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KINETIC AND MOLECULAR WEIGHT STUDIES OF COMPLEXED ALTERNATING COPOLYMERIZATIONS

by

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ABSTRACT

Complexed alternating copolymerizations have been the subject of intense interest for the past five years. However, the mechanism for these reactions is obscure. In this study, the molecular weight distributions of several systems were examined in conjunction with kinetic rate data in order to elucidate the mechanism and to differentiate among competing theories.

The model systems methyl methacrylate-styrene, methyl methacrylate-isoprene, acrylonitrile-styrene, methacrylonitrile-styrene, methyl acrylate-styrene, methyl chloroacrylate-styrene and chloroacrylonitrile-styrene in conjunction with the complexing agents, diethylaluminum chloride, ethylaluminum sesquichloride and zinc chloride have been selected for study.

Major kinetic emphasis is placed on the methyl methacrylate-styrene-diethylaluminum chloride system. The initial reaction is found to be first-order dependent on each monomer, second-order overall: $k_p' = 5.4 \times 10^{-6}$ l mole^{-1}sec.$^{-1}$ at 25°C. The apparent rate constant, k_p', is obtained by two separate methods. The yield of polymer with time gives k_p' by a graphical technique using the integrated rate expression. Variation of initial rate with monomer feed composition provides an alternative method. Kinetic studies conducted between 0°C. and 60°C. show a low overall activation energy, $E_r = +3.9$ kcal mole^{-1}.

Similar studies on the methyl methacrylate-isoprene-ethylaluminum sesquichloride and diethylaluminum chloride

systems show an initial reaction, first-order dependent on methyl methacrylate and one-half order dependent on isoprene; 3/2 order overall. An integrated rate expression for a 3/2 order reaction is derived and provides apparent rate constants, k_p', for the diethylaluminum chloride and ethylaluminum sesquichloride systems as $4.8 \times 10^{-6} l^{1/2}$ mole$^{-1/2}$sec.$^{-1}$ and $2.2 \times 10^{-6} l^{1/2}$mole$^{-1/2}$sec.$^{-1}$ respectively. Kinetic studies conducted between 0^{o}C. and 60^{o}C. show a small negative activation energy of $E_r = -4.2$ kcal mole^{-1} for the methyl methacrylate-isoprene-diethylaluminum chloride reaction. A mechanism involving an isoprene diradical species and consistent with 3/2 order kinetics is proposed.

Molecular weight distributions have been determined using gel permeation chromatography. No change in molecular weight is seen with increased reaction time. Thus mechanisms involving "living" centers are not involved in complexed alternating copolymerization. The number average molecular weights ($\overline{M}_n$) for methyl methacrylate-styrene-diethylaluminum chloride, methyl acrylate-styrene-diethylaluminum chloride, acrylonitrile-styrene-diethylaluminum chloride and methacrylonitrile-styrene-diethylaluminum chloride indicate a steady decrease in $\overline{M}_n$ with increases in the vinyl monomer-diethylaluminum chloride concentration. Rates, however, are found to be maximum at 1:1 monomer feed ratios. A Mayo type plot indicates a non-degradative chain transfer termination mechanism.

An opposite trend in which $\overline{M}_n$ increases with increasing methyl methacrylate-diethylaluminum chloride concentration is seen in the methyl methacrylate-isoprene-diethylaluminum chloride system and is postulated to be due to the incorporation of "dead" polymer into the propagating species.

Monomer chain transfer constants, (C_m), for the complexed monomers, methyl acrylate-diethylaluminum chloride, methyl methacrylate-diethylaluminum chloride, acrylonitrile-diethylaluminum chloride and methacrylonitrile-diethylaluminum chloride are determined to be 7.6×10^{-4}, 7.1×10^{-4}, 3.4×10^{-4} and 4.1×10^{-4} respectively. These are several orders of magnitude greater than C_m values for uncomplexed systems reported in the literature.

The non-degradative chain transfer mechanism is tested by examining $\overline{M}_n$ and vinyl monomer Q value. There is a qualitative dependence between $\overline{M}_n$ and Q which is consistent with a chain transfer mechanism, e.g.: high Q values yielding low $\overline{M}_n$ product.

Copolymer composition (methyl methacrylate-styrene-diethylaluminum chloride) and the molecular weight distributions are determined simultaneously using ^{14}C labelling techniques. The copolymer is strictly alternating throughout the molecular weight distribution and the gross analysis reflects a molecular homogeneity, thus indicating the overall reaction mechanism is devoid of parallel propagation mechanisms.

With zinc chloride complexing agent and α, α'azobisisobutyronitrile, initiator, no change in rate of initiator decomposition is found in the presence of zinc chloride. The decomposition is first-order (k_d 2.0 x 10^{-5}sec.$^{-1}$). This establishes that the high rate of reaction found for α, α'azobisisobutyronitrile initiated systems is not due to an enhanced rate of initiator decomposition.

Solvents capable of complexing with zinc chloride grossly affect alternating copolymerizations and cause the reaction to revert to a random process. For example, methacrylonitrile-styrene-zinc chloride with α, α'azobisisobutyronitrile copolymerized in THF, produces random copolymer.

TO DIANA, KIMBERLEY AND

MY PARENTS

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"When you can measure what you are speaking about and express it in numbers, you know something about it, and when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meager and unsatisfactory kind."

Lord Kelvin

GLOSSARY OF FREQUENTLY-USED TERMS AND ABBREVIATIONS

R_p - Rate of Polymerization

R_o - Initial Rate of Polymerization

n - Reaction Order Coefficient

k_p' - Apparent Rate Constant

k_d - Decomposition Rate Constant

E_r - Overall Activation Energy

$\overline{DP}$ - Average Degree of Polymerization

C_m - Monomer Chain Transfer Constant

$\overline{M}_n$ - Number Average Molecular Weight

$\overline{M}_w$ - Weight Average Molecular Weight

r_1, r_2 - Monomer Reactivity Ratio

DEAC - Diethylaluminum Chloride

EASC - Ethylaluminum Sesquichloride

MMA - Methyl Methacrylate

STY - Styrene

IP - Isoprene

AN - Acrylonitrile

MAN - Methacrylonitrile

MA - Methyl Acrylate

MCA - Methyl Chloroacrylate

CAN - Chloroacrylonitrile

AIBN - α, α'Azobisisobutyronitrile

MMA* - Methyl Methacrylate-Lewis Acid Feed Ratio of 2:1

THF - Tetrahydrofuran

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I. INTRODUCTION

I.1 HISTORY

Before the turn of the century, the first synthetic polymers had been prepared using techniques available from organic chemistry. Although these compounds were merely laboratory curiosities at the time, they provided the beginning of the field of polymer chemistry. The first thirty years of the 20th Century saw a slow build-up of knowledge of some of the basic concepts for this new science.

Although polymeric materials such as polyethylene and nylon were in commercial production before 1939, there is little doubt that the Second World War provided the impetus for much of the research and technological development which has since provided the multitude of polymeric materials that are so common in every day life today.

A large proportion of these useful materials are copolymers and the explosive growth of the field of copolymer chemistry has been attributed to the lack of sufficient supplies of natural rubber during the war years. A large effort was exerted into developing a suitable substitute for natural rubber and the development of the copolymer styrene-butadiene rubber (SBR) resulted. Synthetic copolymers are now found in many applications such as clothing, automobiles, housing and in a growing number of industrial and agricultural applications.

I.2 IMPORTANCE OF COPOLYMERS

A polymerization process whereby two or more monomers are simultaneously polymerized into the same polymeric molecule is termed copolymerization and the product is known as a copolymer. Many monomers that fail to homopolymerize themselves, readily form copolymers in conjunction with other monomers. Hence, monomers with desirable chemical properties that do not homopolymerize, give useful copolymers on copolymerization.

One of the more important aspects of copolymerization is the modification of polymer properties through changes in composition. Polymethyl methacrylate is an attractive, tough plastic used for a large number of industrial applications. This homopolymer unfortunately suffers from poor thermal properties and decomposes above 180°C (1). The addition of styrene as a comonomer in the polymerization of methyl methacrylate provides a more durable and temperature tolerant material. Likewise, polyacrylonitrile, a popular polymer in the textile industry, attains better dying characteristics when copolymerized with vinyl pyridine (2).

I.3 COPOLYMER CONSTITUTION

Copolymers are classified into four general classifications depending on the structural distribution of the monomers along the polymeric chain. For two component copolymers, these classifications are called; random, alternating, block and graft. In a random copolymer, the monomeric units have a random distribution along the chain:

A-B-A-A-B-B-B-A-B-B-A-A-A

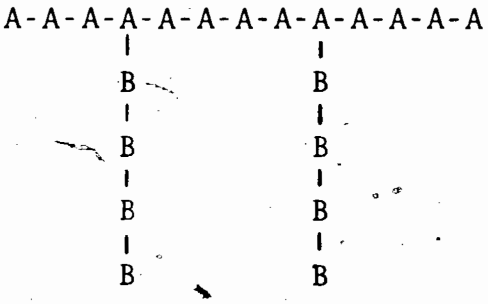
Alternating copolymers have a perfectly alternating sequence of monomer units:

A-B-A-B-A-B-A-B-A-B

Block copolymers are copolymers containing long runs of one monomer:

A-A-A-A-A-A-B-B-B-B-B-B

A graft copolymer has a branch structure consisting of a homopolymer backbone with comonomer side chains:



$$\begin{array}{ccccccccccccccccccccccccc} A&-&A&-&A&-&A&-&A&-&A&-&A&-&A&-&A&-&A&-&A&-&A&-&A \\ &&&&&&|&&&&&&&&&&|&&&&&&&& \\ &&&&&&B&&&&&&&&&&B&&&&&&&& \\ &&&&&&|&&&&&&&&&&|&&&&&&&& \\ &&&&&&B&&&&&&&&&&B&&&&&&&& \\ &&&&&&|&&&&&&&&&&|&&&&&&&& \\ &&&&&&B&&&&&&&&&&B&&&&&&&& \\ &&&&&&|&&&&&&&&&&|&&&&&&&& \\ &&&&&&B&&&&&&&&&&B&&&&&&&& \end{array}$$

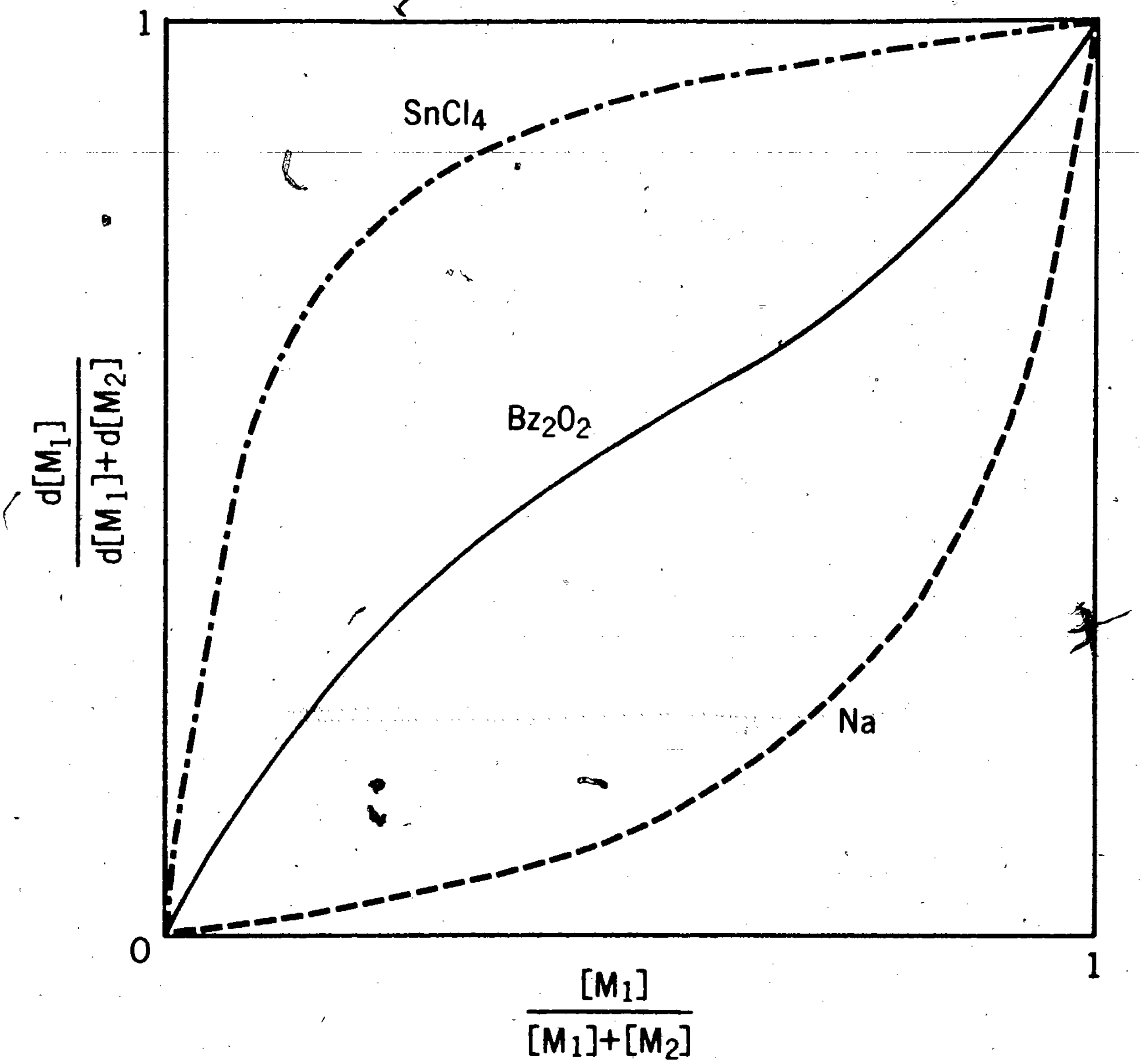
For a given pair of monomers, differences in chain structure provide each of the four types of copolymers with unique physical and chemical properties, of which the most interesting is the alternating structure.

Polymers with alternating structures show high degrees of crystallinity on stretching (3), presumably due to their homogeneous structure. This property is highly desirable in the design of materials with high tensile strength. Poly-(hexamethylene adipamide) is used as both a fibre and a flexible plastic. When moderately crystalline, it is a flexible plastic, however, as this material is stretched it becomes highly crystalline and produces fibres of high strength commonly called nylon 6, 6 (4).

I.4 COPOLYMER COMPOSITION

The monomeric composition of a copolymer is usually measured as a mole percent of each monomer and is independent of the copolymer's constitution. A copolymer of particular composition can be either random, alternating, block or graft. The composition of a copolymer is to a large extent determined by the particular monomer feed composition used to prepare the copolymer as well as reactivity differences between the monomers. The relationship between feed composition for a cationic, anionic and free radical copolymerization of methyl methacrylate and styrene is shown in figure (1). Figure (1) indicates that in the free radical mechanism, a linear relationship does not exist between the monomer feed and the product composition. The non-linear relationship shown on figure (1) is common to a large number of copolymerizations and early research into radical copolymerization devoted much attention to this phenomenon. Dostal (5) was the first to

Figure 1 INCREMENTAL COPOLYMER COMPOSITION AS A FUNCTION OF MONOMER FEED COMPOSITION FOR THE STYRENE (M_1)-METHYL METHACRYLATE (M_2) SYSTEM, POLYMERIZED BY CATIONIC ($SnCl_4$), FREE RADICAL (Bz_2O_2) AND ANIONIC (Na) MECHANISMS (6).


1
0
1
SnCl$_4$
Bz$_2$O$_2$
Na
$\frac{d[M_1]}{d[M_1]+d[M_2]}$
$\frac{[M_1]}{[M_1]+[M_2]}$

attempt to elucidate the mechanisms of copolymerization. His basic assumption was that the rate of addition of monomer units to a growing macroradical was dependent only on the end group. For a two monomer system, M_1 and M_2, this assumption leads to four possible propagation steps:

$$\begin{array}{lcl}
\sim M_1^{\cdot} + M_1 & \xrightarrow{k_{11}} & \sim M_1^{\cdot} \\
\sim M_1^{\cdot} + M_2 & \xrightarrow{k_{12}} & \sim M_2^{\cdot} \\
\sim M_2^{\cdot} + M_1 & \xrightarrow{k_{21}} & \sim M_1^{\cdot} \\
\sim M_2^{\cdot} + M_2 & \xrightarrow{k_{22}} & \sim M_2^{\cdot}
\end{array}$$

Many years after Dostals original work, Mayo and Lewis (7) and Alfrey and Goldfinger (8) separately derived the now familiar copolymerization equation (1-1), (also frequently called the Mayo-Lewis equation). This expression relates the copolymer composition $d[M_1]/d[M_2]$ with the monomer feed composition $[M_1] / [M_2]$ through the use of two terms called the monomer reactivity ratios r_1 and r_2:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])} \qquad 1\text{-}1$$

where:

$$r_1 = \frac{k_{11}}{k_{12}} \quad , \quad r_2 = \frac{k_{22}}{k_{21}}$$

The monomer reactivity ratios are quantitative measures of the preference of a radical to react with its own monomer rather than with the comonomer. Reactivity ratios are not constant for a given monomer but are particular to monomer pairs and to polymerization conditions (Table I).

Whether the polymer product from a radical copolymerization is random, alternating or block, is determined by the values of the reactivity ratios. Random propagation occurs when $r_1 = r_2 = 1$. This situation occurs when the two monomers show equal reactivities toward both propagating species. The product composition is then dependent only on the monomer feed ratio as shown in equation (1-2).

$$\frac{d\,[M_1]}{d\,[M_2]} = \frac{[M_1]}{[M_2]} \qquad 1\text{-}2$$

In cases where r_1 and r_2 differ from unity, e.g., $r_1 > 1$, $r_2 < 1$ or $r_1 < 1$, $r_2 > 1$, one of the monomers is more reactive than the other toward both propagating species. The product will then contain a large proportion of the more reactive monomer in random placement. When $r_1 = r_2 = 0$, regular alternation of monomer units occurs. The two monomers enter into the copolymer in equimolar amounts in a non-random alternating arrangement along the polymer chain. Each of the two types of propagating species preferentially adds the other monomer. The product composition is then independent of the monomer

TABLE I

Some Monomer reactivity ratios
in radical copolymerizations

M_1	r_1	M_2	r_2	T(°C)
Acrylic acid	1.15	Acrylonitrile	0.35	50
	0.25±0.02	Styrene	0.15±0.01	60
	2	Vinyl acetate	0.1	70
Acrylonitrile	0.35	Acrylic acid	1.15	50
	0.02	1,3-Butadiene	0.3	40
	0.14±0.04	t-Butyl vinyl ether	0.0032±0.0002	60
	0.7±0.2	Ethyl vinyl ether	0.03±0.02	80
	0.02±0.02	Isobutylene	1.8±0.2	50
	1.5±0.1	Methyl acrylate	0.84±0.05	50
	0.150±0.080	Methyl methacrylate	1.224±0.100	80
	0.61±0.04	Methyl vinyl ketone	1.78±0.22	60
	0.04±0.04	Styrene	0.40±0.05	60
	4.2	Vinyl acetate	0.05	50
	2.7±0.7	Vinyl chloride	0.04±0.03	60
	0.91±0.10	Vinylidene chloride	0.37±0.10	60
	0.113±0.002	2-Vinylpyridine	0.47±0.03	60
Allyl acetate	0	Methyl methacrylate	23	60
	0.00	Styrene	90±10	60
	0.7	Vinyl acetate	1.0	60
1,3-Butadiene	0.3	Acrylonitrile	0.02	40
	0.75±0.05	Methyl methacrylate	0.25±0.03	90
	1.35±0.12	Styrene	0.58±0.15	50
	8.8	Vinyl chloride	0.035	50
Diethyl fumarate	0	Acrylonitrile	8	60
	0.070±0.007	Styrene	0.30±0.02	60
	0.444±0.003	Vinyl acetate	0.011±0.001	60
	0.12±0.01	Vinyl chloride	0.47±0.05	60
Diethyl maleate	0	Acrylonitrile	12	60
	0	Methyl methacrylate	20	60
	0.0±0.1	Styrene	5±1.5	70
	0.043±0.005	Vinyl acetate	0.17±0.01	60
	0.009±0.003	Vinyl chloride	0.77±0.03	

feed. If r_1 and r_2 are greater than unity, then there is a tendency to form blocks of monomer along the chain. This type of behaviour is uncommon in radical copolymerization. In the few reported cases where it does occur, polymerization is accomplished with the use of co-ordination catalysts (9).

A special situation occurs when one of the reactivity ratios is much larger than the other ($r_1 \gg 1$, $r_2 \ll 1$). Both of the propagating species preferentially add M_1, thus M_1 tends to homopolymerize until it is consumed after which M_2 homopolymerizes. This behaviour is called consecutive homopolymerization. An extreme example is the copolymerization of vinyl acetate-styrene ($r_1 = 0.01$, $r_2 = 55$) (9).

When the product of the reactivity ratios is unity:

$$r_2 = \frac{1}{r_1} \qquad 1\text{-}3$$

the propagating species show the same preference for adding either of the monomer species. This type of behaviour is called ideal copolymerization and the copolymer composition is given by (1-1) and (1-3).

$$\frac{d\,[M_1]}{d\,[M_2]} = \frac{r_1\,[M_1]}{[M_2]} \qquad 1\text{-}4$$

Most comonomer systems lie between the two extremes of alternating and ideal copolymerization. The range of changes in copolymer composition as a function of the reactivity ratios and comonomer feed is shown in figure (2).

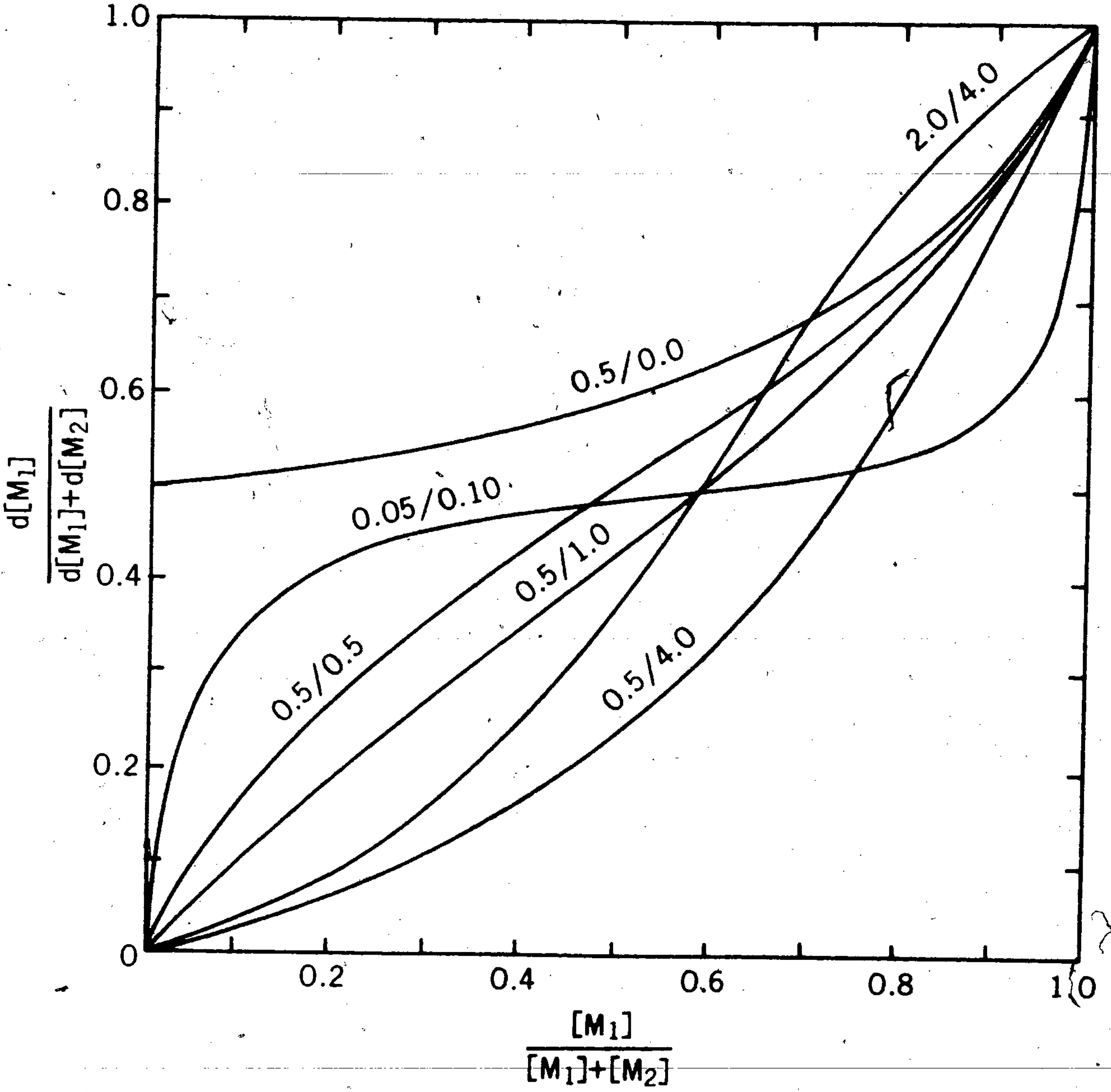
I.5 THE Qe SCHEME OF MONOMER REACTIVITY

The relation between monomer structure and reactivity with free radicals involves resonance, polar and steric factors. The Qe scheme of Alfrey and Price (10, 11) represents an attempt to formulate the first two factors in a quantitative manner. The Qe scheme is an empirical semi-quantitative attempt to relate the reactivity of a given radical-monomer pair to the resonance and polar effects that exist in the monomers and is shown as expression (1-5):

$$k_{ij} = P_i Q_j \exp(-e_i e_j) \qquad 1\text{-}5$$

The terms P and Q relate to resonance effects, where P_i relates to the radical and Q_i to the neutral monomer. Terms e_i and e_j are polarity measures of the radical and monomer respectively. By making the simplifying assumption that the same e value relates to both a monomer and its radical, it is possible to obtain expressions for copolymerization reactivity ratios r_1 and r_2 as:

Figure 2 INCREMENTAL COPOLYMER COMPOSITION AS A FUNCTION OF MONOMER FEED COMPOSITION FOR VARIOUS r_1/r_2 RATIOS (12).


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

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

$$r_2 = \frac{Q_2}{Q_1} \exp\left(-e_2\left(e_2-e_1\right)\right) \qquad 1\text{-}6$$

The Qe scheme, because of its empirical approach, has many deficiencies. In all cases the precision of calculated Q and e values is limited by the inaccuracy of the measured r_1 and r_2 values and several values of Q and e are obtained using published reactivity ratios (13).

Perhaps the most obvious shortcomings of the Qe relationship is the lack of consideration for steric effects. In this respect, Qe values are often meaningless for copolymerization involving 1,1 disubstituted monomers having large bulky substituants (13).

Despite these deficiencies, the Qe scheme is a reasonably quantitative measure of monomeric reactivity and if the individual Q and e values are used only as approximate measures, the behaviour of a comonomer pair can be predicted. Consequently, the Qe values of a large number of monomers have been determined and tabulated (14).

I.6 FACTORS INFLUENCING ALTERNATION IN COPOLYMERIZATION

When the product of the reactivity ratios of a comonomer pair tends toward zero, there is a tendency toward alternation in the copolymer. Price (15) was the first to propose a polarity effect whereby substituents on a radical or neutral molecule polarized the vinyl bond. An alternation effect could then arise from an attraction between a negative double bond and a positive radical or vice versa. This suggestion was explored more closely by Mayo, Lewis and Walling (16, 17) These authors tabulated a series of monomers in order of increasing copolymer alternation as shown in table II. Mayo et al pointed out that the monomers appear in the approximate order of the tendency of the substituent to withdraw electrons from the vinyl bond. It has also been recognized that the monomers in table II follow in order of their e values (17). In cases where the comonomers are far apart in the series, an alternating copolymer results. If the separation is small then the tendency to alternate becomes less and a non-alternating polymer is formed. Ultraviolet spectroscopy has revealed new absorption bands (change transfer bands) attributed to a molecular complex between the monomers (18 - 24). In their studies of alkyl acetate-maleic anhydride copolymerizations, Bartlett and Nozaki (25) proposed a molecular donor-acceptor interaction between monomers as the controlling factor for the observed alternating tendency. Walling et al (26, 27) views the alternating effect as a transition state phenomenon, where the alternating copolymer arises from the most stable transition between the growing macroradical and the monomers. The electron donating and accepting properties are postulated as the important factors leading to transition state stabilization.

TABLE II VALUES OF r_1r_2 IN RADICAL COPOLYMERIZATION (17). e VALUES IN BRACKETS.

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

At the present time two major schools of thought exist for the explanation of the alternating tendency. Gaylord *et al* (28) support the idea of a homopolymerization of donor-acceptor complexes to form the alternating copolymer, whereas Zubov *et al* (29) postulate that donor-acceptor interaction occurs at the chain end. Present opinion is approximately equally divided between the Gaylord view (21, 30-34) and that of Zubov (35-41). More will be said about these mechanisms later.

I.7 ALTERNATING COPOLYMERIZATION WITH LEWIS ACIDS

Acrylic compounds such as acrylonitrile, methyl methacrylate, etc. have been known not to undergo alternating copolymerization with olefinic compounds such as styrene, propylene or ethylene. Hirooka and co-workers (40) showed that acrylic monomers in conjunction with aluminum alkyls formed stable complexes and that these complexes in conjunction with olefins spontaneously produced alternating copolymers. A similar situation was shown in the acrylonitrile-styrene system where zinc chloride was used as a complexing agent for the former monomer. Several complexing agents have been found to be successful in these copolymerizations; $Et_{1.5}AlCl_{1.5}$ (19, 24, 42-60), Et_2AlCl (43, 57), $EtAlCl_2$ (42, 43, 57, 58, 61-63), Et_3Al (64), $ZnCl_2$ (28, 35, 51, 52, 66-72), $AlCl_3$ (31), $iBu_{1.5}AlBr_{1.5}$ (43), $ZnBr_2$ (52) and $SnCl_3$ (53). In addition, some Lewis acid-vanadium oxychloride combinations have been successful (31, 34, 73, 76). These complexing agents dramatically affect the copolymer composition as shown in figures (3) and (4). In both of these examples, the ethylaluminum sesquichloride (EASC) complexed alternating copolymerization is contrasted against products from conventional radical and ionic mechanisms. The most dramatic feature is the apparent insensitivity of the product composition to monomer feed ratio changes. The ability of the Lewis acid to facilitate the spontaneous alternating copolymerization is attributed to the complexation of the Lewis acid onto the nitrile or carbonyl group of the vinyl monomer (30, 56, 77-84). Complexation then delocalizes electron density from the vinyl bond and thus enhances the nucleophilic character of the monomer. Such a process separates the comonomers to a greater degree on the Mayo-Walling series and alternating copolymerization results.

I.8 EVIDENCE FOR AN ALTERNATING STRUCTURE

Equimolar copolymers can be obtained by proper selection of monomer feed ratios. These polymers are not necessarily alternating in structure, but contain a random distribution of monomer units along the chain. Distinction between alternating and random copolymers cannot be accomplished using elemental analysis although unimolar composition independent of feed ratios is strongly suggestive of an alternating mechanism. As a random sequence of equimolar copolymer would contain a high proportion of alternating units, infrared spectroscopy shows no characteristic absorptions assignable to an alternating structure (85).

Figure 3 COPOLYMERIZATION OF METHYL METHACRYLATE AND STYRENE (48).

(o) with ethylaluminum sesquichloride;

(--) radical;

(.....) cationic;

(△) anionic, Na catalyst;

(▽) anionic, BuLi catalyst.

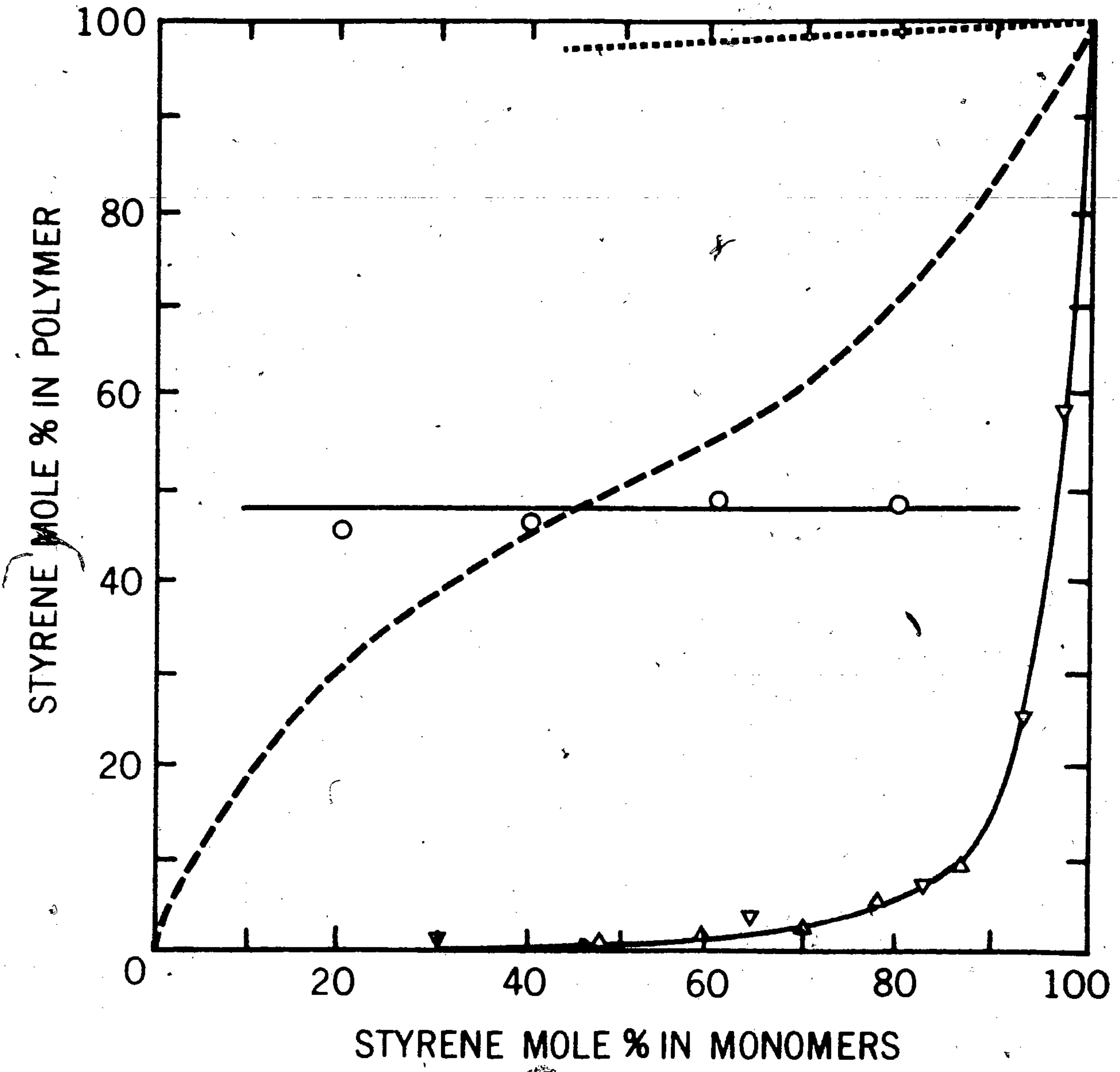
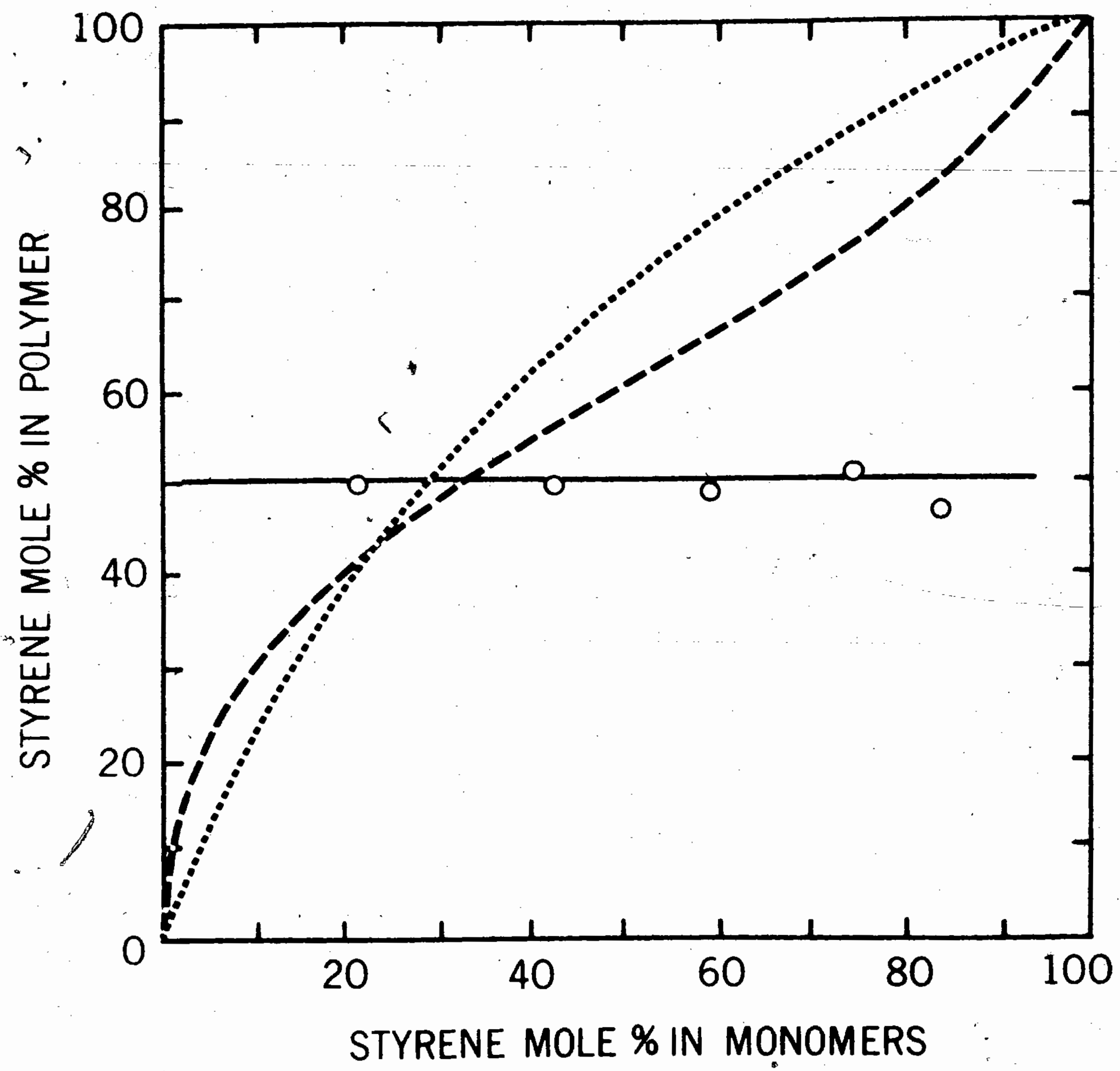

STYRENE MOLE % IN POLYMER
0
20
40
60
80
100
STYRENE MOLE % IN MONOMERS

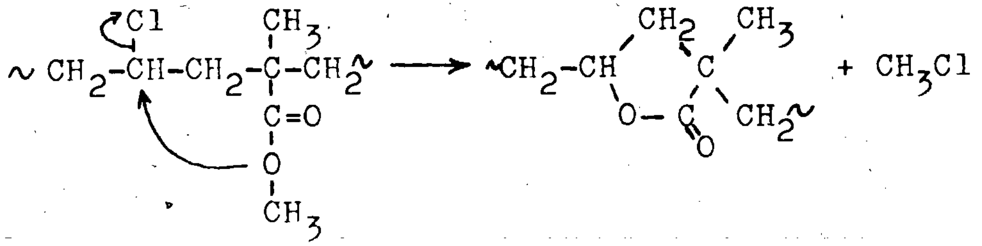
Figure 4 COPOLYMERIZATION OF METHYL ACRYLATE AND STYRENE (48).

(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

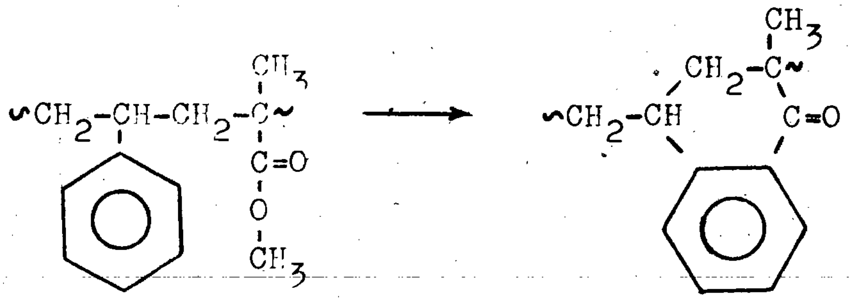
Nuclear magnetic resonance (NMR) has provided a useful method of identification. Both steady state (42, 46, 58, 66, 67, 71, 72, 75, 88-90) and, to a greater degree, pulsed fourier transform NMR (PFT-NMR) (91) provide distinguishing features between random and alternating structures.

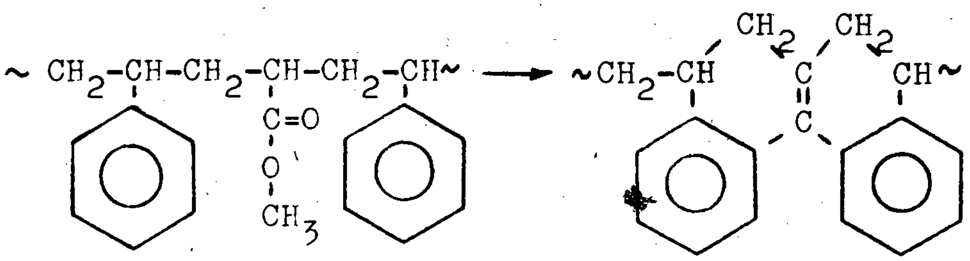
In situations where neighbouring group reactions are possible, cyclization reactions are used as a measure of alternation. For example, vinyl chloride-methyl methacrylate copolymer can cyclize through alternating sequences as shown:



The yield of methyl chloride is proportional to the degree of cyclization and can be related to the degree of alternation (75).

A similar situation exists for methyl methacrylate-styrene and methyl acrylate-styrene copolymers. In these cases, cyclization is accomplished by treatment of the copolymer with polyphosphoric acid. The degree of cyclization can then be examined by NMR (92).





As expected, differences between the non-cyclized and cyclized alternating copolymer are much greater than in the random case. Infrared spectral differences are also seen between cyclized random and alternating copolymer.

I.9 NOMENCLATURE OF ALTERNATING COPOLYMERIZATION WITH LEWIS ACIDS

Evidence for the formation of charge transfer or donor-acceptor complex species in copolymerizations involving

Lewis acids is shown in some instances. This has led to the adoption of the term "donor-acceptor" copolymerization by some authors (48). Other authors view the reactions as a modified radical process and prefer to maintain the name "radical copolymerization" (29, 35-39, 41).

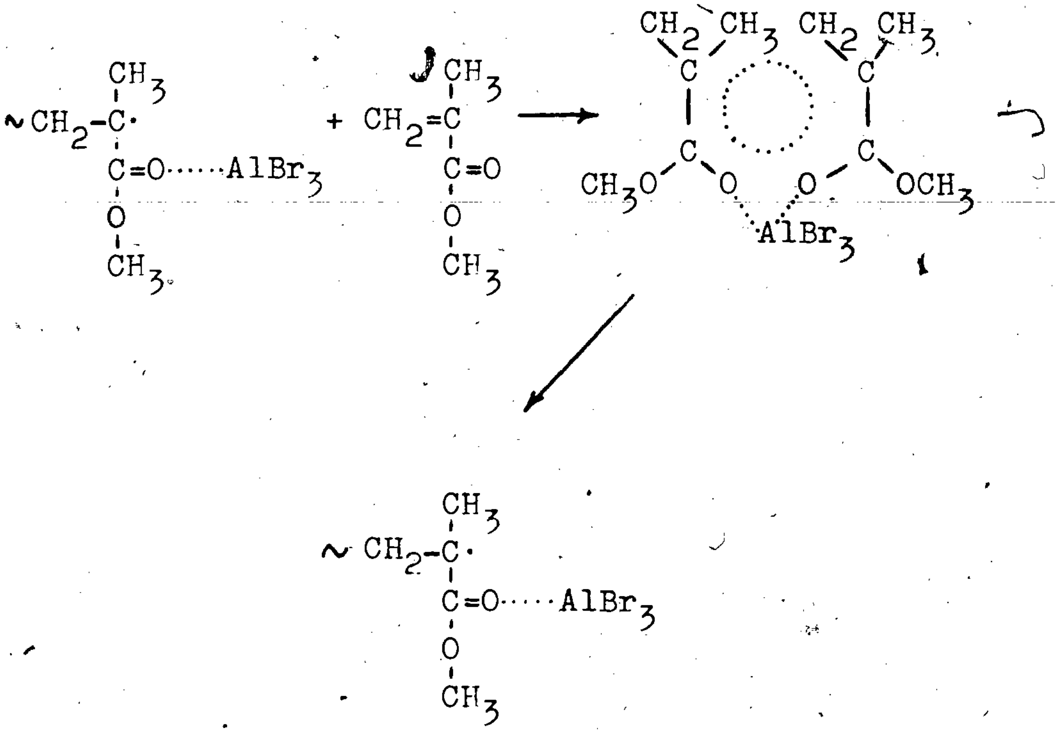
Since no specific features of these copolymerizations are shown in the absence of Lewis acids, the specificity of these reactions is ascribed to the complexing action of the Lewis acid on the nitrile or carbonyl vinyl monomer (40, 94). Thus both Yamada (53) and Hirooka (48, 94) have proposed the use of the terms "complex copolymerization" and "complexed copolymerization" respectively.

As these copolymerizations unequivocally involve some type of complexed species and produce highly alternating copolymer, the nomenclature "complexed alternating copolymerization" is adopted by this author and is used throughout the remainder of this text.

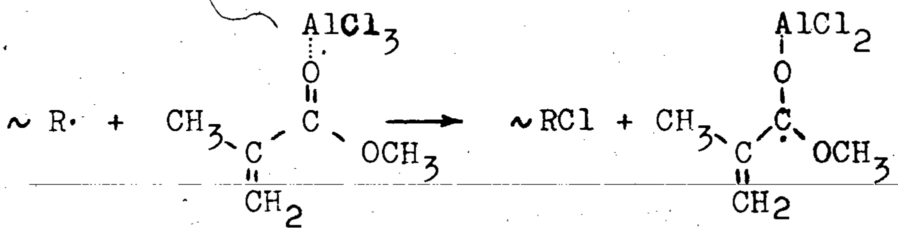
I.10 THE MECHANISM OF COMPLEXED ALTERNATING COPOLYMERIZATIONS

When free radical polymerization of nitrile or carbonyl vinyl monomers are conducted in the presence of Lewis acids such as zinc chloride and alkyl aluminum halides, a rate increase in polymerization is observed (30, 77, 79, 83, 95-98).

Soviet workers (98) have proposed a propagation step for the polymerization of methyl methacrylate in the presence of aluminum bromide as involving the formation of a cyclic transition state at the end of the propagating radical:



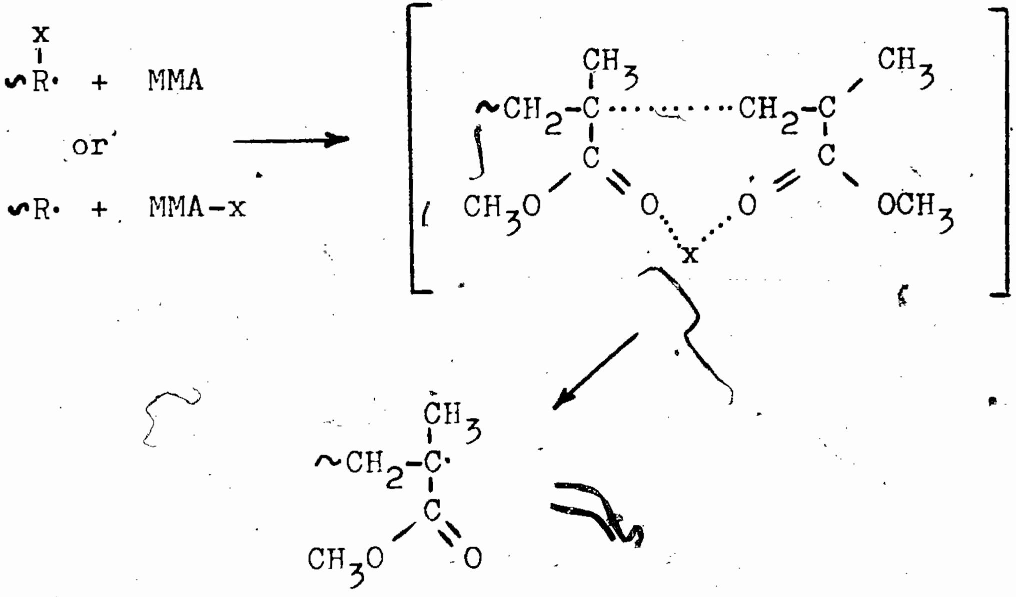
Observations on similar aluminum chloride polymerizations of methyl methacrylate, caused Bamford (96) to propose a transfer reaction between the growing radical and the complexed monomer.



Bamford observed a rate retardation and concluded that the transferred radical was more stable than conventional radicals produced from the monomer.

When Lewis acids are added to copolymerizations containing a monomer with a nitrile or carbonyl function, an enhanced reactivity is also seen. More surprising, however, is the tendency toward a equimolar composition of the product. Yabumoto et al (35) examined the copolymerization of acrylonitrile and styrene with Lewis acids and showed that if three monomeric species were considered; acrylonitrile, complexed acrylonitrile and styrene, that nine propagation steps were possible. Mathematically these nine steps provide a copolymer composition equation identical to the Mayo-Lewis equation with exceptions of different reactivity ratio values. Thus it was shown that a conventional copolymerization in the presence of a Lewis acid could be treated, as far as the relation between the copolymer composition and the monomer reactivity ratios are concerned, as a Lewis acid free copolymerization.

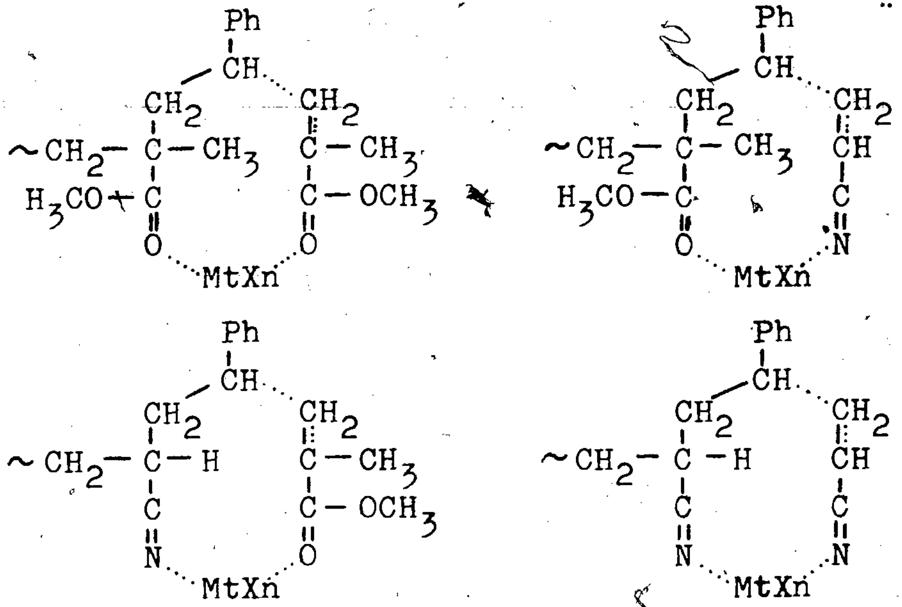
Zubov and co-workers (98) studied the Lewis acid copolymerization of two comonomers, each capable of complexing with the Lewis acid. These workers found that the copolymer composition approached the monomer feed composition as the concentration of the Lewis acid increased. When the ratio of Lewis acid concentration to total monomer concentration was 0.2-0.3, an ideal copolymerization occurred ($r_1 = r_2 = 1$) and the product composition equalled the composition of the feed. Zubov explained these results by assuming that propagation occurs through a transition state where differences in reactivity between the vinyl bonds disappear. Thus the reactivity ratios approach unity and the comonomer composition determines the product composition. Considering a copolymerization involving methyl methacrylate, Zubov's ideas are shown as:



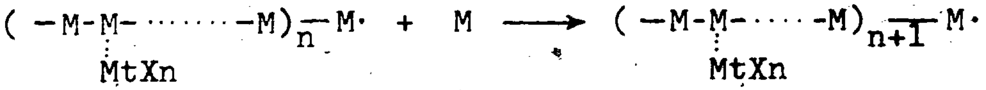
where x represents the Lewis acid complexing agent.

In situations where both comonomers cannot complex with the Lewis acid, the r_1 value can either increase or decrease while r_2 decreases. In most cases, r_1 decreases and a constant composition in the neighbourhood of 50/50 mole % is seen in the product.

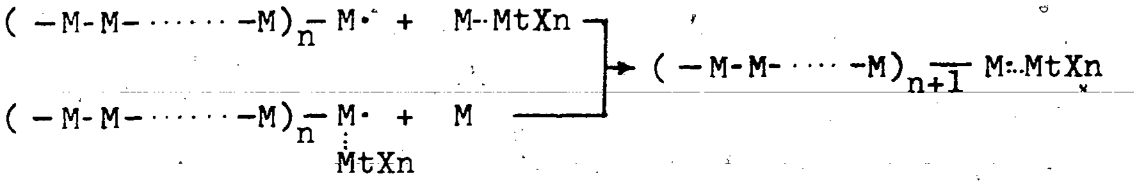
Kutscher and Saitsew (99) examined the terpolymerization of methyl methacrylate and acrylonitrile with styrene in the presence of zinc chloride or diethyl aluminum chloride. Rate data suggested that the copolymerization involved four possible chain end species.



Consequently these workers proposed a mechanism involving a complex bound radical at the propagating chain end similar to that of Zubov et al (98).

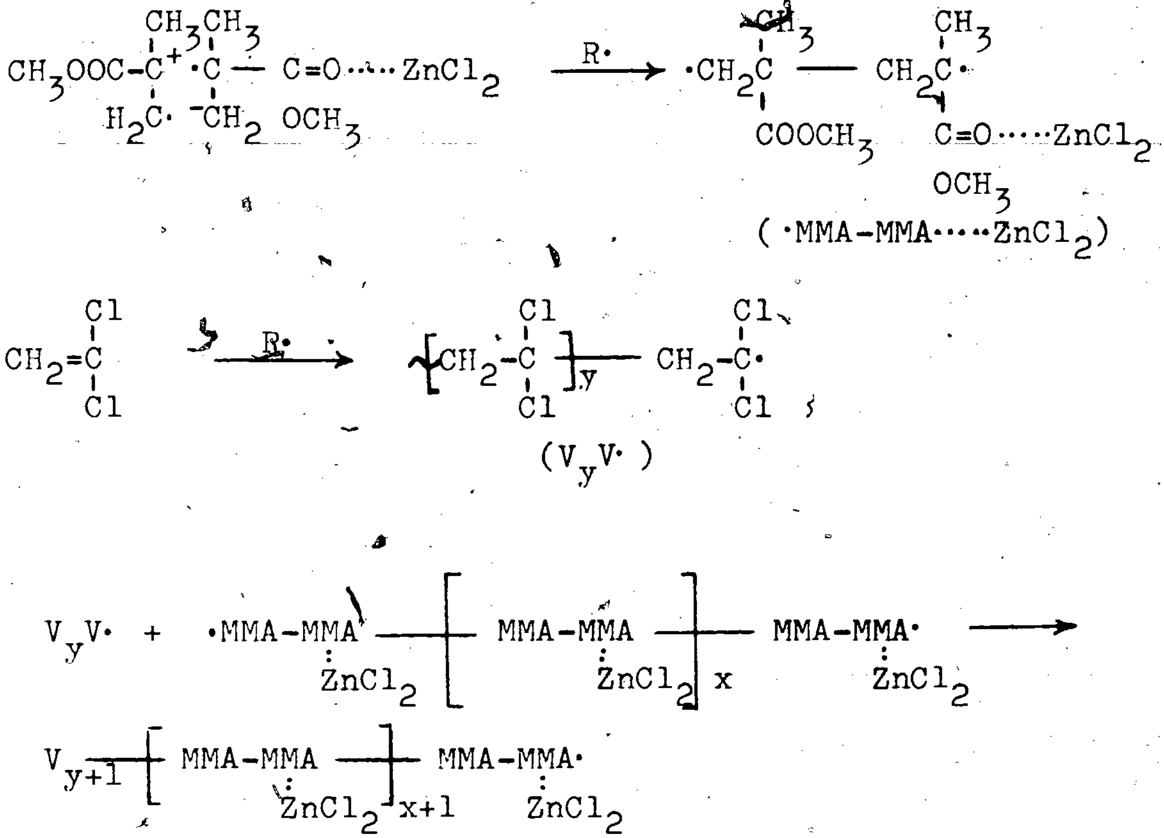


$$(-M\text{-}\underset{\vdots \atop MtXn}{M}-\cdots\cdots-M)_n-M\cdot \;+\; M \longrightarrow (-M\text{-}\underset{\vdots \atop MtXn}{M}-\cdots-M)_{n+1}-M\cdot$$



$$\left.\begin{array}{l} (-M\text{-}M-\cdots\cdots-M)_n-M\cdot \;+\; M\cdots MtXn \\ (-M\text{-}M-\cdots\cdots-M)_n-\underset{\vdots \atop MtXn}{M}\cdot \;+\; M \end{array}\right] \rightarrow (-M\text{-}M-\cdots-M)_{n+1}-M\cdots MtXn$$

In an approach suggested by Gaylord (100), the copolymerization is seen as the homopolymerization of a molecular complex and subsequent polymerization with comonomer. This is shown in the scheme below for the copolymerization of methyl methacrylate and vinylidine chloride in the presence of zinc chloride.



$$V_yV\cdot + \cdot\underset{\vdots\;ZnCl_2}{MMA-MMA}\left[\underset{\vdots\;ZnCl_2}{MMA-MMA}\right]_x \underset{\vdots\;ZnCl_2}{MMA-MMA\cdot} \longrightarrow V_{y+1}\left[\underset{\vdots\;ZnCl_2}{MMA-MMA}\right]_{x+1}\underset{\vdots\;ZnCl_2}{MMA-MMA\cdot}$$

Gaylord and Takahashi (28, 100) were the first to propose the donor-acceptor mechanism for complexed alternating copolymerization. In their studies on the copolymerization of acrylonitrile and olefins with zinc chloride, these workers proposed a diradical species derived from a comonomer donor-acceptor complex.

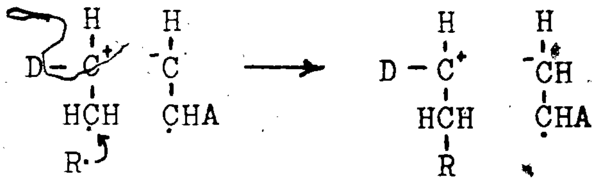
This was later modified to include possible radical coupling in the complex to produce ionic centers (54). Some studies indicate a "living" type mechanism (54) where molecular weight increases with conversion. Later investigations showed that molecular weight, measured as intrinsic viscosity, increases only in the initial stages and a constant molecular weight occurs in the latter stages of the reaction (101-103). It should be pointed out, however, that the data show considerable scatter and that a "living" mechanism is not completely ruled out.

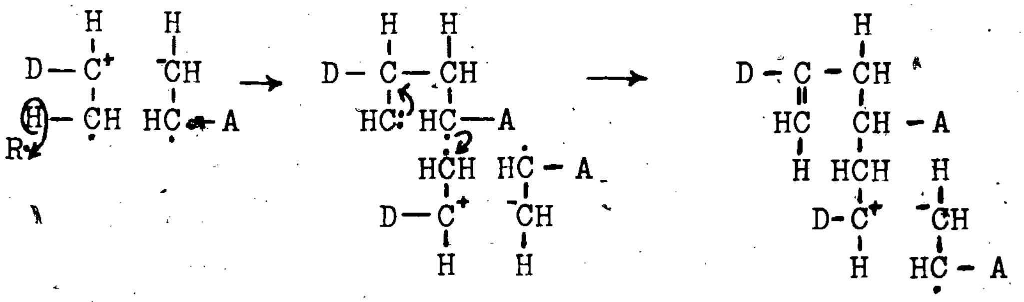
The overall Gaylord donor-acceptor mechanism is shown as the generalized scheme (I) (104). Initiation is seen as a hydrogen abstraction from a donor-acceptor complex by another donor-acceptor complex or radical initiator fragment. Propagation involves subsequent addition of donor-acceptor complexes while termination is provided by intramolecular coupling or reverse electron transfer. This scheme involves considerable speculation. All possible interactions are shown although, in some instances, experimental evidence is lacking.

SCHEME I

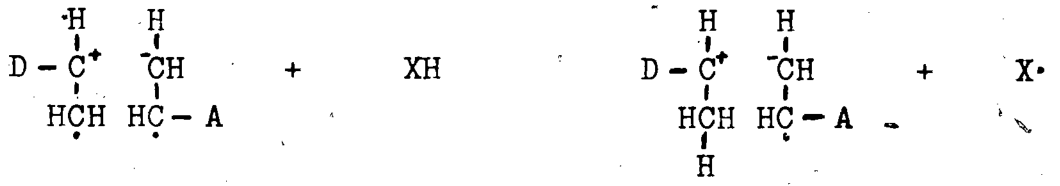
Initiation: D = Electron Donor Substituent; A = Electron Acceptor Substituent

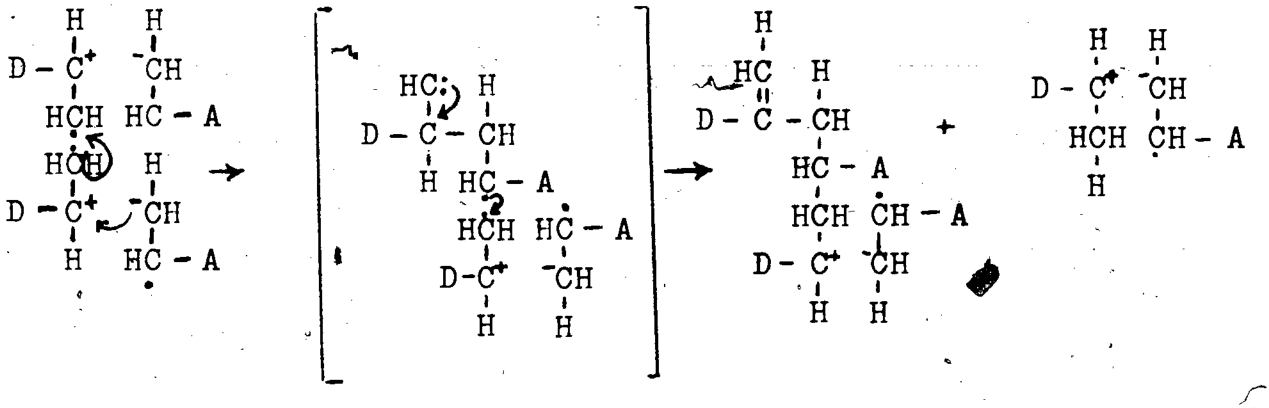
a) Radical Initiation

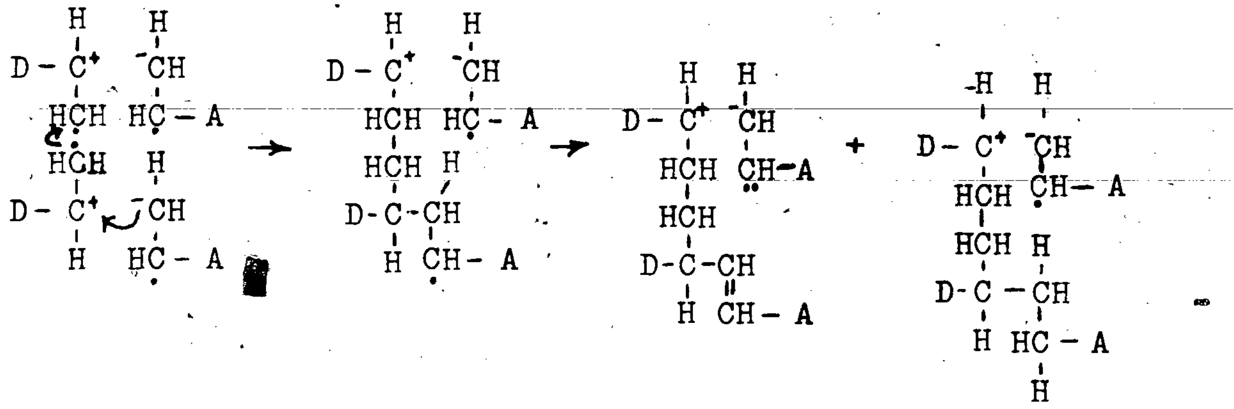




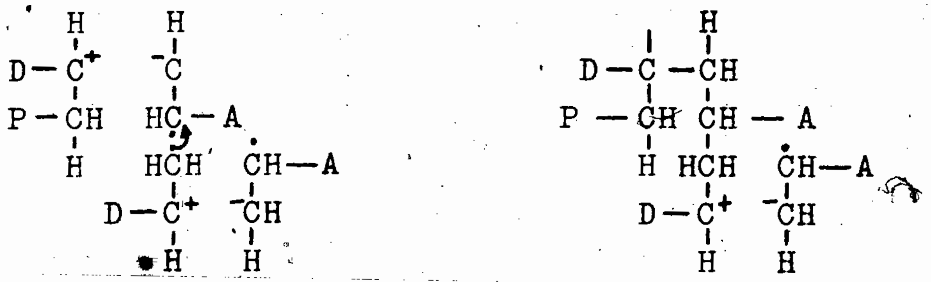
b) Spontaneous Initiation





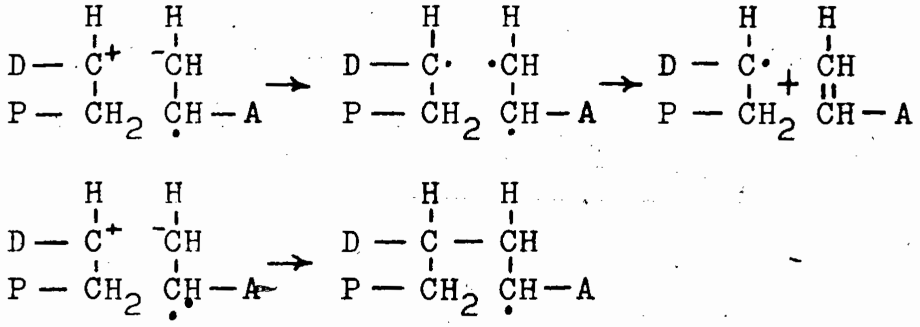


Propagation



$$P - (DA)_x D^{+\cdot}\bar{\cdot}A \quad + \quad [D^{\cdot +}\bar{\cdot}A] \longrightarrow P - (DA)_x DAD^{+\cdot}\bar{\cdot}A$$

Termination

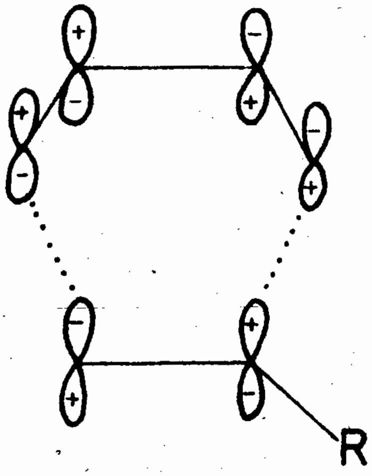


The above mechanisms involve much speculation and several steps are subject to question (loss of hydrid ion in radical initiation). Thus these mechanisms are presented here as Gaylord's proposals and are not wholly supported by this author.

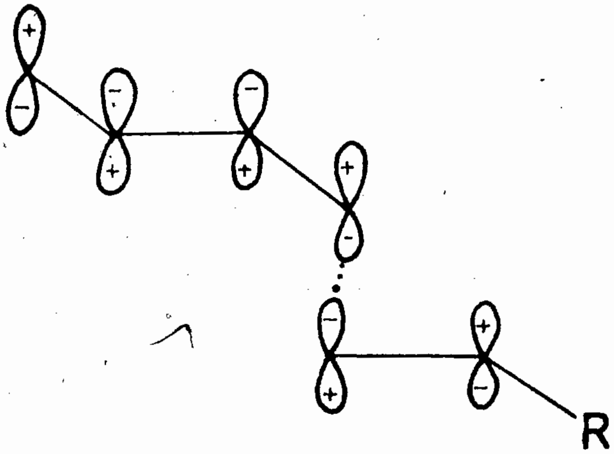
Gaylord (102) followed the intrinsic viscosity changes in the complexed alternating copolymerization of methyl methacrylate and styrene with ethylaluminum sesquichloride and found that in the initial stages of reaction an increasing molecular weight occurred. Later stages of reaction showed a constant molecular weight. This observation required a modification to the original donor-acceptor mechanism. Gaylord (42, 103, 105) proposed that the donor-acceptor complexes arranged themselves into matrixes, the size of which depended on the original concentration of the complexes. Once arranged in an ordered array, these complexes would polymerize into a product of molecular weight dependent on the matrix size. These copolymer molecules, with Lewis acid complexing agent still attached, would act as complexing sites for the production of new donor-acceptor complexes. These new complexes would then polymerize to copolymer of constant molecular weight. When acrylonitrile was substituted for methyl methacrylate (106), however, the molecular weight remained unchanged with conversion; a contrast to the methyl methacrylate situation.

Considerable attention has been devoted to examining the similarities of the Diels-Alder cycloaddition reaction to complexed alternating copolymerization (107, 108, 109). Similar features are shown by the diene-olefin transition state of the Diels-Alder reaction to that of the donor-acceptor complex before polymerization.

The Diels-Alder reaction is envisaged as a concerted cycloaddition of diene and olefin in ground state electronic configurations (110). Under these conditions, orbital symmetries are conducive to electron flow between the diene to the olefin such that the flow occurs from the highest occupied molecular orbital of the diene (HOMO) to the lowest unoccupied orbital of the olefin (LUMO) (111).



If, however, the diene is considered in the excited state, where the HOMO now has the symmetry of Ψ_3 orbital, this situation cannot occur and head to tail addition can only occur.



This situation leads to copolymer and is suggested by the trans structure of alternating butadiene acrylonitrile copolymer produced in the presence of ethylaluminum sesquichloride (108). Several esr investigations have been performed on complexed alternating copolymerizations (98, 108) and in no instances have signals from a charge transfer or donor-acceptor complex radical been seen. Studies (112-114) of the initiation step in these processes report the formation of radicals of the type:

$$\dot{D} - \mathrm{AlX}_3$$

where D = donor molecule; X = C_2H_5 or Cl.

Recent esr studies by Kuran _et al_ on the complexed alternating copolymerization of acrylonitrile with propylene, and acrylonitrile with butadiene in the presence of aluminum alkyls indicated that free radicals can be provided from a alkyl aluminum-acrylonitrile complex. These radicals are seen as both of alkyl and alkyl aluminum complex constitution (115).

$$\mathrm{AN} \;.....\; \underset{\substack{|\\ \mathrm{R}}}{\mathrm{AlCl}_2} \longrightarrow \mathrm{R}^{\cdot} + \mathrm{AN} \;.....\; \dot{\mathrm{A}}\mathrm{lCl}_2$$

With methylaluminum dichloride, the bond dissociation energy for the Al-C bond is high and the population of radicals from the alkyl aluminum-acrylonitrile complex is low. Optimum properties are shown by the ethyl and isobutyl aluminum alkyls, where the Al-C bond energies are sufficiently low (0.8 kcal lower than the methyl case) to provide radicals of high reactivity.

It is generally agreed that the mechanism of complexed alternating copolymerization involves radical species. Thus the rates of copolymerization increase when conventional radical initiators (peroxy and azo compounds) are added (65, 116). Of particular interest is the observation that α,α'azobisisobutyronitrile accelerates these processes even at temperatures below 40°C (101). A possible azo compound-solvent and/or complexing agent, monomer interaction has been examined. Where aluminum alkyls are present, decomposition increases are seen (101). The effect of zinc chloride on the decomposition is unclear with some authors suggesting a rate increase (29), while others indicate no change (83).

I.11 THE PARTICIPATION OF DONOR-ACCEPTOR COMPLEXES AND DEVIATIONS FROM AN ALTERNATING PRODUCT

The spontaneous formation of donor-acceptor complexes is shown to occur in a number of copolymerization systems (20-23, 33, 117-119). When Lewis acids are used in complexed alternating copolymerization, only limited evidence is seen for donor-acceptor interaction. Both UV and NMR data suggest the existence of these complexes in some alternating copolymerization systems (66, 82, 120, 121), while no evidence is seen in others (38, 40, 122). Thus sensitive calorimetric (38) and cryoscopic (40) techniques have failed to indicate the presence of donor-acceptor complexes in the complexed acrylonitrile-hexene and complexed methyl acrylate-styrene systems respectively.

Most complexed comonomer systems that yield alternating product show little evidence for donor-acceptor complexes and if these complexes exist, they must be present in extremely small concentrations. The observed copolymerization reaction would therefore require a very high reactivity between these complexes. High reactivity of loosely bound charge transfer complexes is unlikely (36, 40), consequently the existence of donor-acceptor complexes as intermediates in these reactions is questionable (21, 36). As indicated previously, many complexed systems yield 1:1 alternating copolymers irrespective of monomer feed ratios. This is not universally true, however, and some examples show deviations from 1:1 product composition. When acrylonitrile and styrene are copolymerized at high temperatures or high conversions in the presence of zinc chloride, a non-equimolar polymer of high acrylonitrile content is obtained (69). Similar results are shown in acrylonitrile diene zinc chloride systems (51, 123).

To explain these results, Gaylord (45, 124) suggests the existence of two types of donor-acceptor complexes; a complex incorporating both comonomers and a complex containing two molecules of the same monomer.

$$\mathrm{XA} + \mathrm{D} \longrightarrow \mathrm{XAD}$$
$$\mathrm{XA} + \mathrm{A} \longrightarrow \mathrm{XAA}$$

where X = complexing agent, A = acceptor monomer and D = donor monomer. Thus the participation of XAA in the chain propagation would result in an acceptor rich copolymer product.

When acrylonitrile and styrene are copolymerized in the presence of ethylaluminum sesquichloride (49, 125), styrene rich copolymer is obtained in conjunction with alternating 1:1 copolymer. In this case, dissociation of the terminal complex is involved and gives rise to the conventional addition of comonomer.

$$(\mathrm{DA})_n\,\overset{+}{\mathrm{D}}\cdot \quad \cdot\overset{-}{\mathrm{A}}\,\text{\_ \_ \_}\,\mathrm{X} \longrightarrow (\mathrm{DA})_n\,\overset{+}{\mathrm{D}}\cdot + \cdot\overset{-}{\mathrm{A}}\,\text{\_ \_ \_}\,\mathrm{X}$$
$$(\mathrm{DA})_n\,\overset{+}{\mathrm{D}}\cdot + \mathrm{D} \longrightarrow (\mathrm{DA})_n\,\overset{+}{\mathrm{D}}\mathrm{D}\cdot$$
$$(\mathrm{DA})_n\,\overset{+}{\mathrm{D}}\cdot + \mathrm{A} \longrightarrow (\mathrm{DA})_n\,\overset{+}{\mathrm{D}}\mathrm{A}\cdot$$

I.12 CHAIN TRANSFER

Chain transfer agents normally active in conventional radical polymerizations (126) have little or no effect on complexing alternating copolymerizations (23, 40, 54, 93, 118, 127). In the copolymerization of methyl acrylate and styrene by ethylaluminum sesquichloride, the molecular weight of the copolymer is hardly affected by the addition of carbon tetrachloride and no chlorine is detected in the product (94). Gaylord (54), also, observed the same phenomenon in the copolymerization of acrylonitrile and styrene with ethyl aluminum sesquichloride. Furukawa et al (43) found that no chain transfer to carbon tetrachloride took place in the acrylonitrile, butadiene, ethyl aluminum dichloride-vanadyl trichloride system. A similar phenomenon has, also, been seen in conventional alternating copolymerizations (94).

Tsuchida and Tomono (23) examined the copolymerization of maleic anhydride and styrene and found that the molecular weight of the product could be lowered by strong donor or acceptor compounds such as N,N-dimethyl aniline or naphthalene. These compounds were described as chain transfer agents. Funt and Rhodes (128) investigated the effects of dimethyl analine on the acrylonitrile, styrene zinc bromide system. These researchers found evidence for degradative chain transfer and suggested a competition between dimethyl analine and acrylonitrile for zinc bromide. As dimethyl analine is a much stronger complexing agent than acrylonitrile, preferential complexation occurs between this compound and zinc bromide. This results in a decrease of acrylonitrile complex concentration and reduces the reaction rate. Molecular weight reductions are attributed to chain transfer to uncomplexed dimethyl aniline. Consistent with this approach is the observation that copolymerization is inhibited by polar solvents such as ethers, amides and esters (23, 119). When small concentrations of these materials are added to complexed alternating copolymerizations, slight rate increases are shown (129). Reasons for this are not clear.

I.13 KINETICS OF COMPLEXED ALTERNATING COPOLYMERIZATIONS

Although a large number of reports have been published concerning complexed alternating copolymerization, few of these investigations involve kinetic studies of these processes.

Several papers (35, 98) have provided reactivity ratio values for complexed alternating copolymerization derived from conventional copolymerization kinetics. Some studies, although inconclusive in themselves, do indicate a number of interesting characteristics.

When monomers are in excess of the complexing agent, the conversion vs time curves show two distinctly different regions, the first being curved and the second linear. Studies of the methyl methacrylate styrene ethyl aluminum sesquichloride system indicates the initial non-linear portion of the polymerization could not be distinguished between a first and second order process (55, 102). Thus no rate equation could be provided by these studies.

When the rate of copolymerization of a monomer pair is followed as a function of the monomer feed composition, the rate is found to be maximum at equimolar feed ratios (22, 35, 55, 72, 106, 130, 131). This is explained by both the concept of homopolymerization of donor-acceptor complex monomer (often called the Bernoullian model) (108) and the alternate addition of complexed monomer of enhanced reactivity (the Markovian model) (40). Assuming none of the reaction components enters the polymerization as a single particle and that all components form donor-acceptor complexes, the maximum concentration of these complexes will occur at equimolar feeds. Thus excess of either monomer brings about a decrease in donor-acceptor complex concentration and a lower rate is observed.

The occurrence of a rate maximum at 1:1 feed ratios is not necessarily true for the Markovian model, since the monomer ratio M_1/M_2 for a maximum rate is given by k_{12}/k_{21}. The rate constants k_{12} and k_{21} are rate constants for the addition of M_1 to M_2 and M_2 to M_1 (108). It can be argued, however, that both cross propagation rates are equally enhanced in the Markovian mechanism, hence a rate maximum at or near 1:1 feed ratios is seen.

Activation energies of some complexed alternating copolymerizations have been measured. In some cases, E_a is found to be in the range of 10-15 Kcal/mole, slightly lower than the 15-20 Kcal/mole region for conventional radical copolymerizations (101). In other cases, E_a is found to be very small (29, 108).

I.14 NATURE AND SCOPE OF THIS INVESTIGATION

A variety of mechanisms has been suggested for complexed alternating copolymerization and the present literature, although reasonably extensive, has failed to unequivocally support any one of these proposals. Studies to date have been largely focussed on the attainment of maximum yield, investigations of physical properties, the NMR investigation of structural features and the alternation of mer units in the polymer. No detailed studies involving molecular weight distribution and reaction kinetics have been published. Measurements of molecular weights have been performed by viscosity techniques and kinetic studies have centered mainly on reactivity ratio values.

Molecular weight dependence upon rate of reaction can serve to distinguish different polymerization mechanisms; for example, free radical reactions show a broad molecular weight distribution and an inverse dependence between rate and molecular weight. A reaction involving a continuous growth of "living" centers will show a narrow molecular weight distribution and when these "living" centers are terminated simultaneously, an increased molecular weight with time or conversion is shown. Thus informative and illuminating data can be obtained by examining molecular weight features and reaction kinetics of polymerization reactions.

Much of the complication that exists in the literature of complexed alternating copolymerization is a consequence of the large variety of unrelated systems and conditions studied. Thus a study involving similar relatable systems maintaining identical conditions has obvious advantages. In this research, simple, representative and related systems using common comonomers and conditions are compared by kinetic and molecular weight measurements.

The main objectives of this investigation are: (a) to study kinetic and molecular weight data from a variety of related complexed alternating copolymerization systems in order to select a mechanism consistent with these data; (b) to determine the molecular weight controlling features of these copolymerizations and relate these features to the overall mechanism, and (c) to re-examine some topics of ambiguity with the possible clarification of these issues as an ultimate goal.

II. EXPERIMENTAL METHODS

II.1 REAGENTS

II.1.1 MONOMERS

Methyl methacrylate (MMA) (Matheson), styrene (STY) (Eastman), isoprene (IP) (Matheson), acrylonitrile (AN) (Matheson), methacrylonitrile (MAN) (Matheson) and methylacrylate (MA) (Matheson) were dried by stirring with calcium hydride for 24 hours and distilled through a high efficiency spinning band column (1:1 collection ratio). The middle fraction (≈ 60%) was used in the experiments. Methyl chloroacrylate (MCA) (Polysciences Inc.) and chloroacrylonitrile (CAN) (Polysciences Inc.) were stirred with molecular sieve (3A) for 24 hours, then filtered and distilled under reduced pressure in a micro distillation apparatus. The middle fraction (≈ 50%) was retained for the experiments.

II.1.2 OTHER REAGENTS

α'α azobisisobutyronitrile (AIBN) (Baker) was recrystallized twice from diethyl ether, then dried *in vacuo* and stored in a freezer until used. Zinc chloride (Allied Chemical, A.C.S. Reagent) was dehydrated by heating at 120°C in a vacuum desiccator for 72 hours. The anhydrous salt was stored in tightly stoppered vials until needed. Diethylaluminum chloride (DEAC) and ethylaluminum sesquichloride (EASC) (Texas Alkyls) were obtained as a 25%

toluene solution and were used as received. Polyphosphoric acid (Matheson, practical grade) was used as received. Propionitrile (Aldrich, reagent grade) was stirred over molecular sieve (3A) for 24 hours, then distilled in a micro distillation apparatus and the center fraction ($\approx$ 50%) retained for the experiments.

II.1.3 SOLVENTS

Toluene (Fisher, spectrograde) and tetrahydrofuran (Fisher, histological grade) were refluxed over and distilled from lithium aluminum hydride. Tetrahydrofuran used for gel permeation chromatography (Fisher, histological grade) was used as received.

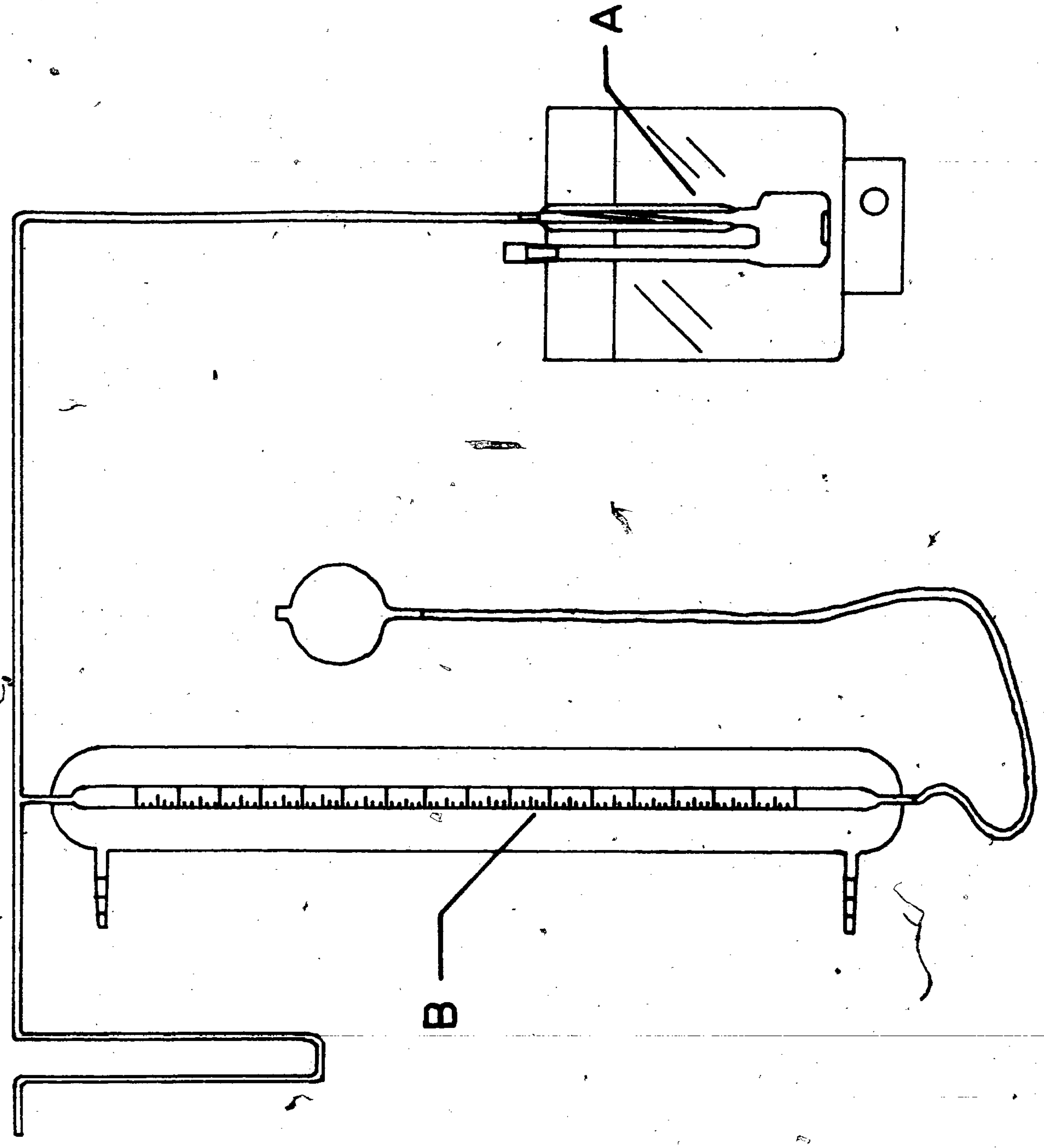
II.2 INITIATOR DECOMPOSITION

The decomposition of AIBN was followed by measuring evolved nitrogen gas on the apparatus described in figure (5). The decomposition cell was thermostated at $70^{\circ}C \pm 0.2^{\circ}C$, while the gas manometer was maintained at $25^{\circ}C \pm 0.1^{\circ}C$. Measured gas volumes were corrected for solvent vapour pressure and converted to standard conditions. All AIBN solutions were presaturated with nitrogen prior to decomposition measurements.

Figure 5 APPARATUS FOR MEASURING THE EVOLVED NITROGEN FROM THE DECOMPOSITION OF AIBN.

A - THERMOSTATED DECOMPOSITION CELL

B - THERMOSTATED MERCURY MANOMETER


A
B

II.3 POLYMERIZATION APPARATUS

Cells used for most polymerizations are shown in figure (6). Where rate studies were conducted, cells described in figure (7) were used.

II.4 POLYMERIZATION PROCEDURE

The reagents were added to the polymerization cells in the following order: acrylic monomer, toluene solvent, and complexing agent. A blanket of dry argon was then applied after which the cell and contents were cooled to 0°C. Styrene was then added and the resulting solution degassed twice. Polymerizations were normally conducted under vacuum. Polymerizations were terminated by tipping the polymerization batch into a large excess of acidified (HCl) methanol. The polymer was then filtered, dried and reprecipitated from THF. The reprecipitated polymer was shaken with cyclohexane and dried in a vacuum desiccator for 12 hours. When rate studies were performed, the cell shown in figure (7) was used as follows: the side arm was stoppered with a screw cap (D) and the reagent added. After degassing was completed, dry argon was introduced into the cell. A slight positive pressure of argon was maintained and the syringe assembly (A,B,C) was attached. Samples were withdrawn at predetermined intervals by drawing solution into the syringe (A), then withdrawing samples through the rubber band septum (B). The sample was then precipitated in acidified methanol and purified as described above.

Figure 6 POLYMERIZATION CELL.

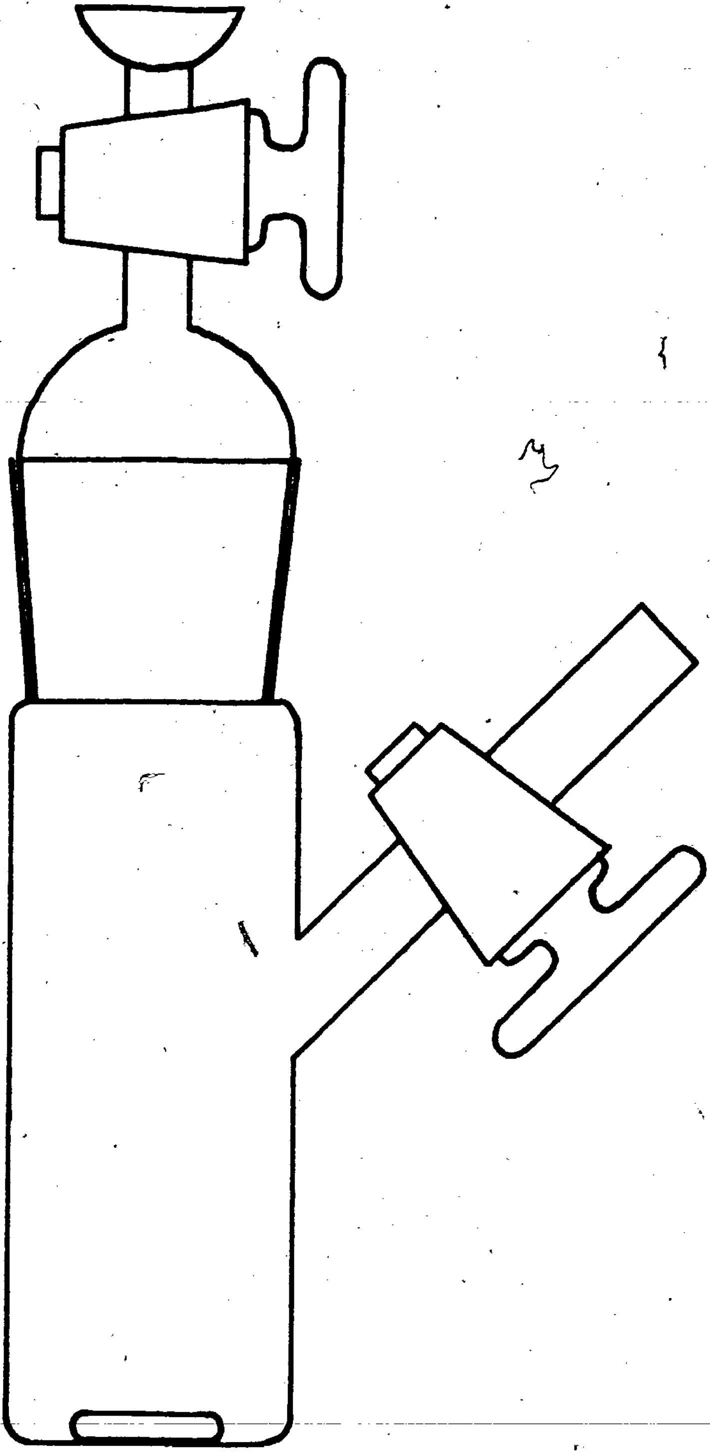


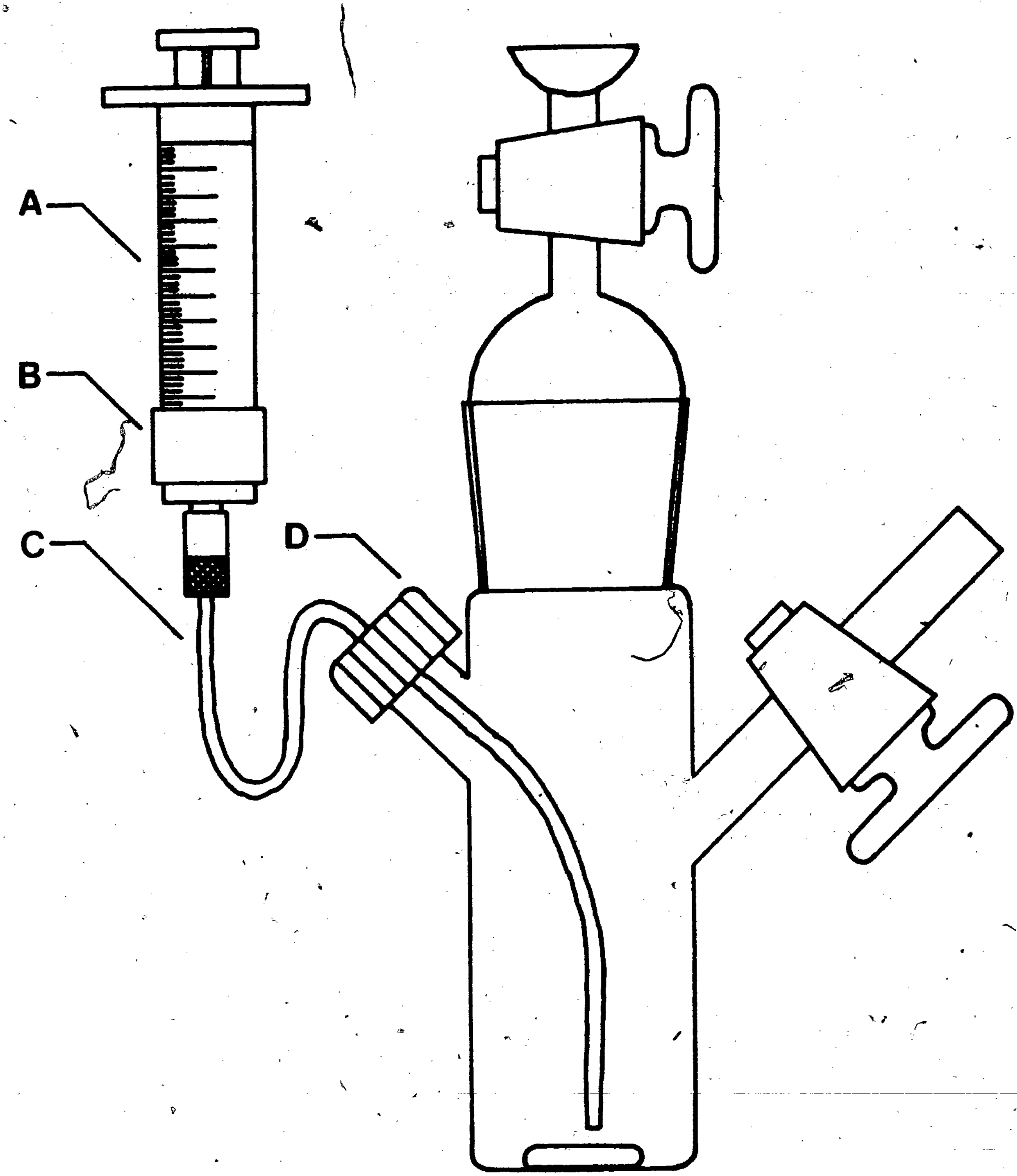
Figure 7 POLYMERIZATION CELL WITH SAMPLE WITHDRAWING SIDE ARM.

A - WITHDRAWING SYRINGE

B - RUBBER BAND SEPTUM

C - TEFLON TUBING

D - SCREW CAP GASKET SEAL


A
B
C
D

II.5 CARBON-14 LABEL EXPERIMENTS

Styrene [μ - ^{14}C] (ICN Inc.) was added to a methyl methacrylate-styrene-diethyl aluminum chloride polymerization to give a product with a total specific activity of 2000 CPM/mg. Samples were polymerized for 2.75 hours, precipitated in methanol, purified and dried *in vacuo*. A 8 mg. sample was inserted into the gel permeation chromatograph and 5 ml. aliquots containing approximately 0-1.5 mg. of polymer were removed from the counting siphon. These aliquots were diluted with 15 ml. of a toluene scintillation cocktail containing 4g./1. of 2,5-diphenyloxazole (PPO) and 50 mg./1. of 1,4-bis-(5-phenyloxazol-2-yl)-benzene (POPOP). Counting was done on a Beckman model LS-200B liquid scintillation counter set at a count interval of 20 minutes and 0.5% preset error.

II.6 POLYMER CHARACTERIZATION

II.6.1 ELEMENTAL ANALYSIS

Elemental analysis of the copolymer for carbon hydrogen and nitrogen were performed on a Perkin Elmer elemental analysis instrument model M240. The copolymer composition was calculated on the percentage nitrogen, where nitrogen was present in the copolymer. Otherwise, carbon analysis was used. Repeated analysis of identical samples showed a ± 2% uncertainty of copolymer composition, when based on nitrogen and a ± 6% uncertainty based on carbon.

II.6.2 INFRARED

Infrared spectroscopic measurements were performed on a Perkin Elmer 457 infrared spectrometer using polymer films cast on sodium chloride discs. Chloroform was used as solvent; spectra of alternating and random copolymer used for comparison are shown in figures (8-12). Infrared spectra of the methacrylonitrile-styrene and methyl methacrylate-isoprene copolymers were obtained in this study and were identified by elemental analysis.

II.6.3 NMR SPECTROSCOPY

The nuclear magnetic resonance spectra of alternating and random copolymer were obtained using a Varian A-56/60A spectrometer. Deuterated chloroform solvent was used in all cases. The spectra of the prepared copolymers were compared with spectra of known alternating and non-alternating polymer described in the literature (42, 46, 67, 90, 92, 132). Comparison spectra are shown in figures (13-17). In addition, methyl methacrylate-styrene copolymer was examined by the chemical cyclization method of Gaylord (92) using polyphosphoric acid. Representative NMR spectra of polymer examined by this method are shown in figure (18).

Figure 8 IR SPECTRA OF METHYL ACRYLATE-STYRENE COPOLYMERS (42).

----- RANDOM

——— ALTERNATING

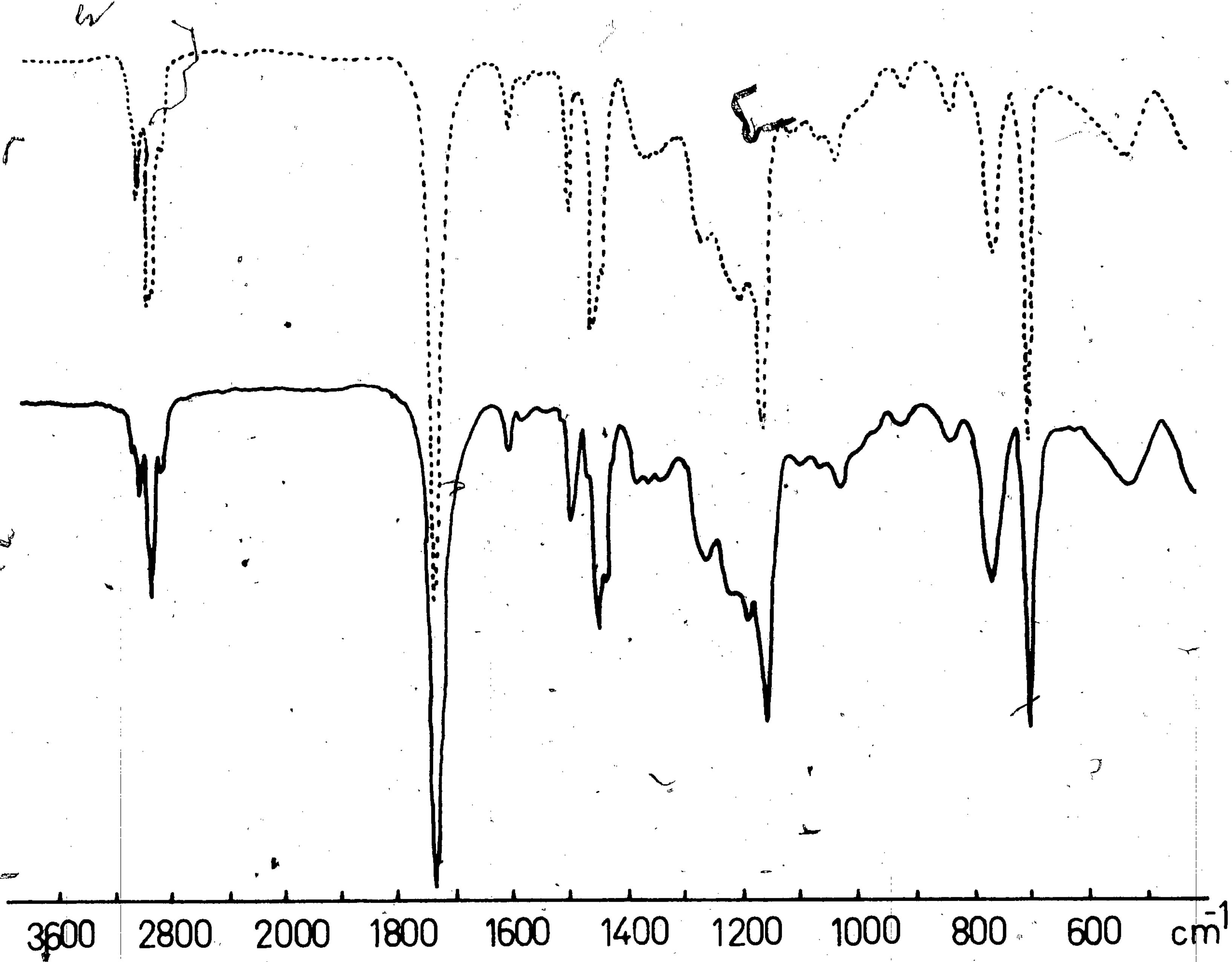

3600
2800
2000
1800
1600
1400
1200
1000
800
600
cm-1

Figure 9 IR SPECTRA OF METHYL METHACRYLATE-STYRENE COPOLYMERS (42).

----- RANDOM

——— ALTERNATING

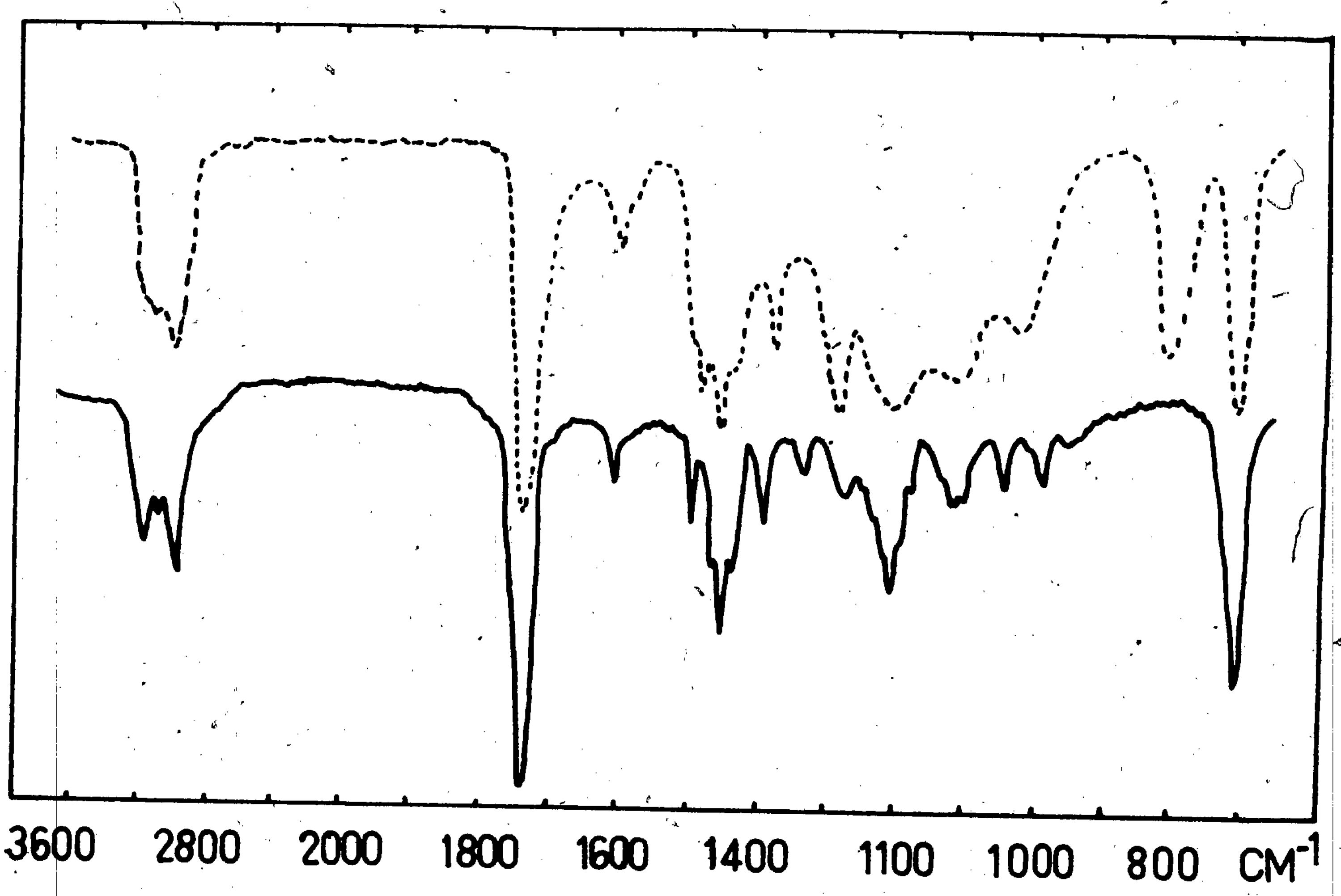

3600
2800
2000
1800
1600
1400
1100
1000
800
CM^{-1}

Figure 10 IR SPECTRA OF ACRYLONITRILE-STYRENE COPOLYMERS (42).

- - - - - RANDOM

——— ALTERNATING

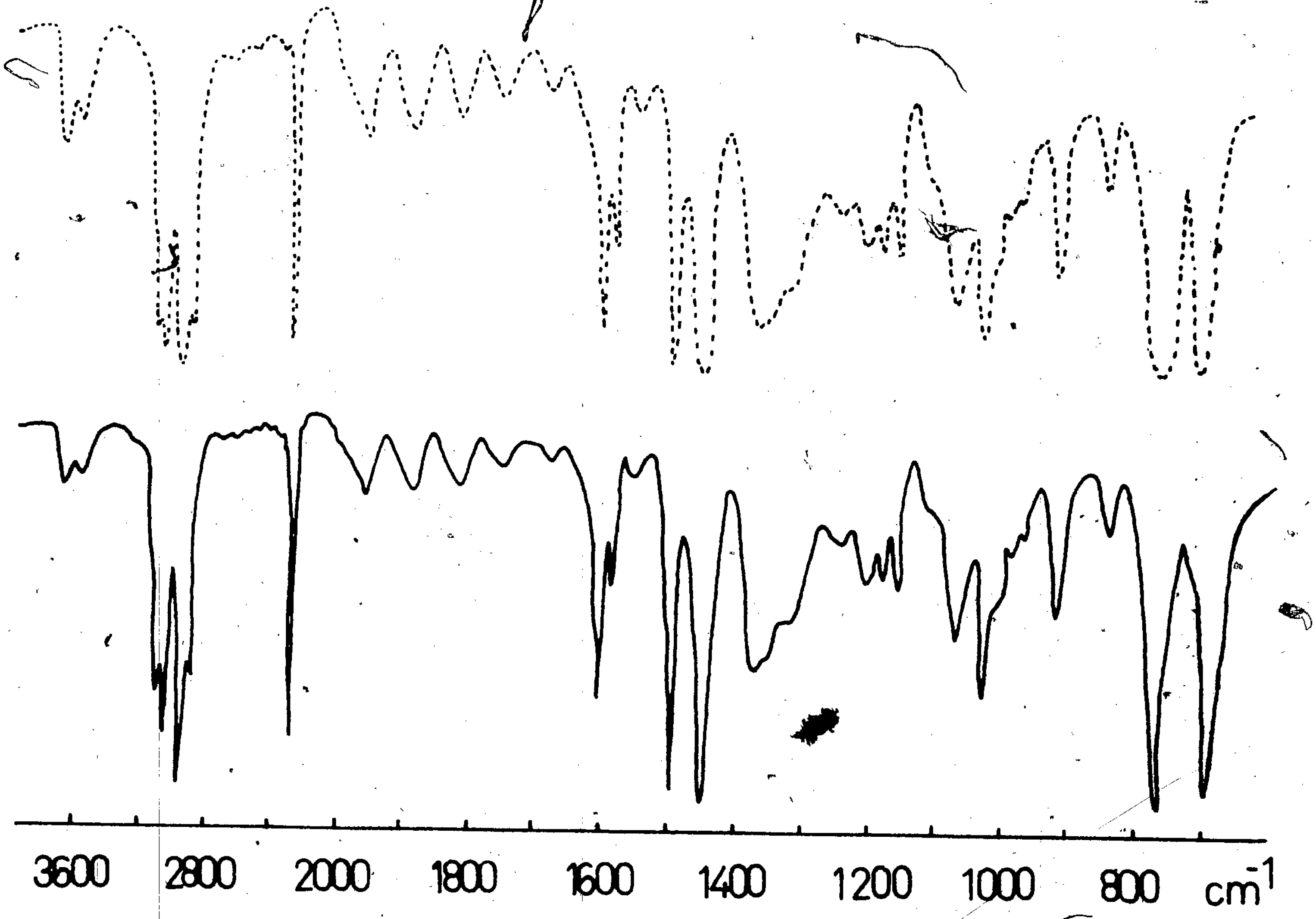

3600
2800
2000
1800
1600
1400
1200
1000
800
cm^{-1}

Figure 11 IR SPECTRA OF METHACRYLONITRILE-STYRENE COPOLYMER.

- - - - ALTERNATING

——— RANDOM

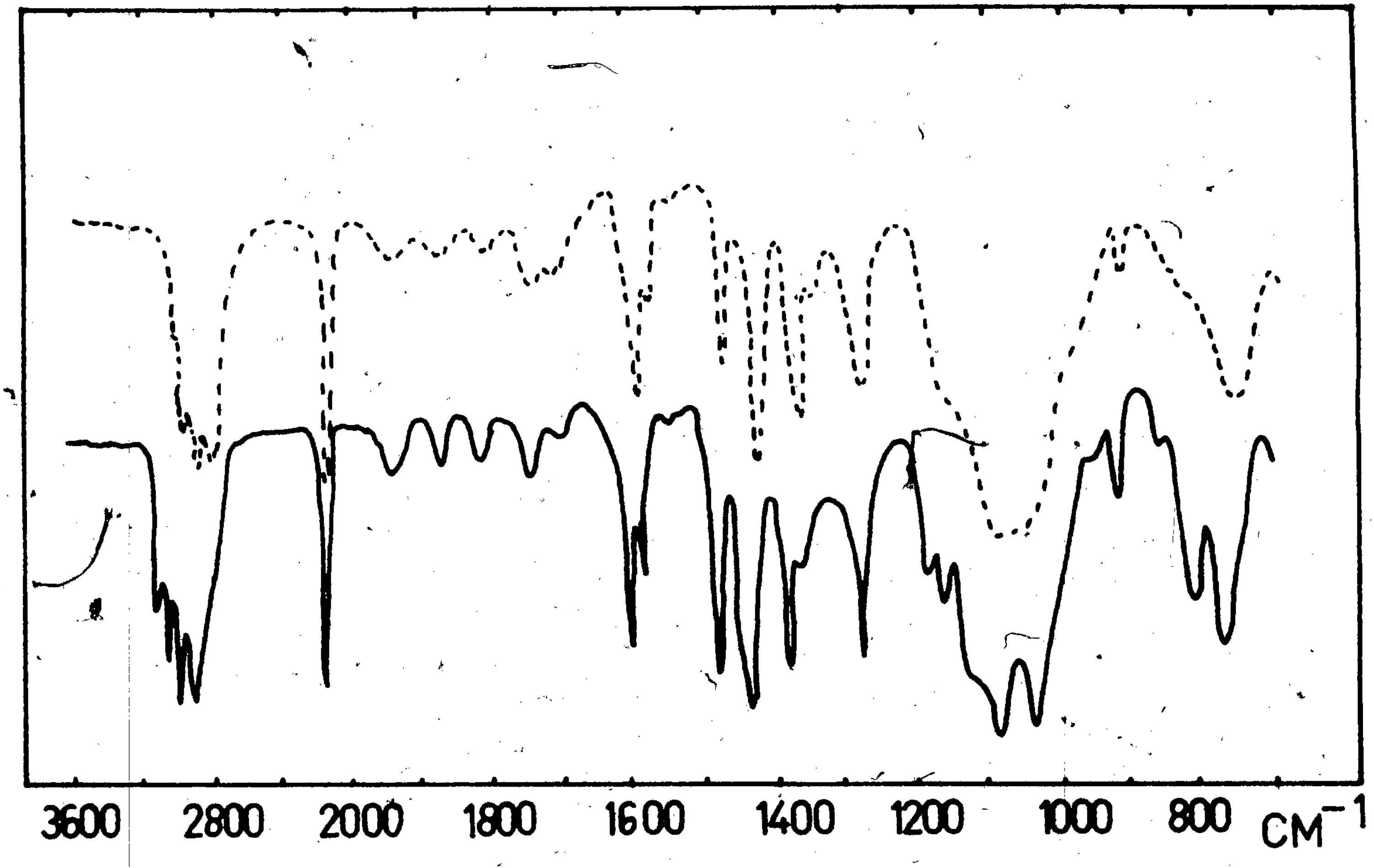

3600
2800
2000
1800
1600
1400
1200
1000
800
CM^{-1}

Figure 12 IR SPECTRA OF METHYL METHACRYLATE-ISOPRENE COPOLYMER.

----- RANDOM

——— ALTERNATING

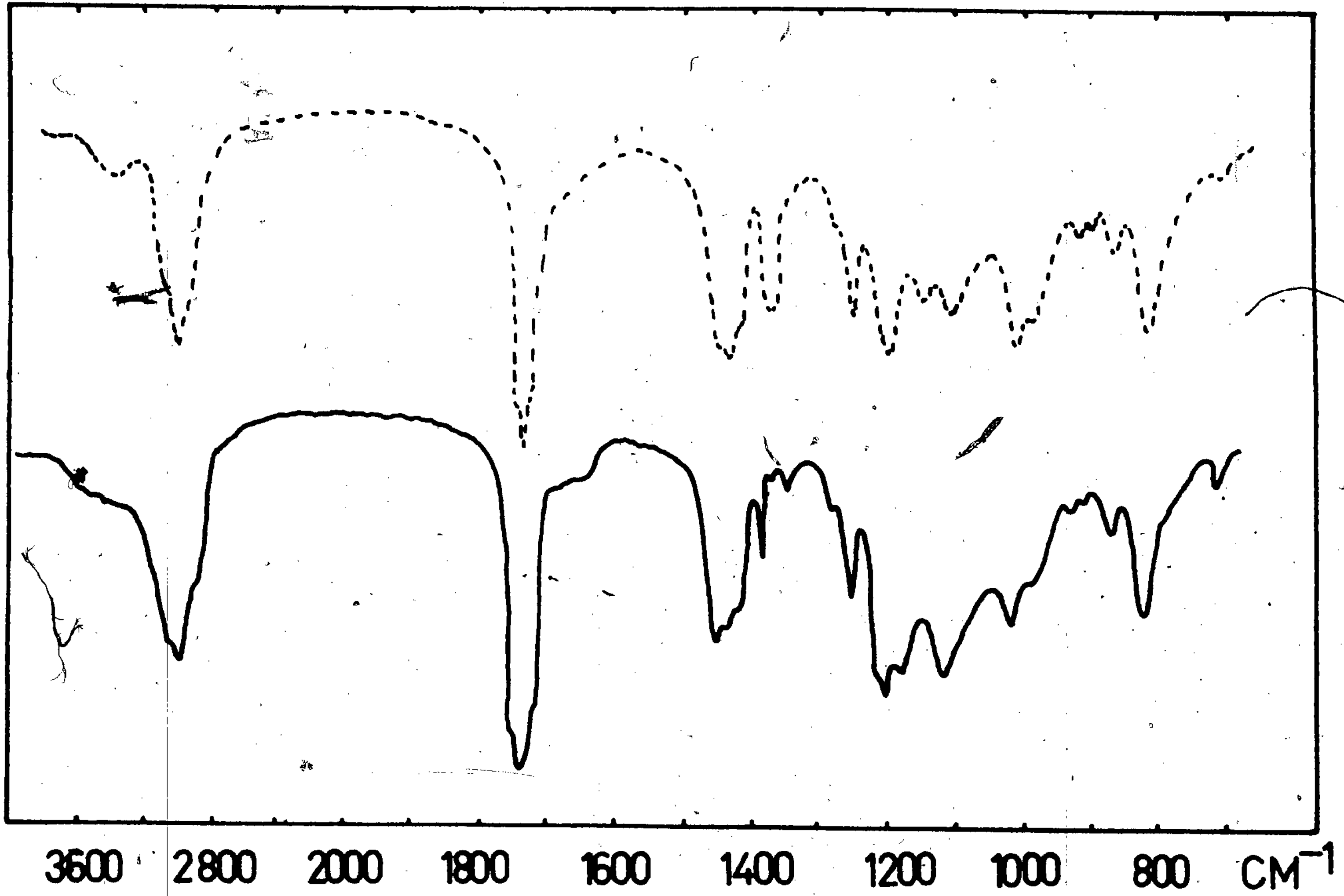

3600
2800
2000
1800
1600
1400
1200
1000
800
CM⁻¹

Figure 13 NMR SPECTRA OF METHYL ACRYLATE-STYRENE COPOLYMER (42).

A) ALTERNATING

B) RANDOM

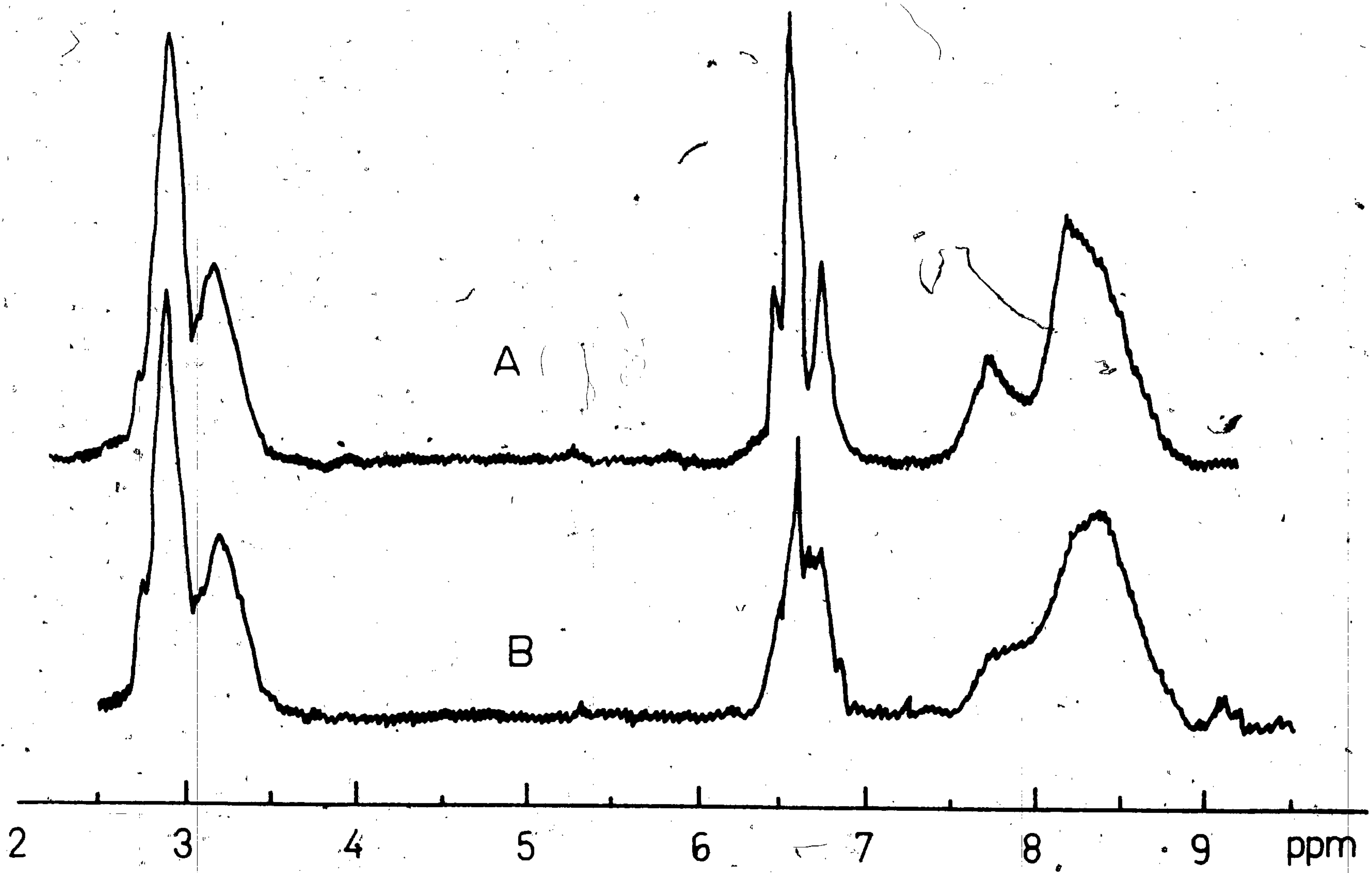

A
B
2
3
4
5
6
7
8
9
ppm

Figure 14 NMR SPECTRA OF METHYL METHACRYLATE-STYRENE COPOLYMER (42).

A) ALTERNATING

B) RANDOM

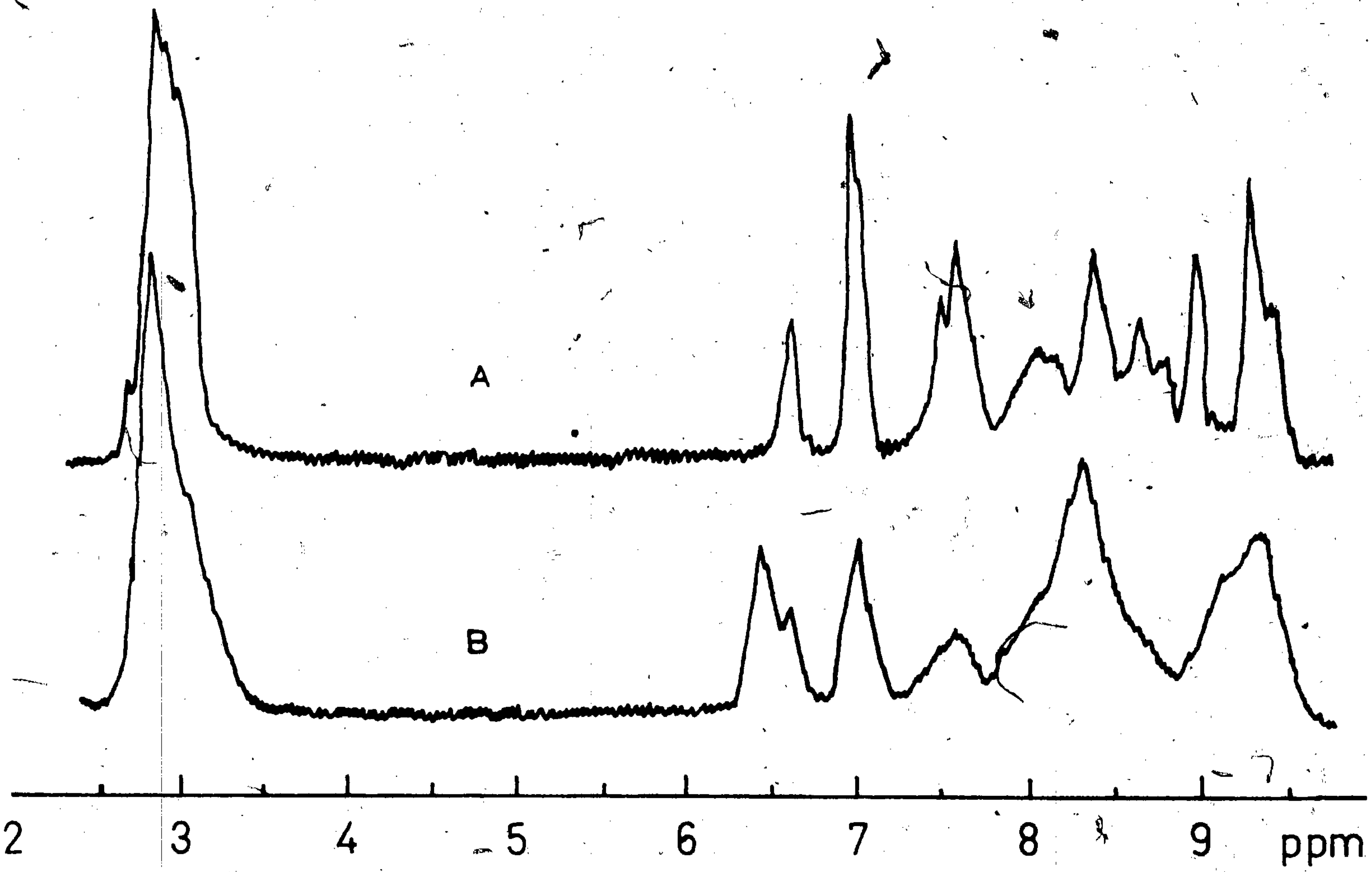

A
B
2
3
4
5
6
7
8
9
ppm

Figure 15 NMR SPECTRA OF STYRENE-ACRYLONITRILE COPOLYMER

A) RANDOM 65/35 (132)

B) ALTERNATING (90, 132)

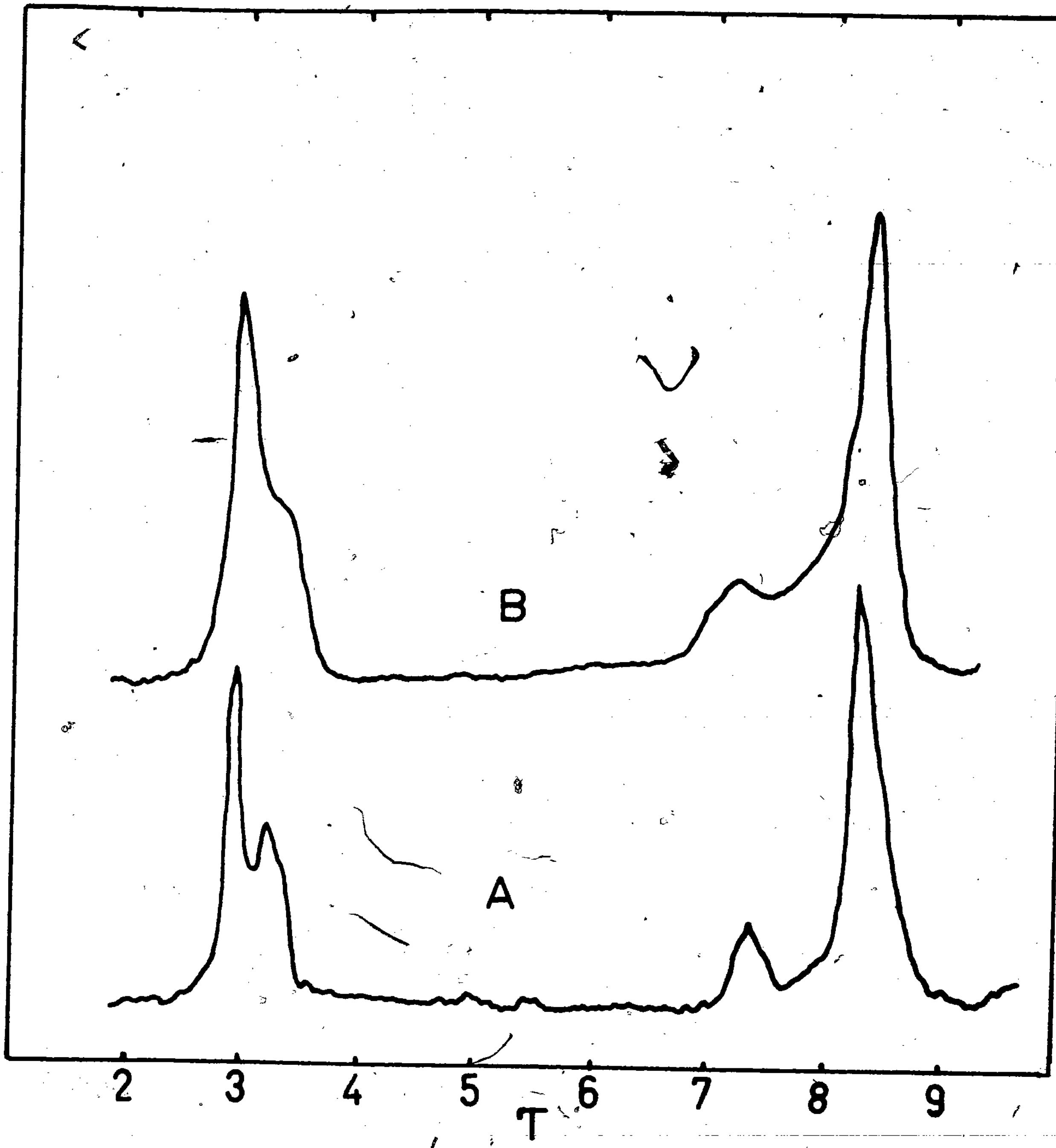

B
A
2
3
4
5
6
7
8
9
τ

Figure 16 NMR SPECTRA OF METHACRYLONITRILE-STYRENE COPOLYMER (46).

A) ALTERNATING

B) RANDOM

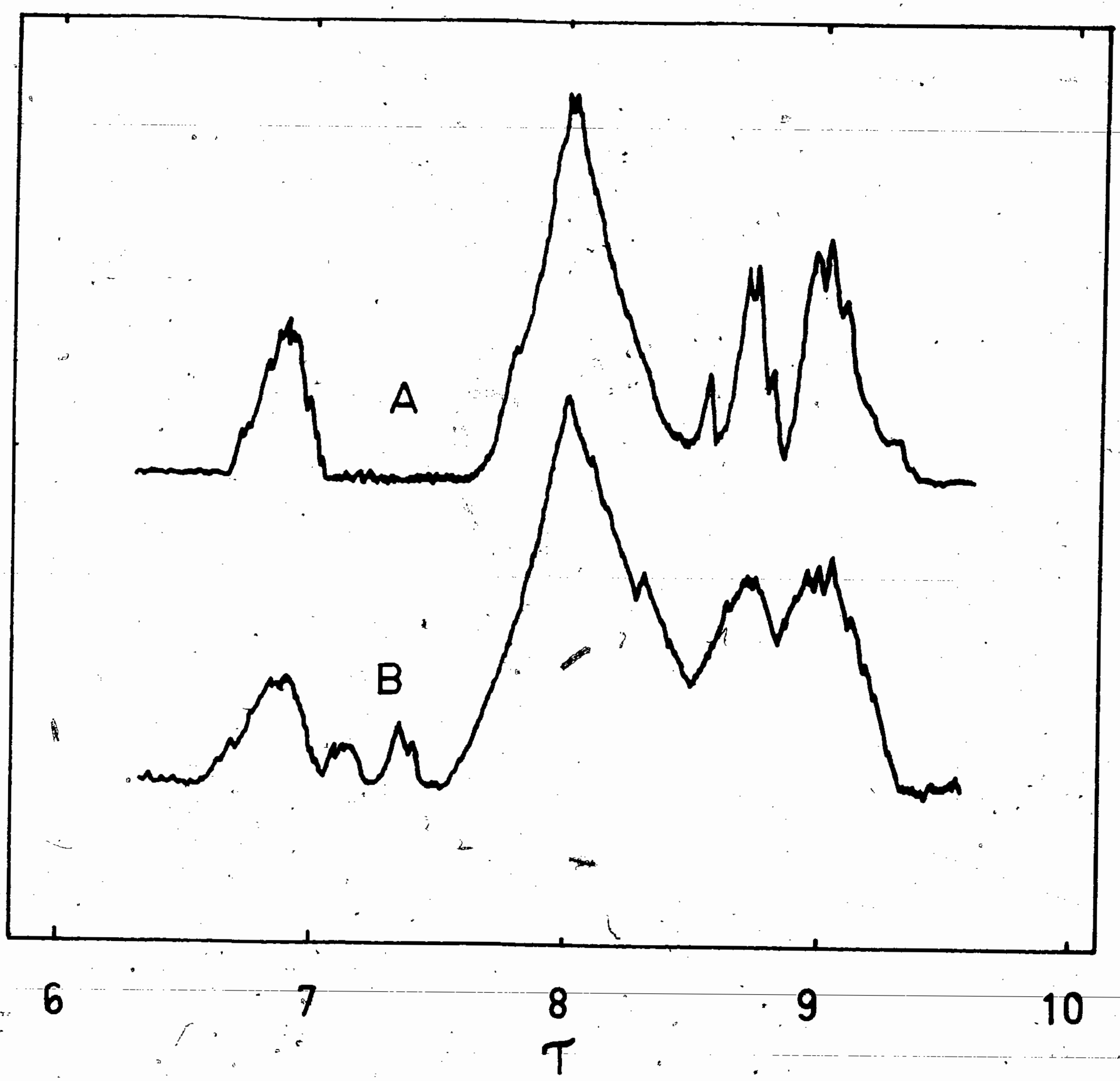

A
B
6
7
8
9
10
τ

Figure 17 NMR SPECTRA OF ISOPRENE-METHYL METHACRYLATE COPOLYMER (67).

A) RANDOM 50/50

B) ALTERNATING

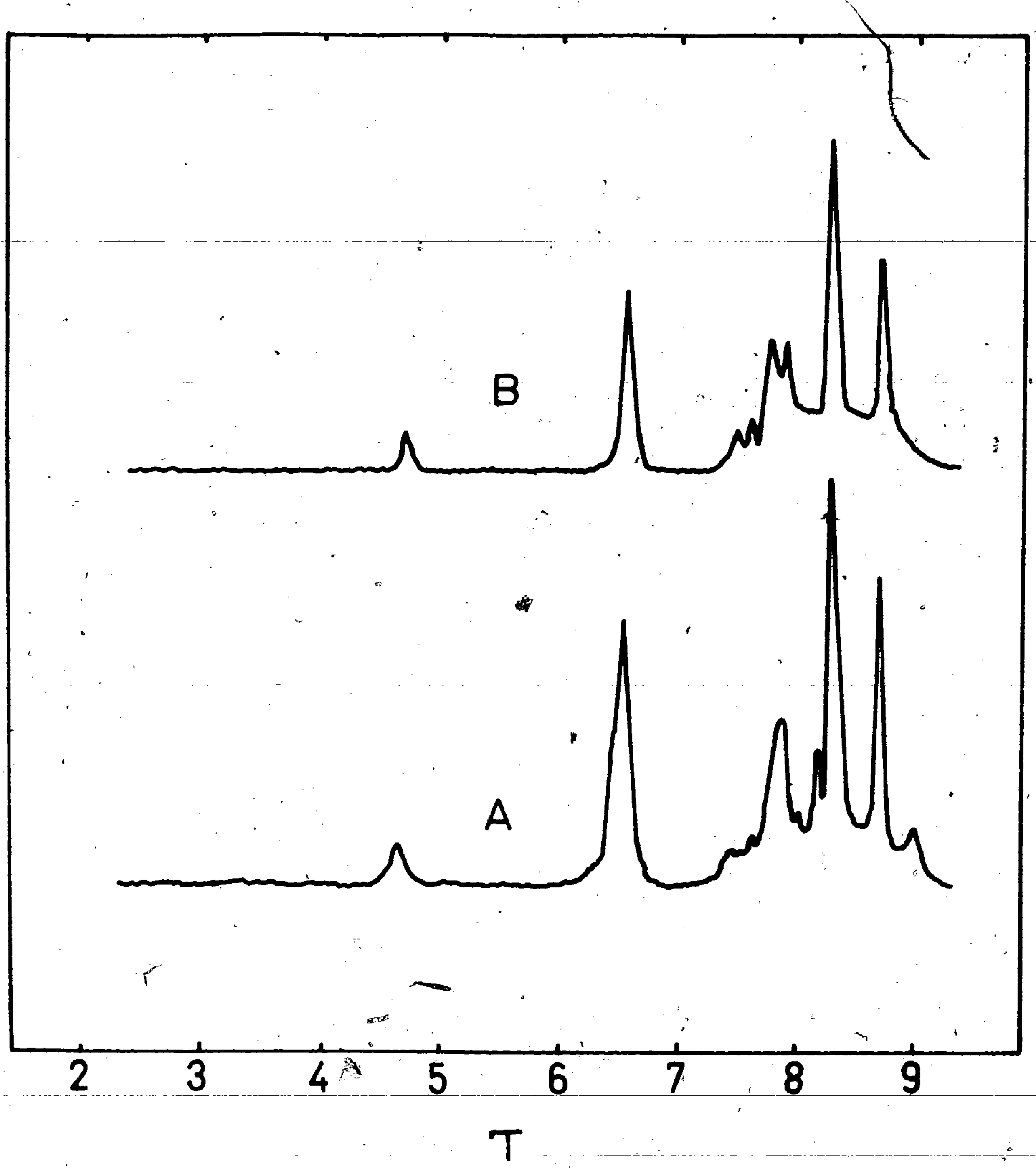
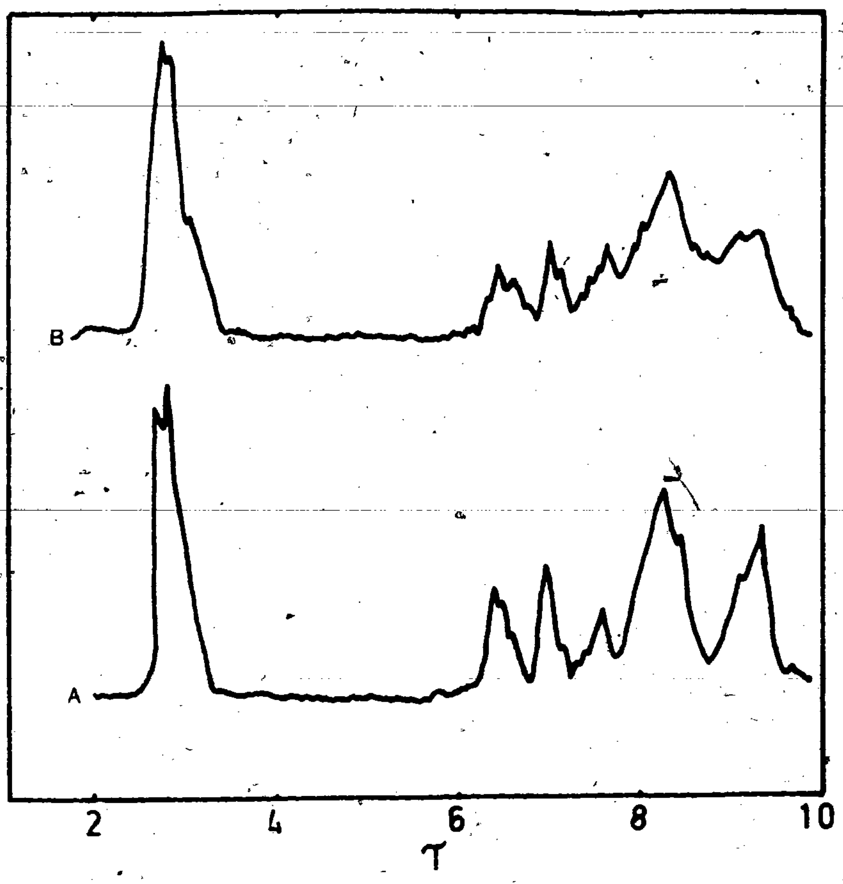

B
A
2
3
4
5
6
7
8
9
τ

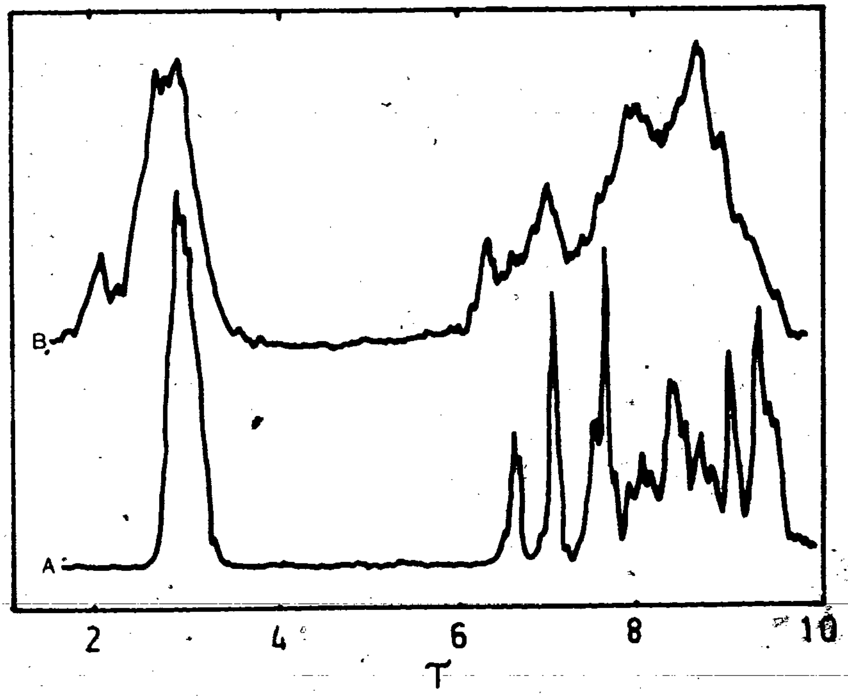
Figure 18 a) NMR SPECTRA OF (A) RANDOM MMA-STY COPOLYMER; (B) CYCLIZED RANDOM MMA-STY COPOLYMER (92).

b) NMR SPECTRA OF (A) ALTERNATING MMA-STY COPOLYMER; (B) CYCLIZED ALTERNATING MMA-STY COPOLYMER (92).

a



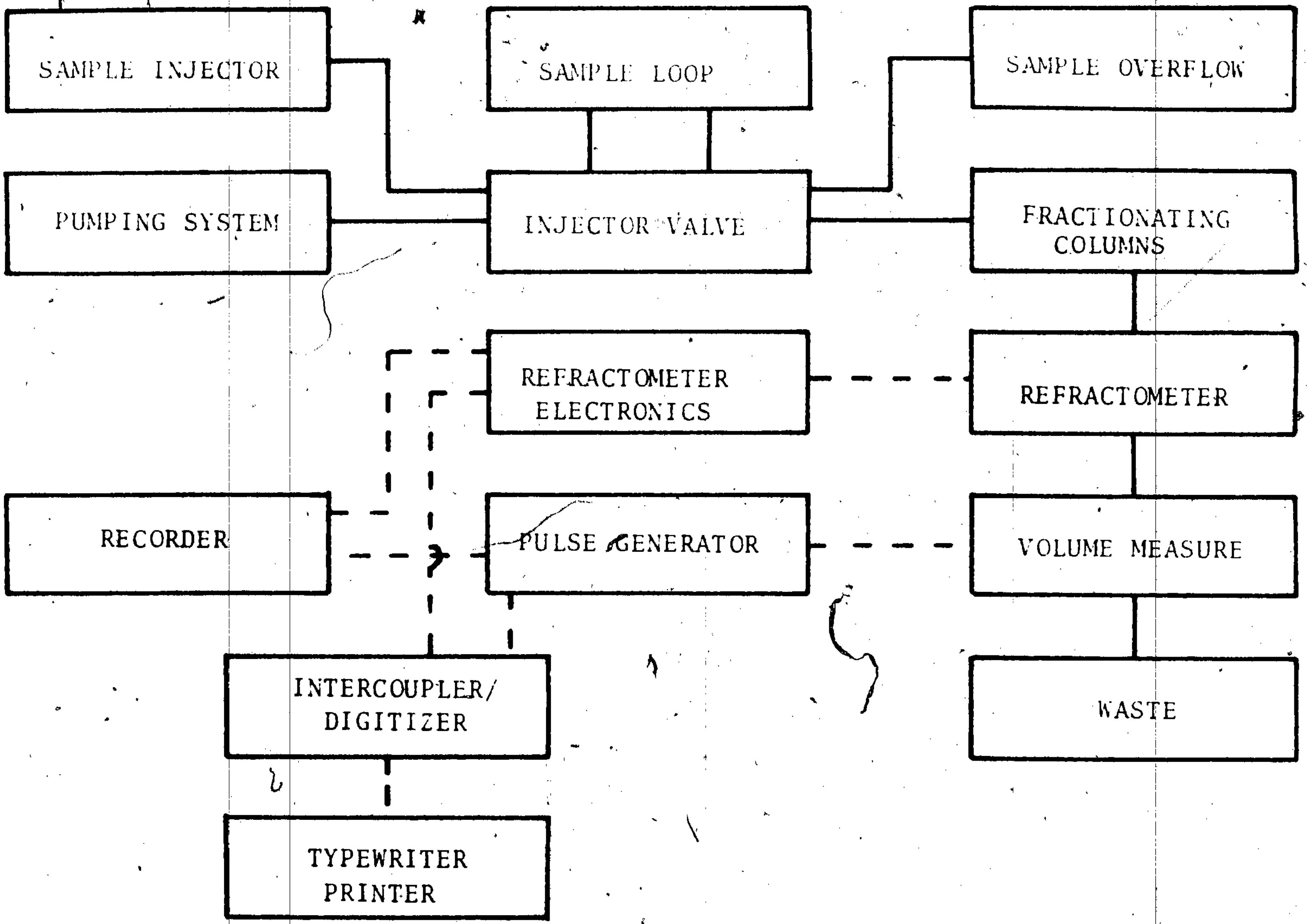
b



II.6.4 GEL PERMEATION CHROMATOGRAPHY

Molecular weight distributions were measured on a Waters Associates model 301A GPC/ALC instrument equipped with styragel columns of the following pore sizes: 2×10^3 A - 5×10^3 A, 2×10^3 A - 7×10^3 A, $2 \times (5 \times 10^3$ A - 1.5×10^4 A) and 1.5×10^4 A - 5×10^4 A. A unique data acquisition system was employed, where the data output from the chromatograph was split and fed simultaneously into a chart recorder and a Beckman model 311B intercoupler. The digital data from the intercoupler was recorded on a teletype model 3JE printer. A block diagram of the gel permeation apparatus is shown in figure (19). Molecular weights ($\overline{M}_n$ and $\overline{M}_w$) and polydispersities ($\overline{M}_w/\overline{M}_n$) were determined from the digital data using the University of Waterloo MWD I computer program according to Chang and Huang (132).

Figure 19 BLOCK DIAGRAM OF THE MODIFIED GEL PERMEATION APPARATUS USED TO OBTAIN MOLECULAR WEIGHT DATA.


SAMPLE INJECTOR
SAMPLE LOOP
SAMPLE OVERFLOW
PUMPING SYSTEM
INJECTOR VALVE
FRACTIONATING COLUMNS
REFRACTOMETER ELECTRONICS
REFRACTOMETER
RECORDER
PULSE GENERATOR
VOLUME MEASURE
INTERCOUPLER/ DIGITIZER
WASTE
TYPEWRITER PRINTER

III. RESULTS AND DISCUSSION

III.1 PRELIMINARY STUDIES

III.1.1 THE EFFECT OF ZINC CHLORIDE ON THE DECOMPOSITION OF α, α'AZOBISISOBUTYRONITRILE

Introduction

An interesting feature of complexed alternating copolymerization is the influence of radical initiation. It has been shown that the addition of either α, α'azobisisobutyronitrile (AIBN) or benzoyl peroxide increases the rate of reaction without influencing the copolymer-monomer relationship (28, 116).

Of interest is the observation that azobisisobutyronitrile catalysed reactions, progress with higher rates at temperatures where the spontaneous thermal rate of azobisisobutyronitrile decomposition is extremely small. Studies have shown that at 10°C the addition of azobisisobutyronitrile produces a significant rate increase in the copolymerization reaction with no detectable evolution of nitrogen (101).

A possible explanation of these observations is increases in azobisisobutyronitrile decomposition due to interactions with other components of the copolymerization solution. Changes in solvent have little effect on the rate of azobisisobutyronitrile decomposition (134). The addition of some transition metal complexes increased the rate of decomposition (135, 136), whereas the addition of lithium salts to radical polymerizations initiated by azobisisobutyronitrile shows no change in overall rate (97).

The effects of both aluminum alkyls and zinc chloride on azobisisobutyronitrile decomposition in alternating copolymerization have been studied. Gaylord et al (137) found an increased rate of azobisisobutyronitrile decomposition in the presence of ethylaluminum sesquichloride, methylmethacrylate and styrene at 60°C. Hirano and co-workers observed enhanced rates of azobisisobutyronitrile decomposition in the presence of triethylaluminum between 50-70°C (138).

With zinc chloride, the effects on azobisisobutyronitrile decomposition are not clear. Zubov et al (29) has reported an increase of azobisisobutyronitrile decomposition with zinc chloride, whereas Imoto and co-workers (83) found the rate unchanged.

As a large volume of experimental data has been accumulated on zinc chloride-azobisisobutyronitrile alternating copolymerization systems, it became an initial objective of this research to determine unequivocally the effect of zinc chloride on azobisisobutyronitrile decomposition.

Results and Discussion

Experiments were designed to duplicate as closely as possible copolymerization conditions where azobisisobutyronitrile decomposition could be followed by conventional nitrogen evolution techniques.

In figure (20a) the first order rate data from azobisisobutyronitrile decomposition in: solvent alone (dichloroethane); solvent and propionitrile (pseudo monomer); and solvent, propionitrile with zinc chloride are shown. A least squares line between all points is also shown. Figure (20b) shows similar data where systems containing azobisisobutyronitrile with; solvent and acrylonitrile; solvent, acrylonitrile and zinc chloride; acrylonitrile, styrene and zinc chloride are indicated. An average slope for all points is also shown. Rate constants for the reactions shown on figures (20a) and (20b) were determined by least squares fits and are given on table (III).

Conclusions

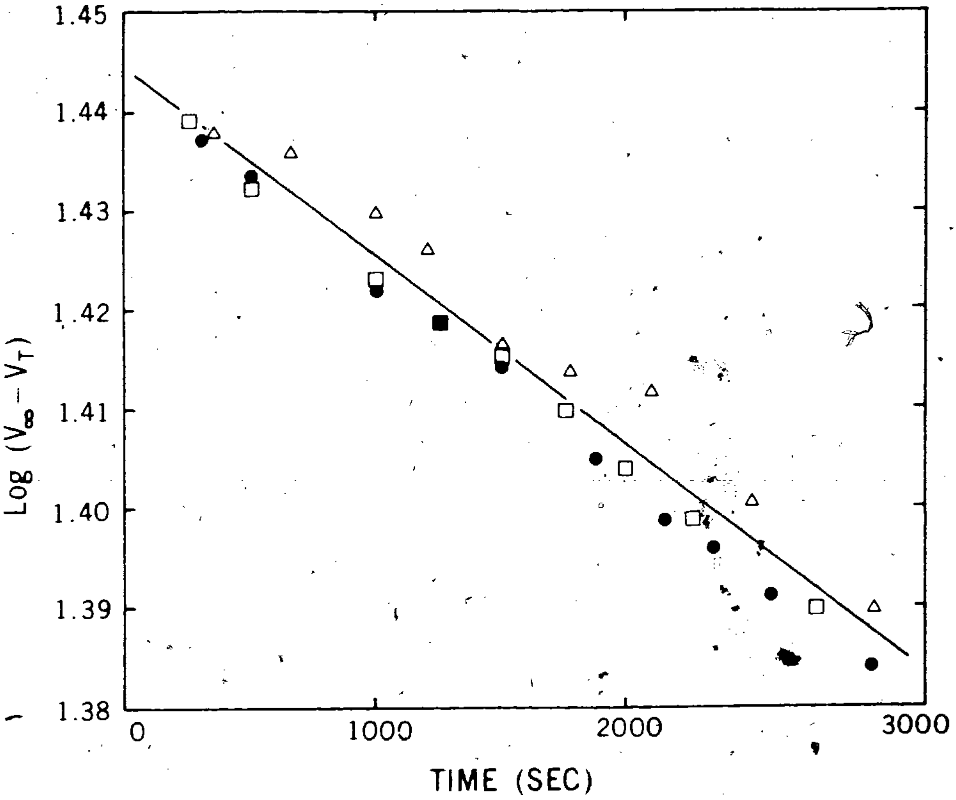
No change in rate of azobisisobutyronitrile decomposition was indicated by the addition of monomer or pseudo monomer, nor was there any change noted on the addition of zinc chloride. The value of k_d (azobisisobutyronitrile) at 70° was determined as 2.01×10^{-5} sec^{-1}. No literature value for k_d at this temperature and solvent could be found, however, a comparison of k_d at 70° for hydrocarbon solvents ($k_d = 3.9 \times 10^{-5}$ sec^{-1}) (139) showed reasonable agreement. The enhanced rates observed in the addition of azobisisobutyronitrile to zinc chloride complexed alternating copolymerizations should thus be attributed to factors other than an increased number of initiating free radicals.

A different situation prevails in systems containing aluminum alkyls. Here, the activation energy is reportedly reduced dramatically from 30.8 kcal/mole to 12 kcal/mole for the triethylaluminum-azobisisobutyronitrile system (138). An interaction between the organo aluminum compound

Figure 20 FIRST ORDER DECOMPOSITION OF AIBN IN DICHLOROETHANE AT 70°C.

a) $[\mathrm{AIBN}] = 2.48 \times 10^{-2}$: AIBN WITH DICHLOROETHANE ●; WITH PROPIONITRILE/DICHLOROETHANE (1:1), □ ; WITH PROPIONITRILE/DICHLOROETHANE (1:1) AND $[\mathrm{ZnCl_2}] = 1.70 \times 10^{-2}$, Δ .

b) $[\mathrm{AIBN}] = 2.48 \times 10^{-2}$: WITH $[\mathrm{AN}] = 5.56 \times 10^{-2}$, ● ; WITH $[\mathrm{AN}] = 5.56 \times 10^{-2}$ AND $[\mathrm{ZnCl_2}] = 1.70 \times 10^{-2}$, □ ; WITH $[\mathrm{AN}] = 5.56 \times 10^{-2}$, $[\mathrm{STY}] = 5.00 \times 10^{-2}$ AND $[\mathrm{ZnCl_2}] = 1.70 \times 10^{-2}$, Δ .


1.45
1.44
1.43
1.42
1.41
1.40
1.39
1.38
Log ($V_\infty - V_T$)
0
1000
2000
3000
TIME (SEC)

a

TABLE III

Rate Constants for the Decomposition of α, α'Azobisisobutyronitrile in Various Solvent-Monomer Systems

Figure	AIBN Solution [AIBN] = 2.48×10^{-2} mole/1	k_d $sec^{-1} \times 10^5$
20a	dichloroethane	2.01±0.02
20a	dichloroethane, propionitrile	1.94±0.03
20a	dichloroethane, propionitrile, zinc chloride	1.72±0.07
20b	dichloroethane, acrylonitrile	1.64±0.06
20b	dichloroethane, acrylonitrile, zinc chloride	1.73±0.05
20b	dichloroethane, styrene, acrylonitrile, zinc chloride	1.68±0.05

and azobisisobutyronitrile is shown by the existence of complexes between these two materials (138).

Reasons for the differences between aluminum alkyls and zinc chloride have not been postulated previously. A possible consideration is the preferential complexation of these agents to the available nitrogen lone pair electrons in azobisisobutyronitrile, (azo and nitrile).

Zinc II because of its filled d orbitals (d^{10}) would preferably complex to the nitrile nitrogen where back donation is possible from the filled d orbitals into empty antibonding orbitals on the nitrile function. In the case of aluminum (d^0) back donation is not possible and complexation to the nitrile lone pair is less likely. Aluminum, however, because of its unfilled d orbitals may coordinate across the azo bond in a bridge fashion incorporating both available azo lone pairs. Bridged aluminum complexes of this type have been proposed between hydrazines and aluminum alkyls (140). In contrast, zinc II cannot accommodate the azo lone pairs in this fashion. The end result of aluminum complexation across the azo linkage would be a reduction of carbon nitrogen bond energies. A decomposition rate increase would then result from more facile scission of the carbon nitrogen bonds.

III.1.2 EFFECT OF α,α'AZOBISISOBUTYRONITRILE ON THE PRODUCT MOLECULAR WEIGHT AND COPOLYMERIZATION RATE OF METHYL METHACRYLATE AND STYRENE IN THE PRESENCE OF DIETHYLALUMINUM CHLORIDE

Introduction

Conventional radical polymerizations initiated by radical initiators obey a square root relationship between the initiator concentration and the reaction rate (141),

$$R_p = k_p \ [M] \left(\frac{fk_d \ [I]}{k_t} \right)^{1/2} \qquad \text{III-1}$$

where the symbols maintain their usual significance. Previous investigations of complexed alternating copolymerization have not indicated this square root relationship (116).

Results and Discussion

Data from a series of copolymerizations of methyl methacrylate and styrene in the presence of diethylaluminum chloride involving various concentrations of azobisisobutyronitrile are shown in table (IV). Figure (21) shows the linear relationship between $[\text{azobisisobutyronitrile}]^{1/2}$ and the copolymerization rate of methyl methacrylate and styrene in the presence of diethylaluminum chloride. Thus, figure (21) indicates an initiation step involving the participation of primary radicals provided by increasing concentrations of azobisisobutyrontrile.

TABLE IV

Rate and Molecular Weight Data for the Copolymerization of the Methyl Methacrylate, Styrene and Diethylaluminum Chloride (2:2:1) System with Various Concentrations of α,α'Azobisisobutyronitrile

$[AIBN]x10^3$	Yield/10K sec.	Initial Rate $x\ 10^6$ mole/1sec.	$[AIBN]^{1/2}x10^2$	$\overline{M}_n$	$\overline{M}_w$
0	11.40 gm/1	5.9	0	130,000	316,000
0.73	12.92 gm/1	6.31	2.7	100,000	272,000
2.5	10.91 gm/1	5.3	5.0	93,000	234,000
7.8	16.27 gm/1	7.9	8.8	70,000	242,000
26.0	16.80 gm/1	8.2	16	60,000	215,000
78.3	21.13 gm/1	10.33	28	66,000	232,000

Figure 21 INITIAL RATE OF COPOLYMERIZATION OF METHYL METHACRYLATE AND STYRENE IN THE PRESENCE OF DIETHYLALUMINUM CHLORIDE VS THE SQUARE ROOT OF CONCENTRATION OF α,α'AZOBISISOBUTYRONITRILE.

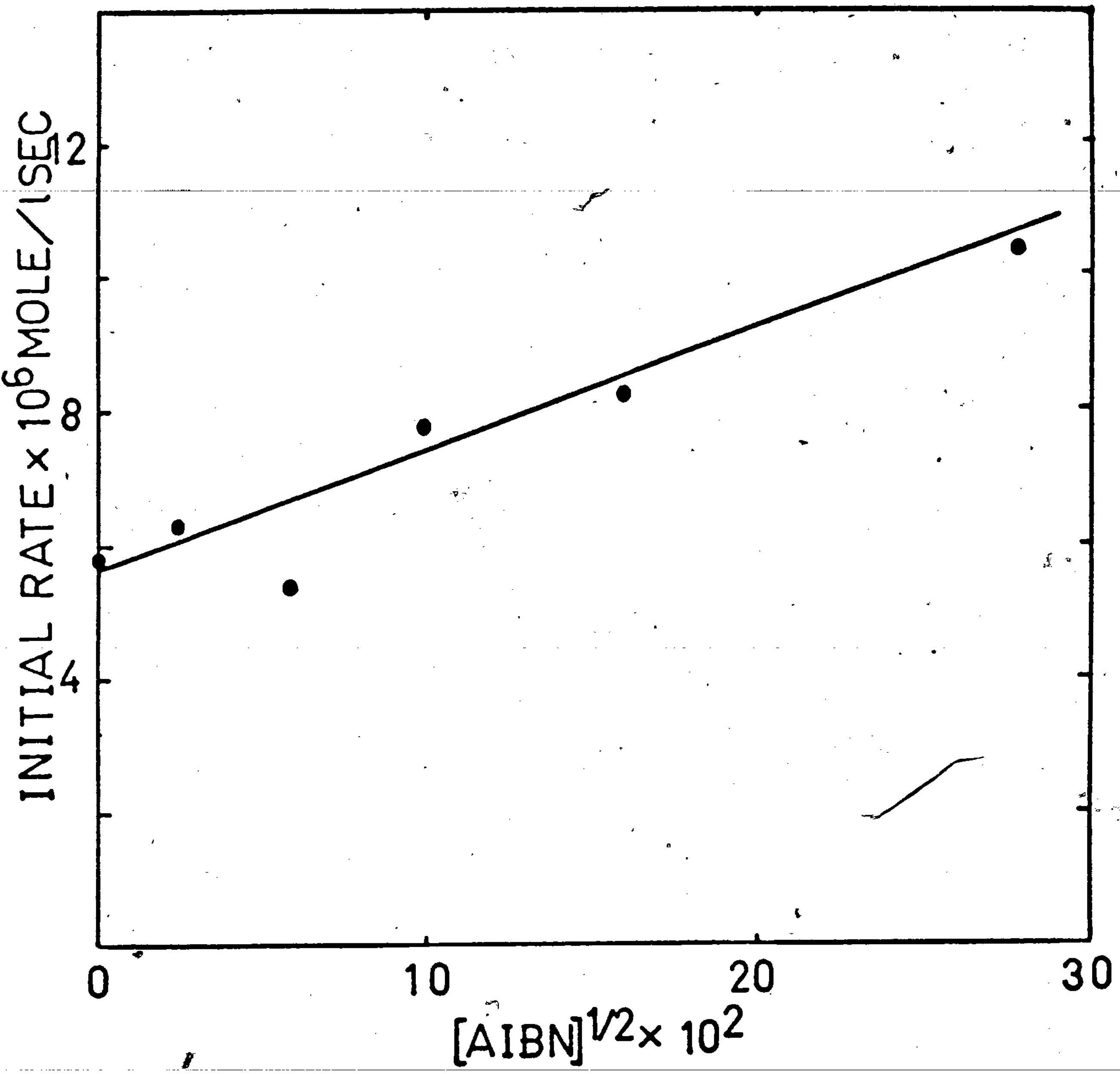

INITIAL RATE × 10^6 MOLE/1SEC
12
8
4
0
10
20
30
[AIBN]$^{1/2}$ × 10^2

Table IV also indicates a gradual decrease in product molecular weight $\overline{M}_n$ as the azobisisobutyronitrile concentration increases. These data are consistent with radical polymerizations, where molecular weight are inversely dependent on the radical concentration.

Conclusions

Complexed alternating copolymerizations containing azobisisobutyronitrile behave in a manner expected of a radically initiated process. The previously reported (116) anomalous behaviour of complexed alternating copolymerizations on addition of azobisisobutyronitrile is not shown in this work.

III.1.3 THE HOMOGENEITY OF COMPOSITION AS A FUNCTION OF MOLECULAR WEIGHT DISTRIBUTION

Introduction

The strongest evidence supporting the concept of alternating copolymerization is the interpretation of NMR data to support the structure of an alternating sequence of mer units within the polymer chain (42, 43, 46, 50, 58, 60, 67, 71, 72, 88-91, 143), (Section I.8).

Where elemental analysis data is obtained, only gross macrocomposition of the polymeric material is known, and the detailed microcomposition of the polymer remains in question.

A crucial test of variation in the reaction mechanism either sequentially during the course of polymerization or

marks on original

as a parallel side reaction during polymerization lies in a measure of composition at various intervals in the molecular weight distribution of the polymer in question. The molecular weight distributions of comonomer rich copolymers (either monomer of a particular pair) or homopolymers of either comonomer would be expected to differ from the molecular weight distribution of the product from alternating copolymerizations of these same monomers. Thus an analysis of the composition of polymer in small molecular weight ranges could provide strong evidence as to the true homogeneity of the overall reaction mechanism. Screaton *et al* recently combined gel permeation chromatography and radio tracer techniques to determine the functional distribution in copolymers of acrylic acid, vinyl alcohol and epoxy resins (144). Their technique, which utilized the molecular weight fractionation capabilities of gel permeation chromatography (GPC) appears well suited for investigation into the microcomposition of alternating copolymers. It was decided to apply this method to compositional studies of complexed alternating copolymerization of methyl methacrylate and ^{14}C styrene copolymer.

Results and Discussion

The data shown in figure (22) indicates that throughout the molecular weight range, the specific radio-activity of the samples remains unchanged. A curve representing the activities lies within experimental error to a curve representing the weight distribution. In addition, selected chromatograph samples were dried and the polymer residue was subjected to microanalysis. Results are shown in table (V).

It is clear from figure (22) and table (V) that there is no change in relative composition of the copolymer over the complete molecular weight range ($2 \times 10^6 - 2 \times 10^3$) covered by GPC elution volume counts 23 to 35. The copolymer is essentially an alternating copolymer over the molecular weight range indicated.

Conclusions

It can be seen from these data that complexed alternating copolymerizations represent copolymer formation that is independent of complexities due to simultaneous homopolymerization or changes in mechanism.

III.1.4 COMPLEXED ALTERNATING COPOLYMERIZATION IN TETRAHYDROFURAN SOLVENT

Introduction

It is desirable to conduct kinetic studies of polymerization reactions in homogeneous solution. Consequently, a solvent in which both the monomer and polymer are soluble is necessary. Tetrahydrofuran (THF), a solvent for a large number of polymers, appears a good candidate.

Tetrahydrofuran is a polar solvent and studies have shown that polar solvents, such as THF, greatly influence complexed alternating copolymerizations (23, 119, 129). Cerciat et al (129) showed that THF in low concentration has a noticeable influence on the complexed alternating copolymerization of

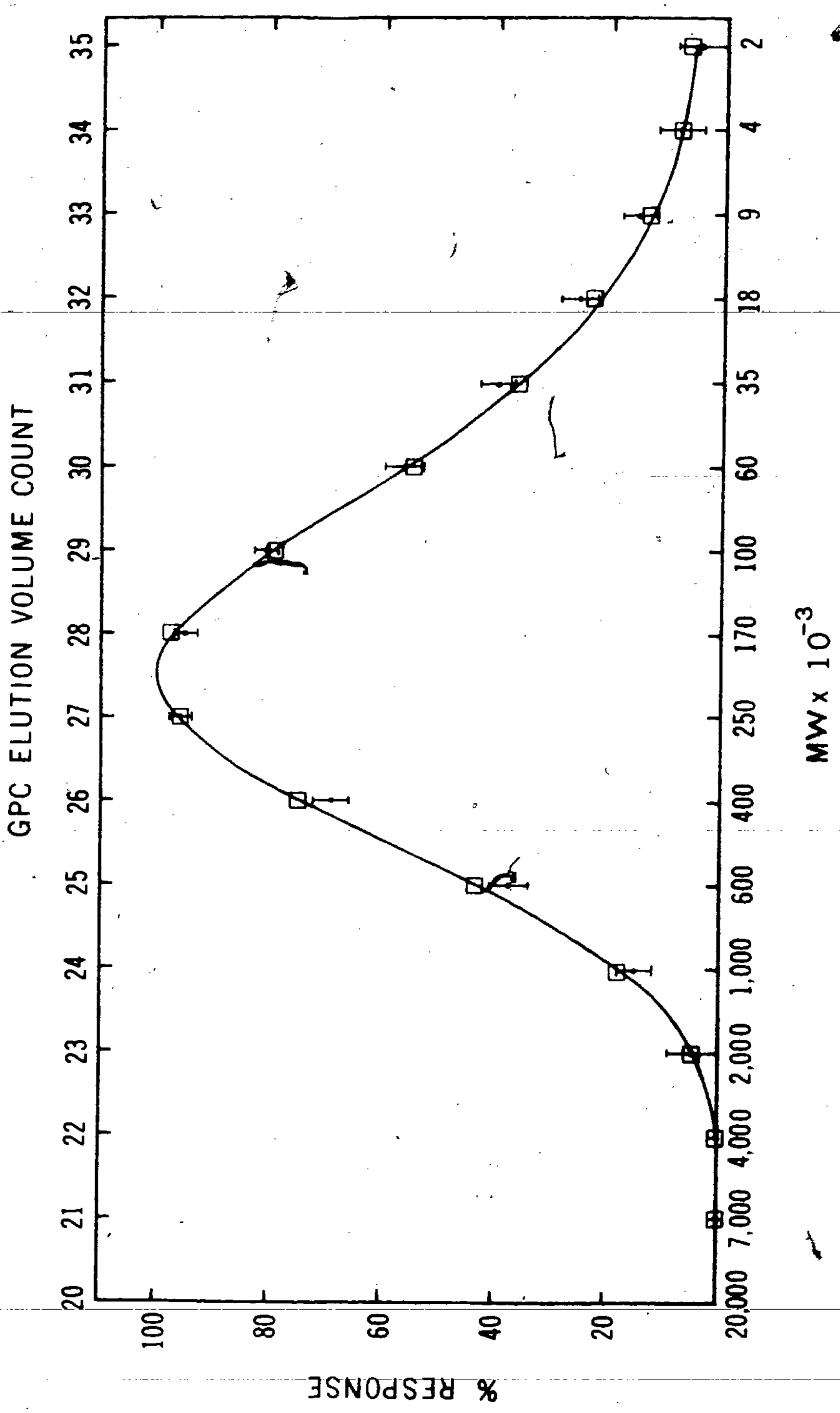

GPC ELUTION VOLUME COUNT
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
% RESPONSE
100
80
60
40
20
MW x 10^{-3}
20,000
7,000
4,000
2,000
1,000
600
400
250
170
100
60
35
18
9
4
2

TABLE V

Microanalysis Results for Selected Gel Permeation Fractionation Samples

Elution Vol. (Count No.)	Microanalysis % Carbon	% MMA from Analysis
23-24	76.25	50%±6%
27-28	76.17	51%±6%
24-30	75.79	52%±6%
32-33	75.70	53%±6%

both acrylonitrile and methyl methacrylate in conjunction with styrene and zinc chloride. These authors found a polymerization rate maximum at a well defined concentration of $THF/ZnCl_2$

$$0.82 < \frac{[THF]}{[ZnCl_2]} < 1.23$$

for methyl methacrylate-styrene and

$$0.62 < \frac{[THF]}{[ZnCl_2]} < 1$$

for acrylonitrile-styrene. It is also found that when THF is present, deviations from a 1:1 comonomer product composition occur. These studies involve the use of peroxy radical initiators and deviations from an equimolar product suggest the possibility of a mechanism change to a conventional radical process.

Results

Data from copolymerizations of methacrylonitrile, styrene and $ZnCl_2$ at various concentrations of THF are shown in table (VI). These data closely resemble the literature (129), and reveal a polymerization rate maximum (conversion) at:

$$1 < \frac{[THF]}{[ZnCl_2]}, < 2$$

Figure (23) indicates the product composition as a function of monomer feed for complexed alternating copolymerizations conducted in THF solvent. Figure (23), also, contains the predicted radical copolymer composition as determined by the Mayo-Lewis copolymerization equation (Section I.4).

It is evident from the data presented, that the products from radically induced complexed alternating copolymerizations conducted in THF, are random copolymers. The composition of these copolymers can be predicted by the Mayo-Lewis copolymerization equation and are due to radical copolymerization of the comonomers.

Tetrahydrofuran can complex with zinc chloride. Hence, if the complexation between THF and zinc chloride is more favourable than complexation between methacrylonitrile and zinc chloride, e.g., ii $\rangle$ i .

$$\text{i)} \quad n\ \mathrm{MAN} + \mathrm{ZnCl_2} \rightleftharpoons \mathrm{MAN_n - ZnCl_2}$$

$$\text{ii)} \quad n\ \mathrm{THF} + \mathrm{ZnCl_2} \rightleftharpoons \mathrm{THF_n - ZnCl_2}$$

the concentration of complexed methacrylonitrile monomer is reduced. Consequently, little complexed alternating copolymerization occurs.

The remaining uncomplexed methacrylonitrile and styrene can copolymerize by a free radical mechanism and the copolymer composition can be predicted by the Mayo-Lewis equation.

Figure 23 COPOLYMER COMPOSITION VS COMONOMER FEED COMPOSITION FOR THE COPOLYMERIZATION OF METHACRYLONITRILE AND STYRENE.

●– – –● WITH $ZnCl_2$, AIBN AND THF

——— COMPOSITION FROM THE MAYO-LEWIS EQUATION USING LITERATURE (14) REACTIVITY RATIOS.

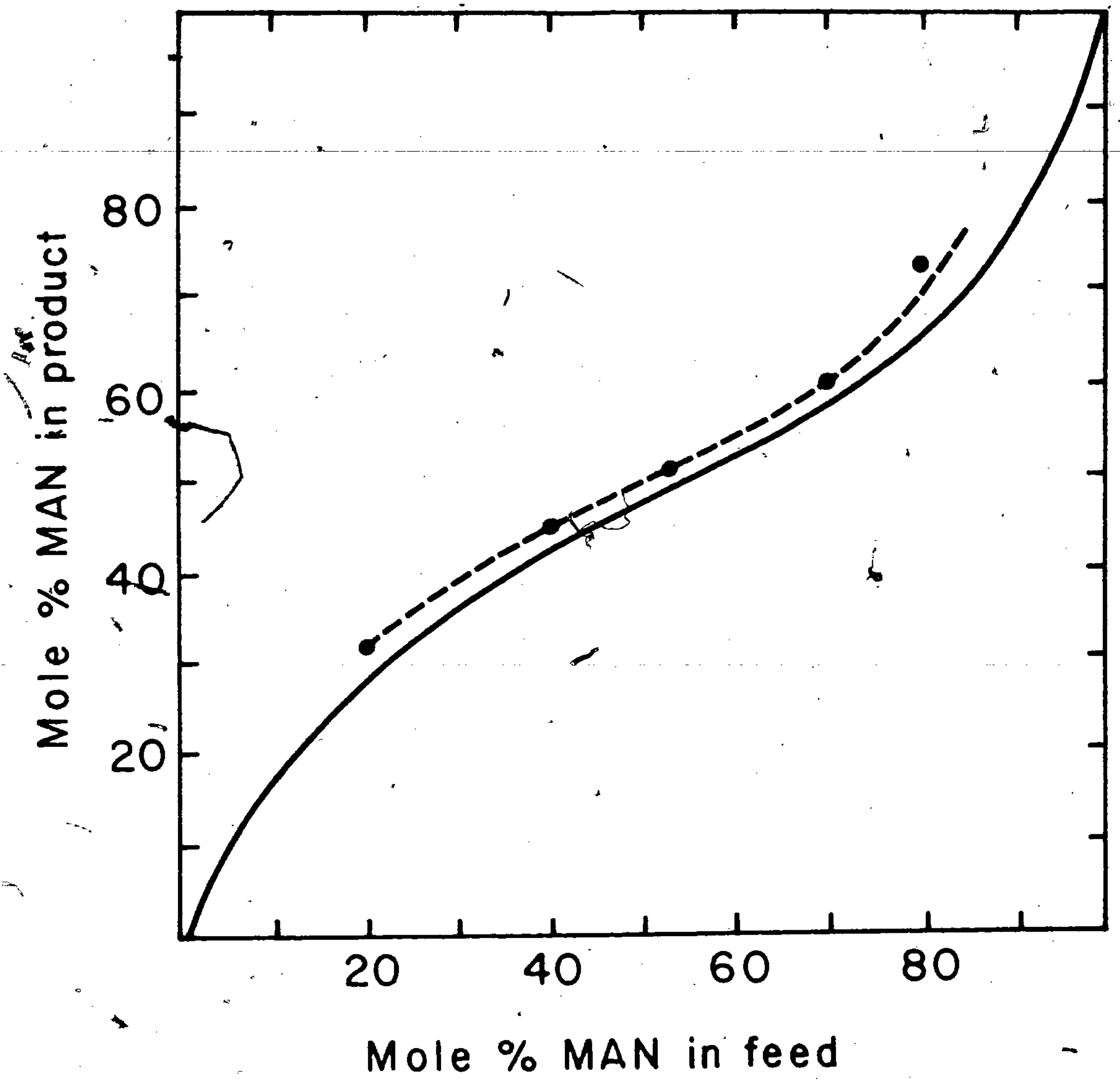

80
60
40
20
Mole % MAN in product
20
40
60
80
Mole % MAN in feed

TABLE VI

Product Composition and % Conversion for the Copolymerization of Methacrylonitrile and Styrene in the Presence of Zinc Chloride, α,α'Azobisisobutyronitrile (6×10^{-3}m) and Tetrahydrofuran ($ZnCl_2$/MAN = 0.33); Temp. = 40°C, Time = 1×10^{4} Sec.

$THF/ZnCl_2$	% Conversion	Mole % MAN In Feed	Polymer Composition % MAN
1.37	3.69	80	73.0
1.64	7.33	70	60.0
3.29	2.89	40	45.0
7.18	3.40	20	31.5

Conclusions

When complexed alternating copolymerizations containing radical initiators are conducted in polar solvents capable of complexing with the complexing agent of the copolymerization, random copolymer is obtained as product. This is a consequence of preferential complexation of the complexing agent to the solvent thus reducing the concentration of the monomer complex necessary for complexed alternating copolymerization. The copolymerization becomes essentially a radical copolymerization and the product composition is predicted by the Mayo-Lewis equation.

III.1.5 CHANGES IN MOLECULAR WEIGHT WITH TIME

Introduction

The molecular weight and molecular weight distribution can, in some cases, provide a distinction between reaction mechanisms. Free radical reactions show broad molecular weight distributions with no change in molecular weight with respect to time, while reactions involving a continuous growth of "living" centers show narrow molecular weight distribution and an increase in molecular weight with time.

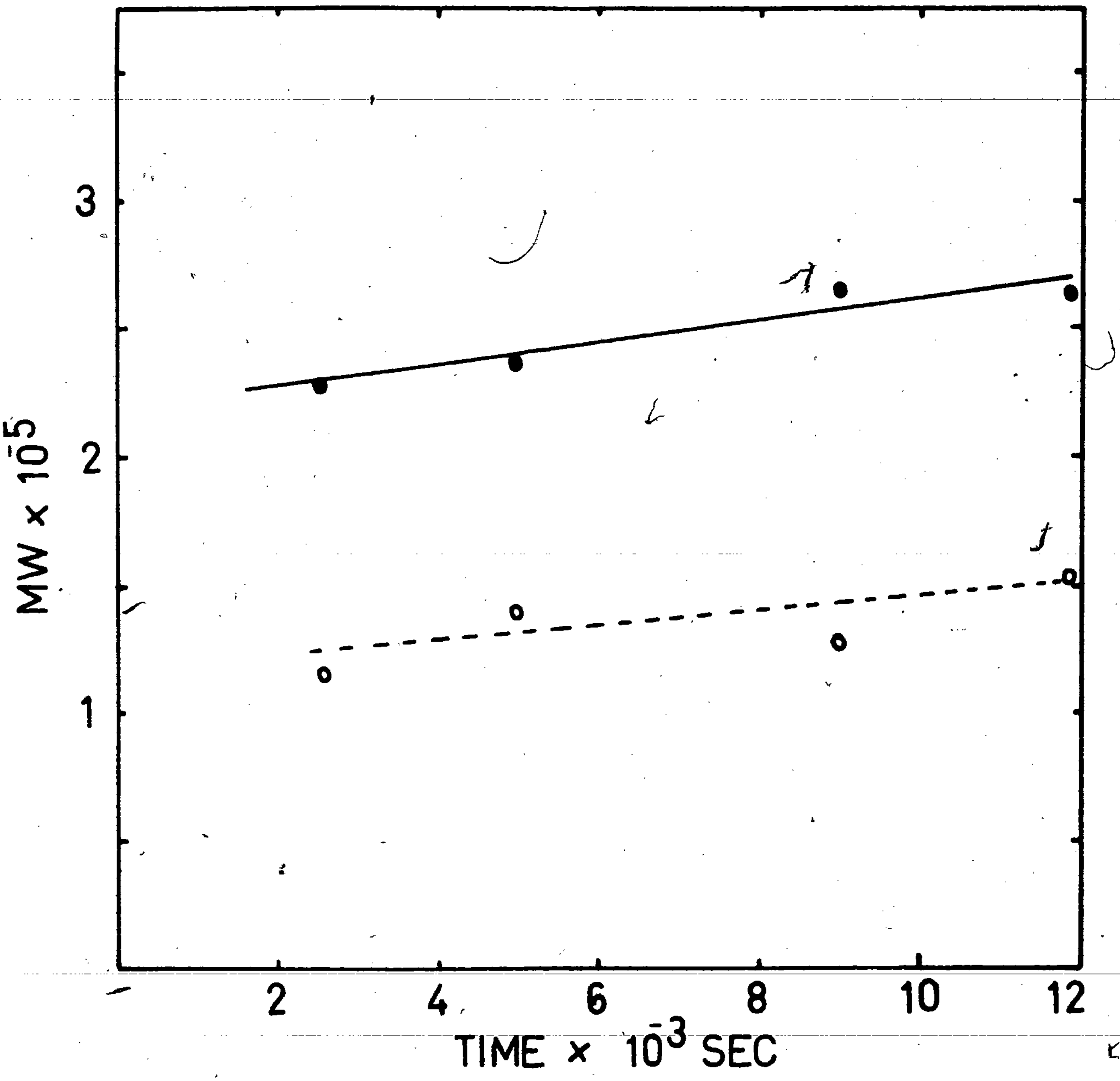
Results and Discussion

Figure (24) shows the $\overline{M}_w$ and $\overline{M}_n$ values during the initial stages of methyl methacrylate-styrene, diethylaluminum chloride complexed alternating copolymerization. No significant variation of molecular weight is shown with the time of reaction.

Figure 24 MMA-STY COPOLYMER MOLECULAR WEIGHT VS REACTION TIME.

• ——— • $\bar{M}_w$

o - - - o $\bar{M}_n$


3
2
1
MW x 10̄5
2
4
6
8
10
12
TIME x 10̄3 SEC

Some mechanistic proposals have involved "living" systems (54). However, figure (24) is not consistent with this picture. It is clear from this figure that no significant change in molecular weight occurs over the initial stages of the reaction and the mechanism of copolymerization is not of a "living" mechanism.

Figure (25) contains the complete molecular weight distribution of the alternating copolymer product obtained after a polymerization time of 1 x 10^4 seconds. Also, included on this figure is the molecular weight distribution of a comparable radical copolymerization of the same monomer pair initiated by organic peroxide. Figure (25) indicates a broad distribution with somewhat higher molecular weight averages than that of the conventional radical counterpart. No change in the distribution is seen with time.

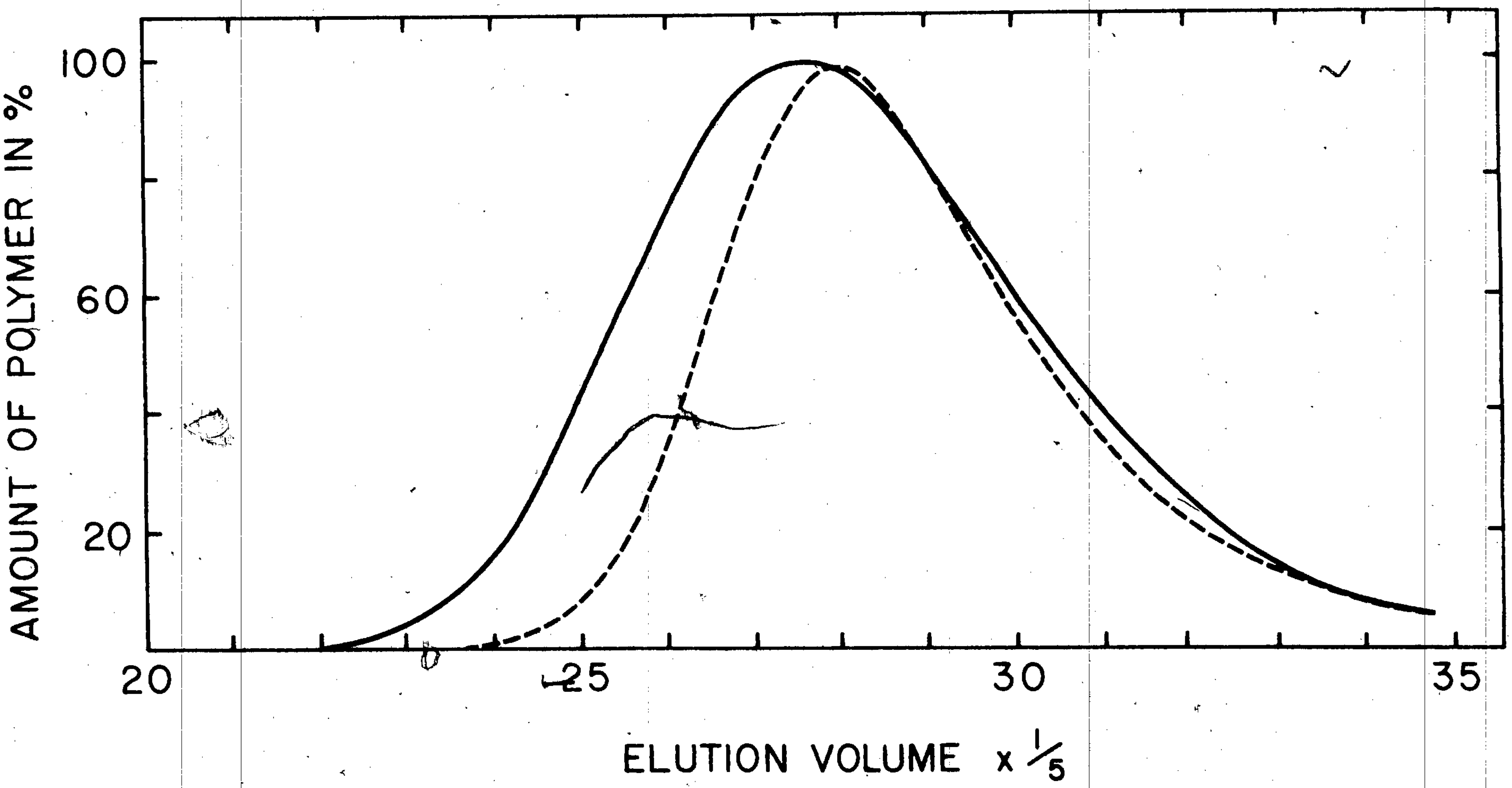
Conclusion

The product molecular weight distribution from the complexed alternating copolymerization of methyl methacrylate and styrene in the presence of diethylaluminum chloride is broad and grossly comparable to that of product from conventional radical copolymerization of the same monomers. Molecular weights of the product are invarient with time. Thus a propagation mechanism devoid of "living" centers is indicated for the copolymerization of methyl methacrylate and styrene in the presence of diethylaluminum chloride.

Figure 25 GPC CHROMATOGRAMS OF AMOUNT OF POLYMER VS ELUTION VOLUME.

——— MMA-STY COPOLYMER FROM DEAC COMPLEXATION

– – – – MMA-STY COPOLYMER FROM ORGANIC PEROXIDE


100
60
20
AMOUNT OF POLYMER IN %
20
25
30
35
ELUTION VOLUME x 1/5

III.2 KINETIC AND MOLECULAR WEIGHT FEATURES OF THE COMPLEXED ALTERNATING COPOLYMERIZATION OF METHYL METHACRYLATE AND STYRENE IN THE PRESENCE OF DIETHYLALUMINUM CHLORIDE

Introduction

Previous kinetic studies of complexed alternating copolymerizations have centered mainly on the effects of monomer concentration on the polymerization rate (Section I.13). No studies have been reported that examine the kinetic features of these reactions in conjunction with molecular weight observations.

Results and Discussion

III.2.1 MONOMER REACTION ORDERS

According to the kinetic relationship:

$$R = k\,[M_1]^{n_1} \times [M_2]^{n_2} \qquad \text{III-2}$$

the reaction order (n_1 and n_2) of each monomer of a copolymerization can be determined by the Van't Hoff method utilizing the logarithmic form of (III-2).

$$\ln R = \ln k + n_1 \ln [M_1] + n_2 \ln [M_2] \qquad \text{III-3}$$

or when $[M_2]$ is constant then:

$$\ln R = \ln k + n_1 \ln [M_1] + C \qquad \text{III-4}$$

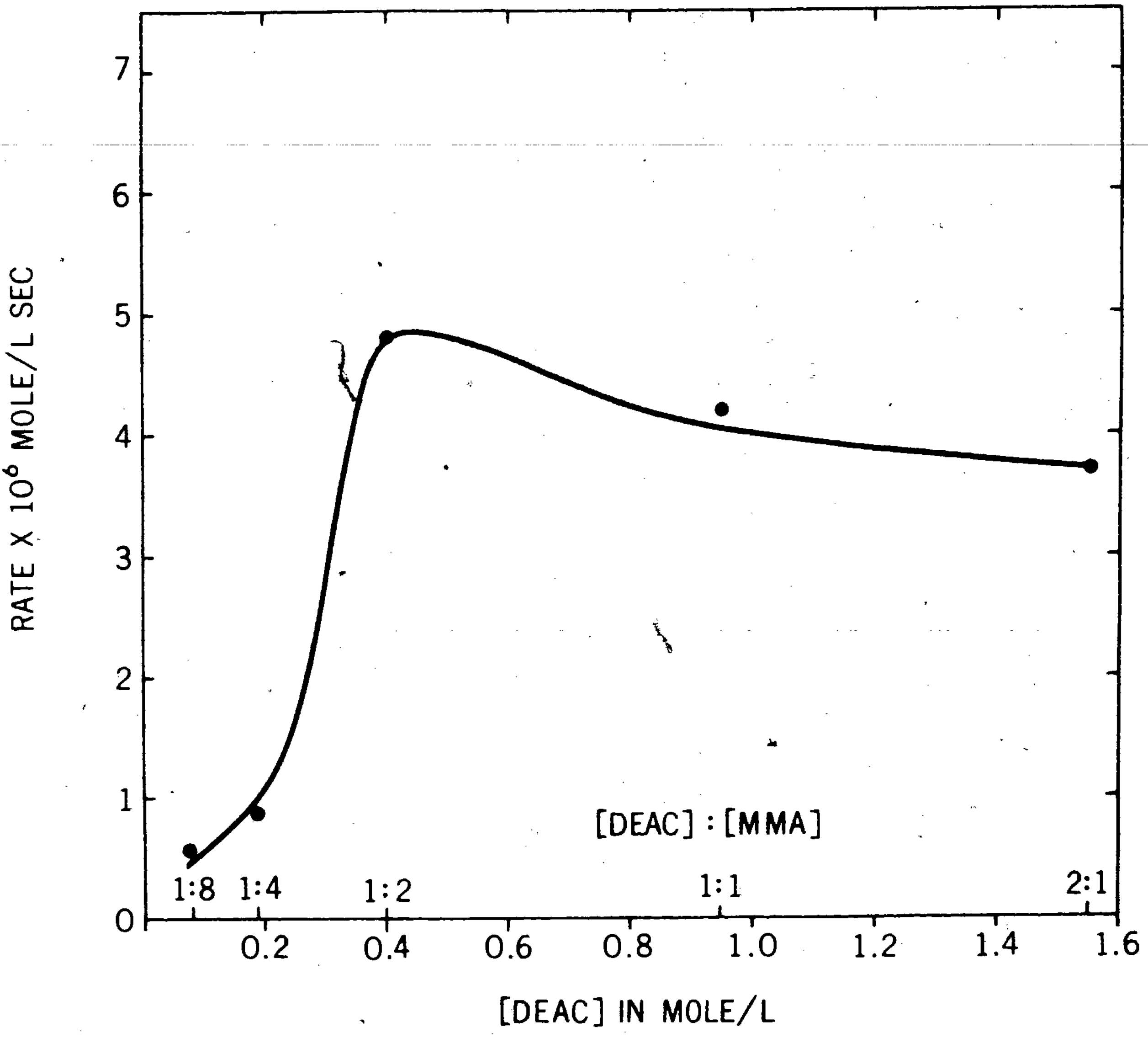
The reaction orders of M_1 and M_2 respectively, are obtained as the slope of the linear plot lnR (initial) vs ln $[M_1]$. Data from experiments where the methyl methacrylate-diethylaluminum chloride complex and styrene were individually varied gave n values of 0.76 and 0.80 for the methyl methacrylate-diethylaluminum chloride complex and styrene respectively. These values are interpreted as approximating 1 in both instances. Experiments were also conducted to determine the reaction order for diethylaluminum chloride; however, a poor correlation resulted and no conclusion as to the diethylaluminum chloride reaction order could be made.

Although controversy exists about the mechanism of complexed alternating copolymerization, the participation of a vinyl monomer - complexing agent complex is generally accepted. The formation of these complexes is conveniently written, as (in the methyl methacrylate-diethylaluminum chloride case):

$$\text{DEAC} + \alpha\text{MMA} \underset{-k}{\overset{k}{\rightleftharpoons}} \text{DEAC-MMA}_{\alpha}$$

where a variety of factors such as temperature, concentration, etc. determine the position of equilibrium. Figure (26) clearly indicates that a stoichiometric α value of 2 provides an optimum observed rate. This has been reported previously (103, 105). Although it would be convenient to consider a 2:1 stoichiometry, it is not apparent from the data that this is universally true. All possible complexes must be considered such that the α value of 2 represents a series of equilibrated adducts, each contributing to the overall value of α. The

Figure 26 DEPENDENCE OF THE RATE OF POLYMERIZATION ON THE CONCENTRATION OF DEAC (MMA:STY = 2:3) AT 25°C


RATE X 10^6 MOLE/L SEC
0
1
2
3
4
5
6
7
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
[DEAC] IN MOLE/L
[DEAC] : [MMA]
1:8
1:4
1:2
1:1
2:1

value of α can be considered as a weighted average of the integral values for all possible discrete complexes. Thus a new symbol [MMA*] is introduced to represent situations where methyl methacrylate and diethylaluminum chloride concentration ratios are 2:1. The reactivity orders obtained from the Van't Hoff method can then be interpreted as consistent with a reaction, first order dependant in each monomer (styrene and MMA*) or second order overall.

$$R_o = k'_p \, [MMA^*] \, [STY] \qquad \text{III-5}$$

III.2.2 THE DETERMINATION OF THE COPOLYMERIZATION RATE CONSTANT

When the second order rate expression (III-5) is integrated, the expression (III-6) is obtained:

$$\frac{1}{[STY]_o - [MMA^*]_o} \ln \frac{[MMA^*]_o \, ([STY]_o - x)}{[STY]_o \, ([MMA^*]_o - x)} = k'_p t \qquad \text{III-6}$$

where x is the concentration of styrene and MMA* consumed. The indicated rate constant, k'_p, is not a propagation rate constant in a true sense. The value of k'_p is a composite of the initiation, propagation and termination rate constants. The use of the apparent rate constant, k'_p, serves only to describe the actual monomer consuming steps and its internal complexity does not detract from the validity of the schemes in which it is used. The apparent rate constant, k_p', is equally significant in the Gaylord and Zubov (Section I.10) mechanistic approaches to complexed alternating copolymerization. In the Gaylord scheme, the propagation step involves the homo propagation between so-called donor-acceptor complex species. As these processes are presumed to involve donor-acceptor complex of 1:1 monomer stoichiometry (89, 100), a second order overall reaction (first in each monomer) would be shown by the homopolymerization of these adducts. The Zubov model, where the cross propagation constants are considered to collectively describe the propagation process, would also describe a second order two component copolymerization. Hence, as k_p' is a composite term involving all monomer consuming processes, no distinction can be made between the mechanisms of Gaylord and Zubov.

A series of polymerizations were performed, where samples were withdrawn from the reaction vessel at 2500 second intervals and the yield determined for these times. These data were plotted according to expression (III-6). The slope of a plot of the left side of (III-6) vs t, provides k_p'. Four copolymerizations involving different monomer feeds were conducted and the data used in expression (III-6). Results are shown on figure (27). The straight lines through these points were fitted by linear least squares and the k_p' values obtained are shown in table (VII). With lower MMA* concentrations, there is less data scatter, however, reasons

Figure 27 PLOT OF THE SECOND ORDER RATE EXPRESSION FOR COPOLYMERIZATIONS INVOLVING:

● —— $[MMA^*]_o = 1.29$; $[STY]_o = 2.57$

○ –·– $[MMA^*]_o = 2.36$; $[STY]_o = 1.59$

Δ ····· $[MMA^*]_o = 1.96$; $[STY]_o = 1.96$

□ --- $[MMA^*]_o = 2.62$; $[STY]_o = 1.31$

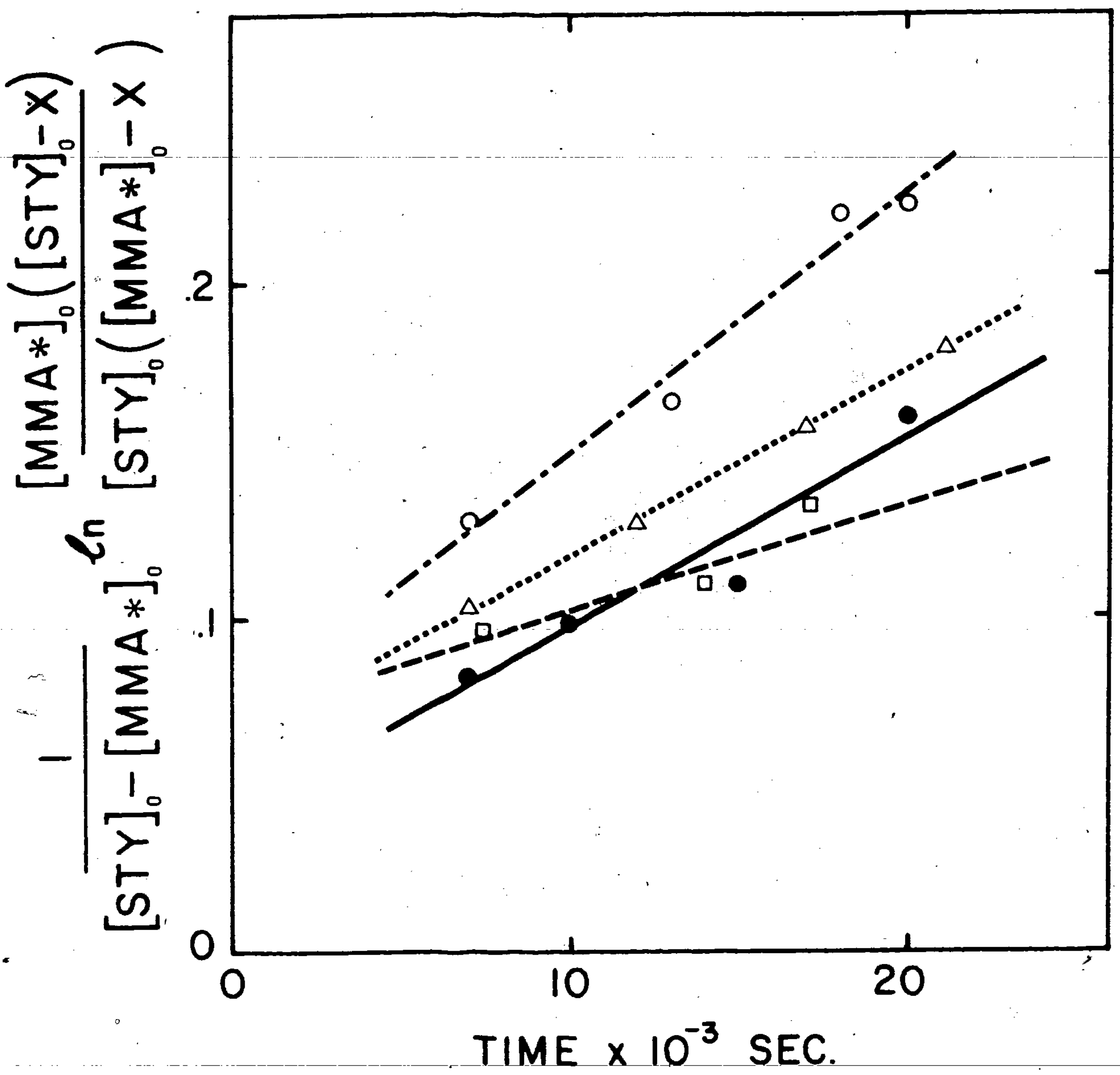

$\frac{1}{[STY]_0-[MMA*]_0}\ell n\frac{[MMA*]_0([STY]_0-X)}{[STY]_0([MMA*]_0-X)}$
.2
.1
0
0
10
20
TIME x 10^{-3} SEC.

TABLE VII

Calculated k'_p Values for Copolymerization Involving Various Concentrations of Comonomer

[MMA*] mole l^{-1}	[STY] mole l^{-1}	k'_p l $mole^{-1}$ $sec.^{-1}$
1.29	2.57	$5.5 \pm 0.5 \times 10^{-6}$
2.36	1.59	$7.6 \pm 0.7 \times 10^{-6}$
1.96	1.96	$5.4 \pm 0.1 \times 10^{-6}$
2.62	1.31	$3.2 \pm 0.8 \times 10^{-6}$

for this are not clear. A weighted average k_p' value, $5.4 \pm 0.3 \times 10^{-6}$ 1/mole sec. was adopted. Failure of the lines in figure 27 to pass through the origin reflects the actual concentration of the complexed monomer (methyl methacrylate-diethylaluminum chloride) in comparison to the stociometric conditions of MMA* (Section III.2.1). The quantity MMA* designates a feed ratio of 2:1 between methyl methacrylate and diethylaluminum chloride. The actual concentration of complexed monomer may be less than this and will be determined by the equilibrium constant for the complex. The y axis intercept indicates a lower complexed monomer concentration than [MMA*] at t=0. The slopes of the lines of figure 27, although offset upward, retain their significance and provide valid k_p' values.

A second method was employed to determine k_p'. Products of the initial monomer concentrations ($[MMA^*]_o [STY]_o$), from a series of alternating copolymerizations containing various initial monomer concentrations were plotted against the observed initial rate, R_o, of polymer formation. The data are summarized in table (VIII). The linear plot, figure (28), provides a k_p' value from the initial rates rather than from data expressed as a function of time as in the integrated rate expression. The average k_p' is determined as $5.2 \pm 0.5 \times 10^{-6}$ 1/mole sec. by this method and agrees with the k_p' value $5.4 \pm 0.3 \times 10^{-6}$ 1/mole sec. obtained from the integrated rate expression.

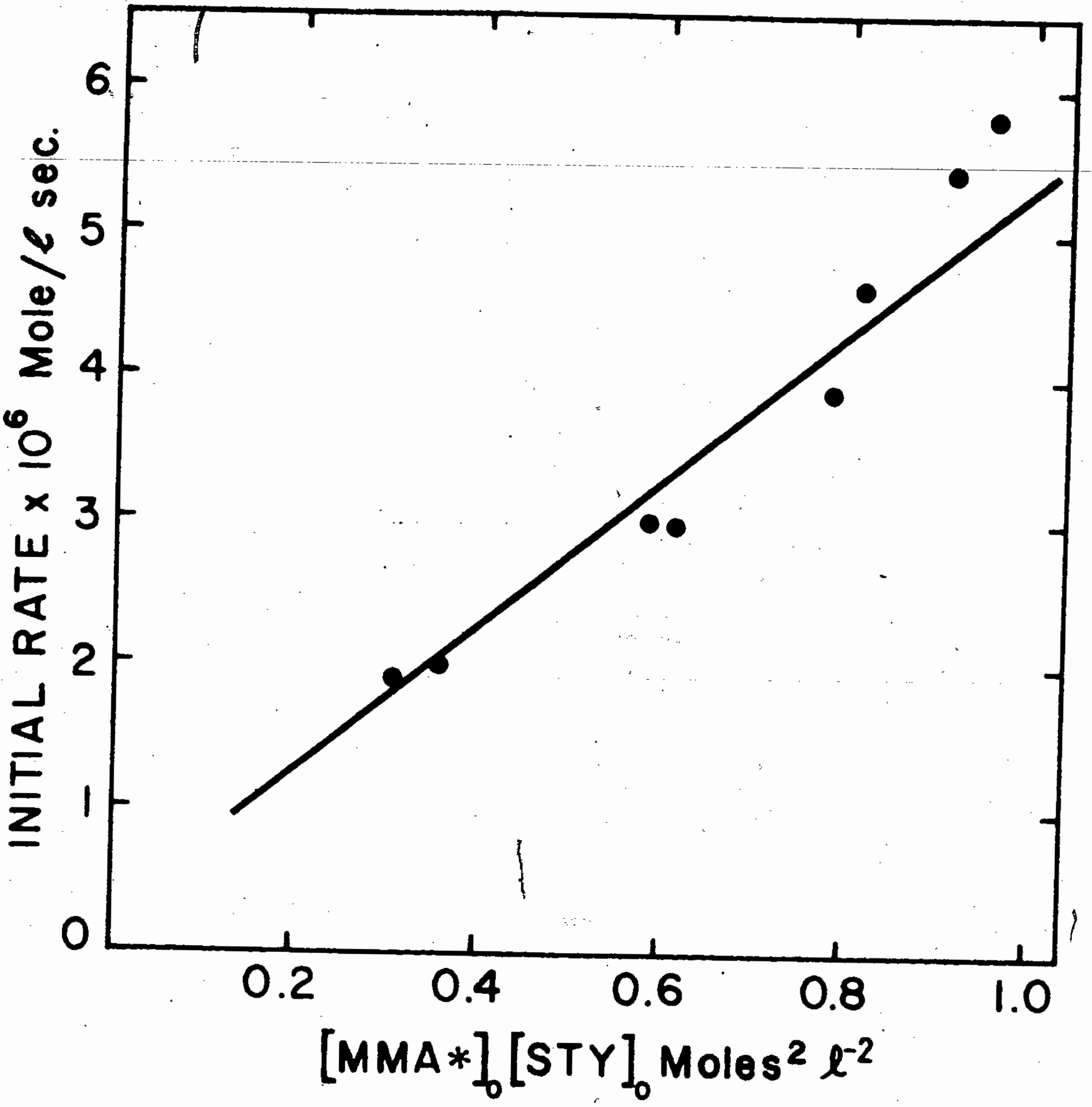
Figure (28) indicates a rate maximum at a maximum value of [MMA*] [STY] i.e. : equimolar monomer concentration. This

TABLE VIII

The Initial Copolymerization Rates of Reactions Containing Various Feed Ratios of Comonomer

Mole % MMA* in Feed	$[MMA^*]_o$ $[STY]_o$ ($Mole^2$ l^{-2})	Initial Rate (Mole l^{-1} $Sec.^{-1}$)
10	0.31	1.9×10^{-6}
20	0.59	3.1×10^{-6}
30	0.79	3.9×10^{-6}
40	0.95	5.9×10^{-6}
60	0.92	5.4×10^{-6}
70	0.82	4.6×10^{-6}
80	0.62	3.0×10^{-6}
90	0.35	2.0×10^{-6}

Figure 28 PLOT OF THE INITIAL RATE OF COPOLYMERIZATION VS THE PRODUCT OF THE COMONOMER CONCENTRATION. SLOPE = k'_p = 5.2 ± 0.5 x 10^{-6} 1/mole sec.


INITIAL RATE x 10^6 Mole/ℓ sec.
0
1
2
3
4
5
6
0.2
0.4
0.6
0.8
1.0
[MMA*]o [STY]o Moles² ℓ⁻²

is in accord with both the Gaylord and Zubov mechanistic models. An equimolar monomer concentration provides a maximum concentration of donor-acceptor complexes and, hence, a rate maximum consistent with the Gaylord model. Conversely, since cross propagation involves both monomer species, a rate maximum in the region of a 1:1 feed ratios would also be expected in the Zubov approach.

III.2.3 ACTIVATION ENERGY

The activation energy of a chemical reaction is normally defined by the Arrhenius Equation.

$$k = Ae^{\frac{-E}{RT}} \qquad \text{III-7}$$

A plot of lnk vs 1/T provides a straight line of slope -E/R. In polymerization kinetics the term E_r is often used to designate the overall activation energy of the process.

Rate constants for copolymerizations conducted at various temperatures are shown in table (IX) and the corresponding Arrhenius plot is figure (29). The slope of the linear least squares line through the points is -2×10^3 and corresponds to an activation energy, E_r of +3.9 kcal mole^{-1}.

Zubov et al (29, 108) has observed low activation energies in other systems. He suggests that if the energy level of the lowest vacant orbital of a radical is close in value to that of the energy of the highest occupied orbital of the comonomer, the activation energy can be near zero.

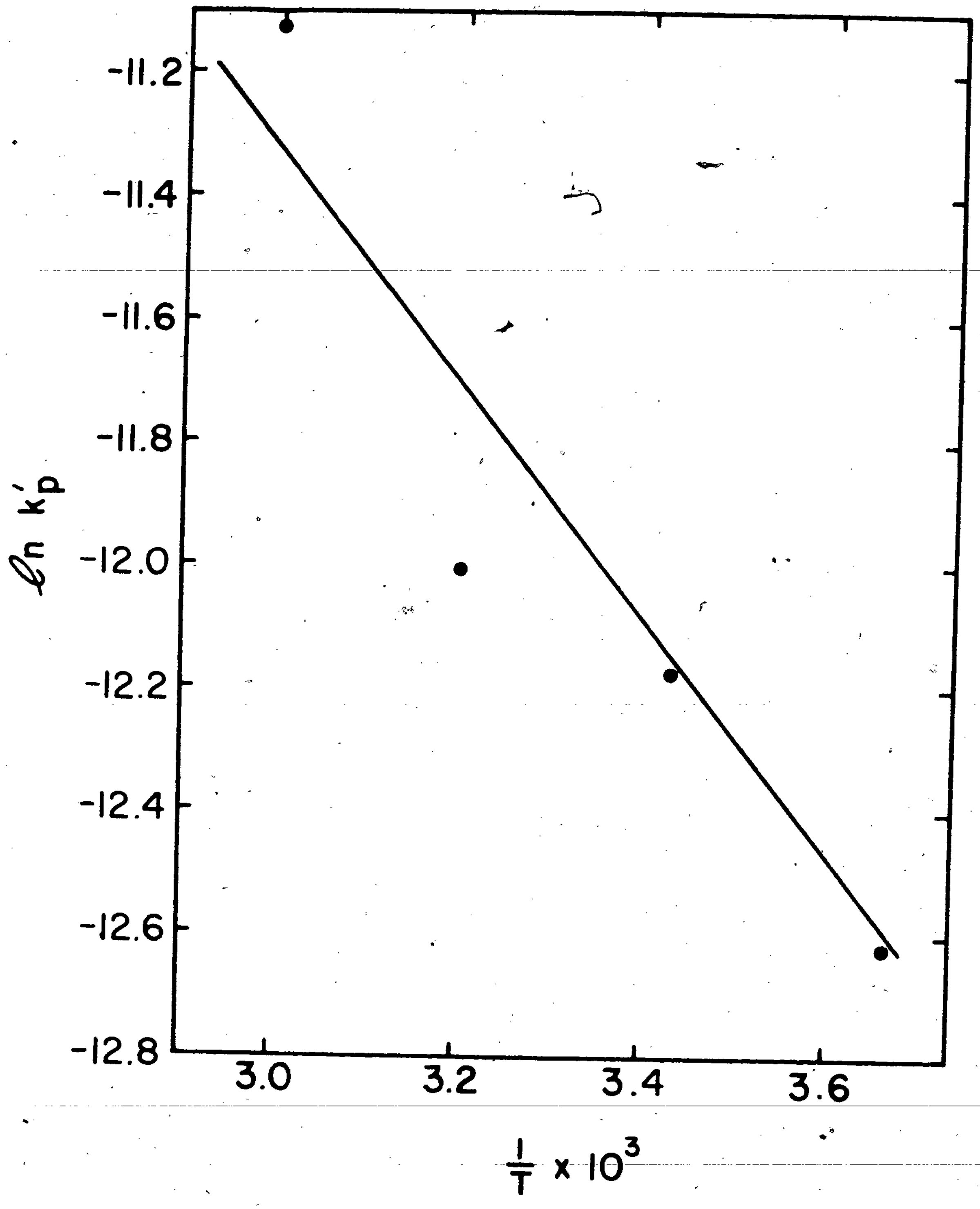
TABLE IX

Rate Constants for the Copolymerization of Methyl Methacrylate and Styrene in the Presence of Diethylaluminum Chloride

(MMA:DEAC = 2:1; MMA = 40 mole %)

k'_p 1 mole^{-1} sec.$^{-1}$	T in ^oK	^oC	1/T x 10^3
3.3	273	0	3.7
5.2	298	25	3.4
6.1	313	40	3.2
14.2	333	60	3.0

Figure 29 ARRHENIUS PLOT FOR COPOLYMERIZATION OF MMA AND STY IN THE PRESENCE OF DEAC CONDUCTED BETWEEN 0 AND 60 DEGREES C.


-11.2
-11.4
-11.6
-11.8
-12.0
-12.2
-12.4
-12.6
-12.8
$\ell n\ k_p'$
3.0
3.2
3.4
3.6
$\frac{1}{T} \times 10^3$

As the orbital energies of a vinyl monomer radical are easily visualized as being lowered by complexation, the Zubov argument becomes particularly attractive.

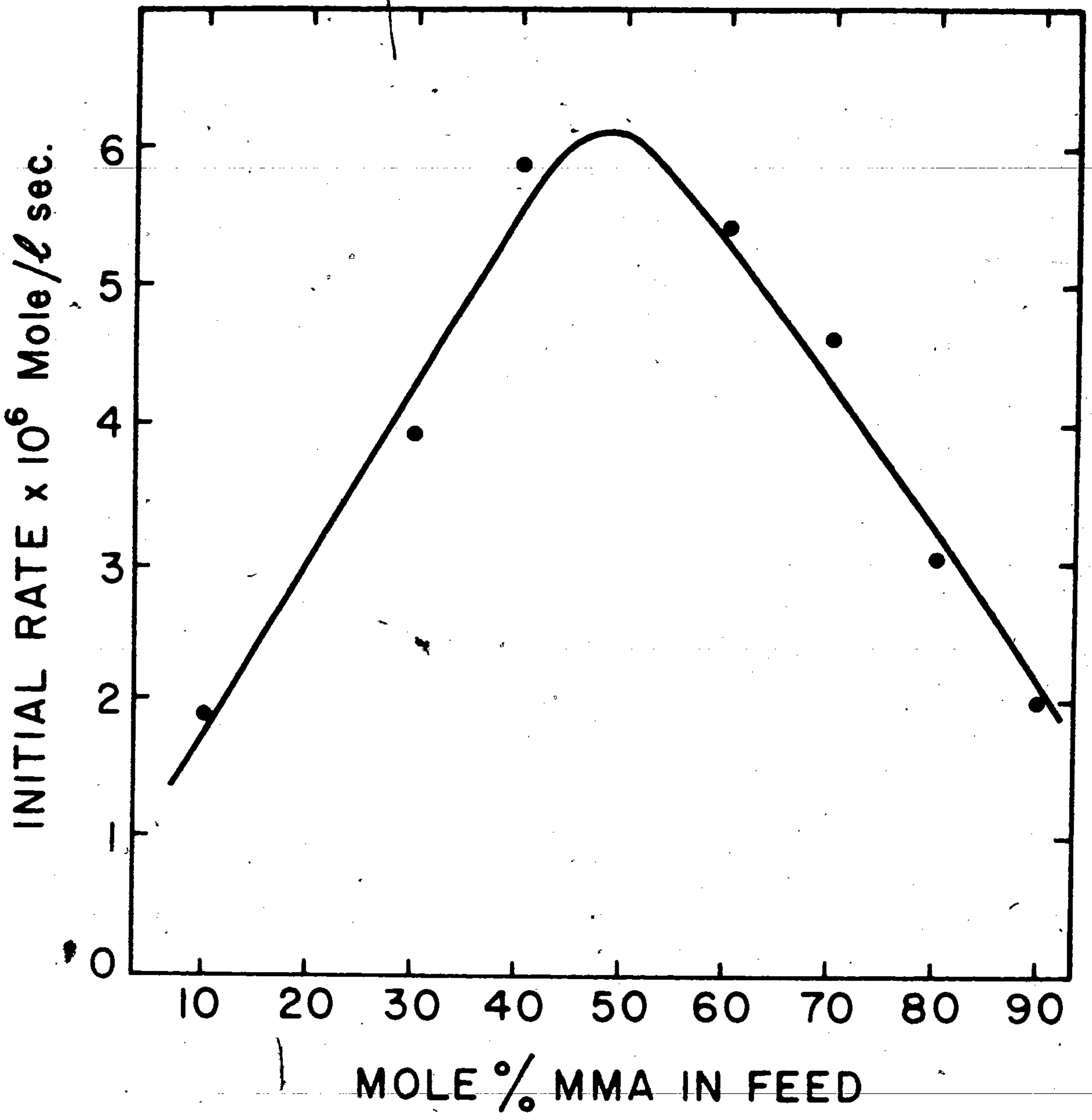
III.2.4 INITIAL REACTION RATE AND FEED RATIO RELATIONSHIPS

Figure (30) shows the relationship between the monomer feed ratio and the rate of polymerization for a series of copolymerization containing methyl methacrylate feeds between 10 and 90 mole %. A rate maximum is found at a feed ratio corresponding to 50 mole % methyl methacrylate. NMR analysis of the products compare with known alternating copolymers of methyl methacrylate and styrene. Hence an addition mechanism providing for the preference for alternating addition of each monomer throughout the propagating chain is indicated in both these data and the data of other workers (101). A rate maximum is expected at a point where a maximum in comonomer monomer concentration (equimolar concentration) exists. The second order kinetics fit of the data reflects this observation.

Normal radical copolymerization is shown to obey expression (III-8) (145).

Figure 30 INITIAL RATE OF THE COPOLYMERIZATION OF MMA AND STY WITH DEAC.

[MMA] + [STY] = 1.94; [MMA] : [DEAC] = 2:1


INITIAL RATE x 10^6 Mole/ℓ sec.
0
1
2
3
4
5
6
10
20
30
40
50
60
70
80
90
MOLE % MMA IN FEED

$$R_p = \frac{(r_1 [M_1]^2 + 2 [M_1] [M_2] + r_2 [M_2]^2) R_i^{1/2}}{(r_1^2 \delta_1^2 [M_1]^2 + 2\phi r_1 r_2 \delta_2 \delta_1 [M_1] [M_2] + r_2^2 \delta_2^2 [M_2]^2)^{1/2}} \qquad \text{III-8}$$

where $\delta_1 = \left(\frac{2k_{t11}}{k_{11}^2}\right)^{1/2}$; $\delta_2 = \left(\frac{2k_{t22}}{k_{22}^2}\right)^{1/2}$

and $\phi = \frac{k_{t12}}{2(k_{t11}k_{t22})^{1/2}}$

and k_{t11} and k_{t12} are the homo termination rate constants. The ϕ value of this expression represents the favourability of cross termination. A ϕ value less than 1 indicates unfavourable cross termination whereas the contrary is true for a ϕ value greater than 1.

The tendency toward alternation parallels the tendency to cross terminate since ϕ increases with decreasing r_1r_2 product (146). Thus ϕ values greater than 1 are required for alternation. In alternating copolymerizations, it is difficult to predict the overall shape of a feed composition vs rate curve due to the offsetting effects of small r_1r_2 products and large ϕ values. Walling (147), however, supported theoretical calculations with experimental evidence and showed feed composition vs rate curves for ϕ values of 1 and 13. Different curve shapes were shown in both instances with a minimum curve shown for the greater ϕ value and a straight line for ϕ equal to 1. The evidence of Walling and others

(148) indicates that systems with a tendency to alternate ($\phi > 1$) show minima in the monomer feed composition vs rate curves. These rate minima are observed in systems where each comonomer is capable of homo polymerization. In situations where one monomer is not capable of homo polymerization, $r_2 = 0$, a rate maximum is predicted (149). The position of this rate maximum depends upon the values of a modified expression, (III-9), from (III-8) where the r_2 value is equated to 0 and the sum of the monomer concentrations is given as 1.

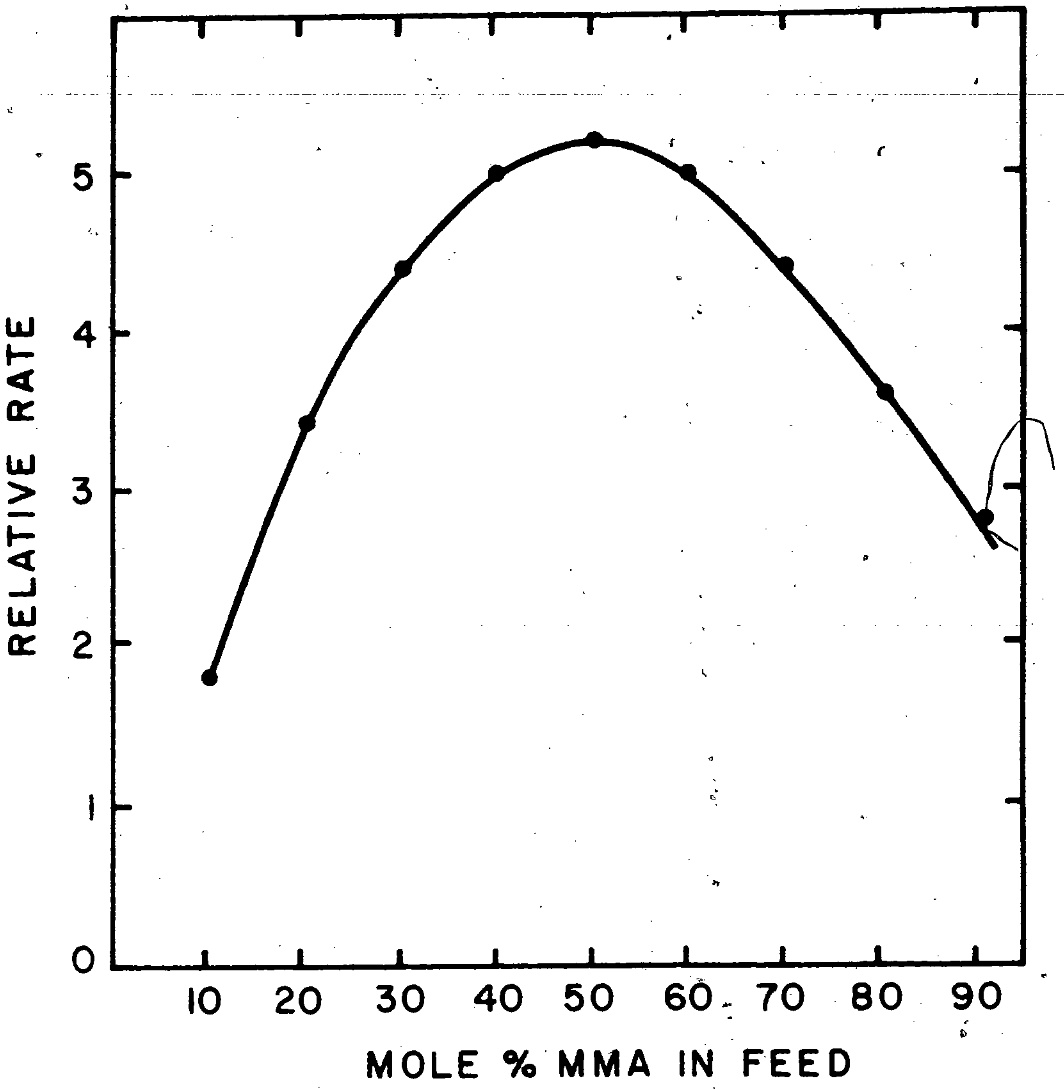
$$R = \frac{(r_1 - 2)A^2 + 2aA}{(XA^2 + 2YA + C^2)1/2} \qquad \text{III-9}$$

where
$$X = r_1^2 \delta_a^2 - 2\phi r_1 \delta_a \xi + \xi^2$$
$$Y = \phi r_1 \delta_a \xi a - a\xi^2$$
$$C = \xi a$$
$$\delta a = (2k_{taa})^{1/2} / k_{paa}$$
$$\xi = (2k_{tbb})^{1/2} / k_{pba}$$
$$\phi = k_{tab} / 2(k_{taa} k_{tbb})^{1/2}$$

An iterative selection of possible values for the above parameters of equation (III-9) is found to provide a theoretical curve, figure (31), with a rate maximum at 50 mole % of each

Figure 31 THEORETICAL PLOT OF THE CHANGE IN RELATIVE RATE WITH RESPECT TO MONOMER FEED.

$r_1 = 0.25$; $r_2 = 0$; $\delta = 12$; $\phi = 0.5$; $\xi = 2$.


RELATIVE RATE
0
1
2
3
4
5
10
20
30
40
50
60
70
80
90
MOLE % MMA IN FEED

monomer. This figure shows a close resemblance to the experimental curve, figure (30). The r_1 value used in the simulation, shown in figure (31), ($r_1 = 0.25$) relates to a monomer favouring cross propagation to homo propagation ($r_1 < 1$). Yamada has shown (53) that in a complexed alternating copolymerization, reactivity ratios of the comonomers are significantly smaller than in the conventional radical situation. He found with acrylonitrile and styrene chloride, the reactivity ratios were at least an order of magnitude lower for both monomers compared to their radical counterparts. Since the monomer used in the equation (III-9) simulation involves a monomer not capable of homo polymerization ($r_2 \ll 1$) and a monomer of preferred cross propagation ($r_1 < 1$), the resulting copolymer would be highly alternating. Hence, normal radical kinetics according to equation (III-8) are consistent with observation of figure (30).

III.2.5 MOLECULAR WEIGHT CHANGES

Molecular weight changes ($\overline{M}_n$) that occur with changes in monomer feed ratios are shown in figure (32). A comparison with published (150) radical molecular weight changes is also shown. It is clearly seen that as the MMA concentration is increased, the $\overline{M}_n$ value decreases. This is in direct contrast to the conventional radical situation. Rate studies, figure (30), show that as the MMA* concentration in the monomer feed increases, rate increases are seen to a maximum value at 50

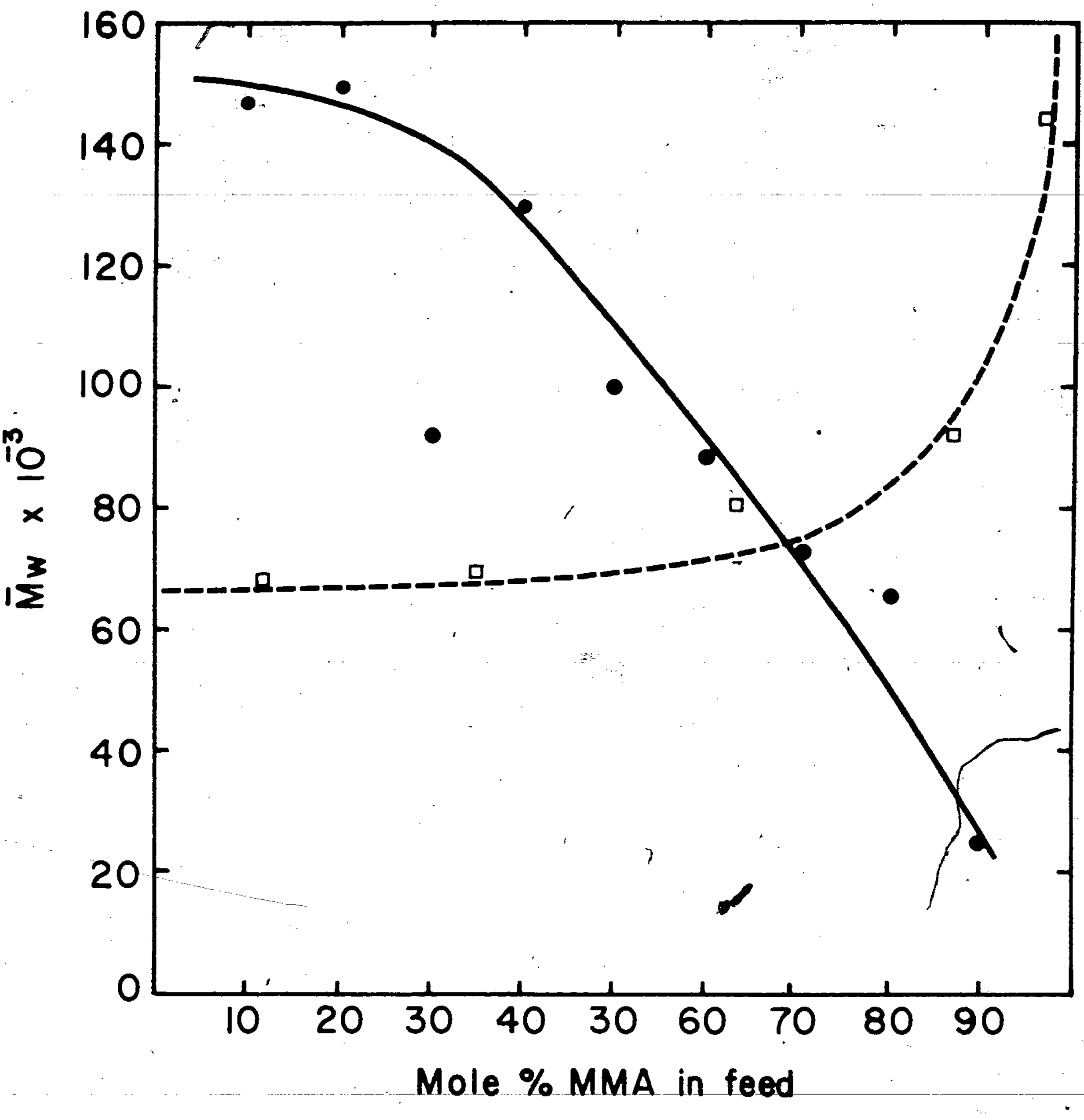
Figure 32 PRODUCT MOLECULAR WEIGHT VS THE MOLE % MMA IN MONOMER FEED.

●——● $\overline{M}_n$ FOR THE COPOLYMERIZATION OF MMA AND STY IN THE PRESENCE OF DEAC

$[MMA] + [STY] = 1.95$;

$[MMA] : [DEAC] = 2:1$ AT 25°C.

□----□ $\overline{M}_w$ FOR RADICAL (AIBN) COPOLYMERIZATION OF MMA AND STY AT 25°C. (150)


160
140
120
100
80
60
40
20
0
$\bar{M}w \times 10^{-3}$
10
20
30
40
30
60
70
80
90
Mole % MMA in feed

mole % MMA*, after which the rate decreases with increasing MMA* concentration in the monomer feed. Hence, it appears that the rate and molecular weight features of these reactions do not show a simple correlation. Normally radical polymerizations show decreases in molecular weight with increasing rates (151). Thus, where a rate maximum is shown, figure (30), a molecular weight minimum would be expected. A plausible explanation for the observed decrease in molecular weight with increases in MMA* concentration is non-degradative chain transfer to the complexed monomer. Figure (33) shows the $\overline{M}_n$ dependence on the diethylaluminum chloride concentration and indicates a high stoichiometric n value (Section III.2.1) for the chain transfer active species. Assuming non-degradative chain transfer is the major molecular weight controlling factor and that the cross propagation reaction is preferred between the complexed monomer and the styrene comonomer, the following will be true:

$$\overline{DP} = \frac{\text{Rate of Propagation}}{\text{Rate of Transfer}} \qquad \text{III-10}$$

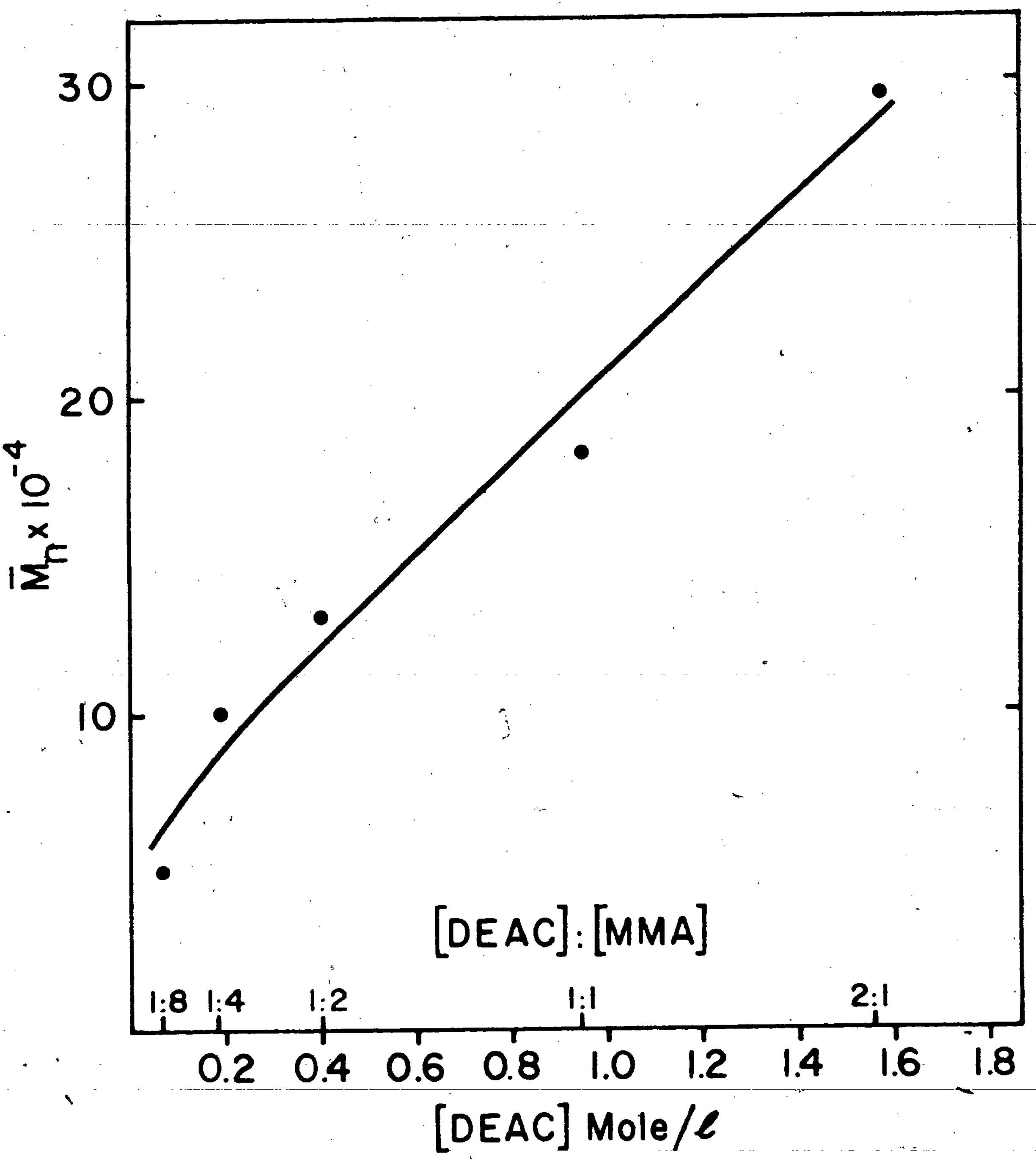
then:

$$\sim M_1^{\bullet} + M_2 \xrightarrow{k_{12}} \text{Polymer}$$

$$\sim M_2^{\bullet} + M_1 \xrightarrow{k_{21}} \text{Polymer}$$

where M_1 is considered as the complexed monomer.

Figure 33 THE DEPENDENCE OF $\overline{M}_n$ ON THE CONCENTRATION OF DEAC ([MMA] : [STY] = 2:3) AT 25°C



30
20
10
$\bar{M}_n \times 10^{-4}$
[DEAC]:[MMA]
1:8
1:4
1:2
1:1
2:1
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
[DEAC] Mole/ℓ

The rate of propagation is:

$$R_p = k_{12}\,[M_1^{\cdot}]\,[M_2] + k_{21}\,[M_2^{\cdot}]\,[M_1] \qquad \text{III-11}$$

Assuming a steady state:

$$k_{12}\,[M_1^{\cdot}]\,[M_2] = k_{21}\,[M_2^{\cdot}]\,[M_1] \qquad \text{III-12}$$

then:

$$R_p = 2k_{12}\,[M_1^{\cdot}]\,[M_2] \qquad \text{III-13}$$

As termination of an individual chain is assumed to be largely due to non-degradative chain transfer, termination can be considered as:

$$\sim M_1^{\cdot} + M_1 \xrightarrow{k_{t11}} \text{Polymer} + M_1^{\cdot}$$

$$\sim M_2^{\cdot} + M_1 \xrightarrow{k_{t12}} \text{Polymer} + M_1^{\cdot}$$

The rate of non-degradative chain transfer is then:

$$R_t = k_{t11}\,[M_1^{\cdot}]\,[M_1] + k_{t21}\,[M_2^{\cdot}]\,[M_1] \qquad \text{III-14}$$

The incorporation of both (III-11) and (III-14) in (III-10) gives (III-15).

$$\overline{DP} = \frac{2k_{12}\,[M_1^{\cdot}]\;[M_2]}{k_{t11}\,[M_1^{\cdot}]\;[M_1] + k_{t21}\,[M_2^{\cdot}]\;[M_1]} \qquad \text{III-15}$$

or

$$\frac{1}{\overline{DP}} = \frac{k_{t11}\,[M_1^{\cdot}]\;[M_1] + k_{t21}\,[M_2^{\cdot}]\;[M_1]}{2k_{12}\,[M_1^{\cdot}]\;[M_2]} \qquad \text{III-16}$$

Simplifying (III-16) gives (III-17).

$$\frac{1}{\overline{DP}} = \left(\frac{[M_1]}{[M_2]}\right)\left(\frac{k_{t11}}{2k_{12}} + \frac{k_{t21}\,[M_2^{\cdot}]}{2k_{12}\,[M_1^{\cdot}]}\right) \qquad \text{III-17}$$

Using the steady state assumption (III-12) gives:

$$M_2 = \frac{k_{12}\,[M_1^{\cdot}]\;[M_2]}{k_{21}\,[M_1]} \qquad \text{III-18}$$

Substituting (III-18) into (III-17) gives (III-19)

$$\frac{1}{\overline{DP}} = \left(\frac{[M_1]}{[M_2]}\right)\left(\frac{k_{t11}}{2k_{12}} + \frac{k_{t21}\;[M_2]}{k_{12}k_{21}[M_1]}\right) \qquad \text{III-19}$$

or

$$\frac{1}{\overline{DP}} = C_1 \frac{[M_1]}{[M_2]} + C_2 \qquad \text{III-20}$$

where

$$C_1 = \frac{k_{t11}}{2k_{12}} \quad \text{and} \quad C_2 = \frac{k_{t21}}{k_{12}\,k_{21}}$$

From (III-20) it can be seen that a test for non-degradative chain transfer is a plot of the monomer ratio vs $1/\ \overline{DP}$ $(1/\ \overline{M}_n)$. Such a plot should provide a straight line if non-degradative chain transfer is a major termination process.

Data from a series a polymerizations involving changes in monomer ratios are plotted in figure (34) according to expression (III-20). Figure (34) indicates good agreement with expression (III-20). Thus the molecular weight controlling factor present in complexed alternating copolymerization systems appears to be non-degradative chain transfer to the complexed monomer; e.g., MMA*.

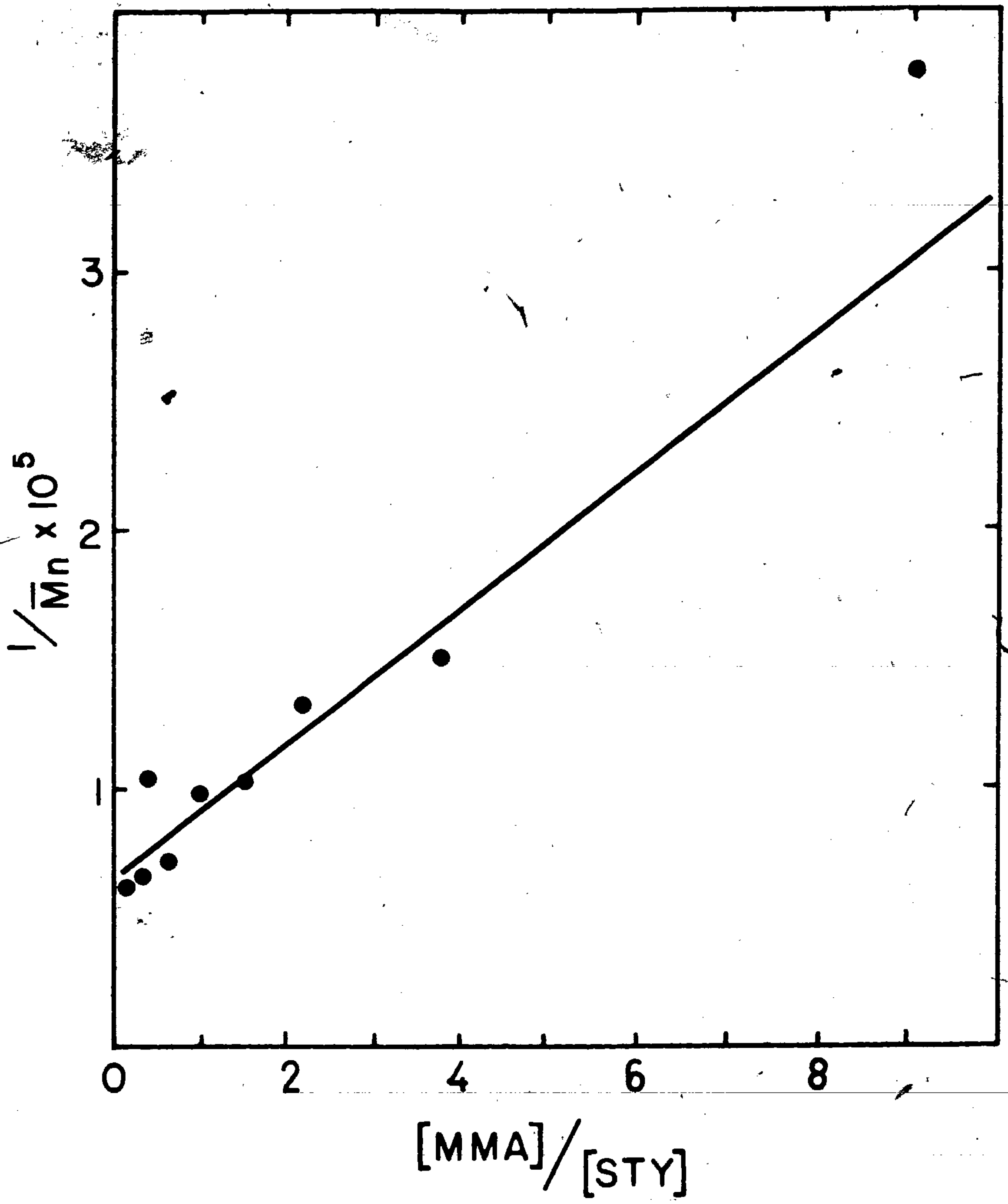
III.3 CHAIN TRANSFER STUDIES

III.3.1 CHAIN TRANSFER CONSTANTS OF COMPLEXED MONOMERS

Introduction

Figure (34) and expression (III-20) show a strong resemblance to a Mayo plot commonly used for the determination of chain transfer constants of chain transfer agents

Figure 34 RECIPROCAL PRODUCT $\overline{M}_n$ VS [MMA] / [STY] FOR THE COPOLYMERIZATION OF MMA AND STY IN THE PRESENCE OF DEAC. [MMA] + [STY] = 1.95; [MMA] : [DEAC] = 2:1.



$1/\overline{M}_n \times 10^5$
3
2
1
0
2
4
6
8
[MMA]/[STY]

(152). In fact, figure (34) suggests that transfer constants for MMA* may be obtained via a Mayo treatment conducted in a situation where the MMA* is in excess of a 1:1 molar ratio with the comonomer (styrene in the present case). If the MMA* in excess of the concentration of styrene is considered as the transfer agent, then expression (III-21) can be applied (153).

$$\frac{1}{\bar{M}_n} = \frac{k_t \; R_p}{k_p^2 \; [M]^2} + C_s \; \frac{[S]}{[M]} \qquad \text{III-21}$$

where [M] is the concentration of styrene and [S] the transfer agent or the excess MMA* complex. The Mayo procedure involves a plot of $1/\bar{M}_n$ vs [S] / [M] whereby a straight line of slope C_s is obtained as $k_t \; R_p \; / \; k_p^2 [M]^2$ is held constant.

Results and Discussion

Figure (35) shows a plot of data obtained from a series of copolymerizations between MMA* complex and styrene where the MMA* concentration is in excess of that of styrene. The linear relationship indicates that $k_t \; R_p \; / \; k_p^2 \; [M]^2$ is constant and chain transfer is indicated. A linear least squares fit of the data in figure (35) provides a chain transfer constant of 7.1×10^{-4} for the MMA* complex. Since the transfer of the radical site from the growing polymer molecule is not considered to affect the kinetic chain, rates will be unaffected with increase in chain transfer.

$$\mathrm{P}\cdot \quad + \quad \mathrm{MMA}^* \longrightarrow \mathrm{P} \quad + \quad \mathrm{MMA}^*$$

$$\mathrm{MMA}^* \quad + \quad \mathrm{STY} \longrightarrow \mathrm{P}\cdot$$

Similar experiments ($1/\overline{M}_n$ vs monomer complex correlations) were performed with methyl acrylate-diethylaluminum chloride, styrene; acrylonitrile-diethylaluminum chloride, styrene; and methacrylonitrile-diethylaluminum chloride, styrene. Mayo plots for these data are shown in figures (36, 37 and 38) respectively. Least squares slopes of these figures provides monomer chain transfer constants approximately two orders of magnitude greater than their uncomplexed counterparts, table (X). In both the complexed and uncomplexed cases, the magnitude of the chain transfer constants rank in the same order, e.g., (methyl acrylate > methyl methacrylate > methacrylonitrile > acrylonitrile). Figure (38) provides a questionable linear correlation and is included for completeness. Least squares treatment does, however, provide a chain transfer constant consistent with the other monomers, although the standard deviation for this curve is large.

Figure 35 MAYO PLOT OF $1/\overline{M}_n$ VS [MMA] - [STY] / [STY] FOR THE COPOLYMERIZATION OF MMA AND STY WITH DEAC. [MMA] = [STY] = 1.95; [MMA] : [DEAC] = 1:1

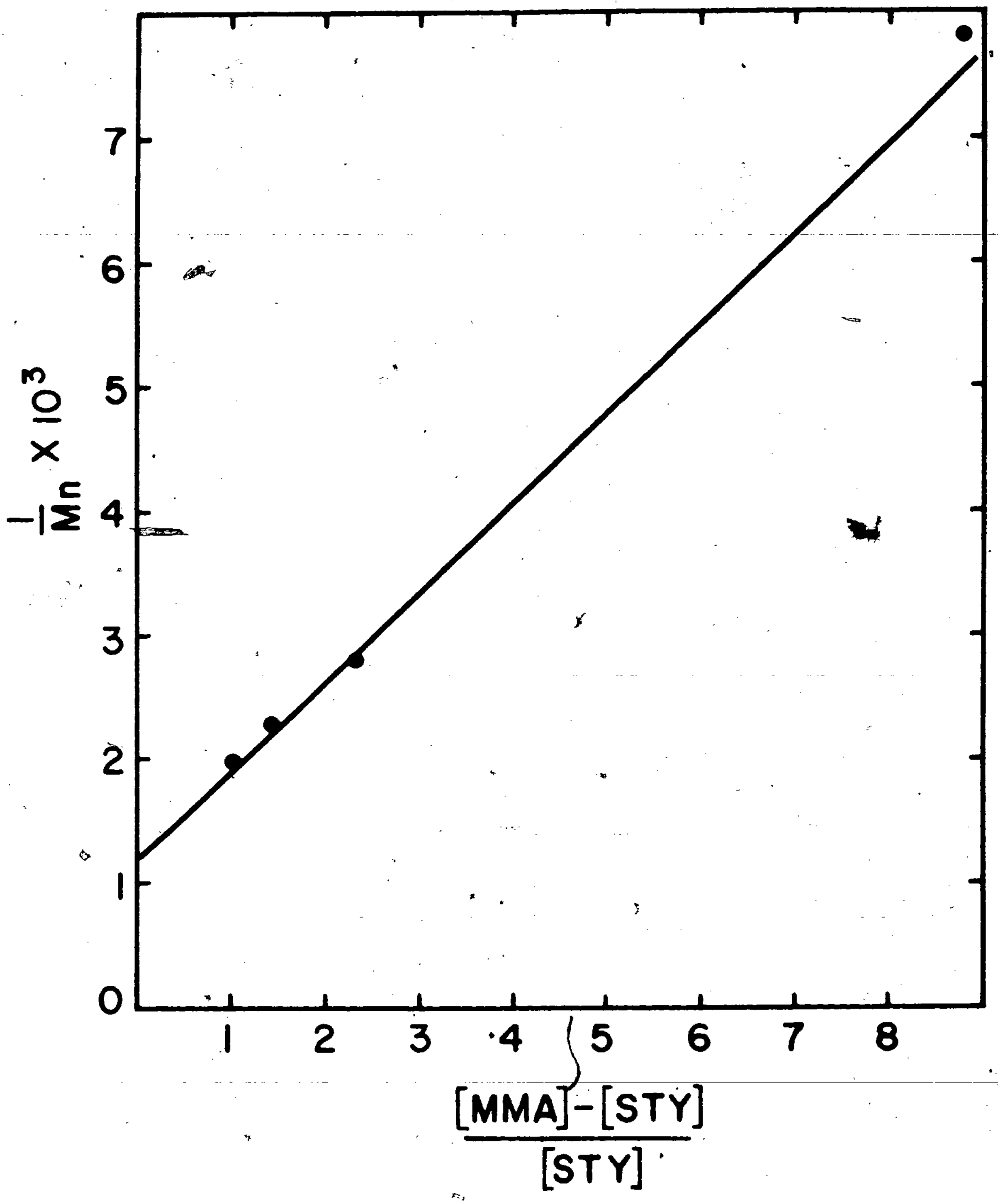

$\frac{1}{\bar{M}n} \times 10^3$
0
1
2
3
4
5
6
7
1
2
3
4
5
6
7
8
$\frac{[MMA]-[STY]}{[STY]}$

Figure 36 MAYO PLOT OF PRODUCT $1/\overline{M}_n$ VS [MA] - [STY] / [STY] FOR THE COPOLYMERIZATION OF MA AND STY IN THE PRESENCE OF DEAC AT 25°C. [MA] + [STY] = 2.10; [MA] : [DEAC] = 2:1.

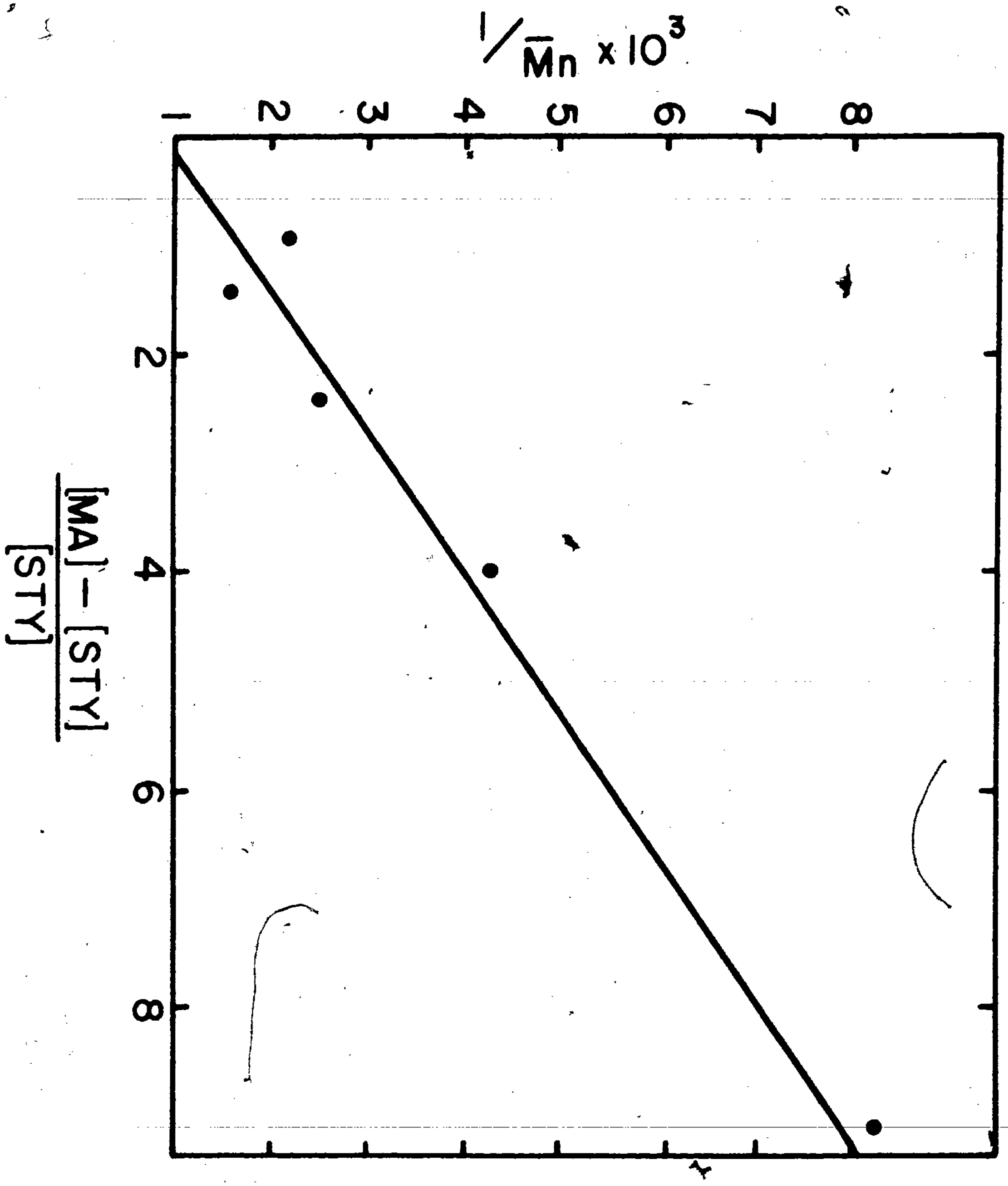

$1/\bar{M}n \times 10^3$
1
2
3
4
5
6
7
8
$\frac{[MA]-[STY]}{[STY]}$
2
4
6
8

Figure 37 MAYO PLOT OF PRODUCT $1/\overline{M}_n$ VS [AN] - [STY] / [STY] FOR THE COPOLYMERIZATION OF AN AND STY IN THE PRESENCE OF DEAC. [AN] + [STY] = 2.70; [AN] : [DEAC] = 2:1.

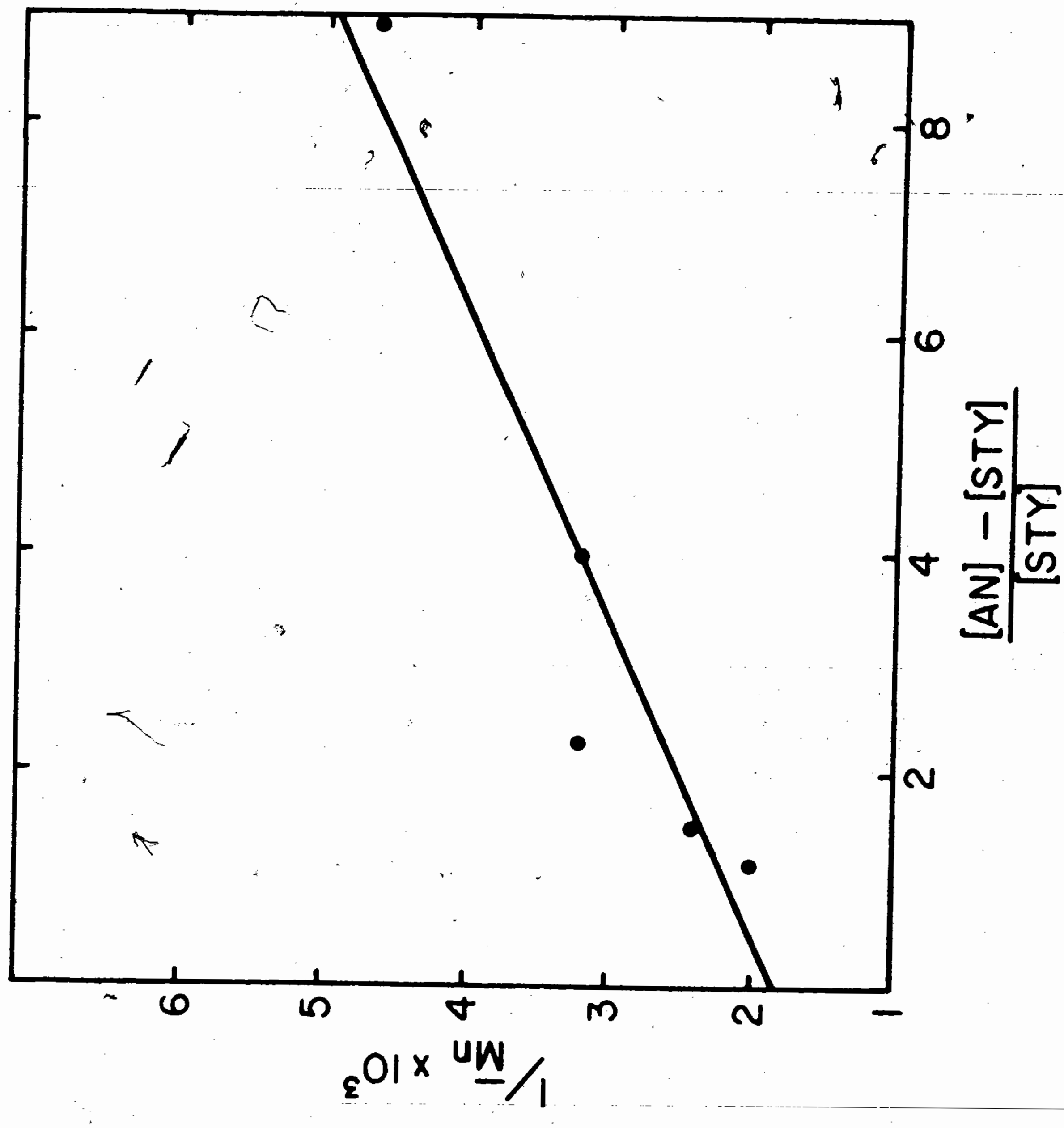

$1/\overline{M}_n \times 10^3$
1
2
3
4
5
6
$\frac{[AN] - [STY]}{[STY]}$
2
4
6
8

Figure 38 MAYO PLOT OF PRODUCT 1/ $\bar{M}_n$ VS [MAN] - [STY] / [STY] FOR THE COPOLYMERIZATION OF MAN AND STY IN THE PRESENCE OF DEAC.[MAN] + [STY] = 2.30, [MAN] : [DEAC] = 2:1.

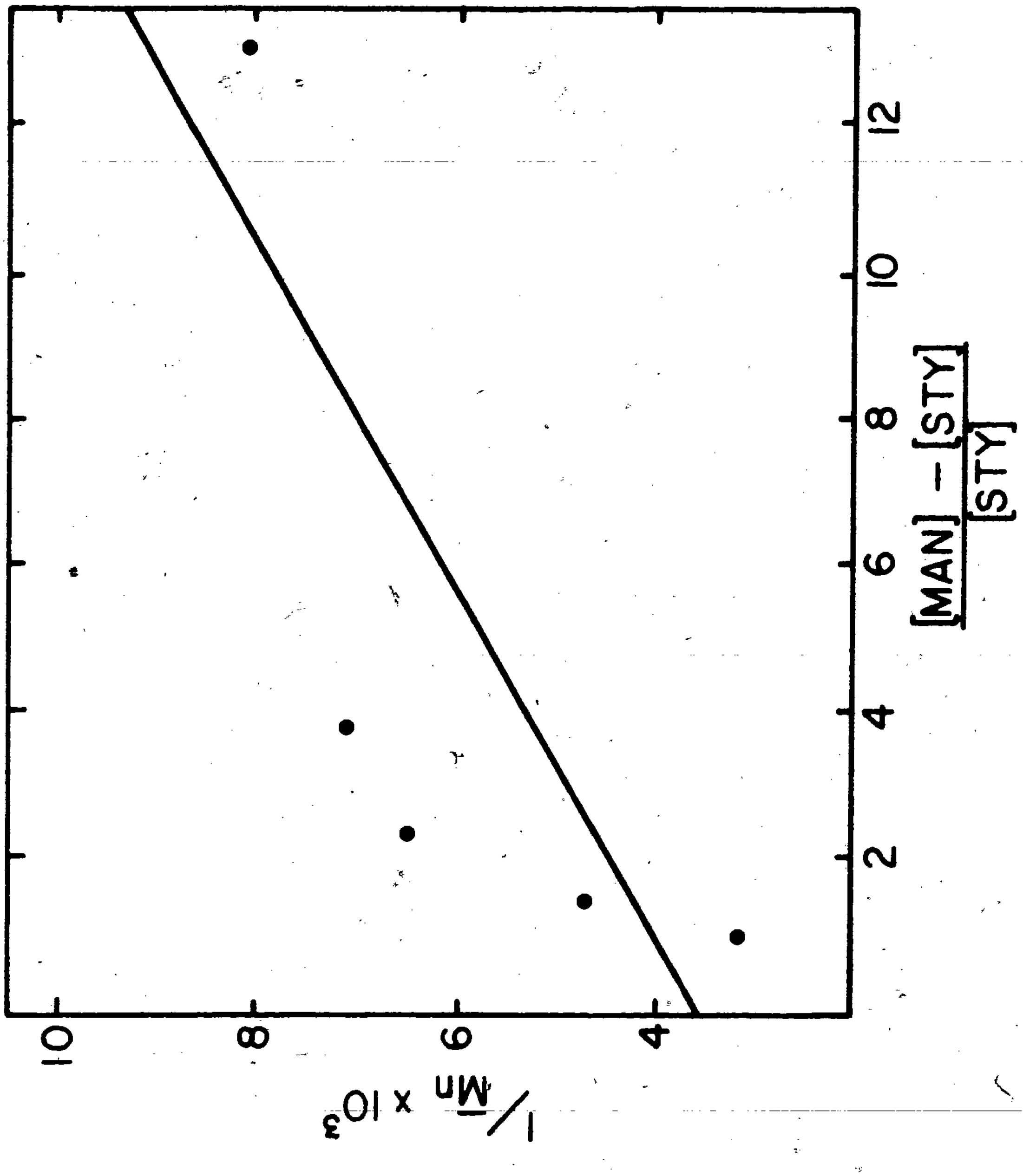

$1/\overline{M}_n \times 10^3$
10
8
6
4
2
4
6
8
10
12
$\frac{[MAN] - [STY]}{[STY]}$

TABLE X

Literature (Radical) (154) C_m Values of the Indicated Monomer with Styrene Comonomer at 25°C and Calculated DEAC Complexed C_m Values with Styrene Comonomer at 25°C

Monomer	Lit. $C_m \times 10^6$	Complexed $C_m \times 10^4$
MA	4.08	7.6 ± 0.2
MMA	2.81	7.1 ± 0.2
MAN	2.38	4 ± 2
AN	2.22	3.4 ± 0.6

III.3.2 CHEMICAL ASPECTS OF CHAIN TRANSFER IN COMPLEXED ALTERNATING COPOLYMERIZATION

The chain transfer constants of diethylaluminum chloride complexed monomer are shown to be approximately two orders of magnitude greater than their uncomplexed counterparts. If the occurrence of chain transfer is facilitated by the abstraction of a hydrogen atom from the transfer moeity (monomer-diethylaluminum chloride complex), then the complexed situation should provide a more facile route for this process as indicated by the higher Cm value. Such a situation would occur if the complexed monomer radical produced from a chain transfer event were more stable than its uncomplexed counterpart, e.g., the more stable the radical the easier the formation.

It has been suggested (155) that π system conjugation in a vinyl monomer is extended by complexation. When a vinyl compound such as acrylonitrile or methyl methacrylate is complexed through functional groups such as CN or C=O evidence for increased delocalization between the vinyl bond and the functional group is seen by IR and NMR (66). Hence, when such a situation occurs, a radical species generated from this complex should be more stable due to the increase in delocalization. As a consequence, it is proposed that the greater delocalization resulting from complexation contributes to a large extent on the ease of non-degradative chain transfer.

III.3.3 CHAIN TRANSER - Q VALUE CORRELATIONS

Various attempts have been made to relate radical monomer reactivities on a quantitative basis in terms of structure and reactivity correlation. A generally useful correlation is the Qe scheme of Alfrey and Price (10). The Qe scheme proposes the rate constants for a radical-monomer reaction can be written as a function of several parameters two of which are Q and e (Section I.5). Molecular orbital treatments have shown that Q values are related to the localization energy of the monomer and the e value has been related to electron affinity (156). Considering that Q value reflects delocalization (more delocalization with greater Q value), the greater Q values will provide more stable radicals with a greater ease of formation. It has been shown (53, 66, 88) that monomer moeities of greater Q value are provided by complexation. Hence, monomers of normally high Q values will provide complexed monomers of even higher Q values. Thus the ease of non-degradative chain transfer is indicated by the magnitudes of the Q values. Consequently, product molecular weights from complexed copolymerizations should be lowest with monomers of high Q values. Table (XI) contains molecular weight and Q value data for copolymerizations involving methyl methacrylate, acrylonitrile, methacrylonitrile, chloroacrylonitrile, and methyl chloroacrylate complexed with diethylaluminum chloride, with styrene comonomer. Similar data are also shown for ethylaluminum sesquichloride complexing agent. The corresponding monomer Q values for these monomers and product

TABLE XI

Product Molecular Weight from Polymerizations Incorporating Monomers of Various Q Values with Styrene and DEAC or EASC

Monomer	Q Value	Mole % in Feed	Complexing Agent	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w \times 10^{-3}$
MMA	0.74	40	DEAC	106	277
			EASC	443	2110
MA	0.42	40	DEAC	87	678
AN	0.60	40	DEAC	80	259
			EASC	132	588
MAN	1.12	40	DEAC	55	120
			EASC	102	285
CAN	1.72	40	DEAC	18	54
			EASC	13	35
MCA	2.02	40	DEAC	15	32
			EASC	18	44

reciprocal molecular weights ($\bar{M}_n$ and $\bar{M}_w$) for both complexing agents are shown plotted on figures (39) and (40). It can clearly be seen from these figures that a definite relationship exists between the Q value and the product molecular weight. Increases in Q value show decreases in molecular weight consistent with the non-degradative chain transfer hypothesis.

III.4 KINETIC AND MOLECULAR WEIGHT STUDIES OF THE COMPLEXED ALTERNATING COPOLYMERIZATION OF METHYL METHACRYLATE AND ISOPRENE IN THE PRESENCE OF DIETHYLALUMINUM CHLORIDE OR ETHYLALUMINUM SESQUICHLORIDE

Introduction

No kinetic and molecular weight studies of complexed alternating copolymerization involving diene monomers have been reported. Kinetics of acrylonitrile-butadiene copolymerization have been reported (157). However, this study involved zinc chloride complexing agent and devoted little attention to molecular weight aspects of that system.

In this research, a study of the methyl methacrylate-isoprene comonomer pair spontaneously copolymerized by either diethylaluminum chloride or ethylaluminum sesquichloride was undertaken. Previous studies of this system (67) showed that the copolymer product was alternating and features of the reaction were consistent with those found in other

Figure 39 RECIPROCAL PRODUCT $\overline{M}_n$ AGAINST MONOMER Q VALUE;

●——— DEAC

○ – – – EASC

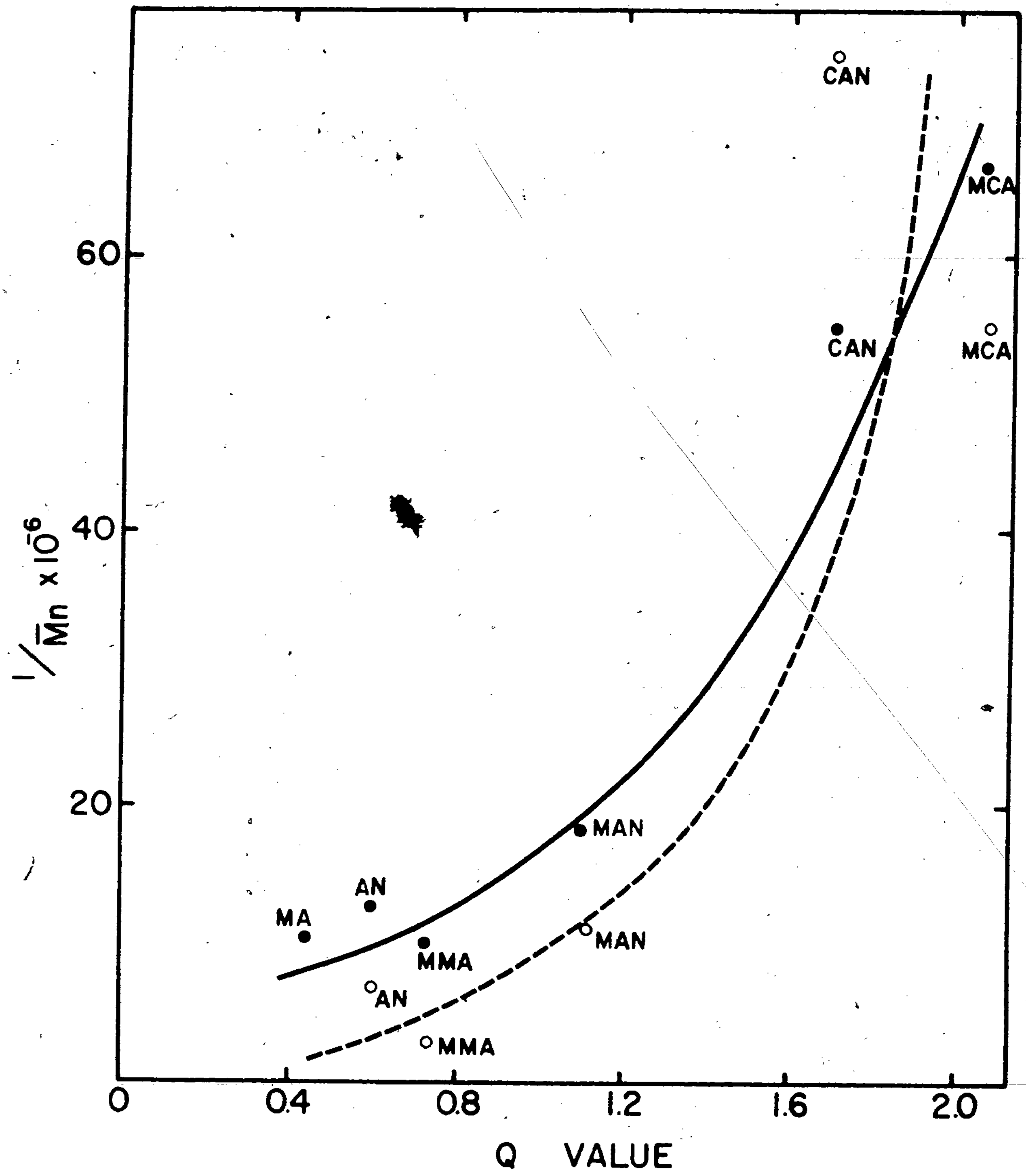
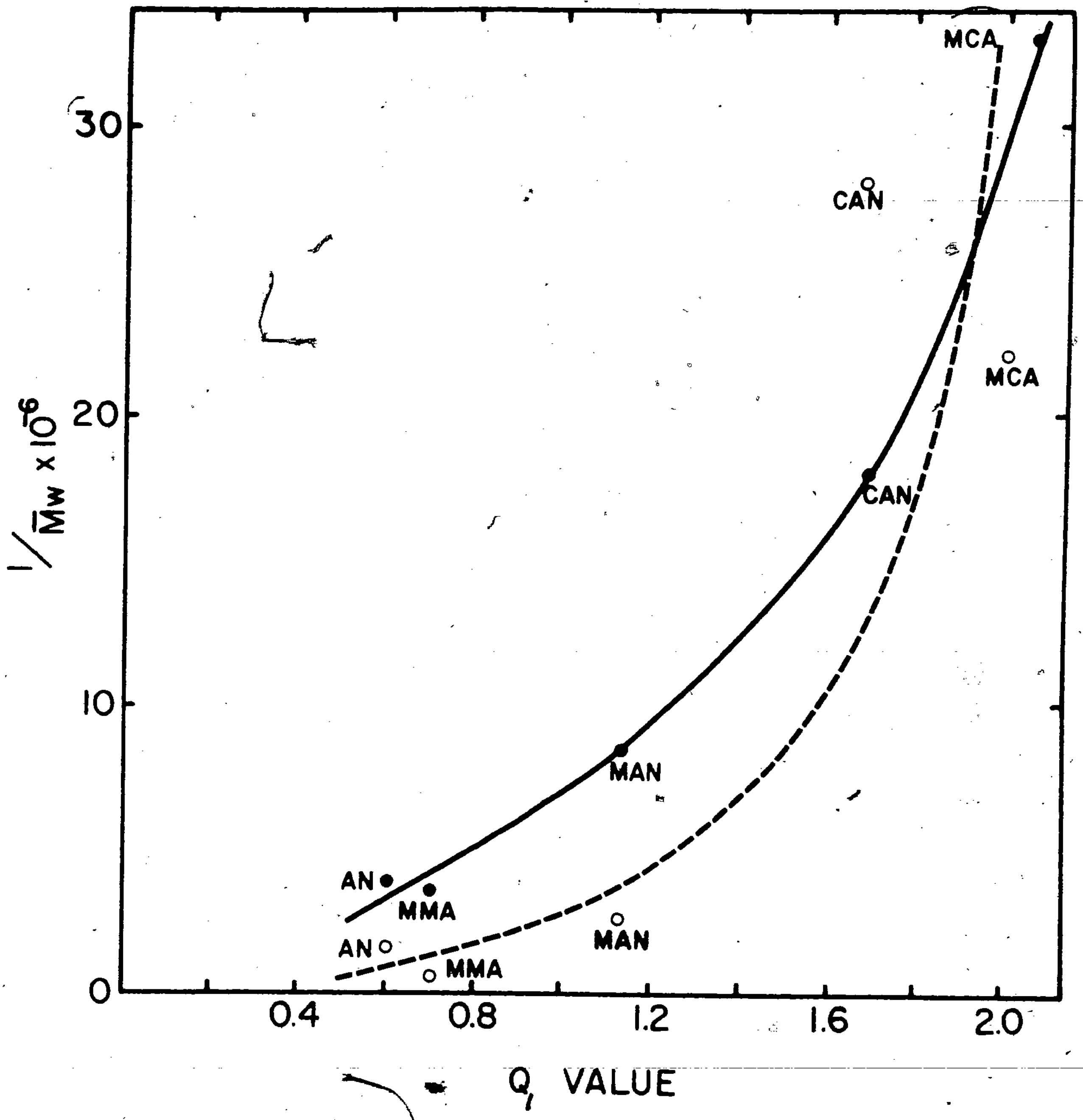

$1/\bar{M}n \times 10^{-6}$
60
40
20
0
0.4
0.8
1.2
1.6
2.0
Q VALUE
CAN
MCA
CAN
MCA
MAN
AN
MA
MMA
AN
MAN
MMA

Figure 40 RECIPROCAL PRODUCT $\bar{M}_w$ AGAINST MONOMER Q VALUE;

● ——— DEAC

○ – – – EASC


1/$\bar{M}_w$ x 10^-6
0
10
20
30
0.4
0.8
1.2
1.6
2.0
Q, VALUE
MCA
CAN
MCA
CAN
MAN
AN
MMA
AN
MAN
MMA

complexed alternating copolymerizations.

Conditions in this study were duplicated as closely as possible to the conditions used in the previous methyl methacrylate-styrene investigation and a comparison between these systems is provided. Methyl methacrylate/complexing agent ratios are maintained at 2:1 and the symbol MMA* is maintained to designate this condition.

Results and Discussion

III.4.1 MONOMER REACTION ORDERS

Van't Hoff plots from experiments, where the MMA* complex (both diethylaluminum chloride and ethylaluminum sesquichloride) and isoprene were individually varied, gave n values of 0.9 and 0.5 for MMA* and isoprene respectively. These values were interpreted as unity in the case of MMA* and 1/2 for isoprene. The overall reaction is indicated as a 3/2 order process corresponding to:

$$R = k_p' \,[\mathrm{MMA}^*] \quad [\mathrm{IP}]^{1/2} \qquad \text{III-22}$$

where the reaction constant k_p' is the apparent reaction constant for the overall process.

III.4.2 DETERMINATION OF THE COPOLYMERIZATION RATE CONSTANT

When the copolymer product produced from the copolymerization is considered, equation (III-22) can be re-written as:

$$\frac{dx}{dt} = k_p' \left([MMA^*]_o - x\right)\left([IP]_o - x\right)^{1/2} \qquad \text{III-23}$$

where x is the concentration of monomer consumed. Rearrangement of (III-23) provides (III-24):

$$\frac{dx}{\left([MMA^*]_o - x\right)\left([IP]_o - x\right)^{1/2}} = k_p' dt \qquad \text{III-24}$$

Integration using standard expressions (158, 159) provides (III-25):

$$\frac{1}{\left([IP]_o - [MMA^*]_o\right)1/2} \ln \left| \frac{\left([IP]_o - x\right)^{1/2} - \left([MMA^*]_o - [IP]_o\right)^{1/2}}{\left([IP]_o - x\right)^{1/2} + \left([MMA^*]_o - [IP]_o\right)^{1/2}} \right| = k_p' t \qquad \text{III-25}$$

A series of copolymerizations were done using various concentrations of comonomer. Samples were obtained at 2500 sec. intervals and yields determined. Expression (III-25) was solved, such that the left side of the expression was plotted against time, and k_p' for the reaction determined as the slope of the least squares line through the points.

Figures (41, 42) are the plots for experiments using diethylaluminum chloride complexing agent and figure (43) indicates the data for ethylaluminum sesquichloride. The k_p' values for these reactions are listed in table (XII). Weighted average k_p' values for diethylaluminum chloride and ethylaluminum sesquichloride systems are $4.8 \pm 0.4 \times 10^{-6}\ l^{1/2}\ \mathrm{mole}^{-1/2}\mathrm{sec}^{-1}$ and $2.2 \pm 0.1 \times 10^{-6}\ l^{1/2}\ \mathrm{mole}^{-1/2}\mathrm{sec}^{-1}$ respectively.

A comparison of k_p' values for both of these systems and that of the MMA* styrene system (Section III.2.2) indicates similar magnitudes in all cases.

A common factor present in these copolymerizations is the methyl methacrylate monomer. Both diethylaluminum chloride and ethylaluminum sesquichloride show similar activity in initiating alternating copolymerization, consequently, a common moeity, MMA*, can be considered in these systems. Similar apparent rate constants can be due to a rate controlling step involving complexed methyl methacrylate. It has been shown (115) that aluminum alkyls, when complexed to vinyl monomers, act as a source of free radicals. Thus any reaction step involving the production of radicals by MMA*, and the subsequent interaction of these radicals with comonomer is common to all these systems and will show similar k_p' values.

Figure 41 PLOTS OF 3/2 ORDER RATE EXPRESSION (III-27) FOR COPOLYMERIZATION OF MMA AND IP IN THE PRESENCE OF DEAC.

●——— $[MMA^*]_o = 0.77$; $[IP]_o = 1.80$

○- - - $[MMA^*]_o = 0.99$; $[IP]_o = 1.48$

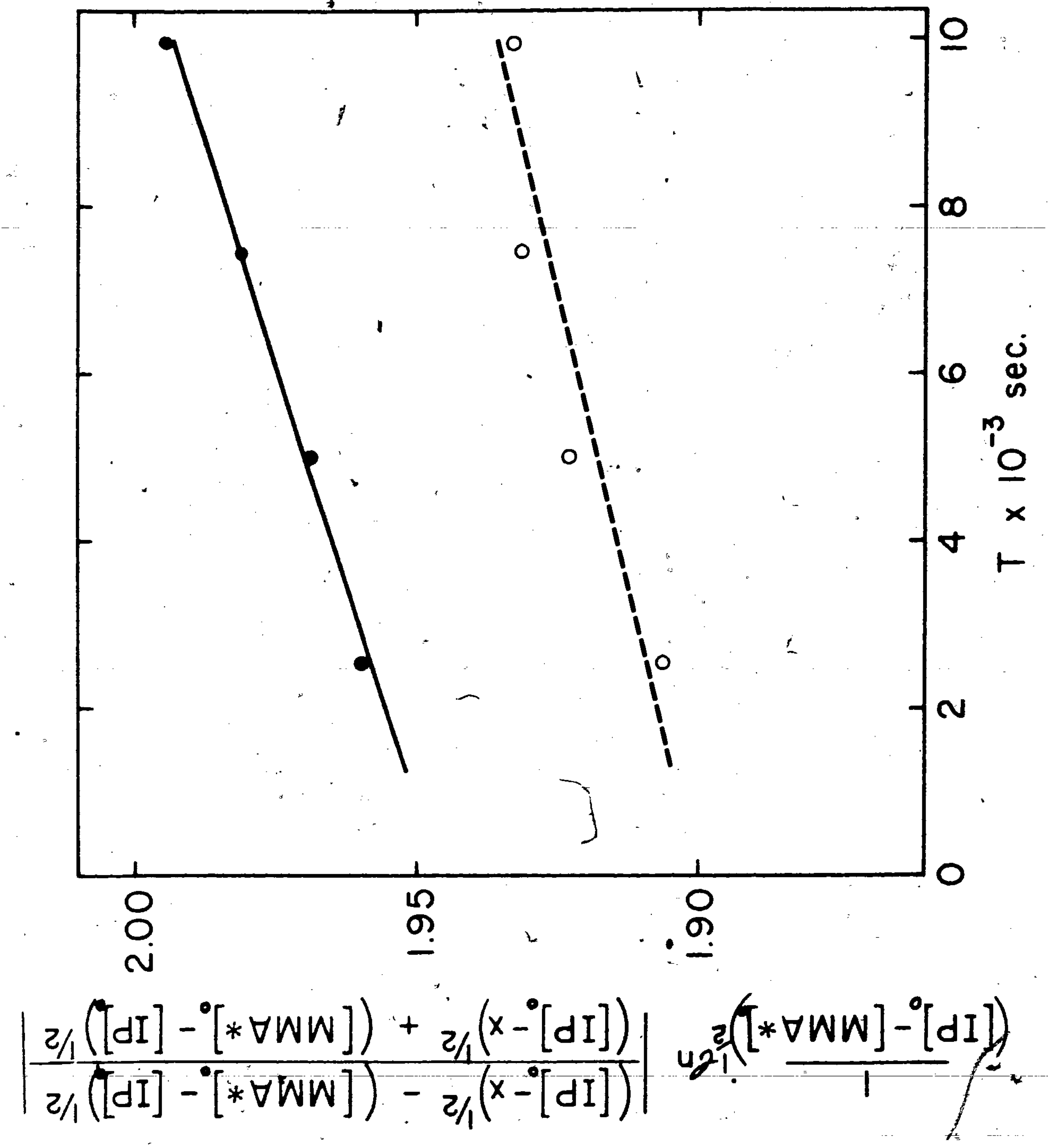

2.00
1.95
1.90
$\frac{1}{([IP]_0-[MMA^*]_0)^{1/2}\,n}\ \ln\left|\frac{([IP]_0-x)^{1/2}-([MMA^*]_0-[IP])^{1/2}}{([IP]_0-x)^{1/2}+([MMA^*]_0-[IP])^{1/2}}\right|$
0
2
4
6
8
10
$T \times 10^{-3}$ sec.

Figure 42 PLOTS OF 3/2 ORDER RATE EXPRESSION (III-27) FOR COPOLYMERIZATION OF MMA AND IP IN THE PRESENCE OF DEAC.

● —— $[MMA^*]_o$ = 1.55; $[IP]_o$ = 0.66

○ - - - - $[MMA^*]_o$ = 1.38; $[IP]_o$ = 0.92

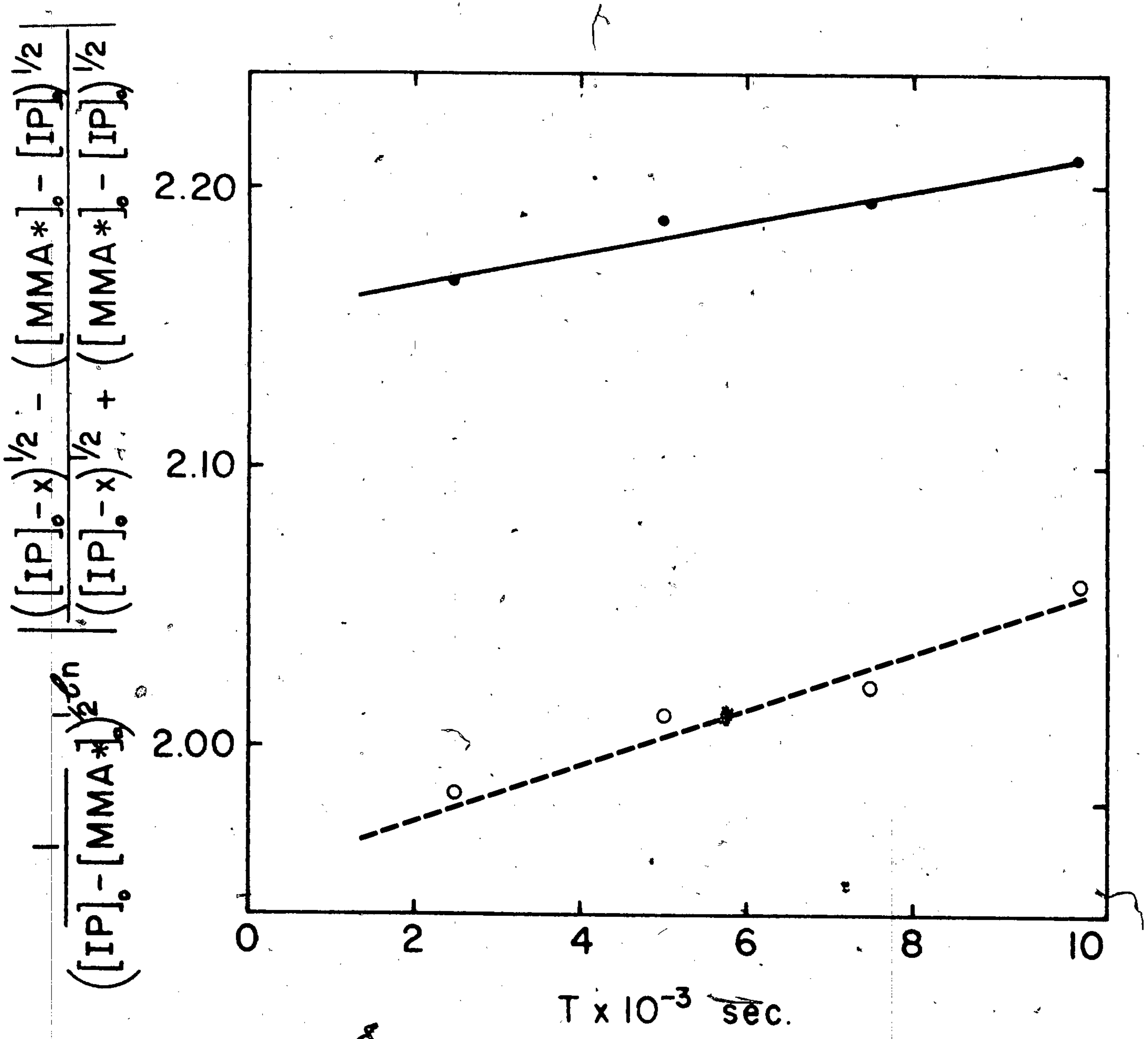

$\frac{1}{([IP]_0-[MMA*]_0)^{1/2}} \ln \left| \frac{([IP]_0-x)^{1/2} - ([MMA*]_0-[IP]_0)^{1/2}}{([IP]_0-x)^{1/2} + ([MMA*]_0-[IP]_0)^{1/2}} \right|$
2.20
2.10
2.00
0
2
4
6
8
10
T x 10^{-3} sec.

Figure 43 PLOTS OF 3/2 ORDER RATE EXPRESSION (III-27) FOR COPOLYMERIZATION OF MMA AND IP IN THE PRESENCE OF EASC.

■ —·— $[\mathrm{MMA}^*]_o = 0.77$; $[\mathrm{IP}]_o = 1.80$

○ ---- $[\mathrm{MMA}^*]_o = 0.99$; $[\mathrm{IP}]_o = 1.48$

● —— $[\mathrm{MMA}^*]_o = 1.38$; $[\mathrm{IP}]_o = 0.92$

□ —·— $[\mathrm{MMA}^*]_o = 1.55$; $[\mathrm{IP}]_o = 0.66$

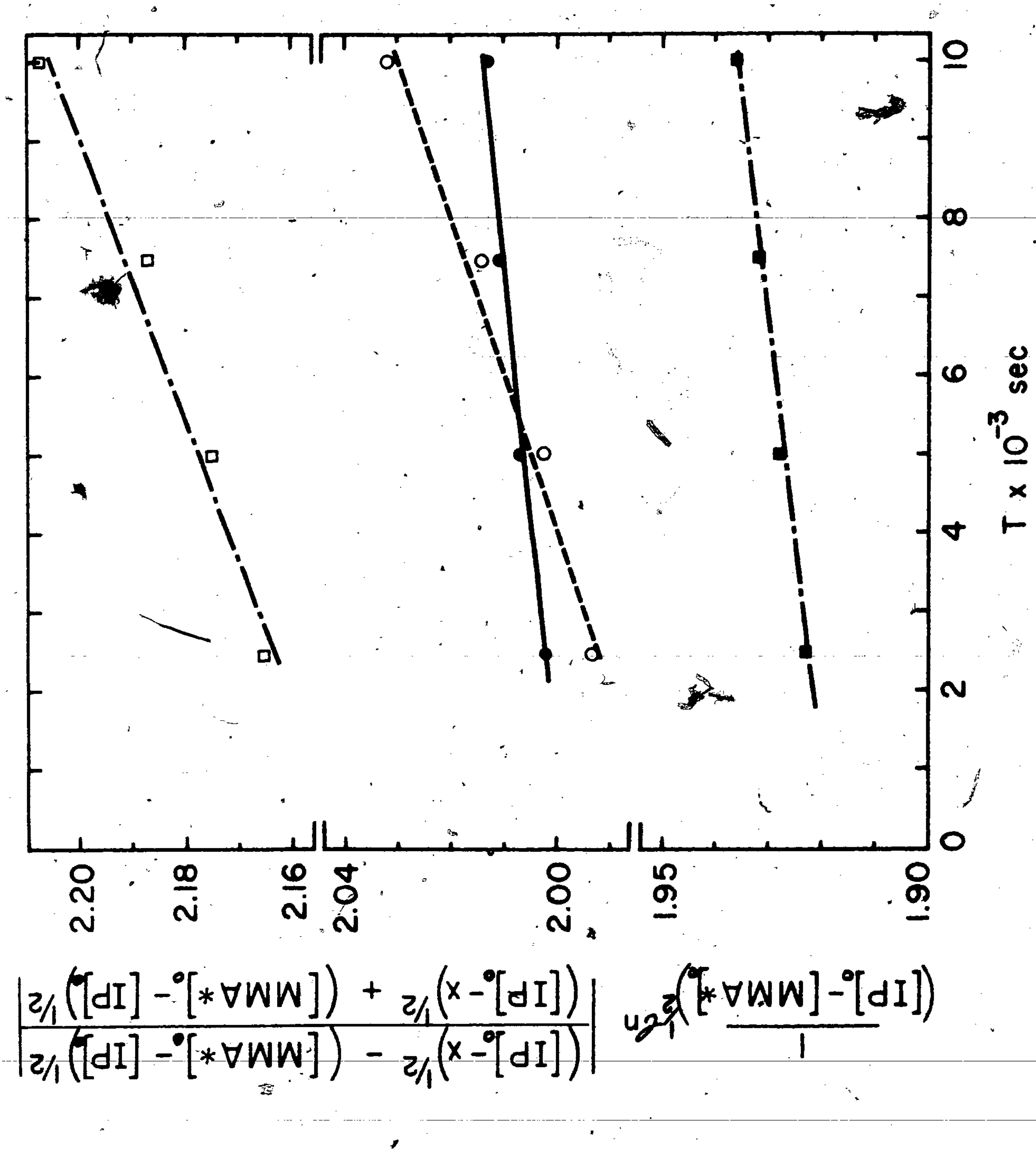

2.20
2.18
2.16
2.04
2.00
1.95
1.90
0
2
4
6
8
10
T x 10^{-3} sec
$\frac{1}{([IP]_0-[MMA*]_0)^{1/2}} \ln \left| \frac{([IP]_0-x)^{1/2} - ([MMA*]_0-[IP]_0)^{1/2}}{([IP]_0-x)^{1/2} + ([MMA*]_0-[IP]_0)^{1/2}} \right|$

TABLE XII

Apparent Rate Constants for the Alternating Copolymerization of MMA-IP Determined from the 3/2 Order Rate Expression (III-25)

[MMA*] mole 1^{-1}	[IP] mole 1^{-1}	Complexing Agent	k'_p $1^{1/2}$mole$^{-1/2}$sec^{-1}
0.77	1.80	DEAC	$4.6\pm0.3 \times 10^{-6}$
0.99	1.48	DEAC	$3.6\pm0.7 \times 10^{-6}$
1.38	0.92	DEAC	$5.5\pm0.5 \times 10^{-6}$
1.55	0.66	DEAC	$5.4\pm0.6 \times 10^{-6}$
0.77	1.80	EASC	$1.4\pm0.1 \times 10^{-6}$
0.99	1.48	EASC	$1.7\pm0.1 \times 10^{-6}$
1.38	0.92	EASC	$5.1\pm0.4 \times 10^{-6}$
1.55	0.66	EASC	$5.8\pm0.6 \times 10^{-6}$

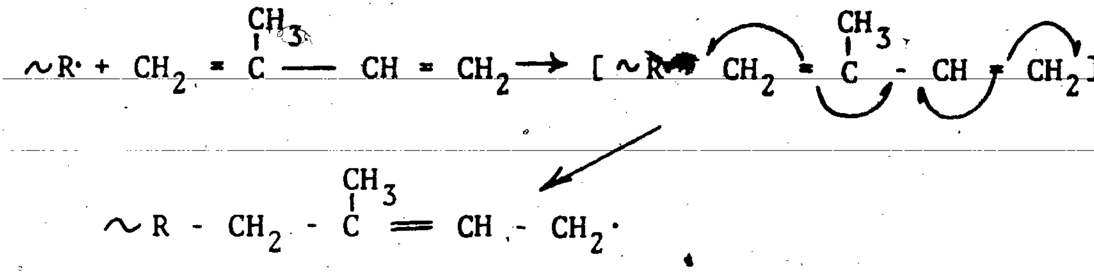
III.4.3 COPOLYMERIZATION RATES

The relationship between the rate of copolymerization (yield) and monomer feed ratio is shown in figure (44). A rate maximum is found at a feed ratio corresponding to 50 mole % MMA*. This is consistent with the literature (67).

III.4.4 MOLECULAR WEIGHT CHANGES

Changes in $\overline{M}_n$ as a function of monomer feed ratios are shown in figure (45). An increase in $\overline{M}_n$ is seen with increases in MMA*. This is in direct contrast with the molecular weight decreases seen in the MMA* styrene system (Section III.2.5). In the copolymerization of MMA* and styrene, non-degradative chain transfer is indicated, and may also be occurring in the MMA*-isoprene system. An added complication in the MMA*-isoprene copolymerization, however, is the possibility of incorporation of dead polymer into the growing polymer chain. Such a situation would obviously increase the molecular weight of the copolymer product.

When isoprene radically polymerizes, unsaturation remains in the monomeric units:



$$\sim R\cdot + CH_2 = \overset{CH_3}{C} - CH = CH_2 \rightarrow [\sim R\cdot\ CH_2 = \overset{CH_3}{C} - CH = CH_2]$$

$$\rightarrow \sim R - CH_2 - \overset{CH_3}{C} = CH - CH_2\cdot$$

Figure 44 RATE OF COPOLYMERIZATION (YIELD) VS FEED COMPOSITION FOR THE MMA-IP SYSTEM.

●——● DEAC

○----○ EASC

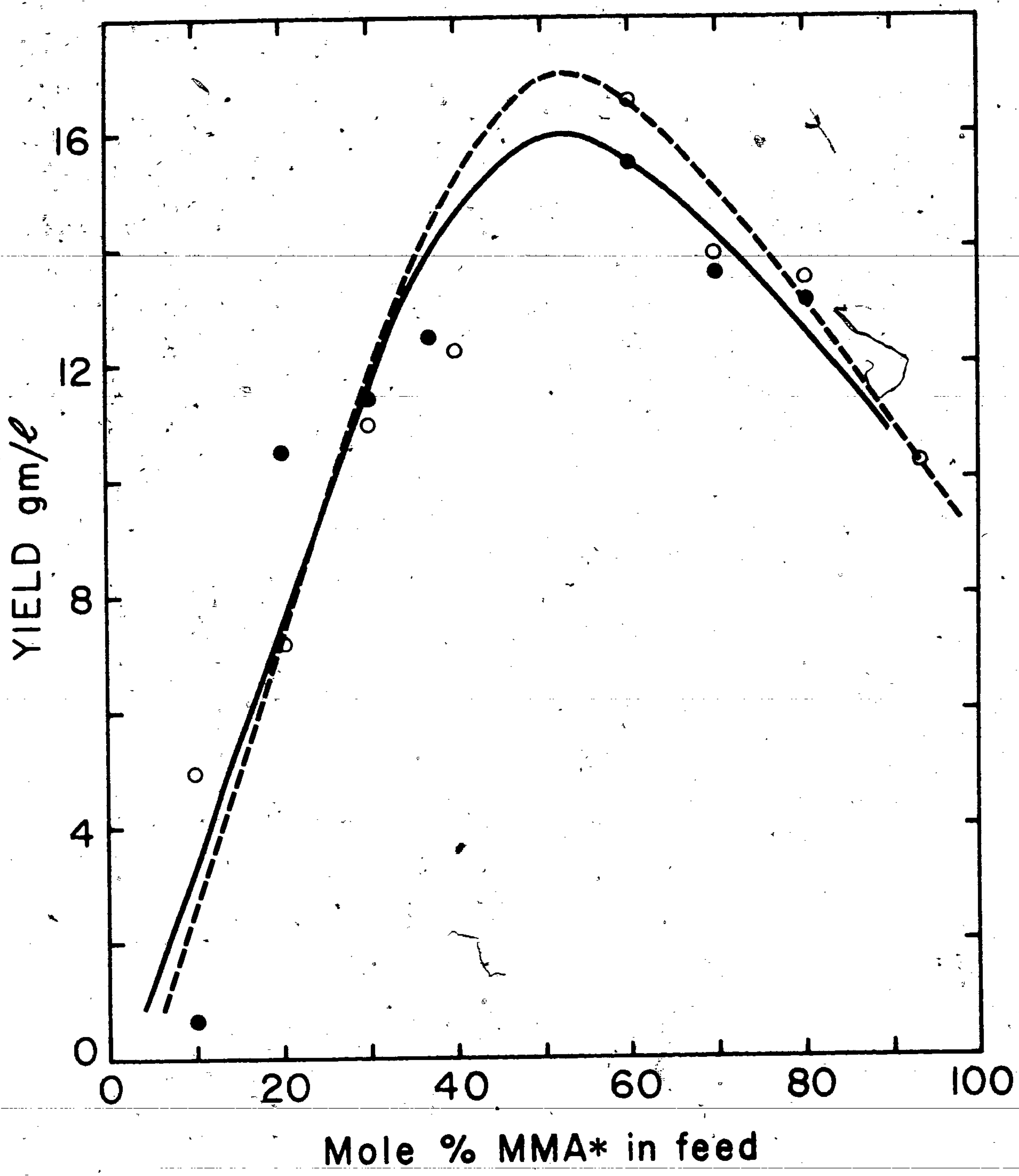
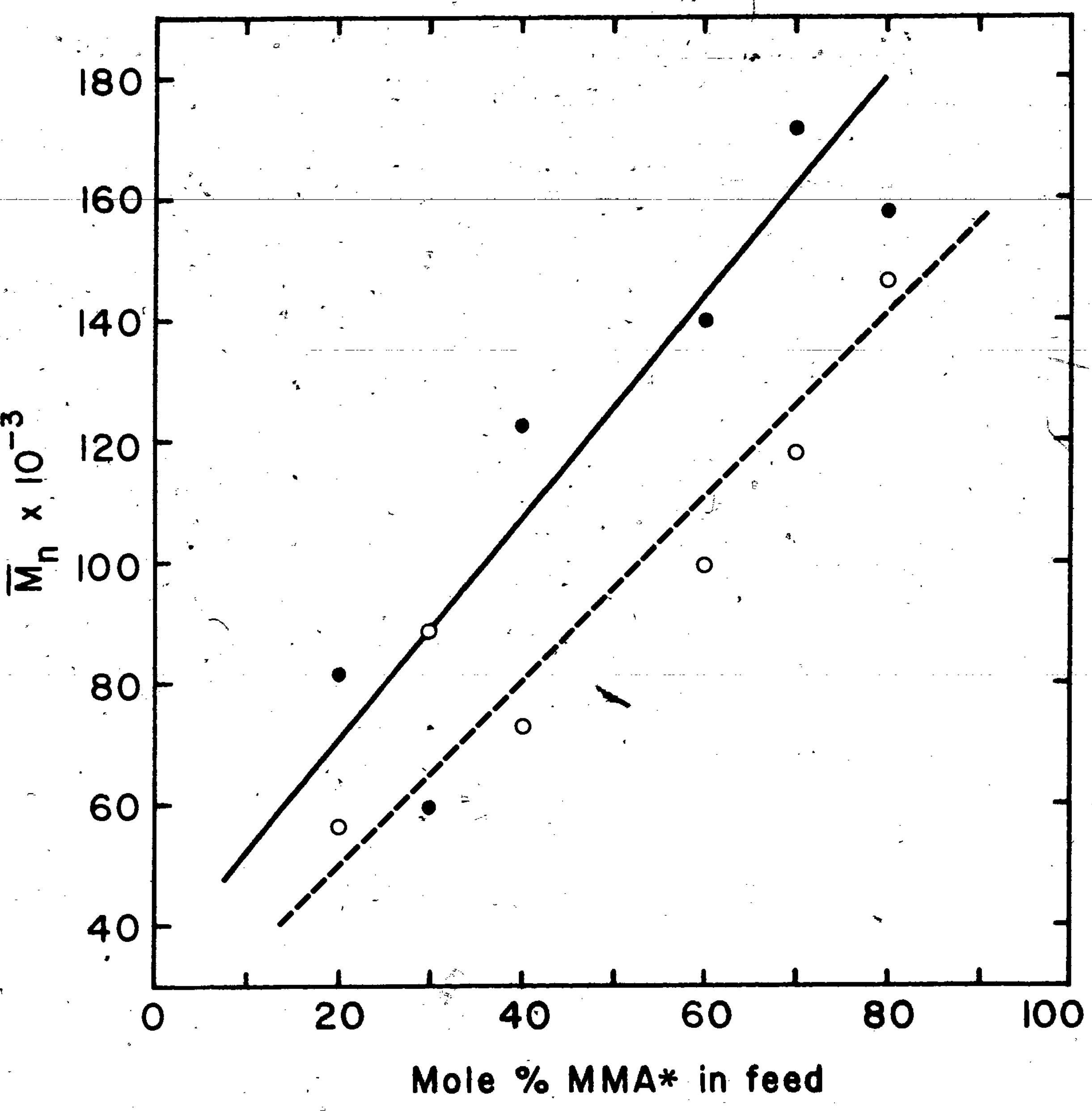

YIELD gm/ℓ
0
4
8
12
16
0
20
40
60
80
100
Mole % MMA* in feed

Figure 45 THE $\overline{M}_n$ OF PRODUCT VS THE MOLE % MMA IN MONOMER FEED FOR THE MMA-IP SYSTEM.

○----○ DEAC COMPLEXING AGENT

●——● EASC COMPLEXING AGENT


$\overline{M}_n \times 10^{-3}$
180
160
140
120
100
80
60
40
0
20
40
60
80
100
Mole % MMA* in feed

It is this unsaturation that provides the important thermosetting properties of many isoprene polymers.

As this unsaturation is capable of acting as a olefinic monomer in the copolymerization, both the dead polymer with this unsaturation and unpolymerized isoprene can copolymerize with MMA* in an alternating fashion. Since the isoprene monomer and the dead polymer are in competition, the degree in which either is incorporated into the growing chain is dependent on the concentration of each. Thus as the concentration of isoprene is reduced, more polymer will be incorporated and a $\bar{M}_n$ increase will be seen.

III.4.5 ACTIVATION ENERGY

An Arrhenius plot of k_p' values obtained at various temperatures (table XIII) is shown in figure (46). The slope of the linear least squares line through the points is 2.1×10^3 and corresponds to an overall activation energy, E_R, of -4.2 kcal mole^{-1}. A poor linear correlation is shown in figure (44) and the validity of the calculated activation energy is uncertain.

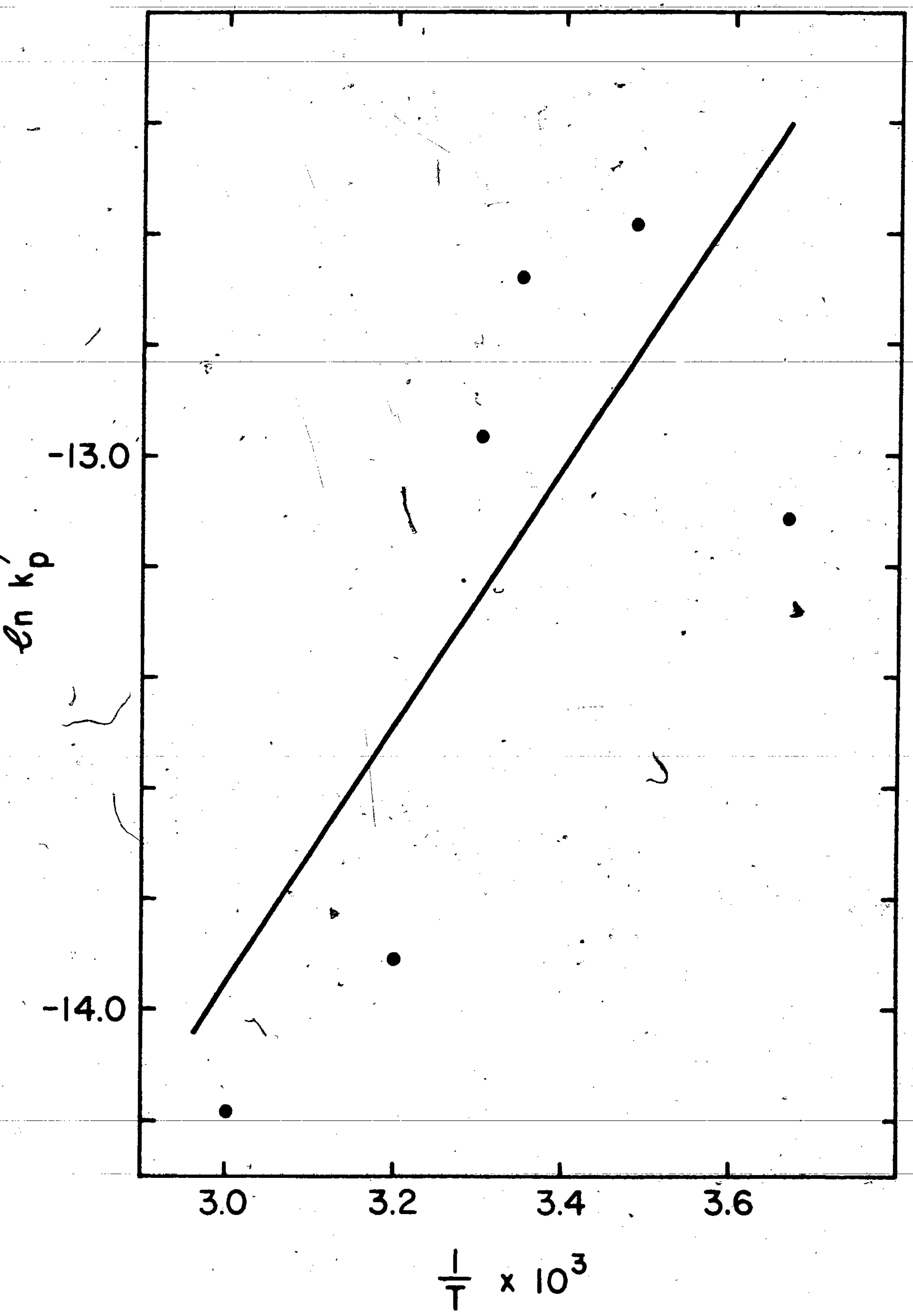
Negative activation energies, although somewhat unexpected in the present system, are not uncommon in polymerization kinetics. Generally overall activation energies for polymerization reactions are composite values, the magnitude of which is dependent on the activation energy of the individual steps of the polymerization reaction:

TABLE XIII

Rate Constants for the Copolymerization
of MMA and IP in the Presence of DEAC
([MMA] : [DEAC] = 2:1; [MMA] = 40 mole %)

k'_p $l^{1/2}$ mole$^{-1/2}$ sec^{-1}	T in °K	°C	1/T
2.0×10^{-6}	273	0	3.7×10^{-3}
3.4×10^{-6}	286	13	3.5×10^{-3}
3.1×10^{-6}	298	25	3.4×10^{-3}
2.3×10^{-6}	303	30	3.3×10^{-3}
0.9×10^{-6}	313	40	3.2×10^{-3}
0.7×10^{-6}	333	60	3.0×10^{-3}

Figure 46 ARRHENIUS PLOT FOR THE COPOLYMERIZATION OF MMA AND IP IN THE PRESENCE OF DEAC CONDUCTED BETWEEN 0 AND 60°C.


-13.0
-14.0
$\ell n\ k_p'$
3.0
3.2
3.4
3.6
$\frac{1}{T} \times 10^3$

$$E_R = E_i + E_p - E_t \qquad \text{III-26}$$

where E_i, E_p and E_t are the activation energies of the initiation, propagation and termination steps respectively. In situations, where the initiation and propagation activation energies are much lower than that of the termination process, low E_R values are seen. For many polymerization systems (usually cationic), E_R is negative and increasing polymerization rates are seen with decreasing temperatures.

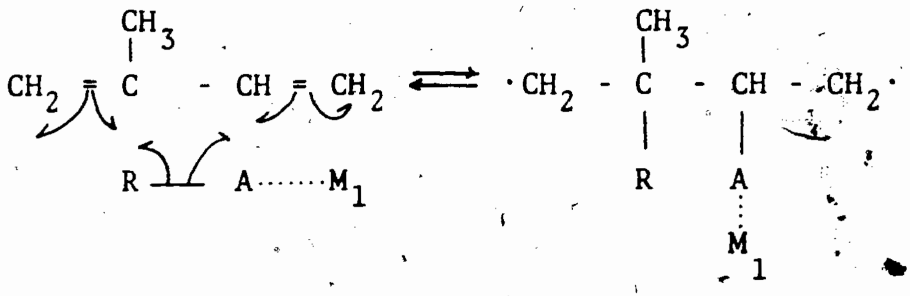
III.5 A PROPOSED MECHANISM FOR COMPLEXED ALTERNATING COPOLYMERIZATION OF METHYL METHACRYLATE-STYRENE AND METHYL METHACRYLATE-ISOPRENE IN THE PRESENCE OF LEWIS ACIDS

Isoprene, because of its diene structure, is a difunctional monomer. Thus the incorporation of isoprene into a polymerization scheme can provide a 1/2 order kinetic relationship for this monomer.

If the generation of radicals results from the decomposition of aluminum alkyl -vinyl monomer complex as shown by Kuran <u>et al</u> (115), the recombination of these radicals becomes an important consideration in the initiation sequence.

$$M_1 \;-\,-\,-\; AR \rightleftharpoons \dot{R} + M_1 \;-\,-\,-\; \dot{A}$$

where AR is an aluminum alkyl molecule and M_1 is the complexable vinyl monomer. If isoprene is present in close proximity to the decomposing complex, both radical species can add to the diene to provide a diradical initiation species.



Thus two active radical polymerization sites are produced. If these active sites are considered individually and designated as I·, then:

$$IP + AR - M_1 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\, I\cdot$$

If species I· is considered as the initiator for the copolymerization reaction, then a kinetic chain will result from each radical site on the isoprene diradical.

The first step in the propagation sequence is the addition of an AR---M_1 complex (shown by the 1:1 monomer composition of the product). This step is rate determining, as the failure of this reaction to occur results in the reversion of the diradical back to isoprene and AR - M_1. The rate determining step can thus be written as:

$$I\cdot + M_1 - AR \xrightarrow{k_p'} p\cdot \text{ (or P)}$$

$$\frac{d\ [P]}{dt} = k_p' \ [I\cdot] \ [M_1 - AR]$$

or where $[M_1 - AR]$ is unknown:

$$\frac{d\ [P]}{dt} = k_p' \ [I\cdot] \ [M_1^*] \qquad \text{III-27}$$

where M_1^* represents a particular M_1 and AR feed ratio relationship similar to MMA* (Section III.2.1).

where p· is the growing polymer chain and P is dead polymer.

Since the generation of I· is an equilibrium process and if the concentration of aluminum alkyl monomer complex is considered constant:

$$k_1 \ [IP] = k_{-1} \ [I\cdot]^2 \qquad \text{III-28}$$

or

$$\frac{k_1}{k_{-1}} = \frac{[I\cdot]^2}{[IP]} = Ke \qquad \text{III-29}$$

where Ke is the equilibrium constant for the generation of I·. Solving (III-29) for I· provides (III-30).

$$[I\cdot] = Ke^{1/2}\ [IP]^{1/2} \qquad \text{III-30}$$

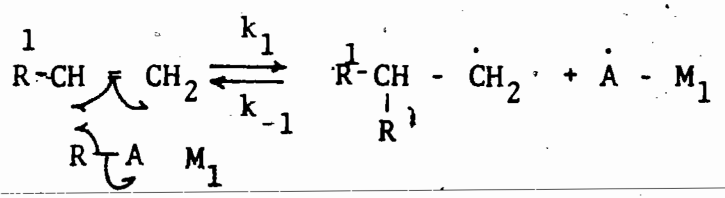
and substitution of (II-30) into the rate expression (III-27) gives (III-31).

$$\frac{d\,[P]}{dt} = k_p'\ Ke^{1/2}\ [M_1^*]\ [IP]^{1/2} \qquad \text{III-31}$$

when applied to the copolymerization of MMA and isoprene in the presence of aluminum alkyl, (III-31) becomes (III-32).

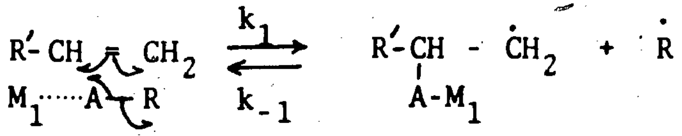
$$\frac{d\,[P]}{dt} = k_p'\ Ke^{1/2}\ [MMA^*]\ [IP]^{1/2} \qquad \text{III-32}$$

A similar treatment can be applied to systems involving olefinic monomers with the aluminum-alkyl monomer complex producing monoradical initiation species.



$$\underset{\displaystyle R - A \quad M_1}{\overset{1}{R}-CH=CH_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \overset{1}{R}-\underset{\displaystyle \overset{|}{R}}{CH}-\dot{C}H_2 + \dot{A}-M_1$$

or



$$\underset{M_1\cdots A-R}{R'-CH=CH_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R'-\underset{A-M_1}{CH}-\dot{C}H_2 + \dot{R}$$

where

$R-\underset{R'}{CH}-\dot{C}H_2$ and $R-\underset{A-M_1}{CH}-\dot{C}H_2$ are considered as monoradicals

Thus the rate expression for this process becomes:

$$\frac{d\,[\text{monoradical}]}{dt} = k_1\,[\text{olefin}]\,[\text{monomer complex}] \qquad \text{III-33}$$

Assuming the rate determining step is the addition of the monoradical to complexed monomer:

$$\text{monoradical} + AR\cdots M_1 \xrightarrow{k_p'} P\cdot \ (\text{or } P)$$

then:

$$\frac{d\,[P]}{dt} = k_p'\,[\text{monoradical}]\,[AR\cdots M_1] \qquad \text{III-34}$$

and considering the equilibrium situation for the production of the olefin radical gives:

$$k_1 \, [\text{monoradical}] = k_{-1} \, [\text{olefin}] \qquad \text{III-35}$$

$$Ke = \frac{[\text{monoradical}]}{[\text{olefin}]} \qquad \text{III-36}$$

Substitution of (III-36) into the rate equation (III-34) gives:

$$\frac{d\,P}{dt} = k_p' \, Ke \, [\text{olefin}] \; [AR \cdots M_1] \qquad \text{III-37}$$

If applied to the methyl methacrylate-styrene, diethylaluminum chloride system previously studied, (Section III.2), this becomes:

$$\frac{d\,[P]}{dt} = k_p' \;\; K\text{[illegible]} \; [STY] \;\; [MMA^*]$$

a second order process.

IV SUMMARY

Introduction

The preparation of alternating copolymers from a large number of vinyl, olefinic and diene comonomer pairs in the presence of Lewis acids has received considerable attention in recent years. Despite the great amount of work carried out to elucidate the mechanism of complexed alternating copolymerization, no general agreement exists.

The major differences of opinion in the mechanism centers around the propagation step. Although it is generally agreed that the propagation reaction is free radical, the exact details have not been clarified.

The salient features from complexed alternating copolymerization are the appearance of a rate maximum at a 1:1 monomer feed ratio and the production of alternating 1:1 copolymer irrespective of monomer feed ratios.

It has been proposed by Gaylord and others (34, 40, 104) that these features are the result of formation of donor-acceptor complexes in which the incomplexed monomers behave as donor molecules and the complexed monomers as acceptor molecules. The propagation reaction is seen as a homopolymerization of these donor-acceptor complexes.

Gaylord (104) invokes a donor-acceptor mechanism whereby propagation occurs via a radical ion-pair chain end. Furukawa (34) invisions a donor-acceptor mechanism involving a vinyl monomer complex radical at the chain end, while Hirooka (40) sees the chain end as a radical complex.

Zubov *et al* (98) maintain that polymerization proceeds in a classical manner by the alternate addition of comonomer. The subsequent 1:1 polymer composition then reflects the stoichiometry of the donor-acceptor complex while maximum rate is seen where the concentration of the donor-acceptor complex is greatest (when the comonomer concentrations are equal).

Zubov (98) states the major argument against such a propagation step is the small concentration (undetected in some cases) of donor-acceptor complex found in these copolymerizations. Zubov proposes an explanation based on the complexation effects of Lewis acids on the cross-propagation rate constants evolving complexed monomer and radicals.

The objective of this research was to compare kinetic and molecular weight data with various mechanistic proposals and to select the mechanism most consistent with the data obtained. Preliminary studies were directed towards the examination of several anomalies of alternating copolymerization that existed in the literature.

EXPERIMENTAL DESIGN

The research was done using simple, yet representative, alternating copolymerization systems. A variety of simple vinyl monomers were complexed to one of three possible complexing agents, (diethylaluminum chloride, ethylaluminum sesquichloride and zinc chloride), with emphasis on diethylaluminum chloride. For simplicity, a common comonomer (styrene) was used in most studies. Studies of complexed alternating copolymerization involving diene monomers were accomplished using isoprene in conjunction with aluminum alkyl complexed methyl methacrylate.

CONCLUSIONS

IV.1 REACTION HOMOGENEITY

Some authors have shown (49, 125) that both alternating and non-alternating copolymerization can occur simultaneously in complexed alternating copolymerizations. Thus the gross composition of the copolymer may reflect a combination of variation in copolymer composition due to the simultaneous occurrence of free radical and complexed polymerization, together with variations in composition due to homopolymer associated with copolymer.

It was initially established in this study that complexed alternating copolymerization is a homogeneous process and equimolar product composition was obtained throughout the molecular weight distribution. Thus a single mechanism is functioning in these systems, rather than several independent processes providing product of different composition at different molecular weights.

IV.2 LIVING MECHANISMS

The possibility of a "living" propagation mechanism has been suggested (101, 103). In this work detailed molecular weight distribution data indicated that the molecular weights of complexed alternating copolymerization product were invariant with time. Thus a "living" system is not indicated in this study.

IV.3 α,α'AZOBISISOBUTYRONITRILE DECOMPOSITION WITH ZINC CHLORIDE AND ALUMINUM ALKYLS

The effects of both aluminum alkyls and zinc chloride on α,α'azobisisobutyronitrile decomposition in alternating copolymerization situations have been studied elsewhere (137, 27, 83). Aluminum alkyls unequivocally increase the rate of α,α'azobisisobutyronitrile decomposition (137), however, the situation regarding zinc chloride is unclear. In this research, no change in rate of initiator decomposition is found in the presence of zinc chloride. The decomposition was found to be first-order ($k_d = 2.0 \times 10^{-5}$ sec^{-1}). Thus increased copolymerization rates seen on introduction of azobisisobutyronitrile to alternating copolymerization systems containing zinc chloride are not due to enhanced rates of initiator decomposition. Differences between the effects of aluminum alkyls and zinc chloride is a consequence of the d orbital chemistry of aluminum and zinc.

IV.4 KINETICS OF THE COMPLEX ALTERNATING COPOLYMERIZATION OF METHYL METHACRYLATE-STYRENE-DIETHYLALUMINUM CHLORIDE

Major kinetic emphasis was placed on the methyl methacrylate-styrene-diethylaluminum chloride system. The initial reaction was first-order dependent on each monomer, second-order overall; $k_p' = 5.4 \times 10^{-6}$ l mole^{-1}sec^{-1} at 25°C. The apparent rate constant, k_p', was obtained using two separate methods. The yield of polymer with time gives k_p' by a graphical method using the integral form of the second-order rate expression for this reaction. An alternative graphical method utilizing initial rate and monomer feed composition provided a nearly identical k_p' value.

Mechanistically the above data are consistent with a radical process where propagation is exclusively between unlike species, e.g., increased cross-propagation kinetics. A rate maximum at a 1:1 monomer feed ratio is shown for methyl methacrylate-styrene-diethylaluminum chloride. A rate maximum is not predicted by conventional radical kinetics, consequently, early workers were directed to a mechanism involving donor-acceptor complexes. Close examination of the Burnett radical copolymerization treatment (149) indicates that the proper selection of kinetic parameters provides a theoretical rate curve similar to the experimental curve. The significant assumption in this approach is a non-homopolmerizable monomer. Thus if a non-homopolymerizable complexed vinyl monomer is considered, the unexpected rate curve for complexed alternating copolymerization is consistent with radical copolymerization.

IV.5 KINETICS OF THE COMPLEXED ALTERNATING COPOLYMERIZATION OF METHYL METHACRYLATE-ISOPRENE-DIETHYLALUMINUM CHLORIDE AND METHYL METHACRYLATE-ISOPRENE-ETHYLALUMINUM SESQUICHLORIDE

The methyl methacrylate-isoprene-diethylaluminum chloride system was examined and an overall 3/2 order was found, first-order dependence on methyl methacrylate and 1/2 order dependence on isoprene. The overall rate constant, k_p', was found to be 4.8 x $10^{-6} l^{1/2} M^{-1/2} sec^{-1}$ in the diethylaluminum chloride case and 2.2 x $10^{-6} l^{1/2} M^{-1/2} sec^{-1}$ for ethylaluminum sesquichloride.

The overall 3/2 order of this reaction is unusual. However, propagation can be considered as a bimolecular process with a rate determining initiation step involving a diradical species, thus providing 3/2 order.

Diradicals have been previously proposed for complexed alternating copolymerization, however, ESR measurements have failed to detect these moities and their existence is in doubt. No ESR measurements have been made with methyl methacrylate-isoprene-diethylaluminum chloride copolymerization.

Normally polymerization involving diradical moities produce high molecular weight product due to diradical termination producing diradicals of much higher molecular weight.

$$\cdot(R_n)\cdot \ + \ \cdot(R_m)\cdot \longrightarrow \cdot(R_{n+m})\cdot$$

Experiments in this work have shown that in complexed alternating copolymerization, the major termination process is non-degradative chain transfer. Thus non-degradative chain transfer to one end of a diradical produces a monoradical from the diradical, and a new monoradical from the chain transfer species, e.g., the complexed monomer M_1 - X:

$$\cdot R\cdot + M_1 - X \longrightarrow \cdot RH + \cdot M_1 - X$$

The process can continue as a conventional monoradical sequence where termination occurs via mutual termination of two radicals or by chain transfer.

In this study, the molecular weight for the methyl methacrylate-styrene-diethylaluminum chloride system was seen to decrease with the complexed vinyl monomer concentration. This is a consequence of non-degradative chain transfer to the complexed vinyl monomer. Thus molecular weight decreases as the complexed vinyl monomer concentration increases. In the methyl methacrylate-isoprene-diethylaluminum chloride situation the opposite trend is found. Unsaturation available in the isoprene copolymer is responsible for this observation. Where isoprene monomer is in limited supply, incorporation of "dead" polymer into the growing macroradical occurs and the molecular weight increases by the molecular weight of the incorporated "dead" polymer chain.

$$R_n^{\cdot} + P_m \longrightarrow R_{n+m}^{\cdot}$$

IV.6 ACTIVATION ENERGIES OF COMPLEXED ALTERNATING COPOLYMERIZATION

Low activation energies are found in these systems and can be explained using molecular orbital theory. This approach has been suggested by Zubov (108).

> "It is easy to show by quantochemical calculations that if the donor-acceptor interaction is strong enough, e.g., the lower vacant energy level of reacting particles, e.g., radical is close in value to the upper occupied energy level of the other particle (monomer), the activation energy of the reaction could be close to zero. This, in fact, had been shown by simple molecular orbital calculations of complexed acrylic and hydrocarbon monomers."

The observations in this study that the methyl methacrylate-styrene-diethylaluminum chloride system has an activation energy of + 3.9 kcal mole^{-1} and that the methyl methacrylate-isoprene-diethylaluminum chloride system has a lower activation energy of - 4.2 kcal mole^{-1}, (the significance of the negative value is questionable due to considerable data scatter) are consistent with Zubov ideas.

IV.7 NON-DEGRADATIVE CHAIN TRANSFER IN COMPLEXED ALTERNATING COPOLYMERIZATION

A significant contribution of this research is the observation that the molecular weight of the products from complexed alternating copolymerization is determined by the non-degradative chain transfer activity of the complexed vinyl monomer. Molecular weights of the product reflect the stability of the radical formed from the vinyl monomer complex after transfer and are predicted by resonance stabilization (Q value) available in the complexed monomer. Thus monomers with greater delocalization (high Q value) provide produ[illegible]of lower molecular weight when compared to monomers with lesser delocalization (low Q value).

A number of anomalies in complexed alternating copolymerization not consistent with a normal radical process can be satisfactorily explained by non-degradative chain transfer.

When radical catalysts are used in these copolymerizations, no catalyst residues are found in the polymer, even though higher rates were observed. Furthermore, when these systems are in the presence of halocarbons, such as chloroform or carbon tetrachloride, no chain transfer occurs and no halogen is found in the polymer. When these halocarbon are in the presence of free radical catalysts, again no halogen is found in the polymer, even though halocarbon initiator should be present.

If these species are considered to chain transfer to the complex vinyl monomer and if the resulting complexed vinyl monomer radical is considered as a propagation initiation species, then the polymer will not be expected to contain halocarbon or radical initiator fragments, e.g.

$$R\cdot + (M_1 - X) \longrightarrow (M_1 - X)\cdot + RH$$

$$R\cdot + CCl_4 \longrightarrow RCl + \cdot CCl_3$$

$$\cdot CCl_3 + (M_1 - X) \longrightarrow CHCl_3 + (M_1 - X)\cdot$$

$$(M_1 - X)\cdot \longrightarrow \text{Polymer}$$

IV.8 A GENERAL MECHANISM FOR COMPLEXED ALTERNATING COPOLYMERIZATION

The following mechanism is proposed to account for the observations found in this thesis.

SCHEME II

Initiation

$$(M_1 - X)\cdot + M_2 \longrightarrow (M_1 - X) - M_2\cdot$$

or

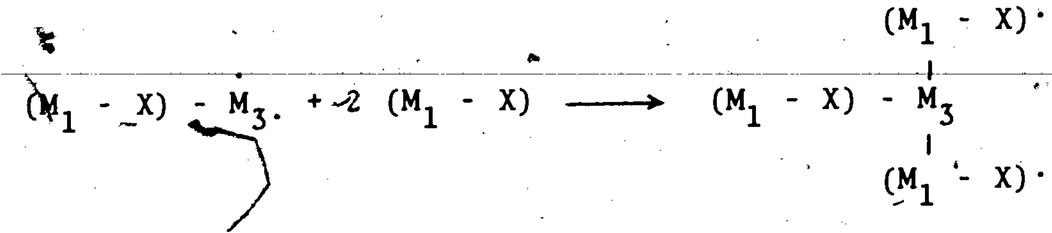
$$(M_1 - X) + M_3 \longrightarrow (M_1 - X) - M_3\cdot$$

Propagation

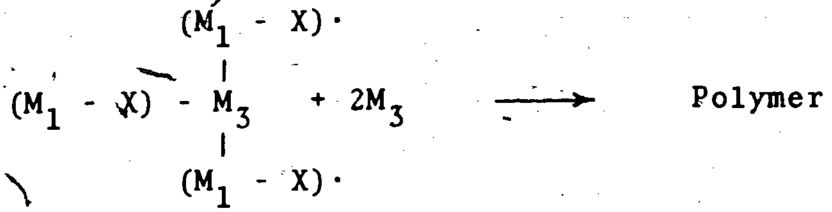
$$(M_1 - X) - M_2\cdot + (M_1 - X) \longrightarrow (M_1 - X) - M_2 - (M_1 - X)\cdot$$

$$(M_1 - X) - M_2 - (M_1 - X)\cdot + M_2 \longrightarrow (M_1 - X) - M_2 - (M_1 - X) - M_2\cdot$$

or



$$(M_1 - X) - M_3\cdot + 2\,(M_1 - X) \longrightarrow (M_1 - X) - \begin{array}{c}(M_1 - X)\cdot \\ | \\ M_3 \\ | \\ (M_1 - X)\cdot\end{array}$$



$$(M_1 - X) - \begin{array}{c}(M_1 - X)\cdot \\ | \\ M_3 \\ | \\ (M_1 - X)\cdot\end{array} + 2M_3 \longrightarrow \text{Polymer}$$

Chain Transfer

$$\sim M_2\cdot + (M_1 - X) \longrightarrow (M_1 - X)\cdot + M_2\sim$$

or

$$\cdot M_3 \sim M_3\cdot + (M_1 - X) \longrightarrow (M_1 - X)\cdot + M_3 \sim M_3\cdot$$

Where $(M_1 - X)$ is the complexed monomer, M_2 is an olefinic comonomer, and M_3 is a diene comonomer. In this thesis the collected data were evaluated in regards to the initiation and propagation steps only. No data are available in this study that are suggestive of a particular termination process, consequently, a termination sequence is not included in the above scheme.

The mechanism shown in (Scheme II) resembles that of Zubov *et al* with the exception of non-degradative chain transfer and the modified initiation steps. Chain transfer is included in the propagation step since it is considered as non-degradative and does not disrupt the kinetic chain.

In conclusion, the author supports the Zubov mechanistic proposal with slight modification. The process of complexed alternating copolymerization can easily be considered as a radical copolymerization involving very high cross-propagation rate constants.

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