumably due to associative interactions between polymer chains. This effect is diminished at low $[Z]_o$, or at higher overall dilution. (However, at high dilution, there is once again a solubility problem with the uncomplexed catalyst when using solvents such as dichloroethane).

Outline of Methods of Extracting Kinetic Parameters from Experimental Data.

The extraction of kinetic parameters from Yield/Time curves is a simple process involving the following major steps.

First, Case I conditions are considered.

(1) Experimental curves are found (at a given set of temperature, solvent and initiator conditions) for $[P_t]$ versus t at various values of $[D]_o$, the initial donor monomer concentration, keeping $[D]_o \gg [Z]_o$.

(2) The curves are then analysed mathematically to provide the parameters E,F and C_2. The actual method of analysis presents

some problems since the expression of $[P_t]$ as a function of t contains a non-linear parameter, $\exp(-C_2t)$. This problem can be overcome however, using one of the following methods.

(a) Curve analysis may be accomplished by arbitrarily choosing a value for the non-linear parameter, C_2, followed by linear least-squares regression to find the best C_2, E and F. Another method is to expand the exponential term as a polynomial and look for the best fit by the least-squares technique.

(b) The preceeding method is generally applicable. However, in the special case, when $k_p \gg k_r$ (see Figure 26) it is possible to get good values of the parameters E,F and C_2 using a two-part linear least-squares regression. Values of the slope, E, and the first estimate of the intercept, F', which ignores the possibility of an inflection point in the curved region, are obtained from the linear portion (high t) of the curve. Using these, it is possible to get a value for C_2 and a final value of F from the shaded part of the graph. This can be seen from equation (73).

$$\log(Et + F' - [P_t]_t) = \log F - C_2t \tag{73}$$

A linear least-squares treatment will give a slope of C_2 and an intercept of logF.

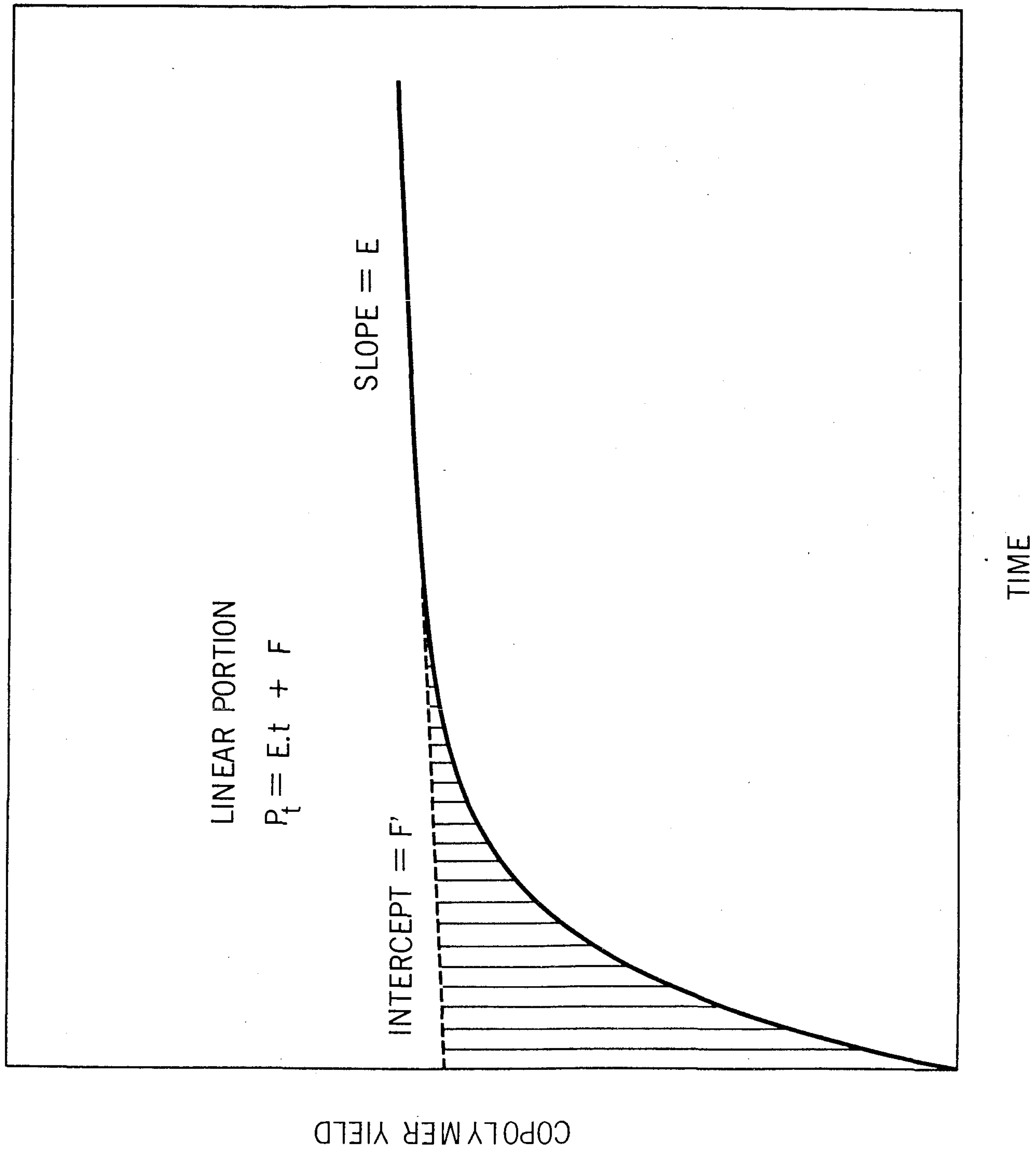
(3) When E, F and C_2 have been found for each value of $[D]_o$, it is then possible to extract m, k_r and k_p as detailed in the following sequence of operations.

(a) Values of k_pR, k_r and m are found by solving the following three simultaneous equations.

$$E = mk_pR([Z]_o - \frac{C_1}{C_2}) = mk_pR[Z]_o(1 - \frac{k_pR}{C_2}) \tag{38}$$

$$F = \frac{mk_pRC_1}{C_2^2} = \frac{m(k_pR)^2[Z]_o}{C_2^2} \tag{39}$$

Figure 26. ANALYSIS OF THE CURVE $[P_t] = Et + F(1 - \exp(-C_2t))$ WHEN $k_p \gg k_r$.


LINEAR PORTION
$P_t = E.t + F$
INTERCEPT = F'
SLOPE = E
TIME
COPOLYMER YIELD

$$C_2 = k_pR + k_r \tag{31}$$

Solution of equations (38), (39) and (31) gives

$$k_pR = \frac{FC_2^2}{E + FC_2} \tag{74}$$

$$m = \frac{FC_2^2}{[Z]_o} \frac{1}{(k_pR)^2} \tag{75}$$

$$k_r = C_2 - k_pR \tag{76}$$

(b) Having values of k_pR for each value of $[D]_o$ and knowing m and k_r which are constants, k_p can be found by the following procedure. Equation (26) is simplified to

$$R = \frac{Q}{1 + Q} \tag{77}$$

on the assumption that $K_o[A]_o \gg 1$.

Now,

$$k_pR = \frac{k_pQ}{1 + Q} \tag{78}$$

After substitution for Q from equation (23) and rearrangement,

$$\frac{1}{k_pR} = \left(\frac{k_{-1} + k_p}{k_pk_1}\right) \frac{1}{[D]_o^m} + \frac{1}{k_p} \tag{79}$$

Thus, when plotting $1/k_pR$ against $1/[D]_o^m$, the intercept is k_p^{-1}.

In Case II (and similarly Case III) once again, the curves of $[P_t]$ against t are determined experimentally for different $[D]_o$ values. A straightforward least-squares analysis of each curve is performed to evaluate C_4 for each $[D]_o$.

Equations (41) and (49) are then combined and rearranged to give

$$\frac{1}{C_4} = \left(\frac{k_{-1} + k_p}{k_p k_1}\right) \frac{1}{[ZA]_o} + \frac{1}{k_p} \tag{80}$$

Thus, a plot of $1/C_4$ against $1/[ZA]_o$ yields an intercept of $1/k_p$. ($[ZA]_o$ may be considered equivalent to $[A]_o$ or $[Z]_o$, whichever is least, assuming that K_o is large, the equilibrium lying heavily on the right hand side).

The assumption was tacitly made in the foregoing treatment that variation of $[D]_o$ does not affect any of the rate constants.

III.2.3. ASSESMENT OF THE APPROXIMATIONS IN THE KINETICS.

Purpose.

The mathematical solution of the equations derived from the foregoing kinetic scheme developed for donor-acceptor complex polymerization was based on the steady state assumption and the applicability of initial concentrations of two components over a range of conversion. The limits imposed on the validity of the solutions by the approximations are to be investigated.

Introduction.

The kinetic scheme of the overall process of the formation of $Z(AD)_m$ and its subsequent polymerization may be described precisely and exactly by the following set of differential equations (k_o and k_{-o} follow from $K_o = k_o/k_{-o}$).

$$\frac{d[Z]}{dt} = k_{-o}[ZA_m] + k_r[P_mZ] - k_o[Z][A]^m \tag{81}$$

$$\frac{d[A]}{dt} = k_{-o}[ZA_m] - k_o[Z][A]^m \tag{82}$$

$$\frac{d[ZA_m]}{dt} = k_o[Z][A]^m + k_{-1}[Z(AD)_m] - k_{-o}[ZA_m] - k_1[ZA_m][D]^m \qquad (83)$$

$$\frac{d[D]}{dt} = k_{-1}[Z(AD)_m] - k_1[ZA_m][D]^m \qquad (84)$$

$$\frac{d[Z(AD)_m]}{dt} = k_1[ZA_m][D]^m - k_{-1}[Z(AD)_m] - k_p[Z(AD)_m]^q \qquad (85)$$

$$\frac{d[P_mZ]}{dt} = k_p[Z(AD)_m]^q - k_r[P_mZ] \qquad (86)$$

$$\frac{d[P_t]}{dt} = mk_p[Z(AD)_m]^q \qquad (87)$$

By applying a general numerical method for the solution of differential equations (81-87), one can calculate each concentration variable (including copolymer concentration) as a function of time for a given set of rate constants and component concentrations. A 4th order Runge-Kutta method was used to provide the numerical solution to these differential equations.

A comparison of the "exact" solutions with those based on the approximations (eqs. 37, 50, 58) demonstrates the validity and utility of the approximate kinetic equations.

The first section of this chapter deals with situations in which the relationships

$$[D] \simeq [D]_o, \quad [A] \simeq [A]_o, \quad [Z] \simeq [Z]_o$$

are not strictly valid. This is the case when the initial concentrations of reactants do not differ sufficiently and/or when polymerization proceeds to high conversion.

The second section examines the applicability of the equations for various combinations of rate constants, not all of which satisfy the steady state assumption (eq. 16).

The graphs have been scaled so that the time and concentration units involved in the rate constants, and [A], [D], [Z], etc., are arbitrary but uniform.

Results.

Concentration Variations.

One of the basic assumptions for the derivation of equations (37), (50) and (58) was virtual constancy of concentration of two of the components. Although valid at low conversion, this approximation becomes unsatisfactory at high conversion. Thus the effect of the extent of conversion on the validity of results obtained by the approximate treatment is of direct interest. Variation of the ratios $[Z]_o/[A]_o$ and $[Z]_o/[D]_o$; $[D]_o/[A]_o$ and $[D]_o/[Z]_o$; $[A]_o/[D]_o$ and $[A]_o/[Z]_o$; for Cases I, II and III, respectively, is also expected to affect the constancy of [A], [D] and [Z] during polymerization.

Because of the similarity between Cases II and III, only Cases I and II are studied. The results of Case II may be applied directly to Case III.

The effects of changes in conversion and component concentration ratios are shown in Figures 27 and 28 for the conditions of Case I and Case II, respectively. The rate constants used in the simulation of the curves were chosen to satisfy the steady state assumption and therefore eliminate any deviation due to the late attainment of a steady state complex concentration. The constants also satisfy the assumed rapid attainment of the equilibrium characterized by K_o, and the rate of regeneration of the complexing salt slow compared to the rate of polymerization.

The corresponding numerical data for curve 4 of Figure 27 and curve 3 of Figure 28 are presented in Tables X and XI. Table X for Case I indicates clearly that the largest error in the approximated solution is in the non-linear portion of the curve. The relative error is insignificant after

Figure 27. VALIDITY TEST. EFFECT OF CONVERSION AND COMPONENT CONCENTRATIONS. CASE I.

The dotted lines represent the approximated solution. The solid lines represent the exact solution.

Curves 1 $[Z]_o/[A]_o = 1/3$
2 $[Z]_o/[A]_o = 1/5$
3 $[Z]_o/[A]_o = 1/10$
4 $[Z]_o/[A]_o = 1/20$

Calculated for: $[A]_o = 1$, $[D]_o = 1$, $m = 1$, $k_o = 8$, $k_{-o} = 4$, $k_1 = 0.4$, $k_{-1} = 0.4$, $k_p = 4$, $k_r = 0.004$

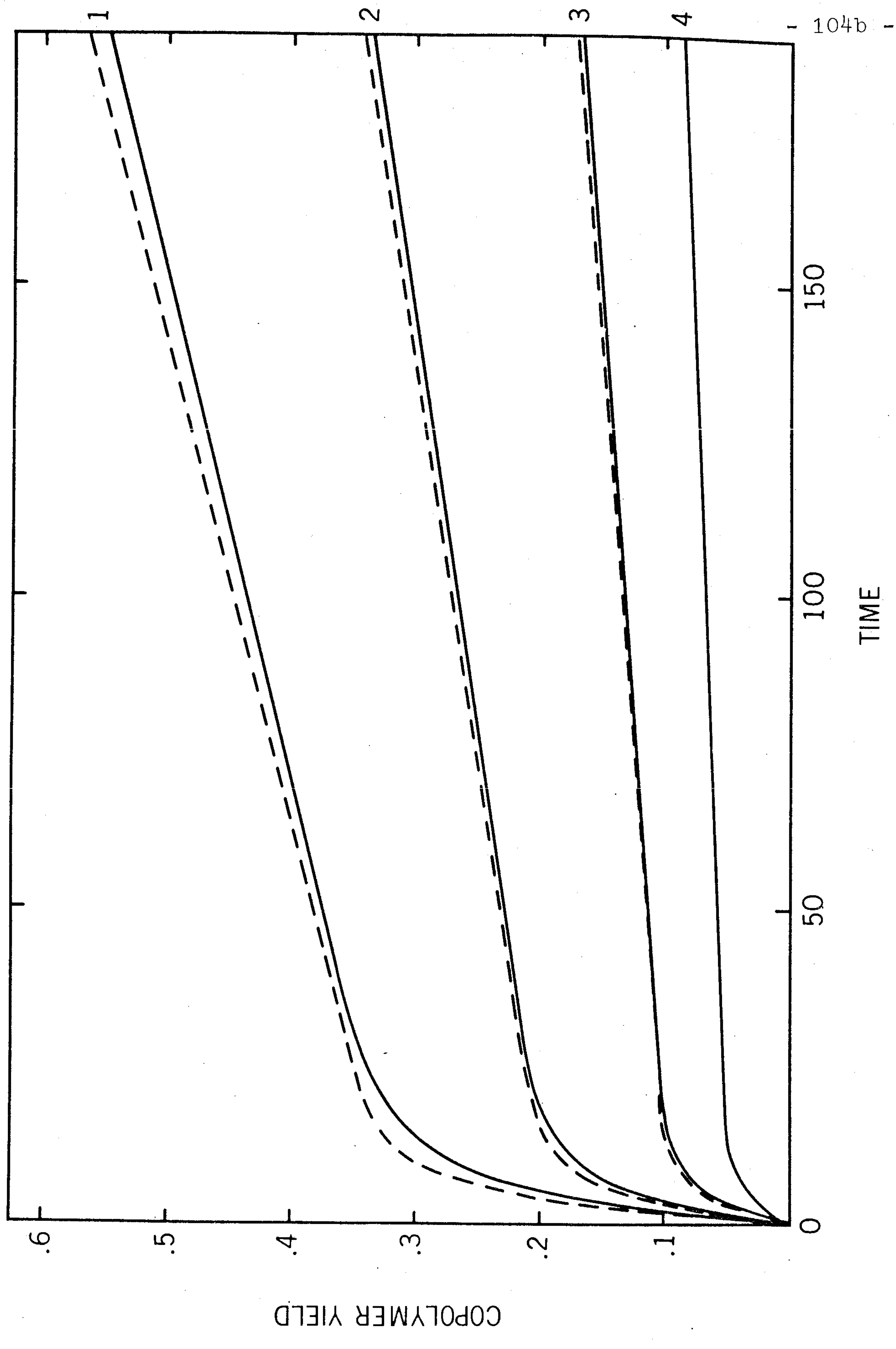
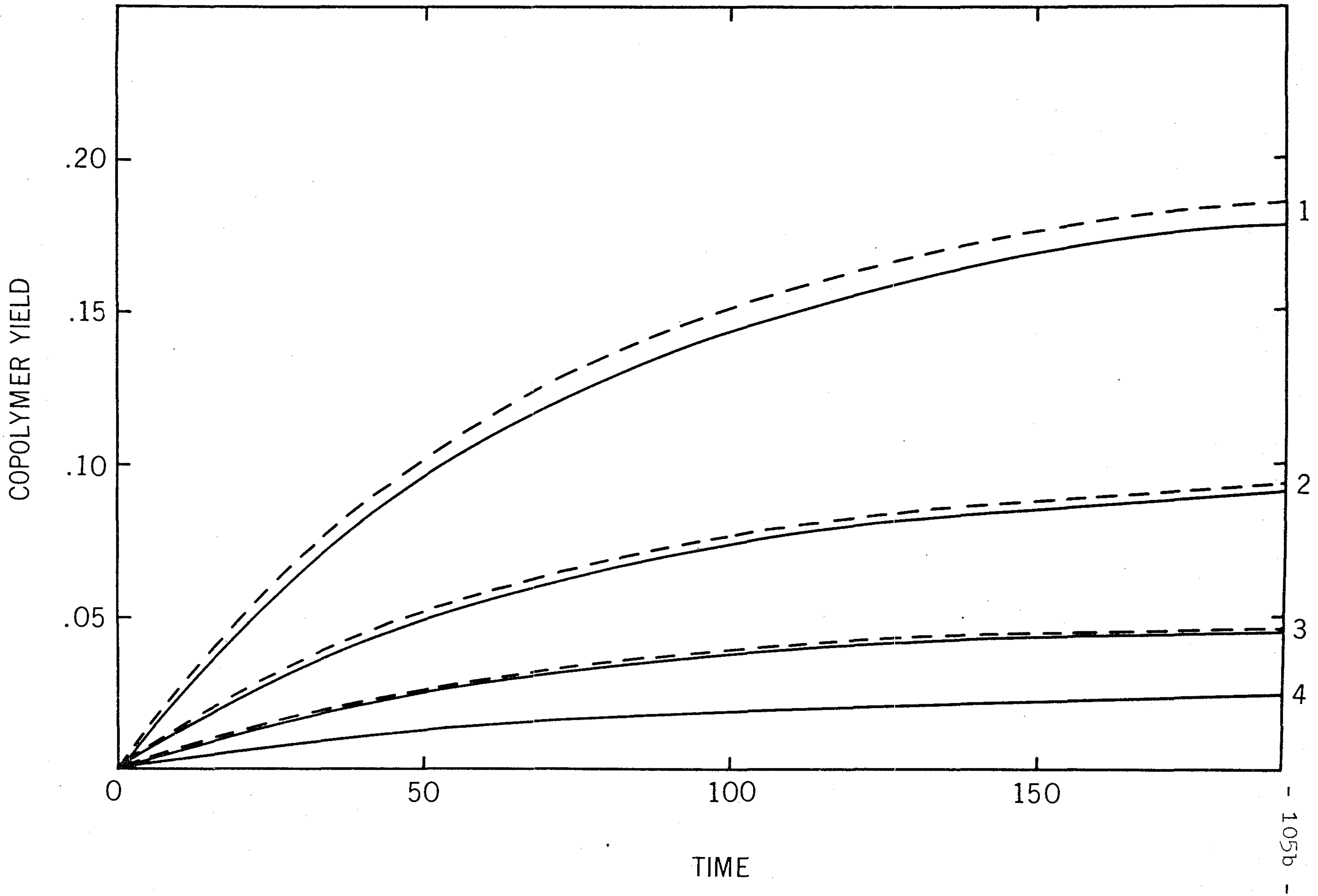

COPOLYMER YIELD
.6
.5
.4
.3
.2
.1
0
50
100
150
TIME
1
2
3
4

Figure 28. VALIDITY TEST. EFFECT OF CONVERSION AND COMPONENT CONCENTRATIONS. CASE II.

The dotted lines represent the approximated solution. The solid lines represent the exact solution.

Curves 1 $[D]_o/[A]_o = 1/5$
2 $[D]_o/[A]_o = 1/10$
3 $[D]_o/[A]_o = 1/20$
4 $[D]_o/[A]_o = 1/40$

Calculated for: $[A]_o = 1$, $[Z]_o = 1$, $m = 1$, $k_o = 8$, $k_{-o} = 0.8$, $k_1 = 0.02$, $k_{-1} = 0.02$, $k_p = 2$, $k_r = 0.0002$


COPOLYMER YIELD
.20
.15
.10
.05
0
50
100
150
TIME
1
2
3
4

the first few percent of conversion. In Case II the error decreases slowly during the reaction.

Table X. Effect of Conversion Under Case I Conditions of Low Complexing Agent Concentration.

Time	Conversion of D (%)		Relative error (%)
	exact	approx.	
3	2.32	2.49	6.97
6	3.67	3.75	2.40
9	4.36	4.41	1.29
12	4.73	4.77	0.82
15	4.95	4.98	0.59
18	5.09	5.11	0.45
25	5.29	5.31	0.32
50	5.80	5.81	0.28
100	6.77	6.79	0.31
150	7.75	7.78	0.33
200	8.73	8.76	0.35

Calculated for: $[A]_o = 1$, $[D]_o = 1$, $[Z]_o = 0.05$, $k_o = 8$, $k_{-o} = 4$, $k_1 = 0.4$, $k_{-1} = 0.4$, $k_p = 4$, $k_r = 0.04$, $m = 1$.

Table XI. Effect of Conversion Under Case II Conditions of Low Donor Monomer Concentration.

Time	Conversion of D (%)		Relative error (%)
	exact	approx.	
4	4.7	5.6	18.8
8	10.0	10.9	8.9
12	14.9	15.8	6.0
16	19.6	20.5	4.7
20	24.0	25.0	4.0
50	50.0	51.2	2.4
100	79.8	81.0	1.8
150	87.2	88.4	1.3
200	93.3	94.2	0.9

Calculated for: $[A]_o = 1$, $[D]_o = 0.05$, $[Z]_o = 1$, $k_o = 8$, $k_{-o} = 0.8$, $k_1 = 0.02$, $k_{-1} = 0.02$, $k_p = 2$, $k_r = 0.0002$, $m = 1$.

The effects of variation of ratios $[Z]_o/[A]_o$ and $[D]_o/[A]_o$ are also shown in Figures 27 and 28. The largest error is generated (as illustrated in Tables X and XI) in the initial portion of the curves. Therefore, the applicability of the approximate equations is judged by the goodness of fit in the regions of low conversion.

Table XII. Effect of Ratio $[Z]_o/[A]_o$.

$[Z]_o/[A]_o$	Conversion of D (%)		Relative error (%)
	exact	approx.	
1/3	5.1	7.3	44.0
1/5	4.9	6.1	24.2
1/10	4.9	5.3	8.1
1/20	5.00	5.03	0.5

Calculated for: $[A]_o = 1$, $[D]_o = 1$, $k_o = 8$, $k_{-o} = 4$, $k_1 = 0.4$, $k_{-1} = 0.4$, $k_p = 4$, $k_r = 0.004$, $m = 1$.

Table XIII. Effect of Ratio $[D]_o/[A]_o$.

$[D]_o/[A]_o$	Conversion of D (%)		Relative error (%)
	exact	approx.	
1/5	9.9	10.8	9.8
1/10	9.9	10.9	9.2
1/20	10.0	10.9	8.9
1/40	9.9	10.9	8.7

Calculated for: $[A]_o = 1$, $[Z]_o = 1$, $k_o = 8$, $k_{-o} = 0.8$, $k_1 = 0.02$, $k_{-1} = 0.02$, $k_p = 2$, $k_r = 0.0002$, $m = 1$.

The results for Case I in Tables X and XII are quite satisfactory. The ratio $[Z]_o/[A]_o = 1/15$ provides a deviation below the error limit resulting from experimental uncertainty. At higher ratios of $[Z]_o$ to $[A]_o$ or under the conditions of Case II the deviation is above acceptable limits. Fortunately, this is a reflection of the choice of the value for k_1 $(= k_{-1}) = k_p/10$ in Case I, and $k_p/100$ in Case II. If higher ratios are encountered the relative error is much less.

For example, an increase of k_p/k_1 (= k_p/k_{-1}) from 100 to 1000 is accompanied by a decrease in the relative error from 11.2% to 1.8% .

One can thus conclude that the degree of conversion of the donor monomer is not critical and, in Case I, a low concentration of complexing agent necessary for a good fit is easily attainable.

Assumption of Steady State Conditions.

The other fundamental assumption reflected in the approximate equations is that a steady state complex concentration is attained and that the concentration is given by equation (17).

The approximate and exact solutions have been simulated and compared for the following combinations of rate constants (L and S are large and small numbers, respectively).

	k_1	k_{-1}	k_p
1	S	L	L
2	S	S	L
3	S	L	S
4	L	L	S
5	S	S	S
6	L	S	S
7	L	S	L

Although other parameters may influence the rate of reaction, these three rate constants are sufficient to define the attainment of the steady state. It would have been desirable to perform the simulations with all other parameters constant. Scaling problems, however, forced the adoption of the following uniform conditions.

$k_o > k_{-o}$, $k_{-o} > k_1$, $k_r \le k_p$ or k_1 (smaller one),
$q = 1$, $m = 1$.

Physically this corresponds to having $[ZA_m]$ determined by a fast pre-equilibrium

$$Z + mA \underset{k_{-o}}{\overset{k_o}{\rightleftarrows}} ZA_m$$

where the regeneration step is never faster than the polymerization step. The simulations were performed for first order reaction. A factor of 100 was used for L/S.

Simulated curves are presented in Figures 29-31. Combinations 1, 2 and 3 (Fig. 29, lines 1-I, 1-II; 2-I, 2-II; 3-I, 3-II; respectively) satisfy the steady state condition, and the approximated and exact solutions are in good accord. Although the conversion region covered by lines 3-I and 3-II is small, the calculations indicate good agreement, as a non-steady state phenomenon would have been indicated at the beginning of the polymerization. Similarly, a good fit is found for the fourth combination of rate constants, the fast pre-equilibrium condition (lines 4-I and 4-II).

However, for the non-steady state conditions 5, 6 and 7 (Fig. 30, lines 5-I and 5-II or 6-I and 6-II; Fig. 31, lines 7-I and 7-II) a discrepancy is evident at low conversion.

Not all of the seven combinations are necessarily realistic. For example, the equilibrium constant $K_1 = k_1/k_{-1}$ is equal to 0.062 l/mole for the system styrene-acrylonitrile-zinc chloride system (52). This excludes consideration of $k_1 \gg k_{-1}$ and therefore limits attention to the steady state combinations 1 to 4 and the non-steady state case 5 for such systems.

Conclusion.

The analysis showed that the degree of conversion was not critical and the percent error in the yield was highest at low conversions.

In the case of low concentration of the complexing agent, the concentration conditions necessary for a good agreement are easily attainable. The kinetic equation may be applied at steady state as well as non-steady state complex concentrations.

When the concentration of either monomer is low, the necessary excess of the other two components may be impracti-

Figure 29. VALIDITY TEST. EFFECT OF RELATIVE MAGNITUDES OF k_1, k_{-1} AND k_p.

The dotted lines represent the approximated solution. The solid lines represent the exact solution.

Curves 1-I, 2-I, 3-I, 4-I :

$$[Z]_o = [A]_o/20 = [D]_o/20$$

Curves 1-II, 2-II, 3-II, 4-II :

$$[D]_o = [A]_o/20 = [Z]_o/20$$

Curves 1-I, 1-II: $k_1 = k_{-1}/100 = k_p/100$

2-I, 2-II: $k_1 = k_{-1} = k_p/100$

3-I, 3-II: $k_1 = k_{-1}/100 = k_p$

4-I, 4-II: $k_1/100 = k_{-1}/100 = k_p$

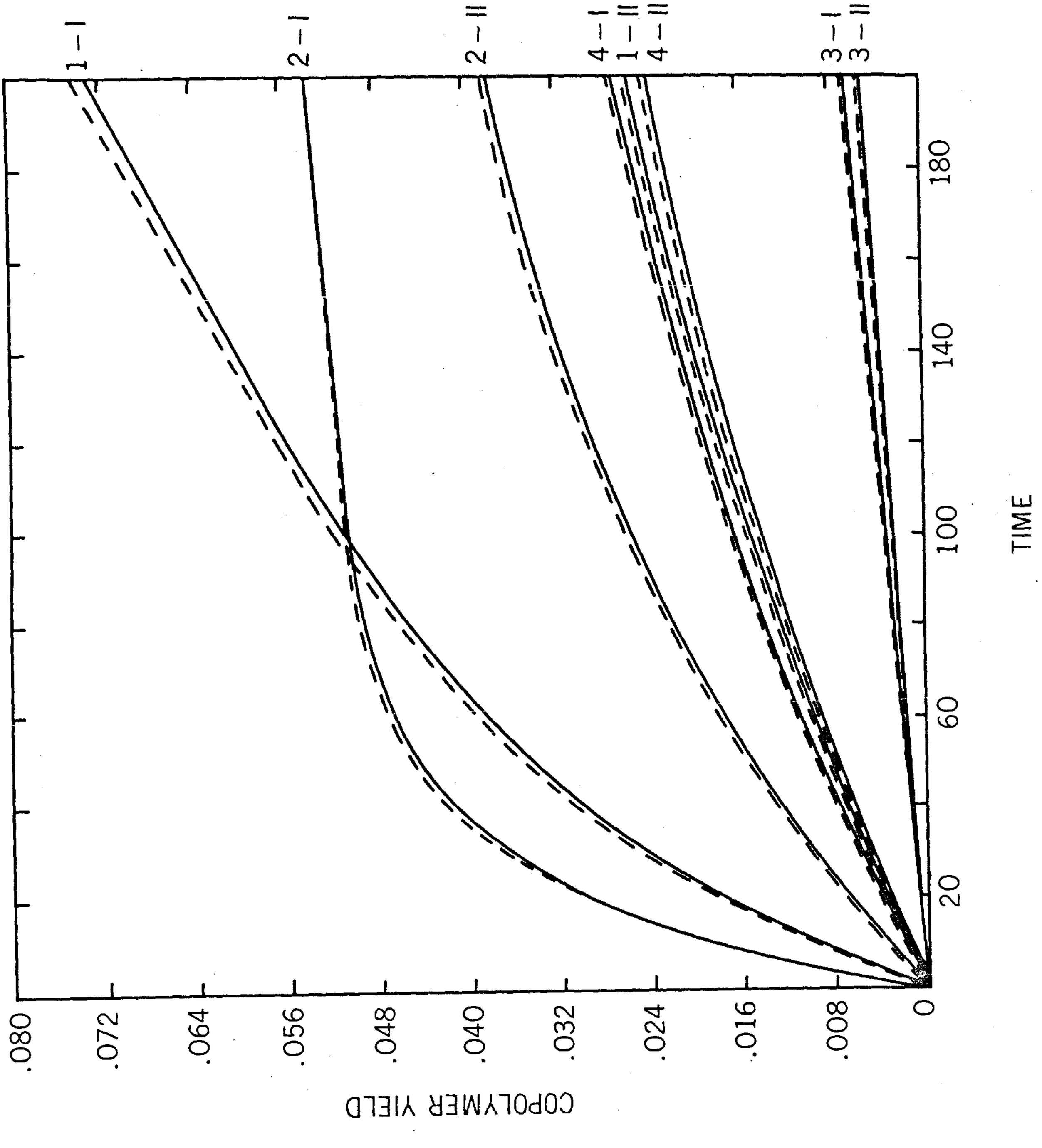

COPOLYMER YIELD
0
.008
.016
.024
.032
.040
.048
.056
.064
.072
.080
TIME
20
60
100
140
180
1 – I
2 – I
2 – II
4 – I
1 – II
4 – II
3 – I
3 – II

Figure 30. VALIDITY TEST. EFFECT OF RELATIVE MAGNITUDES OF k_1, k_{-1} AND k_p.

The dotted lines represent the approximate solution. The solid lines represent the exact solution.

Curves 5-I, 6-I : $[Z]_o = [A]_o/20 = [D]_o/20$
Curves 5-II, 6-II: $[D]_o = [A]_o/20 = [Z]_o/20$

Curves 5-I, 5-II : $k_1 = k_{-1} = k_p$
6-I, 6-II : $k_1/100 = k_{-1} = k_p$

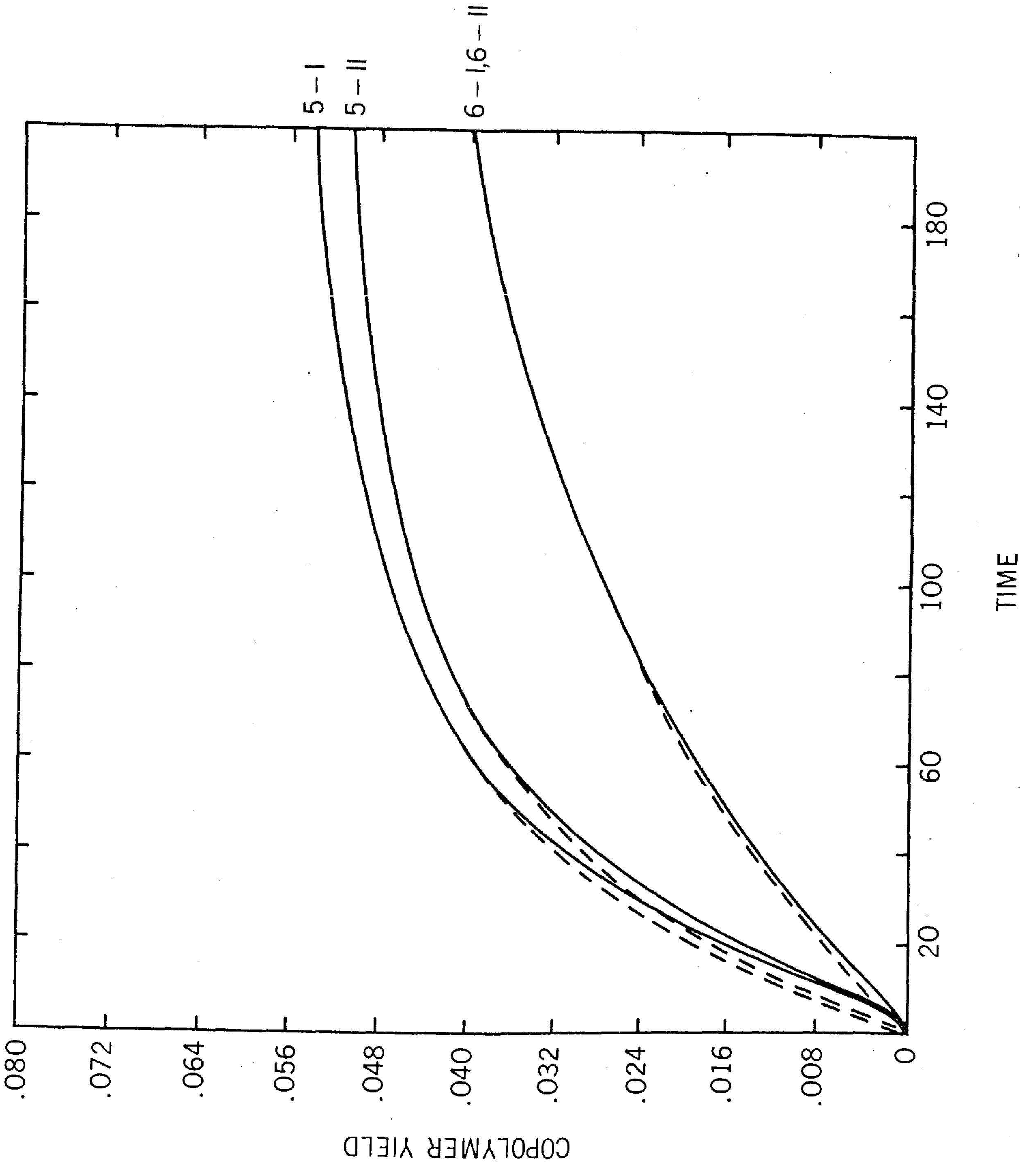
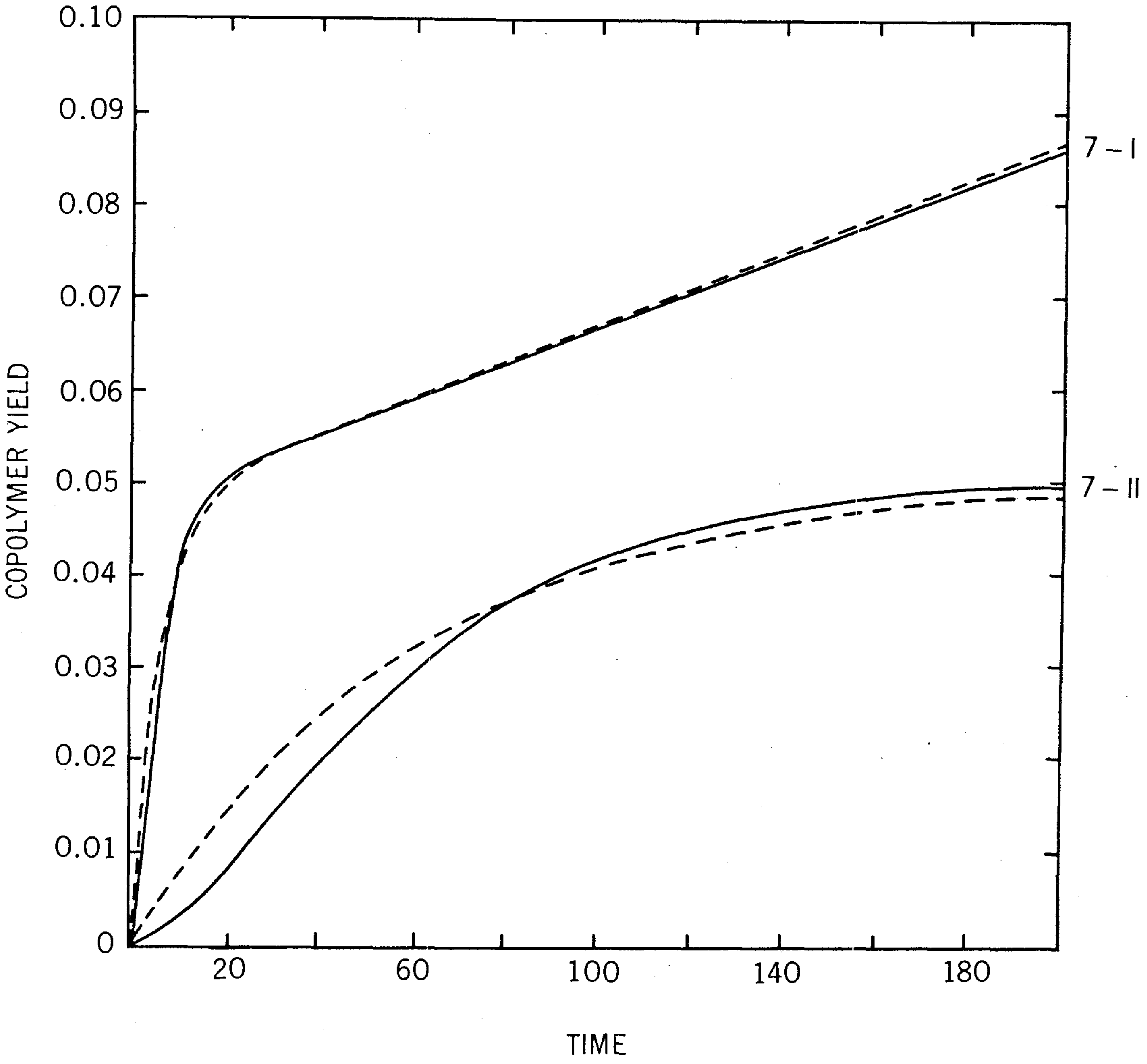

5 – I
5 – II
6 – I,6 – II
COPOLYMER YIELD
.080
.072
.064
.056
.048
.040
.032
.024
.016
.008
0
20
60
100
140
180
TIME

Figure 31. VALIDITY TEST. EFFECT OF RELATIVE MAGNITUDES OF k_1, k_{-1} AND k_p.

The dotted lines represent the approximated solution. The solid lines represent the exact solution.

Curve 7-I : $[Z]_o = [A]_o/20 = [D]_o/20$
Curve 7-II : $[D]_o = [A]_o/20 = [Z]_o/20$

Curves 7-I, 7-II : $k_1/100 = k_{-1} = k_p/100$


COPOLYMER YIELD
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
20
60
100
140
180
TIME
7 – I
7 – II

cally high. Moreover, the kinetic equations can only be applied for a steady state complex concentration.

III.2.4. APPLICATION OF THE KINETICS. LIMITING RATE IN THE BUTADIENE-ACRYLONITRILE COPOLYMERIZATION.

Purpose.

An analysis of the kinetic equations indicated a limit to the yield of polymer which can be produced in a given time when the rate of initiation is increased. In the case in which $k_p \gg k_{-1}$, equation (37),

$$[P_t] = Et + F(1-\exp(-C_2t)) \qquad (37)$$

is independent of the apparent rate constant, k_p, (see eqs. 63-65). Thus, the system should show a limiting rate at the appropriate value of k_p. As this is a function of the rates of initiation, propagation and termination,

$$k_p = f(k_i, k_{pr}, k_t) \qquad (88)$$

it is equivalent to saying that the system should show a limiting rate of polymerization at an appropriate value of the rate of initiation. The purpose of this chapter is to provide an experimental example of such behaviour.

Results.

Variation of the temperature cannot serve as a means for selective variation of k_p because all the equilibria and rate constants would vary as well. However, a change in the rate of initiation was achieved using electropolymerization techniques. During each experiment a constant current was passed through the solution. The effect of varying this current is shown in Figure 32.

A definite plateau is evident. However, the limiting yield may be explained by either of two phenomena. (1)A diffusion process becomes the rate determining step; (2)the complex formation is rate determining, as indicated above.

In order to differentiate between these two possibilities polymerizations were performed at the same current with two different electrode surface areas of 6.4 cm^2 and 3.6 cm^2. However, as is evident from Figure 32, the surface area has no effect on the limiting yield, thus indicating that the process was not diffusion controlled in the range of current densities under investigation. This leads to the conclusion that the rate of polymerization becomes independent of the current as the result of the rate determining step involved in the formation of a charge transfer complex. Since k_p is a function of the rate of initiation and therefore of the current applied, it is equivalent to stating that the rate of polymerization becomes independent of the apparent rate constant of polymerization.

Conclusion.

A definite limitation to the rate of polymerization is observed when the rate of initiation is increased. It was shown that this effect was not due to diffusion control of the rate of initiation. This observation is in accord with the theoretical prediction derived from the kinetics formulated in this work for the donor-acceptor complex polymerization.

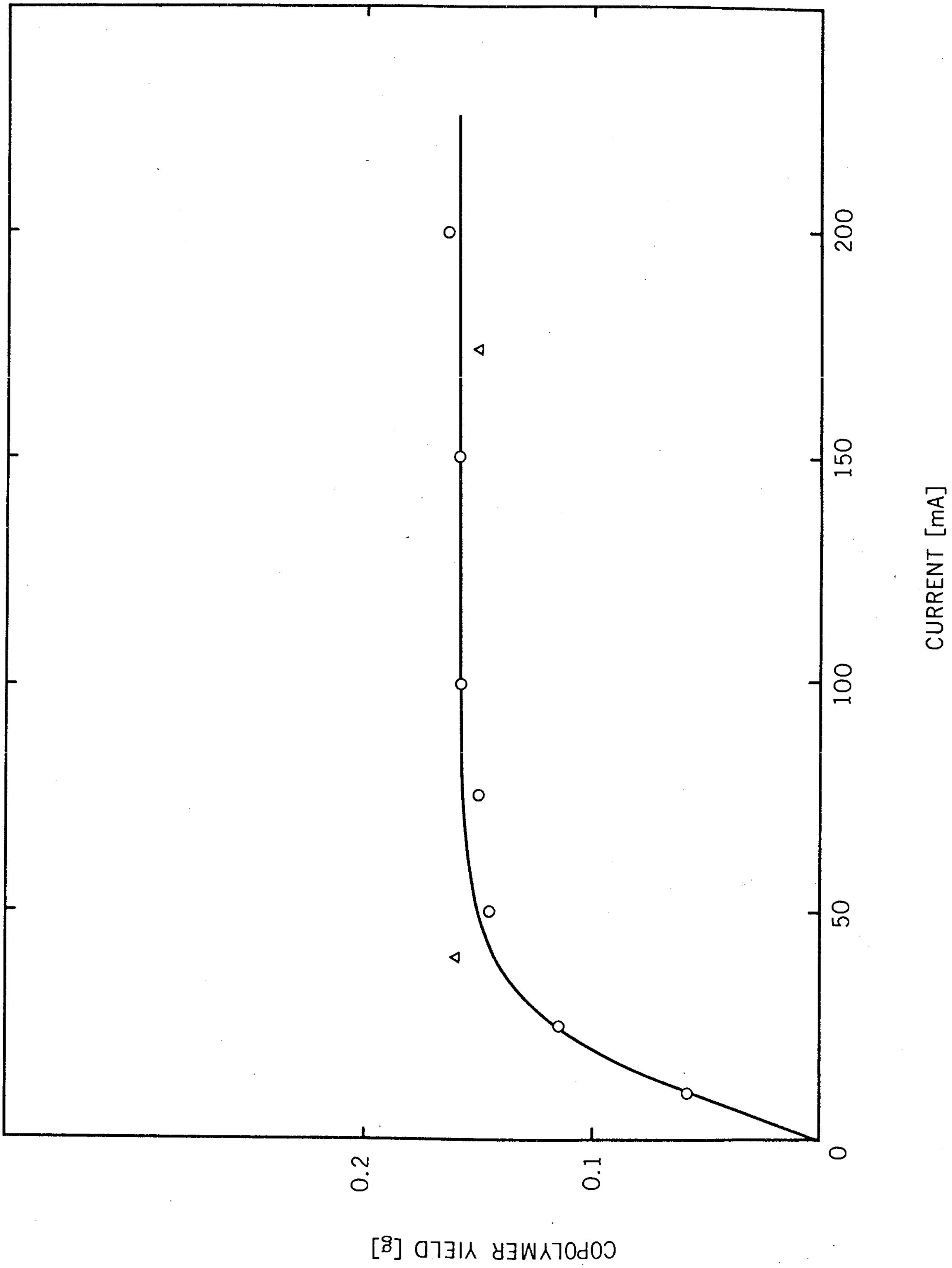
Generally, the observation of a rate determining step in a reaction indicates the presence of two or more descrete reaction steps. In the case of polymerization it suggests that the individual monomers are not the entities undergoing the polymerization process. According to the theories of conventional free radical and ionic chain polymerizations, the rate of polymerization always increases with the rate of initiation (to various powers). However, when the polymerizing entity is formed "in situ", then the rate of production of this complex monomer may limit the rate of polymerization. With reference to the system studied, the limited rate of polymerization justifies the introduction of pre-equilibria into the reaction scheme of donor-acceptor complex polymerization.

Figure 32. COPOLYMER YIELD AS A FUNCTION OF APPLIED CURRENT.

(o) Electrode surface area 6.4 cm^2.

(Δ) Electrode surface area 3.6 cm^2.

Conditions: 3.00 g $ZnCl_2$, 24.0 g AN, 1.7 g BD,
45°C, 30 minutes.


COPOLYMER YIELD [g]
0.2
0.1
0
50
100
150
200
CURRENT [mA]

III.2.5. APPLICATION OF THE KINETICS. DETERMINATION OF ZINC CHLORIDE DISTRIBUTION AND EVALUATION OF KINETIC PARAMETERS IN THE STYRENE-ACRYLONITRILE- $ZnCl_2$ IN DICHLOROETHANE SYSTEM.

Purpose.

It was shown earlier in this work that an experimental curve described by equation (37) could be analysed to find constants E, F and C_2. The simultaneous solution of equations (38), (39) and (31) yields kinetic parameters k_pR, m and k_r. (See chapter "Outline of Methods of Extracting Kinetic Parameters from Experimental Data").

An alternate method of determining k_pR and k_r employs the following equation (derived in chapter III.2.2.) with C_1 and C_2 given by equations (30) and (31).

$$[P_mZ] = \frac{C_1}{C_2}(1 - \exp(-C_2t)) \qquad (29)$$

The first method requires the following of polymer yield as a function of time. The alternate method requires the determination of the distribution of the complexing salt between the polymer and the solution as a function of time. The independent evaluations of the kinetic constants by both methods, and the comparison of the values obtained could support or disprove the overall reaction scheme proposed and used as a basis for the kinetics.

Results.

It was established by elemental analysis and NMR that the product at the highest conversion studied (14% of the least monomer) was an alternating copolymer. When the copolymer composition calculated for conventional free radical polymerization was 35% AN the actual product contained 47% AN. The NMR spectrum of the copolymer is shown in Figure 33. It indicates the alternating structure of the product (cf. Figs. 10 and 11).

Figure 33. NMR SPECTRUM OF THE PRODUCT.

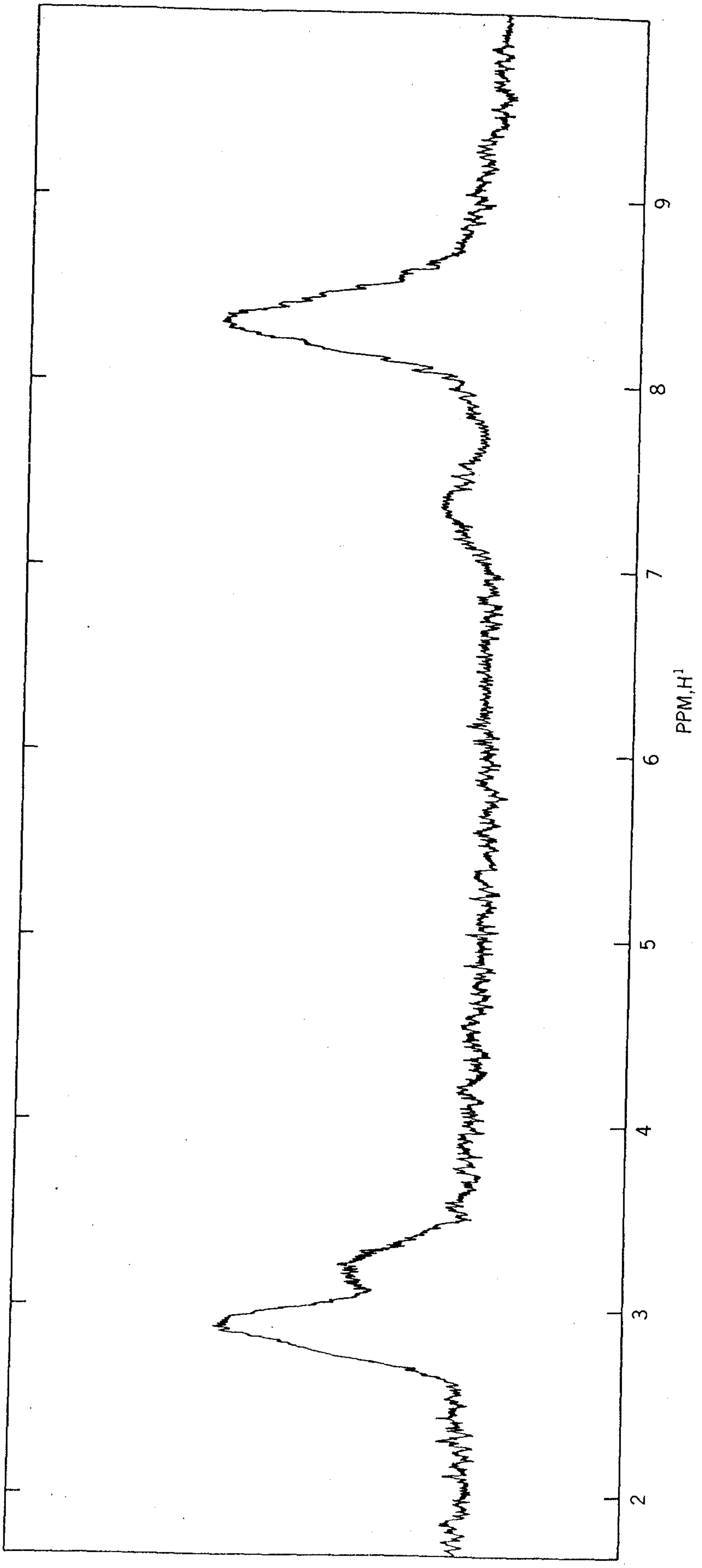

2
3
4
5
6
7
8
9
PPM,H1

Figure 34. $[P_mZ]$ AND $[P_t]$ AS FUNCTIONS OF TIME.

Conditions: $ZnCl_2$ (7.74×10^{-2} mole/l),
STY (1.21 mole/l), AN (1.18 mole/l),
DCE (35.5 g), 60°C.

The solid lines were calculated from the experimental points.

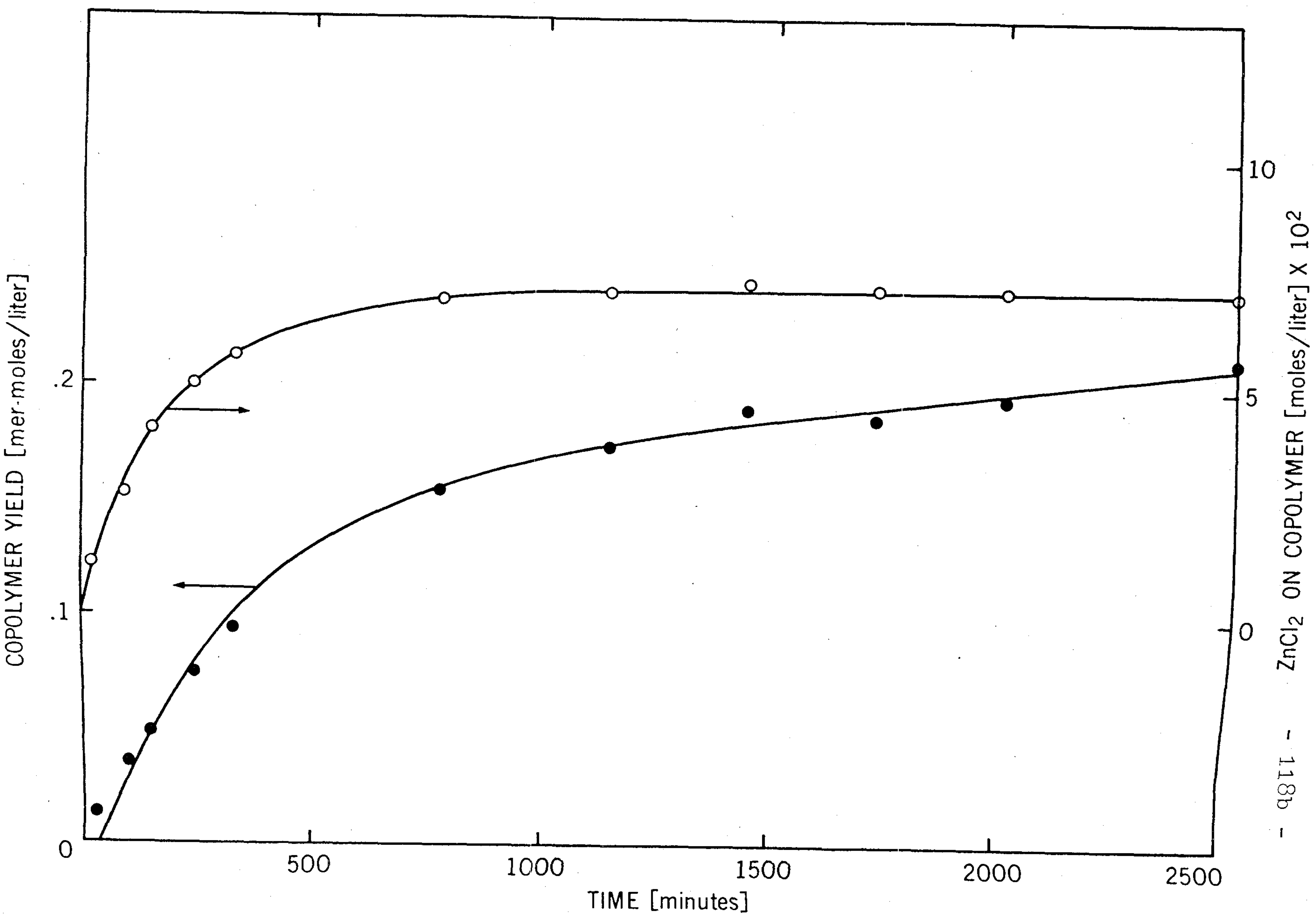

COPOLYMER YIELD [mer-moles/liter]
0
.1
.2
TIME [minutes]
500
1000
1500
2000
2500
$ZnCl_2$ ON COPOLYMER [moles/liter] X 10^2
0
5
10

Figure 34 shows the copolymer yield and the amount of zinc chloride associated with the copolymer as functions of time. (The solid lines were calculated from the experimental points using equations (37) and (29)).

As predicted by the reaction scheme, the rate of polymerization becomes constant when the amount of zinc chloride associated with the copolymer attains a constant value. This value is 7.1×10^{-2}mole/l, slightly below the total zinc chloride concentration, 7.74×10^{-2}mole/l.

From equation (29) it is clear that C_1/C_2 may be determined from the limiting concentration of the zinc chloride associated with the copolymer. One of the constants, C_2, may be determined from a plot of $\log(1-(C_2/C_1)[P_mZ])$ versus time for the non-linear initial portion of the curve. Knowing C_1 and C_2, the constants k_pR and k_r can be evaluated.

The values of the constants as determined from the "Copolymer yield" curve and from the "$ZnCl_2$ on copolymer" curve, are as follows. (The calculation and interpretation of the uncertainties are explained in Appendix III).

From the "Copolymer yield" curve :

$E = 2.3\times10^{-5}$mole/l min

$F = 1.73\times10^{-1}$mole/l

$C_2 = 3.3\times10^{-3}\text{min}^{-1}$

$k_pR = (3.1 \pm 0.8)\times10^{-3}\text{min}^{-1}$ (The limit of error 5.2×10^{-3})

$m = (2.4 \pm 1.3)$ (The limit of error 10)

$k_r = (1 \pm 14)\times10^{-4}\text{min}^{-1}$ (The limit of error 63×10^{-4})

From the "$ZnCl_2$ on copolymer" curve :

$C_1 = 3.6\times10^{-4}$mole/l min

$C_2 = 5.1\times10^{-3}\text{min}^{-1}$

$k_pR = (4.6 \pm 0.1)\times10^{-3}\text{min}^{-1}$ (The limit of error 0.7×10^{-3})

$k_r = (4.5 \pm 1.4)\mathrm{x}10^{-4}\mathrm{min}^{-1}$ (The limit of error $12\mathrm{x}10^{-4}$)

The huge uncertainty in the value of k_r determined from the "Copolymer yield" curve prevents a realistic comparison of the figures for the constants of regeneration of zinc chloride. On the other hand, the errors associated with k_pR allow a reasonable comparison of the two values. The proximity of the result obtained from the "Copolymer yield" curve to that obtained from the "$ZnCl_2$ on copolymer" curve indicates the validity of the overall reaction scheme.

When the uncertainties calculated in both methods of determination of the kinetic parameters are compared, the second method based on the distribution of zinc chloride appears to be far more precise. (This is a consequence of the smaller number of mathematical operations leading from experimental data to the kinetic parameters). Therefore, the determination of the distribution of the complexing agent is an alternate route to the evaluation of k_pR and k_r.

Conclusion.

The two approaches to the evaluation of the kinetic parameter k_pR provided reasonable results and lend some support to the overall reaction scheme proposed. There is strong evidence for the regeneration of the complexing salt from the polymer in the time dependence of the distribution of the salt between the polymer and solution. The concentration of the zinc chloride associated with the copolymer follows from equation (29). As time increases the exponential term becomes less significant and the equation approaches

$$[P_mZ] = C_1/C_2 = \text{constant}$$

A constant concentration of salt associated with the copolymer indicates a constant concentration of salt in solution available for complexation and subsequent polymerization. The time correspondence of the attainment of a constant amount of the zinc chloride associated with the copolymer, and a constant rate of polymerization is an indication that the regeneration step is indeed the process responsible for the constant rate of polymerization attained after the initial stage of reaction. The analytical data probably represent the first direct proof of the regeneration of the complexing agent.

III.2.6. APPLICATION OF THE KINETICS. EVALUATION OF KINETIC PARAMETERS FOR THE BUTADIENE-ACRYLONITRILE-$ZnCl_2$ IN DICHLOROETHANE SYSTEM.

Purpose.

The purpose of this work was to investigate the spontaneous or thermal polymerization of the system defined above in the absence of any additional source of free radicals, and to evaluate kinetic parameters over a range of temperatures.

Results.

Polymerizations were carried out at 35°, 45° and 60°C. Below 35°C the reaction rate was inconveniently low; above 60°C the copolymer produced is not strictly alternating.

The reaction profiles of the polymerizations are shown in Figure 35. (The solid lines have been calculated from the experimental points using equation (37)). The features common to these curves are an initially steep region, corresponding to a fast reaction, and a subsequent linear portion of much smaller slope. The latter corresponds to a stage in which the rate of polymerization is restricted by the rate of regeneration of zinc chloride. The 35°C curve corresponds to a non-steady state of "monomer" concentration. This case has been predicted and analysed (see chapter III.2.3.) and it has been found that the curve can be used to evaluate kinetic parameters.

The numerical results are summarized in Table XIV. Only the experimental points, and not the calculated curves, have been used in the calculations.

Figure 35. COPOLYMER YIELD AS A FUNCTION OF TIME AT VARIOUS TEMPERATURES.

Curve	1	35°C
	2	45°C
	3	60°C

Conditions: $ZnCl_2$ (1.47×10^{-3} moles),
AN (75.4×10^{-3} moles),
BD (33.5×10^{-3} moles), DCE (37.0 g).

The solid lines were calculated from the experimental points.

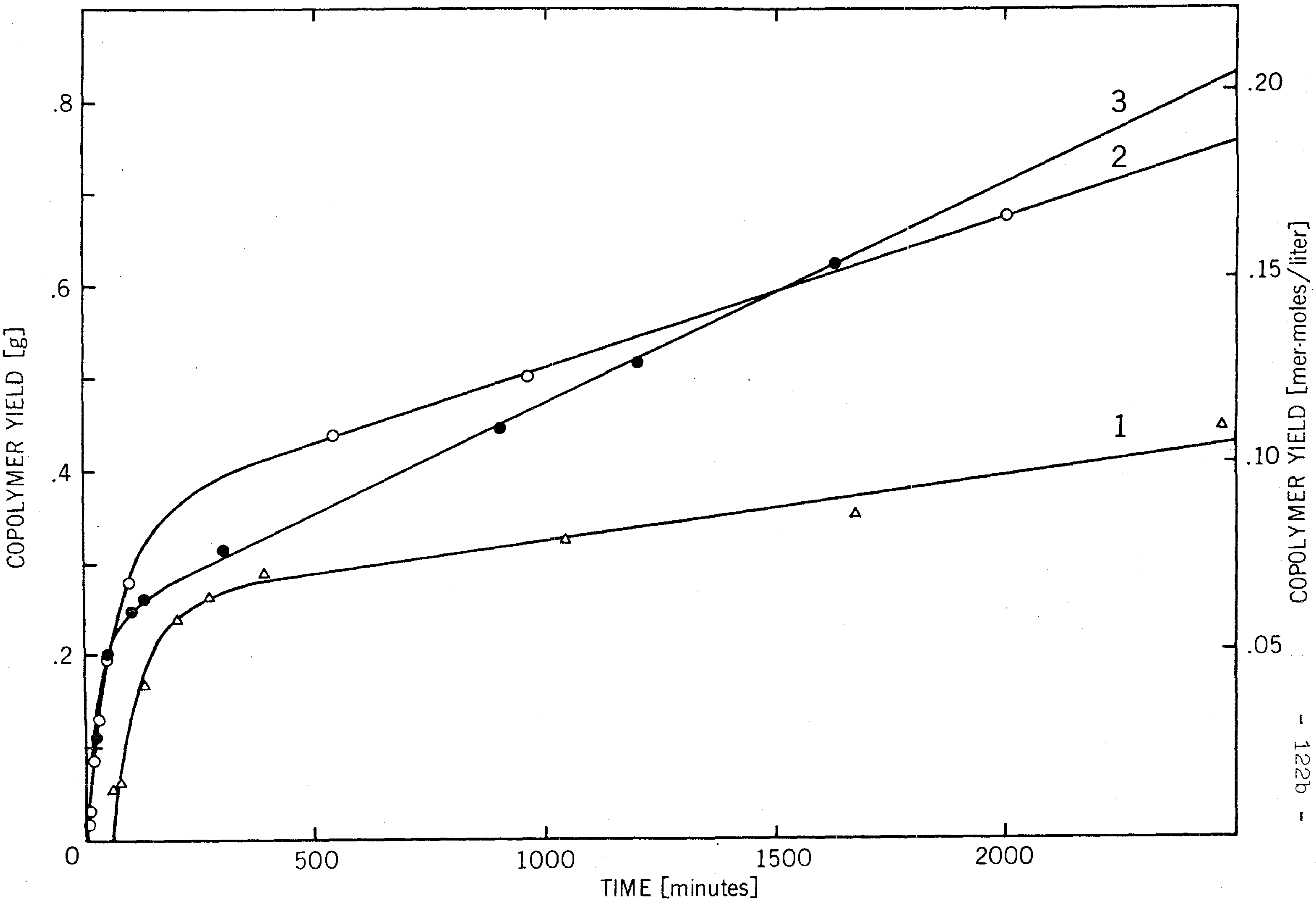

COPOLYMER YIELD [g]
.2
.4
.6
.8
0
500
1000
1500
2000
TIME [minutes]
COPOLYMER YIELD [mer-moles/liter]
.05
.10
.15
.20
1
2
3

Table XIV. Kinetic Parameters at Various Temperatures.

	Temperature (°C)		
	35	45	60
E (mole/l min)x10^5	1.8	4.0	5.6
F (mole/l)x10^1	1.66	0.88	0.48
C_2 (min^{-1})x10^2	1.7	1.5	2.3
k_pR (min^{-1})x10^2	1.7±0.5	1.4±0.4	2.2±0.7
m	4.3±3.0	2.4±1.7	1.4±1.0
k_r (min^{-1})x10^4	1±12	4±46	10±120

In order to be able to judge the reliability of the figures in Table XIV the uncertainties in k_pR, m and k_r were evaluated in a form of the probable errors (see Appendix III). The error analysis indicates an acceptable reliability for k_pR and perhaps m. However, the error in k_r is unduly great. In order to have obtained a reasonable value for k_r the difference (C_2-k_pR) should not have been smaller than the errors in these quantities. This was not the case.

Conclusion.

The kinetic treatment adopted was used to accomodate the experimental data within the framework of the rate constants and equilibria assigned to the polymerization. The data have been analysed to yield parameter m, the complex rate constant k_pR, and the regeneration constant k_r.

The stoichiometric factor m increases with decreasing temperature. The value 4 corresponds to octahedral coordination of the zinc cation with two Cl^- and four AN ligands in the complex (90). At a high temperature m approaches the limiting value 1.

The product k_pR does not show a distinct temperature dependence. However, both k_p and R are complex constants and the temperature effect may be cancelled, or reduced enough to be cancelled within the experimental error.

The regeneration constants k_r were evaluated, but the experimental uncertainty met under the conditions employed was too large for useful quantitative assesment of the regeneration rate for the system studied.

IV. SUMMARY AND DISCUSSION.

In general, polymerizations involving donor-acceptor complexes may be described by the following scheme.

Acceptor monomer (A) + Donor monomer (D) $\rightleftarrows$
Donor-Acceptor complex (AD) $\rightarrow$ Polymeric product

If the donor-acceptor pair does not spontaneously form such an AD complex, then the formation of the latter may be "catalyzed" by the addition of a Lewis acid to the monomer pair. In this case, the acceptor monomer forms an adduct with the Lewis acid as follows.

Lewis acid (Z) + A $\rightleftarrows$ ZA

The adduct ZA may be an entity of sufficient electropositivity to attract a donor monomer and form the donor-acceptor complex. As a consequence of the reaction mechanism, the resulting product is always an alternating copolymer.

In this work, the acrylonitrile-butadiene zinc chloride system was employed to study this type of polymerization. From the ability of related systems to produce polymeric product, and elemental and spectral analyses, it was determined that the product of acrylonitrile-butadiene-$ZnCl_2$ system was a pure alternating copolymer. Various reaction conditions and means of initiation had no effect on the product composition. In this manner it was demonstrated that this system may be used as a representative for detailed studies of donor-acceptor complex polymerization. The effect of monomer concentration on the rate of the reaction indicates that polymerization proceeds via molecular complexes. The rate of polymerization was found to be greatest at the maximum complex concentration.

The rate of copolymer formation was found to be remarkably increased by the addition of chlorinated aliphatic hydrocarbons. Although no simple explanation of the effect was found, the change of the polarity of the reaction medium was definitely excluded as a factor responsible for the rate acceleration. As far as the butadiene-acrylonitrile-$ZnCl_2$ system is concerned, the chloroderivatives of aliphatic hydrocarbons seem to be specific in this matter. Polymerization induced by a solvent was reported (46) for the styrene-maleic anhydride system; only solvents with a labile hydrogen (p-cymene, cumene) induced the formation of the alternating copolymer. It was suggested that the polymerization was "initiated" by the abstraction of hydrogen from the α-position of cumene by the charge transfer complex of styrene and maleic anhydride. This view is in accord with the accelerating effect of the dichloroethane. The negative inductive effect (electron-withdrawing) of the chlorine activates the hydrogen atoms and the proton is readily extracted. On the other hand, benzene is ineffective. In the case of chlorobenzene, the negative inductive effect of the chlorine atom is opposed by the positive mesomeric effect (electron-supplying), the net electron-withdrawing effect being much less than in a molecule of the dichloroethane. Thus, the aromatic chloroderivative is also ineffective.

When the butadiene-acrylonitrile-$ZnCl_2$ system with a low concentration of zinc chloride and an excess of the monomers is polymerized, the reaction profile is characterized by a two-region curve; the initially high rate decreases and is invariant in the second region. Such a curve can be described by a kinetic equation which relates the copolymer yield to time. The derivation of this equation has been a main theoretical achievement of this work. It was based on the following scheme.

$$Z + mA \overset{K_o}{\rightleftharpoons} ZA_m \underset{k_{-1}}{\overset{+mD\quad k_1}{\rightleftharpoons}} Z(AD)_m \xrightarrow{k_p} P_mZ \xrightarrow{k_r} mP + \underset{\text{recycled}}{\underset{\downarrow}{Z}}$$

The initially formed complex between the acceptor monomer and the complexing agent reacts further with the donor monomer to yield a donor-acceptor complex. This is the entity which undergoes polymerization. The complexing agent is regenerated from the polymer and participates in a new reaction cycle.

The final kinetic equation describing the polymer formation in the presence of an excess of the monomers and first order consumption of the complex was found to be

$$[P_t] = Et + F(1 - \exp(-C_2t))$$

where E, F and C_2 are complex constants. At high t the exponential term is negligible and the expression becomes an equation of a straight line.

Because the kinetic equation was derived under certain assumptions (the steady state of the complex concentration, and the constancy of the concentration of the monomers throughout the polymerization) it was necessary to test its validity under various conditions. This was done by comparying the approximate equation with the exact solution found by means of the Runge-Kutta numerical method. A good agreement between the approximate and exact methods was found over a reasonable conversion.The kinetic equations derived for the low concentration of either monomer,

$$[P_t] = [D]_o(1 - \exp(-C_4t)) \qquad (\text{low } [D])$$

$$[P_t] = [A]_o(1 - \exp(-C_6t)) \qquad (\text{low } [A])$$

where C_4 and C_6 are complex constants, bear the disadvantage of being valid only for $m = 1$. Fortunately, these concentration conditions are of little, if any, importance with respect to the solubility problems, high rate of polymerization, viscosity of solution, etc., which may be met when the complexing salt is in an excess over a monomer. The most practical and most frequently used conditions are those with a low concentration of the complexing agent. For this case (Case I) the kinetics has been derived for all m. Also, a polymerization curve of such a system can always be analysed to yield the kinetic parameters irrespective of relative values of the rate constants of the single reaction steps, either satisfying or not satisfying the presupposed steady state concentration of the complex.

The equations relating the polymer yield to time were derived for zero and first order reactions only. A zero order reaction was eliminated by the observation of a non-linear dependence of $[P_t]$ on time. It is feasible to envisage reaction schemes which lead to the first order consumption of $Z(AD)_m$. The latest approach to the charge transfer complex polymerization conceives the initiation step as the activation of a complex from the ground state to an excited state with a high contribution from the ionic structure $^{-}AD^{+}$. The latter may initiate a chain addition reaction leading to a copolymer. In the presence of an organic peroxide or an azo compound, the initiation has been postulated to be an energy transfer from the excited species generated in the decomposition of the organic compounds (116-119) to a charge transfer complex (114, 115). The principal processes can be described as follows.

Thermal or photochemical initiation :

$$Z(AD)_m \xrightarrow{k_a} Z(AD)_m^* \qquad (89)$$

$$R_i = k_a[Z(AD)_m] \qquad (90)$$

Initiation by an organic compound :

$$I \xrightarrow{k_d} R^* \qquad (91)$$

$$R^* + Z(AD)_m \xrightarrow{k_i'} R + Z(AD)_m^* \qquad (92)$$

If reaction (91) is the rate determining step in the initiation process, the rate of initiation is

$$R_i = k_i[I] \qquad (93)$$

where $k_i = k_d f$, f being an efficiency factor.

If reaction (92) is the rate determining step in the initiation process, the rate of initiation is

$$R_i = k_i[Z(AD)_m][I] \qquad (94)$$

where $k_i = k_i^{!}f$.

The propagation step is the reaction of an activated chain-end with a monomer.

$$Z(AD)_m^* + Z(AD)_m \xrightarrow{k_{pr}} Z(AD)_m^* \qquad (95)$$

$$R_{pr} = k_{pr}[Z(AD)_m^*][Z(AD)_m] \qquad (96)$$

The termination can proceed by several means. The hydrogen transfer mechanism (44) suggests monomolecular termination, bimolecular termination by polymer-polymer interaction, or bimolecular termination by polymer-complex interaction. They may be expressed schematically as follows.

$$Z(AD)_m^* \xrightarrow{k_{t1}} Z(AD)_m \qquad (97)$$

$$R_{t1} = k_{t1}[Z(AD)_m^*] \qquad (98)$$

$$Z(AD)_m^* + Z(AD)_m^* \xrightarrow{k_{t2}} Z(AD)_m \qquad (99)$$

$$R_{t2} = k_{t2}[Z(AD)_m^*]^2 \qquad (100)$$

$$Z(AD)_m^* + Z(AD)_m \xrightarrow{k_{t3}} Z(AD)_m \qquad (101)$$

$$R_{t3} = k_{t3}[Z(AD)_m^*][Z(AD)_m] \qquad (102)$$

From the steady state approximation it follows that $R_i = R_t$ and therefore

$$[Z(AD)_m^*] = \left(\frac{R_i}{k_t[Z(AD)_m]^{\beta}}\right)^{1/\alpha} \qquad (103)$$

where α and β are reaction orders with respect to $Z(AD)_m^*$ and $Z(AD)_m$, respectively, in the termination reaction.

The rate of polymerization can be written as

$$R_p \simeq mR_{pr} = m\,k_{pr}\left(\frac{R_i}{k_t[Z(AD)_m]^{\beta}}\right)^{1/\alpha}[Z(AD)_m] \tag{104}$$

The following combinations of the initiation, propagation and termination steps lead to a first order reaction with respect to complex $Z(AD)_m$.

(a) Initiation (90), propagation (96), termination (102).

$$R_p = m\,\frac{k_{pr}k_a}{k_{t3}}[Z(AD)_m] = mk_p[Z(AD)_m] \tag{105}$$

(b) Initiation (93), propagation (96), termination (100).

$$R_p = mk_{pr}\left(\frac{k_i[I]}{k_{t2}}\right)^{1/2}[Z(AD)_m] = mk_p[Z(AD)_m] \tag{106}$$

(c) Initiation (94), propagation (96), termination (102).

$$R_p = mk_{pr}\frac{k_i[I]}{k_{t3}}[Z(AD)_m] = mk_p[Z(AD)_m] \tag{107}$$

(d) Initiation (93), propagation (96), termination (98).

$$R_p = mk_{pr}\frac{k_i[I]}{k_{t1}}[Z(AD)_m] = mk_p[Z(AD)_m] \tag{108}$$

In other words, when the reaction orders of $Z(AD)_m$ in the initiation and termination steps are the same the overall reaction order with respect to the complex is unity.

To confirm or at least support the reaction scheme employing the pre-equilibria , polymerization of the complex and the regeneration of the complexing agent, two parameters involved in the scheme were followed independently: the concentrations of the final product P_t and the intermediate P_mZ. The time functions of these are described by different equations which offer two independent methods for the evaluation of kinetic parameters. A comparison of the magnitudes of k_pR yielded an accord indicating the validity of the kinetic scheme employed in the derivation of the time functions.

A proof of the regeneration step in the scheme has emerged from the observed limiting value of the zinc chloride associated with the polymer. This is apparently the first experimental demonstration of the regeneration of the complexing agent in a donor-acceptor complex polymerization.

The observed plateau on the curve Rate/Current is also in agreement with the theoretical prediction which followed from the kinetics. It was derived that a limiting rate of polymerization should be achieved when the apparent rate constant k_p is large. Because k_p is a complex constant reflecting the initiation, propagation and termination steps, a variation of the current was used to alter k_p. The existence of a rate determining step is general for two- and many-step schemes. When a product is an alternating copolymer it confirms that it was produced by a homopolymerization of a complex between the two monomers formed prior to the polymerization. In other words, the observation of a limiting rate of polymerization justifies the employment of the pre-equilibria, characterized by K_0 and K_1 . Thus, while the distribution of zinc chloride in the polymerization system confirmed the part of the scheme subsequent to the polymerization step, the limit in the rate of polymerization confirmed the part of the scheme preceeding the polymerization step. Therefore, with the exception of the reaction order in the complex polymerization, the whole proposition including the prior formation of "monomer" in the pre-equilibria, polymerization of the "monomer", and the salt regeneration after the "monomer" is polymerized, has been supported experimentally.

APPENDIX I

Systems Reported to Yield Alternating Copolymers.

(The polymerizations were initiated by radical initiators, UV irradiation, electrochemically or thermally).

Donor	Acceptor	Compl. agent	Refr.
1,3-butadiene	acrylonitrile	ethylaluminum sesquichloride	38,54
		$ZnCl_2$	38,54,55
		$AlEtCl_2/VOCl_3$	94,95
		$ZnCl_2/VOCl_3$	74
		$SnCl_4/VOCl_3$	74
		$AlCl_3/VOCl_3$	74
	ethyl methacrylate	ethylaluminum sesquichloride	69
		ethylaluminum sesquibromide	69
		iso-butylaluminum sesquibromide	69
	maleic anhydride	-	131,137
	methyl methacrylate	$AlEt_2Cl$	69
		ethylaluminum sesquichloride	69
		$AlEtCl_2$	69
		$AlEtCl_2/VOCl_3$	96
n-butyl vinyl ether	maleic anhydride	-	27
i-butyl vinyl ether		-	27
t-butyl vinyl ether		-	27
cyclopentene	acrylonitrile	ethylaluminum sesquichloride	47
	methyl acrylate		47
p-dioxene	maleic anhydride	-	24
divinyl ether	Cl-maleic anhydride	-	29

Donor	Acceptor	Compl. agent	Refr.
ethyl vinyl ether	chlorotrifluoroethylene	-	41
ethylene	methyl acrylate	ethylaluminum sesquichloride	39
furan	maleic anhydride	-	26
indene	methyl acrylate	ethylaluminum sesquichloride	135
	methyl methacrylate		135
isoprene	acrylonitrile		38,54
		$ZnCl_2$	34,38,54,55
	ethyl methacrylate	ethylaluminum sesquichloride	69
		ethylaluminum sesquibromide	69
	methyl methacrylate	$ZnCl_2$	35
5-methylene bicyclo (2,2,1)-2-heptene	maleic anhydride	-	36
α-methyl styrene	acrylonitrile	ethylaluminum sesquichloride	59,60,66
	β-cyanoacrolein	-	25
	methacrylonitrile	ethylaluminum sesquichloride	57,60
β-i-propenyl naphthalene	maleic anhydride	-	132
propylene	acrylonitrile	$AlEtCl_2$	39,58
		ethylaluminum sesquichloride	58
		ethylaluminum sesquibromide	58
	methyl acrylate	$AlEtCl_2$	39
	methyl vinyl ketone		77
		$AlMeCl_2$	77
styrene	acrylonitrile	ethylaluminum sesquichloride	39,57,62 65,66
		$AlEt_3$	78
		$ZnCl_2$	34,43,51-53

Donor	Acceptor	Compl. agent	Refr.
styrene	acrylonitrile	$ZnBr_2$	71,73
		$MgCl_2.6H_2O$	34
		$NiCl_2.6H_2O$	34
	α-Cl acrylonitrile	ethylaluminum sesquichloride	57,70
		$ZnCl_2$	57
	α -cyanomethyl acrolein		40
	methacrolein		56
	methyl acrylate	ethylaluminum sesquichloride	39
	methacrylonitrile		60
	methyl methacrylate	$AlEt_3$	78
		ethylaluminum sesquichloride	39,42,45 57,63,67 68,133
		$ZnCl_2$	52
		$ZnBr_2$	72
vinyl chloride	acrylonitrile	$AlEtCl_2$	61,75,76
		ethylaluminum sesquichloride	61
		$AlEt_2Cl$	61
	methyl methacrylate	$AlEtCl_2/VOCl_3$	93,134
vinylidene chloride	acrylonitrile	ethylaluminum sesquichloride	64
		$AlEtCl_2$	64

APPENDIX II

Solutions of Some Integrals.

(1)

$$\frac{dy}{dx} = a - by$$

$$\int \frac{dy}{a - by} = \int dx$$

$$y = \frac{a}{b}(1 - \exp(-bx))$$

(2)

$$dy = a dx + b \exp(-cx) dx$$

$$\int dy = a\int dx + b\int \exp(-cx) dx$$

$$y = ax + \frac{b}{c}(1 - \exp(-cx))$$

APPENDIX III

Error Calculations.

Outline of the Calculations.

The error calculations were performed according to the pattern set by Shoemaker and Garland in "Experiments in Physical Chemistry", McGraw-Hill Book Comp., New York, 1967, p. 30-35.

Two kinds of uncertainties were calculated.

(1) The limit of error, $\lambda(F)$, by the propagation-of-error treatment, which determines a maximum possible error in a quantity, and is given by

$$\lambda(F) = \left|\frac{\delta F}{\delta x_1}\right|\lambda(x_1) + \left|\frac{\delta F}{\delta x_2}\right|\lambda(x_2) + \ldots \left|\frac{\delta F}{\delta x_n}\right|\lambda(x_n) \qquad \text{(A1)}$$

(2) The probable error, Q, defined as a quantity with such a value that the probability that the magnitude of an error will be less than Q is equal to the probability that it will exceed Q, was calculated using the relationship

$$Q = \lambda/3.8 \qquad \text{(A2)}$$

For this purpose, the limit of error, λ, was calculated by a treatment which takes into consideration the probability that when several variables are involved the errors may cancel one another.

$$\lambda(F) = \{(\frac{\delta F}{\delta x_1})^2[\lambda(x_1)]^2+(\frac{\delta F}{\delta x_2})^2[\lambda(x_2)]^2+..(\frac{\delta F}{\delta x_n})^2[\lambda(x_n)]^2\}^{1/2} \qquad \text{(A3)}$$

When a graphical method of determining the limit of error was employed, it was based on the drawing of a rectangle with width $2\lambda(x_i)$ and height $2\lambda(y_i)$ around each experimental point (x_i,y_i). The error in measuring the reaction time t was negligible and accordingly treated as zero. The limit of error in the polymer yield was estimated from the polymerization experiments carried out under identical conditions, which yielded: 1.481 g, 1.497 g and 1.422 g. From these the standard error (or estimated standard deviation) was calculated and found to be 2.6% . Although three points are too few to calculate the standard error, this value was accepted as it is in agreement with the usual uncertainties in polymerization experiments.

The limits of error in slope E and intercept F' of the polymerization curves were determined graphically. From $\lambda(E)$ and $\lambda(F')$, the error limit in the extrapolated yield P_{ex} was determined according to equation (A1) and

$$[P_{ex}] = Et + F'$$

$$\lambda([P_{ex}]) = t\,\lambda(E) + \lambda(F') \qquad (A4)$$

The limit of error in the $([P_{ex}] - [P_t])$ term is

$$\lambda([P_{ex}] - [P_t]) = \lambda([P_{ex}]) + \lambda([P_t]) \qquad (A5)$$

The maximum error in $\log([P_{ex}] - [P_t])$ is given by

$$\lambda(\log([P_{ex}] - [P_t])) = \frac{\lambda([P_{ex}] - [P_t])}{[P_{ex}] - [P_t]} \qquad (A6)$$

By plotting $\log([P_{ex}] - [P_t])$ versus time, the limits of errors in parameters F and C_2 were determined graphically. The uncertainty in the slope provides the uncertainty in constant C_2. The uncertainty in the intercept yields the uncertainty in logF. The latter was subsequently used in

$$\lambda(F) = F\,\lambda(\log F) \qquad (A7)$$

From equations (74), (75) and (76), the total differentials were derived and transformed to the error limit expressions:

$$\lambda(k_pR) = \left(\frac{FC_2^3}{(E+FC_2)^2} + \frac{C_2^2}{E+FC_2} \right) \lambda(F) + \frac{FC_2^2}{(E+FC_2)^2} \lambda(E) + \\ + \left(\left(\frac{FC_2}{E+FC_2}\right)^2 + \frac{2FC_2}{E+FC_2} \right) \lambda(C_2) \qquad (A8)$$

$$\lambda(m) = \frac{C_2^2}{[Z]_o \, (k_pR)^2} \lambda(F) + \frac{2C_2F}{[Z]_o \, (k_pR)^2} \lambda(C_2) + \\ + \frac{FC_2^2}{[Z]_o^2 \, (k_pR)^2} \lambda([Z]_o) + \frac{2FC_2^2}{[Z]_o \, (k_pR)^3} \lambda(k_pR) \qquad (A9)$$

$$\lambda(k_r) = \lambda(C_2) + \lambda(k_pR) \qquad (A10)$$

When the kinetic parameters were evaluated from a "$ZnCl_2$ on copolymer versus time" curve, the limits of errors were calculated in the following manner. The last five points on the corresponding curve in Figure 34 (supposedly lying on a plateau) were used to determine the maximum possible error in the "$ZnCl_2$ on copolymer" values. It is

$$\lambda([P_mZ]) = 2x10^{-3}\text{mole/l} = 2.8\%$$

This is also the limit of error of C_1/C_2, as follows from equation (29).

$$\lambda(C_1/C_2) = 2x10^{-3}\text{mole/l} = 2.8\%$$

Also from equation (29), the error limit in constant C_2 is

$$\lambda(C_2) = \frac{[P_mZ]}{t(1 - \frac{C_2}{C_1} [P_mZ])} \lambda(C_2/C_1) + \frac{C_2/C_1}{t(1 - \frac{C_2}{C_1} [P_mZ])} \lambda([P_mZ]) \qquad (A11)$$

Since $C_1 = (C_1/C_2)C_2$, the limit of error in constant C_1 is given by

$$\lambda(C_1) = C_2\ \lambda(C_1/C_2) + \lambda(C_2)C_1/C_2 \qquad (A12)$$

For $k_pR = C_1/[Z]o$, the limit of error is

$$\lambda(k_pR) = \frac{1}{[Z]o}\lambda(C_1) + \frac{C_1}{[Z]_o^2}\lambda([Z]o) \qquad (A13)$$

For $k_r = C_2 - k_pR$, the error limit was calculated from

$$\lambda(k_r) = \lambda(C_2) + \lambda(k_pR) \qquad (A14)$$

Calculations for Chapter III.2.5.

The uncertainties in the component quantities were:

$\lambda(ZnCl_2) = \pm\ 0.005$ g
$\lambda(AN) = \pm\ 0.2$ ml
$\lambda(STY) = \pm\ 0.2$ ml
$\lambda(DCE) = \pm\ 0.5$ ml

These gave $\lambda([Z]o) = 2.1\text{x}10^{-3}$mole/l

The graphical method yielded

$\lambda(E) = 4\text{x}10^{-6}$mole/l min
$\lambda(F') = 1.5\text{x}10^{-2}$mole/l

Consiquently,

$\lambda([P_{ex}]) = 16.6\text{x}10^{-3}$mole/l (for t = 400 min)
$\lambda([P_{ex}] - [P_t]) = 19.4\text{x}10^{-3}$mole/l (for t = 400 min)
$\lambda(\log([P_{ex}]-[P_t])) = 0.36$ (for t = 400 min)
$= 12\%$ (for any t)
$\lambda(C_2) = 1.08\text{x}10^{-3}\text{min}^{-1}$
$\lambda(F) = 6.0\text{x}10^{-2}$mole/l

The following values were used to calculate $\lambda(k_pR)$, $\lambda(m)$ and $\lambda(k_r)$.

E $= 2.321\text{x}10^{-5}$mole/l min
F $= 1.727\text{x}10^{-1}$mole/l

$C_2 = 3.266\times10^{-3}\text{min}^{-1}$
$[Z]_o = 7.74\times10^{-2}\text{mole/l}$
$\lambda(E) = 4\times10^{-6}\text{mole/l min}$
$\lambda(F) = 6.0\times10^{-2}\text{mole/l}$
$\lambda(C_2) = 1.08\times10^{-3}\text{min}^{-1}$
$\lambda([Z]_o) = 2.1\times10^{-3}\text{mole/l}$

$$\lambda(k_pR) = 3.563\times10^{-2} \times 6.0\times10^{-2} + 5.3 \times 4\times10^{-6} + 2.8447 \times 1.08\times10^{-3}$$
$$= \underline{5.2313\times10^{-3}\text{min}^{-1}}$$

$$\lambda(m) = 14 \times 6.0\times10^{-2} + 1481 \times 1.08\times10^{-3} + 31.26 \times 2.1\times10^{-3} + 1543 \times 5.2313\times10^{-3}$$
$$= \underline{10.5}$$

$$\lambda(k_r) = 1.08\times10^{-3} + 5.23\times10^{-3}$$
$$= \underline{6.31\times10^{-3}\text{min}^{-1}}$$

The probable errors, Q, were determined as follows. Equation (A3) was used instead of equation (A1) in all numerical calculations. The results obtained are:

$\lambda([P_{ex}]) = 15.1\times10^{-3}\text{mole/l}$ (for $t = 400$ min)
$\lambda([P_{ex}] - [P_t]) = 15.4\times10^{-3}\text{mole/l}$ (for $t = 400$ min)
$\lambda(\log([P_{ex}] - [P_t])) = 0.28$ (for $t = 400$ min)
$= 9.6\%$ (for any t)
$\lambda(C_2) = 0.87\times10^{-3}\text{min}^{-1}$
$\lambda(F) = 4.8\times10^{-2}\text{mole/l}$

Now, with the new $\lambda(F)$ anf $\lambda(C_2)$, the following values were calculated for the limits of error.

$$\lambda(k_pR) = \{(3.563\times10^{-2})^2 (4.8\times10^{-2})^2 + 5.3^2(4\times10^{-6})^2 + 2.8447^2(8.7\times10^{-4})^2 \}^{1/2}$$
$$= 3.01\times10^{-3}\text{min}^{-1}$$

$$\lambda(m) = \{14^2(4.8\times10^{-2})^2 + 1481^2(8.7\times10^{-4})^2 + 31.26^2(2.1\times10^{-3})^2 + 1543^2(3.01\times10^{-3})^2 \}^{1/2}$$
$$= 4.8$$

$\lambda(k_r) = \{(1.08\text{x}10^{-3})^2 + (5.23\text{x}10^{-3})^2\}^{1/2}$
$= 5.3\text{x}10^{-3}\text{min}^{-1}$

Using equation (A2), the probable errors were calculated to be :

$Q(k_pR) = \underline{0.8\text{x}10^{-3}\text{min}^{-1}}$
$Q(m) = \underline{1.3}$
$Q(k_r) = \underline{1.4\text{x}10^{-3}\text{min}^{-1}}$

The limits of error in k_pR and k_r determined from the "$ZnCl_2$ on copolymer" curve were calculated using equations (A11) to (A14) and

$t = 200$ minutes
$[P_mZ] = 4.6\text{x}10^{-2}$mole/l
$[Z]_o = 7.74\text{x}10^{-2}$mole/l
$C_1 = 3.6\text{x}10^{-4}$mole/l min
$C_2/C_1 = 14.17$ l/mole
$C_2 = 5.1\text{x}10^{-3}\text{min}^{-1}$
$C_1/C_2 = 7.1\text{x}10^{-2}$mole/l
$\lambda([P_mZ]) = 1.28\text{x}10^{-3}$mole/l
$\lambda([Z]_o) = 2.1\text{x}10^{-3}$mole/l
$\lambda(C_2/C_1) = 3.97\text{x}10^{-1}$l/mole
$\lambda(C_1/C_2) = 2.0\text{x}10^{-3}$mole/l

Consequently,

$\lambda(C_2) = 6.60\text{x}10^{-4} \text{ x } 3.97\text{x}10^{-1} + 2.03\text{x}10^{-1} \text{ x } 1.28\text{x}10^{-3}$
$= 5.22\text{x}10^{-4}\text{min}^{-1}$

$\lambda(C_1) = 5.1\text{x}10^{-3} \text{ x } 2.0\text{x}10^{-3} + 7.1\text{x}10^{-2} \text{ x } 5.22\text{x}10^{-4}$
$= 4.73\text{x}10^{-5}$mole/l min

$\lambda(k_pR) = 12.92 \text{ x } 4.73\text{x}10^{-5} + 6.01\text{x}10^{-2} \text{ x } 2.1\text{x}10^{-3}$
$= \underline{7.373\text{x}10^{-4}\text{min}^{-1}}$

$\lambda(k_r) = 5.22\text{x}10^{-4} + 7.37\text{x}10^{-4}$
$= \underline{1.259\text{x}10^{-3}\text{min}^{-1}}$

The probable errors, Q, were determined using equations (A2) and (A3). The calculations yielded

$$\lambda(C_2) = \{(6.60\text{x}10^{-4})^2\ (3.97\text{x}10^{-1})^2 + (2.03\text{x}10^{-1})^2\ (1.28\text{x}10^{-3})^2\ \}^{1/2}$$
$$= 3.7\text{x}10^{-4}\text{min}^{-1}$$

$$\lambda(C_1) = \{(5.1\text{x}10^{-3})^2\ (2\text{x}10^{-3})^2 + (7.1\text{x}10^{-2})^2\ (3.7\text{x}10^{-4})^2\ \}^{1/2}$$
$$= 2.82\text{x}10^{-5}\text{mole/l min}$$

$$\lambda(k_pR) = \{12.92^2\ (2.82\text{x}10^{-5})^2 + (6.01\text{x}10^{-2})^2\ (2.1\text{x}10^{-3})^2\ \}^{1/2}$$
$$= 3.85\text{x}10^{-4}\text{min}^{-1}$$

$$\lambda(k_r) = \{(3.7\text{x}10^{-4})^2 + (3.85\text{x}10^{-4})^2\ \}^{1/2}$$
$$= 5.34\text{x}10^{-4}\text{min}^{-1}$$

$$Q(k_pR) = \underline{1.01\text{x}10^{-4}\text{min}^{-1}}$$
$$Q(k_r) = \underline{1.40\text{x}10^{-4}\text{min}^{-1}}$$

Calculations for Chapter III.2.6.

The curve for 45°C was selected as a representative of all the three curves. It was assumed that the limits of error, when expressed as percentages, were similar for all the three experimental series. This greatly reduced the calculations.

The uncertainties in the component quantities were:

$\lambda(ZnCl_2) = \pm\ 0.005$ g
$\lambda(AN) = \pm\ 0.2$ ml
$\lambda(BD) = \pm\ 1$ mm $= \pm\ 0.016$ g
$\lambda(DCE) = \pm\ 0.5$ ml

These values yielded $\lambda([Z]_o) = 1.66\text{x}10^{-3}\text{mole/l}$
The graphical method of determining the limits of error in the intercept and slope gave
$\lambda(E) = 2.5\text{x}10^{-6}\text{mole/l min}$
$\lambda(F') = 1.1\text{x}10^{-2}\text{mole/l}$

Hence,

$\lambda([P_{ex}]) = 11.1\text{x}10^{-3}\text{mole/l}$ (for $t = 50$ min)

$\lambda([P_{ex}] - [P_t]) = 12.4\text{x}10^{-3}\text{mole/l}$ (for $t = 50$ min)

$\lambda(\log([P_{ex}] - [P_t])) = 0.30$ (for $t = 50$ min)

$= 9\%$ (for any t)

$\lambda(C_2) = 5.9\text{x}10^{-3}\text{min}^{-1}$

$\lambda(F) = 2.20\text{x}10^{-2}\text{mole/l}$

The following values were used to calculate $\lambda(k_pR)$, $\lambda(m)$ and $\lambda(k_r)$.

$E = 4.0\text{x}10^{-5}\text{mole/l min}$

$F = 8.8\text{x}10^{-2}\text{mole/l}$

$C_2 = 1.5\text{x}10^{-2}\text{min}^{-1}$

$[Z]o = 3.868\text{x}10^{-2}\text{mole/l}$

$\lambda(E) = 2.5\text{x}10^{-6}\text{mole/l min}$

$\lambda(F) = 2.20\text{x}10^{-2}\text{mole/l}$

$\lambda(C_2) = 5.9\text{x}10^{-3}\text{min}^{-1}$

$\lambda([Z]o) = 1.66\text{x}10^{-3}\text{mole/l}$

$$\lambda(k_pR) = 3.26\text{x}10^{-1} \text{ x } 2.2\text{x}10^{-2} + 10.7 \text{ x } 2.5\text{x}10^{-6} + 2.88 \text{ x } 5.9\text{x}10^{-3}$$

$$= \underline{2.42\text{x}10^{-2}\text{min}^{-1}}$$

$$\lambda(m) = 29.7 \text{ x } 2.2\text{x}10^{-2} + 348 \text{ x } 5.9\text{x}10^{-3} + 67.5 \text{ x } 1.66\text{x}10^{-3} + 374 \text{ x } 2.42\text{x}10^{-2}$$

$$= \underline{11.86}$$

$$\lambda(k_r) = 5.9\text{x}10^{-3} + 24.2\text{x}10^{-3}$$

$$= \underline{30.1\text{x}10^{-3}\text{min}^{-1}}$$

The probable errors were determined by employing equations (A2) and (A3). The results are as follows.

$\lambda([P_{ex}]) = 1.10\text{x}10^{-2}\text{mole/l}$ (for $t = 50$ min)

$\lambda([P_{ex}] - [P_t]) = 1.12\text{x}10^{-2}\text{mole/l}$ (for $t = 50$ min)

$\lambda(\log([P_{ex}] - [P_t])) = 0.27$ (for $t = 50$ min)

$= 8\%$ (for any t)

$\lambda(C_2) = 5.4\text{x}10^{-3}\text{min}^{-1}$
$\lambda(F) = 1.98\text{x}10^{-2}\text{mole/l}$

Now, with the new values for $\lambda(C_2)$ and $\lambda(F)$, the limits of error were found to be:

$$\lambda(k_pR) = \{(3.26\text{x}10^{-1})^2\ (1.98\text{x}10^{-2})^2 + 10.7^2(2.5\text{x}10^{-6})^2 + 2.88^2(5.4\text{x}10^{-3})^2\ \}^{1/2}$$
$$= 1.68\text{x}10^{-2}\text{min}^{-1}$$

$$\lambda(m) = \{29.7^2(1.98\text{x}10^{-2})^2 + 348^2(5.4\text{x}10^{-3})^2 + 67.5^2(1.66\text{x}10^{-3})^2 + 374^2(1.68\text{x}10^{-2})^2\ \}^{1/2}$$
$$= 6.6$$

$$\lambda(k_r) = \{(5.4\text{x}10^{-3})^2 + (1.68\text{x}10^{-2})^2\ \}^{1/2}$$
$$= 17.6\text{x}10^{-3}\text{min}^{-1}$$

From equation (A2),

$Q(k_pR) = \underline{0.44\text{x}10^{-2}\text{min}^{-1}}$ (= 31%)

$Q(m) = \underline{1.7}$ (= 71%)

$Q(k_r) = \underline{4.6\text{x}10^{-3}\text{min}^{-1}}$ (= 1045%)

When these figures are expressed as the percentages of the corresponding constants and the same percent error is assumed for the kinetic parameters evaluated at 35°C and 60°C, the probable errors are found to be :

At temperature 35°C,
$Q(k_pR) = 0.53\text{x}10^{-2}\text{min}^{-1}$
$Q(m) = 3.0$
$Q(k_r) = 1.2\text{x}10^{-3}\text{min}^{-1}$

At temperature 60°C,
$Q(k_pR) = 0.68\text{x}10^{-2}\text{min}^{-1}$
$Q(m) = 1.0$
$Q(k_r) = 11.7\text{x}10^{-3}\text{min}^{-1}$

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