COPOLYMERIZATION PARAMETERS OF ITACONIC ANHYDRIDE IN FREE-RADICAL POLYMERIZATION

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This is to certify that the

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ABSTRACT

COPOLYMERIZATION PARAMETERS OF ITACONIC ANHYDRIDE IN FREE-RADICAL POLYMERIZATION

by Moustafa Mokhtar Sharabash

Itaconic anhydride (M_1) was copolymerized with four comonomers (M_2) having different polarities, namely: vinyl acetate, 2-chloroethyl acrylate, acrylonitrile and styrene.

The monomer reactivity ratios (r_1, r_2) for these four systems were determined in benzene, and the reactivity ratios for the itaconic anhydride with the first two comonomers were also determined in tetrahydrofuran. The values of the reactivity ratios are given in the following table:

Table 1. The Reactivity Ratios of Itaconic Anhydride (M_1) with Different Comonomers (M_2)

Comonomer (M_2)	In benzene		In T.H.F.	
	r_1	r_2	r_1	r_2
Vinyl acetate	5.75	0.08	3.50	0.08
2-Chloroethyl acrylate	2.7	0.065	2.25	0.34
Acrylonitrile	4.8	0.13	--	--
Styrene	0.53	0.018	--	--

Six Q-e scheme values were calculated for itaconic anhydride, using the reactivity ratios given in Table 1. These values are given in the following table:

Table 2. Calculated Q-e Values for Itaconic Anhydride (M_1)

Comonomer (M_2)	In benzene		In T.H.F.	
	Q_1	e_1	Q_1	e_1
Vinyl acetate	2.88	0.66	2.54	0.90
2-Chloroethyl acrylate	12.79	1.85	1.59	1.05
Acrylonitrile	10.46	1.89	--	--
Styrene	9.68	1.37	--	--

By plotting log Q_1 vs. e_1, the average Q-e values for itaconic anhydride were determined.

$$Q = 9.8 \qquad e = 2.0$$

An improved technique for the homopolymerization as well as the copolymerization of solid and liquid vinyl type monomers was developed and used to obtain the data presented in this thesis.

A quantitative determination of the copolymer composition of itaconic anhydride co vinyl acetate and itaconic anhydride co 2-chloroethyl acrylate, based on a method employing infra-red spectra was developed.

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By

Moustafa Mokhtar Sharabash

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To My Wife: KAMILIA

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INTRODUCTION

The first publication on itaconic anhydride as a monomer was published by Drougas and Guile in 1961 (1). Since that time, very little has been published concerning the properties of this monomer in copolymerization reactions (2,3).

The copolymers of itaconic anhydride have been the subject of increasing industrial interest (4,5,6,7).

The purpose of this investigation is to study the free-radical copolymerization of itaconic anhydride with several monomers, and to determine the related copolymerization parameters.

HISTORICAL

The reaction of copolymerization was first described in 1914 by Klatte (8) who carried out the polymerization of a mixture of vinyl esters. In a subsequent period of intensive research, interest in copolymerization was spurred by the observation that copolymers such as vinylite (9) and vinyon (10), frequently had more desirable physical properties than either polymers of the individual monomers, or a mixture of their homopolymers. Investigation of the exact nature of copolymerization was slow due to the complexity of the reaction. During the 1930's, evidence accumulated that striking differences existed in the tendencies of the monomers to enter into copolymers. When Staudinger and Schneiders (11) fractionated a vinyl chloride-vinyl acetate copolymer made from a 1:1 reaction mixture of monomers, they obtained fractions containing the two monomer moieties in the ratios, 9:3, 7:3, 5:3 and 5:7 but none in the ratio 1:1. Further, marked differences in the ability of divinyl compounds to enter into copolymerization with styrene or methyl methacrylate were noted by Norrish and Brookman (12) from the relative tendencies of mixtures to form insoluble gels. Their studies also provided one of the first demonstrations that inclusion of the two monomer types in the same polymer chain actually occurred. Similarly, in vinyl chloride-acrylic ester copolymers, the acrylate was found to enter the copolymer faster than the chloride, so that the first polymer formed was rich in acrylate and the last was rich in vinyl chloride moiety. Empirically, it was observed that the heterogeneity could be controlled and a uniform composition copolymer obtained by adding the more reactive monomer gradually during the copolymerization (13).

Further studies of copolymerization phenomena indicated that it was a unique process markedly different from homopolymerization. Maleic anhydride and some related compounds which are very difficult to homopolymerize [maleic anhydride was polymerized in this laboratory under mild conditions] were capable of copolymerizing readily with a polymerizable monomer such as styrene and vinyl chloride (14). Still, more surprisingly, the pairs stilbene-maleic anhydride (15) and isobutylene-fumaric ester (16) readily gave high molecular weight 1:1 copolymers regardless of the initial composition of the monomers in the reaction mixture in spite of the fact that none of the monomers homopolymerized under the same conditions. Furthermore, although a styrene-vinyl acetate (or styrene-vinyl chloride) mixture would polymerize to give mixtures of the two polymers (17), a copolymer containing all three monomer moieties could be obtained in the presence of an acrylic or maleic ester.

The first attempt to give a quantitative treatment to results of the sort just described and to develop an adequate theory of copolymerization was made by Dostal (18) in 1936. In his treatment, Dostal assumed that the behavior of an active center depends solely upon the terminal group (defined as the monomer unit last added to the chain) and is, independent of the length or the overall composition of the polymer chain. Under these conditions, only two types of active centers exist in the copolymerization of any two monomers, and for long polymer chains, the formation of the copolymer is determined by the four reactions:

Reaction	Rate
$M_1^* + M_1 \longrightarrow M_1^*$	$k_{11}\ [M_1^*]\ [M_1]$ ---- (1a)
$M_1^* + M_2 \longrightarrow M_2^*$	$k_{12}\ [M_1^*]\ [M_2]$ ---- (1b)
$M_2^* + M_2 \longrightarrow M_2^*$	$k_{22}\ [M_2^*]\ [M_2]$ ---- (1c)
$M_2^* + M_1 \longrightarrow M_1^*$	$k_{21}\ [M_2^*]\ [M_1]$ ---- (1d)

where M_1 and M_2 represent the two monomers and M_1^* and M_2^* represent the chains ending in M_1 and M_2 units respectively. Dostal wrote expressions for the rate of polymerization and the composition of a copolymer in these terms. However, since his expressions involved four or more unknown rate constants, he devised no experimental test of his conclusions.

Norrish and Brookman (19) carried out a careful experimental study of the rates of polymerization of styrene and methyl methacrylate and their mixtures. They made an additional assumption that the concentration of free radicals would be the same in all mixtures at the same catalyst concentration, an assumption that was shown to be unjustified (20). Wall (21) made an important advance in suggesting that absolute rate be neglected in copolymerization and that the relative reactivities of the monomers be studied by investigating the copolymer compositions. He suggested that if the relative reactivities of the monomers were the same toward each monomer and if $k_{11}/k_{12} = k_{21}/k_{22} = \alpha$, then it followed that:

$$\frac{d[M_1]}{d[M_2]} = \alpha \frac{[M_1]}{[M_2]} \quad \text{or} \quad \log \left(\frac{[M_1]_0}{[M_1]}\right) = \alpha \log \left(\frac{[M_2]_0}{[M_2]}\right) \text{----} (2)$$

and the composition of the copolymer would be described in terms of the initial monomer concentrations and a single, easily measured constant (α). Although early tests of this equation (22,23) appeared to justify Wall's assumptions, careful studies showed that α varies with the initial monomer ratio.

Although the four reactions of chain growth in copolymerization were first recognized by Dostal in 1936, and the necessity of expressing copolymer composition in terms of an easily measurable parameter was realized by Wall in 1941, no combination of the two principles was developed. This was largely due to inadequate data since most of the data available were obtained from experiments carried out to a high percent conversion to copolymer and did not cover a sufficiently wide range of initial monomer concentrations.

In 1944, three independent derivations of what is now known as the "copolymerization equation" were published by Alfrey and Goldfinger (24), by Mayo and Lewis (20) and by Wall (25). In each case, the derivation was based on the following assumptions: first, that one was dealing with a chain reaction involving long chains so that consumption of monomer could be discussed in terms of chain propagation reactions; second, that these chains have very short lives compared to the duration of the overall reaction, so that steady state expressions might be set up for the concentrations of the active centers, and finally, the propagation reactions could be adequately described by equations (1a-1d). From these equations, the rate of disappearance of the two monomers in a copolymerization and hence the appearance of the monomer moieties in the copolymer can be given by,

$$\frac{-d[M_1]}{dt} = k_{11} \; [M_1^*] \; [M_1] + k_{21} \; [M_2^*] \; [M_1] \text{ -------- } (3a)$$

$$\frac{-d[M_2]}{dt} = k_{12} \; [M_1^*] \; [M_2] + k_{22} \; [M_2^*] \; [M_2] \text{ -------- } (3b)$$

and the relation between $[M_1]$ and $[M_2]$ is given by the steady state expression:

$$k_{21} \; [M_2^*] \; [M_1] = k_{12} \; [M_1^*] \; [M_2] \text{ -------- } (4)$$

Dividing equation (3a) by (3b), eliminating the concentrations of active centers by combining the result with equation (4), and introducing the parameters $r_1 = \frac{k_{11}}{k_{12}}$ and $r_2 = \frac{k_{22}}{k_{21}}$, leads to the final copolymerization equation:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \text{ --------- } (5)$$

The quantity $\frac{d[M_1]}{d[M_2]}$ represents the ratio of the two monomers in that increment of copolymer formed when the ratio of unreacted monomers is $\frac{[M_1]}{[M_2]}$.

The validity of the copolymerization equation was first established by Mayo and Lewis for the styrene-methyl methacrylate system (20) and has been confirmed by many subsequent investigators.

The monomer reactivity ratio (r) is the ratio of the two rate constants for the reaction of a chain radical with a given monomer unit at the growing end with its own type of monomer and with the other type of monomer. This reactivity ratio should be applicable in copolymerization of pure monomers (bulk polymerization), solvent soluble systems of monomers (solution polymerization), and heterogeneous systems (emulsion polymerization). The r_1, r_2 parameters should also remain fundamentally constant in systems where the polymer stays in solution or precipitates as it is formed (26,20,27).

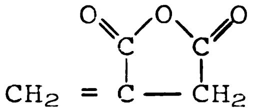
In general, and where there is no change in copolymerization mechanism, a single pair of reactivity ratios suffices to describe the copolymerization of a given pair of monomers under all conditions at a particular temperature. The thermal polymerization of styrene was found to proceed at identical rates in a variety of solvents (28,29,30). One must recognize that there are three quite different mechanistic types of addition polymerization: free radical, anionic, and cationic mechanisms. The reactivity ratios determined for a pair of monomers in a copolymerization proceeding by one of these three mechanisms, cannot be used to describe the reactivity ratios of the same pair of monomers in a copolymerization proceeding by one of the other two mechanisms. A pair of monomers should have different reactivity ratios, for each mechanism followed in the copolymerization.

The great majority of the reactivity ratios reported in the literature are for systems involving free radical type polymerization (31). Many copolymerization parameters have been reported for maleic anhydride (32-37), and citraconic (methyl maleic) anhydride (38). Only one set of reactivity ratios for itaconic anhydride has been reported so far (1).

REAGENTS

I. Monomers

a. Itaconic anhydride



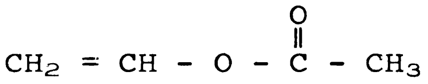
Preparation and purification

A mixture of 50 gm (0.39 mole) of itaconic acid (Chas. Pfizer Co.), and 100 ml. of acetyl chloride was refluxed for one hour during which time the itaconic acid reacted to form the anhydride which dissolved in the excess acetyl chloride. Heating was continued for about fifteen minutes after solution and the reaction mixture was immediately distilled to remove most of the excess acetyl chloride and acetic acid. The distillation was carried out at a temperature below 80°C. under a reduced pressure of 25 m.m. in a nitrogen atmosphere. In order to insure complete removal of the acetyl chloride and acetic acid, the reaction mixture was co-distilled with toluene. Two consecutive 60-ml. portions of toluene were added and then removed by vacuum distillation at a temperature below 80°C. Eighty degrees is a critical temperature above which decomposition and polymerization occurs. After distillation of the second portion of toluene, a syrupy residue remained which was then cooled and transferred to an Erlenmeyer flask. One hundred milliliters of anhydrous ether were added to precipitate the itaconic anhydride. Approximately 32.0 gms. of itaconic anhydride (m.p. 68-69°C.) were obtained. Concentration of the ethereal solution yielded an additional 8.0 gms. of crude anhydride (m.p. 63-66°). The preparation requires about four hours, and should be continuous through the removal of all the excess acetyl chloride and acetic acid and the precipitation by anhydrous ether. The crude anhydride was recrystallized twice from chloroform to give a product m.p. 68.5°C. ± 0.2°C. An average yield of itaconic anhydride was 80% based on the itaconic acid.

Itaconic anhydride may be prepared from itaconic acid by reaction with thionyl chloride (39), phosphorus pentoxide (40), acetyl chloride (41), or acetic anhydride (42).

Itaconic acid is produced commercially by the submerged culture fermentation of a glucose media by "Aspergillus terreus." A laboratory method of preparation consists of rapid distillation of citric acid (43).

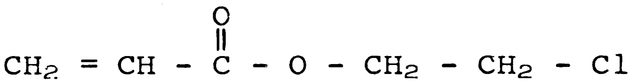
b. Vinyl acetate



$CH_2 = CH - O - \overset{\overset{O}{\|}}{C} - CH_3$

Vinyl acetate (Union Carbide Chem. Co.) containing diphenylamine as inhibitor, was stored over anhydrous sodium sulfate for one week. It was then distilled and the fraction boiling at 72.4-72.6°C was collected. The refractive index of the material used was $\eta_D^{20} = 1.3953$.

c. 2-Chloroethyl acrylate (β-chloroethyl acrylate)



$CH_2 = CH - \overset{\overset{O}{\|}}{C} - O - CH_2 - CH_2 - Cl$

This monomer (The Borden Chem. Co.) was first washed with 5% sodium hydroxide solution to remove the inhibitor, then it was stored over anhydrous sodium sulfate for one week.

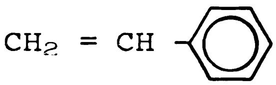
It was distilled under reduced pressure and the fraction boiling at 64-66°C. at 20 mm. was collected and used.

d. Acrylonitrile

$CH_2{=}CH{-}CN$

Acrylonitrile (Matheson Coleman and Bell Co.) was washed with sulfuric acid to remove the inhibitor, then with water until neutral to litmus. The uninhibited material was stored over anhydrous sodium sulfate in a refrigerator for one week and then distilled. The material used had a boiling point of 77.5 ± 0.2°C. at 760 m.m., and a refractive index of $\eta_D^{20} = 1.3890$.

e. Styrene

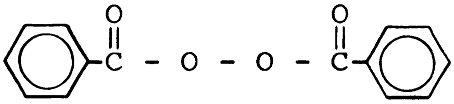


Styrene (Dow Chem. Co.) was washed with three successive portions of 10% sodium hydroxide solution to remove the inhibitor. It was then washed with water until the washings were neutral to litmus, and stored over anhydrous sodium sulfate in a refrigerator for one week. The dry styrene was distilled under reduced pressure in a nitrogen atmosphere. The boiling point of the material used was 36-37°C. at 30 m.m. and the refractive index was $\eta_D^{20} = 1.5430$.

Before using styrene in any copolymerization, it was tested for the presence of polystyrene. This test was made by addition of methanol to a sample of styrene. Since polystyrene is insoluble in methanol, the absence of a precipitate indicated that the styrene was free of polystyrene.

II. Catalyst

Benzoyl peroxide



Benzoyl peroxide (Matheson, Coleman and Bell Co.) was purified and recrystallized from a mixed solvent consisting of one part chloroform and two parts methanol. The crude benzoyl peroxide was dissolved in an appropriate amount of chloroform and the solution was filtered by suction. Twice its volume of methanol was added. The crystals, which separated at room temperature were filtered by suction and dried in vacuum at room temperature (25°C.).

III. Solvents and non-solvents

a. Anhydrous benzene (44)

Thiophene-free benzene was vigorously stirred for one-half hour with concentrated sulfuric acid. This process was repeated twice with fresh portions of the acid. The benzene was then washed with 10% solution of sodium bicarbonate followed by water until the washings were neutral to litmus. The washed benzene was stored over anhydrous calcium chloride and then over metallic sodium. It was distilled from sodium, the first portion of the distillate (5% of the original volume) was discarded and the fraction collected at 80°C.± 0.5°C. was used in all reactions.

b. Tetrahydrofuran

Tetrahydrofuran (Eastman Chemical Co.) was stored over solid potassium hydroxide for at least one week. It was then refluxed with lithium aluminum hydride for about twelve hours and distilled. The first portion of the distillate was discarded (5% of the original volume), and the fraction boiling at 64-65°C. was collected for use. Since tetrahydrofuran readily absorbs moisture from the atmosphere, care was exercised in transferring and measuring the anhydrous tetrahydrofuran into the reaction vessel. All-glass equipment was used and was always thoroughly dried.

c. Acetonitrile

Spectro grade acetonitrile (Matheson, Coleman and Bell Co.) used in the infra-red analysis was purified in the following manner (45):

It was stored over phosphorus pentoxide, and fresh portions of the pentoxide were added until there was no change in the color of a freshly added portion. The color change in the phosphorus pentoxide was from a nearly white solid to a bright yellow. The acetonitrile was transferred into a distilling flask containing fresh phosphorus pentoxide and refluxed for six hours. It was then distilled and the fraction boiling at 82°C. ± 0.2°C. was collected. The refractive index of the acetonitrile used was $\eta_D^{20} = 1.3459$.

d. Anhydrous ether

Diethyl ether (anhydrous grade) was stored over sodium metal for two days. It was refluxed over lithium aluminum hydride for about five hours, and distilled from the hydride. The boiling point of the anhydrous ether used was 34°C. ± 0.5°C.

IV. Fieser Solution

Twenty grams of potassium hydroxide were dissolved in 100 ml. of distilled water. To this solution, 2 gms. of sodium anthraquinone-β sulfonate and 15 gms. of commercial sodium hyposulfite were added. The mixture was stirred until all the components were dissolved and allowed to cool to room temperature. The solution has a blood-red color. One hundred milliliters of this solution will absorb about 750 ml. of oxygen. The exhaustion of the solution is indicated by a change in color to dull-red or brown, or the formation of a precipitate (46).

PART I

THE REACTIVITY RATIOS

EXPERIMENTAL

A. Polymerization Technique

The following technique was used for all the homopolymerization and copolymerization reactions throughout this investigation.

The monomer or monomers and the initiator were dissolved in the appropriate solvent in the reaction vessel of the polymerization apparatus, Fig. 1. The reaction vessel was fitted with two necks, a small one (₮ 10/14) through which the nitrogen bubbler was inserted, and a standard size neck (₮ 24/40). To the latter was attached an adaptor with a side arm. The reaction was stirred continuously by a magnetic stirrer. Nitrogen was passed into the system through the bubbler, and the side arm on the adaptor was used to introduce small pieces of dry ice into the reaction vessel. Approximately 10 gms. of dry ice were introduced and allowed to dissolve in the reaction mixture. After all the dry-ice had disappeared, the apparatus was evacuated to a pressure of 30-40 m.m. In order to avoid any loss of the solvent and any of the monomers, a dry-ice-acetone-cooled trap was inserted between the top of the condenser and the vacuum line. When the pressure inside the apparatus reached 30-40 m.m., nitrogen was turned on and allowed to bubble through the reaction mixture and evacuation was stopped. The vacuum inside the apparatus was replaced by nitrogen. An inflatable rubber bladder inserted between the nitrogen tank and the apparatus enabled the operator to control the restoration of the pressure inside the apparatus to atmospheric pressure. Prepurified nitrogen was used which was passed through Fieser solution to remove any traces of oxygen. It was then passed through an anhydrous calcium chloride drying tower before entering the apparatus. This sweeping process was carried out twice before each reaction was started in order to eliminate all traces of oxygen from the reaction mixture. The reaction was protected against moisture of the atmosphere by a calcium chloride filled drying tower connected to the top of the condenser. After the sweeping treatment was completed, any material collected in the dry ice-acetone cooled trap was allowed to thaw and returned to the reaction vessel through the top of the condenser. The temperature was raised to the desired level using an oil bath which was composed of an all glass container [bottom part of a resin flask] heated with a nichrome heating coil controlled by a "Variac."

B. Evaluation of Monomer Reactivity Ratios

A series of copolymerizations of itaconic anhydride (M_1) and each of the four comonomers (M_2) were carried out at the molar ratios of:

M_1/M_2: 1/9, 2/8, 3/7, 4/6, 5/5, 6/4, 7/3, 8/2 and 9/1

Each reaction was allowed to proceed to approximately 5% conversion to polymer, when it was stopped and the copolymer isolated according to the appropriate specific procedure described for the copolymerization in each solvent system.

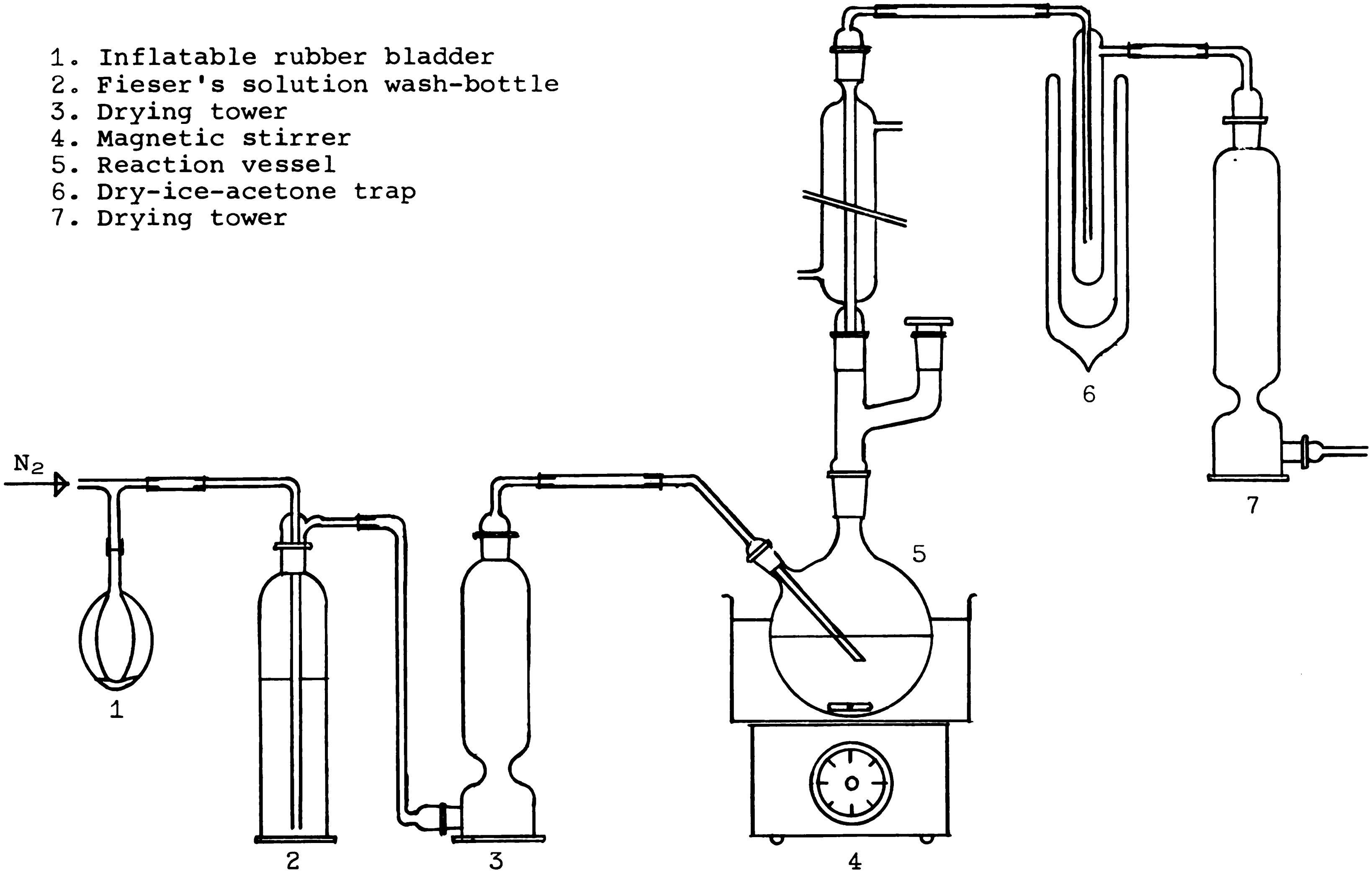


Figure 1. Schematic drawing of the apparatus used for the polymerization experiments.

The percent polymerization was calculated according to:

$$\text{Percent polymerization} = \frac{\text{weight of polymer}}{\text{total weight of monomers}} \times 100$$

The copolymers were analyzed for the quantity of the moiety of the anhydride and the comonomer moiety in the copolymers. A copolymerization composition graph was obtained by plotting m_1 as the ordinate and M_1 as the abscissa where:

M_1 = Mole fraction of itaconic anhydride in the initial reaction mixture

m_1 = Mole fraction of itaconic anhydride moiety in the copolymer.

The determinations of copolymer compositions were carried out by elemental analysis, or by infra-red spectroscopy, or by both as specified for each system.

I. Procedure for Copolymerization in Benzene:

A measured amount of anhydrous benzene, sufficient to make the total molarity of the reaction mixture equal to 0.2 molar, was introduced into the reaction flask. The calculated amount of itaconic anhydride (M_1) was then added and allowed to dissolve at room temperature. In most cases, only ten minutes were needed for the anhydride to dissolve. To this solution, the calculated amount of the comonomer (M_2) was then added and the flask was inserted into the polymerization apparatus. The catalyst-benzoyl peroxide was added to the reaction mixture and allowed to dissolve. The catalyst concentration was always kept at 0.2% wt./vol. The clear reaction mixture was then subjected to the previously described sweeping process to eliminate oxygen. The reaction temperature was then raised to reflux temperature (about 80°C.) and the time was recorded. The reaction was maintained at all times under a dry nitrogen atmosphere.

When the desired percent polymerization (as indicated by visual inspection of the amount of copolymer precipitated) had occurred, the reaction was stopped and the contents of the reaction flask were transferred quantitatively into a bottle and immersed in a dry ice-acetone mixture for at least ten minutes to quench the reaction. It was then removed and allowed to thaw. The copolymer was isolated by centrifugation and washed several times with hot benzene to remove any traces of itaconic anhydride that might remain. To insure that the copolymer was free from any monomeric itaconic anhydride, a portion of the last benzene-washing was evaporated. If no residue was obtained, it was assumed that the copolymer was free of monomers. The copolymer was dried at 56°C. under reduced pressure (0.2 m.m.) for twenty-four hours and weighed.

II. Procedure for Copolymerization in Tetrahydrofuran:

The copolymerization of itaconic anhydride (M_1) and two comonomers (M_2) namely vinyl acetate and 2-chloroethyl acrylate was studied in tetrahydrofuran.

The copolymerization procedure was the same as described for the polymerization in benzene. After the reaction mixture was removed from the dry ice-acetone bath, the following steps were taken to isolate and purify each copolymer sample.

The reaction mixture was concentrated by evaporating the tetrahydrofuran at room temperature (25^{o}C. maintained by a water bath) under reduced pressure (about 20 m.m.). The volume was reduced to 50 ml. This treatment was necessary in order to obtain a precipitate that could be isolated from the reaction mixture. The concentrated reaction mixture was quantitatively transferred into a vial and kept in a refrigerator for at least twenty-four hours. During that time most of the unreacted itaconic anhydride crystallized out. This procedure was used to remove excess itaconic anhydride that would be precipitated by the anhydrous ether and thus contaminate the precipitated copolymer. The polymer was precipitated using ten volumes of anhydrous ether to one volume of the reaction mixture (500 ml. ether). Diethyl ether was found to be the best non-solvent for precipitating the copolymers prepared in this work and yielded solid easy-to-handle precipitates. The copolymer was separated by centrifugation and washed several times in the centrifuge tube with anhydrous ether followed by a wash with anhydrous benzene in order to remove the last traces of monomeric itaconic anhydride. The copolymers were then dried at 56^{o}C. under reduced pressure (0.2 m.m.) for twenty-four hours.

C. Calculation of the Reactivity-ratio Values

The intersection method originated by Mayo and Lewis (20) was used to determine the monomer reactivity ratios. This method is as follows:

The copolymerization equation:

$$\frac{d[M_1]}{d[M_2]} = \frac{M_1}{M_2} \cdot \frac{r_1M_1 + M_2}{r_2M_2 + M_1} \qquad \text{------ (5)}$$

can be rearranged to

$$r_2 = \frac{M_1}{M_2} \left[\frac{m_2}{m_1} \left(1 + \frac{M_1}{M_2} r_1\right) - 1\right] \qquad \text{------ (6)}$$

assuming that $\frac{d[M_1]}{d[M_2]} = \frac{m_1}{m_2}$ for very low conversions.

Where:

M_1 = mole percent of itaconic anhydride in the initial amount of monomers used in a copolymerization

M_2 = mole percent of the comonomer in the initial amount of monomers used

m_1 = mole percent of the itaconic anhydride moiety in copolymer

m_2 = mole percent of the comonomer moiety in copolymer.

Substitution of the values of M_1, M_2, m_1 and m_2 in equation (2) was made for the various reactions. This resulted in a series of equations which gave straight line graphs when r_1 was plotted against r_2.

Assumed values of r_1 (from +0.1 to -0.1) were substituted in equation (2) to give corresponding values of r_2. A sample calculation using data for experiment 5 recorded in Table 3 follows:

$M_1 = 0.5$ and $m_1 = 0.845$

$M_2 = 0.5$ $m_2 = 0.155$

$$r_2 = \frac{M_1}{M_2} \left[\frac{m_2}{m_1} \left(1 + \frac{M_1}{M_2} r_1\right) - 1\right]$$

$$= 1 \left[0.183 \left(1 + 1\ r_1\right) - 1\right]$$

Taking

$r_1 = +0.1$ $r_2 = -0.799$

$r_1 = 0.0$ $r_2 = -0.817$

$r_1 = -0.1$ $r_2 = -0.835$

Two substitutions of r_1 in equation (2) are sufficient to obtain two values for r_2 which would determine the straight line r_1 vs r_2 for a particular copolymerization reaction. However, a third value of r_1 was assumed and a third value of r_2 evaluated to serve as a check on the calculation.

The r_1 values were plotted against the respective r_2 for each system studied. This was done for each of several copolymerizations. If there were no experimental error, all lines would meet at the same point, the coordinates of which are the proper values of r_1 and r_2. However, an average point of intersection had to be determined which represented the best experimental pair of r_1 and r_2 values (see Figures 9, 13, 21, 25, 28, 31).

D. Infra-red Analysis of the Copolymers

Infra-red spectra of the homopolymers and the copolymers were obtained using a "Perkin-Elmer-237B" spectrophotometer, and matching sodium chloride cells. The slit opening was set at 5 and the scanning was done at the slow speed [7 min./ spectrum].

The procedure of analysis was as follows:

Solutions of 0.5% of each of the homopolymers in anhydrous acetonitrile were prepared. The spectra for these solutions were obtained and are shown in Figures 2, 3 and 15. A standard curve was made by mixing the solution of polyitaconic anhydride with that of either polyvinyl acetate or poly-(2-chloroethyl acrylate) in the following proportions:

20/80 , 40/60 , 60/40 , 80/20

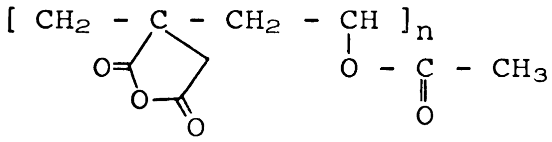
The infra-red spectra for these mixtures were obtained and a standard curve was made by plotting the known concentrations of polyitaconic anhydride versus the peak-areas of the anhydride peaks at 1864 cm^{-1}. A straight line graph was obtained. A "Keuffel & Esser 4236" planimeter was used to measure the peak-areas.

To analyze the copolymers, 0.5% solutions in anhydrous acetonitrile were prepared and their spectra were obtained. The areas of the anhydride peaks at 1864 cm^{-1} were measured, and the content of itaconic anhydride moiety in the copolymer was determined using the standard curve. The infra-red spectra were obtained in duplicates to eliminate any experimental error or instrumental variations.

RESULTS

I. Copolymerization of Itaconic Anhydride and Vinyl Acetate

A theoretical repeating unit for a completely alternating copolymer of itaconic anhydride-vinyl acetate ($r_1 \cdot r_2 \simeq 0$) is illustrated by the following formula:



Itaconic anhydride was copolymerized with vinyl acetate in two solvents: a) benzene, where the polymer precipitates out during the reaction, and b) tetrahydrofuran where the polymer stays in solution and is isolated by precipitation with diethyl ether.

The data from which the reactivity ratios were calculated, are shown in Table 3. The copolymers obtained were analyzed by infra-red following the change in the area of the anhydride peak at 1860 cm^{-1}. Figures 2 and 3 show the spectra of polyitaconic anhydride, and polyvinyl acetate respectively. It can be seen that the polyitaconic anhydride has two carbonyl peaks, one at 1864 cm^{-1}, the other at 1785 cm^{-1}. The polyvinyl acetate spectrum shows an ester carbonyl peak at 1739 cm^{-1}. Figure 4 shows the infra-red carbonyl absorbances of mixtures of 0.5% solutions of polyitaconic anhydride and polyvinyl acetate with distinct peaks at 1864 cm^{-1}, 1785 cm^{-1}, and 1739 cm^{-1}. The areas of the peaks at 1864 cm^{-1} were measured and plotted against the anhydride content as shown in Figure 5. Figures 6 and 7 show the infra-red carbonyl absorbances of the copolymers obtained from the different copolymerization experiments. The areas of the peaks at 1860 cm^{-1} were measured and the respective anhydride contents were determined using the graph in Figure 5. A copolymer composition graph was then drawn and is shown in Figure 8. The copolymerization equation was solved for r_1 and r_2 values for the copolymers of several experiments and the graphical solution is shown in Figure 9. The data from which the reactivity ratios were calculated for the copolymerization in tetrahydrofuran are shown in Table 4. Figures 10 and 11 show the infra-red absorbances of the different copolymers. Figure 12 shows the copolymer composition graph, and Figure 13 shows the graphical solution of the copolymerization equation.

Table 3. Reactivity Ratio Data for Itaconic Anhydride-Vinyl Acetate Copolymerization in Benzene

Exp. No.	M_1 Grams	M_1 Mole Fraction	Yield Grams	Conversion Percent	Peak Area Sq. in.	m_1 Mole Fraction	Reaction Time Minutes
1	2.24	0.1	0.632	3.57	0.470	0.600	80
2	4.48	0.2	0.713	3.91	0.540	0.710	75
3	6.72	0.3	1.050	5.59	0.580	0.770	75
4	8.96	0.4	0.857	4.44	0.605	0.810	60
5	11.20	0.5	0.460	2.32	0.625	0.845	55
6	13.44	0.6	0.711	3.51	0.655	0.890	60
7	15.68	0.7	0.739	3.52	0.665	0.910	60
8	17.92	0.8	0.714	3.34	0.685	0.940	60
9	20.16	0.9	1.142	5.22	0.705	0.970	60

M_1 = Mole fraction of itaconic anhydride in reaction mixture.
m_1 = Mole fraction of itaconic anhydride moiety in copolymer.

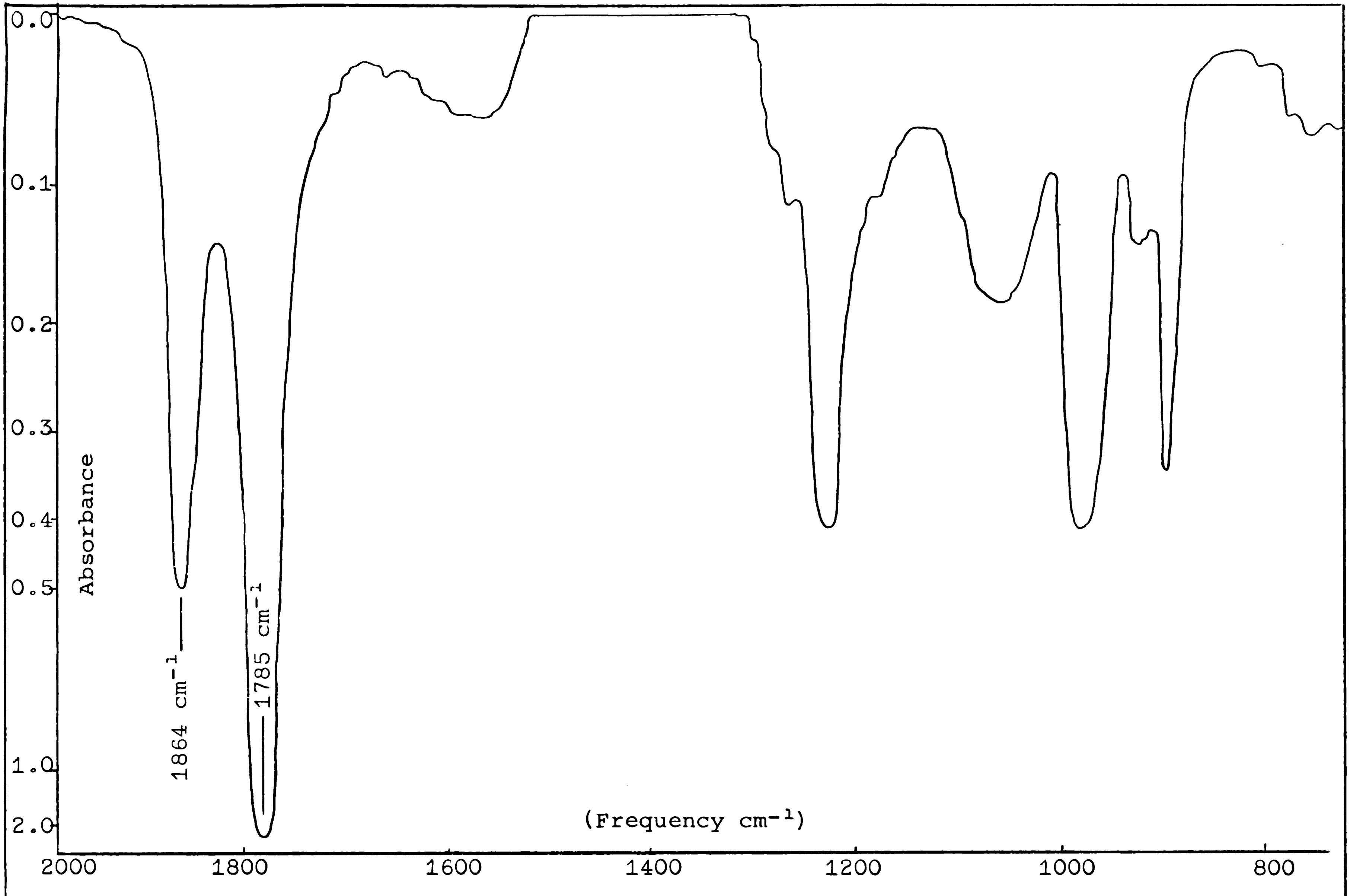


Figure 2. Infra-red spectrum of polyitaconic anhydride.

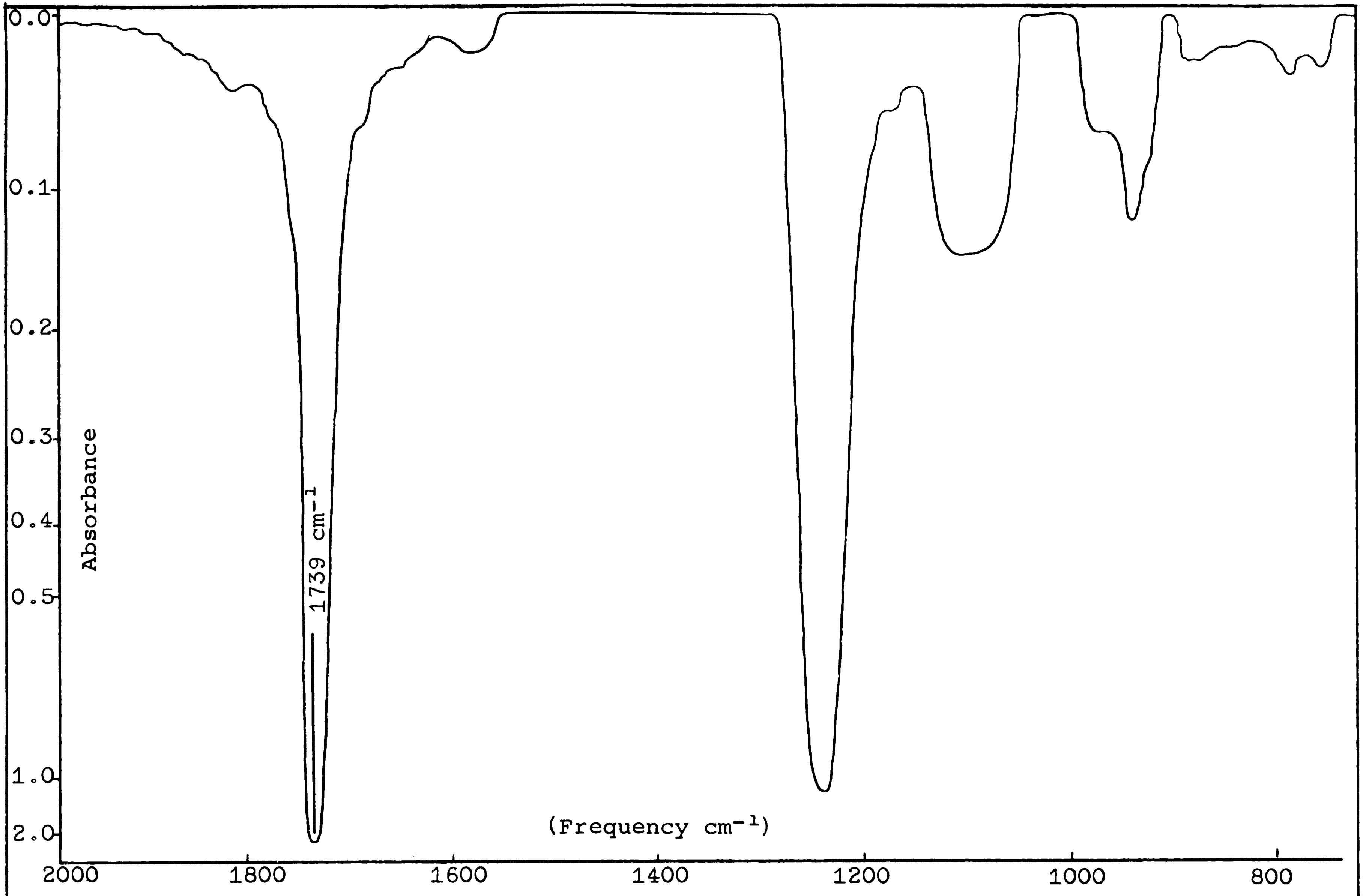


Figure 3. Infra-red spectra of polyvinyl acetate.

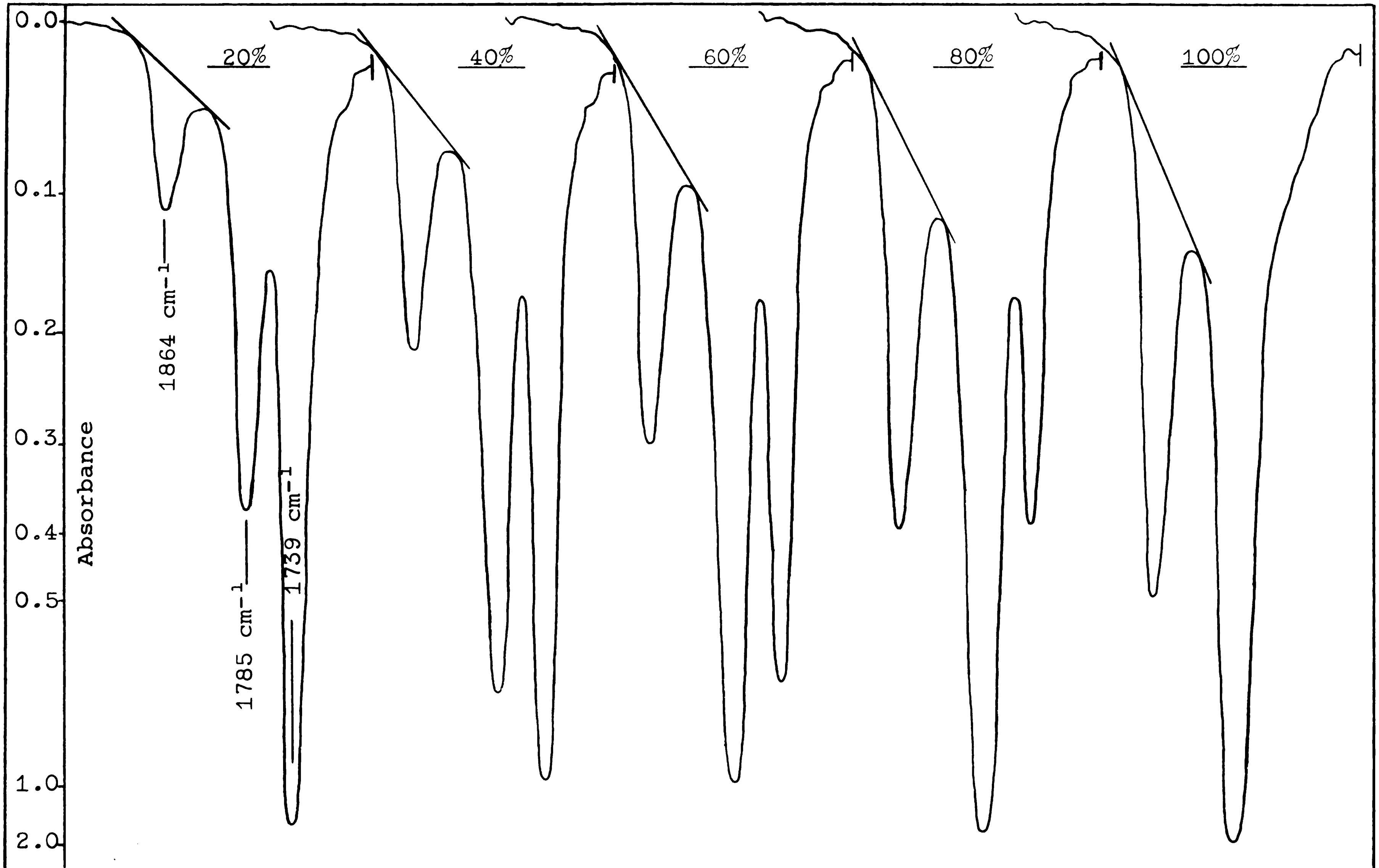


Figure 4. Infra-red carbonyl absorbances of mixtures of polyitaconic anhydride and polyvinyl acetate arranged in increasing order of the anhydride content.

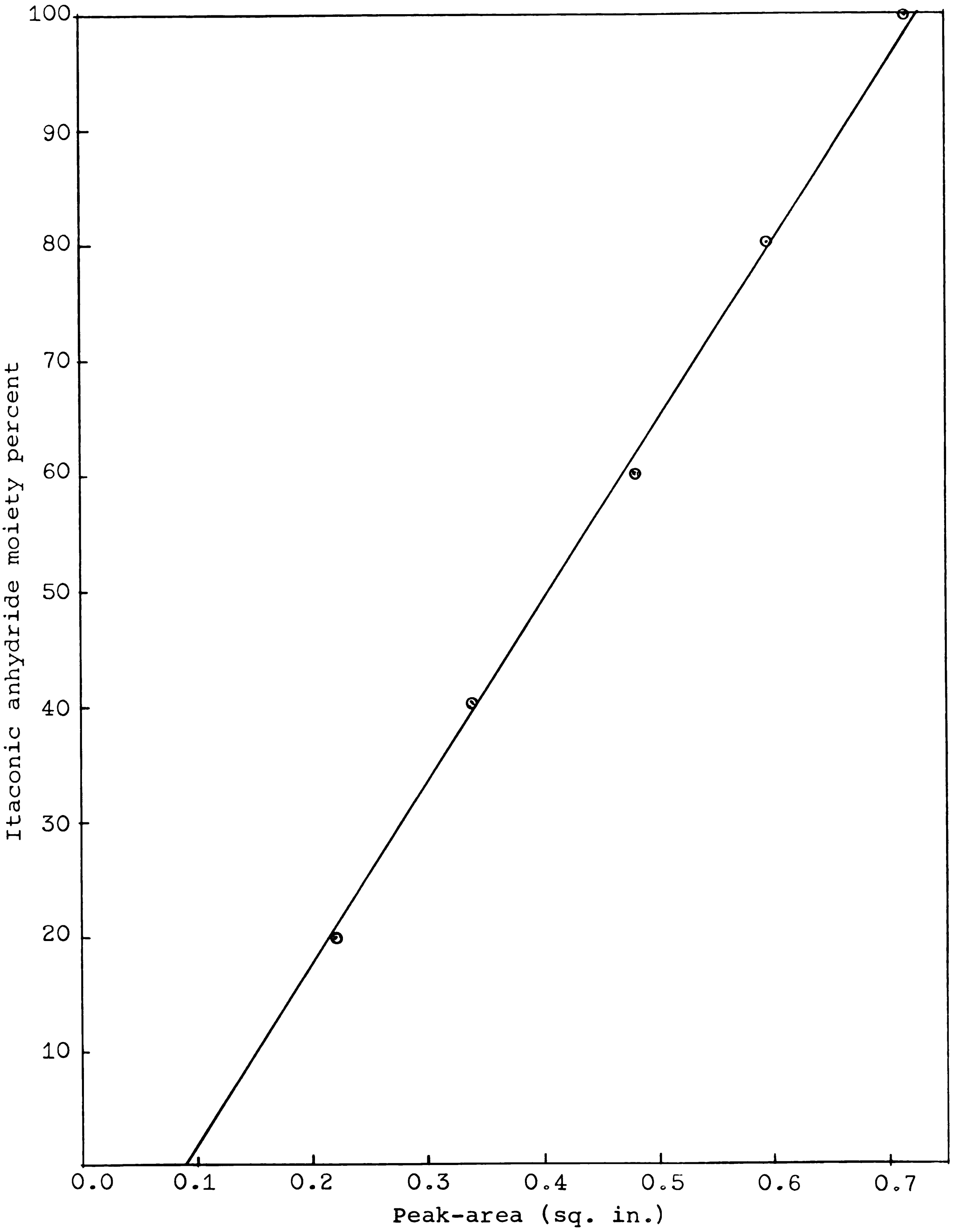


Figure 5. A graph of the area of the anhydride peak at 1864 cm^{-1} against the anhydride moiety content in mixtures of polyitaconic anhydride and polyvinyl acetate.

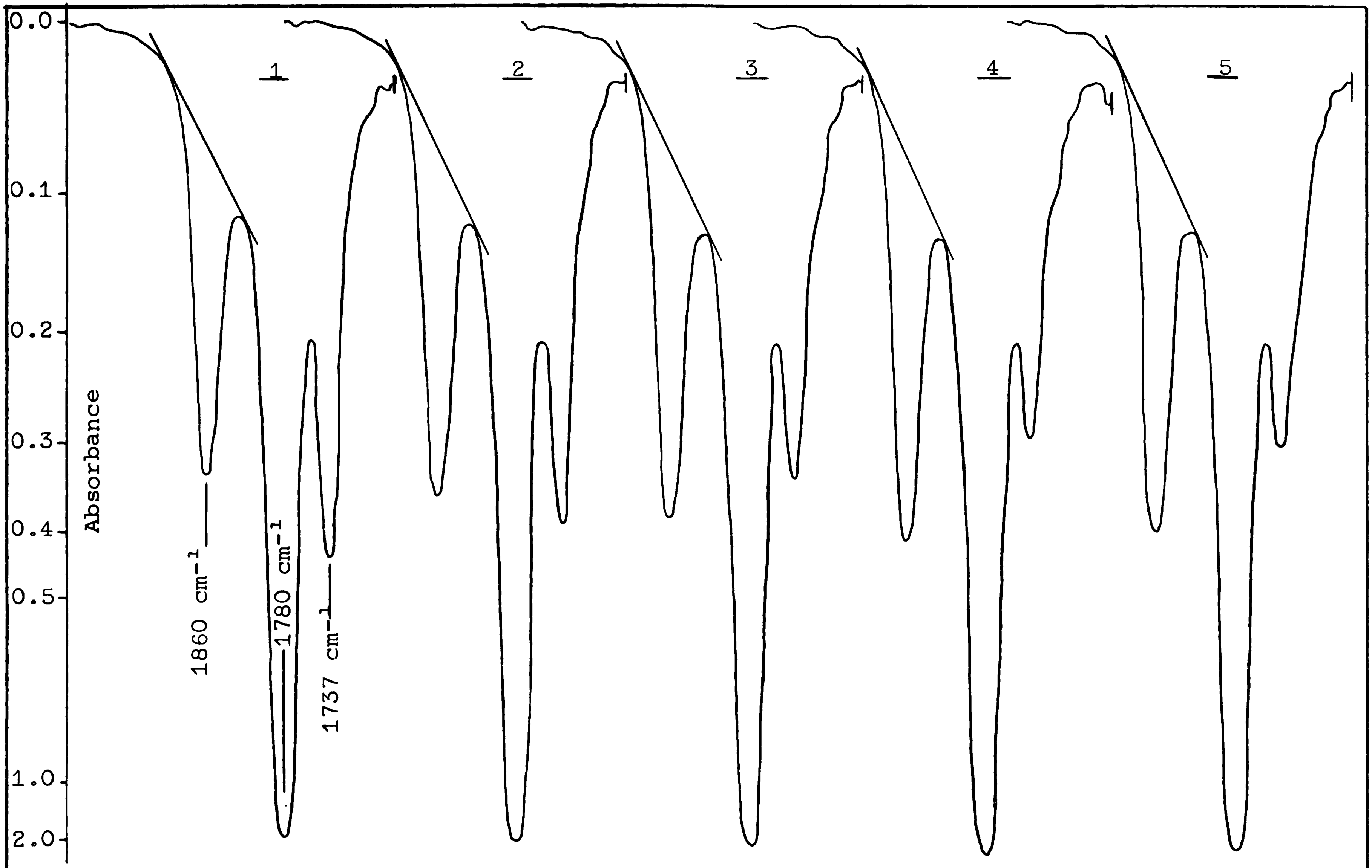


Figure 6. Infra-red carbonyl absorbances of copolymers obtained from copolymerization of itaconic anhydride and vinyl acetate in benzene (Experiments 1-5 in Table 3).

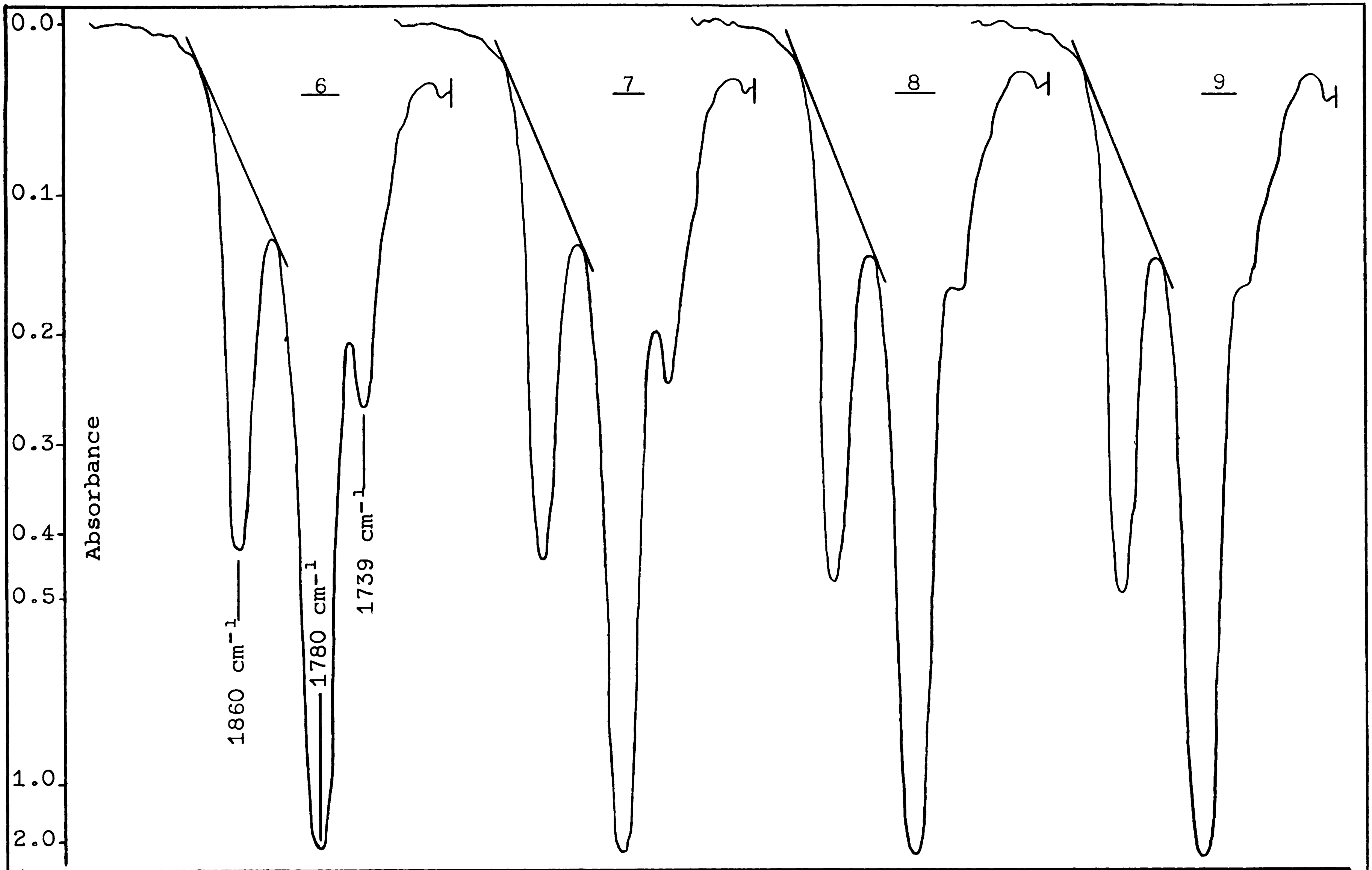


Figure 7. Infra-red carbonyl absorbances of copolymers obtained from copolymerization of itaconic anhydride and vinyl acetate in benzene (Experiments 6-9 in Table 3).

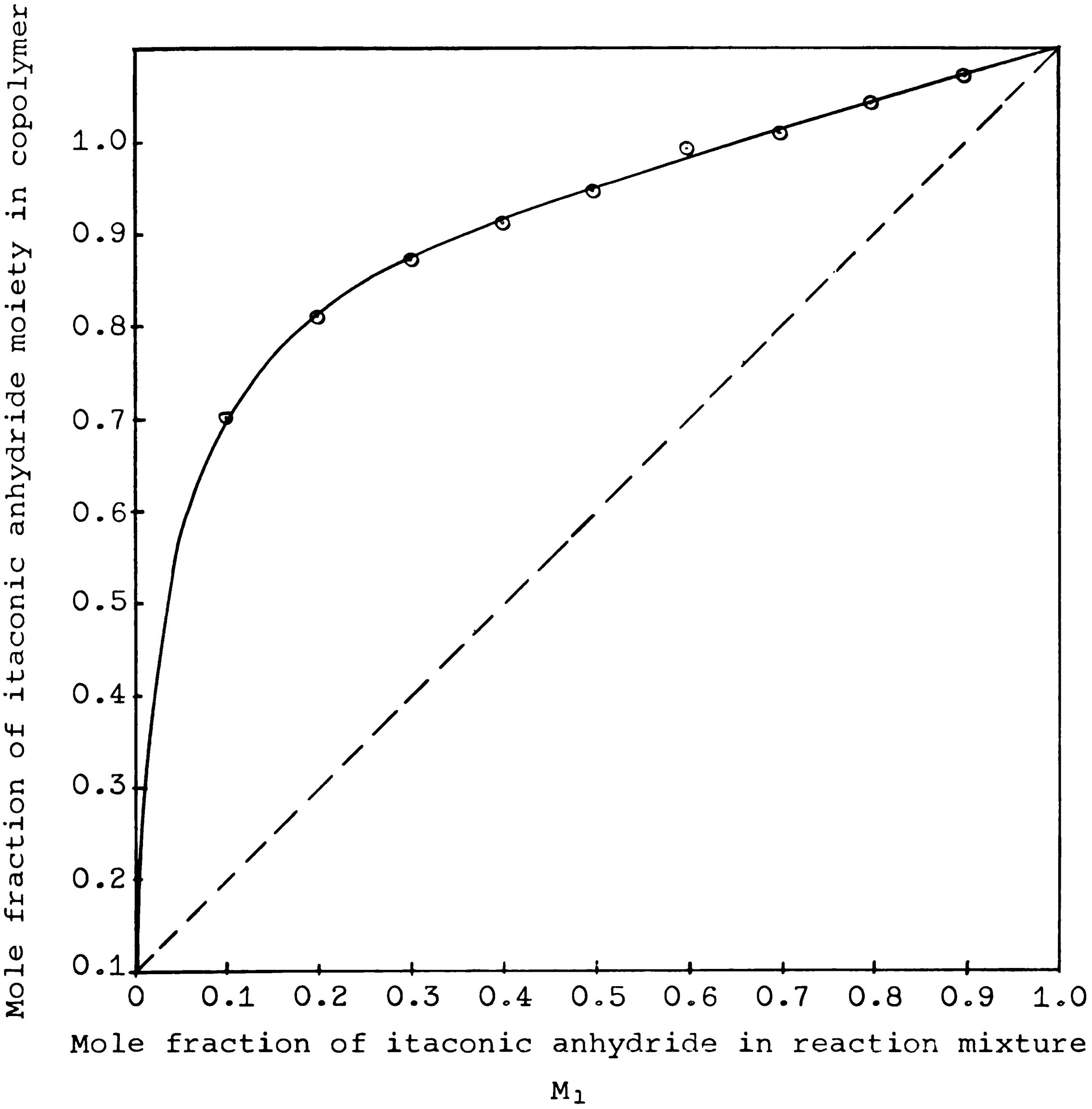


Figure 8. Copolymer composition curve of itaconic anhydride-vinyl acetate copolymerization in benzene.

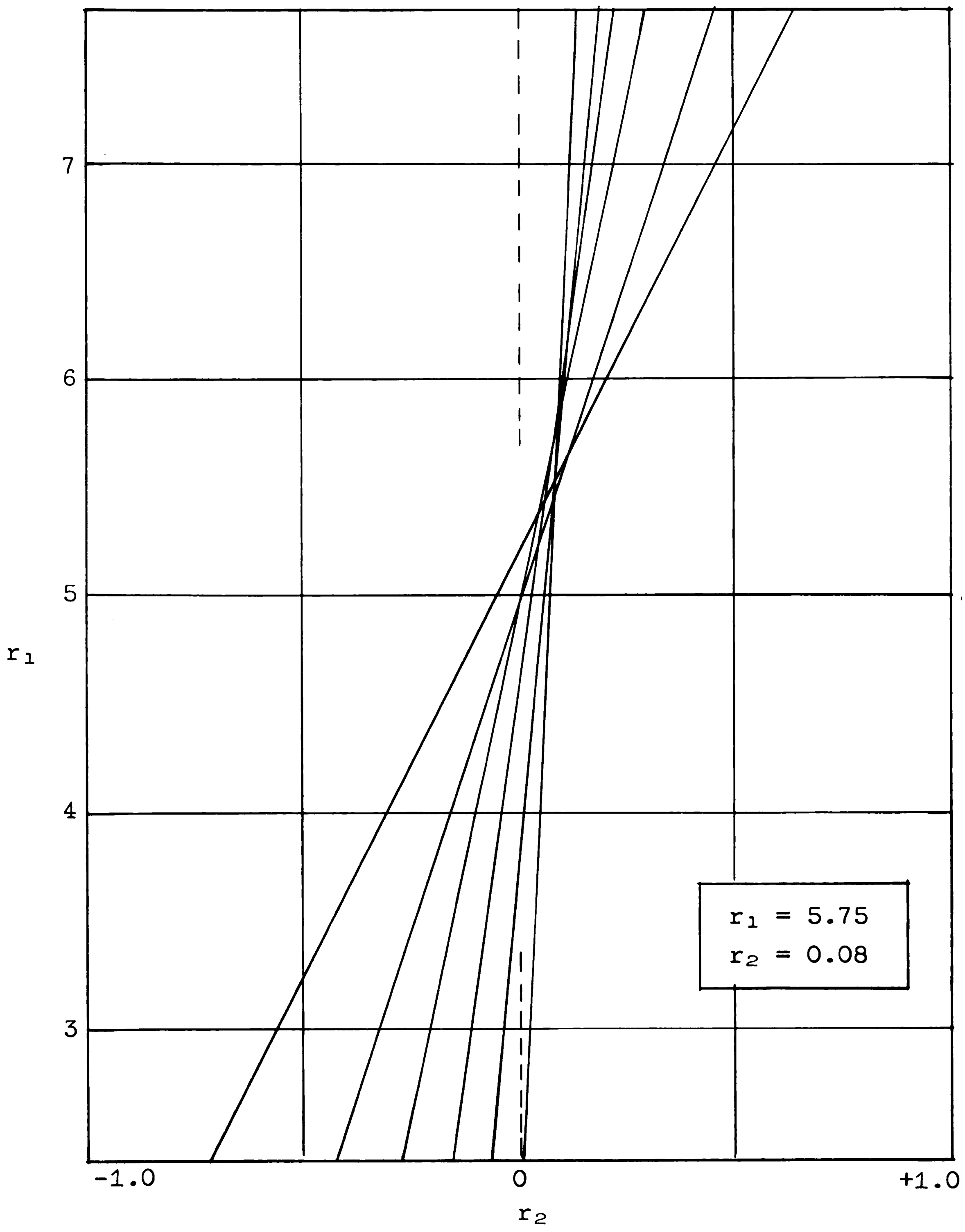


Figure 9. Graphical solution of copolymerization equation for itaconic anhydride-vinyl acetate in benzene.

Table 4. Reactivity Ratio Data for Itaconic Anhydride-Vinyl Acetate Copolymerization in Tetrahydrofuran

Exp. No.	M_1		Yield Grams	Conversion Percent	Peak Area Sq. in.	m_1 Mole Fraction	Reaction Time Minutes
	Grams	Mole Fraction					
1	1.40	0.1	0.60	5.40	0.385	0.46	180
2	2.80	0.2	0.52	4.59	0.470	0.60	210
3	4.20	0.3	0.68	5.88	0.530	0.70	210
4	5.60	0.4	0.71	5.89	0.565	0.75	210
5	6.45	0.5	0.66	5.33	0.605	0.81	210
6	8.40	0.6	0.56	4.41	0.620	0.84	220
7	9.80	0.7	0.52	3.91	0.630	0.86	150
8	11.20	0.8	0.67	5.01	0.660	0.90	210
9	12.60	0.9	0.82	6.00	0.690	0.94	240

M_1 = Mole fraction of itaconic anhydride in reaction mixture.
m_1 = Mole fraction of itaconic anhydride moiety in copolymer.

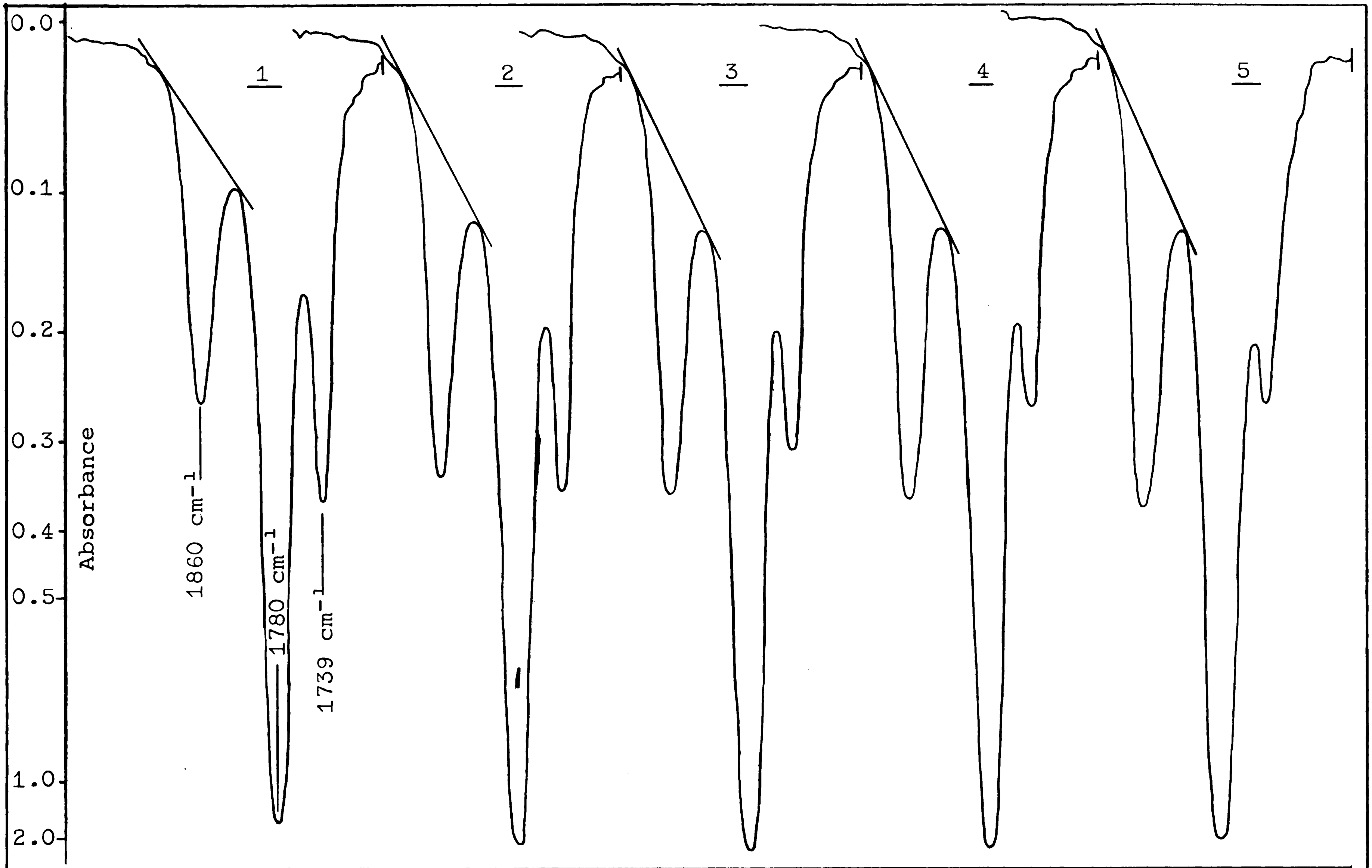


Figure 10. Infra-red carbonyl absorbances of copolymers obtained from copolymerization of itaconic anhydride and vinyl acetate in tetrahydrofuran (Experiments 1-5 in Table 4).

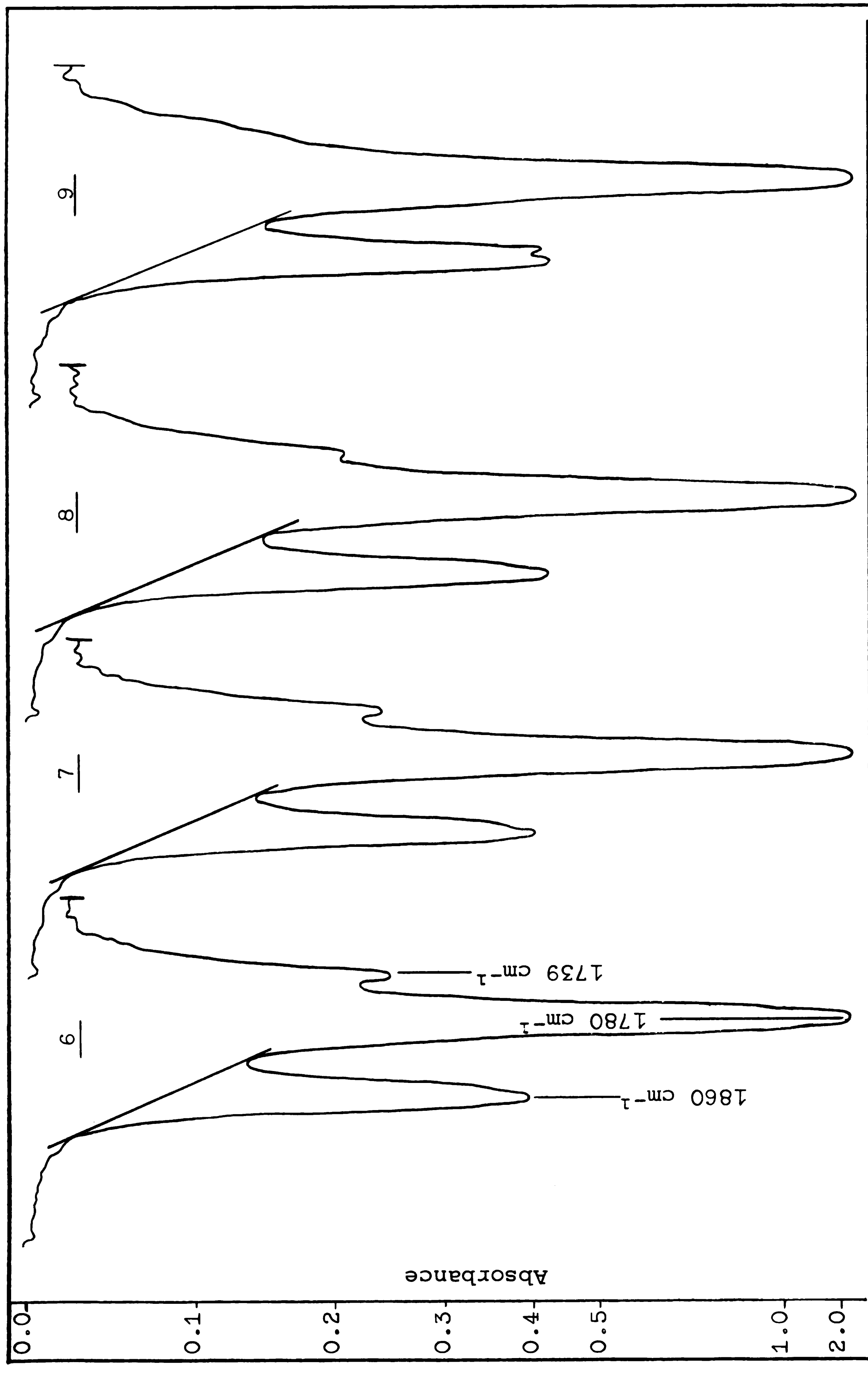


Figure 11. Infra-red carbonyl absorbances of copolymers obtained from copolymerization of itaconic anhydride and vinyl acetate in tetrahydrofuran (Experiments 6-9 in Table 4).

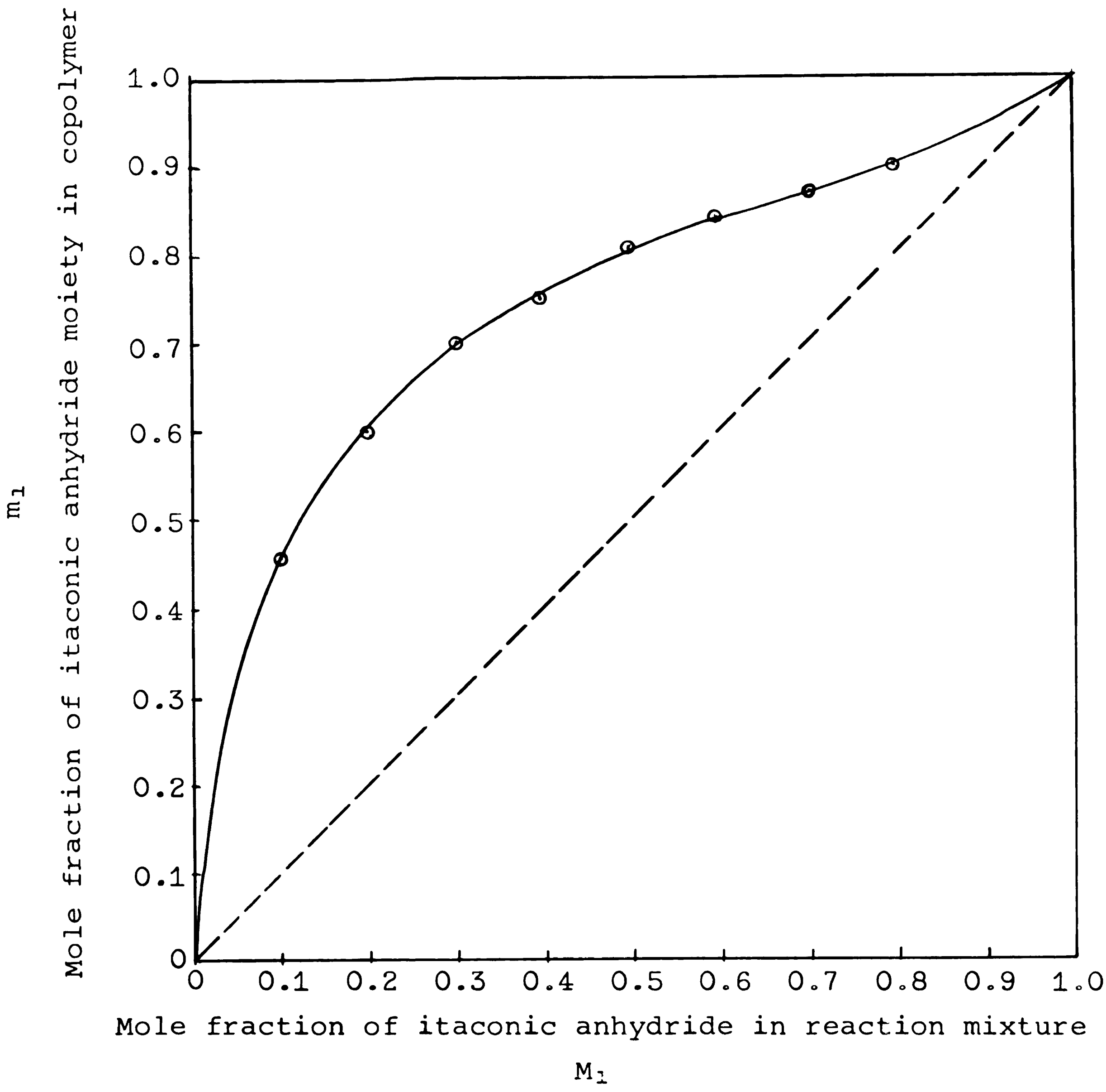


Figure 12. Copolymer composition curve of itaconic anhydride-vinyl acetate copolymerization in tetrahydrofuran.

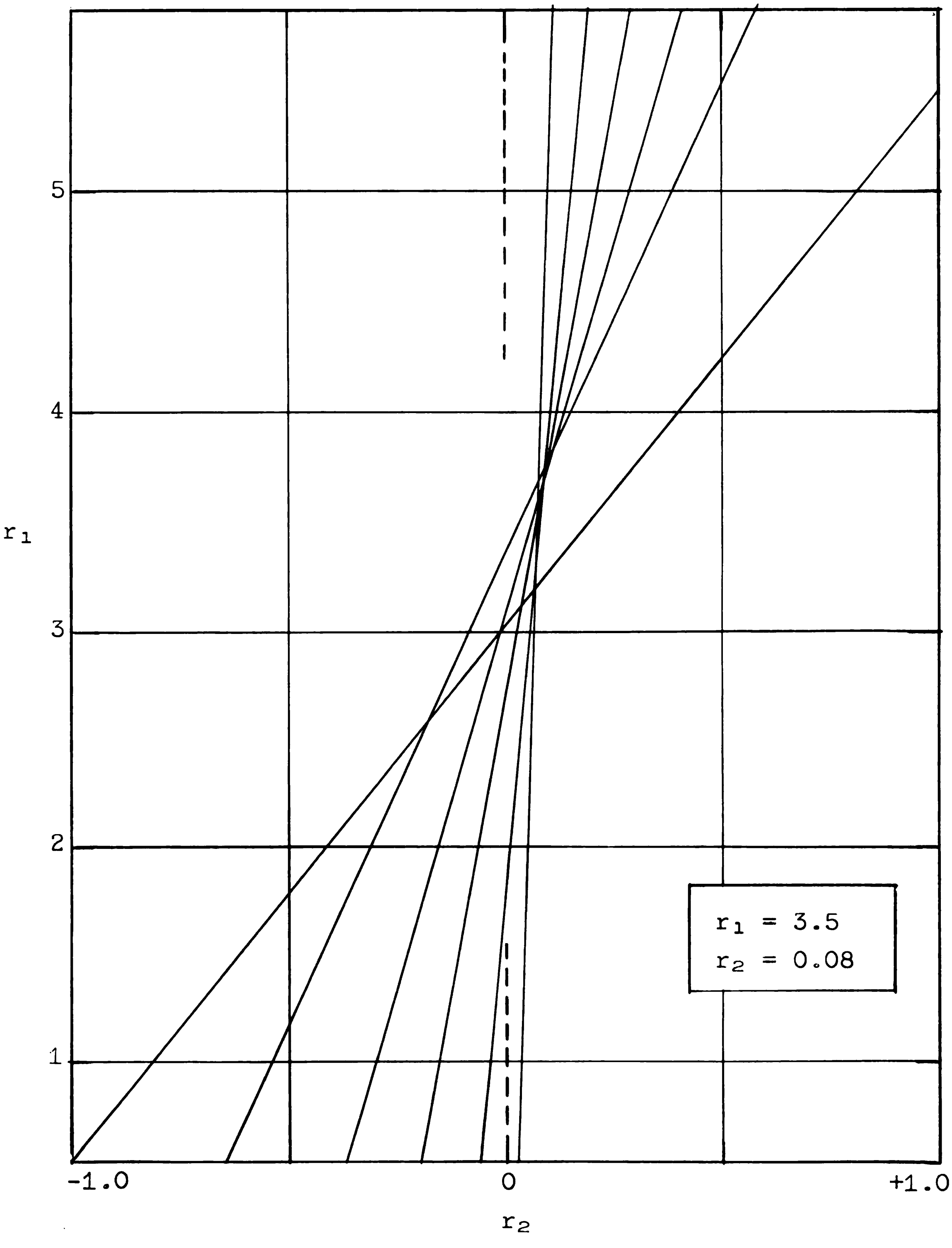
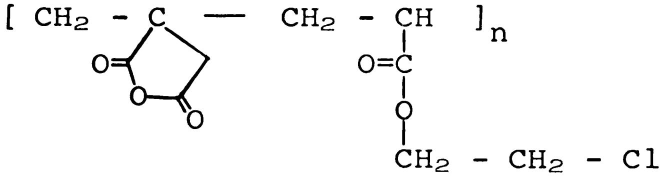


Figure 13. Graphical solution of copolymerization equation for itaconic anhydride-vinyl acetate in tetrahydrofuran.

II. Copolymerization of Itaconic Anhydride and 2-Chloroethyl Acrylate

A theoretical repeating unit for a completely alternating copolymer of itaconic anhydride--2-chloroethyl acrylate ($r_1 \cdot r_2 \simeq 0$) is illustrated by the following formula:



Itaconic anhydride was copolymerized with 2-chloroethyl acrylate in two solvents: a] benzene [the polymer precipitates out during the reaction] and b] tetrahydrofuran [the polymer stays in solution, and is isolated by precipitation by diethyl ether].

The data from which the reactivity ratios were determined are shown in Table 5. The copolymers obtained in the different experiments were analyzed by elemental analysis for chlorine content as well as by infra-red following the change in the area of the anhydride peak at 1860 cm^{-1}.

Figure 14 shows the calculated chlorine content of itaconic anhydride — 2-chloroethyl acrylate copolymers of varying anhydride content. Figure 15 shows the infra-red spectrum of poly-(2-chloroethyl acrylate), and the ester carbonyl peak at 1736 cm^{-1}. The infra-red carbonyl absorbances of mixtures of 0.5% solutions of polyitaconic anhydride and poly-(2-chloroethyl acrylate), with distinct peaks at

1860 cm^{-1}, 1782 cm^{-1} and 1736 cm^{-1}, are shown in Figure 16.

The areas of the peaks at 1860 cm^{-1} were measured and plotted against the anhydride content as shown in Figure 17. The infra-red absorbances of the copolymers obtained from different copolymerization experiments are shown in Figures 18 and 19. The areas of the peaks at 1860 cm^{-1} were measured and the respective anhydride contents were determined using the graph in Figure 17. A copolymer composition graph was then drawn and is shown in Figure 20. The copolymerization equation was solved for r_1 and r_2 values for the copolymers of several experiments and the graphical solution of the copolymerization equation is shown in Figure 21.

The data from which the reactivity ratios were calculated for the copolymerization in tetrahydrofuran are shown in Table 6. Figures 22 and 23 show the infra-red absorbances of the different copolymers. Figure 24 shows the copolymer composition graph, and Figure 25 shows the graphical solution of the copolymerization equation.

Table 5. Reactivity Ratio Data for Itaconic Anhydride-2-Chloroethyl Acrylate Copolymerization in Benzene

Exp. No.	M_1 Grams	M_1 Mole Fraction	Yield Grams	Con- version Percent	Cl_2- Content Percent	m_1	Peak Area Sq. in.	m_1 Mole Fraction	Reaction Time Minutes
1	1.025	0.1	0.423	3.50	14.94	0.480	0.37	0.46	30
2	2.80	0.2	0.430	2.70	11.00	0.620	0.45	0.59	30
3	4.20	0.3	0.431	2.70	9.05	0.690	0.49	0.66	45
4	5.60	0.4	1.020	6.50	9.02	0.700	0.52	0.70	65
5	7.00	0.5	0.744	4.83	7.60	0.750	0.56	0.76	30
6	8.40	0.6	0.770	5.09	6.60	0.785	0.59	0.81	50
7	9.80	0.7	0.710	4.70	4.50	0.855	0.61	0.84	40
8	11.20	0.8	0.670	4.50	3.17	0.920	0.64	0.89	35
9	12.60	0.9	0.840	5.90	1.90	0.945	0.68	0.95	45

M_1 = Mole fraction of itaconic anhydride in reaction mixture.
m_1 = Mole fraction of itaconic anhydride moiety in copolymer.

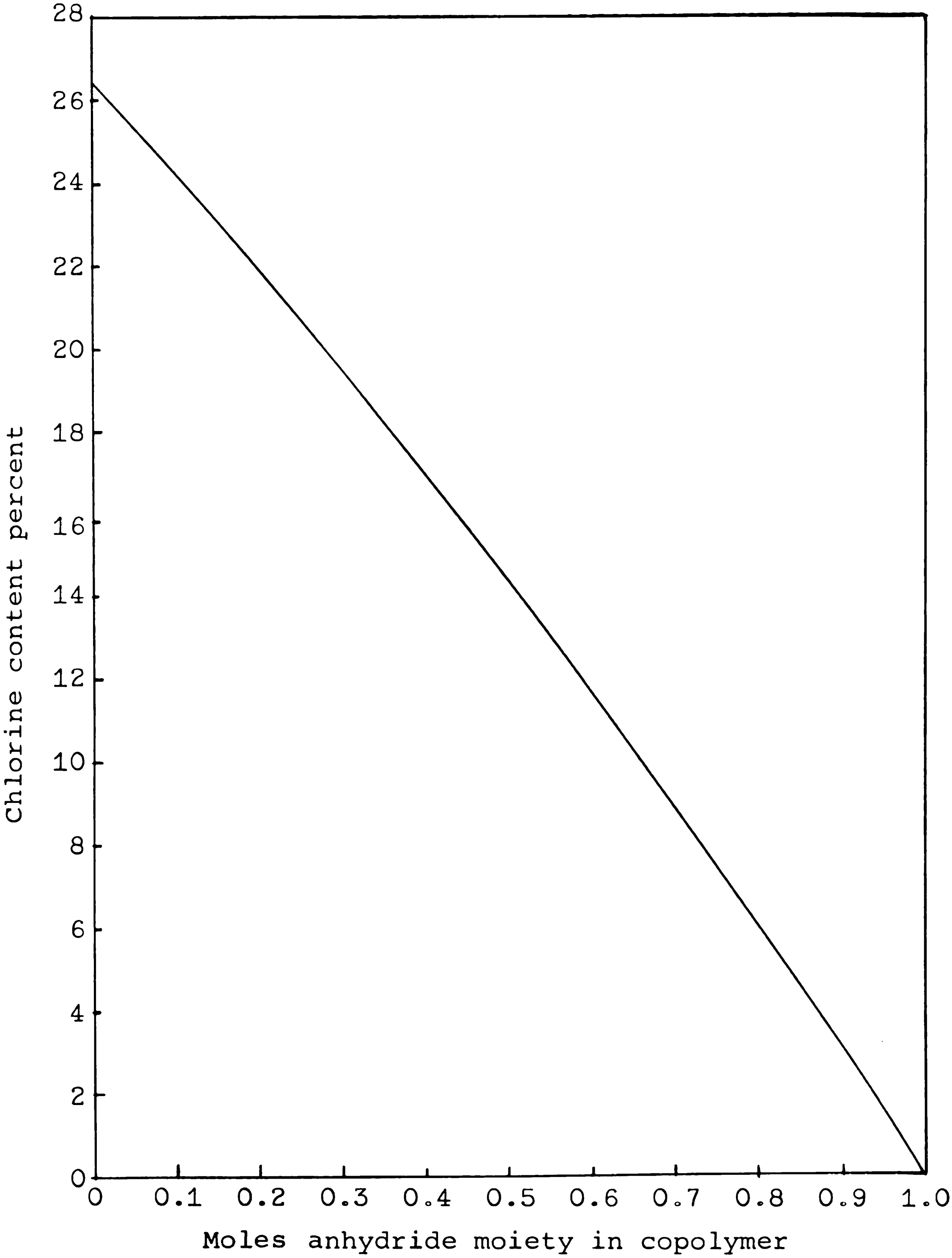


Figure 14. Calculated chlorine content in copolymers of itaconic anhydride-2-chloroethyl acrylate of varying composition.

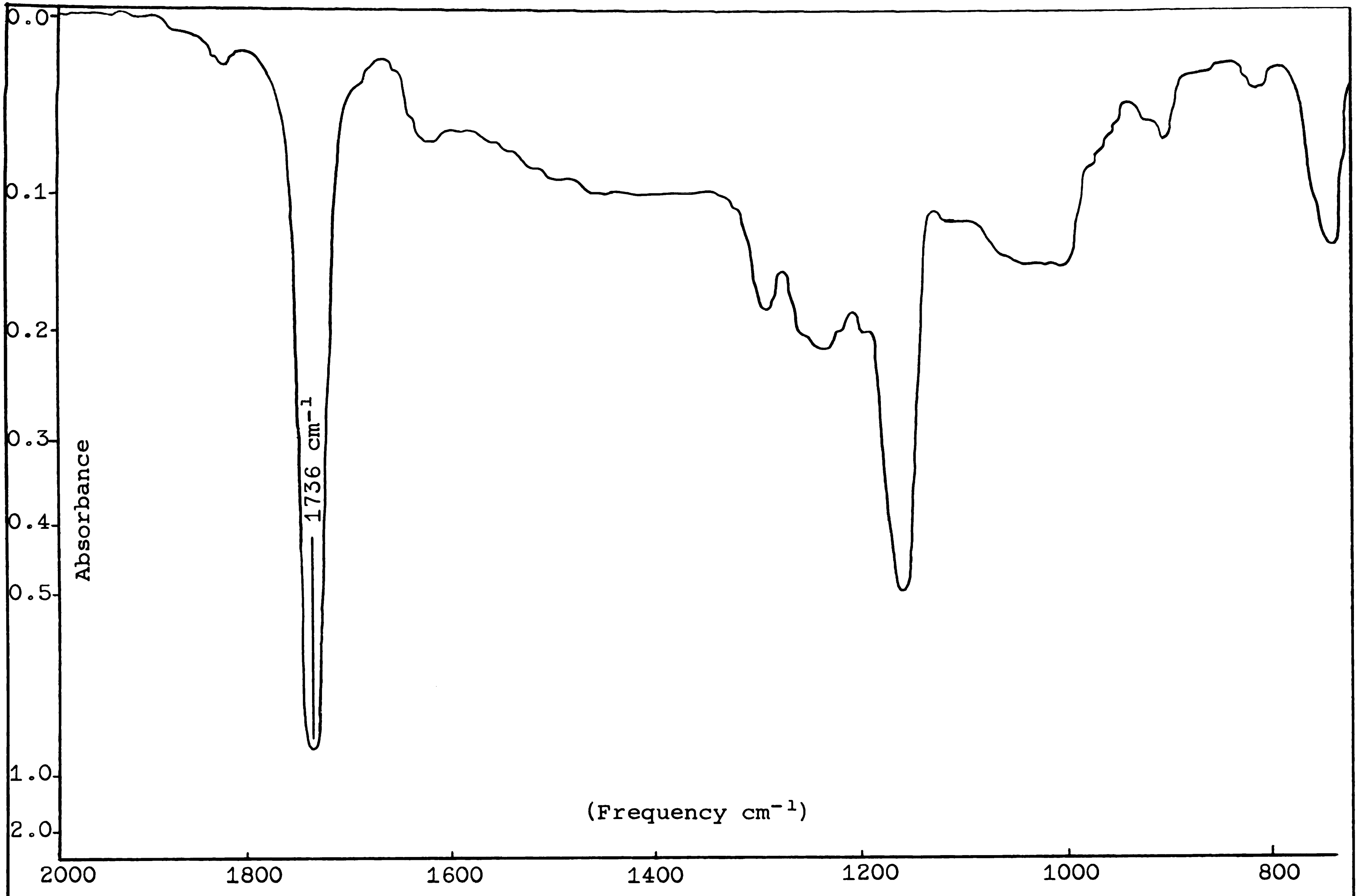


Figure 15. Infra-red spectrum of poly-(2-chloroethyl acrylate).


80°
60°
40°
20°

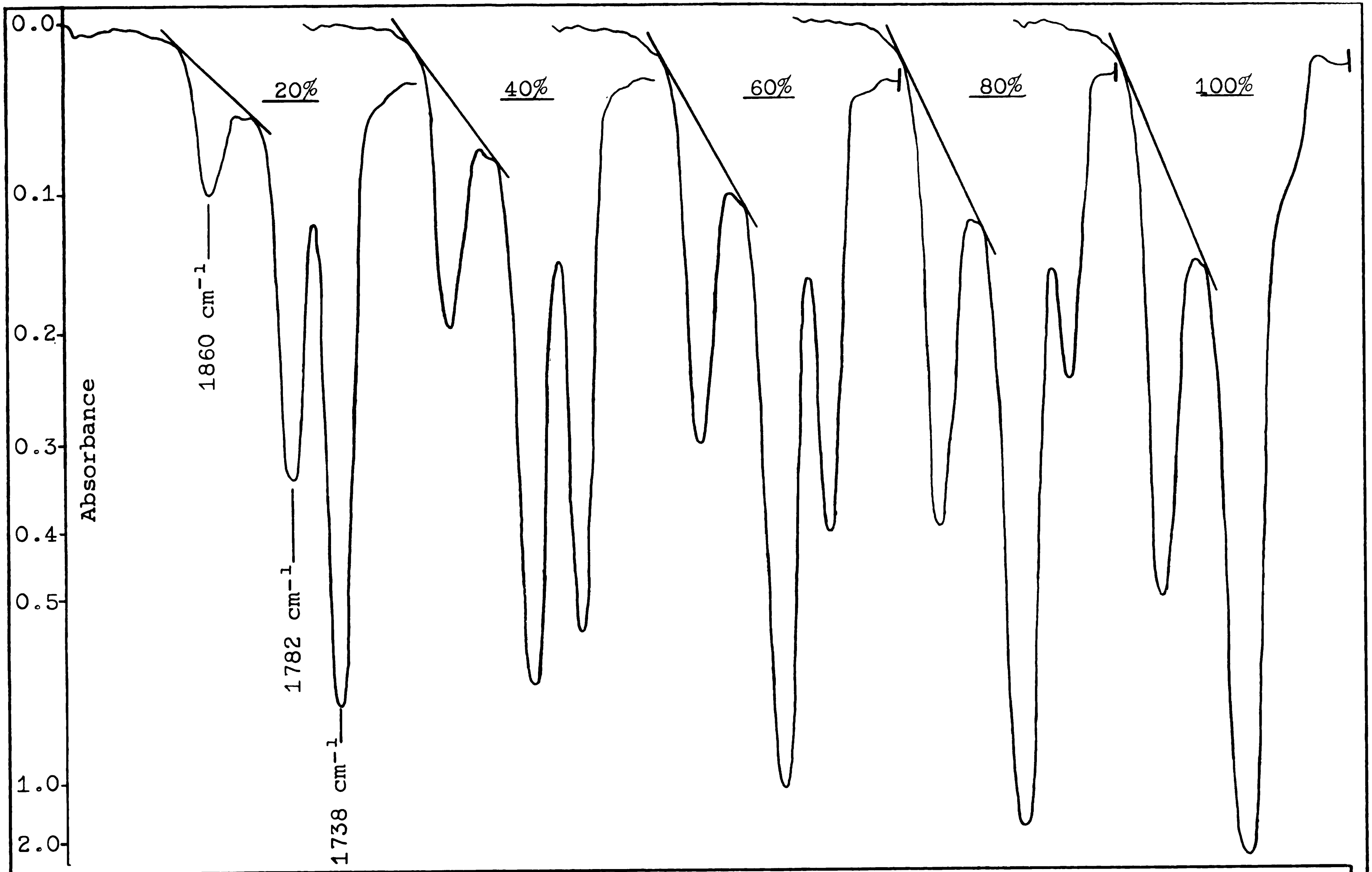


Figure 16. Infra-red carbonyl absorbances of mixtures of polyitaconic anhydride and poly-(2-chloroethyl acrylate) arranged in increasing order of the anhydride content.

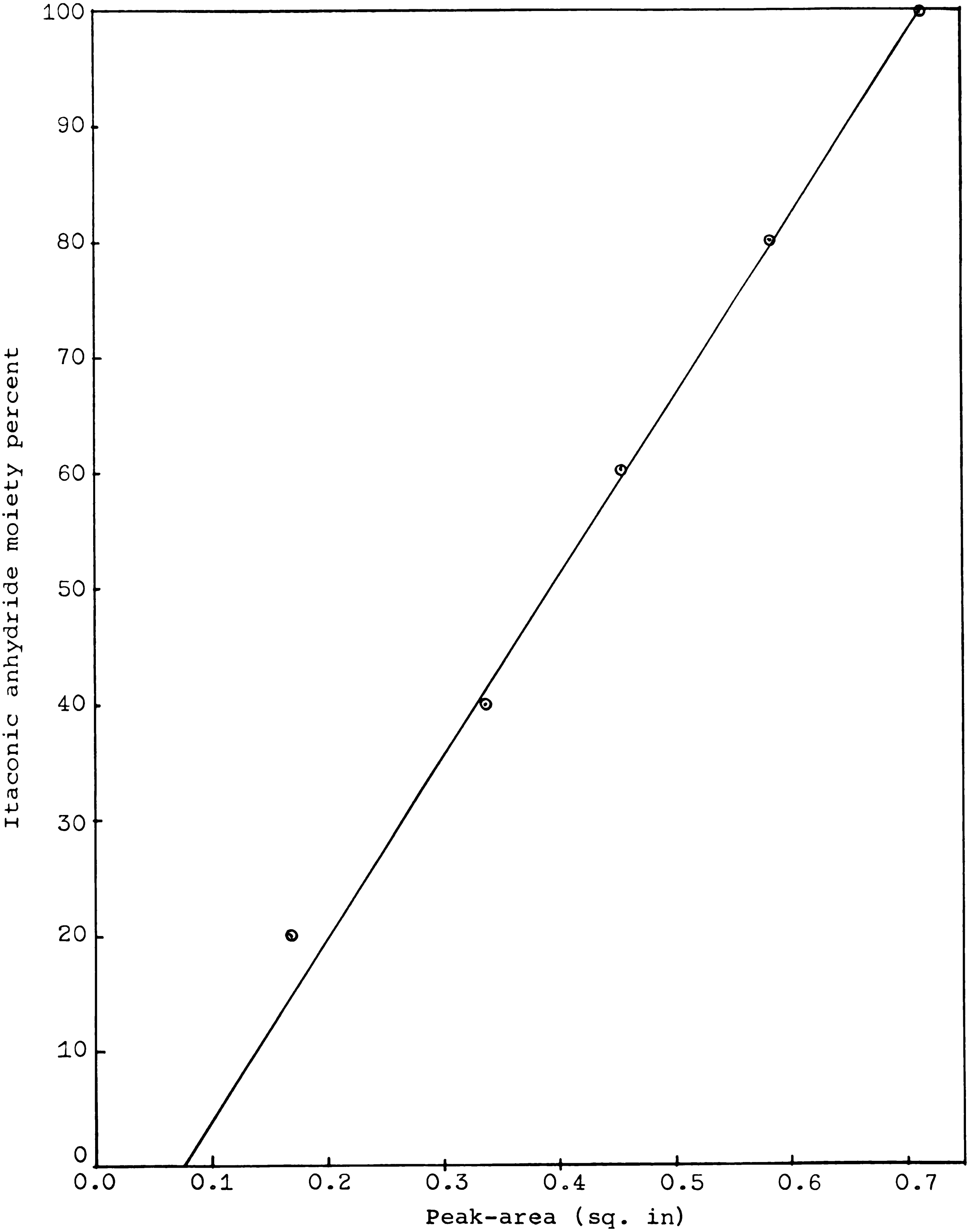


Figure 17. A graph of the area of the anhydride peak at 1860 cm^{-1} against the anhydride moiety content in mixtures of polyitaconic anhydride and poly(2-chloroethyl acrylate).

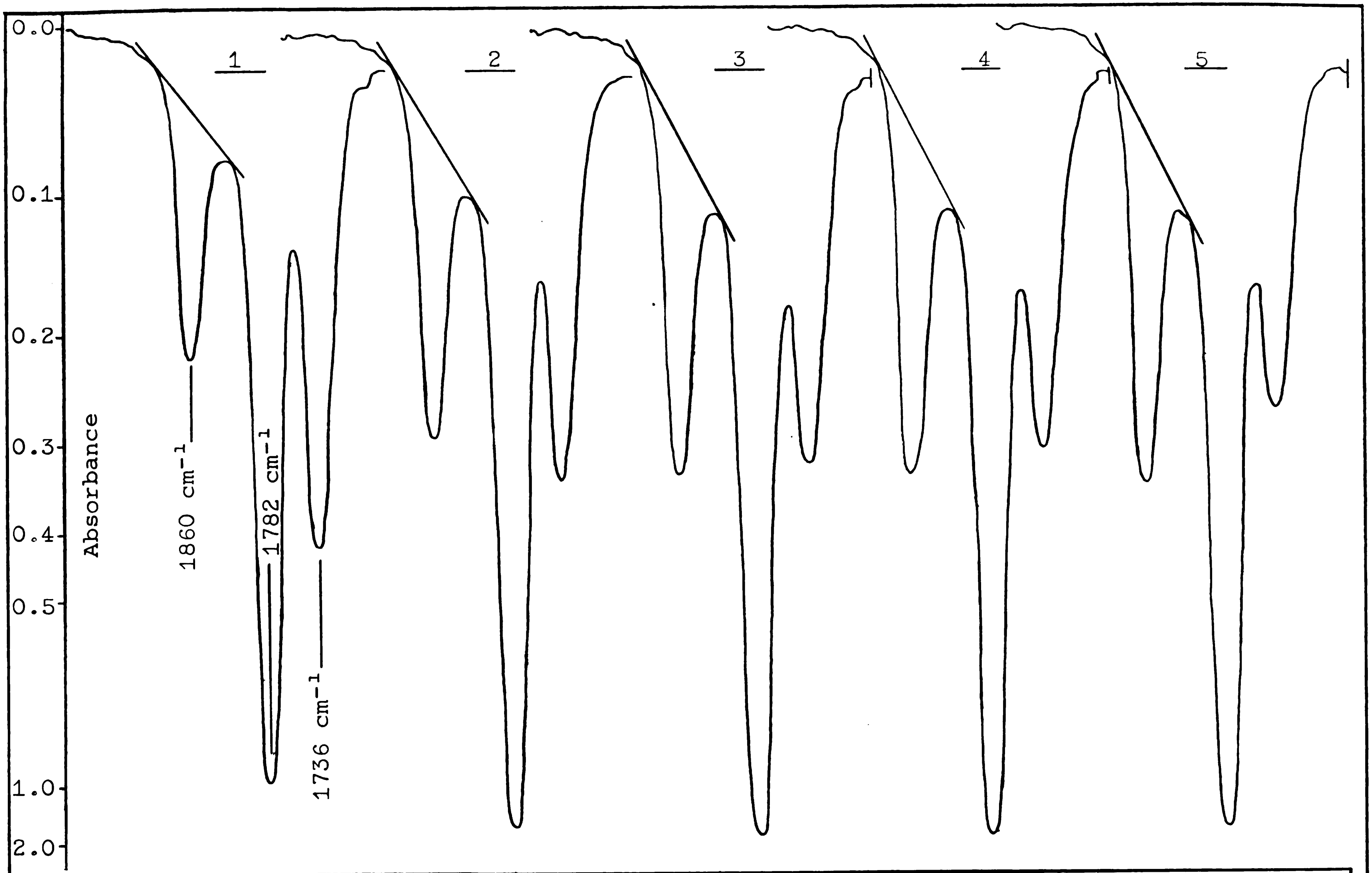


Figure 18. Infra-red carbonyl absorbances of copolymers obtained from copolymerization of itaconic anhydride and 2-chloroethyl acrylate in benzene (Experiments 1-5 in Table 5).

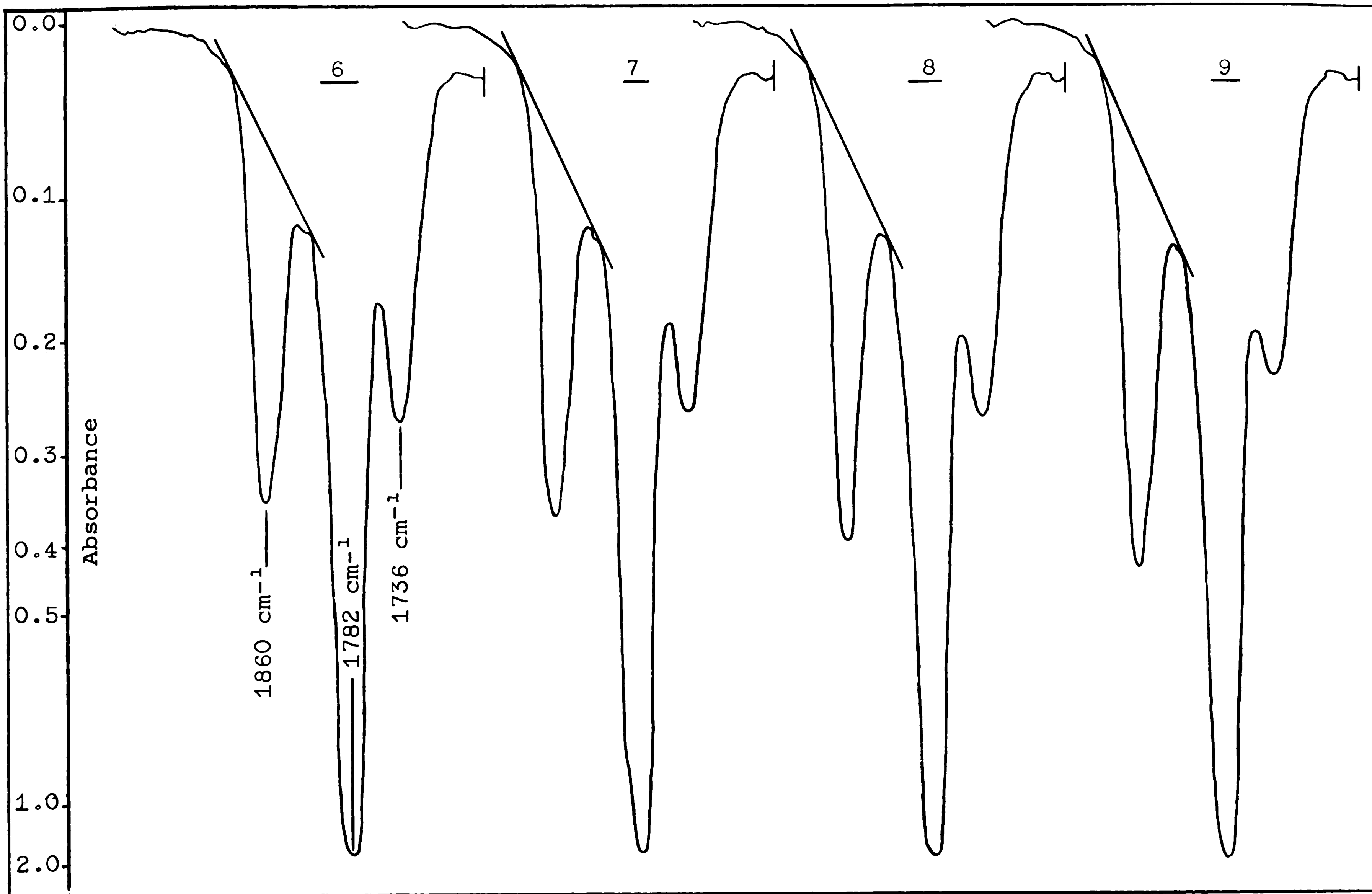


Figure 19. Infra-red carbonyl absorbances of copolymers obtained from copolymerization of itaconic anhydride and 2-chloroethyl acrylate in benzene (Experiments 6-9 in Table 5).

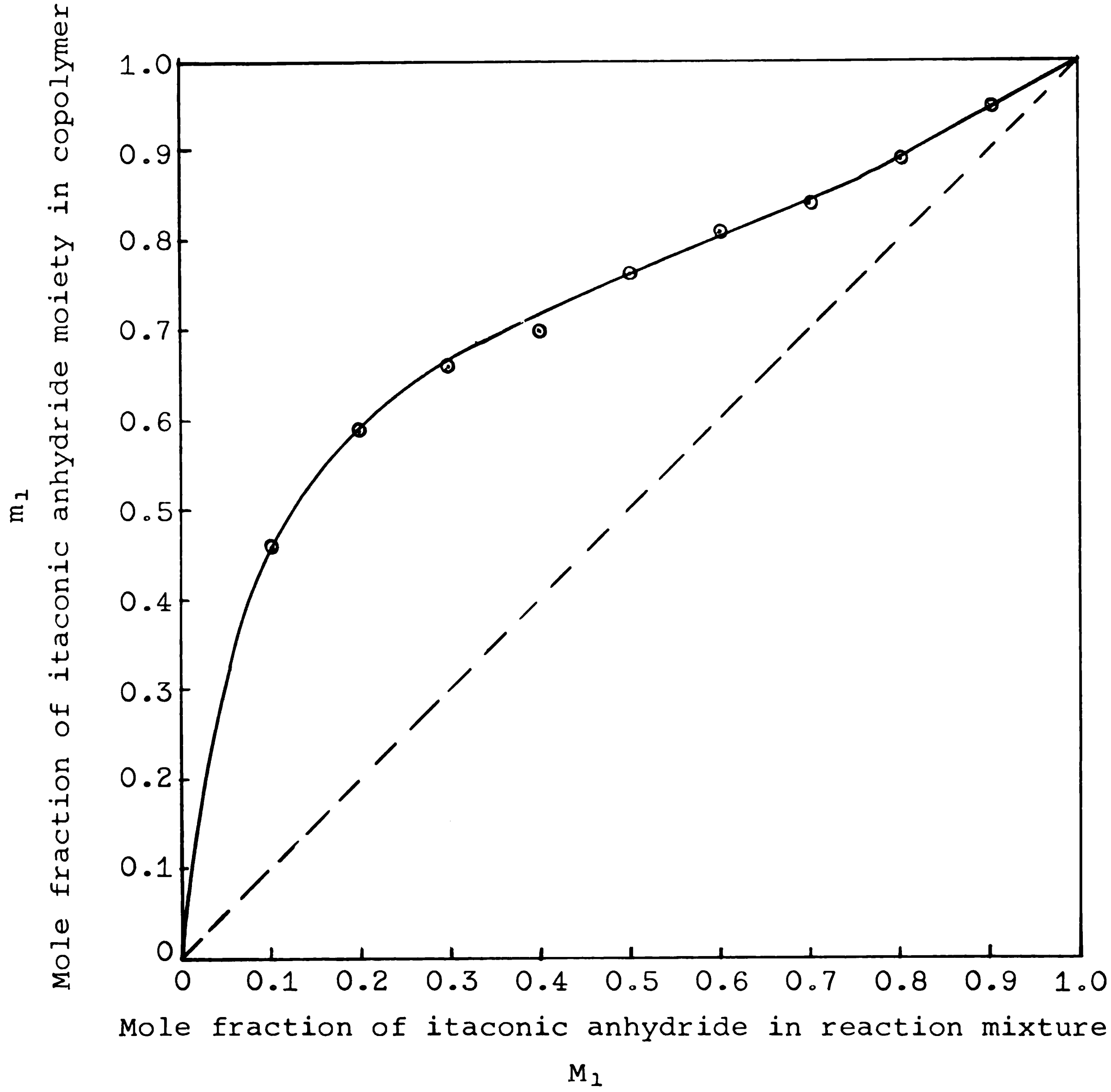


Figure 20. Copolymer composition curve of itaconic anhydride-2-chloroethyl acrylate copolymerization in benzene.

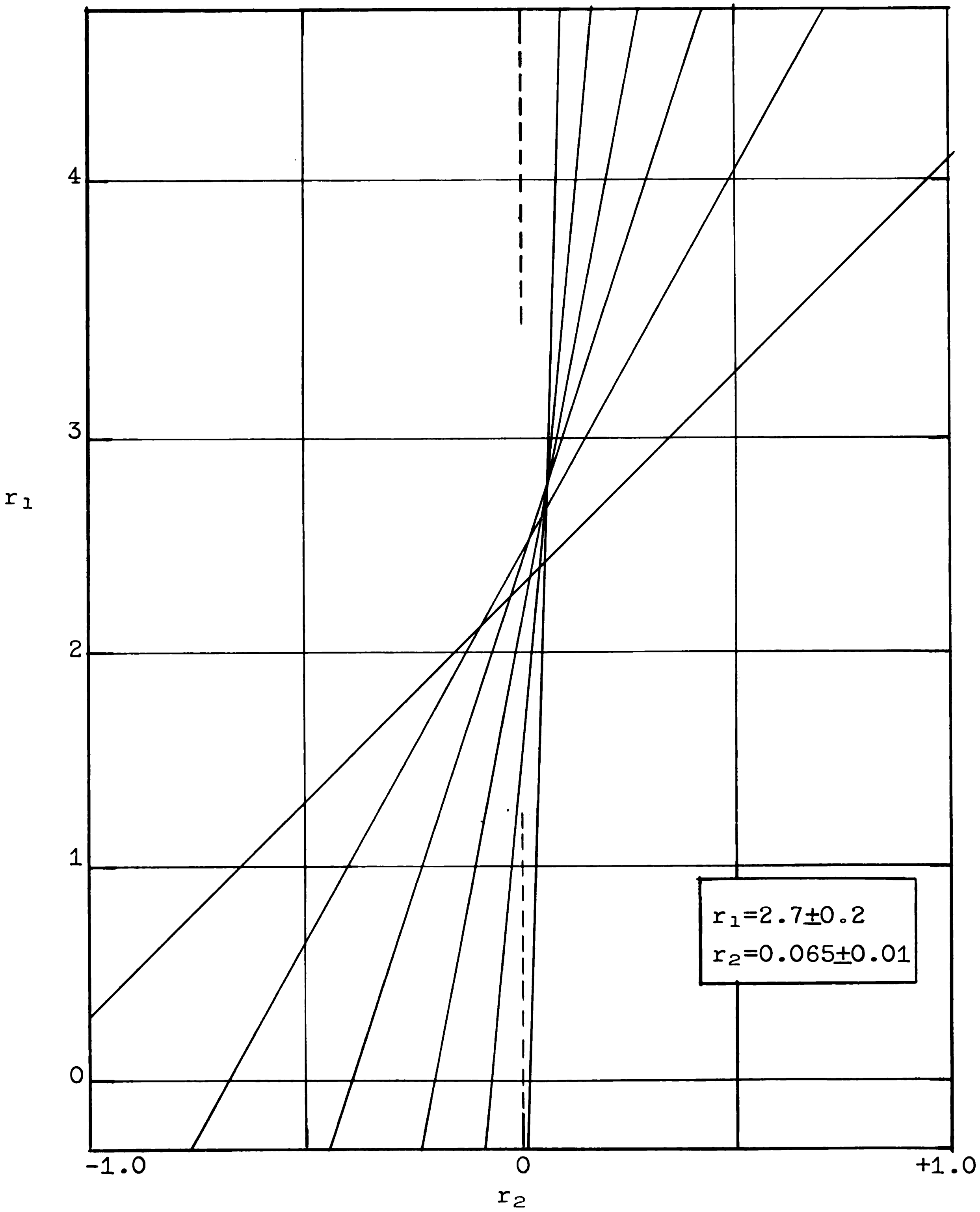


Figure 21. Graphical solution of copolymerization equation for itaconic anhydride-2-chloroethyl acrylate in benzene.

Table 6. Reactivity Ratios Data for Itaconic Anhydride-2-Chloroethyl Acrylate Copolymerization in Tetrahydrofuran

Exp. No.	M_1 Grams	M_1 Mole Fraction	Yield Grams	Conversion Percent	Peak Area Sq. in.	m_1 Mole Fraction	Reaction Time Minutes
1	1.4	0.1	0.99	6.00	0.22	0.23	135
2	2.8	0.2	1.22	7.28	0.33	0.40	150
3	4.2	0.3	0.92	5.80	0.40	0.52	210
4	5.6	0.4	0.85	5.42	0.48	0.63	210
5	7.0	0.5	0.93	6.04	0.53	0.71	210
6	8.4	0.6	0.72	4.76	0.56	0.76	210
7	9.8	0.7	0.57	3.85	--	--	210
8	11.2	0.8	0.59	4.05	0.62	0.85	210
9	12.6	0.9	0.37	2.59	0.66	0.91	240

M_1 = Mole fraction of itaconic anhydride in reaction mixture.
m_1 = Mole fraction of itaconic anhydride moiety in copolymer.

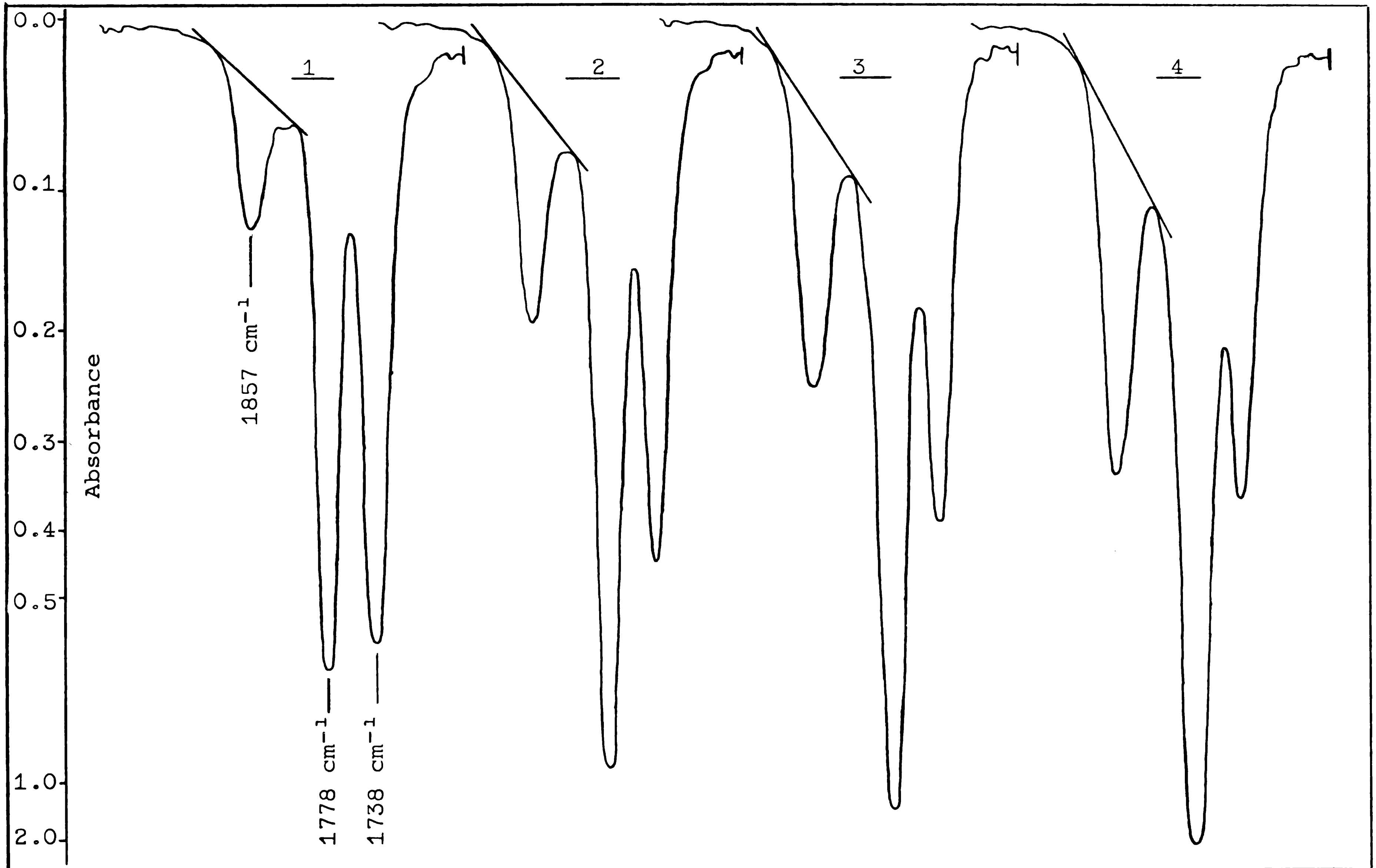


Figure 22. Infra-red carbonyl absorbances of copolymers obtained from copolymerization of itaconic anhydride and 2-chloroethyl acrylate in tetrahydrofuran (Experiments 1-4 in Table 6).

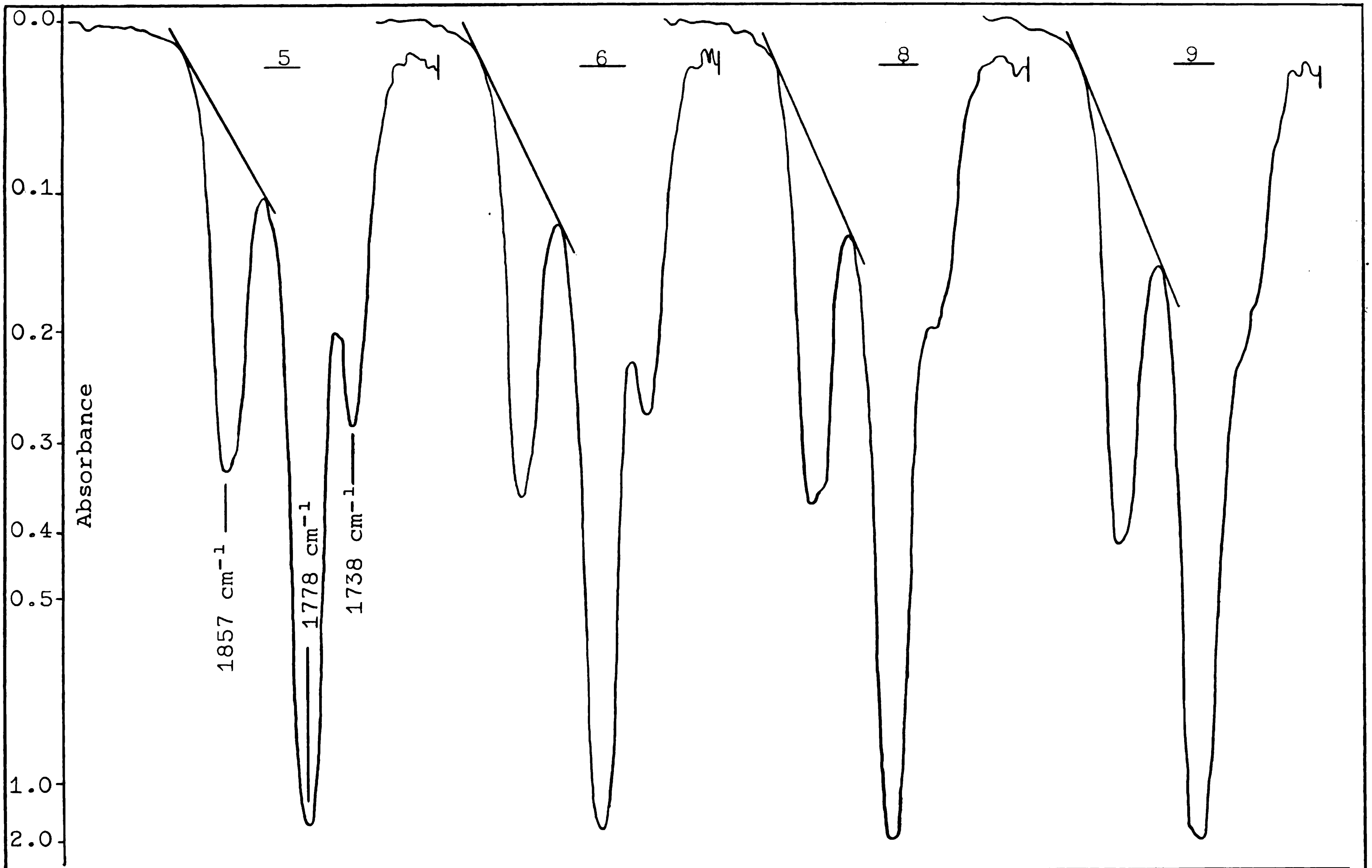


Figure 23. Infra-red spectra of copolymers obtained from copolymerization of itaconic anhydride and 2-chloroethyl acrylate in tetrahydrofuran (Experiments 5-9 in Table 6).

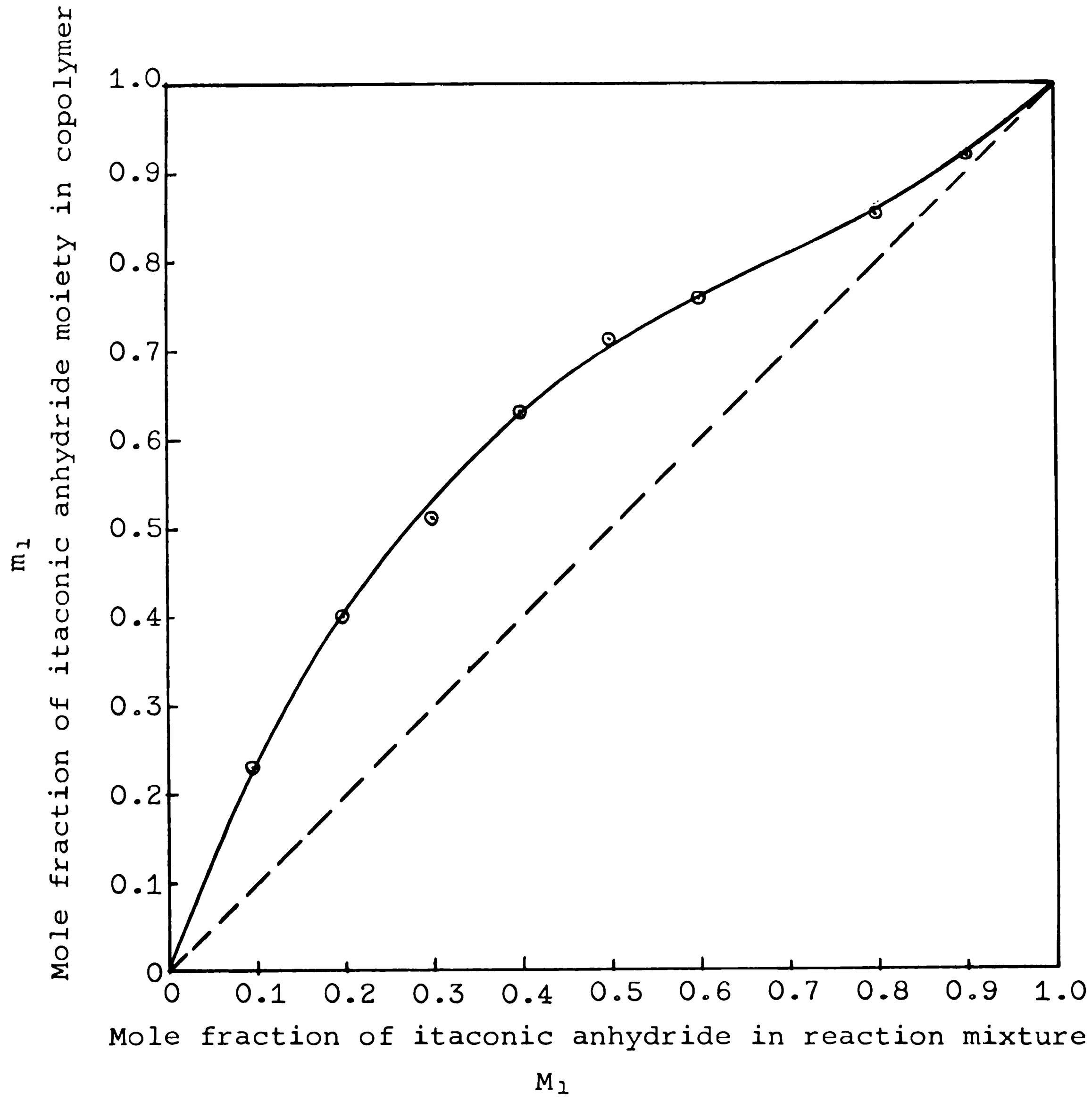


Figure 24. Copolymer composition curve for itaconic anhydride-2-chloroethyl acrylate copolymerization in tetrahydrofuran.

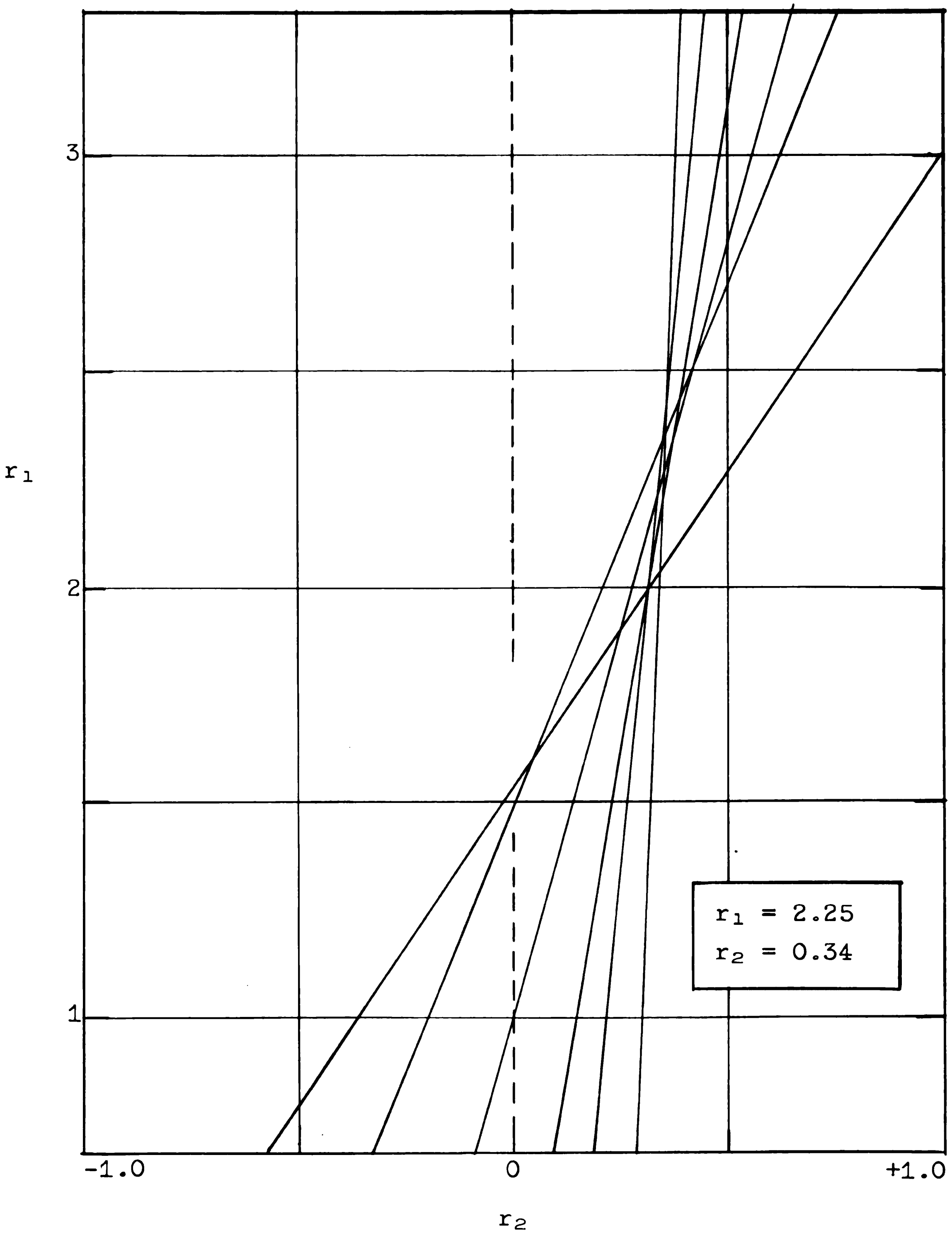
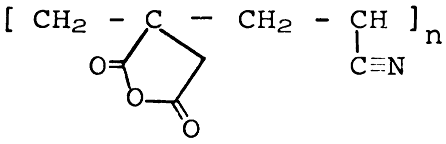


Figure 25. Graphical solution of copolymerization equation for itaconic anhydride-2-chloroethyl acrylate in tetrahydrofuran.

III. Copolymerization of Itaconic Anhydride and Acrylonitrile

A theoretical repeating unit for a completely alternating copolymer of itaconic anhydride-acrylonitrile ($r_1 \cdot r_2 \simeq 0$) is illustrated by the following formula:



Itaconic anhydride was copolymerized with acrylonitrile in benzene. The data from which the reactivity ratios were calculated are shown in Table 7. The copolymers obtained in the different experiments were analyzed by elemental analysis for nitrogen content. Figure 26 shows the calculated nitrogen contents of itaconic anhydride co acrylonitrile copolymers of varying anhydride content. Figure 27 shows the copolymer composition graph. The graphical solution of the copolymerization equation is shown in Figure 28.

Table 7. Reactivity Ratio Data for Itaconic Anhydride-Acrylonitrile Copolymerization in Benzene

Exp. No.	M_1		Yield Grams	Conversion Percent	N_2 Content Percent	m_1 Mole Fraction	Reaction Time Minutes
	Grams	Mole Fraction					
1	2.80	0.1	0.566	3.88	8.93	0.48	210
2	5.60	0.2	0.736	4.54	5.07	0.67	190
3	8.40	0.3	0.486	4.78	3.81	0.74	190
4	11.20	0.4	0.685	3.56	2.60	0.81	150
5	14.00	0.5	0.928	4.50	2.20	0.85	95
6	16.80	0.6	1.232	5.57	1.70	0.88	120
7	19.60	0.7	1.291	5.25	1.12	0.92	95
8	22.40	0.8	1.342	5.75	0.60	0.95	85
9	25.40	0.9	1.594	6.00	0.31	0.97	90

M_1 = Mole fraction of itaconic anhydride in reaction mixture.
m_1 = Mole fraction of itaconic anhydride moiety in copolymer.

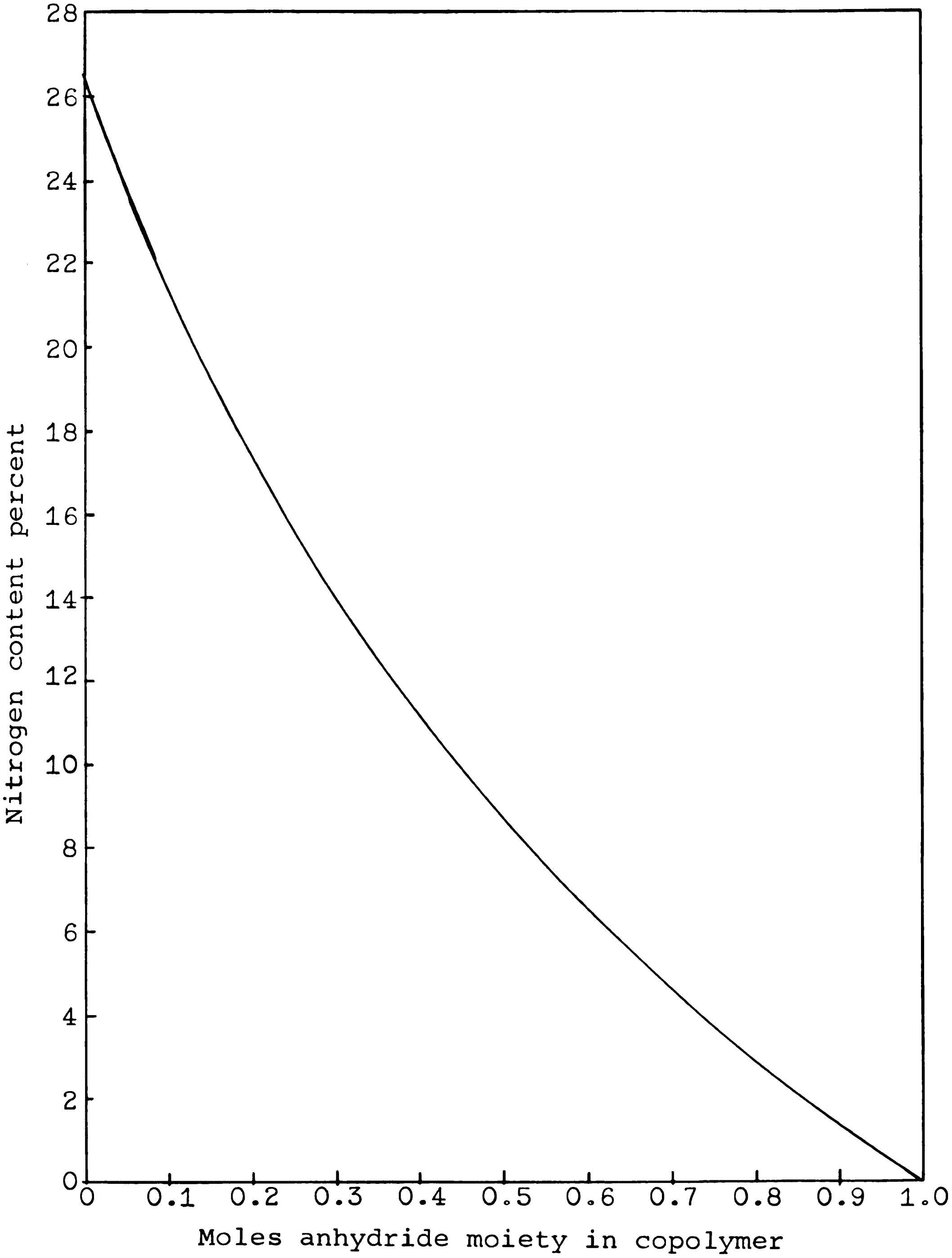


Figure 26. Calculated nitrogen content in copolymers of itaconic anhydride-acrylonitrile of varying composition.

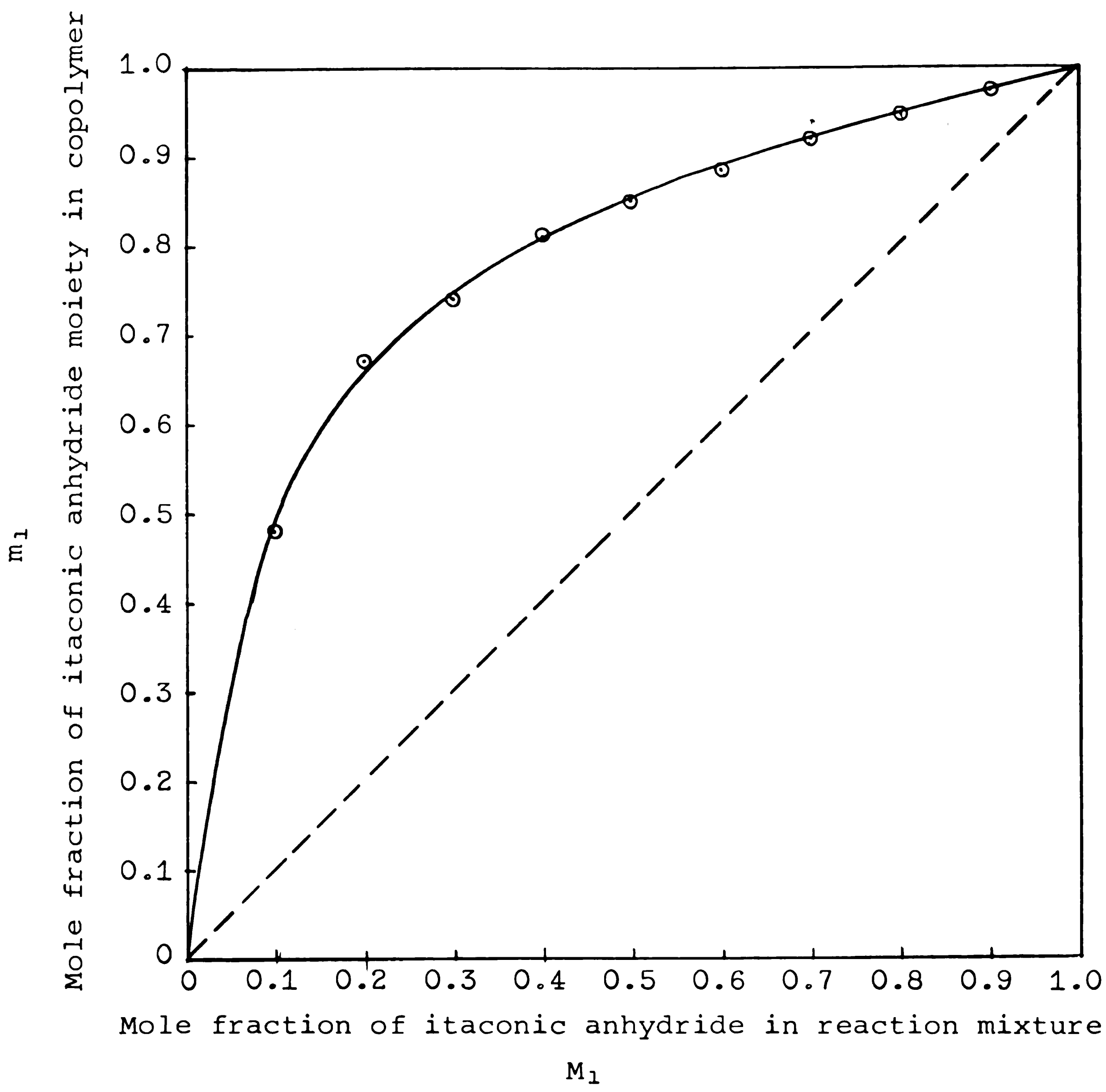


Figure 27. Copolymer composition curve of itaconic anhydride-acrylonitrile copolymerization in benzene.

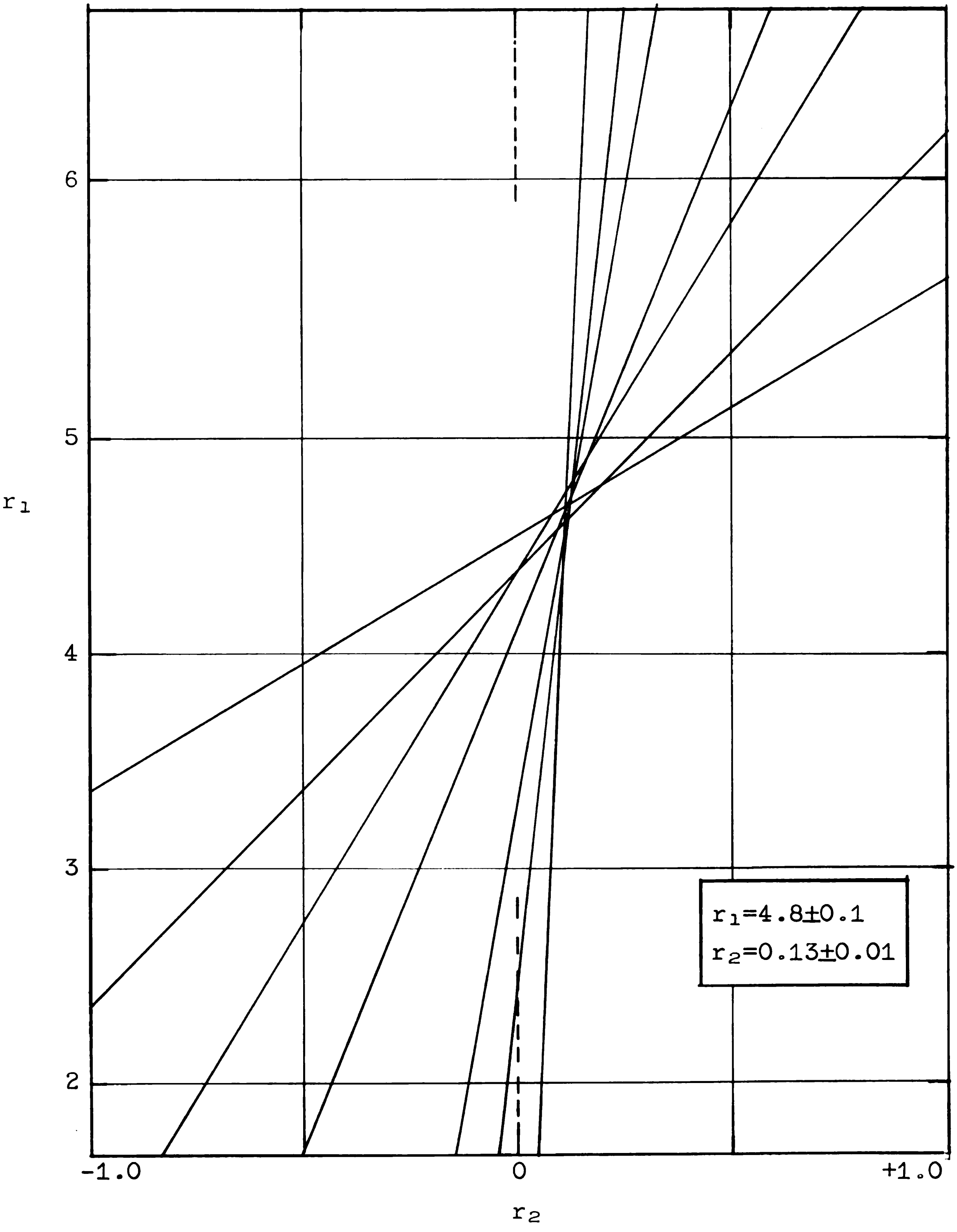
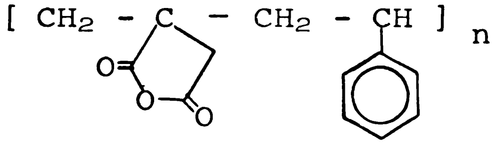


Figure 28. Graphical solution of copolymerization equation for itaconic anhydride-acrylonitrile in benzene.

IV. Copolymerization of Itaconic Anhydride and Styrene

A theoretical repeating unit of a completely alternating copolymer of itaconic anhydride-styrene ($r_1 \cdot r_2 \simeq 0$) is illustrated in the following formula:



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Itaconic anhydride was copolymerized with styrene in benzene. The data from which the reactivity ratios were calculated are shown in Table 8. The copolymers obtained in the different copolymerization experiments were analyzed by elemental analysis for carbon content. Figure 29 shows the calculated carbon contents of itaconic anhydride co styrene copolymers of varying anhydride content. Figure 30 shows the copolymer composition graph. The graphical solution of the copolymerization equation is shown in Figure 31.

Table 8. Reactivity Ratio Data for Itaconic Anhydride-Styrene Copolymerization in Benzene

Exp. No.	M_1		Yield Grams	Conversion Percent	C-Content Percent	m_1 Mole Fraction	Reaction Time Minutes
	Grams	Mole Fraction					
1	1.12	0.1	0.250	2.40	73.00	0.480	90
2	2.24	0.2	0.450	4.29	71.61	0.520	30
3	3.36	0.3	0.725	6.70	70.23	0.550	30
4	4.48	0.4	0.560	5.22	69.72	0.565	30
5	5.60	0.5	0.630	5.83	68.60	0.590	30
6	6.72	0.6	0.610	5.60	67.83	0.615	40
7	7.84	0.7	0.535	4.88	66.31	0.650	35
8	8.96	0.8	0.761	6.80	65.32	0.700	30
9	10.08	0.9	0.555	5.00	61.60	0.780	30

M_1 = Mole fraction of itaconic anhydride in reaction mixture.
m_1 = Mole fraction of itaconic anhydride moiety in copolymer.

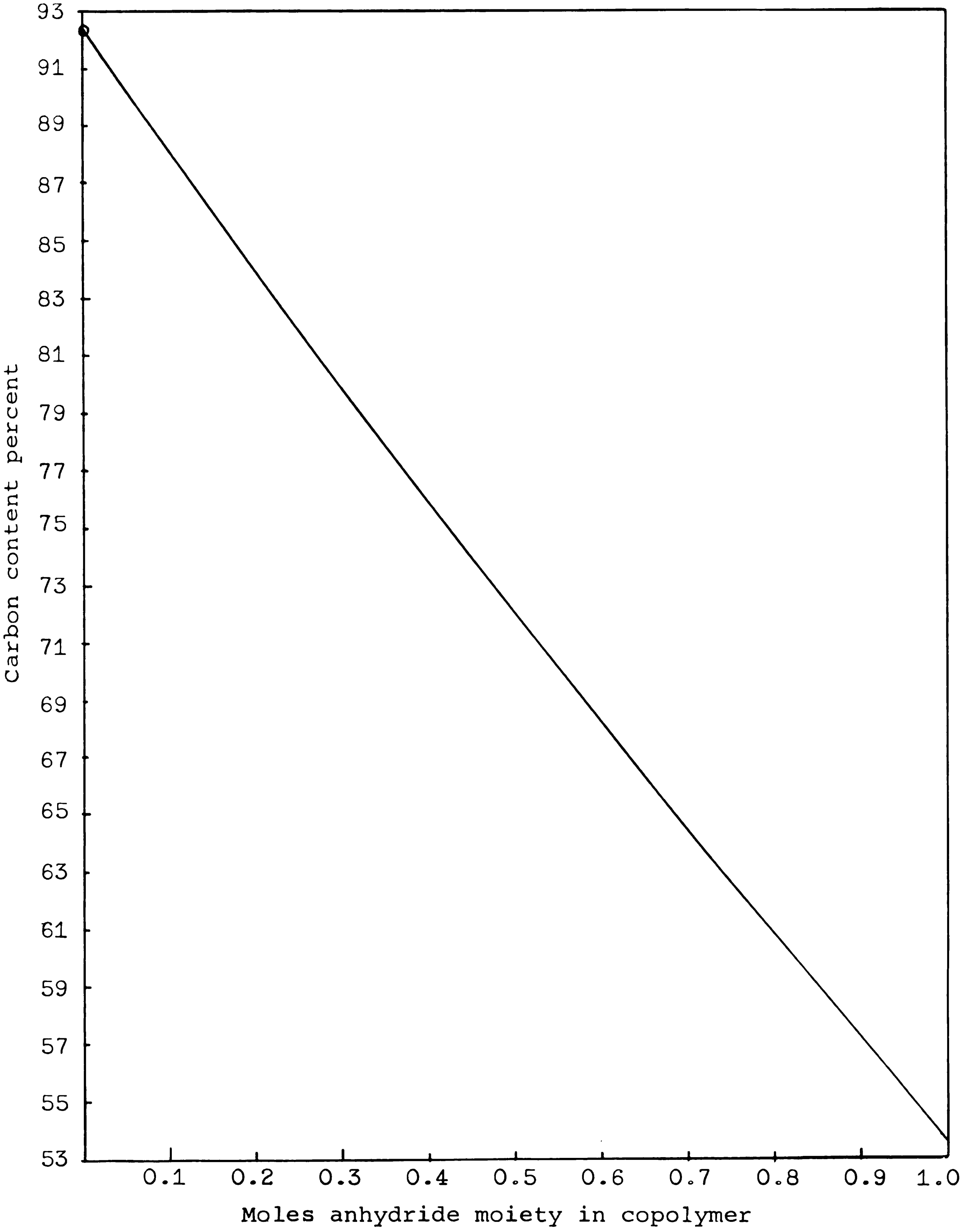


Figure 29. Calculated carbon content in copolymers of itaconic anhydride co styrene of varying composition.

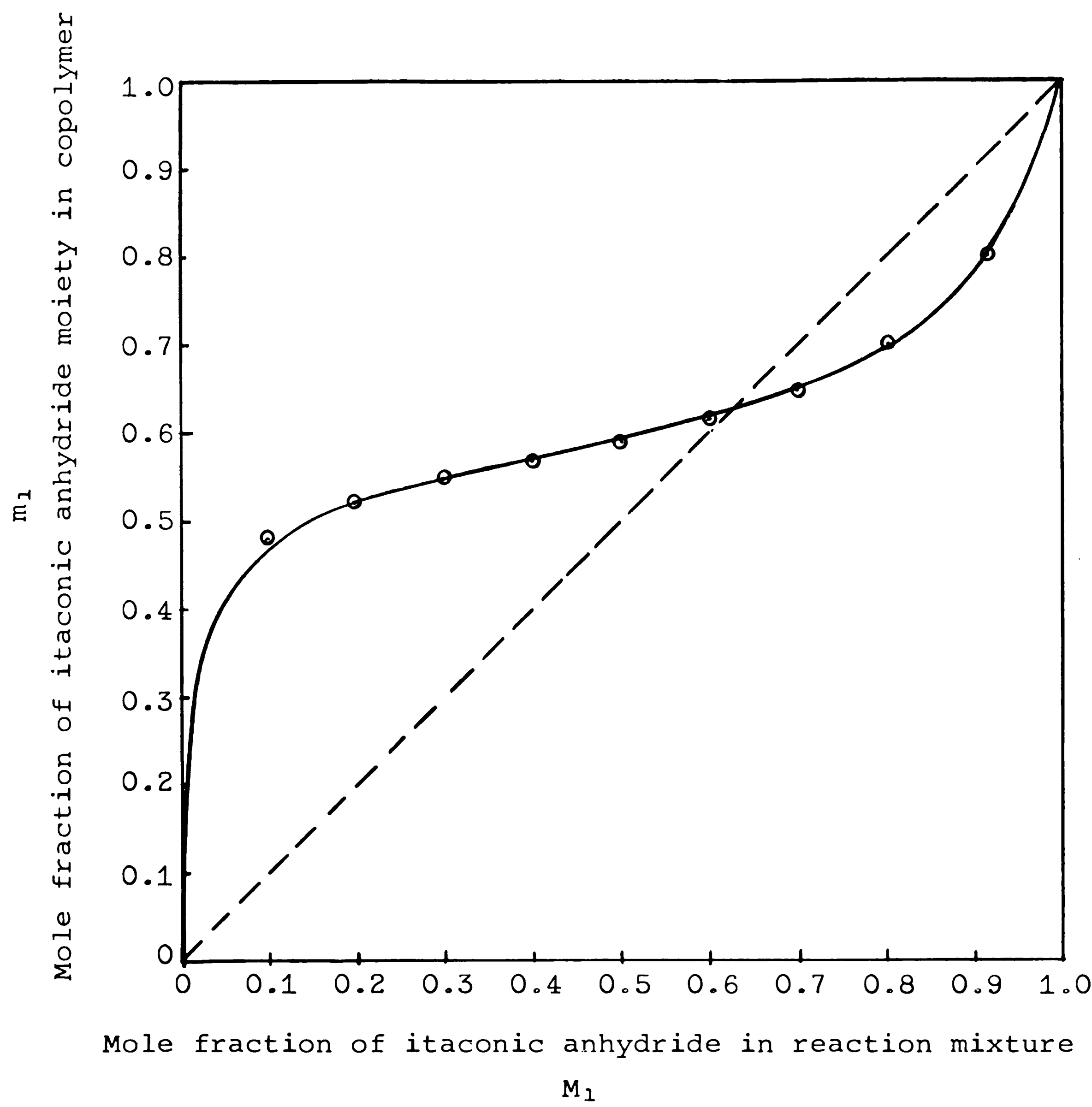


Figure 30. Copolymer composition curve of itaconic anhydride-styrene copolymerization in benzene.

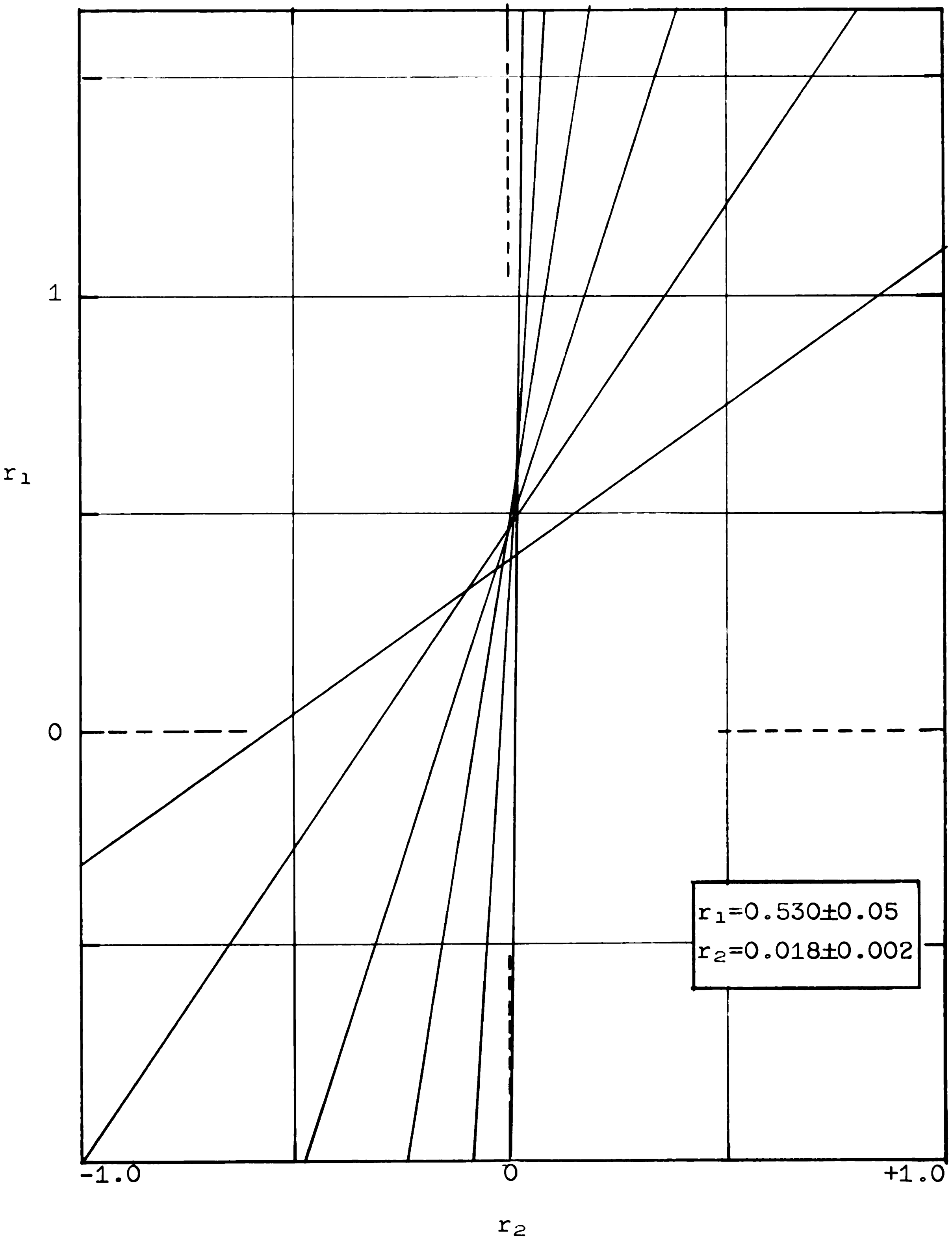


Figure 31. Graphical solution of copolymerization equation for itaconic anhydride-styrene in benzene.

DISCUSSION

I. Monomer Reactivity Ratios:

The composition of a polymeric substance is usually described in terms of its structural units. Generally these may be defined as groups having a valence of two or more. The structural units are connected to one another in the polymer molecule or polymeric chain by covalent bonds. The generation of the entire structure by repetition of one or a few elementary units is the basic characteristic of polymeric substances as implied by the word "polymer" meaning many units.

The polymers prepared in this investigation were formed from monomers which enter into two and only two linkages with other structural units. The structural units of these polymers are repeated in a linear sequence. In accordance with the functionality concept introduced by Carothers (47,48), all monomers which when polymerized may join with two other monomers are termed "bifunctional." A bifunctional unit is one which is attached to two other units. Linear polymers are composed of bifunctional units.

Polymeric substances containing two or more structural units combined in a more or less random sequence are called copolymers. A linear copolymer composed of two bifunctional units M_1 and M_2 may be represented in several ways. The structural units may alternate, that is $- M_1 M_2 M_1 M_2 M_1 -$, or there may be predominance of long sequence of like units: $- M_1 M_1 M_1 M_2 M_2 M_2 M_2 M_1 M_1 M_1 -$; or the structure may be randomly oriented: $- M_1 M_2 M_2 M_1 M_2 M_1 M_1 M_2 M_1 -$. In the event that the units alternate with perfect regularity, the copolymer is regarded as a polymer of the repeating unit $\dagger M_1 M_2 \dagger$. The tendency towards alternation is usual in copolymerization.

The term copolymerization implies that the monomers combine in the same polymer chain. In the event that the monomers polymerized separately to form molecularly distinct species, each having a different repeating unit, the product will simply be a mixture of two polymers and not a copolymer.

According to the classification applied by Carothers (49), the copolymers prepared in this investigation would be called "addition copolymers," since the molecular formula of the structural units is identical with that of the monomers from which the copolymer is derived.

Addition polymerization of unsaturated monomers leading to the formation of high molecular weight products almost always proceedsby a chain reaction mechanism:

$$\text{Monomer} \xrightarrow{\text{activation}} M^*$$
$$M^* + nM \xrightarrow{\text{propagation}} M^*_{n+1}$$
$$M^*_{n+1} \xrightarrow{\text{termination}} \text{polymer}$$

Initial activation of a monomer or a pair of monomers is followed by the addition of other monomers in rapid succession. This process continues until the growing chain is eventually deactivated or terminated.

The activated center, which is located at the growing end of the polymer chain may be a free-radical, a carbonium ion or a carbanion. Free radical type polymerizations have been investigated to a much greater extent than either of the other two types and are most widely used to produce commercial polymers. The majority of free radical polymerizations are commonly induced by an initiator such as decomposing peroxides, or by thermal or photolytic energy. Almost all the terminations of polymer chains in free radical polymerizations have been shown to be by combination of two growing polymer chain radicals.

The following free radical mechanism, first suggested by Taylor and Bates (50) to explain the polymerization of ethylene induced by free radicals in the gas phse, and independently proposed by Staudinger (51) for liquid phase polymerizations, offers an explanation for the general features of vinyl polymerization:

$$R^* \xrightarrow{CH_2=CHX} R-CH_2-\overset{X}{\overset{|}{CH}}{}^* \xrightarrow{CH_2=CHX} R-CH_2-\overset{X}{\overset{|}{CH}}-CH_2-\overset{X}{\overset{|}{CH}}{}^* \quad . \; . \; . \text{ etc.}$$

As in all chain reactions, the over-all polymerization involves two other processes: 1) chain initiation which depends on a reaction which introduces free radicals in the system, and 2) chain termination in which the terminal radical on a growing chain is deactivated.

The number of types of chain radicals to be considered is equal to the number of monomers present. In the copolymerization of two monomers, two types of chain radicals and only two are considered to be present. Addition of the two monomers to each of the two radicals is expressed by four simultaneous propagation reactions (see Historical, equation 1a-1d).

The entire polymer molecule is formed within a matter of a few seconds or less. At any time, therefore, during the polymerization, the reaction mixture consists of unreacted monomers, high polymer and a few radicals. The length of time during which a polymerization is carried out depends on the quantity of polymer desired (percent conversion to polymer) and is largely unrelated to the molecular weight of the polymers already present or being formed. There are practically no polymer species at intermediate stages of growth. Polymers that form even in the initial stages of a polymerization reaction compare favorably in molecular weight with those in the polymer mass at an advanced stage of the same polymerization (52). Thus it can be seen that the individual polymer molecules grow while most of the monomer molecules remain unchanged. This is in accord with the common feature of vinyl polymerization that the active center of the kinetic chain is retained by a single polymer molecule during the entire course of growth. If the active centers which convert the monomer into polymer were transferred randomly from one molecule to another, all molecular species would be present in all stages of the reaction. All polymer molecules would, then, grow more or less simultaneously and species such as dimers, trimers and tetramers would be present at the early stages in the polymerization. These species would then increase in size as the polymerization progresses. Such intermediate species are practically non-existent. This has been demonstrated by Staudinger (53) who pointed out that the known dimers and trimers of styrene are relatively inert to further polymerization. Thus, it can be concluded that a given polymer chain is formed by consecutive steps of a single chain process set off by the generation of some active center. It is apparent that the active center is retained by a growing polymer chain from the addition of one monomer molecule to the next.

The monomer reactivity ratios, r_1 and r_2 are defined by:

$$r_1 = \frac{k_{11}}{k_{12}}$$

$$r_2 = \frac{k_{22}}{k_{21}}$$

r_1 represents the ratio of the rate constant for the reactions of a radical M_1^* with monomer M_1 and with monomer M_2. Similarly, r_2 expresses the relative reactivity of an M_2^* radical towards an M_2 monomer compared with an M_1 monomer.

If the two radicals show the same preference for one of the monomers over the other, then

$$\frac{k_{11}}{k_{12}} = \frac{k_{21}}{k_{22}} \qquad \text{i.e.} \qquad r_1 = \frac{1}{r_2}$$

or $\quad r_1 \cdot r_2 = 1$

In such a case the sequence of the moieties in the polymer chain tends to be random. In the ideal case broken line in Figures 8, 12, 20, 24, 27, 30 , $k_{11} = k_{12}$ and $k_{22} = k_{21}$, that is the two monomers are equally reactive with each radical. In this case $r_1 = r_2 = 1$ and the sequence of monomer units must be random. The probability of the occurrence of an M_1 unit immediately following an M_1 unit is the same as for an M_1 unit to follow M_2 unit. The probability of either unit at any place in the chain is always equal to its mole fraction in an ideal copolymer.

If $r_1 . r_2 < 1$ there will be a greater tendency for the radicals of a given kind to generate radicals of the other monomer (alternation) rather than to regenerate their own species.

If $r_1 . r_2 > 1$, radicals of a given kind tend to regenerate a radical similar to themselves. Copolymers resulting in this case, will contain groups of like units in greater abundance than in a random copolymer.

Wall (25) indicated the close analogy between copolymer-monomer mixture composition relationships and the vapor-liquid equilibria in binary systems. The monomer reactivity ratio r_1, corresponds to the ratio of the vapor pressures $\frac{P_1^o}{P_2^o}$ of the pure components of the ideal mixture. He introduced the term ideal copolymerization for the case $r_1 . r_2 = 1$ in analogy to the vapor-liquid equilibria for ideal liquid mixtures.

When $r_1 > 1$ the polymer (vapor) is richer in M_1 than is the monomer mixture (liquid). If $r_1 < 1$ the reverse is true. Wall also introduced the term "copolymerization azeotropes" which refers to a copolymerization in which the copolymer produced has the same composition as the monomer mixture. The copolymer composition curve crosses the broken line which represents $M_1 = m_1$ as shown in Figure 30 at the azeotropic composition. Azeotropes will exist if <u>both</u> r_1 and r_2 are greater or less than unity. If one of the reactivity ratios is greater than unity while the other is less than unity, no azeotrope will be formed.

In the following discussion, r_1 will refer to the monomer reactivity ratio of itaconic anhydride.

For the copolymerization of itaconic anhydride with vinyl acetate in benzene, $r_1 = 5.75$. This means that the itaconic anhydride radical is about six times more reactive towards its own monomer than it is towards vinyl acetate. The r_2 value is 0.08, this means that the vinyl acetate radical is twelve and a half times more reactive towards itaconic anhydride than it is toward its own monomer. From the product $r_1 \cdot r_2 = 0.46$, one would conclude that the units in this copolymer tend to alternate, but not to a high degree.

For the same system in tetrahydrofuran, $r_1 = 3.5$. This means that the itaconic anhydride radical is three and a half times more reactive towards its own monomer than it is towards vinyl acetate. The r_2 value is 0.08, and again the vinyl acetate radical is twelve and a half times more reaction with the itaconic anhydride than it is with its own monomer. The product $r_1 \cdot r_2 = 0.28$ which indicates that, in tetrahydrofuran, the structure of itaconic anhydride-vinyl acetate copolymers tend to be alternating. The degree of alternation for the copolymers prepared in tetrahydrofuran is higher than that for the copolymers prepared in benzene. It is quite clear that the copolymerization of itaconic anhydride and vinyl acetate does not lead to an azeotrope when prepared in either benzene or in tetrahydrofuran since r_1 is greater than unity while r_2 is smaller than unity.

For the copolymerization of itaconic anhydride with 2-chloroethyl acrylate in benzene, $r_1 = 2.7$ and thus the itaconic anhydride radical is almost three times more reactive towards its own monomer than it is with the 2-chloroethyl acrylate. The fact that $r_2 = 0.065$ indicates that the 2-chloroethyl acrylate radical is about fifteen times more reactive towards itaconic anhydride than it is towards its own monomer. The product $r_1 \cdot r_2 = 0.1755$, and it can be seen that the itaconic anhydride co 2-chloroethyl acrylate polymers in benzene tend to be highly alternating.

For the copolymerization of the same system in tetrahydrofuran, $r_1 = 2.25$ which shows that the itaconic anhydride radical is more than twice as reactive towards monomeric itaconic anhydride than it is towards 2-chloroethyl acrylate. Since $r_2 = 0.34$, it follows that the acrylate radical is three times more reactive towards itaconic anhydride than it is towards its own monomer. From the product of r_1 and r_2 which is 0.765, it can be seen that the structure of itaconic anhydride Co s-chloroethyl acrylate polymer prepared in tetrahydrofuran is more random ($r_1 \cdot r_2 = 1$ for a completely random structure) than alternating. The value of r_1 is greater than unity while that of r_2 is smaller than unity. Thus, it can be seen that the copolymerization of itaconic anhydride with 2-chloroethyl acrylate does not form an azeotrope when prepared in either benzene or tetrahydrofuran.

For the copolymerization of itaconic anhydride with acrylonitrile in benzene, $r_1 = 4.8$. It follows that the itaconic anhydride radical is about five times more reactive towards its own monomer than it is towards the acrylonitrile monomer. The r_2 is 0.13, which means that the acrylonitrile radical is about eight times more reactive towards the anhydride monomer than it is towards its own monomer. The product $r_1 \cdot r_2 = 0.644$ and the structure of the copolymer will tend to be more random than alternating. No azeotrope is formed in this copolymerization since r_1 is greater than unity and r_2 is smaller than unity.

For the copolymerization of itaconic anhydride with styrene in benzene, $r_1 = 0.53$ which means that the itaconic anhydride radical is two times more reactive towards the styrene monomer than it is with its own monomer. The value of r_2 was 0.018, and it follows that styrene radical is about

about fifty-five times more reactive with the anhydride monomer than it is towards its own monomer. The product $r_1 \cdot r_2 = 0.0095$, which indicates that the structure of this copolymer will be almost completely alternating. It is worthy to note that this is the only system in this investigation that formed an azeotrope (both r_1 and r_2 are smaller than unity).

From all the above consideration, it can be concluded that: a) itaconic anhydride is an extremely active monomer in copolymerization. This is evident from the composition graphs (see Figures 8, 12, 20, 24, 27, 30). The extreme relative reactivity of itaconic anhydride may be explained on the basis that it forms a tertiary free radical type which is more easily formed (lower energy of activation) than a secondary free radical. In all the systems studied, itaconic anhydride had the highest relative reactivity, and it is the only monomer that forms a tertiary radical. Vinyl acetate forms a secondary radical which is probably very active since it does have almost no resonance stabilization. Its high activity should result in a radical with a relatively short life. The radical might be destroyed rapidly by one of several ways: 1) it may cross-terminate with another radical or 2) it may react with an anhydride monomer, ($r_2 = 0.08$), since it prefers to react with the anhydride rather than with its own monomer, or 3) by hydrogen transfer with the solvent or a polymer chain. This rapid destruction of vinyl acetate radical reduces the concentration of this type radical in the reaction mixture and allows the more stable but sufficiently active anhydride radicals to control the composition of the copolymer.

The higher relative reactivity of itaconic anhydride compared with that of 2-chloroethyl acrylate and acrylonitrile can be explained on the basis of the stability of the tertiary anhydride radical formed. Although the acrylate and the acrylonitrile radicals are also stabilized by resonance, they are destroyed by reacting with the anhydride monomer (the r values show that these radicals prefer the anhydride monomer over their own monomer) thus forming itaconic anhydride type radicals which prefer to react with the anhydride monomer resulting in a copolymer rich in the itaconic anhydride moiety.

In case of itaconic anhydride and styrene, the difference in the relative reactivities can be rationalized by the difference in the polarity of the monomer. Both radicals are stabilized by resonance, and are almost of the same stability. The difference in the polarity of the monomer may very well play an important role in this case. It seems that the itaconic anhydride being a polar monomer will be adsorbed on the polymer chain more than will the styrene monomer.

The high reactivity ratio of itaconic anhydride, i.e., the high tendency of the itaconic anhydride radical to react with its own monomer, can be explained by the ease of the formation of a tertiary radical. It would be rather interesting to copolymerize itaconic anhydride with a methacrylate ester (which also gives a tertiary radical) and see if there is any wide difference between the reactivity ratios in such a system. Another factor that might play a role could be the structure of the growing chain carrying the active center, and in particular the unit next to the active center. Barb (54) suggested that the activity of an active center is influenced by the penultimate unit of such a center.

b) The structures of copolymers prepared ranged from moderate to high alternation. Thus the itaconic anhydride co 2-chloroethyl acrylate polymer prepared in tetrahydrofuran has a highly random structure ($r_1 \cdot r_2 = 0.775$). On the other hand, itaconic anhydride co styrene polymer had a highly alternating structure ($r_1 \cdot r_2 = 0.0095$).

Itaconic anhydride co vinyl acetate polymers tend to have an alternating structure, however the degree of alternation was not very high. The degree of alternation for these polymers prepared in tetrahydrofuran ($r_1 \cdot r_2 = 0.28$) was relatively higher than those prepared in benzene ($r_1 \cdot r_2 = 0.48$).

Itaconic anhydride co acrylonitrile polymers ($r_1 \cdot r_2 = 0.13$) as well as itaconic anhydride co 2-chloroethylate ($r_1 . r_2 = 0.1755$) prepared in benzene show a slight tendency towards alternation.

c) The monomer reactivity ratio of itaconic anhydride in the copolymerization with vinyl acetate and with

2-chloroethyl acrylate varies in different solvents (see Table 1). In benzene, where the polymer precipitates the monomer reactivity ratio is higher. This, in our opinion, does not reflect any differences in the reactivity of the active centers, but may result from the difference in the degree of adsorption of the two monomers on the precipitated copolymer. Mayo and Walling (55) have described this phenomenon and gave a similar explanation. Itaconic anhydride appears to be adsorbed to a greater extent on the surface of the precipitated copolymer where it will be exposed to a greater extent to the active centers on the precipitated copolymer chains.

In tetrahydrofuran, however, this selective adsorption may not be as significant, though it may well be a factor operating in respect to the active polymer molecules that still remain in solution.

II. Infra-red Analysis

The infra-red method for the determination of the copolymer composition was developed mainly for the determination of the itaconic anhydride moiety in the itaconic anhydride o vinyl acetate polymers. This determination was impossible by the method of elemental analysis for carbon and hydrogen. The carbon percent of vinyl acetate is 55.81%, and that of itaconic anhydride is 53.57%. The greatest difference in carbon content for any combination of the two monomer units is 2.24%, which is too small to show any variation in copolymer composition. Most of the good solvents for the itaconic anhydride copolymers are carbonyl compounds (e.g., acetone, dimethyl formamide), or have a high boiling point and a high viscosity at room temperature such as dimethyl sulfoxide, and thus are not suitable for quantitative work with the copolymers in the infra-red analyses. Of the many solvents tested, acetonitrile was found to be an excellent solvent for the itaconic anhydride-vinyl acetate copolymers. It does not absorb in the carbonyl region, and the anhydride carbonyl peaks are distinctly separated from the ester carbonyl peak (separation of about 45 cm^{-1}).

In order to check the accuracy of the infra-red method, another series of copolymers of which elemental analysis data was meaningful, namely the itaconic anhydride co 2-chloroethyl acrylate were analyzed both by elemental chlorine analysis and infra-red. The difference in the copolymer compositions determined by these two methods was ±2-3% (Table 5). It is interesting to note that the standard curves drawn for mixtures of the homopolymers of itaconic anhydride and vinyl acetate, and that for mixtures of polyitaconic anhydride and poly-(2-chloroethyl acrylate) are almost superimposable. This points out that it may be possible to construct such standard curves using polyitaconic anhydride together with the model unit of the comonomer e.g., sec. butyl acetate for vinyl acetate. It also points out that the variation in the anhydride moiety can be easily followed regardless of the type of the other homopolymers in the mixtures.

III. Sweeping Technique:

The sweeping technique applied in all polymerization reactions was developed in order to free the reaction mixtures from the inhibitory agent generated from molecular oxygen. It is well-known (56) that molecular oxygen inhibits the homopolymerization of vinyl type monomers. In many attempts, in this laboratory, to homopolymerize vinyl acetate in benzene, no polymer was formed over a period of one week even though the initiator was varied as to type and concentration. Vinyl acetate polymerized rapidly in benzene when the sweeping technique (see Experimental) was applied. We have also succeeded in polymerizing maleic anhydride in benzene under mild condition using a low concentration of initiator. It has often been reported that maleic anhydride will not form a homopolymer. It has, however, been polymerized under rather drastic conditions and using a relatively high concentration of the initiator (57,58).

In view of the fact that trace amounts of oxygen leading to oxygen inhibitors vary with the type of monomer and solvent, their purification, and their storage, it is our opinion that kinetic studies in copolymerization as well as homopolymerization will be valid and valuable only where all traces of oxygen have been removed from the reactants and reaction mixtures. In our experience, this removal of oxygen was evidenced by nearly zero induction time. The sweeping method developed in this thesis is an additional technique to insure the removal of all traces of oxygen.

PART II

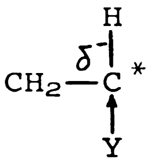
The Q-e Scheme

The relation between the monomer structure and the monomer reactivity with free radicals involves a resonance, a polar, and a steric factor. The Q-e scheme proposed by Alfrey and Price (59) represents an attempt to formulate the first two factors. Although steric factors are not accommodated in the Q-e scheme, they do impose limitations on its applicability.

Alfrey and Price justified the initiation of such a scheme in the following manner: It would be extremely useful if a simple pattern of copolymerization behavior could be found which would allow each individual monomer to be described by characteristic constants. This would simplify the task of determining the behavior of a large number of monomer pairs in copolymerization reactions without the need for excessive experimental work. If it were possible to copolymerize a given monomer with a limited number of "reference monomers," compute the values of constants characteristic of the individual monomer from these results, and then to predict the behavior of this monomer in other (unstudied) combinations, the practical advantages of such a procedure would be considerable. Furthermore, if each monomer, rather than each pair of monomers (the theory of copolymerization permits quantitative description of any pair of monomers in terms of r_1 and r_2), can be characterized by a set of numerical constants, the correlation of reactivity with molecular structure of the monomers should be feasible. It should even be possible to predict the relative reactivities of individual monomers.

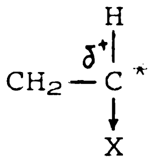
It was suggested (60) that there may be a general order of activity of the monomers toward radicals which is complicated by the tendency of some pairs to alternate in copolymerization. This alternation seems, sometimes, to be due to steric effects, to dipole effects, or to specific interaction between the monomers.

The idea of monomer-polarity was developed in some details (61,62). It is evident that the monomer pairs which are most readily copolymerized are those in which one of the pair has an electron-rich double band (type A) and the other has an electron-poor double bond (type B). If one assumes that the substituent which influenced the polarity of the double bond can similarly influence the polarity of an adjacent free radical, then from a monomer of type "A," the odd electron will be on a relatively negative carbon, while that from a monomer of type "B" will be on a relatively positive carbon:



$CH_2-\overset{\overset{H}{\delta^{-}|}}{\underset{\underset{Y}{\uparrow}}{C}}{}^{*}$

Type "A" radical



$CH_2-\overset{\overset{H}{\delta^{+}|}}{\underset{\underset{X}{\downarrow}}{C}}{}^{*}$

Type "B" radical

It is then the attraction of the relatively negative (or positive) radical for the relatively positive (or negative) double bond which is an important factor in facilitating copolymerization, presumably by decreasing the activation energy for chain propagation.

Alfrey and Price (63) attempted to place this concept, together with the over-all activity associated with resonance stabilization, on a general and semi-quantitative basis, the Q-e scheme.

The central assumption for the Q-e scheme is that the rate constant, k_{iy}, for the attack of radical i upon monomer "y" is given by

$$k_{iy} = P_i Q_y \quad \exp(-e_i e_y) \text{ ----------} \qquad (1)$$

Here P_i is characteristic of radical i
Q_y is the mean reactivity of monomer y
e_i and e_y are measures of the polarity of the radical and its monomer respectively.

The same polarity factor e, is used for a monomer and its adduct radical. When equation (1) is applied to the relative rate constants for two monomers (y and x) with given free radical (i) the radical reactivity factor, P_i, cancels out leaving:

$$\frac{k_{iy}}{k_{ix}} = \left(\frac{Q_y}{Q_x}\right) \quad \exp\{-e_i(e_y - e_x)\} \text{ ---------} \qquad (2)$$

For a binary copolymerization:

$$r_1 = \frac{k_{11}}{k_{12}} = \left(\frac{Q_1}{Q_2}\right) \quad \exp\{-e_1(e_1 - e_2)\} \text{ ----} \qquad (3)$$

$$r_2 = \left(\frac{k_{22}}{k_{21}}\right) = \left(\frac{Q_2}{Q_1}\right) \quad \exp\{-e_2(e_2 - e_1)\} \text{ ----} \qquad (4)$$

Thus each monomer is characterized by two numbers Q and e which together can be used to estimate the reactivity ratios of any chosen monomer pair.

Although several investigators have proposed theoretical interpretations of the significance of these parameters (64-69), the Q-e scheme is still generally regarded as an empirical method of correlation.

The Q-e values were calculated by the use of the following two equations:

$$e_1 = e_2 \pm (- \ln r_1 r_2)^{\frac{1}{2}} \text{ ------------ } (5)$$

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

Values for the Q_2 and e_2 for the respective monomers were obtained from the literature and the calculation was made using the monomer reactivity ratios of itaconic anhydride in Table 1.

For each system studied, two values of e were obtained from equation (5) and were used in equation (6) to calculate the Q value. Two Q values were obtained for each system. The Q and e values obtained from the literature (70) are shown in the following table.

Table 9. Q-e Values for the Comonomers

Monomer	Q_2	e_2
Vinyl acetate	0.026	-0.22
2-Chloroethyl acrylate	0.41	0.54
Acrylonitrile	0.60	1.20
Styrene*	1.00	-0.80

*Values for styrene are assumed values. Styrene is taken as the standard for the Q-e scheme.

Using the values in Table 9, the Q and e values for itaconic anhydride were calculated and are tabulated in the following table:

Table 10.* Calculated Values of Q-e Scheme for Itaconic Anhydride

	A		B	
	Q_1	e_1	Q_1	e_1
a	2.88	0.66	0.39	-1.10
b	2.54	0.90	0.41	-1.34
c	12.79	1.85	3.11	-0.77
d	1.59	1.05	0.90	+0.02
e	10.46	1.88	2.03	+0.51
f	9.68	1.37	310.20	-2.97

*Column "A" of Table 10 shows the value for Q_1 and e_1 calculated for itaconic anhydride using equation (5) when the component $(-\ln r_1 \cdot r_2)^{\frac{1}{2}}$ is positive.

Column "B" shows the values for Q_1 and e_1 calculated in the same manner when the component $(-\ln r_1 \cdot r_2)^{\frac{1}{2}}$ is negative.

a: $r_1.r_2$ used, corresponds to itaconic anhydride co vinyl acetate in benzene.
b: $r_1.r_2$ used, corresponds to itaconic anhydride co vinyl acetate in T.H.F.
c: $r_1.r_2$ used, corresponds to itaconic anhydride co 2-chloroethyl acrylate in benzene.
d: $r_1.r_2$ used, corresponds to itaconic anhydride co 2-chloroethyl acrylate in T.H.F.
e: $r_1.r_2$ used, corresponds to itatonic anhydride co acrylonitrile in benzene.
f: $r_1.r_2$ used, corresponds to itaconic anhydride co styrene in benzene.

Since itaconic anhydride is an electron-poor monomer, it should have a positive e-value. Careful examination of Table 10 shows that the values in Column "A" fulfills this requirement consistently. These values were the ones selected as the Q-e values for itaconic anhydride.

By plotting log Q versus e, for the values in both columns A and B, one may get--in rare cases--a point of intersection which determines the Q-e values for the monomer in question. However, a dense cluster of points at the intersections of the straight lines drawn can serve as a guide in determining the Q-e scheme value for the monomer under investigation. The plot made using the data in Table 10 gave a dense cluster of points of intersection. The center point for the triangle constituting these points corresponded to the values:

$$Q = 9.8$$

$$e = 2.0$$

These values show that the choice of the set of data in column "A" of Table 10, which was based on the structural polarity of the itaconic anhydride, was valid. It also points out that itaconic anhydride is an exceptionally active monomer.

SUMMARY

1. Itaconic anhydride was found to be an extremely active monomer in free-radical copolymerization.

2. The copolymerization of itaconic anhydride with four co-monomers of different polarities, namely: vinyl acetate, 2-chloroethyl acrylate, acrylonitrile, and styrene was studied in benzene, and the reactivity ratios (r_1 and r_2) were determined for each system.

3. Two of the systems studied above namely itaconic anhydride co vinyl acetate and itaconic anhydride co 2-chloroethyl acrylate were also studied in tetrahydrofuran, and the reactivity ratios were determined.

4. The reactivity ratios of itaconic anhydride were found to be higher for the copolymerization in benzene than for the copolymerization in tetrahydrofuran.

5. A sweeping technique has been developed to remove traces of oxygen from the polymerization reaction.

6. An application of infra-red spectroscopy for the quantitative analysis of copolymer composition was developed.

7. The Q-e scheme value for itaconic anhydride was determined.

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