A DETERMINATION OF THE MICROSTRUCTURE OF COPOLYMERS

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ABSTRACT

A DETERMINATION OF THE MICROSTRUCTURE OF COPOLYMERS

by Theodore M. Fischer Jr.

A series of vinylidene chloride (VCl_2)-isobutylene (IB) copolymers and vinylidene chloride-vinyl chloride (VCl) copolymers were polymerized to low conversions. The copolymers were dissolved in bromobenzene and an NMR spectrum run of the solutions. From these spectra, sequences of diads and tetrads were determined for the VCl_2-IB copolymers and diad sequences were determined for the VCl_2-VCl copolymers.

The experimental measurements of the diad sequences in the VCl_2-IB copolymer system were used to determine the reactivity ratios for the monomers in this system assuming a terminal kinetic mechanism of copolymerization. This represents a new technique for determining reactivity ratios which is independent of chemical or spectrographic analysis of the mole fractions of the mers. The values of these reactivity ratios were used to calculate theoretical tetrads but the results correlated poorly with the experimental tetrads. Sufficient experimental detail was available to determine the four parameters of the penultimate kinetic mechanism of copolymerization. Good correlation for the mole fractions of the monomers, diads and tetrads were found using the experimentally determined values $r_1=2.95$, $r_1'=6.22$, $r_2=0.15$, and $r_2'=0.02$ from the penultimate mechanism.

In the VCl_2-VCl copolymer system the experimental measurements of the diad sequences were used to obtain the monomer reactivity ratios

based on the terminal mechanism of copolymerization. Good agreement was obtained between calculated and experimental values for the diads with the values for r_1=3.75 and r_2=0.18. However, the possibility of another copolymerization mechanism could not be ruled out because as Berger and Kuntz pointed out longer sequences are needed for a critical analysis and only diad sequences could be measured in this copolymer system.

Two series of VCl_2-IB copolymers were made at various conversions up to 50% to investigate the dependence of diad sequences on conversion. A theoretical treatment has been developed for the terminal mechanism of copolymerization and the trends predicted between average diads and conversion by this theory using the values r_1=3.30 and r_2=0.05 correspond to the experimentally predicted curves.

A DETERMINATION OF THE MICROSTRUCTURE OF COPOLYMERS

By

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HISTORICAL INTRODUCTION

Before 1959 the only Nuclear Magnetic Resonance (NMR) studies of polymers undertaken were limited to broadline studies of solid polymers. The first paper on high resolution NMR was published by Bovey, Tiers, and Filipovich (1) who investigated the NMR spectrum of a carbon tetrachloride solution of polystyrene. The local field effects were overcome by dissolving the polymer in a suitable liquid to separate the nuclei and Bovey and Tiers hoped to obtain a narrow peak spectrum similar to the spectra of organic liquids. The spectrum they obtained was broader than normally found for ordinary organic liquids, but still much narrower and with greater detail than found in the broadline spectra of solid or molten polymers.

The polystyrene solution spectrum consisted of two main peaks with the larger one downfield split into two poorly resolved peaks at 3.1τ and 3.5τ where τ equals

$$10 - \frac{\Delta(\mathrm{Me_4Si})\cdot 10^6}{\text{Oscillator frequency (cps.)}}$$

and Δ is the line separation between sample and reference in cycles per second (cps.) (2). The peak further upfield was at 8.4τ. The doublet downfield was attributed to resonances of the protons on the phenyl group, and the peak upfield was assigned to the methylene protons of the polymer chain. A third peak was expected for the α-hydrogens but was not located.

To investigate the cause of the splitting of the proton resonances of the phenyl group Bovey, Tiers, and co-workers ran spectra of some substituted polystyrenes (poly-2-chlorostyrene, poly-3-chlorostyrene, and poly-4-chlorostyrene). The smaller peak was not found in the poly-2-chlorostyrene but was detected in both the others. From this it was concluded that the smaller peak was due to the resonance of the ortho hydrogens of the phenyl group.

Bovey, Tiers, and co-workers identified the expected α-hydrogen peak by running an NMR spectrum of poly-β,β-d_2-Styrene. This polymer had no methylene protons, but a peak was present in the region where the methylene proton resonance was found in the polystyrene spectrum. They concluded that the α-hydrogens resonated further upfield than expected from the spectra of small molecule analogs.

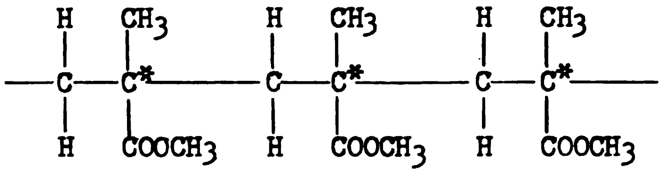
Bovey, Tiers, and co-workers noted that the width of the larger phenyl peak was about 20 cps. wide compared to about 5 cps. for the phenyl peak in cumene which is a small molecule analog of polystyrene. Thus it was established that although some of the finer details could not be seen in high resolution NMR of polymers as in ordinary organic liquids, much information could be obtained from these data.

Bovey, Tiers, and co-workers observed that the line width of the spectrum was independent of the molecular weight of the polystyrene at least down to a molecular weight of 10,000. NMR spectra of several different high molecular weight species of polystyrene were run but the line width remained constant. The line width was shown also to be independent of the concentration of the polymer provided it was less than 50-60% wt./vol. Bovey and Tiers concluded that the peak widths were essentially independent of macroscopic viscosity and were a measure of local viscosity in the immediate vicinity of each chain segment.

Bovey, Tiers, and co-workers noticed that the spectrum of polystyrene with less than 10 units lost the ortho phenyl peak and the larger peak shifted to correspond to the one for cumene at 2.84τ. The α-hydrogen resonance peak was observed in this short chain polystyrene. They also took NMR spectra of some polystyrene samples of different tacticities but obtained identical spectra for all of them. From this data Bovey, Tiers, and co-workers concluded that due to steric restrictions polystyrene of more than 10 units existed in a quasi-crystalline state in solution which placed the ortho hydrogens of one phenyl ring more in the diamagnetic region of its neighboring phenyl rings than the meta or para hydrogens.

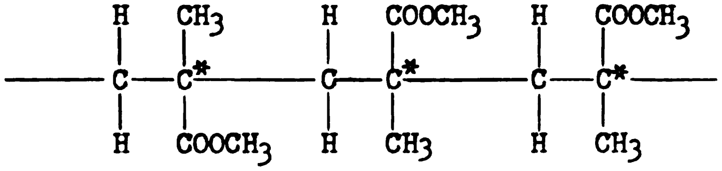
Kern and Pustinger (3) in another early investigation of polystyrene observed partially resolved α-hydrogen and methylene proton peaks for isotactic polystyrene, whereas, an NMR spectrum of a commercial atactic polystyrene sample showed only one peak for these protons.

The NMR study of tacticity or stereosequences has been the main subject of NMR investigations in the field of polymer microstructure. A second paper by Bovey and Tiers (4) dealt with the NMR study of the poly(methylmethacrylate)(PMMA). The NMR spectra of two differently prepared PMMA samples were run in the solvent, chloroform. One sample was synthesized with a free radical initiator which gave a random distribution of stereosequences, whereas the other was synthesized with an anionic catalyst and led predominately to an isotactic polymer. Bovey and Tiers designated three different stereosequences in the chain, an isotactic sequence, "i", a heterotactic sequence, "h", and a syndiotactic sequence, "s". Each of these sequences contains three monomer units as pictured below.



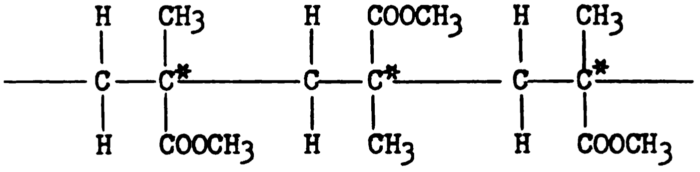
$$\begin{array}{ccccccccccccc} & H & & CH_3 & & H & & CH_3 & & H & & CH_3 & \\ & | & & | & & | & & | & & | & & | & \\ - & C & - & C^* & - & C & - & C^* & - & C & - & C^* & - \\ & | & & | & & | & & | & & | & & | & \\ & H & & COOCH_3 & & H & & COOCH_3 & & H & & COOCH_3 & \end{array}$$

"i"



$$\begin{array}{ccccccccccccc} & H & & CH_3 & & H & & COOCH_3 & & H & & COOCH_3 & \\ & | & & | & & | & & | & & | & & | & \\ - & C & - & C^* & - & C & - & C^* & - & C & - & C^* & - \\ & | & & | & & | & & | & & | & & | & \\ & H & & COOCH_3 & & H & & CH_3 & & H & & CH_3 & \end{array}$$

"h"



$$\begin{array}{ccccccccccccc} & H & & CH_3 & & H & & COOCH_3 & & H & & CH_3 & \\ & | & & | & & | & & | & & | & & | & \\ - & C & - & C^* & - & C & - & C^* & - & C & - & C^* & - \\ & | & & | & & | & & | & & | & & | & \\ & H & & COOCH_3 & & H & & CH_3 & & H & & COOCH_3 & \end{array}$$

"s"

Where C^* represents an asymmetric carbon.

In the PMMA polymer spectra the proton resonances of the α-methyl group consisted of three peaks. These peaks were assigned to the three different stereosequences. The per cent of each stereosequence in the polymer is proportional to the area under each peak.

Bovey and Tiers designated a parameter, σ , as the probability that a polymer chain would add a monomer unit to give the same configuration as the last unit of the chain. This assumes that σ is independent of the penultimate unit. Thus propagation could be described by a single value of σ and the probabilities of the three stereosequences were described as follows:

$$P_i = \sigma^2 \quad (1.1)$$

$$P_s = (1 - \sigma)^2 \quad (1.2)$$

$$P_h = 1 - P_i - P_s = 2(\sigma - \sigma^2) \quad (1.3)$$

For free radical polymerizations this relationship was shown to hold within experimental error, but it was in poor agreement for stereopolymers formed by ionic polymerization. A typical plot of the above relations is depicted in Figure 1.

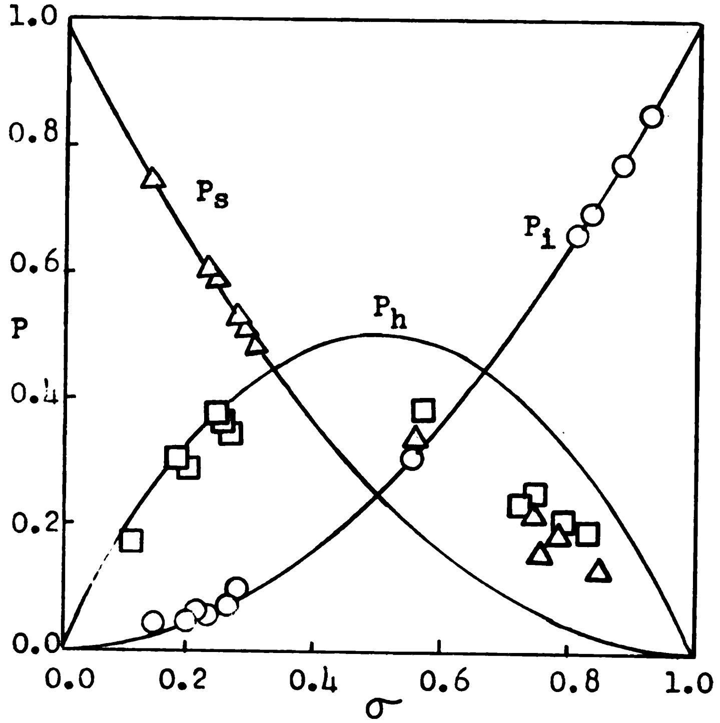


Fig. 1. A typical plot of the probabilities of the stereosequences versus σ for styrene-methyl methacrylate copolymer. (○) isotactic; (□)heterotactic; (△) syndiotactic. Solid lines represent theoretical values.

Another important contribution made by Bovey and co-workers appeared in a paper in 1963 (5), where he and co-workers reported studies on several polymer systems, among them was poly(vinyl chloride). They used H-H spin decoupling to aid in the determination of the structure and configuration of the polymer. They were able to discern that the complex methylene proton region consisted of two overlapping triplets which originated from the racemic and meso methylene configurations. The decoupled α-proton resonance area consisted of three peaks corresponding to the three different possible stereosequences. The undecoupled α-hydrogen spectrum was more complex and was interpreted to consist of three overlapping quintets which would have been difficult to resolve without the aid of the H-H spin decoupling.

Miller and co-workers (6) studied the configuration of poly-(methacrylic anhydride). They prepared several samples of the polymer by different polymerization methods and obtained an NMR spectrum of each. They found disagreement with the simple P vs. σ relations (1.1), (1.2), and (1.3) of Bovey and Tiers. They interpreted this poor agreement to the assumption that σ was independent of the penultimate effect and explained their results by invoking a penultimate mechanism for their system.

Brownstein and co-workers (7) investigated a series of poly-α-methyl styrenes. They prepared polymers by cationic, anionic, and free radical initiation and found the fraction of each stereosequence in the polymers from the areas under the three different peaks of the proton resonances of the α-methyl group. They constructed a P vs. σ graph and obtained a reasonable fit with experimental results.

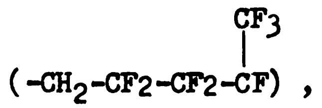
In the last two or three years considerable work has been undertaken in high resolution NMR of polymers. This work has been concentrated for the most part in two main areas: stereosequential studies of homopolymers and sequence distribution studies of copolymers.

The stereosequential studies of homopolymers have been reported on a number of polymers including poly-(propylene)(8-10), poly(styrene) (11, 12), poly(α-methylstyrene)(7, 13), poly(vinyl chloride)(5, 13-19), poly(vinyl fluoride)(5, 20), poly(trifluorochloroethylene)(21), poly(vinyl methyl ether)(5, 22, 23), poly(α-methylvinyl methyl ether) (24), poly(vinyl acetate)(5, 25), poly(vinyl trifluoroacetate)(25), poly(vinyl alcohol)(25), poly(isopropyl acrylate)(26), poly(methylacrylate)

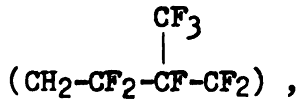
(27, 28), poly(methyl methacrylate)(4, 29-33), poly(acetaldehyde)(34), and poly(acrylonitrile)(62,63). Considerable information on homopolymer structure has now been obtained from these studies. One important outcome has been the detection of sequence lengths of four monomeric units in NMR spectra.

Compared to the tacticity studies of homopolymers few studies of sequence distributions in copolymers have been undertaken. Bovey reported the first proton NMR study of a copolymer (35). He studied the copolymer of methylmethacrylate and styrene by varying the monomer ratios in a series of copolymerizations. Unfortunately the spectra of these samples were rather complicated and while an attempt was made to interpret the spectra, Bovey admitted that his results were rather inconclusive and that additional work was needed in this area.

The best resolution in copolymers was reported by Ferguson who in 1960 (36) studied the copolymers of vinylidene fluoride-hexafluoropropylene utilizing F^{19} NMR. These copolymers were prepared by persulfate initiated emulsion polymerization. Ferguson deduced the fraction of different types of repeating units in the chain of which four were possible according to his analysis. The units were designated as:



$$(-CH_2-CF_2-CF_2-\overset{\overset{\large CF_3}{|}}{C}F) \;,$$



$$(CH_2-CF_2-\overset{\overset{\large CF_3}{|}}{C}F-CF_2) \;,$$

$$(CH_2-CF_2-CH_2-CF_2) \;,$$

and $$(-CH_2-CF_2-CF_2-CH_2)$$

which he called U, V, W, and X respectively. No hexafluoropropylene-hexafluoropropylene repeat units were found to be present. Ferguson defined a quantity "n" as the fraction of vinylidene fluoride units in W and X and analyzed the gross structure from NMR as:

$$(U_{0.93}V_{0.07})_{1-n}(W_{0.95}X_{0.05})_{n/2}$$

which showed that a slight amount of head-head and tail-tail polymerization took place.

Wilson in 1962 (37) published a short note on F^{19} NMR study of a copolymer of tetrafluoroethylene and hexafluoropropylene. The bulk copolymer sample was heated to 310° C before a narrow band spectrum was obtained. The spectrum consisted of three peaks, one peak due to the F^{19} resonance of a CF_3 group, a peak due to the F^{19} resonance of a CF_2 group, and a peak due to the F^{19} resonance of a CF group. Wilson reported a determination for only one sample called Teflon-100 and stated that the mole % of hexafluoropropylene was 9.0% ± 1.5%.

Chujo and co-workers in 1964 (38) reported a proton NMR study of the vinyl chloride-vinylidene chloride copolymerization system. In this paper they proposed that some of the vinylidene chloride units polymerized in head-head sequences although there is no evidence of head-head polymerization in the homopolymer of vinylidene chloride. They based their interpretation on the NMR study of a series of copolymers prepared from different monomer feed ratios plus the NMR of polyvinylidene chloride, poly-2,3-dichlorobutadiene and partially chlorinated poly-2,3-dichlorobutadiene. Their interpretation of their spectra is questionable as no full spectra were shown in the publication and only a partial spectrum of one copolymer was displayed. An alternate interpretation which may explain their results is contained in this work.

Recently two notes pertaining to the NMR study of the copolymerization of styrene and methyl methacrylate have been published (39, 40). Both papers base their analysis on the proton resonance peaks of the methoxy groups which are two atoms removed from the backbone of the chain. The note by Harwood and Ritchey (39) attempts to correlate the interpretation of the data with Bovey's three previous assumptions (35) that: (a) only adjoining monomer units affect the resonance of the methoxy protons; (b) the distribution of a given type of triad of monomer units among isotactic, syndiotactic, or heterotactic configurations was constant throughout the copolymers; and (c) the resonance of methoxy protons centered in a triad of three methylmethacrylate (MMA) units occurred entirely in the lowest field methoxy peak, irrespective of the triad configuration just as in PMMA. From assumption (a) the three methoxy resonance areas should be related to the distribution of MMA centered triads in the copolymers.

The methoxy resonance occurred in three peaks at 6.50τ, 7.05τ, and 7.45τ. According to Ritchey and Harwood if Bovey's assumptions were valid the percentage of methoxy resonance (P) which occurred in each peak should be related by equation (1.4) to the percentage distribution of the MMA centered triads (% MMM, % SMM, and % SMS) in a copolymer and should also be related to the respective fractions (X, Y, Z) of triad resonances which occurred in each peak.

$$P = X \cdot \%\ \mathrm{SMS} + Y \cdot \%\ \mathrm{SMM} + Z \cdot \%\ \mathrm{MMM} \tag{1.4}$$

From assumption (c) Z should equal unity for the lowest field methoxy resonance (6.50τ) and zero for the other two resonances. The following rearranged equations were then obtained from equation (1.4) and used in a simple test of the validity of Bovey's assumptions.

$$\frac{(P_{6.50} - \%\ \mathrm{MMM})}{\%\ \mathrm{SMS}} = X + Y \cdot \frac{\%\ \mathrm{SMM}}{\%\ \mathrm{SMS}} \tag{1.5}$$

$$\frac{P_{7.05}}{\%\ \mathrm{SMS}} = X' + Y' \cdot \frac{\%\ \mathrm{SMM}}{\%\ \mathrm{SMS}} \qquad (1.6)$$

$$\frac{P_{7.45}}{\%\ \mathrm{SMS}} = X'' + Y'' \cdot \frac{\%\ \mathrm{SMM}}{\%\ \mathrm{SMS}} \qquad (1.7)$$

A plot of the left hand side of the equations (1.5, 1.6, and 1.7) vs. (% SMM / % SMS) should give straight lines with slopes Y, Y', and Y" respectively and intercepts of X, X', and X" respectively. Harwood and Ritchey's data show the predicted straight line behavior when the spectra were obtained with the polymer dissolved in carbon tetrachloride, however, for the copolymers dissolved in o-dichlorobenzene the lines had definite curvature to them. Harwood and Ritchey proposed that the o-dichlorobenzene spectra could be correlated with calculated MMA data centered pentad distributions. Their calculations showed good agreement between experimental and calculated values if they used monomer reactivity ratios of 0.52 and 0.46 for the copolymerization parameters for styrene and MMA respectively. They assigned six of the ten possible MMA centered pentads to specific methoxy resonance peaks. These assignments are in Table I.

Table I. Peak assignments in methoxy proton region by Harwood and Ritchey

Peak A, 6.5τ	Peak B, 7.05τ	Peak C, 7.45τ
MMM SMMSM $\frac{1}{2}$[SSMSM] $\frac{1}{4}$(SSMSS)	MSMMM SSMMM SSMMS $\frac{1}{2}$[SSMSM] $\frac{1}{4}$(SSMSS)	MSMSM $\frac{1}{2}$(SSMSS)

Because of stereochemical effects Harwood and Ritchey believe some of the pentads show in all three peaks. However, no absolute experimental proof on small molecule models or deuterated species was offered for these assignments.

The same copolymer system was studied by Ito and Yamashita (40), but they proposed a different interpretation. They concluded the three peaks in the methoxy resonance region were spectroscopically distinguishable as three kinds of MMA units. They assigned the various possible MMA centered triads to these peaks and included the configurations of the triads in their assignment. The various triads and their configurations are depicted in Figure 2 where the units above the horizontal bar are in the d configuration relative to the central M unit and those below the bar in the l configuration. The assignments of the various peaks are listed in Table II. For simplicity the peak designations are the same as those of Harwood and Ritchey. This interpretation does not extend to the pentads but it is not in conflict with the triad assignments proposed by Harwood and Ritchey. Ito and Yamashita introduced a parameter, σ, which they defined as the probability of alternating M and S units taking the same configuration (dd or ll). From the theory of copolymerization they calculated the triad mole fractions from literature values of the monomer reactivity ratios. Using these calculated values they then calculated a value for σ of 0.48 ± 0.04. From this value of σ they calculated the areas under the three peaks of the methoxy protons and compared them with the measured areas. They claimed good agreement was obtained.

Ito and Yamashita (41) also studied the NMR spectra of several styrene-methyl acrylate copolymers obtained by free radical intitiation

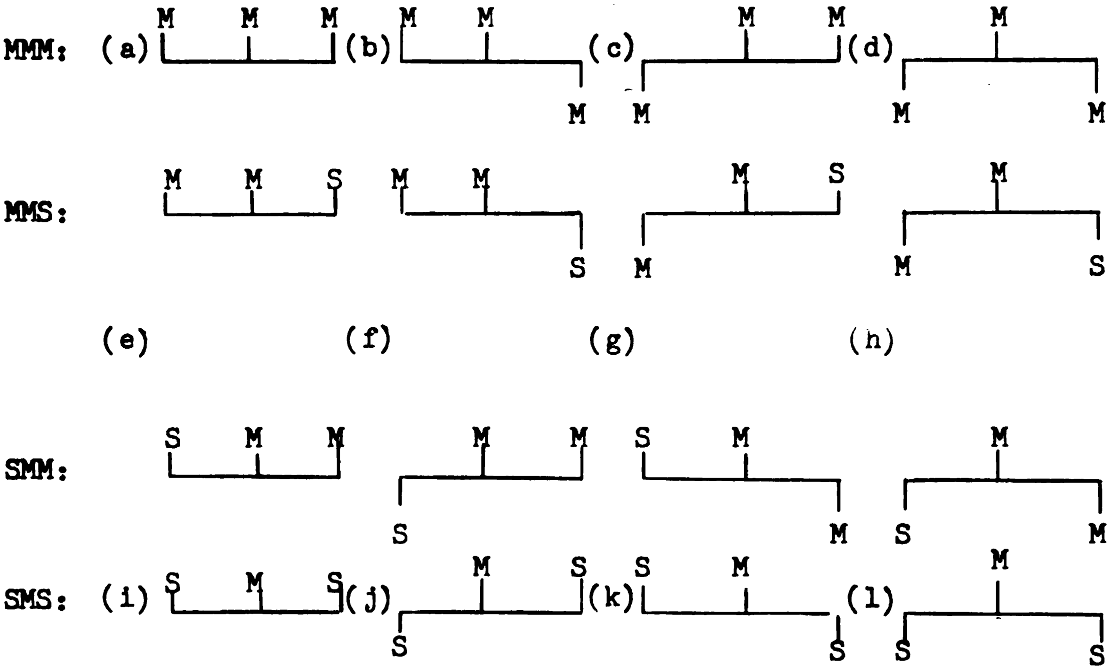


Fig. 2 Methylmethacrylate centered triad configurations of Ito and Yamashita

Table II. Peak assignments in methoxy proton region by Ito and Yamashita

Peak A	Peak B	Peak C
a,b,c,d, f,h,l	e,g, j,k	i*

*Letters refer to configurations of Figure 2 and used the same type of analysis as they conducted in the styrene-methylmethacrylate systems. The resolution of the peaks was poor and the results were not as good. They obtained a $\sigma = 0.80$ for this system.

Two earlier reports by Kato and co-workers (42, 43) on the NMR spectra of sytrene-methyl methacrylate copolymers have been reported, but because of poor resolution only relative amounts of styrene and methyl methacrylate in the copolymers were determined and monomer reactivity ratios were computed. These values compared favorably with previous literature values.

Much more recent work subsequent to this work in this area with the better instrumentation now available has been done on copolymers of methyl methacrylate and methyacrylate (64) and copolymers of vinylidene chloride with vinyl acetate (65, 66, 67), methyl methacrylate (66), α-methyl styrene and styrene (66). A comprehensive review of the NMR studies of elastomers in solution was just published this year (68).

The NMR spectra of copolymer systems studied to date have been complicated by the asymmetric centers in the copolymers. The interpretation of the NMR spectra of these copolymers has been very difficult because of the various stereosequential configurations possible for each copolymer sequence.

In this study two copolymer systems were studied. The first system was the vinylidene chloride-isobutylene system which consists of two symmetrical monomers whose favorable geometry eliminated all complications due to asymmetric centers and much of the poor resolution in spectra observed by earlier workers. The second system studied was vinylidene chloride-vinyl chloride which can be interpreted despite the presence of an unsymmetrical monomer.

THEORY

In free radical copolymerization as in ordinary free radical homopolymerization the simple mechanistic chain reactions which lead to the formation of a polymer molecule consists of three steps; initiation, propagation, and termination. The chemical composition of high molecular weight copolymers is dependent in first approximation only on the propagation step of the chain reaction.

If one of the monomers in a copolymer is designated A and the other B it can be shown that if the addition of these monomers to the growing radical were dependent on the makeup of the entire polymer radical then an infinite number of different reaction rates would occur since the process would be chain length and composition dependent. It was postulated as early as 1936 by Dostal (44) that the kinetic behavior of the chain radical was dependent only on the terminal group (the monomer unit last added to the growing chain) and the kinetic behavior was independent of the length or over-all composition of the polymer chain.

Under these conditions the composition of the copolymer chain is determined by the following four propagation reactions:

$$\sim A\cdot + A \rightarrow \sim AA\cdot \qquad (2.1)$$

$$\sim A\cdot + B \rightarrow \sim AB\cdot \qquad (2.2)$$

$$\sim B\cdot + B \rightarrow \sim BB\cdot \qquad (2.3)$$

$$\sim B\cdot + A \rightarrow \sim BA\cdot \qquad (2.4)$$

whose forward rates are written as:

$$k_{11} \; [A\cdot] \; [A] \qquad (2.5)$$

$$k_{12} \; [A\cdot] \; [B] \qquad (2.6)$$

$$k_{22} \; [B\cdot] \; [B] \qquad (2.7)$$

$$k_{21} \; [B\cdot] \; [A] \qquad (2.8)$$

Dostal was able to write correct mathematical expressions for the rate of copolymerization and the composition of a copolymer in terms of these rates, but since four unknown rate constants were designated he could not devise any experimental tests for his conclusions.

Wall in 1941 (45) showed that the chemical composition of copolymers was dependent only on relative reactivities of the two monomers to the two radicals. He expressed these relative reactivities in the form of ratios called "monomer reactivity ratios" and defined them as:

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

Mayo and Lewis (46) in a classic work, undertook a systematic study of copolymerization and arrived at the following rate expressions for the consumption of monomers A and B:

$$\frac{-d\,[A]}{dt} = k_{11} \, [A\cdot] \, [A] + k_{21} \, [B\cdot][A] \qquad (2.09)$$

$$\frac{-d\,[B]}{dt} = k_{12} \, [A\cdot] \, [B] + k_{22} \, [B\cdot][B] \qquad (2.10)$$

In the steady state of copolymerization the different types of free radicals must be maintained at a steady concentration, therefore, $k_{12} \, [A\cdot] \, [B] = k_{21} [B\cdot] \, [A]$. This means that in the steady state the rate at which (A•) is destroyed is equal to the rate at which (B•) is destroyed. It is then possible to solve for the concentration of one of the radicals in the steady state in terms of the other. Mayo and Lewis applied this steady state assumption to the ratio of the disappearance of the two monomers and arrived at the following relation:

$$\frac{d\,[A]}{d\,[B]} = \left(\frac{[A]}{[B]}\right) \frac{\left(\frac{k_{11}}{k_{12}}\right) [A] + [B]}{\left(\frac{k_{22}}{k_{21}}\right) [B] + [A]} \qquad (2.11)$$

which using the definition of monomer reactivity ratios defined by Wall can be simplified to:

$$\frac{d\,[A]}{d\,[B]} = \left(\frac{[A]}{[B]}\right) \frac{r_1\,[A] + [B]}{r_2\,[B] + [A]} \qquad (2.12)$$

It follows that the ratio of the rates of disappearance of the two monomers is also the ratio of the molar concentrations of the two monomers in the copolymer. Defining the instantaneous concentration of monomer A in the copolymer as "a" and the concentration of monomer B in the copolymer as "b" then;

$$\frac{a}{b} = \left(\frac{[A]}{[B]}\right) \frac{r_1\,[A] + [B]}{r_2\,[B] + [A]} \qquad (2.13)$$

This equation is known as the "copolymer composition equation". This same equation was derived independently by Alfrey and Goldfinger (47) at approximately the same time using the same reasoning.

The copolymer composition equation has been used primarily for the evaluation of the monomer reactivity ratios, r_1 and r_2. The experimental technique has been developed into a standard routine and consists of preparing a series of the copolymers for a given A and B by varying the monomer concentrations and analyzing the resulting copolymers for the concentration of "a" and "b". The conversion of the copolymerizations in this series must be kept low because equation (2.13) is valid for instantaneous copolymerization and the assumption is made that low conversion copolymerization approximates instantaneous copolymerization. The most common method of determining r_1 and r_2 from this data is the method of Fineman and Ross (48). It consists of rearranging the copolymer composition equation to the linear form;

$$F(f - 1)/f = r_1 F^2/f - r_2 \tag{2.14}$$

where $F=\frac{A}{B}$ and $f=\frac{a}{b}$. A plot of $\frac{F(f - 1)}{f}$ vs. F^2/f will result in a straight line with a slope of r_1 and an intercept on the $\frac{F(f - 1)}{f}$ axis of $-r_2$. This method gives the most accurate results because the data can be plotted and a least squares method or a nonlinear least square can be applied to determine the slope and intercept. Since the derivation of the copolymer composition equation, its use has been extended to include other aspects of copolymer composition. Most recently it has been used to calculate various monomer sequences in copolymer chains.

Merz and co-workers (49) derived a copolymer composition equation in 1946 which included the effect of the penultimate unit on the addition of a monomer in a growing chain. The derivation is similar to the derivation of the simple copolymer composition equation for the terminal effect, however, eight propagation reactions and four monomer reactivity ratios or two additional parameters are needed to define the propagation steps. The monomer reactivity ratios were defined as

$$r_1 = \frac{k_{111}}{k_{112}}$$

$$r_1' = \frac{k_{211}}{k_{212}}$$

$$r_2 = \frac{k_{222}}{k_{221}}$$

$$r_2{}' = \frac{k_{122}}{k_{121}}$$

where the subscripts describe the propagation reaction according to monomeric units. The copolymer composition equation was:

$$\frac{dA}{dB} = \frac{a}{b} = \frac{1 + \left(\frac{r_1 A}{B}\right)\left(\frac{r_1{}'B + A}{r_1 B + A}\right)}{1 + \left(\frac{r_2 B}{A}\right)\left(\frac{r_2{}'B + A}{r_1 B + A}\right)} \qquad (2.15)$$

Equation (2.15) reduces to (2.13) by setting $r_1{}' = r_1$ and $r_2{}' = r_2$.

Since copolymerization is a discrete statistical process, Merz and co-workers (49) also found it convenient to describe the copolymerization process in terms of four conditional Markov probabilities. One can define a general Markov conditional probability P_{ij} as the probability that monomer "j" adds to a polymer chain whose terminal unit is "i". For a copolymerization system four permutations of this probability exist, P_{11}, P_{12}, P_{21}, and P_{22}. These probabilities are defined as follows:

$$P_{11} = \frac{k_{11}A}{k_{11}A + k_{12}B} = \frac{r_1 A}{r_1 A + B} \qquad (2.16)$$

$$P_{12} = \frac{k_{12}B}{k_{11}A + k_{12}B} = \frac{B}{r_1 A + B} \qquad (2.17)$$

$$P_{21} = \frac{k_{21}A}{k_{21}A + k_{22}B} = \frac{A}{A + r_2 B} \qquad (2.18)$$

$$P_{22} = \frac{k_{22}B}{k_{21}A + k_{22}B} = \frac{r_2B}{A + r_2B} \qquad (2.19)$$

With these definitions the distribution of various sequence lengths of A and B in the copolymer chain can be calculated in the following manner. A sequence is defined as any run of A's or B's. The probability that a sequence starting with an A is followed by an A is P_{11} according to the principle of succeeding probabilities. If the sequence then contains nA units the probability for this run would be $P_{11}^{(n-1)}$. Since the run is terminated by a B unit the probability of termination is P_{12} or $(1-P_{11})$. Thus the probability that an A sequence picked at random contains just nA members is:

$$N(a,n_1) = P_{11}^{(n_1-1)}(1-P_{11}) \qquad (2.20)$$

This is called the "number distribution function" for the lengths of A sequences and was first derived by Merz and Alfrey.

More recently Price (50) utilized a matrix method to realize the copolymerization process in terms of Markov chain theory. He applied the matrix scheme to the three simplest examples of copolymerization: the terminal unit effect (considering the active end to be just the last monomer unit added), the penultimate unit effect (considering the last two monomer units as the active end), and the penpenultimate unit effect (active end consisting of the last three monomer units).

Price preferred binary notation for a polymer chain. By labeling one monomer "0" and the other monomer "1" he designated any chain sequence by the decimal equivalent of the binary number, e.g. a chain segment 1001 would be 9 in the decimal system.

A Markov process is defined by two probabilities: the a priori probability, $P_j^{(k)}$, and the conditional probability, P_{rs}. The a priori $P_j^{(k)}$ is the fraction of unit sequences of length k. Thus the letter "k" signifies the number of units which affect the addition of a monomer unit. The letter "j" is the decimal equivalent of the binary notation described by the sequence, e.g. $P_2^{(2)}$ is the probability that a given pair is 10. P_{rs} is the conditional probability that a given state "r" is followed by a state "s" where "r" and "s" are expressed as decimal notations of the binary sequences.

Thus any sequence may be described by an initial probability of finding the first one, two, three, etc. units multiplied by the conditional probabilities of converting the initial sequence to various other sequences, e.g. for the case of the terminal effect the sequence 011001 may be described by $P_0^{(1)}P_{01}P_{11}P_{10}P_{00}P_{01}$, for a penultimate unit effect the same sequence would be described by $P_1^{(2)}P_{13}P_{32}P_{20}P_{01}$. The conditional probabilities P_{rs} are subject to the restriction $\sum\limits_s P_{rs} = 1$ since a given terminal sequence must add a 0 or a 1, and since a given singlet, diad, triad, etc. must be in some state $\sum\limits_j P_j^{(k)} = 1$.

Since the conditional probabilities which are more often called transitional probabilities depend only on the initial and final state resulting from the addition of a single unit to the end of a chain and do not depend on the state of the chain at any prior time they then fit the definition of a Markov chain.

To solve for the copolymer composition for any specific (k) the transitional probabilities are arranged in a matrix (P) the elements of which are P_{rs} where r is the column and is is the row.* The steady-state distribution of singlets if k=1, diads if k = 2, etc. in states 0 to 2^k-1 is given by solutions of the equation $(P)V^{(k)} = \lambda\, V^{(k)}$ where $V^{(k)}$ is a 2^k element column vector whose components represent the relative concentrations of the various states and is a constant. Because of the restriction that $\sum_s Prs = 1$, the matrix (P) is stochastic. Using the fact that the matrix is stochastic the various components, $V_j^{(k)}$, can be found (see Appendix I for detailed solution). If N_0 is defined as the number of 0's in the completed chain and N_1 as the number of 1's in the completed chain then an equation for $\frac{N_0}{N_1}$ can be derived from this matrix. According to Price it is:

$$N_0 = \frac{\sum_{o}^{2^{(k-2)}} V_e}{\sum_{1}^{2^{(k-1)}} V_d} \qquad (2.21)$$

where 'e' is an even integer and 'd' is an odd integer. An expression for $\frac{N_0}{N_1}$ in terms of the various probabilities is obtained by substituting the appropriate probabilities into the $V_j^{(k)}$ expressions. It should be noted that $\frac{N_0}{N_1}$ is Price's nomenclature for the expression $\frac{a}{b}$ in equation (2.21).

Price defined k_{r0} and k_{r1} as the specific rate constants for addition of monomers 0 and 1 respectively to the growing chains ending

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*Price's preference here is unfortunately not the usual nomenclature used in Markov chain matrix theory in that r is generally given as the row and s the column.

in terminal sequence "r" and he defined M_0 and M_1 as the monomer feed concentrations of 0 and 1 respectively. These notations differ from previous work, therefore the table below is given to aid in translating Price's work into the more familiar terminology.

NOMENCLATURE

Price	Mayo
$\frac{N_0}{N_1}$	$\frac{a}{b}$
M_0, M_1	A, B
r_0, r_1 (terminal mechanism)	r_1, r_2 (terminal mechanism)
r_0, r_2, r_3, r_1 (penultimate mechanism)	r_1, r_1', r_2, r_2' (penultimate mechanism)

The rate constants used by most workers contain two subscripts for the terminal mechanism, three for the penultimate mechanism and so forth in contrast to only two subscripts in Price's rate constants regardless of the mechanism under consideration. He further defined $r_n = \frac{k_{n0}}{k_{n1}}$ when "n" is even and $\frac{k_{n1}}{k_{n0}}$ when "n" is odd and further sets

$$Prs = \frac{k_{ru}M_u}{k_{rt}Mt} \qquad (2.22)$$

where $u = 0$ when "s" is even and $u = 1$ when "s" is odd. By substituting this expression for the transitional probabilities into the equation for $\frac{N_0}{N_1}$ and letting $\frac{M_0}{M_1} = F_0$ Price obtains copolymer composition equations in terms of F_0 and the reactivity ratios r_n for the three different copolymerization mechanisms (See Appendix I for a specific example). The expressions derived by this method for the penultimate and terminal mechanisms are the same as those derived by earlier workers, showing that Price has not proposed any new mechanism but only a new mathematical tool for arriving at these more complex expressions.

Price also derived general formulas for the fraction of monomer 0 in the copolymer, the fraction of 01 monomer sequences in the copolymer, and the fraction of sequences containing only monomer "0" or monomer "1" for a given length n. These equations are given in Table III.

In addition to these, equations can be obtained from this method for the fraction of sequences of any length from any "active end sequence" in terms of the parameters, the monomer reactivity ratios, and initial monomer concentrations, provided the conversion is kept low.

In the past decade a number of copolymer systems have appeared to have compositions whose values do not correlate well with the terminal mechanism for copolymerization. Previous to high resolution NMR studies, however, all compositional data had been based only on the mer fractions in copolymer chains. The accuracy of these data are highly variable depending on the particular method of analysis and justification for invoking the penultimate mechanism as an explanation for these discrepancies is subject to considerable question. This was first shown by Berger and Kuntz (51) in 1964 whose analysis of reasonably high precision compositional data taking into account the drift in monomer feed over the conversion range could not justify distinguishing between the terminal and penultimate mechanisms. They further concluded that additional information on the sequence lengths or copolymer microstructure would be needed to make this distinction.

Table III. Equations for monomer and sequence fractions

$$f_0^{(k)} = \frac{N_0}{N_0 + N_1} = \frac{\sum_{m=0}^{2^{k-1}} V_{2m}^{(k)}}{\sum_{i=0}^{2^{k-1}} V_i^{(k)}}$$

$k = 1 \quad f_{01} = f_0^{(1)} P_{01}$

$k = 2 \quad f_{01} = V_1^{(2)} / \sum_{i=0}^{3} V_i^{(2)}$

$k = 3 \quad f_{01} = (V_2^{(3)} + V_3^{(3)}) / \sum_{i=0}^{7} V_i^{(3)}$

$$P_n^{(x)} = P_x^{(k)} P_{xx}^{(n-k)}$$

Where n = number of 0's or 1's in the sequence

$x = 0$ or 1

$$P_x^{(k)} = V_x^{(k)} / \sum_{i=0}^{2^{k-1}} V_i^{(k)}$$

To further complicate the nomenclature problem Harwood and Ritchey (52) introduced a new parameter, R, called the run number and defined it as the average number of monomer sequences occurring in the copolymer per 100 monomer units. They used this parameter and the ratio of the monomer concentration to derive an equation similar to that of the Ross-Fineman equation except for the insertion of the parameter R.

A problem which has only recently received attention is the determination of copolymerization reactivity ratios at higher conversions; that is, drift in monomer feed ratios. The theoretical treatments which have been discussed previously are all valid only for instantaneous copolymerization which allows F to be treated as a constant, F_0. As long as the copolymerization proceeds to no more than a few percent in conversion these treatments can be assumed to be valid, however, if the reaction is allowed to proceed to any great extent these equations will no longer apply. They are not valid because as the process continues one of the monomers will enter into the copolymer chain more rapidly than the other unless the monomer reactivity ratios are equal and this will change the ratio of the monomer feed. The theoretical treatments discussed previously are all dependent on the ratio of the monomer concentration thus the results based on these treatments will change with the degree of conversion.

A general formula for obtaining the copolymer composition for any conversion was developed by Skiest (53) and is shown below:

$$\ln \frac{M}{M_0} = \int_{f_1^\circ}^{f_1} \frac{1}{F_1 - f_1}\, df_1 \qquad (2.23)$$

where $M=M_1 + M_2$ and $M_o=M_{1_o}+ M_{2_o}$. For given values of the reactivity ratios, graphical or numerical methods can be used to calculate the expected change in the monomer mixture and copolymer composition corresponding to the mole conversion, $1 - \frac{M}{M_o}$.

For an ordinary binary copolymerization assuming only terminal unit effects Meyer and Lowry (54) have recently developed an analytical solution to Skiest's equation. Meyer and Lowry noted the equation for the mole fraction of monomer M_1 in the feed.

$$F_1 = \frac{(r_1 - 1)f_1^{\,2} + f_1}{(r_1 + r_2 - 2)\, f_1^{\,2} + 2(1-r_2)\, f_1 + r_2} \tag{2.24}$$

could be substituted into Skiest's equation and rearranged to obtain:

$$\ln \frac{M}{M_o} = \frac{1}{(2-r_1-r_2)} \int_{f_1^{o}}^{f_1} \frac{(r_1+ r_2-{}^{2})\;\; f_1^{\,2} + 2(1-r_2)\, f_1 + r_2{}'}{f\;\; (f_1-1)\; \left(f_1 - \frac{1 - r_2}{2 - r_1-r_2}\right)} df_1 \tag{2.25}$$

In this form the equation can be expanded and integrated where the final integrated equation is:

$$\frac{M}{M_o} = \left(\frac{f_1}{f_1{}^{o}}\right)^{\alpha} \left(\frac{f_2}{f_2{}^{o}}\right)^{\beta} \left(\frac{f_1{}^{o} - \delta}{f_1 \;\, - \delta}\right)^{\gamma} \tag{2.26}$$

where $\alpha = \frac{r_2}{(1 - r_1)}$

$\beta = \frac{r_1}{(1 - r_1)}$

$\gamma = \frac{1 - r_1 r_2}{(1 - r_1)(1 - r_2)}$

$$\delta = \frac{1 - r_2}{(2 - r_1 - r_2)}$$

with the condition $r_1 \neq 1$ and $r_2 \neq 1$.

Kinsinger (55) used different nomenclature and solved the problem in a different manner and obtained the same relationship. Since the present work uses the nomenclature of Kinsinger, his definitions are listed below:

$[M_1]$ and $[M_2]$ = monomer concentrations in the feed at any total conversion.
$[M_1{}^o]$ and $[M_2{}^o]$ = initial monomer concentrations.
α_1 = conversion of monomer 1.
α_2 = conversion of monomer 2.

$$\alpha = 1 - \frac{M}{M^o} = 1 - \frac{(M_1 + M_2)}{(M_1{}^o + M_2{}^o)} \tag{2.27}$$

$$1 - \alpha = f_1{}^o(1 - \alpha_1) + f_2{}^o(1 - \alpha_2) \tag{2.28}$$

$$f_1{}^o = \frac{[M_1{}^o]}{[M_1{}^o] + [M_2{}^o]}; \qquad f_2{}^o = \frac{[M_2{}^o]}{[M_1{}^o] + [M_2{}^o]} \tag{2.29}$$

$$f(\alpha) = \frac{f_1}{f_2} = \frac{f_1{}^o(1 - \alpha_1)}{f_2{}^o(1 - \alpha_2)} = F_o\frac{(1 - \alpha_1)}{(1 - \alpha_2)} \tag{2.30}$$

The differential equation expressing the momentary ratio of the disappearance of the two monomers is shown below using the nomenclature of Kinsinger and is identical to (2.12) on page 16.

$$\frac{d(M_1)}{d(M_2)} = F_o\frac{d(1 - \alpha_1)}{d(1 - \alpha_2)} = F\frac{(r_1F + 1)}{(r_2 + F)} \tag{2.31}$$

By substitution of equation (2.30) with (2.31) and elimination of $d(1-\alpha_1)$ and $(1-\alpha_1)$ the equation can be integrated in the limits from 1 to $(1-\alpha_2)$. The completed integration is:

$$\ln(1-\alpha_2) = \frac{r_2}{1-r_2} \ln \frac{F}{F_o} + \frac{1-r_1r_2}{(r_1-1)(1-r_2)} \ln \left[\frac{(r_1-1)F+(1-r_2)}{(r_1-1)F_o+(1-r_2)} \right] \qquad (2.32)$$

It is possible to rearrange (2.28) so that:

$$(1-\alpha) = (1-\alpha_2) f_2^o \left[F + 1 \right] \qquad (2.33)$$

and substituting into (2.32) one obtains:

$$\ln(1-\alpha) = \ln f_2^o + \ln[F+1] + \frac{r_2}{(1-r_2)} \ln \frac{F}{F_o} +$$

$$\frac{1-r_1r_2}{(r_1-1)(1-r_2)} \ln \left[\frac{(r_1-1)F+(1-r_2)}{(r_1-1)F_o+(1-r_2)} \right] \qquad (2.34)$$

An equation similar to equation (2.32) can be derived from equation (2.30) by applying equation (2.29) and eliminating $d(1-\alpha_2)$ and $(1-\alpha_2)$. Using the same procedure one obtains:

$$\ln(1-\alpha) = \ln \left[\frac{F+1}{F} \right] + \frac{1}{1-r_2} \ln \frac{F}{F_o} +$$

$$\frac{1-r_1r_2}{(r_1-1)(1-r_2)} \ln \left[\frac{(r_1-1)F+(1-r_2)}{(r_1-1)F_o+(1-r_2)} \right] \qquad (2.35)$$

By combining (2.34) and (2.35) and rearranging them one obtains:

$$(1-\alpha) = \left[\frac{(r_1-1)F+(1-r_2)}{(r_1-1)F_o+(1-r_2)} \right]^a + f_1^o \left[\frac{F}{F_o} \right]^b + f_2^o \left[\frac{F}{F_2} \right]^c \qquad (2.36)$$

where $a = \dfrac{1-r_1r_2}{(r_1-1)(1-r_2)}$

$$b = \frac{1}{1 - r_2}$$

$$c = \frac{r_2}{1 - r_2}$$

If the substitutions $\frac{f_1 f_2^o}{f_2 f_1^o} = \frac{F}{F_o}$ and $1 - \alpha = \frac{M}{M_o}$ are made and the equation rearranged one obtains the expression of Meyer and Lowry.

Kinsinger has also developed a set of equations for obtaining the average value of the mole fraction of the various sequences at any conversion (α). He obtained this set of equations by integrating the equations for the various instantaneous diads between the limits of F_o and F, where F_o is the ratio of the initial monomer concentrations and F is the ratio of the monomer concentrations after any conversion. The instantaneous diad fractions and their integrated forms are displayed in Tables IV and V.

Before the present work no experimental work was published on the mole fraction of diads or higher sequences as a function of conversion.

Table IV. Instantaneous diad fractions

$$f_{AA} = \frac{r_1F_o^{\,2}}{r_1F_o^{\,2} + 2F_o + r_2}$$

$$2f_{AB} = \frac{2F_o}{r_1F_o^{\,2} + 2F_o + r_2}$$

$$f_{BB} = \frac{r_2}{r_1F_o^{\,2} + 2F_o + r_2}$$

Table V. Average diad mole fraction after conversion

$$\bar{f}_{AA} = \int_{F_o}^{F} \frac{r_1F_o^2}{r_1F_o^2 + 2F_o + r_2}\, dF$$

$$= \frac{-\frac{1}{r_1}\ln R_1 + \frac{2 - r_1r_2}{2r_1\sqrt{1-r_1r_2}}\ln R_2}{F - F_o} + 1 \quad \left(\text{for } r_1r_2 < 1\right)$$

$$2\bar{f}_{AB} = \int_{F_o}^{F} \frac{2F_o^2}{r_1F_o^2 + 2F_o + r_2}\, dF$$

$$= \frac{\frac{1}{r_1}\ln R_1 - \frac{1}{2r_1\sqrt{1 - r_1r_2}}\ln R_2}{F - F_o} \quad \left(\text{for } r_1r_2 < 1\right)$$

$$\bar{f}_{BB} = \int_{F_o}^{F} \frac{r_2}{r_1F_o^2 + 2F_o + r_2}\, dF$$

$$= \frac{\frac{r_2}{2\sqrt{1 - r_1r_2}}\ln R_2}{F - F_o}$$

Where $R_1 = \dfrac{r_1F^2 + 2F + r_2}{r_1F_o^2 + 2F_o + r_2}$

and R_2 $\left[\dfrac{r_1F + 1 - \sqrt{1 - r_1r_2}}{r_1F + 1 + \sqrt{1 - r_1r_2}}\right] \left[\dfrac{r_1F_o + 1 + \sqrt{1 - r_1r_2}}{r_1F_o + 1 - \sqrt{1 - r_1r_2}}\right]$

EXPERIMENTAL

Purification of Monomers and Initiator

1. Azo-bis-isobutyronitrile (AIBN) - The AIBN obtained from Monomer-Polymer Laboratories was purified by recrystallization from acetone. A large quantity was dissolved in warm acetone until a saturated solution was obtained. The solution was filtered through a Buchner funnel under vacuum and transferred to a beaker. The beaker was cooled in an ice-water bath for thirty minutes and a copious crop of crystals precipitated. The contents of the beaker were again filtered through a Buchner funnel under vacuum and the residue placed in a vacuum oven to dry at room temperature.

After drying, the purified, crystalline AIBN was stored in two twelve dram vials in a refrigerator until needed.

2. Vinylidene Chloride (VCl_2) - The VCl_2 was purchased from Monomer-Polymer Laboratories. The container was stored in a refrigerator with only the approximate amount needed for each run withdrawn at one time. The sample withdrawn was separated from dissolved inhibitors by pouring it through a column of activated alumina (56), then it was transferred directly into the polymerization tubes.

3. Isobutylene (IB) - A two pound cylinder of IB was obtained from Matheson Co., Inc. To free the monomer of moisture, it was passed through a column of drierite then into a condenser surrounded by a dry ice-acetone bath. The IB was liquified directly into the vessel in which it would be used.

4. Vinyl Chloride (VCl) - The VCl was obtained in a gas cylinder from Matheson Co.,Inc. To purify the monomer of HCl it was bubbled through a 40% aqueous potassium hydroxide solution,then passed through a column of drierite and soda lime,then passed into a condenser surrounded by a dry ice-acetone bath and liquified directly into the vessel in which it would be used.

Preparation of Low Conversion VCl_2-IB Copolymers

Heavy walled combustion tubes (15 x 20 x 250 mm.) were used for the copolymerizations. The tubes were modified by narrowing the necks and sealing a 24/40 female joint to the top. The initiator (AIBN) was weighed separately and then charged to the tube. The amount of AIBN used never exceeded 1% by weight of the total charge. The tube containing the initiator was closed with a ground glass stopper then weighed on a Mettler balance. Next the solvent, tetrahydrofuran, (THF) was added and weighed. This liquid was found to be a convenient solvent for the reaction since the copolymer was insoluble in the monomer mixtures. The amount of THF added varied according to the amount of VCl_2 since greater portions of solvent were needed to effect a homogeneous polymerization for the greater concentrations of VCl_2. The amount of solvent never exceeded one third of the total weight of the mixture. Next the purified VCl_2 was added and the tube was reweighed. The amount of VCl_2 varied from one charge to another as a series of copolymerizations with varying monomer concentrations were planned. After weighing the VCl_2 charge the tube was placed in a dry ice-acetone bath and the IB condensed directly into it. When sufficient IB had been added, the tube was connected with a unit consisting of a vacuum stopcock and a male ball joint. The tube with the stopcock in the closed position was then transferred to a Dewar flask containing liquid nitrogen. After the contents had solidified the tube was attached to a vacuum line via the ball joint and degassed for three minutes. At the end of this time the tube was sealed off at the narrowed neck. After cooling, both parts of the tube were weighed to obtain the weight of the IB by difference.

The sealed tube was placed in a 30° C water bath. After the contents reached bath temperature the tube was taken from the bath, shaken and replaced into the bath where it was irradiated with U.V. light from a Hanovia S-H lamp. The proper polymerization time for low conversion was judged by eye and depended upon the nature of the charge. The samples which contained large portions of IB polymerized slowly while those with large amounts of VCl_2 needed a much shorter time. Table VI shows the relative amounts of each monomer in the charge, the weight percentage of AIBN, the length of the polymerization, and the conversion for the series. All runs were kept to low conversion.

Polymerization was stopped by removing the tube from the water bath and freezing it with liquid nitrogen. After the contents were solidified the tube was broken and the contents after warming were poured through a coarse sinter glass filter into methanol where the copolymer precipitated. The polymer was allowed to settle until the supernatant was clear then the solution was decanted and more methanol was added. This solution was allowed to stand for 24 hours then decanted from the solids. The copolymer was then placed in a vacuum oven at 40° C and dried until constant weight was achieved. The length of time necessary to attain constant weight varied according to the nature of the copolymer. The greater the amount of IB in the copolymer the longer it took for a

Table VI Copolymerization of vinylidene chloride and isobutylene

Sample	Mole Fraction VCl_2	Mole Fraction IB	Wt % AIBN	Polymerization time in minutes	% conversion
VI-32-2	0.584	0.416	1.0	150	4.0
VI-24-2	0.505	0.495	0.85	100	7.4
VI-12-1	0.471	0.529	0.78	250	1.1
VI-22-2	0.418	0.582	0.75	250	6.0
VI-28-2	0.391	0.609	0.80	300	6.2
VI-30-2	0.353	0.647	0.88	330	5.5
VI-20-1	0.318	0.682	0.82	420	4.5
VI-23-1	0.317	0.683	0.74	300	2.6
VI-26-2	0.288	0.712	0.83	390	5.6
VI-17-2	0.247	0.753	1.67	570	9.4
VI-20-2	0.225	0.775	0.94	480	6.1
VI-25-1	0.213	0.787	0.77	420	2.0
VI-25-2	0.206	0.794	0.84	420	3.8
VI-26-1	0.198	0.802	0.80	420	2.2
VI-18-2	0.159	0.841	1.25	660	7.3
VI-16-2	0.130	0.870	0.92	1200	8.8
VI-29-1	0.126	0.874	0.87	690	2.4
VI-34-1	0.121	0.879	0.93	750	2.8
VI-19-2	0.083	0.917	1.00	720	3.3

constant weight to be reached. The drying time varied from 2 days to as much as 10 days.

Preparation of Low Conversion VCl_2-VCl Copolymers

Since the boiling point of VCl is approximately that of IB the same preparative technique was used for this system as described in the previous system. The time needed for these copolymerizations was considerably shorter, but the technique was the same in all other respects. As with the VCl_2-IB system enough THF was used in each polymerization to keep a homogeneous solution and no precipitation of the polymer from the solution occurred. Table VII shows the mole fraction of each monomer in the charge, the weight percentage of AIBN, the length of the polymerization, and the conversion.

Preparation of High Conversion Copolymers

To study the effect of conversion on sequence distribution a series of VCl_2-IB copolymers were made with the same initial monomer concentrations but with a range of conversions.

The approximate amounts of catalyst, THF, VCl_2, and IB needed for the series of conversions to be made were calculated on the basis of approximately 20 grams of solution for each polymerization tube.

A single neck, 500 ml. round bottom flask was equipped with a stopcock, ball joint, and tube from the stopcock running to the bottom of the flask. Enough AIBN for the series was weighed separately and charged to the flask.

The flask was weighed after the AIBN was added, then the approximate amount of THF was measured volumetrically and added to the flask. Next

Table VII Copolymerization of vinylidene chloride and vinyl chloride

Sample	Mole Fraction VCl_2	Mole Fraction VCl	Wt % AIBN	Polymerization time in minutes	% Conversion
VVCl-63-2	0.691	0.309	1.04	30	0.67
VVCl-62-2	0.576	0.424	1.32	120	4.13
VVCl-36-2	0.470	0.530	0.97	120	3.55
VVCl-67-2	0.395	0.605	1.00	180	4.64
VVCl-64-2	0.355	0.645	1.15	180	6.23
VVCl-61-2	0.272	0.728	0.64	120	3.33
VVCl-69-2	0.240	0.760	1.03	180	4.47
VVCl-66-2	0.203	0.797	1.21	180	4.09
VVCl-65-2	0.169	0.831	0.78	195	3.82
VVCl-47-2	0.098	0.912	0.63	150	4.98
VVCl-70-2	0.066	0.934	1.06	180	0.40

the VCl_2 was measured and added to the flask, and the flask was again weighed.

The flask was then placed in a Dewar filled with acetone and dry ice was added until the temperature was approximately -20° C. It was found that cooling the flask to the normal dry ice-acetone bath temperature of -68° C caused the AIBN to precipitate from the solution.

After cooling to -20° C the IB which had been condensed into a separate cylinder was added to the flask. The flask and contents were then quickly removed from the cold bath, weighed, and returned to the bath.

A tared polymerization tube, equipped with a stopcock and ball joint was placed in a dry ice-acetone bath and attached to the vacuum line. The tube remained under vacuum for 20 seconds then the stopcock was closed and the tube was connected at its ball joint to the ball joint of the round bottom flask. The stopcock of the round bottom flask was opened, then the stopcock of the polymerization tube was opened slowly and a portion of the solution was transferred to the polymerization tube. When enough of the solution was transferred both stopcocks were closed and the ball joints were disconnected. The polymerization tube was then placed in a Dewar filled with liquid nitrogen, degassed, and sealed. Both parts of the tube were retained and the top part weighed immediately.

This procedure was repeated until all of the charge was transferred from the round bottom flask. All sealed tubes were stored in a large Dewar at liquid nitrogen temperature until ready for polymerization. The tubes were removed from the liquid nitrogen when ready for polymerization and placed in the 30° C bath. After warming to bath temperature they were removed, shaken, weighed, and returned to the bath then subjected to U.V. light. All copolymerizations took place with no precipitation of the polymer from the charge solution. Two series were run and Table VIII lists the initial conditions, the length of time of each run, and the conversion for that run.

The copolymers from these polymerizations were precipitated and dried the same as has been previously described for the low conversion copolymerizations.

Preparation of Copolymers for NMR Analysis

Approximately 0.2 g. of the dried copolymer was weighed into a 1 ml. volumetric flask. The flask was then filled to the mark with the solvent which in most cases was bromobenzene. One sample was also prepared in tetrachloroethylene and the same procedure was used. To aid polymer dissolution the volumetric flask was warmed in hot water until the copolymer passed into solution. The solution was then transferred to 0.5 mm. wall NMR tubes. The solution was allowed to cool and three or four drops of the reference standard, tetramethylsilane (TMS), were added to the tube.

If spectra of the samples were to be taken at elevated temperatures, the tubes were placed in liquid nitrogen and attached to a vacuum line. The solution in the tube was degassed for two minutes, removed from the Dewar, and allowed to warm to room temperature. The tube was then returned to the Dewar of liquid nitrogen and subjected to a vacuum for another two minutes. This procedure was repeated one more time except the tube was not removed from the Dewar after the third degassing but was sealed.

Table VIII High conversion copolymerization runs of vinylidene chloride and isobutylene

Sample	Polymerization time in hours	% Conversion
	Run #VI-49-2	
Wt. IB=33.41 gms	Wt. VCL_2=57.21 gms	Wt. THF=50.43 gms
Wt. AIBN=1.0606 gms	F_o=0.940	
VI-49-2-7	4.0	4.6
VI-49-2-4	15.3	17.0
VI-49-2-2	30.0	28.4
VI-49-2-5	48.0	36.2
VI-49-2-8	168.0	46.3
VI-49-2-6	72.0	47.7
VI-49-2-3	106.0	52.7
	Run #VI-1-3	
Wt. IB=29.50 gms	Wt. VCl_2=20.18 gms	Wt. THF=21.43 gms
Wt. AIBN=0.6175 gms	F_o=0.395	
VI-1-3-1	8.0	5.38
VI-1-3-2	24.0	17.83
VI-1-3-3	75.0	25.12
VI-1-3-4	116.0	38.66

INSTRUMENTATION

Methods For NMR Spectra

All NMR spectra were obtained with a Varian A-60 NMR spectrometer equipped with a variable temperature probe. The spectra of all the VCl_2-IB copolymers were taken at room temperature in bromobenzene. In addition to these spectra a series of spectra of sample VI-23-1 dissolved in bromobenzene were obtained at instrument temperature, 64° C, 80° C, 97° C, 118° C, and 137° C. This sample was also dissolved in tetrachloroethylene and an NMR spectrum obtained to study solvent effect. Although some of the other VCl_2-IB samples were originally run at a higher temperature all data reported for this system will be from the spectra taken at instrument temperature. The data will be reported for only the room temperature spectra because of the reduced noise level of the spectra at this temperature when compared to the spectra taken at higher temperatures.

With the exception of two samples all the VCl_2-VCl copolymers were run at room temperature. The two samples which were not run at room temperature were run at an elevated temperature because the copolymer precipitated from solution at room temperature.

All chemical shifts were measured using tetramethylsilane (TMS) as an internal reference and peaks are reported in τ values.

The spectra of the VCl_2-IB system were run once at a 500 cps. sweep width to obtain the relation of the peaks of the solvent to those of the copolymer and to optimize the performance of the spectrometer for the individual samples. To aid in obtaining the areas under the peaks the spectra were rerun at a 250 cps. width. All peaks of the copolymer and that of the reference were visible in this sweep width but the solvent peaks were not.

Because the signals of the polymer peaks were very weak all spectra of the VCl_2-IB system were run at an amplitude setting of between 8 and 12.5. Other typical settings were: Filter Band Width 0.2; Radio Frequency Field = 0.06 and a Sweep Time of 500 seconds. Because of the high spectrum amplitude setting, noise was quite evident in the spectra which introduced error in the peak area measurements. To minimize the effect of the noise each spectrum was repeated and superimposed three times on the original spectrum. This averaged the noise somewhat permitting the areas to be traced with greater accuracy.

All spectra of the VCl_2-VCl copolymer were run at a 500 cps. width. This line width was chosen because these peaks were much broader than those of the VCl_2-IB copolymers and they could not have been scanned at a 250 cps. sweep width. The signals from the peaks in these copolymers were weaker than those in the VCl_2-IB copolymers and the spectrum amplitude had to be increased. Most of the spectra were taken at an amplitude setting of 50 or 63. Other settings for the spectra of the VCl_2-VCl copolymers were: Filter Band Width = 0.1; Radio Frequency Field = 0.2 and Sweep Time = 500 seconds.

Since there was considerable noise in the spectra they were repeated three times superimposing each repeat on the original spectrum as in the VCl_2-IB copolymers. This enabled the areas under the curves to be measured more accurately.

Method of Measuring Areas Under Peaks

The areas underneath the peaks in the NMR spectra were obtained by first placing the spectra on a light table then tracing the portion which was to be measured on a piece of white paper. In this manner the noise could be smoothed and the spectra would not have to be used for the measurement thus keeping them free from possible damage.

Areas were measured with a planimeter. The planimeter was guided over the area once then repeated usually with the planimeter in a different position. If the two areas did not agree by two or three units the measurements were repeated until good agreement was obtained. All areas were measured in this manner. The agreement obtained can be seen for a typical sample, VI-20-2: Area X readings were 153 and 153; Area Y readings were 253 and 255; Area Z readings were 444 and 446.

INTERPRETATION OF NMR SPECTRA

Assignments of Peaks in VCl_2-IB Copolymer Spectra

Figure 3 displays comparative proton resonance spectra of two copolymers of the VCl_2-IB system with different compositions and the spectra of the two corresponding homopolymers. The spectrum A is of pure poly(isobutylene), spectrum B is of a copolymer with a large amount of IB in the monomer charge, spectrum C is of a copolymer with approximately equal amounts of each monomer in the charge, spectrum D is of pure poly(vinylidene chloride). The spectra of the copolymers are divided into three main regions labeled X, Y, and Z.

In Figure 3 it can be seen by comparison of the two copolymer spectra with the spectrum of pure poly(vinylidene chloride) that area X of the copolymers is in the same region as the only peak in the homopolymer. This peak in the homopolymer arises from the methylene protons of the polymer chain. Since these are methylene protons between two carbons bonded to chlorine the area X in the copolymer chain is assigned to the methylene protons of an AA diad where A refers to a vinylidene chloride unit in the copolymer chain and B refers to an isobutylene unit in the copolymer chain.

Area Z in the copolymer spectra is in the same region as the methylene proton and methyl proton peaks of the spectrum of pure poly(isobutylene) and is interpreted as arising from the methylene protons of a BB diad and the methyl protons from all B sequences in the copolymer.

Area Y in the copolymer spectra is mid-way between areas X and Z. There are no peaks in this region in the spectra of either of the

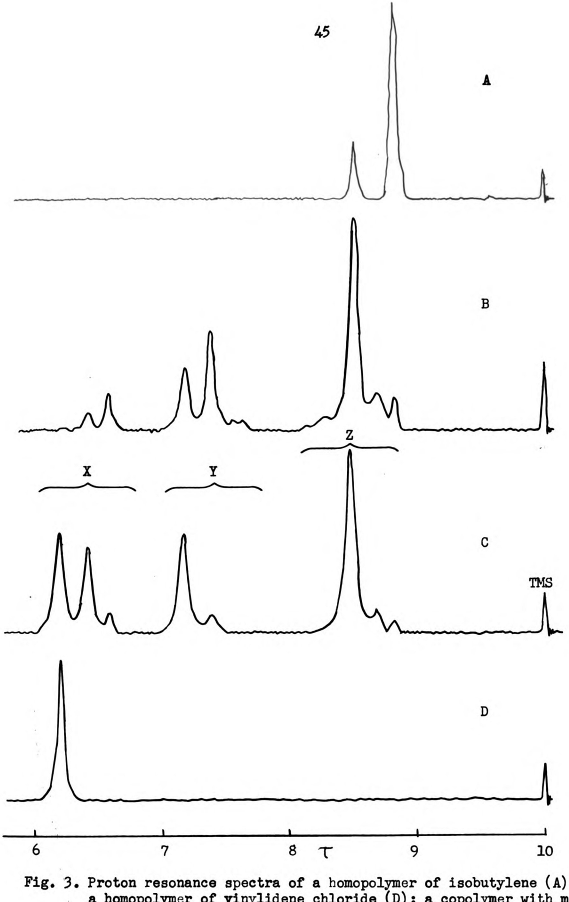


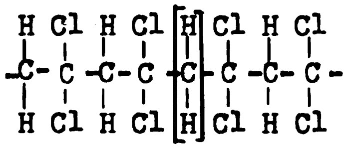
Fig. 3. Proton resonance spectra of a homopolymer of isobutylene (A); a homopolymer of vinylidene chloride (D); a copolymer with mole fraction 0.48 isobutylene and 0.51 vinylidene chloride (B); a copolymer with mole fraction 0.24 isobutylene and 0.76 vinylidene chloride (C).

homopolymers. Because this area does lie mid-way between the areas of the two homopolymers it was deduced that this area arises from the methylene protons of an AB diad.

One major difficulty in the interpretation of the copolymer spectra with regard to the various diads was the appearance of more peaks than were anticipated. Since there is no sound evidence to the contrary, it is assumed in this interpretation that the copolymerization resulted only from head-tail addition. This is a reasonable assumption because of the steric factors involved in both monomers and the polarity of the vinylidene chloride monomer and the experimental evidence which indicated head to tail addition only, in a wide variety of similar systems. Therefore to interpret the spectra it was necessary to consider sequences longer than diads. Figure 4 displays the different possible four unit sequences of the copolymer. All the methylene protons in the brackets in Figure 4 (a, b, and c) are part of an AA diad but upon closer examination it can be seen that each is from a different set of tetrads. "a" is an AAAA tetrad, b is an AAAB tetrad, and c is a BAAB tetrad where A = VCl_2 and B = IB. If the screening effect of the tetrads are significant then the peak of the AA group should split into three smaller peaks arising from the three possible tetrads formed therefrom. The AAAA tetrad peak can readily be identified since it is the one which would be present in the pure homopolymer of poly (vinylidene chloride). It is located at 6.18τ. It is well known (2) that substituting a halide for a methyl group causes the chemical shift of the proton under investigation to be moved downfield. On this basis a reasonable assignment of the peak at 6.40τ is to the AAAB tetrad and the peak at 6.59 to the BAAB tetrad. In Figure 4 (d, e, f, and g) the methylene protons

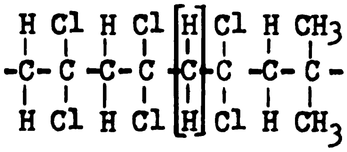
Fig. 4

a



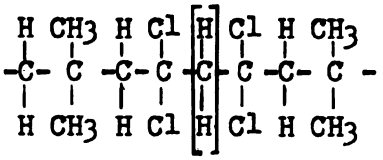
$$-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{C}}}-\left[\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\right]-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{C}}}-$$

b



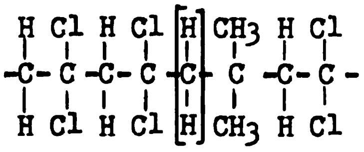
$$-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{C}}}-\left[\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\right]-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-$$

c



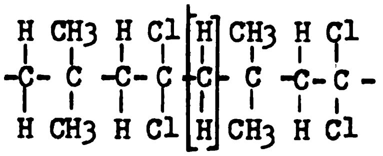
$$-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{C}}}-\left[\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\right]-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-$$

d



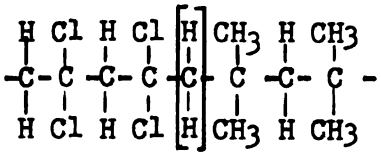
$$-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{C}}}-\left[\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\right]-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{C}}}-$$

e



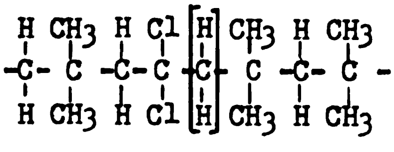
$$-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{C}}}-\left[\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\right]-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{C}}}-$$

f



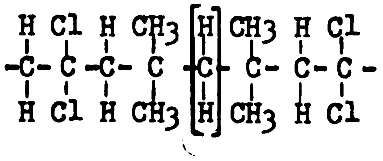
$$-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{C}}}-\left[\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\right]-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-$$

g



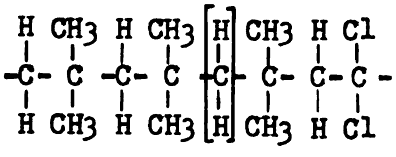
$$-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{C}}}-\left[\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\right]-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-$$

h



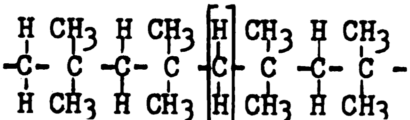
$$-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\left[\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\right]-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{C}}}-$$

i



$$-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\left[\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\right]-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{C}}}-$$

j



$$-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\left[\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\right]-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-$$

in the brackets represent the four possible tetrads (AABA, ABAB, AABB, and BAAB) which are possible from an AB diad. If each tetrad affects the central methylene protons in a different manner then four peaks should be present in the area arising from the methylene protons of the AB diad. Most of the NMR spectra of the VCl_2-IB copolymers obtained in this work show only two peaks in the AB diad region of the spectrum. However, the copolymers made with a high concentration of IB in the monomer charge show a spectra in which the AB region does consist of four peaks. The reason that such a large concentration of IB is needed in the monomer charge lies in the relative reactivity of the two monomers as will be discussed in the next section.

Using the same argument presented for the interpretation of the tetrad peaks in the AA region the tetrads for the AB diads were assigned as follows: progressing from the furtherest peak downfield toward the reference standard there is the AABA tetrad (7.16τ), the ABAB tetrad (7.36τ), the AABB tetrad (7.54τ), and finally the BABB tetrad (7.62τ). The assignment of the peak (7.36τ) to the ABAB sequences and the peak (7.54τ) to the AABB sequences is based on the empirical results rather than on theoretical grounds. To make the reverse assignment would be illogical as all experimental evidence will later show that it is extremely difficult to obtain a BB diad in this system and the peak (7.54τ) appears only when the most favorable conditions exist for AABB tetrads and BB diads.

In Figure 4 (h, i, j) the bracketed methylene protons all arise from BB diads but from different tetrads. The BBBB tetrad should be shifted upfield toward the TMS resonance and correspond to the methylene proton peak in the homopolymer of poly(isobutylene). In spectra B and C this peak is much larger than would be expected from the reactivity of the monomers and the mole fraction of B in the copolymer. It is also larger than the peak which corresponds to the methyl group of the pure homopolymer of poly(isobutylene). Therefore it seems evident that there are other protons in addition to the methylene protons of the BBBB tetrads giving rise to this peak. It will be shown later that the other protons influencing this peak are from the methyl group protons of a triad. If this interpretation is correct two peaks should be found downfield from this large peak corresponding to the other two tetrads of the BB diad. In spectrum B in Figure 3 these two predicted peaks are faintly noticeable. This is the spectrum of the copolymer containing the greatest concentration of IB in the monomer charge. Most of the spectra have the appearance of spectrum C of Figure 3 where these two peaks are not apparent.

In Figure 5 are depicted three chain segments with a central IB unit. If the chemical shift of each methyl group was dependent only on the groups bonded to the adjacent carbons in the chain then all would have the same chemical shift as each has a methylene hydrogen group on each side. But if the carbon atom β to the  $-\overset{CH_3}{\underset{CH_3}{C}}-$ group on the chain is examined and it is assumed that the groups bonded to these carbons affect the chemical shift of the methyl groups then each of the three methyl groups depicted in Figure 5 will display a different chemical shift.

The chemical shift of the methyl group in the chain segment shown in Figure 5 (c) should be the same as the methyl group in pure poly(isobutylene). In Figure 3, Spectra B and C, this chemical shift corresponds to the peak (8.74τ) which is furthest upfield in the two spectra. By applying the same logic as was previously used for the methylene group the next peak downfield (8.67τ) was assigned to the

methyl group in Figure 4 (b) or an ABB triad and the large peak (8.48τ) was interpreted as the chain segment depicted in Figure 5 (a), an ABA triad. This assignment correlates with the reactivities of the two monomers which predict the ABA peak should be the largest.

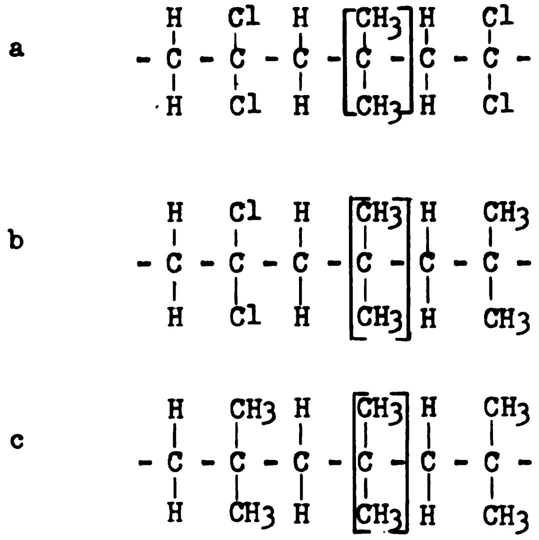


Fig. 5

In Figure 6 are displayed the spectra of three additional VCl_2-IB copolymers which give further evidence to support the interpretations discussed above. Figure 6 (A) is the spectrum of VI-18-2, Figure 6 (B) is the spectrum of VI-17-2 and Figure 6 (C) is the spectrum of VI-22-2. From Table VI it is shown that the amount of IB in the monomer charge increases from the copolymer in Figure 6 (C) to the copolymer in Figure 6 (A). In all three samples the mole fraction of IB in the monomer charge is greater than that in Figure 3 (C) but less than that in Figure 3 (B). The areas underneath the peaks all vary in the manner one would expect if this interpretation is valid. As the amount of IB in the copolymer increases area X decreases and the peak X_1 is drastically

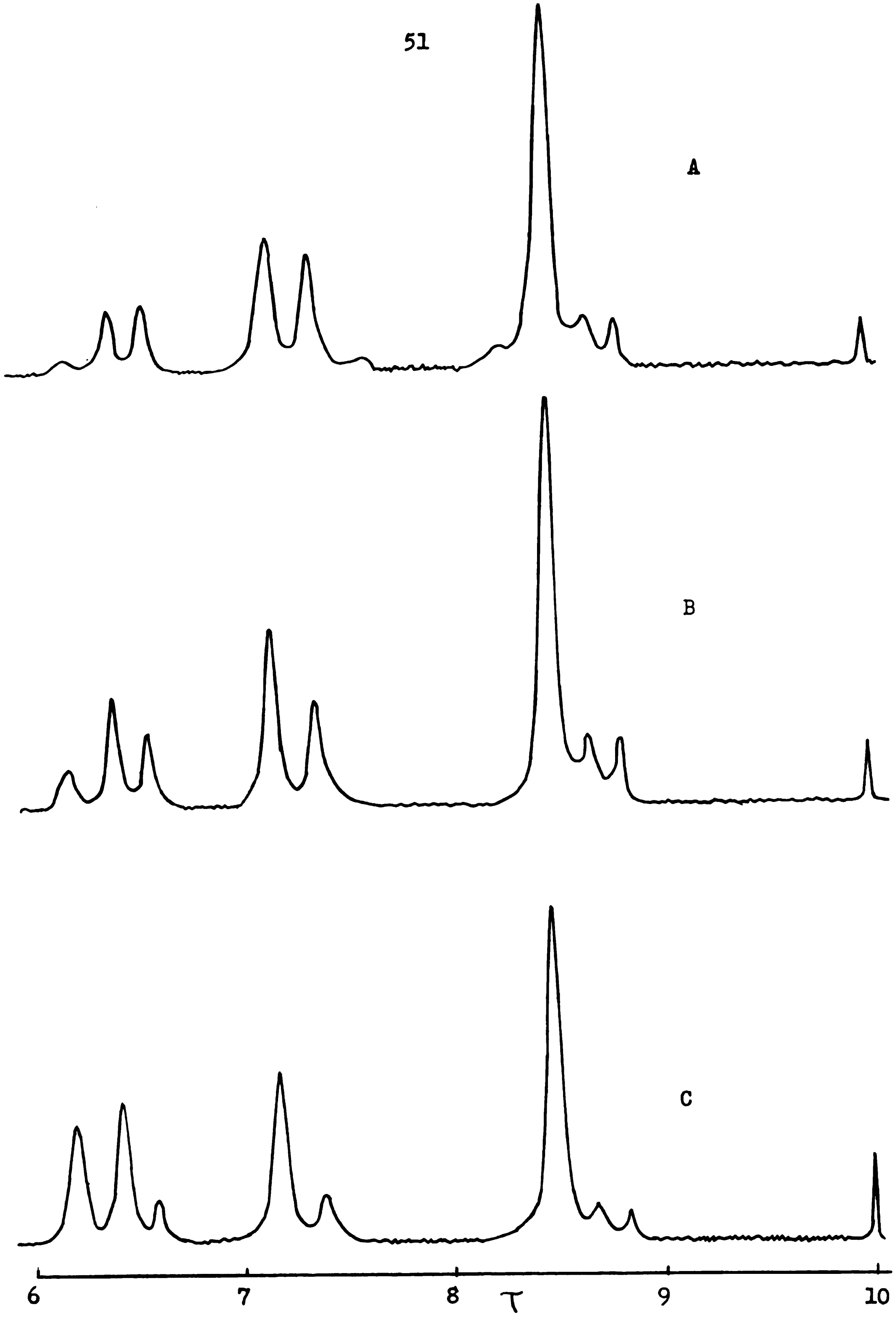


Fig. 6. Proton resonance spectra of a copolymer with mole fraction 0.39 isobutylene and 0.61 vinylidene chloride (A); a copolymer with mole fraction 0.33 isobutylene and 0.67 vinylidene chloride (B); a copolymer with mole fraction 0.24 isobutylene and 0.76 vinylidene chloride (C).

effected because there are fewer and fewer AAAA tetrad sequences. Area Y increases but the area under peak Y_1 relative to the area under Y_2 becomes smaller due to the fewer A units in the copolymer.

Peak Assignments in Vinylidene Chloride-Vinyl Chloride Copolymer Spectra

Figures 7 and 8 are NMR spectra of copolymers of VCl_2 and VCl. The spectra are arranged with the amount of VCl in the copolymer increasing from the top of Figure 7 to the bottom of Figure 8. Because of the introduction of an asymmetric center into the various copolymer sequences only diads were able to be unambiguousily identified in this system. The peak furtherest downfield (5.13τ) is designated peak M and is assigned to the α-hydrogens of the VCl in agreement with previous workers (5, 13-19). The next peak upfield, N, (6.42τ) corresponds to that of pure poly(vinylidene chloride) and is due to AA diads. The peak at 7.70τ, R, is the same as the methylene protons in pure poly (vinyl chloride) and is due to BB diads. The remaining peak, P, at 6.93τ is half way between the AA methylene proton peak and the BB methylene proton peak. Arguing analogously to the VCl_2-IB copolymer system this must be due to the methylene protons of an AB diad.

Because the AA diad will be free of any stereosequential effects this would be the logical place to observe splitting due to tetrads if they are observable. In Figures 7 and 8 all the spectra except spectrum D in Figure 8 displays two peaks in the AA diad region. In spectrum D the AA diad region is composed of a large peak with a shoulder on each side. The peaks in spectra A, B, and C are at 6.30τ and 6.42τ while those in spectrum E are at 6.42τ and 6.58τ. The two shoulders in spectrum D are

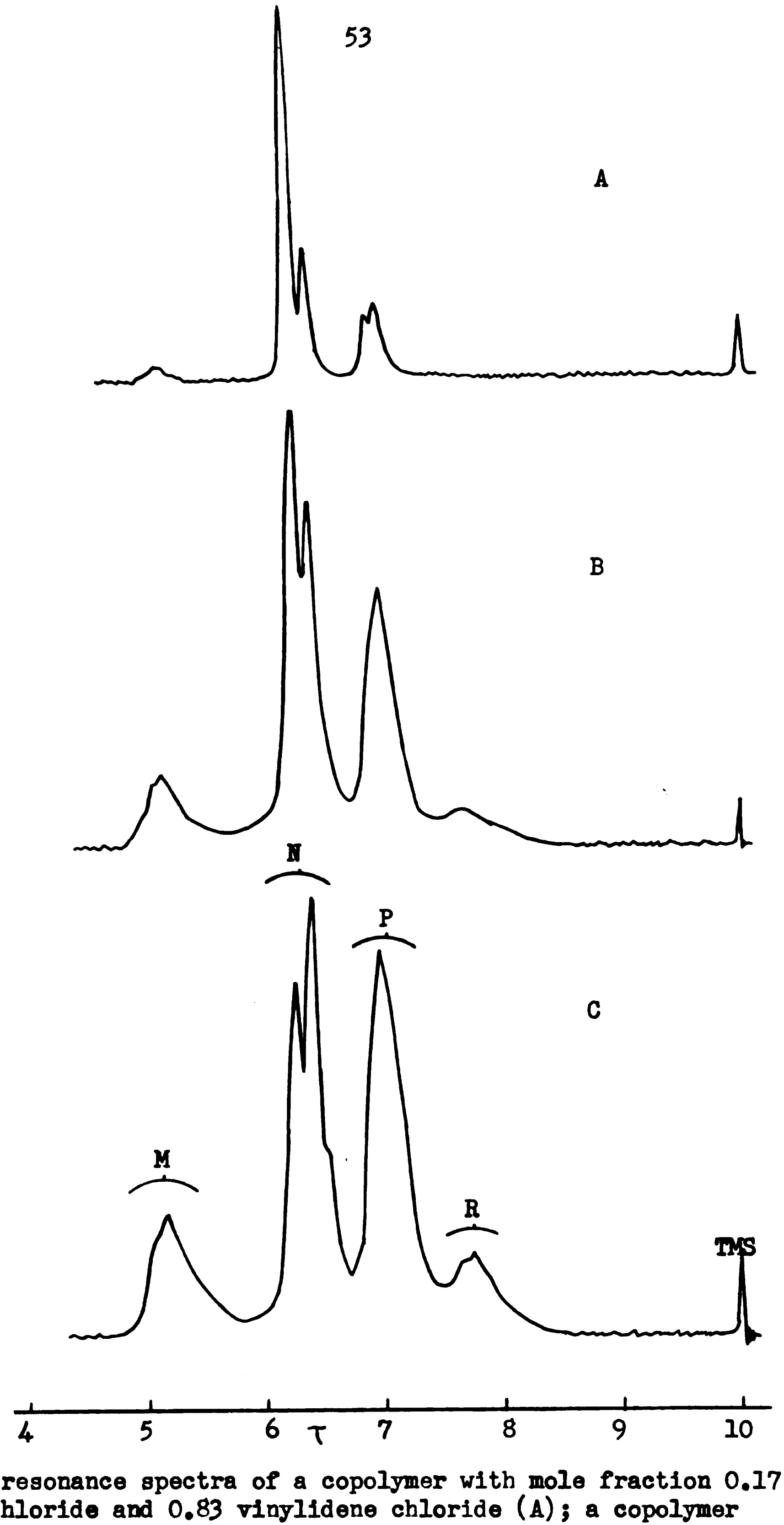


Fig. 7. Proton resonance spectra of a copolymer with mole fraction 0.17 vinyl chloride and 0.83 vinylidene chloride (A); a copolymer with mole fraction 0.26 vinyl chloride and 0.74 vinylidene chloride (B); a copolymer with mole fraction 0.37 vinyl chloride and 0.63 vinylidene chloride.

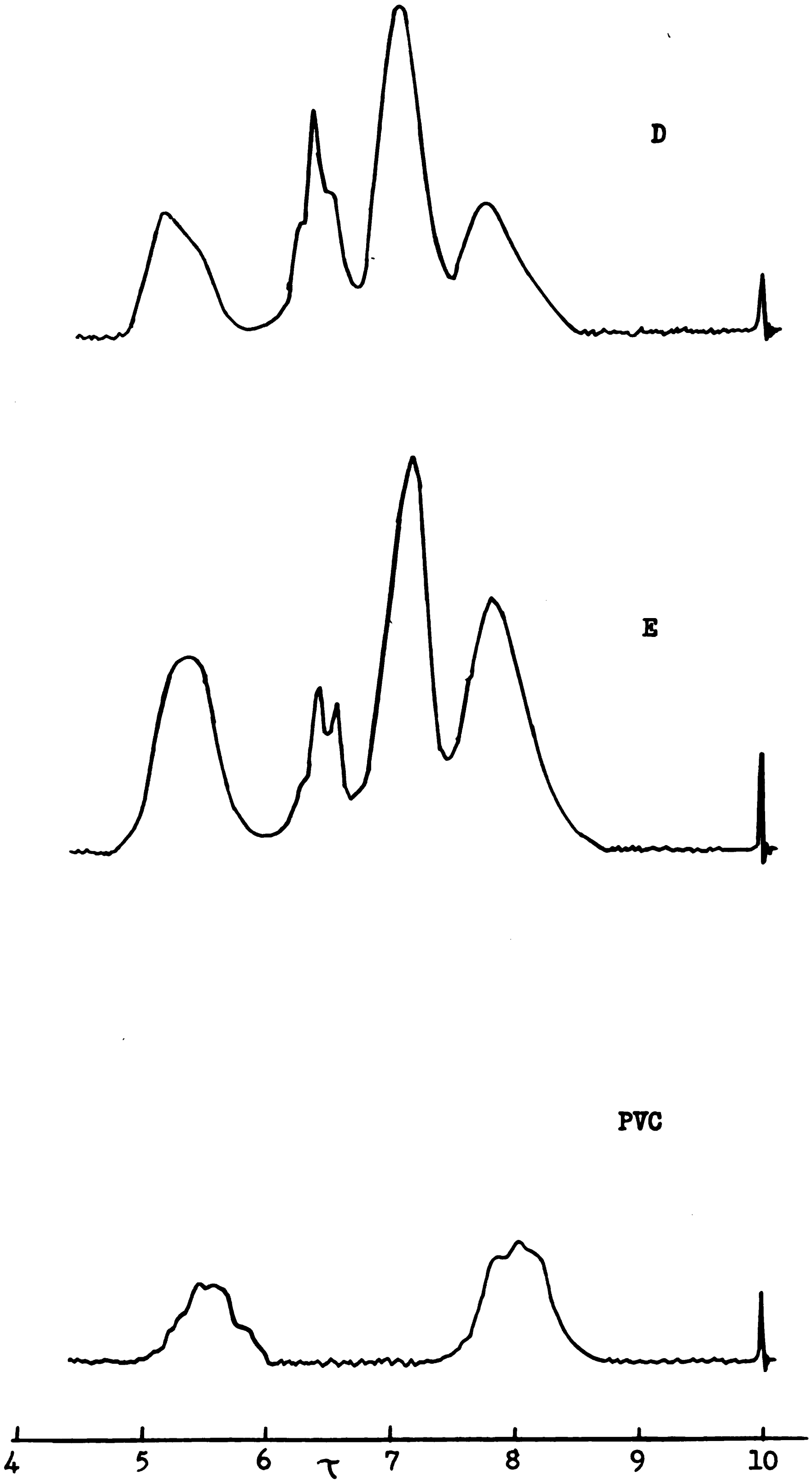


Fig. 8. Proton resonance spectra of a homopolymer of vinyl chloride (PVC); a copolymer with mole fraction 0.51 vinyl chloride and 0.49 vinylidene chloride (D); a copolymer with mole fraction 0.66 vinyl chloride and 0.34 vinylidene chloride (E).

at 6.30τ and 6.58τ with the main peak at 6.42τ. From these results it can be concluded that the AA diad region contains three peaks which are poorly resolved. These peaks would correspond to the three possible tetrads which arise from an AA diad. Because the resolution of these peaks is poor it was not possible to measure the area underneath the individual peaks and calculate the tetrad structures. However, if one looks qualitatively at the height of the peaks they increase and decrease in the manner corresponding to the reactivities of the two monomers.

A different interpretation of an NMR spectrum of a VCl_2-VCl copolymer is offered in the paper by Chujo and co-workers (38). They claim only two peaks are in the methylene region assigned to the AA diads in this work and that these two peaks result from the normal head to tail polymerized segments of VCl_2 and an abnormal head to head polymerization. For proof of their interpretation they compare the spectrum of one VCl_2-VCl copolymer with that of poly-2,3-dichlorobutadiene (PDCB) and partially chlorinated poly-2,3-dichlorobutadiene (PCPDCB). Unfortunately although they claim to have synthesized six low conversion copolymers of varying feed ratios they show no complete spectra and only one partial spectrum which depicts just the region in question. This partial spectrum was from a copolymer synthesized from a VCl_2/VCl feed ratio of 85/15 which should contain approximately 95 % or more VCl_2. The copolymer spectrum peak which they claim corresponds to the peak in the NMR spectrum of PCPDCB falls 0.45τ further downfield than the PCPDCB peak which is very poor correlation. The data offered by these workers is poor and sparse leading to a lack of confidence in their interpretation, but their data is freely interpretable according to the assignments presented in this work.

Normalization of the NMR Spectra

In Figure 3 the areas labeled X and Y arise from the resonance of only the methylene protons of the VCl_2-IB system, whereas the area labeled Z is the result of both methylene proton resonance and methyl proton resonance. Since the areas under the curves are proportional to the number of protons in a given configuration the normalization is achieved in the following way:

$X = C\left[\text{number of AA diads (methylene only)}\right] = C\text{x}(AA)$

$Y = C\left[2 \text{ x number of AB diads (methylene only)}\right] = C\text{x}(2AB)$

$Z = C\left[\text{number of BB diads (methylene only) + number of AB diads (methyl only) + number of BB diads (methyl only)}\right]$

Where A = VCl_2 unit, B = IB unit, and C = constant of proportionality. In an IB unit there are three times as many methyl protons as methylene protons, thus:

$Z = C\left[4 \text{ x number of BB diads (methylene equivalents) + 3 x number of AB diads (methylene equivalents)}\right]$

Since Y is proportional to 2AB, by subtracting $\frac{3}{2}$ Y from Z and dividing the result by four one obtains a direct proportion to the number of BB diads, i.e. the number of BB diads is proportional to $(\frac{Z}{4} - \frac{3Y}{8})$.

The mole (or number) fraction of each diad is given by the following equations where the symbols AA etc. represent the number of each species;

$$f_{AA} = \frac{AA}{AA + AB + BA + BB} = \frac{AA}{AA + 2AB + BB} \qquad (5.1)$$

$$2f_{AB} = \frac{2AB}{AA + 2AB + BB} \qquad (5.2)$$

$$f_{BB} = \frac{BB}{AA + 2AB + BB} \tag{5.3}$$

Since all possible diads are defined the sum must equal one.

By applying the relationships between the diads and the NMR areas the following equations for the mole fraction of the diads are obtained:

$$f_{AA} = \frac{X}{X + Y + \frac{Z}{4} - \frac{3Y}{8}} = \frac{X}{X + \frac{5Y}{8} + \frac{Z}{4}} \tag{5.4}$$

$$2f_{AB} = \frac{Y}{X + \frac{5Y}{8} + \frac{Z}{4}} \tag{5.5}$$

$$f_{BB} = \frac{\frac{Z}{4} - \frac{3Y}{8}}{X + \frac{5Y}{8} + \frac{Z}{4}} \tag{5.6}$$

From this derivation it is also possible to determine the mole fraction of monomer units since,

$$f_A = f_{AA} + f_{AB} \qquad \text{and} \tag{5.7}$$

$$f_B = f_{BA} + f_{BB} \tag{5.8}$$

Only five of the ten possible tetrads are large enough to be measurable by NMR, but the mole fraction of these tetrads can still be calculated because the tetrad signals all arise from the methylene protons and the normalization constant of these protons is the same as C_p the proportionality constant for the diads. Therefore the mole fractions of the various tetrads are obtained by dividing the area of the tetrad peak by the factor $X+\frac{5Y}{8}+\frac{Z}{4}$. Labelling the peaks in a typical copolymer spectrum in the X region from left to right as X_1, X_2, and X_3 and the peaks in the Y region from left to right as Y_1 and Y_2 the following results are obtained for the tetrads:

$$f_{AAAA} = \frac{X_1}{D} \qquad (5.9)$$

$$2f_{AAAB} = \frac{X_2}{D} \qquad (5.10)$$

$$f_{BAAB} = \frac{X_3}{D} \qquad (5.11)$$

$$2f_{AABA} = \frac{Y_1}{D} \qquad (5.12)$$

$$2f_{ABAB} = \frac{Y_2}{D} \qquad (5.13)$$

Where $D = X + \frac{5Y}{8} + \frac{Z}{4}$

The analysis of the VCl_2-VCl system spectra is more straightforward than that of the VCl_2-IB system. In the copolymer spectra in Figures 7 and 8 there are four main areas all arising from separate groups of protons. From the interpretation discussed previously the following relationships were obtained:

M = C [number of B units in polymer (α -hydrogens)] = Cx(B)

N = C [number of AA diads (methylene only)] = Cx(AA)

P = C [2 x number of AB diads (methylene only)] = Cx(2AB)

R = C [number of BB diads (methylene only)] = Cx(BB)

where A = VCl_2 unit, B = VCl unit, and C = constant of proportionality.

Equations (5.1), (5.2), and (5.3) are the equations for the mole (or number) fractions of the various diads and by substituting the above relations into these equations one obtains:

$$f_{AA} = \frac{N}{N + P + R} \tag{5.14}$$

$$2f_{AB} = \frac{P}{N + P + R} \tag{5.15}$$

$$f_{BB} = \frac{R}{N + P + R} \tag{5.16}$$

The mole fraction of vinyl chloride in the polymer is obtained from the spectrum by multiplying the area of the α-hydrogen peak by two and dividing this number by the total area of the methylene protons, i.e.,

$$f_B = \frac{2M}{N + P + R} \tag{5.17}$$

This procedure constitutes an independent check of the mole fractions in the copolymer and should correspond to the values obtained through (5.7) and (5.8).

Internal consistency indicates valid assignments of the spectra.

RESULTS AND DISCUSSION

Results for VCl_2-IB Copolymer System

From Price's matrix formulation (50) it is possible to derive equations for the mole fraction of the various diads in terms of the ratio of the monomer concentrations in the charge, F_o, and the reactivity ratios, r_1 and r_2, (where 1 refers to VCl_2 and 2 refers to IB) assuming that only the terminal unit affects the addition of the next monomer unit and constant monomer feed. The equations (shown below) are the same as those derived previously by Wall (45) but are in the nomenclature of Kinsinger and Colton (57).

$$f_{AA} = \frac{r_1 F_o^2}{r_1 F_o + 2F_o + r_2} \tag{6.1}$$

$$2f_{AB} = \frac{2F_o}{r_1 F_o + 2F_o + r_2} \tag{6.2}$$

$$f_{BB} = \frac{r_2}{r_1 F_o^2 + 2F_o + r_2} \tag{6.3}$$

Each of these equations can be rearranged in linear form so that values for r_1 and r_2 can be easily obtained(58). In the VCl_2-IB system only the first two equations are used because they correspond with the more accurate experimental measurements. Rearranging equation (6.1) one obtains;

$$2F_o = \frac{F_o^2(1-f_{AA})}{f_{AA}} \quad r_1 - r_2 \qquad (6.4)$$

By plotting $2F_o$ vs. $\frac{F_o^2(1 - f_{AA})}{f_{AA}}$ a straight line with a slope of r_1 and an intercept of $-r2$ is obtained. Rearranging equation (6.2) one obtains:

$$\frac{2F_o(1 - 2f_{AB})}{2f_{AB}} = F_o^2 r_1 + r_2 \qquad (6.5)$$

and by plotting the left hand side of (6.5) vs. F_o^2 a slope of r_1 and an intercept of r_2 are obtained.

The monomer reactivity ratios can also be calculated from mole fractions of monomers in the copolymer by applying the Ross-Fineman (48) equation (2.14) which is also restricted to the low conversion terminal effect mechanism.

Table IX lists the mole fractions of the various diads, the monomer charges, and the mole fraction of VCl_2 in the copolymer as determined by NMR, and the more common standard, carbon analysis and chlorine analysis. In addition to these results the experimental tetrad values are listed in Table X.

Plots of these methods for obtaining r_1 and r_2 from the diad and monomer mole fraction data for the terminal mechanism are displayed in Figures 9, 10, 11, and 12. Figure 9 represents the f_{AA} diad data; Figure 10 shows the $2f_{AB}$ data plotted according to (6.5); Figure 11 displays a Ross-Fineman (48) plot of the mole fraction data of the monomers in the polymer from NMR and the carbon analysis of the copolymers; Figure 12 is another Ross-Fineman plot for the mole fractions obtained from chlorine analysis of the copolymers.

Table IX. Mole fractions of diads

Sample	MF_{VCl_2}	MF_{IB}	Mf_{VCl_2} Carbon	Mf_{VCl_2} Cl	Mf_{VCl_2} NMR	f_{AA}	$2f_{AB}$	f_{BB}
VI-32-2	0.584	0.416	-----	-----	0.83	0.68	0.29	0.03
VI-24-2	0.505	0.495	0.845	0.738	0.80	0.61	0.36	0.03
VI-12-1	0.471	0.529	0.794	0.765	0.79	0.59	0.38	0.02
VI-22-2	0.418	0.582	0.769	0.752	0.76	0.55	0.43	0.03
VI-28-2	0.391	0.609	0.757	0.727	0.74	0.51	0.46	0.03
VI-30-2	0.353	0.647	-----	-----	0.72	0.48	0.49	0.04
VI-20-1	0.318	0.682	0.718	0.706	0.71	0.45	0.52	0.04
VI-23-1	0.317	0.683	0.715	0.691	0.71	0.44	0.52	0.04
VI-26-2	0.288	0.712	0.712	0.678	0.70	0.42	0.54	0.04
VI-17-2	0.247	0.753	0.681	0.659	0.67	0.38	0.58	0.04
VI-20-2	0.225	0.775	0.681	0.651	0.66	0.36	0.60	0.04
VI-25-1	0.213	0.787	0.686	0.678	0.65	0.34	0.62	0.04
VI-25-2	0.206	0.794	0.681	0.663	0.64	0.33	0.63	0.04
VI-26-1	0.198	0.802	0.635	0.530	0.64	0.32	0.64	0.05
VI-18-2	0.159	0.841	0.632	0.623	0.61	0.29	0.65	0.06
VI-16-2	0.130	0.870	0.589	0.585	0.59	0.25	0.67	0.08
VI-29-1	0.126	0.874	0.577	0.580	0.58	0.24	0.66	0.10
VI-34-1	0.121	0.879	0.587	0.587	0.58	0.23	0.66	0.10
VI-19-2	0.083	0.917	0.581	0.572	0.52	0.19	0.64	0.17

Table X. Mole fraction of tetrads

Sample	f_{AAAA}	f_{AAAB}	f_{BAAB}	f_{AABA}	f_{ABAB}
VI-32-2	0.41	0.22	0.04	0.23	0.06
VI-24-2	0.32	0.24	0.05	0.31	0.06
VI-12-1	0.28	0.26	0.05	0.31	0.07
VI-22-2	0.23	0.25	0.05	0.33	0.10
VI-28-2	0.21	0.24	0.06	0.37	0.10
VI-30-2	0.18	0.23	0.06	0.38	0.10
VI-20-1	0.17	0.22	0.06	0.39	0.12
VI-23-1	0.17	0.22	0.07	0.38	0.13
VI-26-2	0.11	0.22	0.09	0.38	0.15
VI-17-2	0.08	0.18	0.11	0.38	0.18
VI-20-2	0.07	0.18	0.11	0.38	0.21
VI-25-1	0.06	0.17	0.12	0.38	0.21
VI-25-2	0.05	0.16	0.12	0.38	0.22
VI-26-1	0.04	0.15	0.12	0.36	0.24
VI-18-2	0.03	0.13	0.13	0.34	0.28
VI-16-2	0.02	0.11	0.12	0.29	0.35
VI-29-1	0.02	0.11	0.12	0.29	0.35
VI-34-1	0.01	0.09	0.12	0.27	0.36
VI-19-2	0.01	0.07	0.11	0.27	0.37

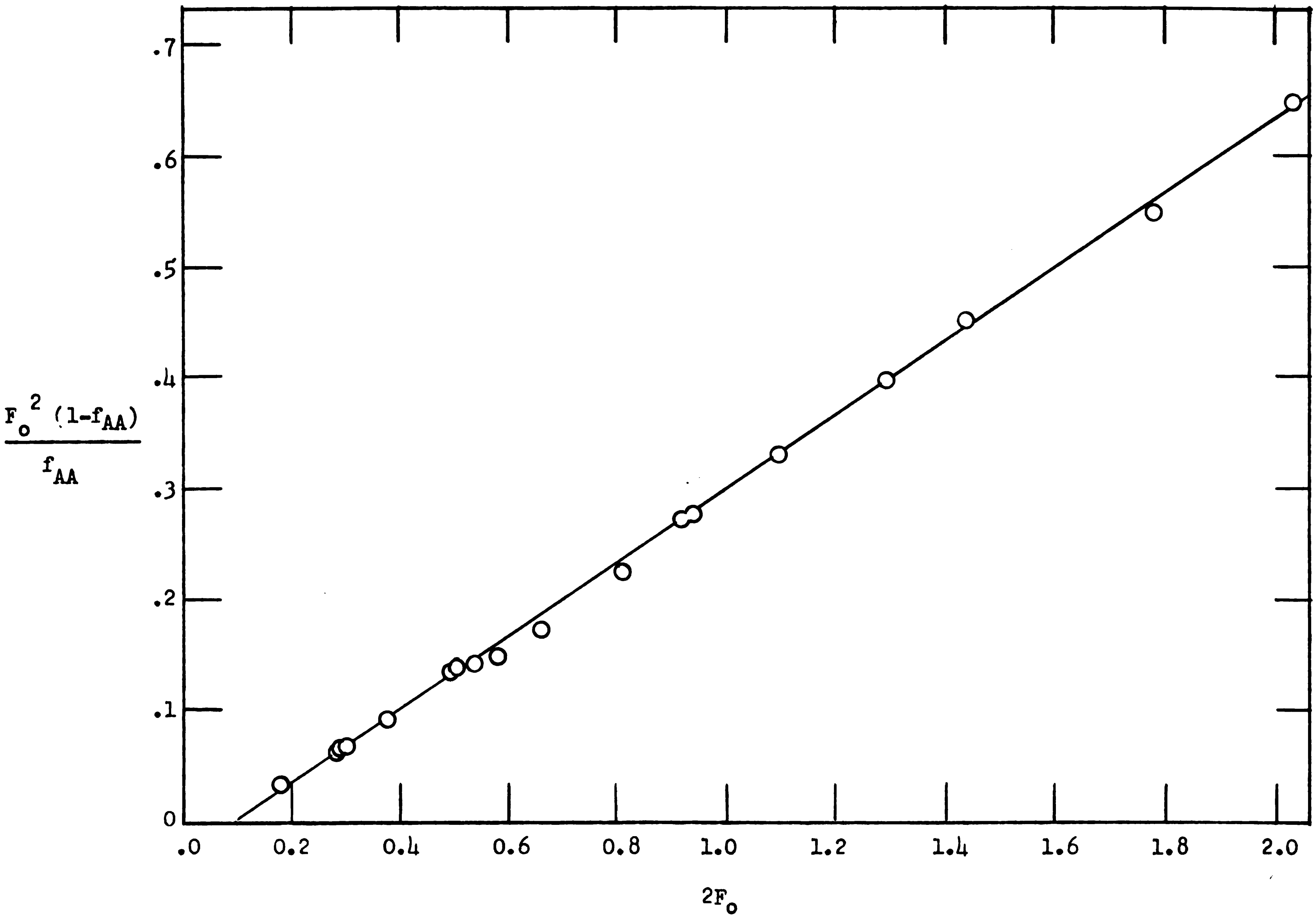


Fig. 9. Linear plot of the relationship $2F_o = F_o^2(1-f_{AA})r_1/f_{AA}-r_2$ where f_{AA} = mole fraction of AA diads

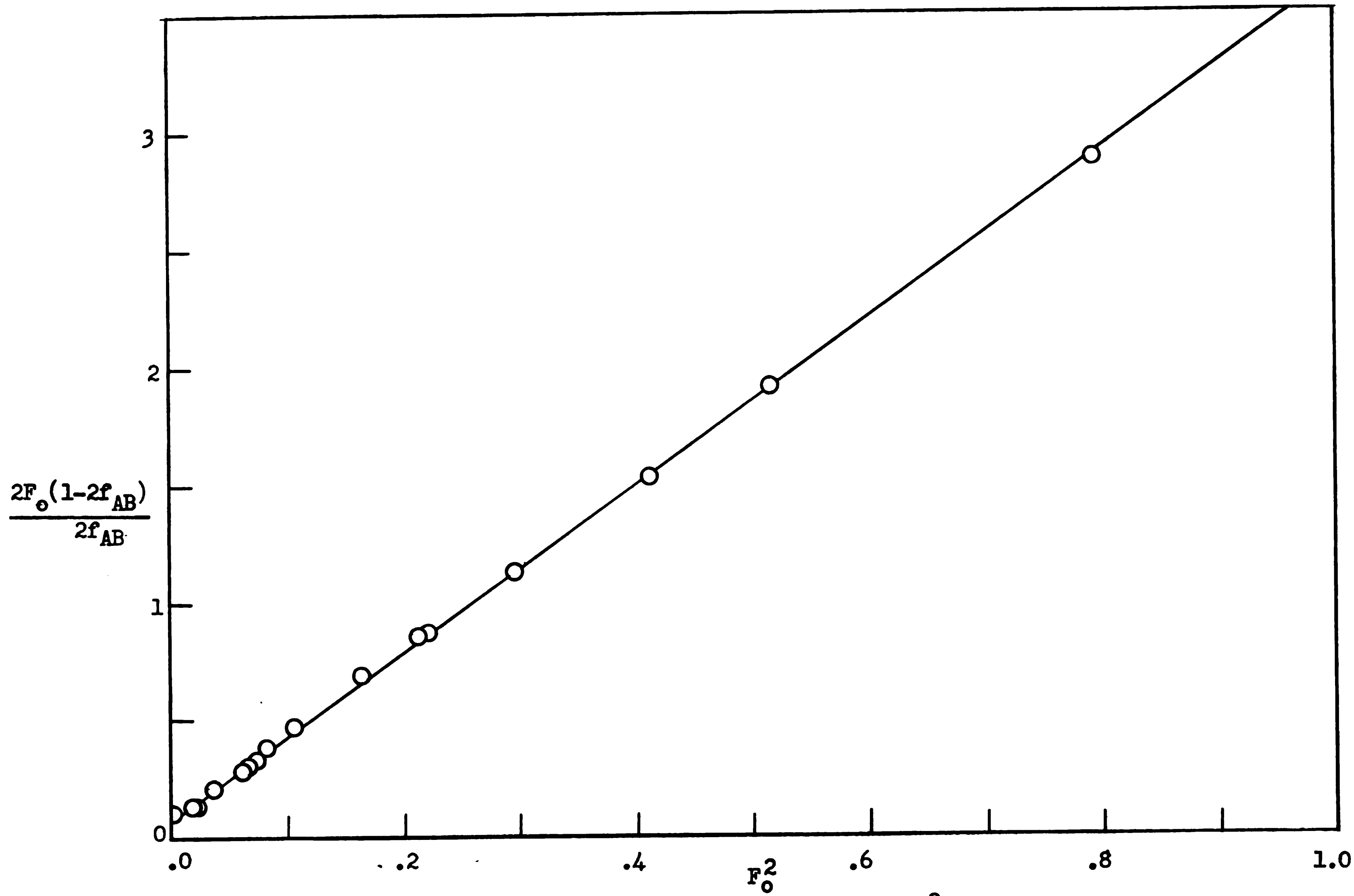


Fig. 10. Linear plot of the relationship $2F_o(1-2f_{AB})/2f_{AB} = F_o^2 r_1 + r_2$ where f_{AB} = mole fraction of AB diads

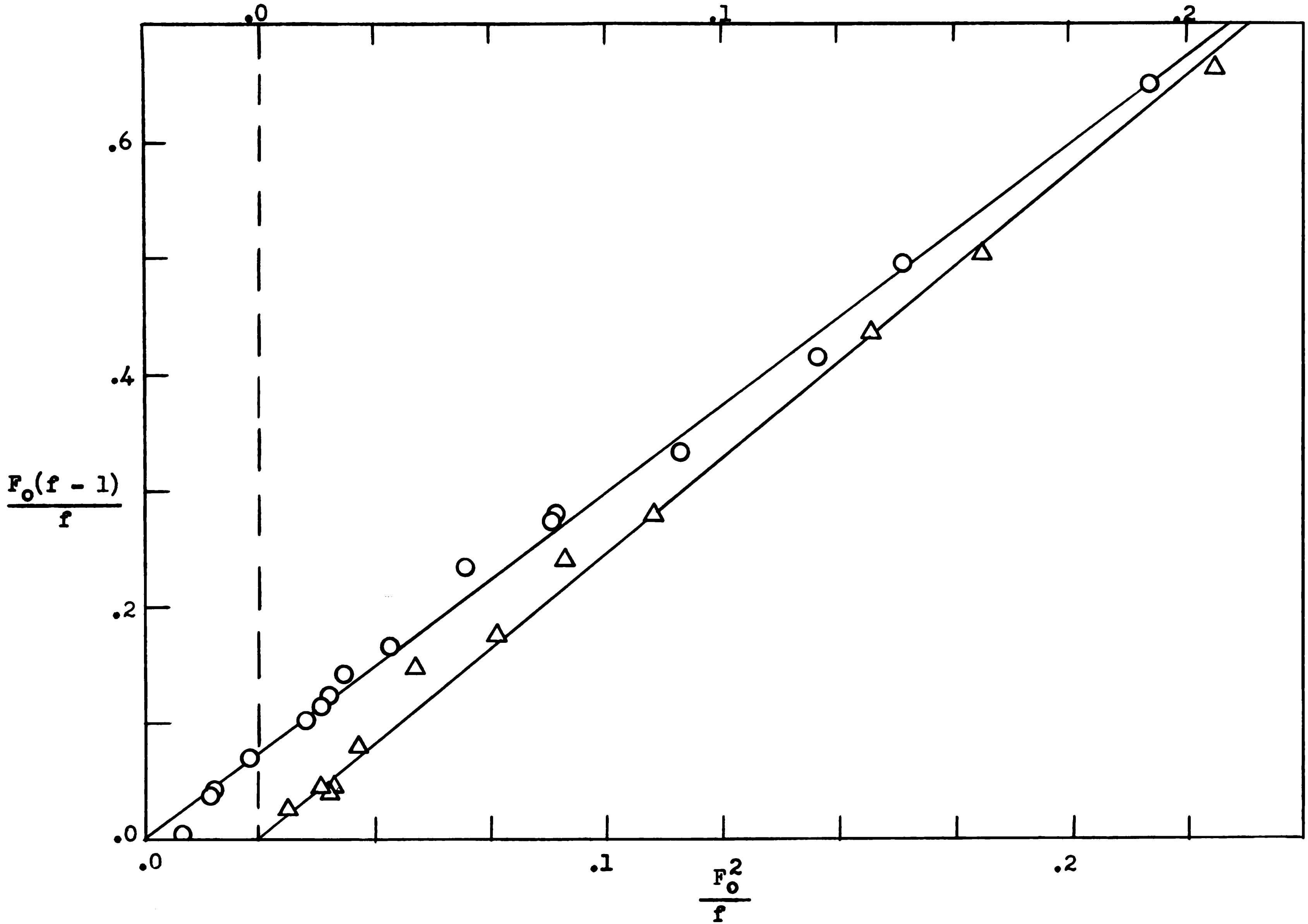


Fig. 11. Linear plot of the Ross-Fineman relationship, $F_o(f-1)/f = r_1F_o^2/f - r_2$ where F_o = mole ratio of monomers in the feed and f = mole ratio of monomers in the copolymer: (○) represent NMR data; (△) represent carbon analysis data on an x axis shifted for clarity.

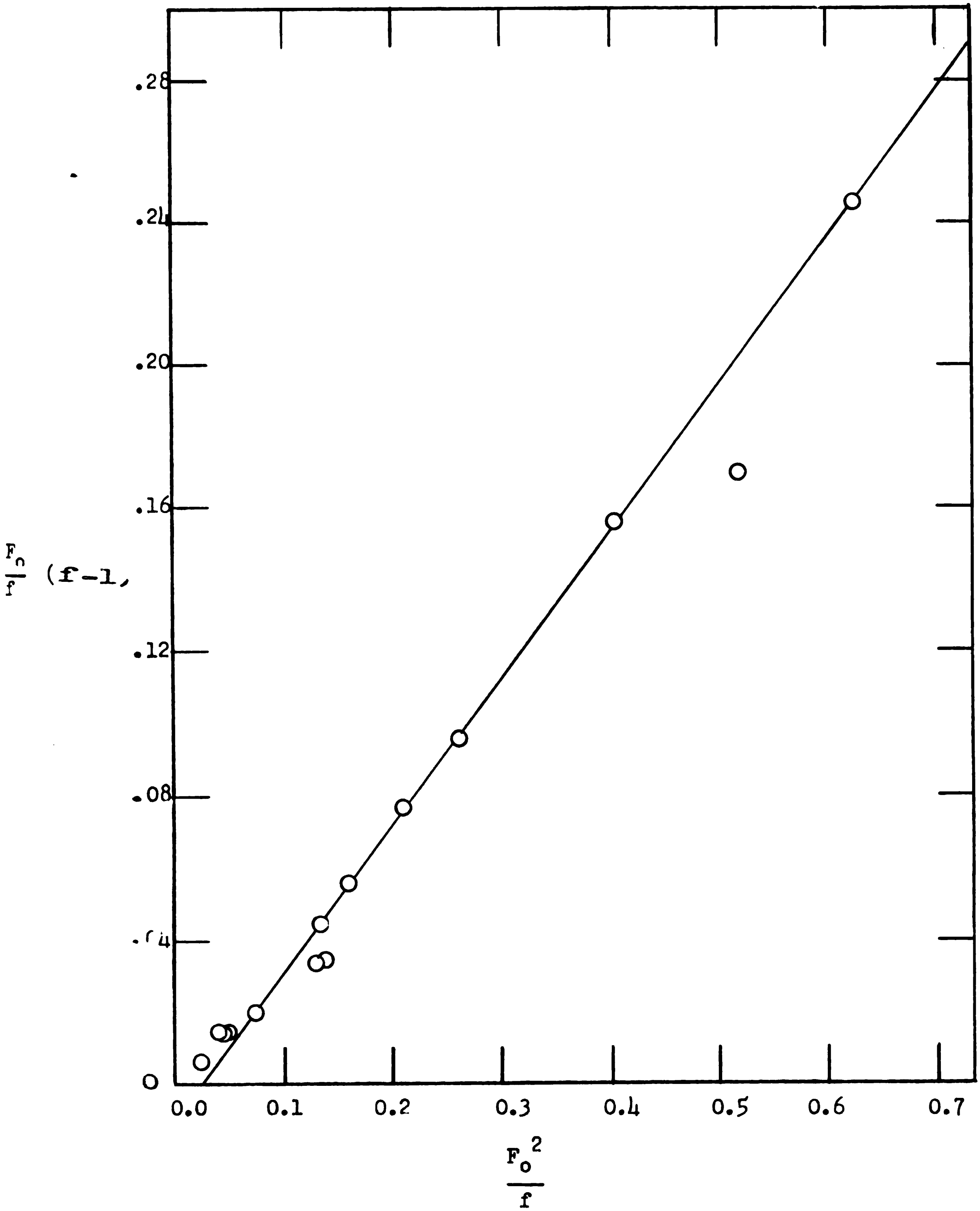


Fig. 12. Same coordinates as Fig. 11. Experimental data is from chlorine analysis of the copolymer.

The results for r_1 and r_2 from these plots are listed in Table XI. The r_2 values obtained from the experimental data are small and in some cases have negative values, however, this is not an unusual occurrence when small values of r_1 or r_2 (less than 0.1) are determined by normal copolymer analysis. For such cases the "r" value is usually listed as zero but a least squares analysis of the data in the present work show the negative value for r_2 to be significant. With an average value of $r_1 = 3.3$ and r_2 chosen to be 0.05 a plot of the mole fractions of the three diads vs. the mole fraction of VCl_2 in the monomer charge was constructed and is depicted in Figure 13. The correlation between the theoretical curves using these values for r_1 and r_2 and the experimental values is good, however, some deviation is noted particularly at low concentration of VCl_2 in the monomer charge. Small changes consistent with the scatter in the results for r_1 and r_2 did not improve the fit with experimental data.

Since the experimental tetrad values were available for the first time the method for calculating the mole fractions of the tetrads had to be derived.

The equations for calculating the mole fractions of the various tetrads for a terminal mechanism can be calculated as outlined from the theory in Chapter 2 by multiplying the mole fractions of the appropriate diad by the corresponding conditional probabilities for obtaining the desired tetrad, e.g.

$$f_{AAAA} = f_{AA} \times P_{AA} \times P_{AA} = f_{AA} \times (P_{AA})^2 \qquad (6.6)$$

Since only five of the tetrads were large enough to be measured experimentally equations were derived for these five and are listed below:

Table XI Copolymerization reactivity ratios from various data for vinylidene chloride (1) - isobutylene (2) system

Method	r1	$\sigma_1^{\dagger}$	r2	σ_2
1. Carbon analysis Ross-Fineman Plot	3.240	0.155	-0.007	0.009
2. Chlorine analysis Ross-Fineman Plot	2.520	0.082	-0.030	0.007
3. f_{VCl_2} from NMR Ross-Fineman Plot	2.999	0.057	0.000	0.001
4. *f_{AA} from NMR $2F_o$ vs $\frac{F_o^2(1 - f_{AA})}{f_{AA}}$	3.062	0.081	-0.098	0.014
5. *f_{AA} from NMR $F_o \frac{(1 - f_{AA})}{f_{AA}}$ vs $\frac{1}{F_o}$	3.145	-----	-0.079	-----
6. $2f_{AB}$ from NMR $\frac{2F_o(1 - 2f_{AB})}{2f_{AB}}$ vs F_o^2	3.470	0.020	0.088	0.006

*4 and 5 represent only two different ways of plotting the same data.

† = STANDARD DEVIATION

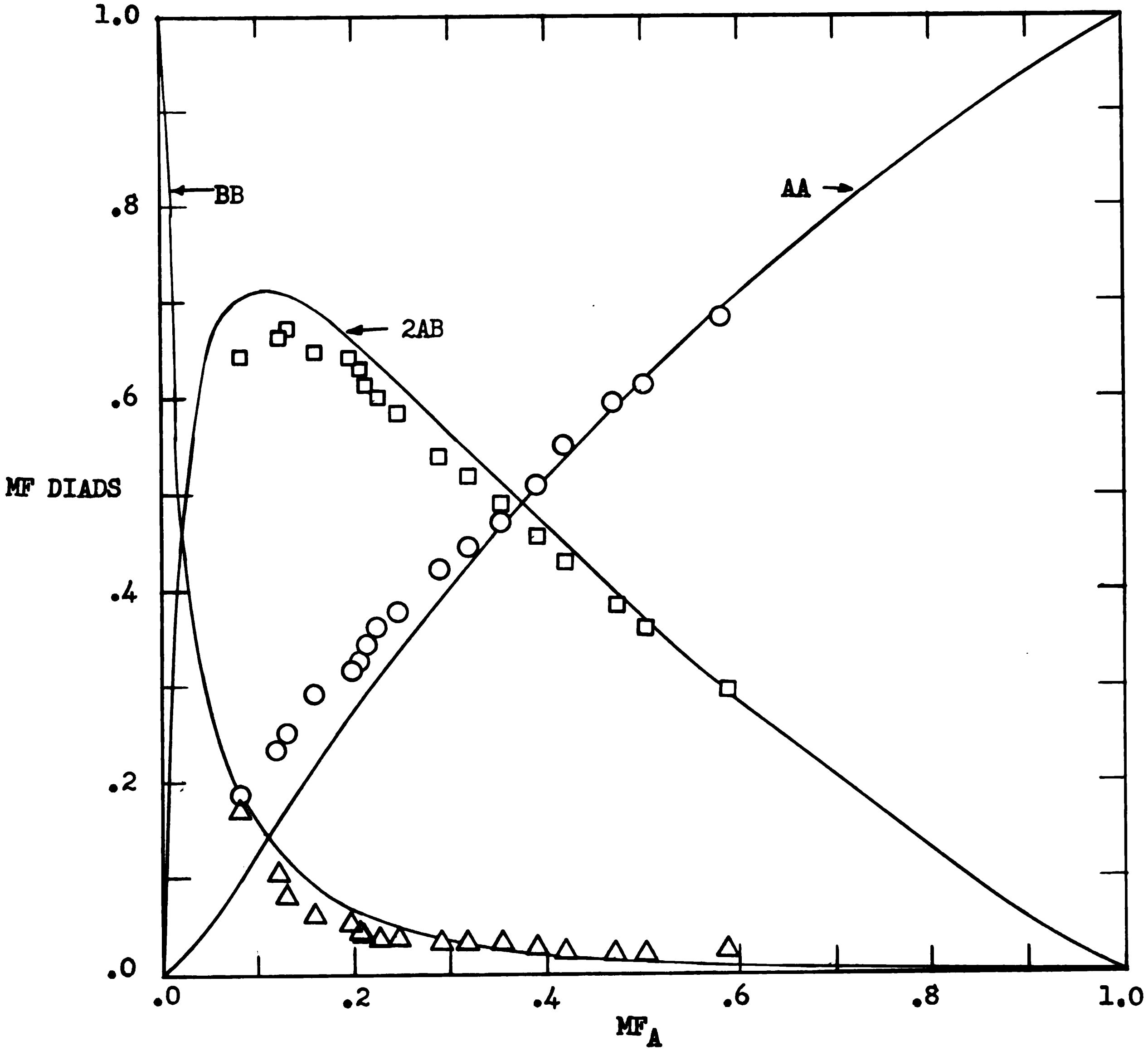


Fig. 13. Mole fraction of diads versus mole fraction of vinylidene chloride in monomer feed; (○) f_{AA}; (□) $2f_{AB}$; (△) f_{BB}. Solid lines terminal mechanism $r_1 = 3.30$, $r_2 = 0.05$.

$$f_{AAAA} = f_{AA} \times (P_{AA})^2 \tag{6.7}$$

$$2f_{AAAB} = 2f_{AB} \times (P_{AA})^2 \tag{6.8}$$

$$f_{BAAB} = f_{AB} \times P_{AA} \times P_{AB} \tag{6.9}$$

$$2f_{AABA} = 2f_{AB} \times P_{BA} \times P_{AA} \tag{6.10}$$

$$2f_{ABAB} = 2f_{AB} \times P_{BA} \times P_{AB} \tag{6.11}$$

Substituting the various expressions for the probabilities in the case of the terminal mechanism as derived from Price's paper one obtains:

$$f_{AAAA} = f_{AA} \times \left(\frac{r_1F_o}{r_1F_o + 1}\right)^2 \tag{6.12}$$

$$2f_{AAAB} = 2f_{AB} \times \left(\frac{r_1F_o}{r_1F_o + 1}\right)^2 \tag{6.13}$$

$$f_{BAAB} = \frac{2f_{AB}}{2} \times \left(\frac{r_1F_o}{r_1F_o + 1}\right) \times \left(\frac{1}{r_1F_o + 1}\right) \tag{6.14}$$

$$2f_{AABA} = 2f_{AB} \times \left(\frac{F_o}{r_2 + F_o}\right) \times \left(\frac{r_1F_o}{r_1F_o + 1}\right) \tag{6.15}$$

$$2f_{ABAB} = 2f_{AB} \times \left(\frac{F_o}{r_2 + F_o}\right) \times \left(\frac{1}{r_1F_o + 1}\right) \tag{6.16}$$

The calculated values for the tetrads employing the above equations with the same r values as used previously were plotted against the mole fraction of VCl_2 in the charge and compared with the experimental values. Figures 14 and 15 depict these plots. The agreement between the experimental and calculated values is reasonable in Figure 14 but these three tetrads are less dependent on small changes in r values than are the two

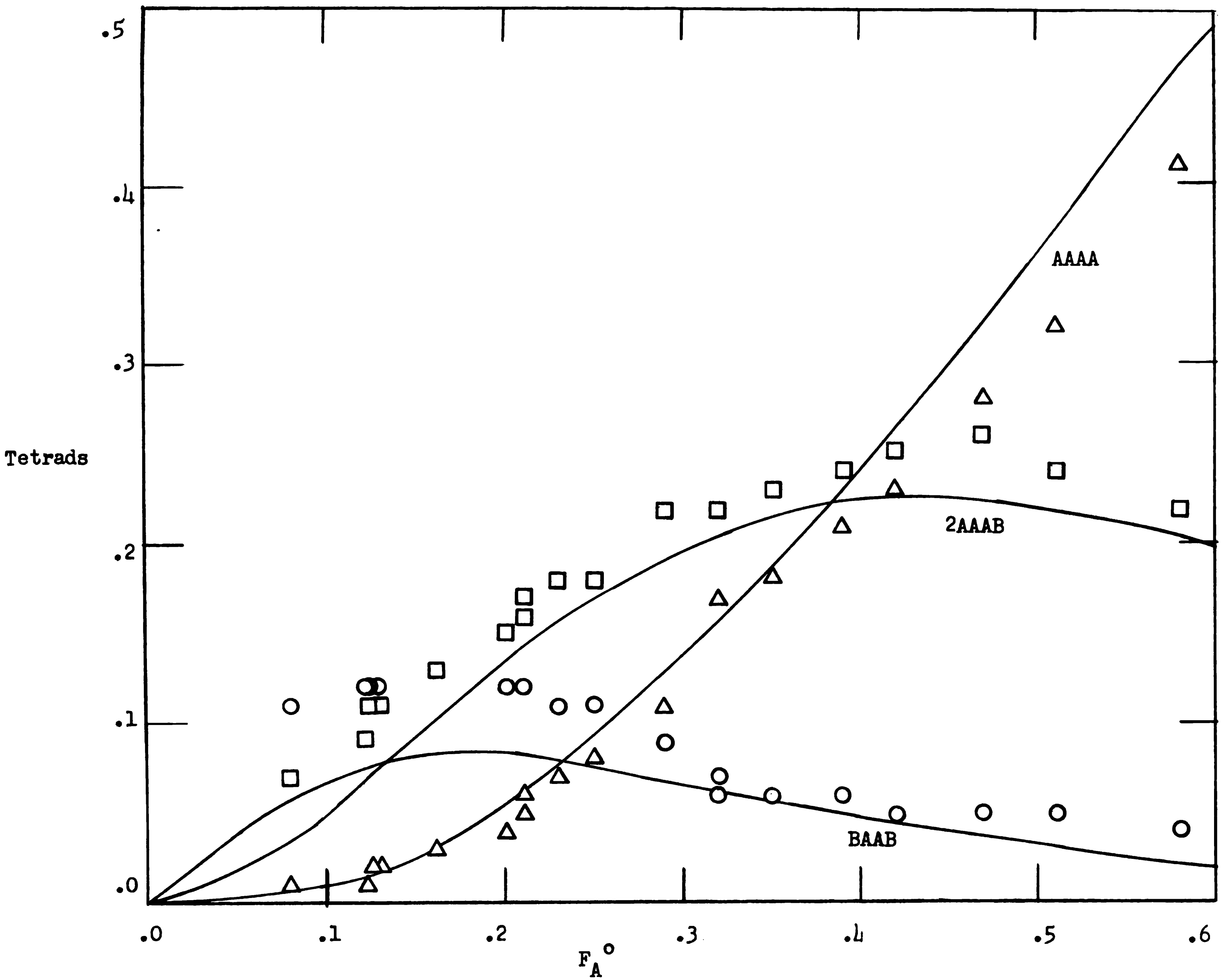


Fig. 14. Mole fraction of tetrads versus mole fraction of vinylidene chloride in monomer mix: (△)f_{AAAA}; (□)$2f_{AAAB}$; (○)f_{BAAB}. Solid lines terminal mechanism $r_1 = 3.30$, $r_2 = 0.05$.

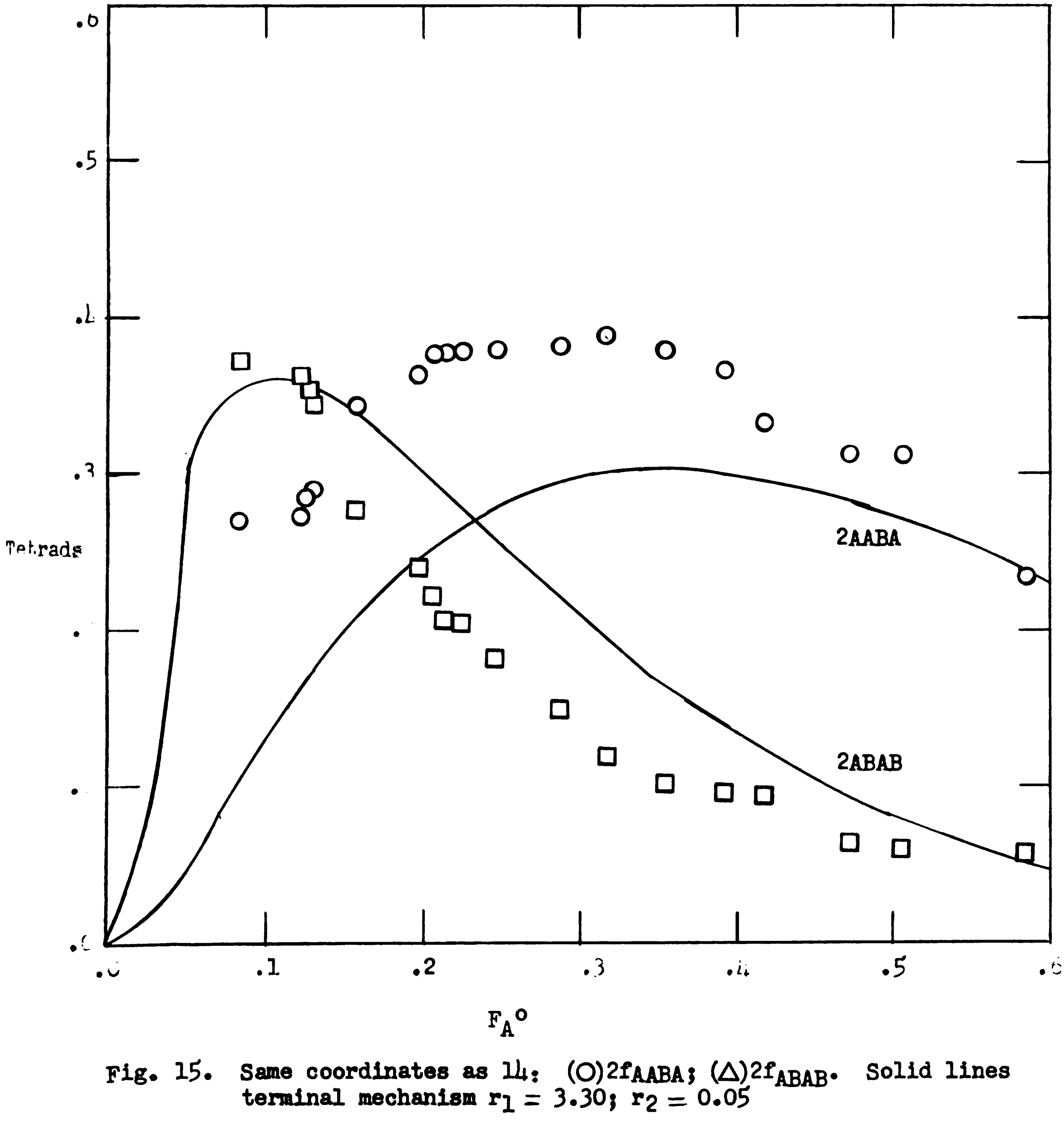


Fig. 15. Same coordinates as 14: (O)$2f_{AABA}$; (△)$2f_{ABAB}$. Solid lines terminal mechanism $r_1 = 3.30$; $r_2 = 0.05$

tetrads plotted in Figure 15 where correlation between the experimental and calculated values is poor. Since the r values used were averages of several values other r values within reason were tried but there was no improvement in correlation between the experimental and calculated values for the tetrads.

The small divergence between calculated and experimental diads and the larger divergence of the tetrads is the trend predicted by Berger and Kuntz (51) in their paper on the distinction between terminal and penultimate mechanisms when the assumed copolymerization mechanism is not the correct one. They point out the need to know the distribution of more than just the monomers and diads in the copolymer in order to distinguish between the two mechanisms. Before the present work no accurate work was presented which permitted the determination of the mole fraction of sequences of higher order than diads.

Based on this evidence the assumption that the terminal mechanism is the correct mechanism for this copolymer system does not appear a valid assumption.

Since the terminal mechanism appears invalid another mechanism must be offered to explain the microstructure of this copolymer system. The second simplest copolymerization mechanism is the penultimate unit mechanism and this mechanism was tested next.

When the penultimate unit mechanism is assumed the equations for the diads become more complex since additional parameters are introduced. The equations for the mole fractions of the various diads for the penultimate mechanism were derived from the procedure outlined in Price's paper (50). The results are listed below:

$$f_{AA} = \frac{\alpha}{\alpha + 2\beta + \gamma} \tag{6.17}$$

$$2f_{AB} = \frac{2\beta}{\alpha + 2\beta + \gamma} \tag{6.18}$$

$$f_{BB} \quad \frac{\gamma}{\alpha + 2\beta + \gamma} \tag{6.19}$$

Where $\alpha = \dfrac{r_1{}'F_o{}^2}{r_1{}'F_o{}^2 + r_1r_2F_o + F_o + r_2}$

$$2\beta = \frac{2F_o}{r_1F_o{}^2 + r_1r_2F_o + F_o + r_2}$$

$$\gamma = \frac{r_2{}'}{r_1F_o{}^2 + r_1r_2{}'F_o + F_o + r_2{}'}$$

and $r_1 = \dfrac{k_{AAA}}{k_{AAB}}$, $r_1{}' = \dfrac{k_{BAA}}{k_{BAB}}$, $r_2 = \dfrac{k_{BBB}}{k_{BBA}}$, and $r_2{}' = \dfrac{k_{ABB}}{k_{ABA}}$.

Note that the penultimate case requires four independent parameters whereas the diads give just two independent pieces of data. Because these equations for the mole fraction of the diads are of a quadratic form in F_o, no linear plot could be derived to determine the various r values. However, by deriving the equations for the mole fractions of the five measureable tetrads and applying simple algebra it was possible to determine the various r values.

The equations for the tetrad mole fractions are derived in a manner similar to those of the terminal case and are listed below:

$$f_{AAAA} = f_{AA} \times \left(\frac{r_1F_o}{r_1F_o + 1}\right)^2 \tag{6.20}$$

$$2f_{AAAB} = 2f_{AB} \times \left(\frac{r_1F_o}{r_1F_o + 1}\right) \times \left(\frac{r_1'F_o}{r_1'F_o + 1}\right) \qquad (6.21)$$

$$f_{BAAB} = f_{AB} \times \left(\frac{r_1'F_o}{r_1'F_o + 1}\right) \times \left(\frac{1}{1 + r_1F_o}\right) \qquad (6.22)$$

$$2f_{AABA} = 2f_{AB} \times \left(\frac{r_1'F_o}{r_1'F_o + 1}\right) \times \left(\frac{F_o}{F_o + r_2'}\right) \qquad (6.23)$$

$$2f_{ABAB} = 2f_{AB} \times \left(\frac{F_o}{F_o + r_2'}\right) \times \left(\frac{1}{1 + r_1'F_o}\right) \qquad (6.24)$$

The ratio of f_{AAAB}/f_{BAAB} gives r_1F_o (59). By plotting this ratio versus F_o, r_1 is obtained from the slope. In a similar manner the ratio of f_{AABA}/f_{ABAB} gives $r_1'F_o$ and from the slope of a similar plot r_1' is obtained. The parameter r_2' can be obtained through the ratio (R) of f_{AB}/f_{AABA}. A linear plot of $(R - 1)F_o^2$ versus F_o gives an independent value for r_1' and r_2'. Finally r_2 is obtained by substituting the other parameters into a diad formula and calculating r_2 for the series of F_o's. An average r_2 over the complete set of data was then calculated. Figures 16 through 18 depict these various plots. The values obtained from these ratios and plots were: $r_1 = 2.95$, $r_1' = 6.22$, $r_2 = 0.15$, and $r_2' = 0.02$.

These values were employed to calculate the various diads and tetrads. The calculated and experimental diad and tetrad values versus MF_{VCl_2} are displayed in Figures 19, 20, and 21. The agreement between the experimental and calculated values is excellent in all three figures.

Figure 15 shows that the experimental values for the ABAB sequences were lower than those calculated using the reactivity ratio values derived from the terminal mechanism. A possible explanation for this discrepancy

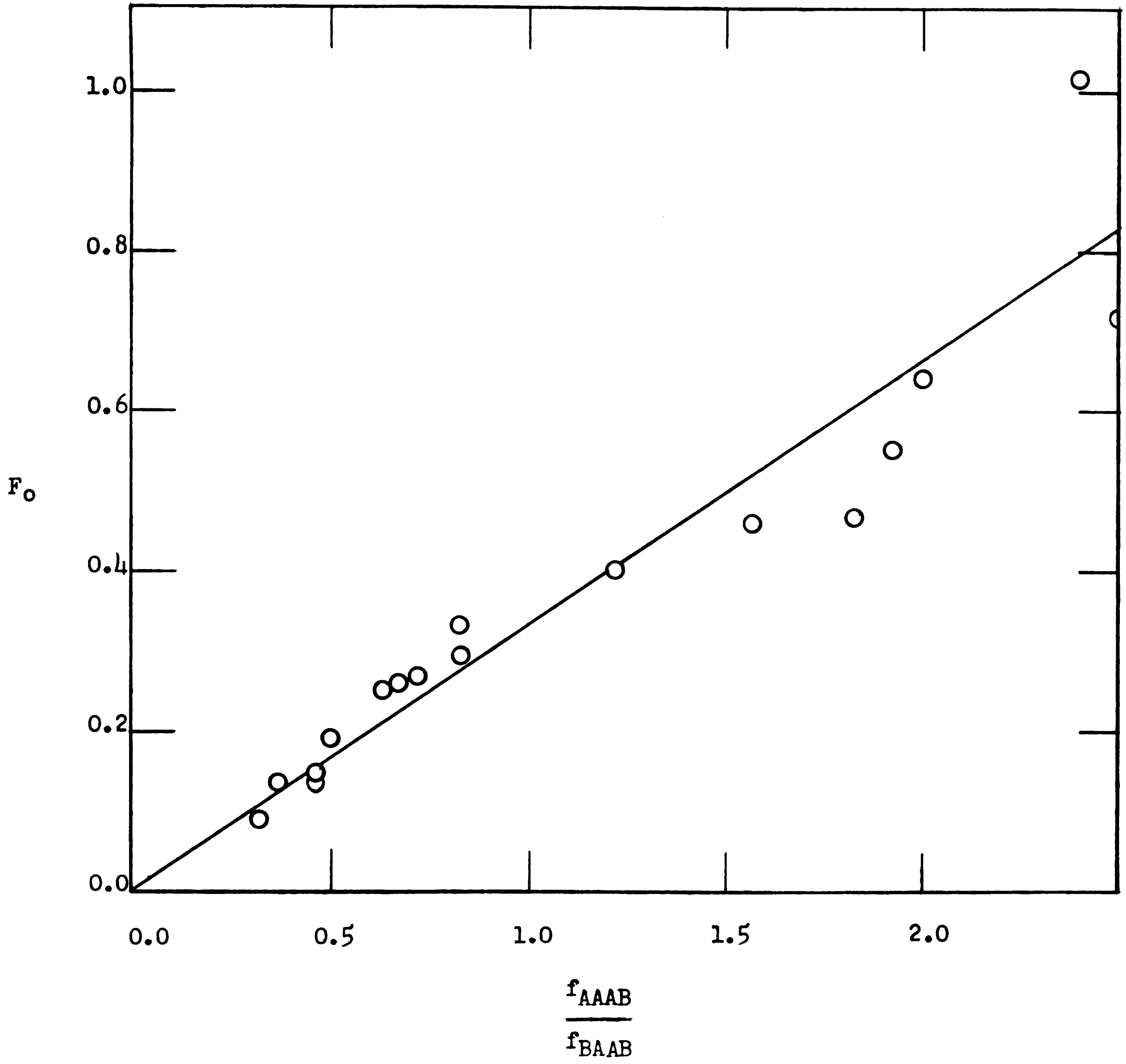


Fig. 16. Ratio of f_{AAAB}/f_{BAAB} versus F_o. Slope equals r_1 for penultimate mechanism.

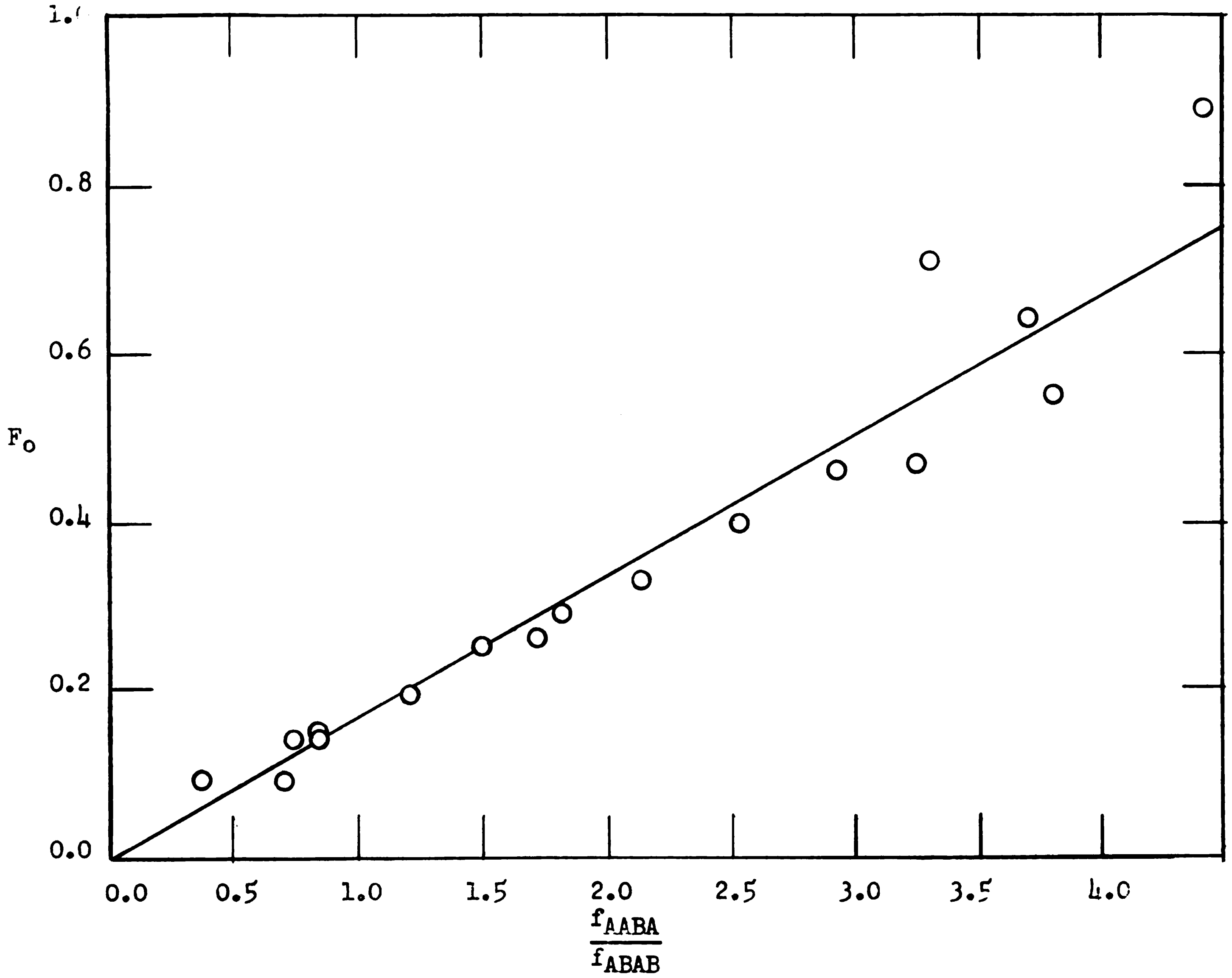


Fig. 17. Ratio of f_{AABA}/f_{ABAB} versus F_o. Slope equals r_1' for penultimate mechanism.

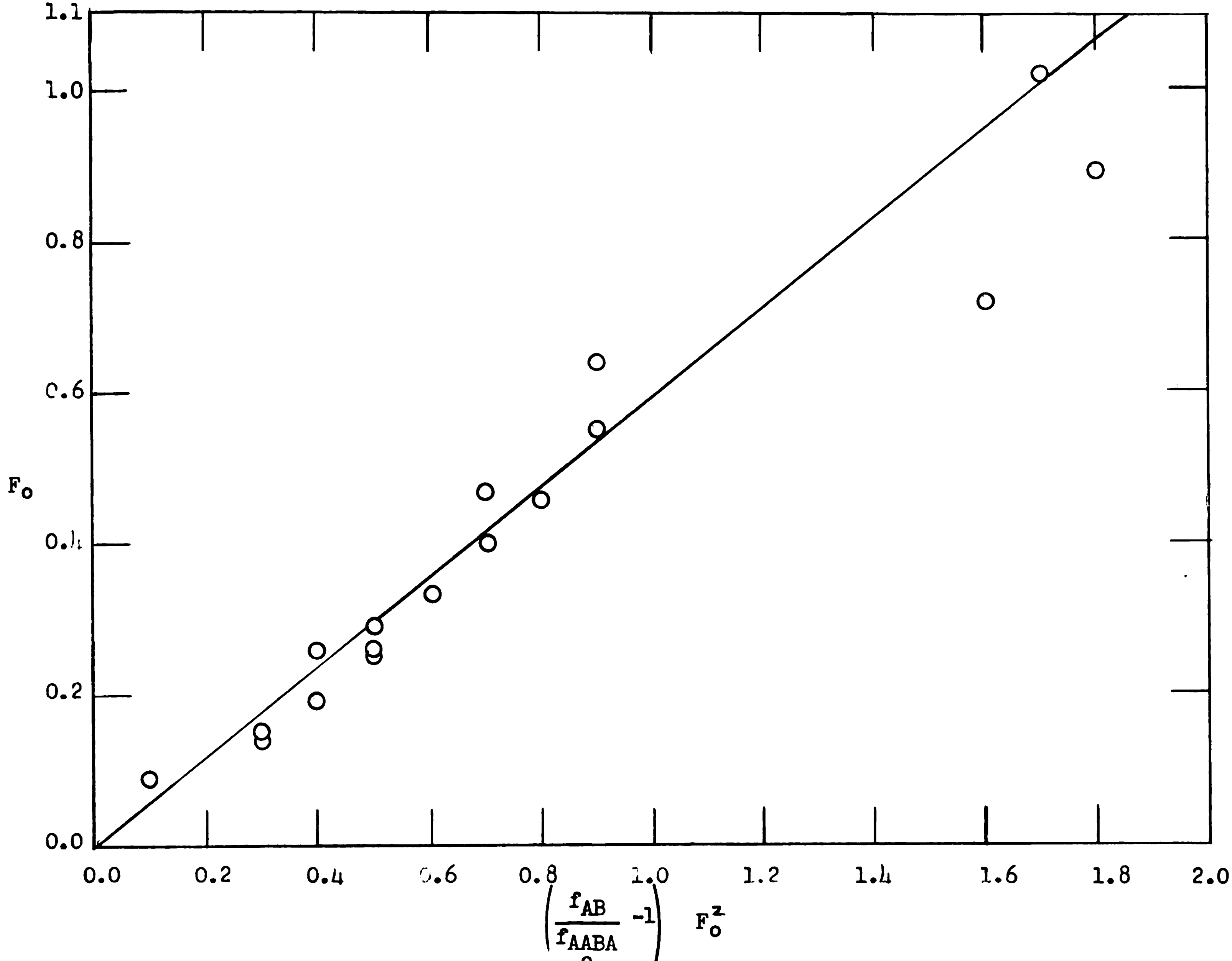


Fig. 18. A linear plot of $(f_{AB}/f_{AABA}-1)F_o^2$ versus F_o. The value of r_2' for the penultimate mechanism is determined from this relationship.

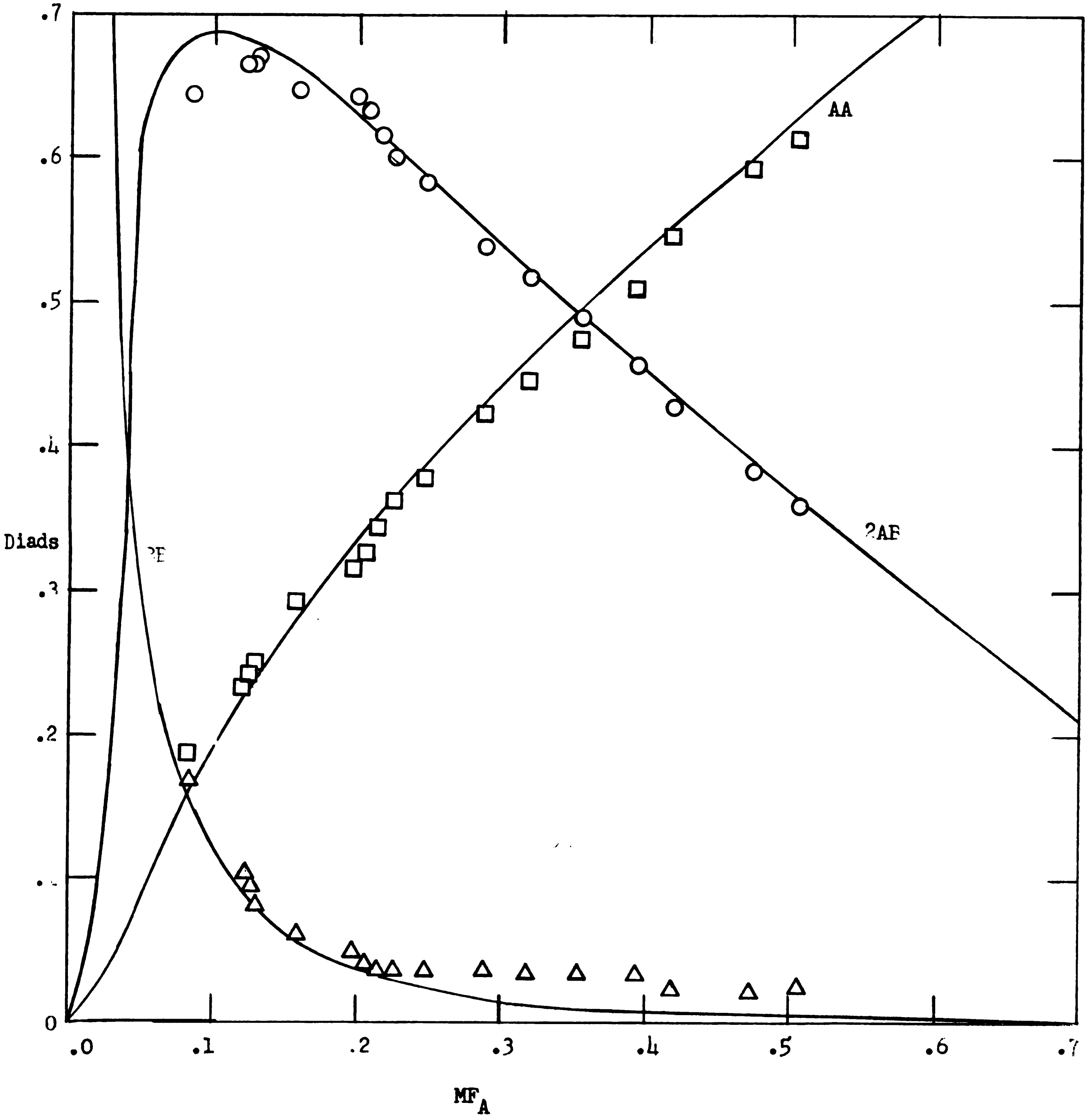


Fig. 19. Same coordinates as Fig. 13; (□)f_{AA}; (○)$2f_{AB}$; (△)f_{BB}. Solid lines penultimate mechanism $r_1 = 2.95$; $r_1' = 6.22$; $r_2 = 0.15$; $r_2' = 0.02$.

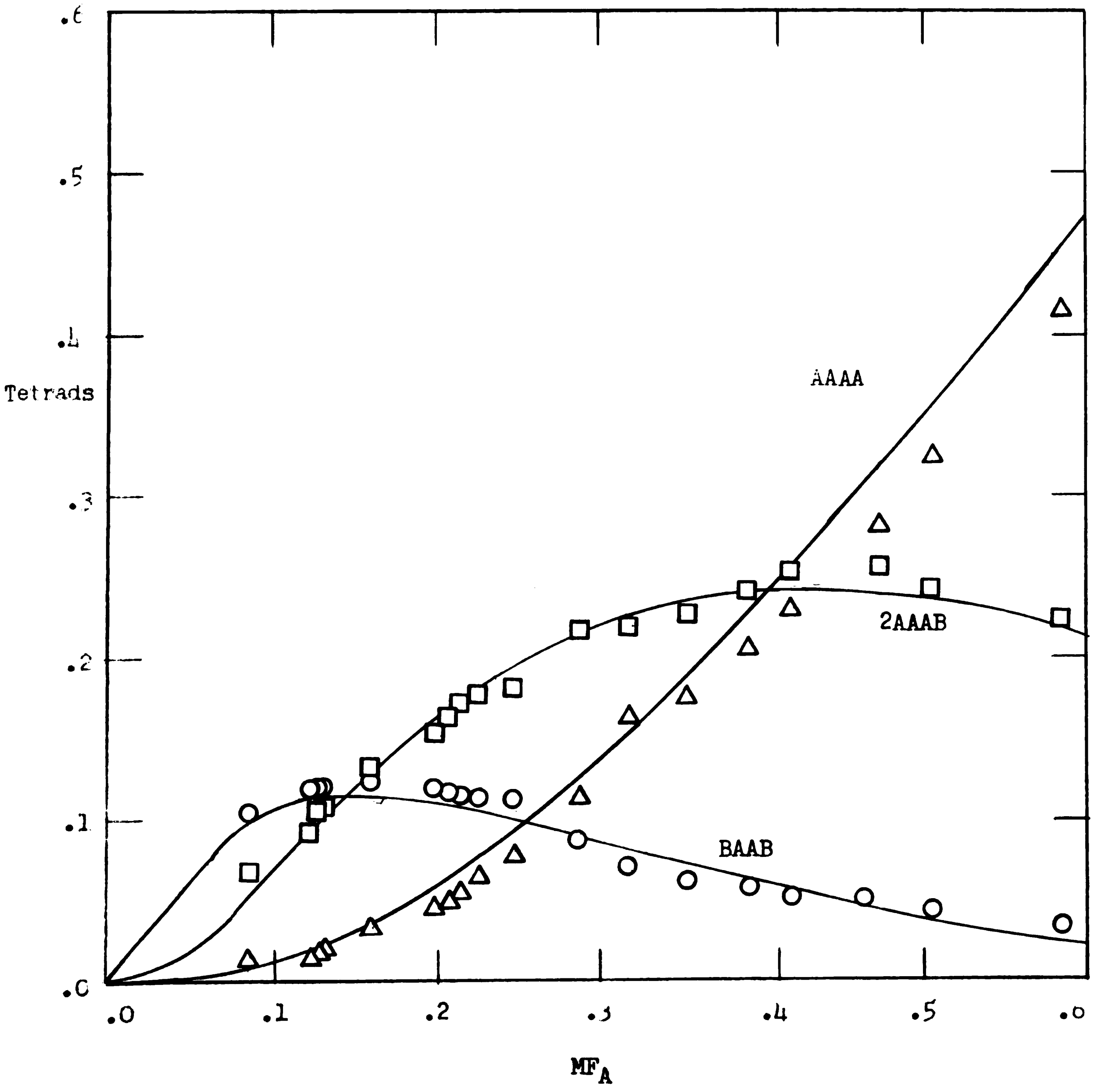


Fig. 20. Same coordinates as 14: (△)f_{AAAA}; (□)$2f_{AAAB}$; (○)f_{BAAB}. Solid lines penultimate mechanism $r_1 = 2.95$; $r_1' = 6.22$; $r_2' = 0.02.$; $r_2 = 0.15$

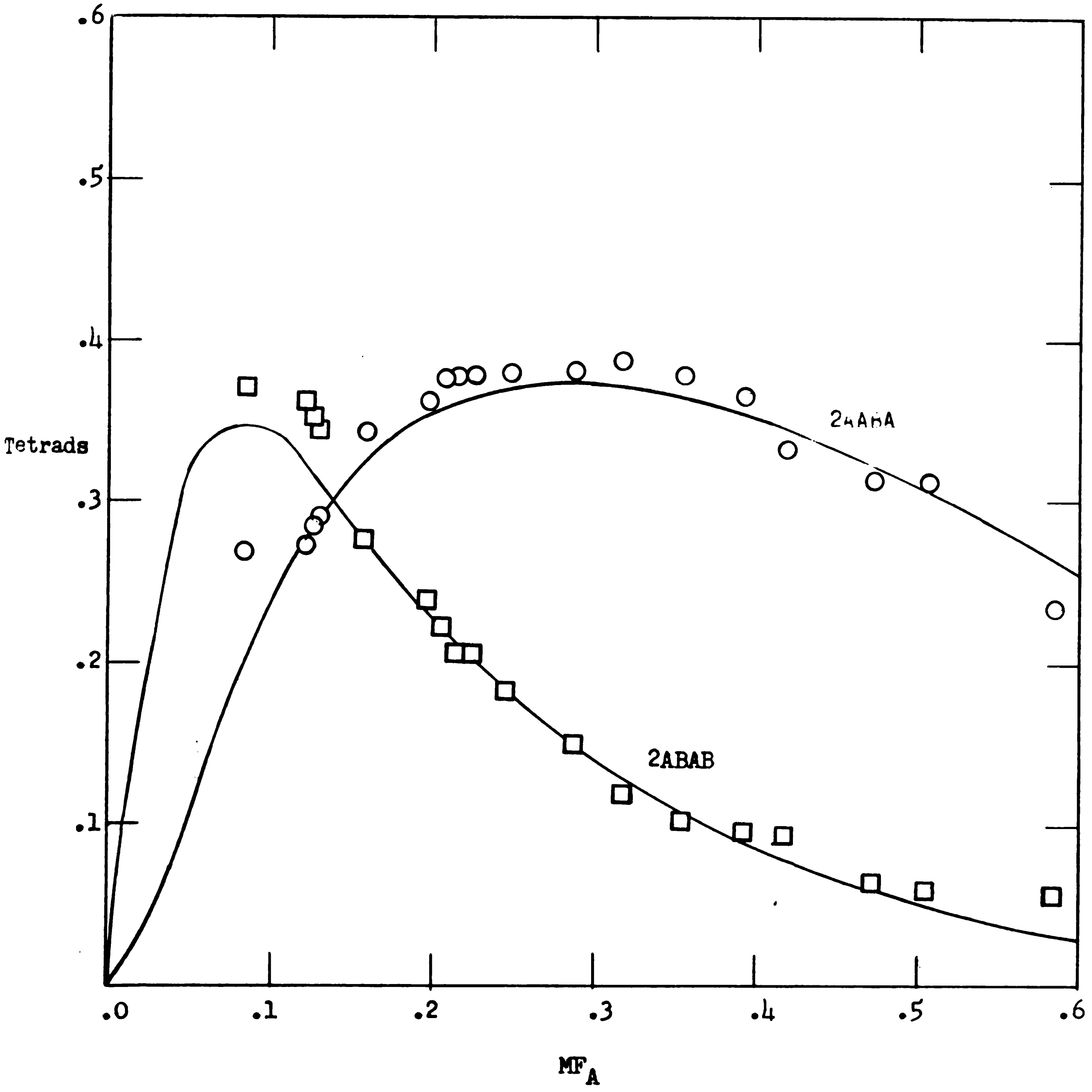


Fig. 21. Same coordinates as 14: (○)$2f_{AABA}$; (□)$2f_{ABAB}$. Solid lines penultimate mechanism $r_1 = 2.95$; $r_1' = 6.22$; $r_2 = 0.15$; $r_2' = 0.02$.

is shown by the reactivity ratios calculated assuming the penultimate mechanism. The values of r_2 and r_2' are close to the r_2 values of the terminal mechanism and the r_1 value is close to the r_1 value of the terminal mechanism. However, the r_1' value is almost twice as large as r_1. The value r_1' is a ratio of $\frac{k_{BAA}}{k_{BAB}}$ and since this value is greater than r_1 it seems to indicate that placing an IB unit next to a terminal VCl_2 unit enhances the addition of another VCl_2 unit to a greater degree than placing a VCl_2 next to a terminal VCl_2. This would result in fewer BABA sequences than predicted by the terminal mechanism.

In Summary

The study has presented a new set of linear equations for the mole fraction of diads in terms of monomer feed ratios. From these equations values for r_1 and r_2 can be determined from diad sequences which are independent of the mole fraction of mers in the chain.

The choice of vinylidene chloride and isobutylene as monomers for the copolymerization was based strictly on the favorable symmetrical geometry and the simplicity of the proton enviroments in the monomers and homopolymers. The chemical shifts of the methylene proton resonances in the two homopolymers were sufficiently spread to lead to a well defined and resolvable series of peaks in the copolymer spectrum. Although a total analysis of the spectrum was not completed the assignments and subsequent calculations of the r_1 and r_2 values as determined from the chemical analysis and the diad NMR analysis correspond and are ample evidence that these assignments are correct. Further proof of the validity of these assignments can be found in a recent publication by Hellwege and co-workers (60) who independently studied this copolymer system and are in complete agreement with the interpretation presented in this work. Innumerable earlier attempts to assign these peaks and normalize the data resulted in a complete breakdown or disagreement with the simple theory.

The results of the NMR study of this copolymer system demonstrate the validity of the work of Berger and Kuntz. The knowledge of sequences of higher order obtained by NMR has permitted the terminal mechanism to be ruled out in this system. The penultimate mechanism has been proposed as the correct one and seems to explain the data in a satisfactory manner. However, it should be noted that according to their e values this monomer pair is not one which would be predicted to obey such a mechanism. Alternate mechanisms can be proposed which may also account for the microstructure and still be consistent with the reactivity of the monomers. The study of the microstructure of this system is the first bonafide example of such a study for copolymers.

Results for VCl_2-VCl Copolymer System

Table XII lists the mole fraction of VCl_2 in the copolymer by NMR and chemical analysis, the mole fraction of VCl_2 in the monomer charge, and the mole fractions of the various diads.

The diad equations for f_{AA} and $2f_{AB}$ along with the Ross-Fineman equation for monomer concentrations were used to calculate r_1 and r_2 for the terminal mechanism. The graphs for these equations are shown in Figures 22, 23, znd 24. Figure 25 shows a Ross-Fineman plot using the two chemical analysis (carbon and chlorine) to determine the mole fraction of monomer in the polymer. The results of the various plots are shown in Table XIII along with the standard deviation of each method.

Average values of the monomer reactivity ratios excluding chemical analysis were computed and the results were; $r_1 = 3.75$ and $r_2 \simeq 0.18$. These values were employed to construct a plot of the mole fractions of the three

Table XII. Vinylidene chloride-vinyl chloride copolymerization

Sample	MF_{VCl_2}	Mf_{VCl_2} NMR	f_{AA}	$2f_{AB}$	f_{BB}	Mf_{VCl_2} carbon	Mf_{VCl_2} Cl
VVCl-63-2	0.691	0.887	0.807	0.183	0.010	-----	-----
VVCl-62-2	0.576	0.832	0.716	0.265	0.019	0.872	0.933
VVCl-36-2	0.470	0.769	0.619	0.320	0.059	0.701	0.751
VVCl-67-2	0.395	0.743	0.544	0.394	0.062	-----	-----
VVCl-64-2	0.355	0.724	0.493	0.428	0.079	0.671	0.669
VVCl-61-2	0.272	0.627	0.387	0.496	0.117	0.505	0.584
VVCl-69-2	0.240	0.603	0.343	0.497	0.160	-----	-----
VVCl-66-2	0.203	0.542	0.287	0.512	0.201	0.423	0.459
VVCl-65-2	0.169	0.493	0.227	0.521	0.252	-----	-----
VVCl-47-2	0.098	0.341	0.121	0.457	0.424	0.331	0.327
VVCl-70-2	0.066	0.266	0.063	0.389	0.548	-----	-----

Table XIII Copolymerization reactivity ratios from various data for vinylidene chloride(1)-vinyl chloride (2) system.

Method	r_1	σ_1	r_2	σ_2
1. Carbon analysis Ross-Fineman plot	3.36	2.72	.07	.20
2. Chlorine analysis Ross-Fineman plot	3.31	1.29	.26	.14
3. f_{VCl_2} from NMR Ross-Fineman plot	3.30	0.085	.13	.015
4. f_{AA} from NMR $F_o\frac{(1 - f_{AA})}{f_{AA}}$ vs. $\frac{1}{F_o}$	4.02	0.007	.15	.002
5. $2f_{AB}$ from NMR $\frac{2f_o(1 - 2f_{AB})}{2f_{AB}}$ vs. F_o^2	3.95	0.042	.26	.059
6. Literature value	3.2		.30	

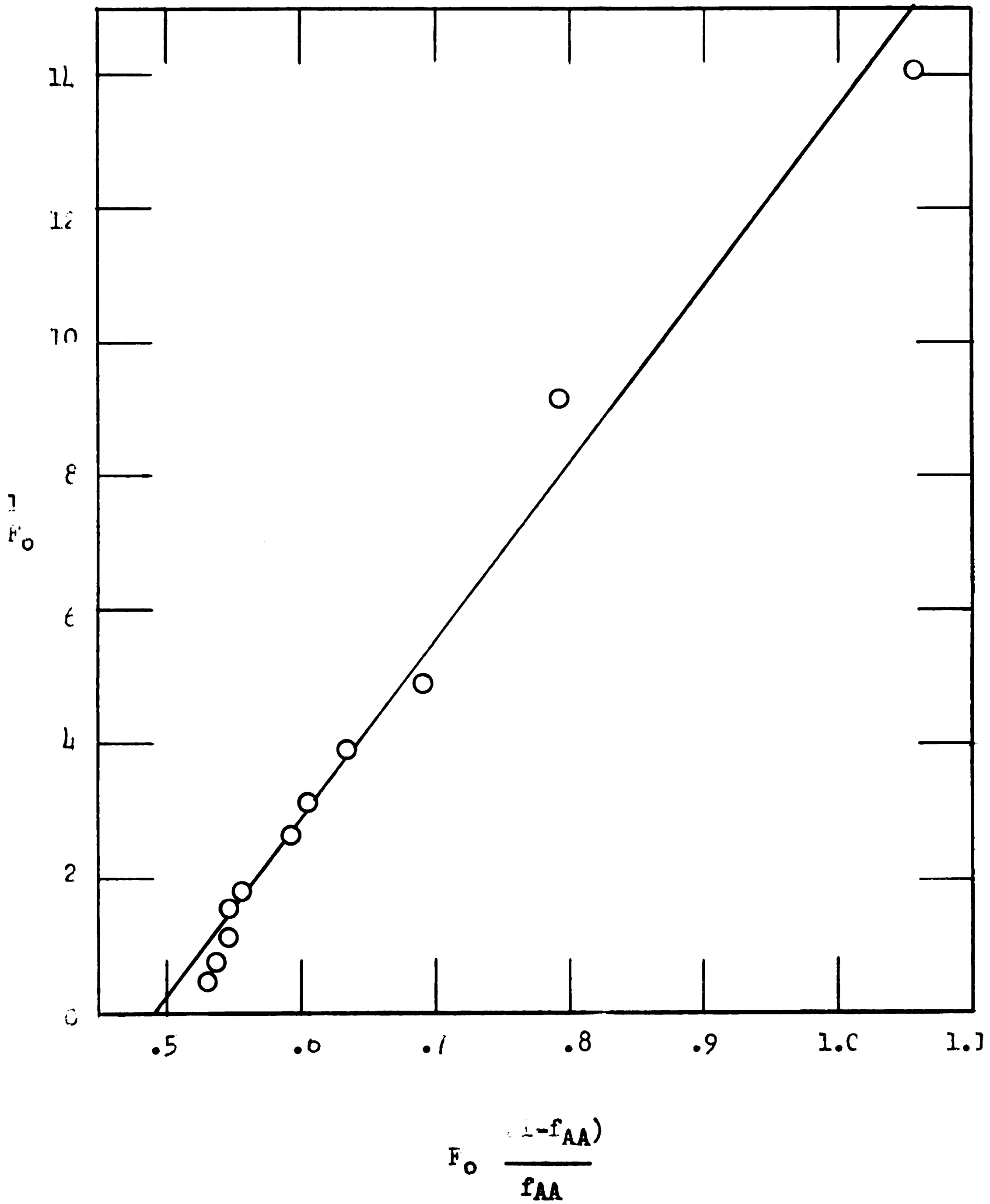


Fig. 22. Linear plot of the relationship $F_o(1-f_{AA})/f_{AA} = r_2/F_o - r_1$ where f_{AA} = mole fraction of AA diads.

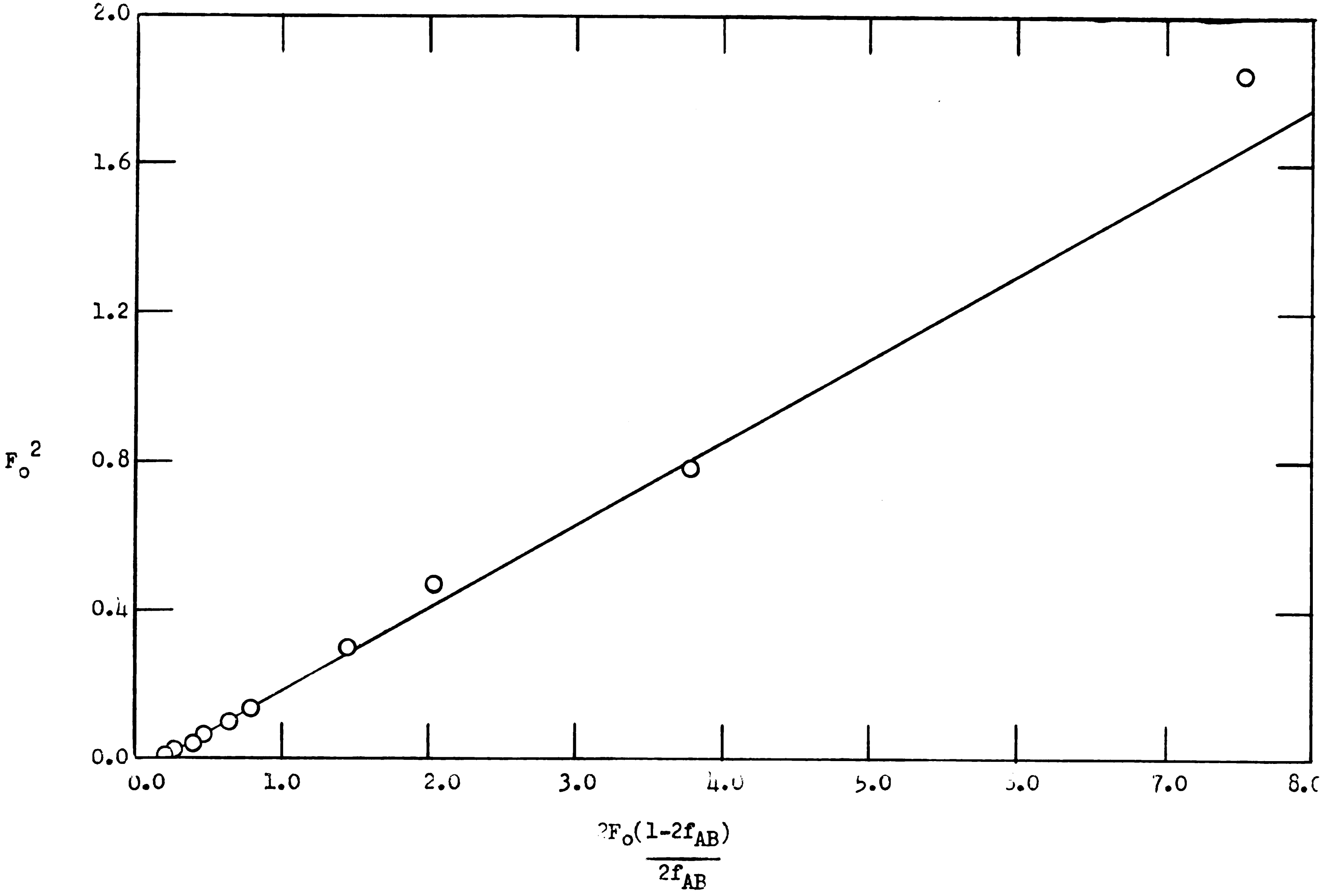


Fig. 23. Linear plot of the relationship $2F_o(1-2f_{AB})/2f_{AB} = F_o^2 r_1 + r_2$ where f_{AB} = mole fraction of AB diads.

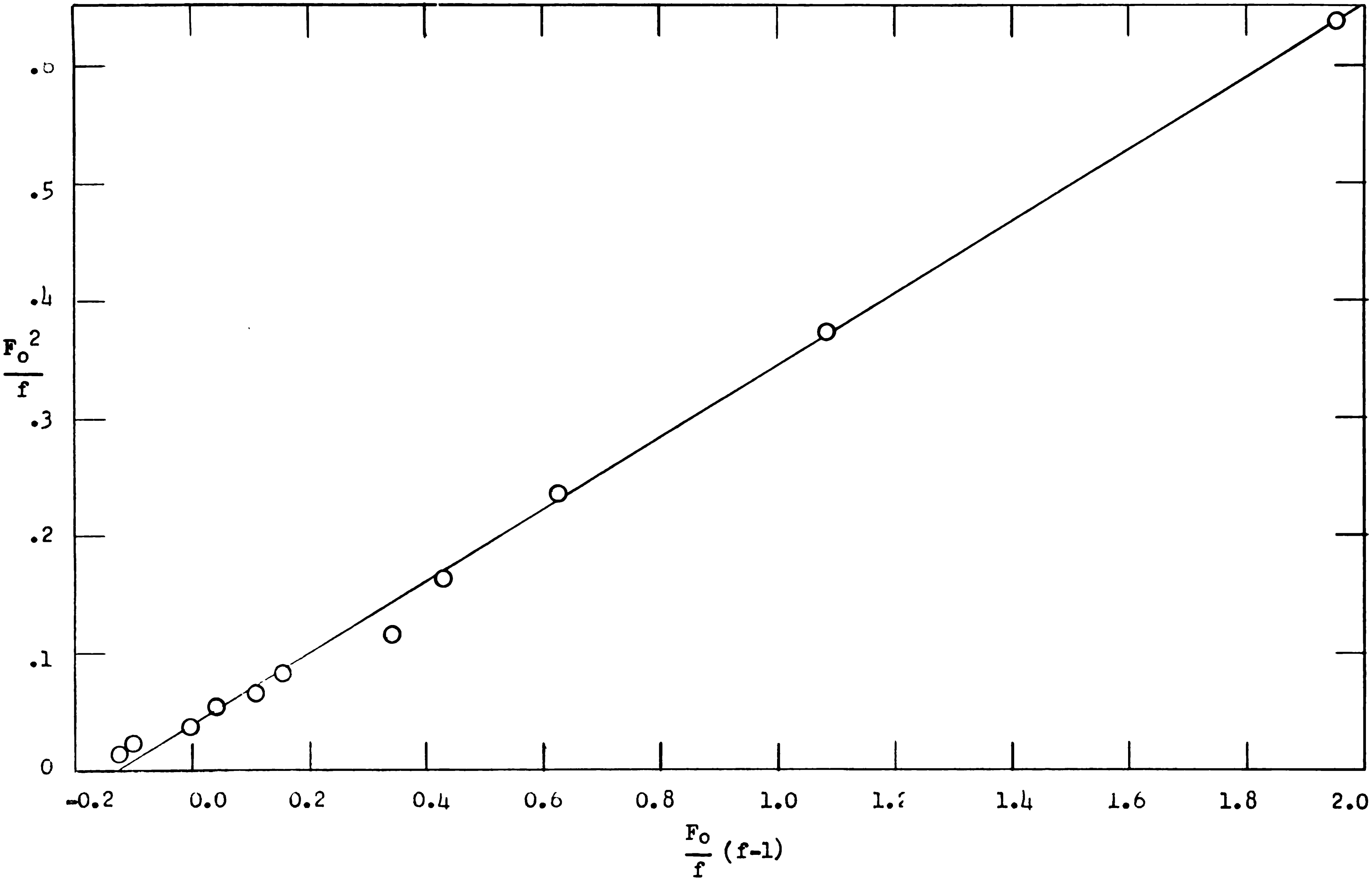


Fig. 24. Linear plot of the Ross-Fineman relationship. Experimental data from NMR analysis.

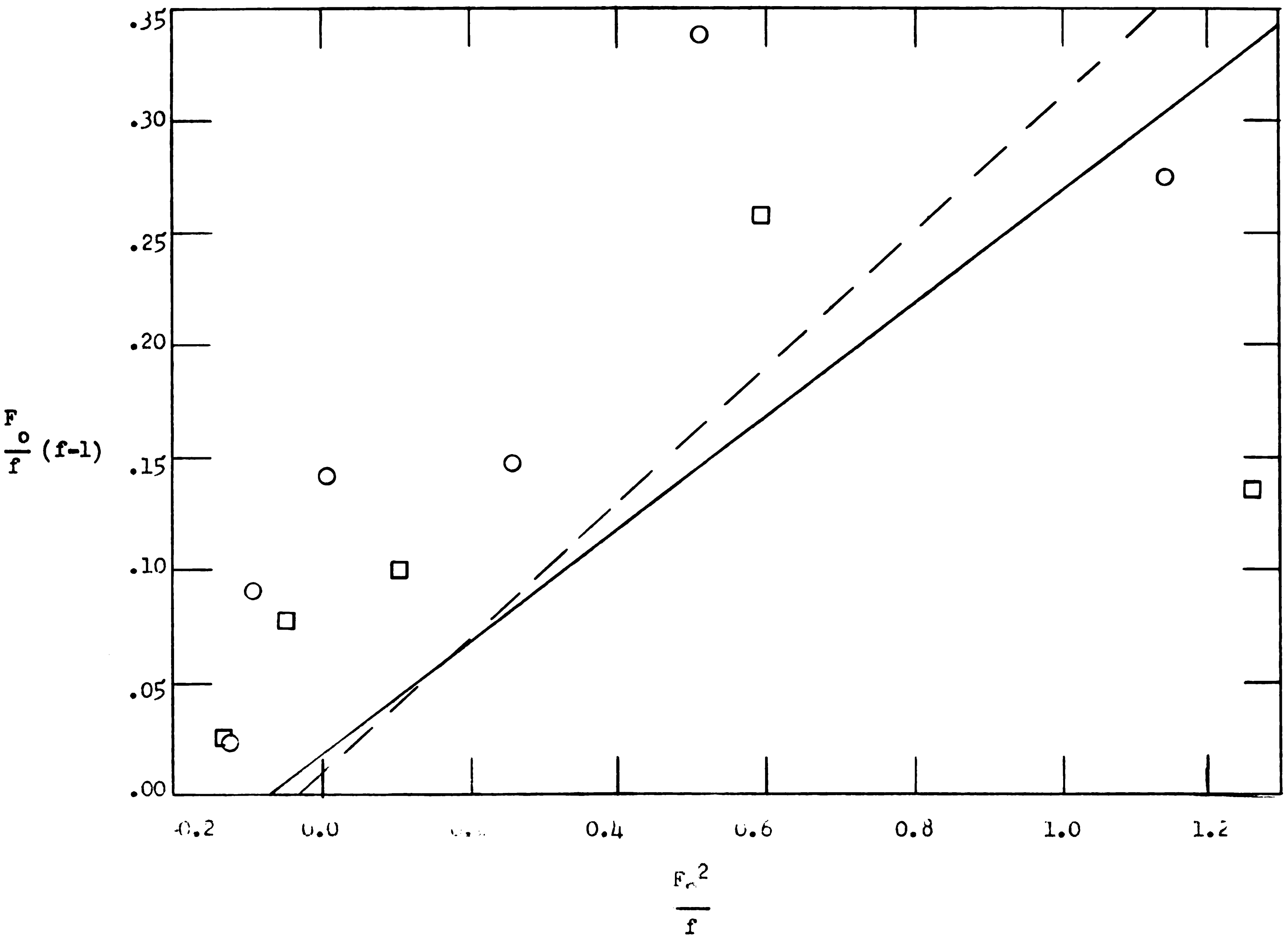


Fig. 25. Linear plot of the Ross-Fineman relationship: (□) and dotted line are from carbon analysis, (○) and continuous line are from chlorine analysis.

diads versus the mole fraction of VCl_2 in the monomer charge. The experimental diad mole fractions were included for comparison and the results displayed in Figure 26. The values obtained from this analysis compare favorably with those found in the literature (61).

Because the NMR spectra of the VCl_2-VCl system were not as sharply defined as were the NMR spectra of the VCl_2-IB copolymers due in part to the poorer solubility and in part to the different possible stereosequences they could not be analyzed for tetrads. Although the terminal mechanism of copolymerization was assumed in this work and the agreement between the calculated diad values and experimental diad values is good one cannot discard the possibility of another copolymerization mechanism without data on longer sequences.

Results of Conversion Study

Prior to the discovery that the terminal mechanism does not seem to be the correct one for the VCl_2-IB system a study of the effect of conversion on the various sequences was undertaken. Since the theoretical development has only progressed considering this effect of conversion on diads and since the terminal mechanism gives moderate correlation with the experimental diads, the results presented in this work are assumed to be valid within experimental error for the terminal mechanism. Two series of conversion runs were made with this system. The results for these series are listed in Table XIV. Figures 27 and 28 are plots of conversion versus mole fraction of monomers in the polymer and conversion versus mole fraction of diads for the series with $F_o = 0.941$. The line represents the calculated values which were obtained from a computer program of equations (2.36) and equations in Table V assuming $r_1 = 3.3$ and $r_2 = 0.05$.

Table XIV. Vinylidene chloride-isobutylene copolymer conversion series

Sample	F_o	$MF^o_{VCl_2}$	% Conv.	f_{AA}	$2f_{AB}$	f_{BB}	f_A	F
VI-49-7-2	0.940	0.62	4.6	0.571	0.396	0.033	0.769	0.914
VI-49-4-2	0.940	0.62	17.0	0.534	0.432	0.034	0.750	0.842
VI-49-2-2	0.940	0.62	28.4	0.528	0.442	0.030	0.750	0.760
VI-49-6-2	0.940	0.62	47.7	0.510	0.440	0.050	0.733	0.618
VI-49-5-2	0.940	0.62	36.2	0.496	0.467	0.037	0.731	0.726
VI-49-8-2	0.940	0.62	46.3	0.493	0.466	0.041	0.726	0.647
VI-49-3-2	0.940	0.62	52.7	0.486	0.468	0.046	0.722	0.592
VI-1-3-1	0.395	0.283	5.4	0.435	0.515	0.050	0.693	0.351
VI-1-3-2	0.395	0.283	17.8	0.421	0.533	0.047	0.688	0.286
VI-1-3-3	0.395	0.283	25.1	0.413	0.546	0.041	0.686	0.156
VI-1-3-4	0.395	0.283	38.7	0.340	0.598	0.062	0.639	0.184

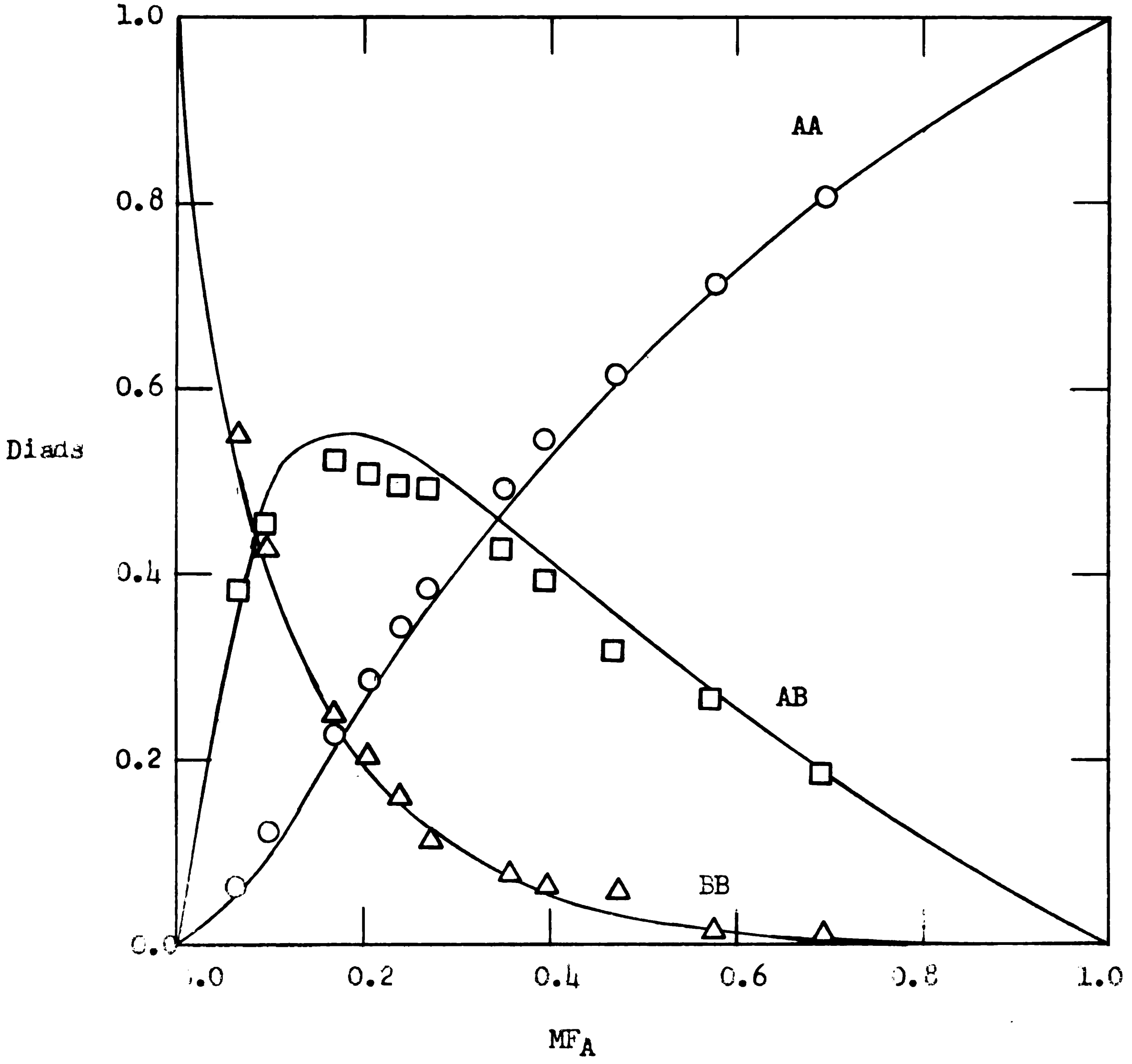


Fig. 26. Mole fraction of diads of VCl-VCl_2 system versus mole fraction of vinylidene chloride in monomer mix; (○)f_{AA}; (□)$2f_{AB}$; (△)f_{BB}. Solid lines terminal mechanism $r_1 = 3.75$ $r_2 = 0.18$.

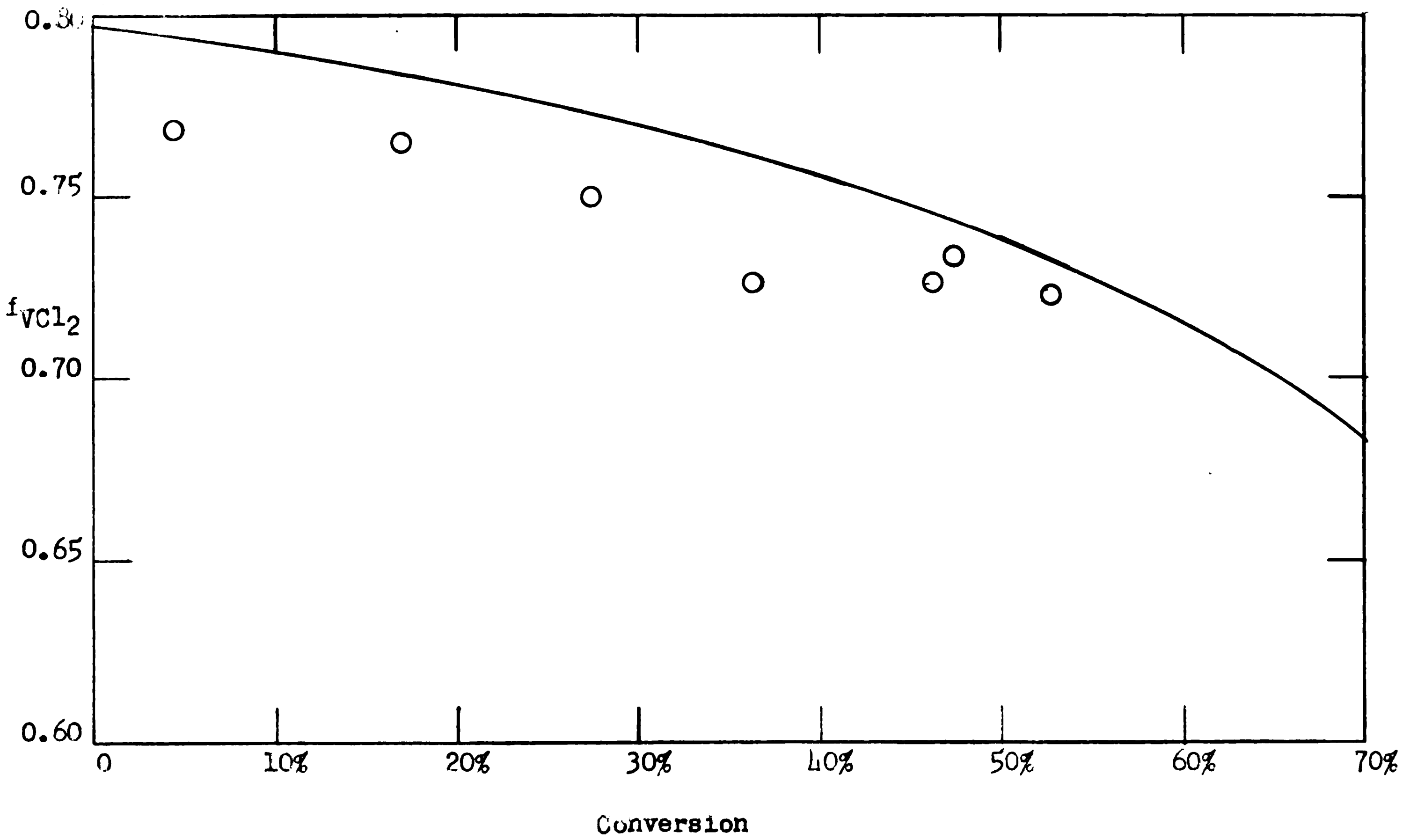


Fig. 27. **Plot of mole fraction of vinylidene chloride in VCl_2-IB copolymer versus per cent conversion. Line represents terminal mechanism $r_1 = 3.0$, $r_2 = 0.05$.**

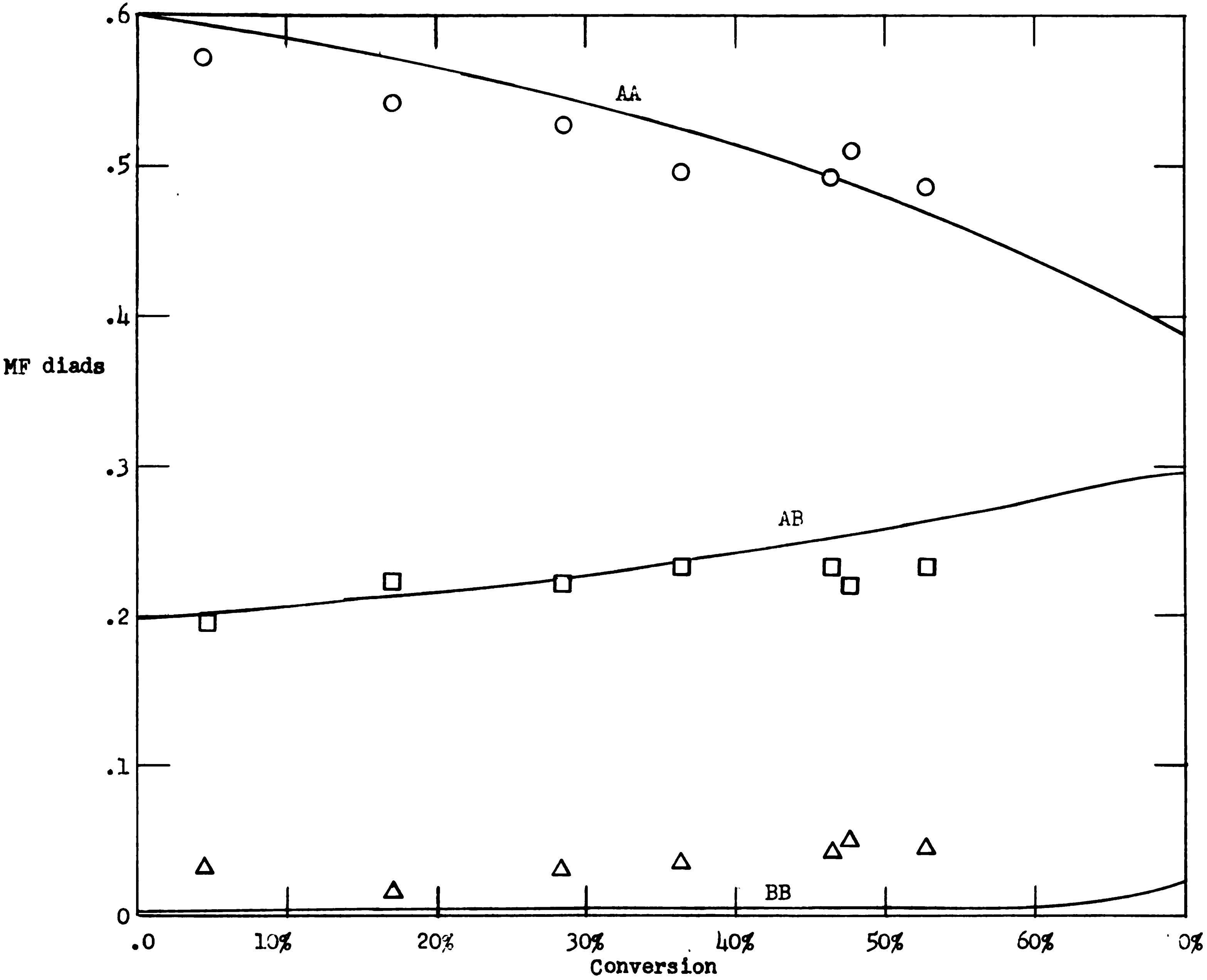


Fig. 28. Plot of mole fraction of diads in VCl_2-IB copolymer system versus per cent conversion. (o)f_{AA}; (□)f_{AB}; (△)f_{BB}. Line represents terminal mechanism $r_1 = 3.0; r_2 = 0.05$.

The trends of the experimental diad mole fractions are in the same direction as the calculated values indicating the equations are a reasonable approximation of the actual process.

Much more work needs to be done in this particular area but the work presented here has demonstrated the feasibility of such a study. With the aid of computers the calculations involved in the theoretical aspects of this problem will become less tedious and it may be possible to extend the theory to other copolymerization kinetic mechanisms.

Conclusion

The results of this work have shown NMR to be an acceptable working tool for the polymer chemist in the determination of the microstructure of copolymers. There are several advantages and some limitations in the use of NMR for microstructure determinations.

There is more information available on the microstructure through NMR than has previously been determined with other methods of analysis. No microstructure units any larger than diads have been reported on synthetic copolymers by other means. With NMR one does not have to rely only on chemical analysis to determine reactivity ratios or mole fractions of the monomer in the copolymer. Because the copolymer needs only to be dissolved in a solvent to be run in the NMR it is not destroyed and can be used for further testing. Another plus factor is the reproducibility of the results obtained from the NMR data of the systems studied.

NMR studies of copolymers do have some limitations. The choice of monomers is the greatest limitation. The copolymer produced from the monomers must be soluble in suitable solvents i.e. solvents which dissolve the copolymer but do not interfere with the copolymer spectra. It is also desirable for the chemical shift of the methylene protons of the two homopolymers to be far enough apart to permit the detection of another peak or group of peaks which will arise from the AB pairs. The two systems of the present work meet this requirement quite readily especially in the case of the VCl_2-IB system where the AB peaks are easily resolvable from either of the homopolymer peaks. Signals from other protons of the homopolymers such as the methyl group protons in IB must not interfere with the regions of the methylene proton peaks in such a manner that makes interpretation of the spectra impossible. In the NMR spectra of the VCl_2-IB system there was overlap of the methyl and methylene proton peaks in the Z region of the spectra. This overlap was overcome by normalization of the peak areas as explained in Chapter V. The α-hydrogens of the VCl in the VCl_2-VCl system did not interfere with the rest of the spectra and were, in fact, an independent check on the mole fractions of each monomer found in the polymer.

The results of the studies of the two systems show that the mathematical treatments of copolymerization which have been proposed by Price and his predecessors are valid. The results of both systems show that calculated values and experimental values agree within the limits of the experiments. The fit of the equations for the mole fraction of diads is good in both copolymer systems when the penultimate mechanism was assumed for the first system and the terminal mechanism was assumed for the second system. In addition to the good agreement for the diads the experimental and calculated tetrad values were also in good agreement in the VCl2-IB system when the penultimate mechanism was assumed.

The experimental results of the conversion study of the VCl_2-IB system have shown trends in the direction predicted by theory and although further work needs to be done in this area the work done to date has not refuted the theoretical assumptions.

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APPENDIX I

Solutions For $V_j^{(k)}$ and the Copolymer Composition Equation for $k = 2$ Utilizing F. Price's Methods.

1. Solutions For $V_j^{(2)}$

The $V_j^{(2)}$ are components of a four column vector $V^{(2)}$ which represent the relative concentrations of diads in the various states.

The solutions for $V_j^{(2)}$ which we want are given by the equation

$$V_j^{(2)} = cA^{js}$$

where A^{js} is the cofactor of the element A_{js} in the determinant $|A|$ and c is the constant.

Because the matrix (P) which is an arrangement of transition probabilities as shown below is stochastic, it can be shown that the determinant $|A|$ can be formed by subtracting unity from each element of the diagonal of the matrix (P). Thus:

$$(P) = \begin{pmatrix} P_{oo} & 0 & 1-P_{21} & 0 \\ 1-P_{oo} & 0 & P_{21} & 0 \\ 0 & P_{12} & 0 & 1-P_{33} \\ 0 & 1-P_{12} & 0 & P_{33} \end{pmatrix}$$

and

$$|A| = \begin{vmatrix} P_{oo}-1 & 0 & 1-P_{21} & 0 \\ 1-P_{oo} & -1 & P_{21} & 0 \\ 0 & P_{12} & -1 & 1-P_{33} \\ 0 & 1-P_{12} & 0 & P_{33}-1 \end{vmatrix}$$

and to obtain solutions for the various $V_j^{(2)}$ all we need to do is obtain the appropriate cofactors. Thus

$$V_o^{(2)} = c\begin{vmatrix} -1 & P_{21} & 0 \\ P_{12} & -1 & 1-P_{33} \\ 1-P_{12} & 0 & P_{33}-1 \end{vmatrix}$$

$$= c\left\{(-1)(-1)(P_{33}-1)-P_{21}\left[P_{12}(P_{33}-1)-(1-P_{33})(1-P_{12})\right]\right\}$$

$$= c(P_{33}-1)(1-P_{21})$$

and

$$V_1^{(2)} = c\begin{vmatrix} 1-P_{oo} & P_{21} & 0 \\ 0 & -1 & 1-P_{33} \\ 0 & 0 & P_{33}-1 \end{vmatrix}$$

$$= c(1-P_{oo})(P_{33}-1)$$

and similarly

$$V_2^{(2)} = c\begin{vmatrix} 1-P_{oo} & -1 & 0 \\ 0 & P_{12} & 1-P_{33} \\ 0 & 1-P_{12} & P_{33}-1 \end{vmatrix}$$

$$= c(1-P_{oo})(P_{33}-1) = V_1^{(2)}$$

Also

$$V_3^{(2)} = c\begin{vmatrix} 1-P_{oo} & -1 & P_{21} \\ 0 & P_{12} & -1 \\ 0 & 1-P_{12} & 0 \end{vmatrix}$$

$$= c(1-P_{oo})(1-P_{12})$$

2. Solution For Copolymer Composition Equation

From equation 2.21

$$\frac{N_o}{N_1} = \frac{V_o^{(2)} + V_2^{(2)}}{V_1^{(2)} + V_3^{(2)}}$$

We can then substitute the previously determined values for the $V_j^{(2)}$'s and obtain

$$\frac{N_o}{N_1} = \frac{(P_{33}-1)(1-P_{21}) + (1-P_{oo})(P_{33}-1)}{(1-P_{oo})(P_{33}-1) + (1-P_{oo})(1-P_{12})}$$

which can be written

$$\frac{N_o}{N_1} = \frac{1 + \dfrac{(1-P_{21})}{(1-P_{oo})}}{1 + \dfrac{(1-P_{12})}{(1-P_{33})}}$$

To place this equation in a form utilizing the reactivity ratios and initial concentrations of the monomers, the definitions and equation 2.22 in chapter two must be used. The definitions used: $r_n = \frac{k_{no}}{k_{n1}}$ when n is even, $r_n = \frac{k_{n1}}{k_{no}}$ when n is odd and $\frac{M_o}{M_1} = F_o$.

Applying equation 2.22

$$P_{oo} = \frac{k_{oo}M_o}{k_{oo}M_o + k_{01}M_1}$$

By dividing both top and bottom of the right hand side by $k_{01}M_1$ and applying the definitions we obtain

$$P_{oo} = \frac{r_oF_o}{r_oF_o + 1}$$

Similarly $P_{12} = \dfrac{k_{10}M_0}{k_{10}M_0 + k_{11}M_1} = \dfrac{F_o}{r_1 + F_0}$

and $P_{21} = \dfrac{k_{21}M_1}{k_{20}M_0 + k_{21}M_1} = \dfrac{1}{1 + r_0F_0}$

also $P_{33} = \dfrac{k_{31}M_1}{k_{31}M_1 + k_{30}M_0} = \dfrac{r_3}{r_3 + F_0}$

Substituting these expressions in the equation for $\frac{N_0}{N_1}$ one obtains:

$$\frac{N_0}{N_1} = \frac{1 + \dfrac{\left(1 - \dfrac{1}{1 + r_2F_0}\right)}{\left(1 - \dfrac{r_0F_0}{r_0F_0 + 1}\right)}}{1 + \dfrac{\left(1 - \dfrac{F_0}{F_0 + r_1}\right)}{\left(1 - \dfrac{r_3}{r_3 + F_0}\right)}}$$

This is the identical equation derived by Alfrey and Goldfinger for the penultimate mechanism of copolymerization.