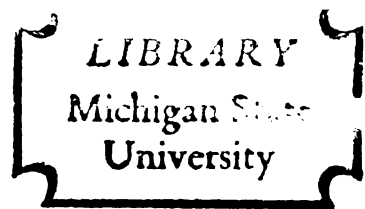# INVESTIGATION OF THE FREE RADICAL COPOLYMERIZATION OF ITACONIC ANHYDRIDE IN SEVERAL BINARY SYSTEMS

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ABSTRACT

INVESTIGATION OF THE FREE RADICAL COPOLYMERIZATION
OF ITACONIC ANHYDRIDE IN SEVERAL BINARY SYSTEMS

by Abdoljalil Mostashari

Binary copolymerizations of itaconic anhydride with six comonomers (vinyl pyrrolidine, 4-methoxystyrene, 2-chlorostyrene, 3-chlorostyrene, styrene and divinyl ether) were carried out in tetrahydrofuran using 2,2'-azodiisobutyronitrile as an initiator.

Reactivity ratios were determined for the systems itaconic anhydride M_1 with methyl methacrylate M_2 ----r_1 = 2.25, r_2 = 0.1 and itaconic anhydride M_1 with 4-methoxystyrene M_2 --- r_1 = 0.47, r_2 = 0.03 when copolymerized in benzene with 2,2'-azodiisobutyronitrile initiator.

Quantitative infra-red analysis was applied to the samples of itaconic anhydride co methyl methacrylate and itaconic anhydride co 4-methoxystyrene for the determination of copolymer compositions.

Values obtained by infra-red analysis were found to be in good agreement with the values obtained by elemental analysis of the samples of itaconic anhydride co 4-methoxystyrene.

A model compound, p-secondary butylanisole, was used to prepare the reference calibration graphs for the percent

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anhydride moiety in the itaconic anhydride co 4-methoxy-styrene since the homopolymer of 4-methoxystyrene was insoluble in acetonitrile.

A series of itaconic anhydride M_1-styrene M_2 copolymers prepared for the determination of the reactivity ratios of this system were analyzed by infra-red for anhydride moiety content. The r_1 and r_2 values calculated from the infra-red data were r_1 = 0.35 and r_2 = 0.02. These values are in reasonable agreement with the values obtained for this system when the composition of these samples was determined by carbon analysis.

The quantitative infra-red reference calibration graphs prepared for itaconic anhydride co styrene, itaconic anhydride co 4-methoxystyrene and itaconic anhydride co methyl methacrylate can be used for a quick and accurate infra-red analysis of the composition of these types of copolymers.

It has been shown that quantitative infra-red reference calibration graphs can be constructed for use in the determination of the amount of itaconic anhydride moiety in a co-polymer using known mixtures of the two homopolymers.

In some cases different concentrations of the single homopolymer, polyitaconic anhydride, can be used to construct these reference calibration graphs but in others different concentrations of polyitaconic anhydride and a model compound similar to the comonomer unit must be employed.

INVESTIGATION OF THE FREE RADICAL COPOLYMERIZATION

OF ITACONIC ANHYDRIDE IN SEVERAL BINARY SYSTEMS

By

Abdoljalil Mostashari

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INTRODUCTION

Free radical copolymerization of itaconic anhydride with various monomers have been studied in this laboratory (20,21). The present work was initiated to extend the studies on the copolymerization of itaconic anhydride and to determine the reactivity ratios for the two systems itaconic anhydride-methyl methacrylate and itaconic anhydride-4-methoxystyrene.

Quantitative infra-red analysis of itaconic anhydride type copolymers had been applied in a limited number of cases (21).

Further work on the quantitative infra-red analysis of the copolymers of itaconic anhydride-styrene and an extension of this technique to itaconic anhydride-co-methyl methacrylate and itaconic anhydride-co-4-methoxystyrene appeared desirable.

HISTORICAL

Although the phenomenon of polymerization of organic compounds has been known for over a century (1), the simultaneous polymerization of two or more monomers was not investigated until around 1911, when the copolymerization of isoprene and butadiene was patented (2). A year later Kandakov published a paper on copolymerization of butadiene and dimethyl butadiene (3). The initial work on copolymerization emphasized the study of the properties of copolymers and very little was reported on the mechanism and kinetics of the reactions. During the 1930's it was found that monomers differed in their tendency to enter the copolymers, and that copolymer samples withdrawn at different degrees of conversion contained the two components in different ratios (4). It was also reported that maleic anhydride, stilbene, isobutylene and fumaric ester, compounds which homopolymerize with great difficulty, easily form copolymers with each other or with other polymerizable monomers, such as styrene and vinyl chloride (5,6,7).

Kinetic work on copolymerization was started in the mid-thirties by Dostal (8). In his treatment, he assumed that the rate of addition of monomer to a growing free radical chain depended only on the nature of the end group on the radical chain. Thus monomers M_1 and M_2 lead to radicals of types M_1^* and M_2^*. There are four possible ways in which

monomer can add:

reaction	rate	
$M_1^* + M_1 \longrightarrow M_1^*$	$k_{11} [M_1^*] [M_1]$	
$M_1^* + M_2 \longrightarrow M_2^*$	$k_{12} [M_1^*] [M_2]$	I
$M_2^* + M_1 \longrightarrow M_1^*$	$k_{21} [M_2^*] [M_1]$	
$M_2^* + M_2 \longrightarrow M_2^*$	$k_{22} [M_2^*] [M_2]$	
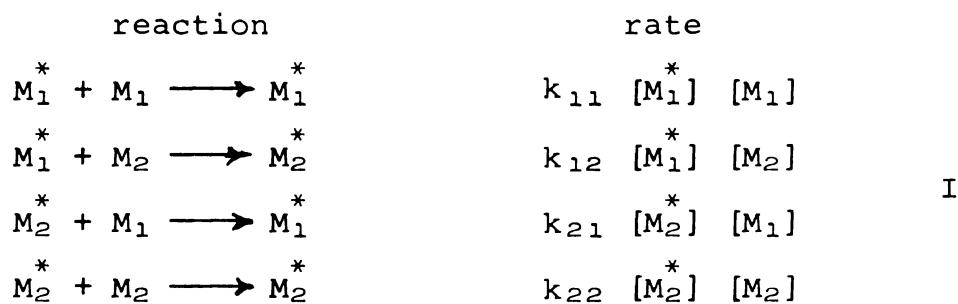
Since four independent rate constants were involved, Dostal made no attempt to test his assumption experimentally. In 1939 Norrish and Brookman (9) published an experimental study of copolymerization of styrene and methyl methacrylate which provided reliable data for a theoretical analysis of the co-polymerization reaction.

The next important step was contributed by Wall (10) in 1941, who suggested that the chemical composition of a co-polymer would depend only upon the relative reactivities of the two monomers towards the two radicals.

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

After several unsuccessful approaches, the kinetics of co-polymerization was elucidated in 1944 by Alfrey (11), Mayo (12), Simha (13), and Wall (14). To Dostal's reaction scheme they added the assumption of the steady state applied to each radical type. This steady state required that each type of free radical must be maintained at a certain fixed characteristic concentration i.e., each type of radical disappears into a polymer chain at the same rate at which it is formed.

$$k_{12} \ [M_1^*] \ [M_2] = k_{21} \ [M_2^*] \ [M_1] \hspace{3cm} \text{III}$$

which states that the rate of conversion of M_1 to M_2 must equal that of conversion of M_2^* to M_1^*.

The rate of disappearance of monomer M_1 is given by:

$$-\frac{d \, [M_1]}{dt} = k_{11} \, [M_1^*] \, [M_1] + k_{21} \, [M_2^*] \, [M_1] \hspace{2cm} \text{IV}$$

similarly, the rate of disappearance of monomer M_2 is given by:

$$-\frac{d \, [M_2]}{dt} = k_{22} \, [M_2^*] \, [M_2] + k_{12} \, [M_1^*] \, [M_2] \hspace{2cm} \text{V}$$

Since the relation between $[M_1]$ and $[M_2]$ is given by the steady state expression (Eq. III), the ratio between the rates of disappearance of M_2 and M_1 could be written in the following form:

$$\frac{d \, [M_1]}{d \, [M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{(\frac{k_{11}}{k_{12}}) \, [M_1] + [M_2]}{(\frac{k_{22}}{k_{21}}) \, [M_2] + [M_1]} \hspace{2cm} \text{VI}$$

If one substitutes the reactivity ratios of Wall (II) in Eq. (VI) one gets the following:

$$\frac{d \, [M_1]}{d \, [M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1 \, [M_1] + [M_2]}{r_2 \, [M_2] + [M_1]} \hspace{2cm} \text{VII}$$

Equation (VII) is the differential form of the copolymerization equation. However, if the percentage of conversion of mono-mers into copolymers is low, the concentration of each of the monomers, M_1 and M_2 at this low conversion will be nearly equal to the initial concentration of monomers, and the ratio of concentrations of the monomers in the copolymers, equal to the

ratio of disappearance of the monomers.

$$\frac{d[M_1]}{d[M_2]} = \frac{m_1}{m_2} \qquad\qquad\qquad \text{VIII}$$

Hence, Eq. VII could be written as follows:

$$\frac{m_1}{m_2} = \frac{M_1}{M_2} \cdot \frac{r_1 M_1 + M_2}{r_2 M_2 + M_1} \qquad\qquad \text{IX}$$

It should be recognized that IX is valid only for very low conversions, otherwise the integrated form of Eq. VII must be used (12)

$$r_2 = \frac{\log \frac{[M_2]}{[M_2^o]} - [\frac{1}{p} \log \frac{1-p(M_1/M_2)}{1-p(M_1^o/M_2^o)}]}{\log \frac{[M_1^o]}{[M_1]} + [\log \frac{1-p(M_1/M_2)}{1-p(M_1^o/M_2^o)}]} \qquad\qquad \text{X}$$

where:

$$p = (1 - r_1)/(1 - r_2)$$

Copolymerization data for the cyclic anhydride monomer maleic anhydride has been reported by numerous investigators (15-19), but the only reported data on itaconic anhydride, has been from this laboratory (20,21). The copolymers of itaconic anhydride, however, have been the subject of increasing patent and industrial interest (22,23).

A variety of analytical methods have been used to determine the composition of various copolymers. These methods differ depending on the copolymer to be analyzed. If the carbon percent of one of the monomers is much higher than the other, or one monomer contains elements such as halogens,

sulfur or nitrogen, elemental analysis may be used for co-
polymer composition determinations. High frequency and
potentiometric titrations of the acid function in acid and
anhydride containing copolymers has also been used (24,25).
Spectrophotometric methods (especially infra-red and ultra-
violet) have recently been employed for copolymer composition
determinations (26,27,28). Measurement of the anhydride peak
in the infra-red spectra of the copolymers containing such an
anhydride moiety was first utilized in this laboratory (21)
to determine the composition of itaconic anhydride copolymers.

REAGENTS AND MONOMERS

I - Monomers

Preparation and Purification

    a - Itaconic anhydride (methylene succinic anhydride)

    Itaconic anhydride was prepared from itaconic acid by dehydration using acetyl chloride. The crude anhydride obtained had a melting point of 68-69°C. and was recrystallized from dry chloroform to give pure anhydride (m.p. 68.5 ± 0.2°C.). Itaconic anhydride may also be prepared from itaconic acid using thionyl chloride (29), phosphorous pentoxide (30), acetic anhydride (31) or 98% sulfuric acid (32). Itaconic acid and anhydride along with citraconic acid and anhydride are prepared from the distillation of anhydrous citric acid (33), or the distillation of concentrated aqueous solution of citric acid under vacuum at 230°C. (34). Itaconic acid is commercially produced by submerged culture fermentation of glucose media by "Aspergillus terrus".

    b - 4-Methoxystyrene (p-vinyl anisole)

    4-Methoxystyrene (Monomer-Polymer Laboratories, Borden Chemical Co.) containing 1% hydroquinone inhibitor was washed with 5% sodium hydroxide to remove the inhibitor. It was then stored over anhydrous magnesium sulfate for 5 days. The dry monomer was then flash distilled in a Rotavapor at a reduced pressure of 2-4 mm., and the fraction with the boiling point of 54-56°C. was collected as monomer. The distilled uninhibited monomer was then stored over anhydrous sodium sulfate, in a refrigerator, and used as soon as convenient (usually in

less than 24 hours). To insure that no polymerization had occurred before use, the monomer was tested with methanol. Poly 4-methoxystyrene is precipitated as a white precipitate by methanol, and the monomeric 4-methoxystyrene remains in solution.

Some of the 4-methoxystyrene was prepared in this laboratory by the following two step procedure:

Step I - Synthesis of p-methoxycinnamic acid (35)

One mole (136 grams) of anisaldehyde was added to one mole (126 grams) of malonic acid and one mole (93 grams) of α-picoline in a three neck flask fitted with a reflux condenser and a mechanical stirrer. The mixture was heated over a boiling water bath for two to three hours. At the end of this period, evolution of carbon dioxide ceased, and after cooling a solid crystalline mixture was obtained. The solid product was then dissolved in a minimum amount of ammonium hydroxide solution. This solution was boiled with 1-2 grams of decolorizing charcoal and then filtered. To the cooled filtrate sufficient amount of concentrated hydrochloric acid was added, with stirring, to make the solution acid to Congo red. p-Methoxycinnamic acid precipitated. It was filtered and washed with several portions of cold water and dried. The melting point was 167-168°C.

Step II - Decarboxylation of p-Methoxycinnamic acid (36).

Decarboxylation was carried out in a three neck distilling flask fitted with a thermometer and an adaptor attached

to a condenser. Sixty grams of p-methoxycinnamic acid in
100 milliliters of quinoline were heated in the presence of
5 grams of refined copper powder. The reaction mixture was
allowed to distill at such a rate that during the bulk of
the reaction, the temperature of the vapor remained below
220°C. The reaction was considered to be complete when the
temperature of the vapors reached 237°C. (boiling point of
quinoline). At the end of the reaction, a resinous residue
(probably polymer) was left in the flask. To the distillate,
containing 4-methoxystyrene, one gram of hydroquinone was
added to inhibit polymerization. It was then dissolved in
ether and washed with cold 2.4 N. hydrochloric acid and water
to remove the quinoline. The ether was removed by distilla-
tion under reduced pressure at room temperature, and the
product was dried over anhydrous calcium sulfate. The impure
product was then fractionally distilled under vacuum, and the
fraction boiling at 98-101 at 9-10 mm. was collected. To the
4-methoxystyrene thus prepared 0.1% hydroquinone was added
as inhibitor. The overall yield was 30%, based on anisaldehyde.
Yields as high as 50% have been reported in the literature.

c - Methyl methacrylate

Methyl methacrylate (Matheson, Coleman and Bell Co.)
(b.p. $100-1^{\circ}$C.) containing hydroquinone was washed rapidly
with 5% sodium hydroxide solution and stored over anhydrous
sodium sulfate in a refrigerator for approximately three days.
The monomer was distilled and the fraction having the boiling

point of 24-25°C. at 7-8 mm. was collected, and stored over anhydrous magnesium sulfate. Before using methyl methacrylate in any polymerization, it was tested for the presence of polymeric methyl methacrylate. A small volume of the monomer was added to an 80% aqueous solution of ethanol. Since the polymethyl methacrylate is insoluble (37) in the solution, the absence of a precipitate indicated that the monomer was free from polymer.

II - Initiator

2,2'-Azobis-(2-methylpropionitrile)—2,2'(azodiisobutyro-nitrile(CH_3)$_2$C(CN)N:NC(CN)(CH_3)$_2$) (Eastman Organic Chemicals) was dissolved in an aqueous solution of ethanol (80%) and filtered. The filtrate was then diluted with distilled water. The diisobutyronitrile was precipitated, collected and dried in a dessicator under vacuum at room temperature.

III - Solvents and Non-Solvents

a - Tetrahydrofuran

Tetrahydrofuran was stored over potassium hydroxide pellets for two weeks. It was stored over metallic sodium for 5-7 days. The tetrahydrofuran was then refluxed with lithium aluminum hydride for about twelve hours and distilled. A fraction boiling at 64-65°C. was collected for use. Since tetrahydrofuran is highly hygroscopic, a freshly distilled portion was used for each copolymerization reaction.

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b - Anhydrous benzene

Benzene was washed with two to three consecutive batches of concentrated sulfuric acid to remove the thiophene and other impurities. The benzene was then washed with 10% solution of sodium bicarbonate to remove the traces of acid. It was then washed several times with distilled water until the washings were neutral to litmus. Thiophene free benzene was stored over anhydrous calcium chloride and then over sodium wire. The benzene was finally refluxed over metallic sodium for 12 to 24 hours and distilled, a fraction collected at 80-80.5°C. at atmospheric pressure, was used.

c - Acetonitrile

Spectrograde acetonitrile (Matheson, Coleman and Bell Co.) was stored over phosphorous pentoxide followed by refluxing for approximately six hours over fresh phosphorous pentoxide. It was distilled and the fraction boiling at 82°C. at ordinary pressure was collected for use.

d - Anhydrous ether

Anhydrous grade diethyl ether was stored over sodium metal for about a week. It was refluxed over lithium-aluminum hydride for 5 to 10 hours, and distilled. The fraction boiling at 34°C. at ordinary atmospheric pressure was collected for use.

IV - Fieser's Solution

Fieser's solution was prepared by dissolving 20 g. of potassium hydroxide in 100 milliliters of distilled water (freshly distilled from all glass equipment) and adding 2 g. of sodium anthraquinone-β-sulphonate and 15 g. of commercial sodium hyposulphite (85 percent) to the warm solution, which was stirred until all the reagents had dissolved. The exhaustion of this solution is indicated by the change in color from blood red to dull red or brown, or when a precipitate due to sodium hydrogen sulfate appears (38).

$$Na_2S_2O_4 + O_2 + H_2O \overline{} NaHSO_4 + NaHSO_3$$
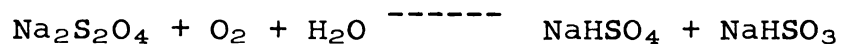
V - p-Sec. butyl anisole (39)

One mole (108 grams) of anisole and 0.75 moles (103 grams) of sec. butyl bromide were dissolved in 100 ml. petroleum ether. The solution was placed in a dropping funnel and was gradually added to 0.125 moles (17 grams) of anhydrous aluminum chloride suspended in 100 milliliters of petroleum ether, at room temperature. The reaction was allowed to proceed for three to four hours. The intensely colored reaction mixture was then poured in to 50 milliliters of concentrated hydrochloric acid and approximately 200 g. of ice. A two layer system resulted. The ether layer, was separated from the aqueous acidic layer. The petroleum ether was removed from the ether layer by distillation and the residue was fractionally distilled under vacuum. The fraction boiling at 24-25°C. at 3 mm., $n_D^{22.5} = 1.514$ was the p-sec. butyl anisole.

EXPERIMENTAL

PART I

Preliminary Copolymerization of Itaconic Anhydride
with Some Comonomers in Tetrahydrofuran

Copolymerization of Itaconic Anhydride with Some Comonomers

Itaconic anhydride was copolymerized with vinyl pyrrolidine, 4-methoxystyrene, styrene, 2-chlorostyrene, 3-chlorostyrene and divinyl ether in tetrahydrofuran. 2,2'-Azodiisobutyronitrile was used as an initiator. Initial concentration was 50:50 of itaconic anhydride and the co-monomer.

Polymerization Technique

A calculated amount of itaconic anhydride was dissolved in 250 milliliters of tetrahydrofuran in the reaction vessel. After solution of the anhydride, the approximate amount of the comonomer (in all cases it was liquid), and 200 milligrams of the initiator were added. Then the reaction flask was heated in an oil bath to the reflux temperature of tetrahydrofuran. The reaction vessel was a 500 ml. two neck round bottom flask. Through the small, side neck ($ 10/14) a nitrogen bubbler was inserted. To the center neck ($ 24/40) a reflux condenser was attached which was equipped with a drying tube filled with anhydrous calcium chloride. The reaction was stirred continuously throughout the reaction period by a magnetic stirrer. The polymerization was allowed to proceed for 12-14 hours. The flask was then removed from the oil bath, and the polymer solution was transferred to the distilling flask of a Rota-vapor and the solvent was evaporated to obtain an optimum concentration for precipitating by a non-solvent. The polymer

was then precipitated using a non-solvent such as: anhydrous ether, petroleum ether, or a mixture of both, such that an easily handled precipitate was obtained. There was a critical optimum concentration, below which, a very small amount of precipitation occurs, and above which, polymer will be separated as a viscous liquid which can not be removed by filtration. The precipitated polymers were filtered, dried, and extracted with benzene to remove unreacted amounts of anhydride. They were then dried in an Abderhalden drying pistol under vacuum at the reflux temperature of acetone. The polymers were weighed to 0.1 gram and the percentage of conversion of monomers to copolymers were calculated for each copolymer. Table 1 gives a summary of initial composition of monomers, percentage of conversion and conditions for the above mentioned copolymerizations.

Table 1. Data and Conditions of Copolymerization of Itaconic Anhydride with Some Monomers in Tetrahydrofuran

Experiment Number	Comonomer M_2	M_1 gr	M_2 gr	Weight of Polymer	Conversion Percent	Non-solvent for precipitation	Time hrs
1	Vinyl pyrrolidine	16.8	10.65	2.9	11.0	Pet. ether	24
2	4-Methoxystyrene	16.8	20.10	15.0	40.8	Pet. ether and Diethyl ether	24
3	Styrene	16.8	15.60	4.0	12.0	Pet. ether and Diethyl ether	3
4	2-Chlorostyrene	4.48	5.54	1.0	10.0	Pet. ether	24
5	3-Chlorostyrene	4.48	5.54	2.1	20.0	Pet. ether	24
6	Divinyl ether	11.2	7.00	3.2	12.1	Pet. ether	12

PART II

Reactivity Ratios of Itaconic Anhydride with
Methyl methacrylate and 4-Methoxystyrene

Copolymerization Process and Technique

A series of copolymerizations of itaconic anhydride
(M_1) and each of the other two comonomers (M_2) were made in
benzene at the molar ratio of:

M_1/M_2; 1/9, 2/8, 3/7, 4/6, 5/5, 6/4, 7/3, 8/2, 9/1.
The copolymerizations were carried out in a 500 milliliter,
two neck flask, which was fitted with a nitrogen inlet and a
reflux condenser. Gaseous nitrogen from a cylinder of puri-
fied nitrogen was passed through Fieser's solution in order to
remove traces of oxygen and then dried by anhydrous calcium
chloride. The apparatus was protected against moisture using
a drying tube filled with anhydrous calcium chloride.

The appropriate amount of itaconic anhydride was dis-
solved in 200 milliliters of anhydrous benzene at room tempera-
ture with stirring. A calculated amount of comonomer was then
added and oxygen was removed from the apparatus and reactants
using a sweeping process (21). The total amount of both
monomers in the reaction was 0.1 mole and the solvent 200
milliliters resulting in a concentration of monomer of 0.5
mole liter^{-1}. Two hundred milligrams of purified 2,2'-azobis-
isobutyronitrile was used (0.1% wt/volume) to initiate the
copolymerization. The temperature of the reaction was increased
to reflux of the solvent and maintained at this temperature
throughout copolymerization. There was almost no induction
time and a slight turbidity was observed almost immediately
when the solvent began to reflux. An exception to this was

was noted in the case of itaconic anhydride-methyl methacrylate $M_1/M_2 = 1/9$, since the polymer was soluble in the solvent. When the appropriate percent of polymerization (judged by the amount of precipitated copolymer or by the time of reaction in the case of copolymerization of methyl methacrylate) had occurred, the flask was taken out of the oil bath, and the content was transferred to a bottle and immersed in a dry ice-acetone mixture to quench the reaction. The solidified mixture was then allowed to thaw, and copolymer was separated by centrifugation and washed several times with hot benzene to remove traces of unreacted monomers. The copolymer was then dried, first in a dessicator under reduced pressure (20-25 mm) at room temperature, and then in Abderhalden drying pistol under vacuum, at boiling point of acetone (56°C.) for twenty-four hours. In the latter drying process, any residue of itaconic anhydride sublimed out of the copolymer. The dry polymer was weighed and the percent of copolymerization was calculated as follows:

Percent of copolymerization = (weight of copolymer/total weight of monomers) x 100

Analysis of Copolymers

To find the reactivity ratios, it was necessary to determine the mole fraction of itaconic anhydride (M_1) and the mole fraction of the comonomer (M_2), in the copolymer. In order to get the mole fractions in the copolymer, quantitative

infrared analysis of the copolymer was obtained using a
"Perkin-Elmer 237B" spectrophotometer, and matching sodium
chloride cells. The scanning was done at low speed (8 min./
spectrum), and the slit opening was set at 5. The thickness
of the solution in cell was 0.5 mm. The analysis of the
amount of itaconic anhydride moiety in the itaconic anhydride
co methyl methacrylate polymer, was carried out in the follow-
ing manner: polyitaconic anhydride - 0.05 grams and poly-
methyl methacrylate 0.05 grams, were each dissolved in 10
milliliters of anhydrous acetonitrile in volumetric flasks.
The 0.5% solutions thus prepared were used to make a series
of solutions in the following proportions:

Polyitaconic anhydride	0	0.4	0.8	1.2	1.6	2
Polymethyl methacrylate	2	1.6	1.2	0.8	0.4	0
Total volume	2	2	2	2	2	2
Percent anhydride	0%	20%	40%	60%	80%	100%

The standard solution for the determination of itaconic an-
hydride moiety in the copolymer of itaconic anhydride with
4-methoxystyrene, was prepared and diluted in the above
described manner, using 0.5% solution of p-sec. butyl anisole
(A model compound of poly—4-methoxystyrene) in the place of
4-methoxystyrene (which was insoluble in acetonitrile). The
standard solutions for the determination of the composition
of itaconic anhydride co styrene polymer were prepared using
a 0.5 percent solution of polyitaconic anhydride (initiated
with benzoylperoxide) and diluting it with anhydrous aceto-
nitrile to 80%, 60%, 40%, 20% of the original concentration.

Infra-red spectra of these three series were obtained. Peak areas of the anhydride peaks at 1865 cm^{-1} for different concentration of anhydride were measured. For these measurements a "Keuffel & Esser 620022" Planimeter was used.

Plotting the known percentage of polyitaconic anhydride in the standard solutions versus the peak areas, gave three straight line graphs, which were used as standard reference graphs, assumed to be related to the percent of anhydride moiety in the various copolymers. In the same manner, 0.5% solutions of different copolymers were made, by dissolving 0.01 grams of each copolymer in 2 ml of anhydrous acetonitrile. The infra-red spectra of these copolymers were obtained and the peak areas of the anhydride peak at 1865 cm^{-1} were plotted against the itaconic anhydride moiety content to construct a calibration curve. The infra-red spectra of the copolymers were obtained and the percentages of itaconic anhydride moiety in the copolymers were determined using the standard graph. From the percent by weight of the itaconic anhydride moiety, the mole fractions (m_1 and m_2) were calculated according to the following procedure.

Let A = percent of itaconic anhydride moiety
  B = 100-A = percent comonomer moiety
  M = molecular weight of comonomer

112 = molecular weight of itaconic anhydride

A/112 = x number of moles of anhydride moiety in 100 grams of copolymer
  B/M = y number of moles of comonomer moiety in 100 grams copolymer
  x+y = z total number of moles of monomer moieties in copolymer

mole fraction of each monomer is simply obtained by $x/z = m_1$

$y/z = 1 - m_1 = m_2$.

Calculation of the Reactivity Ratio Values

Copolymerization equation (I), gives the relationship between reactivity ratios r_1 and r_2 and initial and final concentration of monomers in the reaction mixture.

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \qquad \text{I}$$

assuming very low conversions

$$\frac{m_1}{m_2} = \frac{d[M_1]}{d[M_2]} = \frac{M_1}{M_2} \cdot \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \qquad \text{II}$$

where

> M_1 = mole fraction of itaconic anhydride in the initial reaction mixture
> M_2 = mole fraction of the comonomer in the initial reaction mixture
> m_1 = mole fraction of itaconic anhydride moiety in the copolymer
> m_2 = mole fraction of the comonomer moiety in the copolymer
> r_1 = reactivity ratio for itaconic anhydride radical
> r_2 = reactivity ratio for the comonomer radical

Assuming:

$$\frac{m_1}{m_2} = f \text{ and } \frac{M_1}{M_2} = F$$

Equation (II) can be rearranged into the following forms:

$$r_2 = F(1/f(1 + Fr_1) - 1) \qquad \text{III}$$

$$\frac{F}{f}(f - 1) = r_1\frac{F^2}{f} - r^2 \qquad \text{IV}$$

From equation III, it is readily concluded that any experimental

values of F, f are represented as straight lines, when r_1 is plotted versus r_2. Assumed values of r_1 (+0.1, 0, -0.1) were therefore substituted in equation (III), and plotted against observed values of r_2. Using different values of r_1 and r_2, for different compositions of the copolymer, several straight lines were obtained. The point of intersection of these lines is at the r_1 and r_2 values for a system. Besides the above mentioned method of intersection, equation IV can also be used in determination of r_1, r_2 values, by plotting $\frac{F^2}{f}$ against $\frac{F}{f}(f - 1)$. This results in a straight line graph, the slope of which is equal to r_1 and the value of the point of intersection of the extrapolated line with the $\frac{F^2}{f}$ axis is $-r_2$. This method was first suggested by Fineman and Ross (40).

RESULTS

I - Copolymerization of Itaconic Anhydride
with Methyl methacrylate

Itaconic anhydride was copolymerized with methyl methacrylate
in benzene, using 2,2'-azobisisobutyronitrile as initiator.
The copolymers were analyzed by infra-red spectrophotometry,
following the changes in the area of anhydride carbonyl peak
at 1870-1830 cm^{-1}. It should be noticed that cyclic anhydrides
have two absorption peaks in this area, one at 1800-1760 cm^{-1}
(5.56-5.68 μ), and the other at 1870-1830 cm^{-1} (5.35-5.46 μ),
(41). Methyl methacrylate shows a peak at 1750-1735 (5.71-
5.76 μ). Figures I and II show the spectra of polyitaconic
anhydride, and polymethyl methacrylate respectively, while
Figure III shows the infra-red of C=O stretching absorption
peaks of the different mixtures of 0.5% solution of poly-
itaconic anhydride and polymethyl methacrylate.

The areas of the peaks at 1865 cm^{-1} were measured, and
plotted against the anhydride percent, as shown in Figure IV.
Figures V and VI show the infra-red carbonyl peaks of the co-
polymers obtained from different copolymerization experiments.
The areas of peaks at 1865 cm^{-1} were measured and the respective
anhydride moiety percents were obtained from the calibration
curve (Figure IV). From the percentages of anhydride moiety
in the copolymers, the mole fractions were calculated. The
data from which the reactivity ratios were determined are shown
in Table 2. A copolymer composition graph was drawn plotting
m_1 versus M_1 (Figure VII). The differential form of the co-
polymerization equation was solved for r_1, r_2 values, for every
copolymerization carried out in this series, and r_1, r_2 were de-
termined graphically by the method of intersection (Figure VIII).

The rearranged copolymerization equation was also used to plot $\frac{F^2}{f}$ versus $\frac{F}{f}(f-1)$, and the r_1, r_2 values were determined by the Fineman and Ross method (Figure IX).
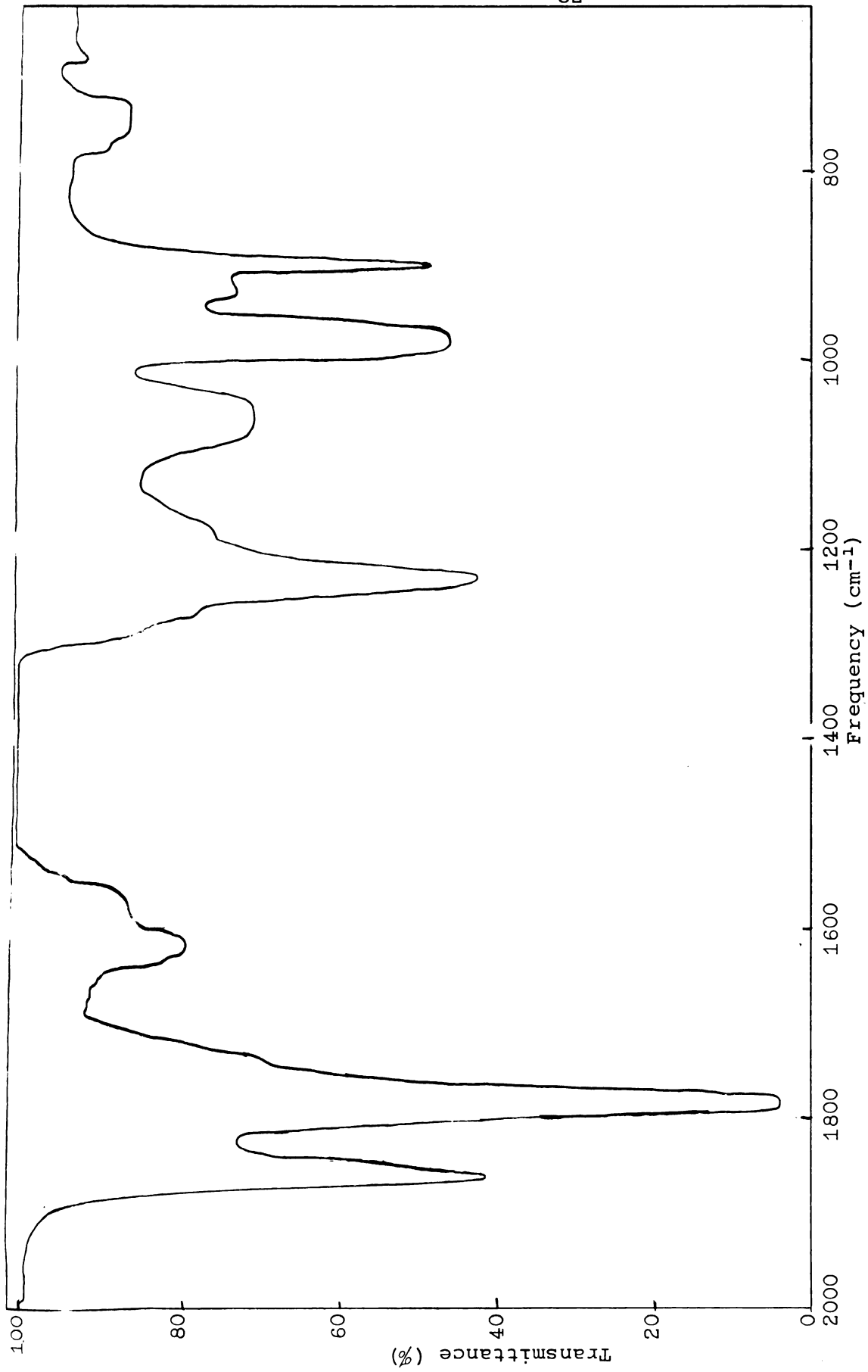
Figure I. Infra-red spectrum of polyitaconic anhydride (0.5%).

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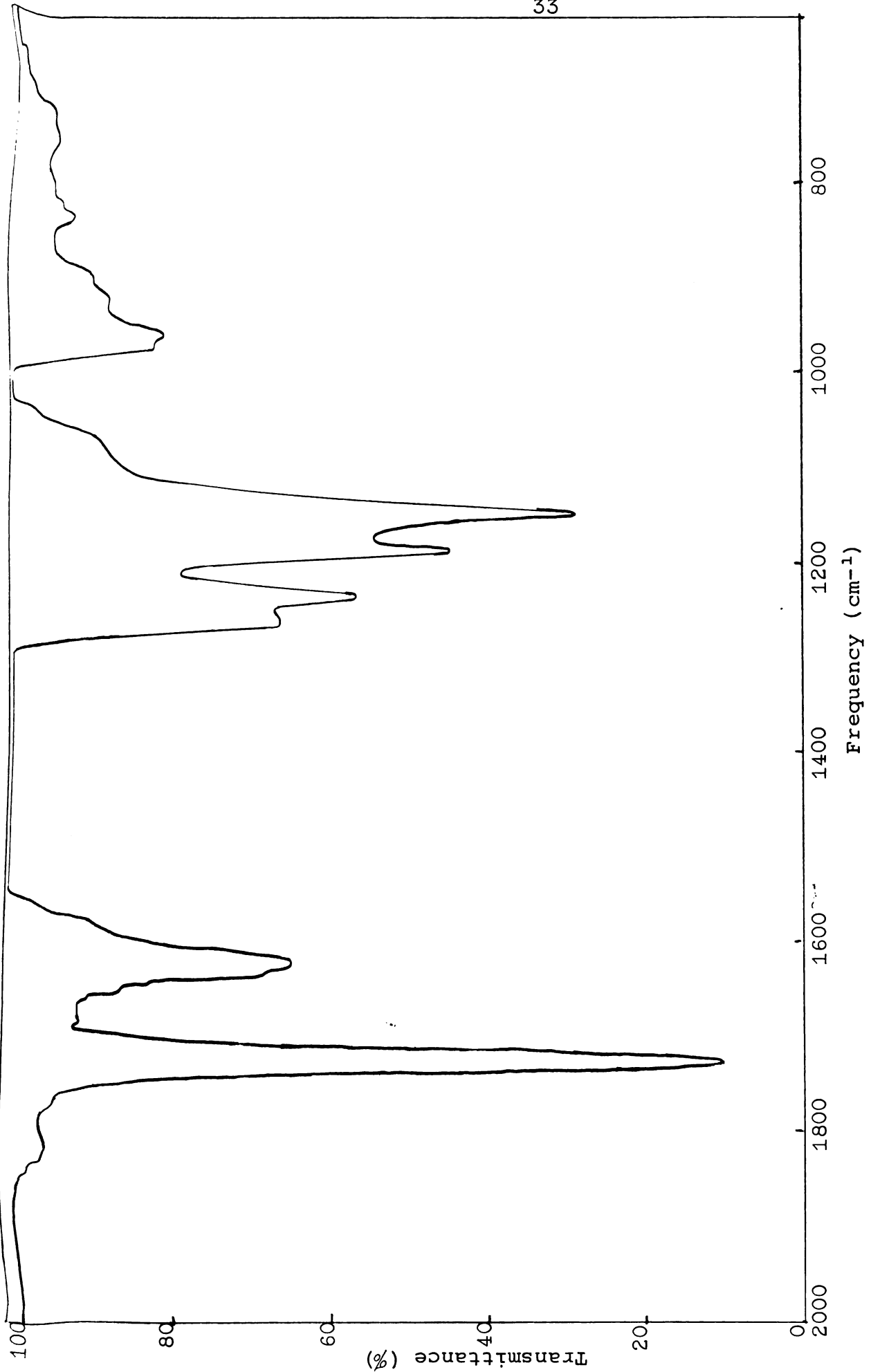Figure II. Infra-red spectrum of polymethyl methacrylate (0.5% solution).
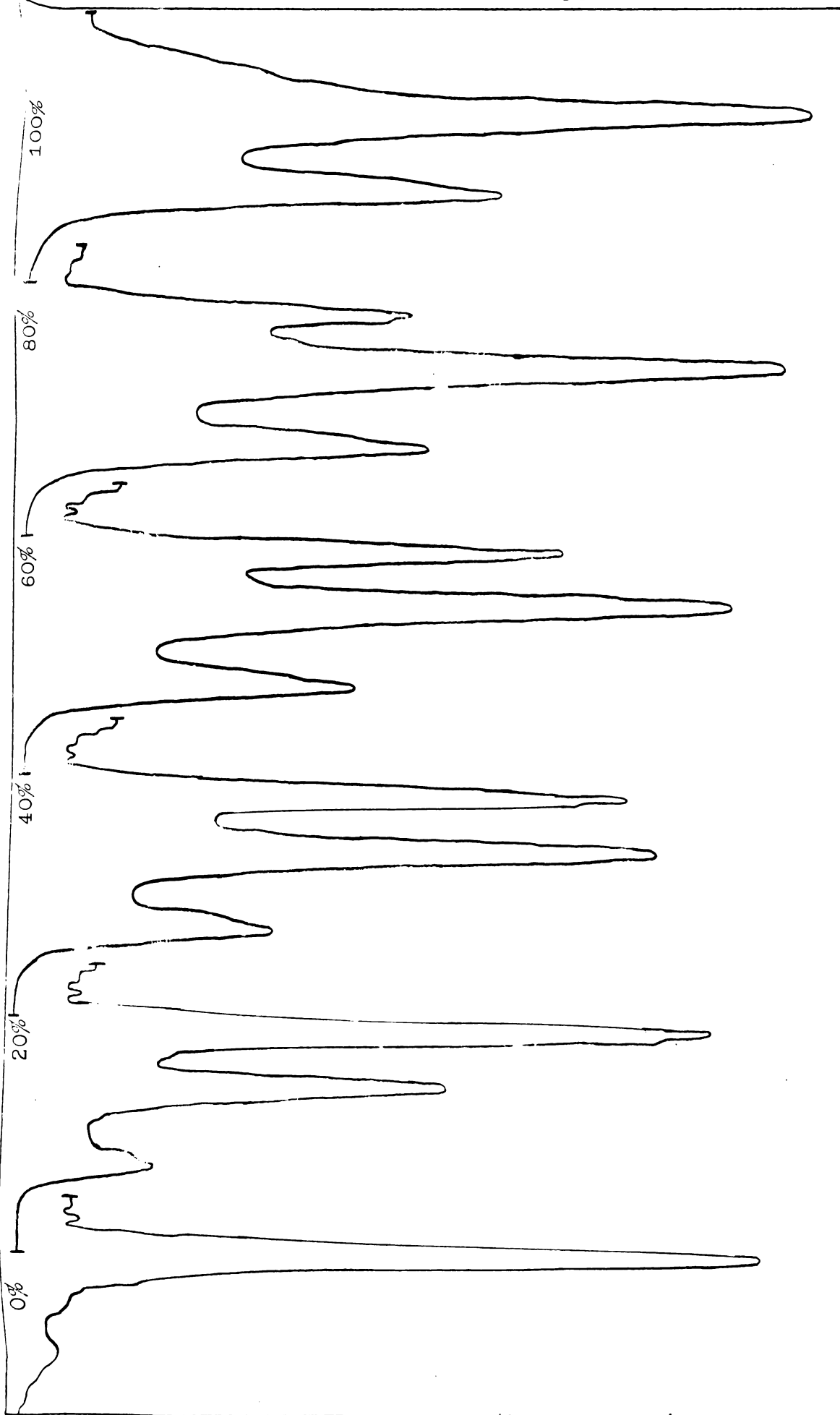
Figure III. Infra-red spectra of carbonyl absorbances of mixtures of polyitaconic anhydride and polymethyl methacrylate.
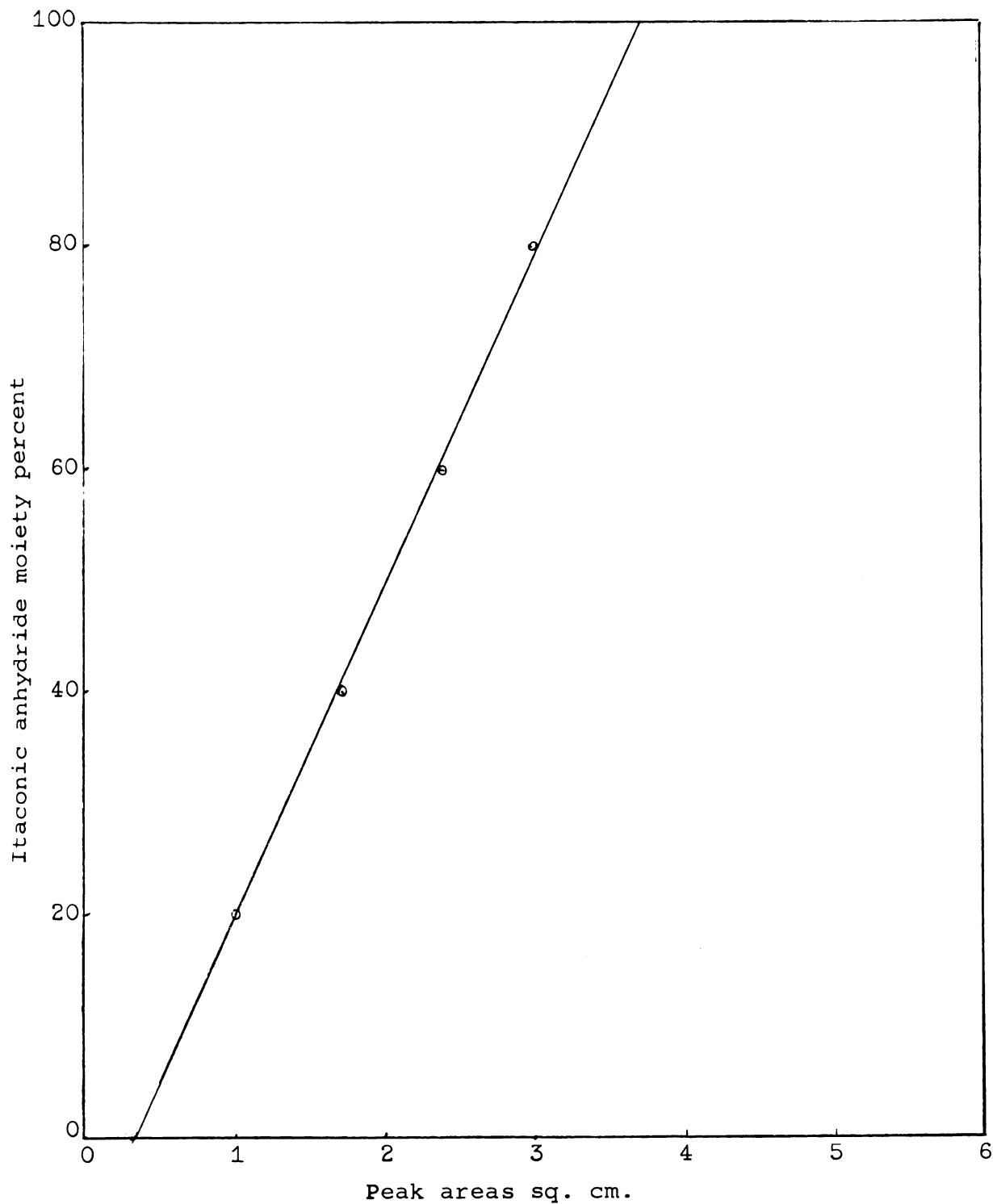
Figure IV. A graph of the area of the anhydride peak
            at 1865 cm^{-1} against the anhydride moiety
            content in mixtures of polyitaconic anhydride
            and polymethyl methacrylate.

Figure V. Infra-red carbonyl absorbances of copolymers obtained from copolymeri-
zation of itaconic anhydride and methyl methacrylate in benzene
(Experiments 1-5 in Table 2).
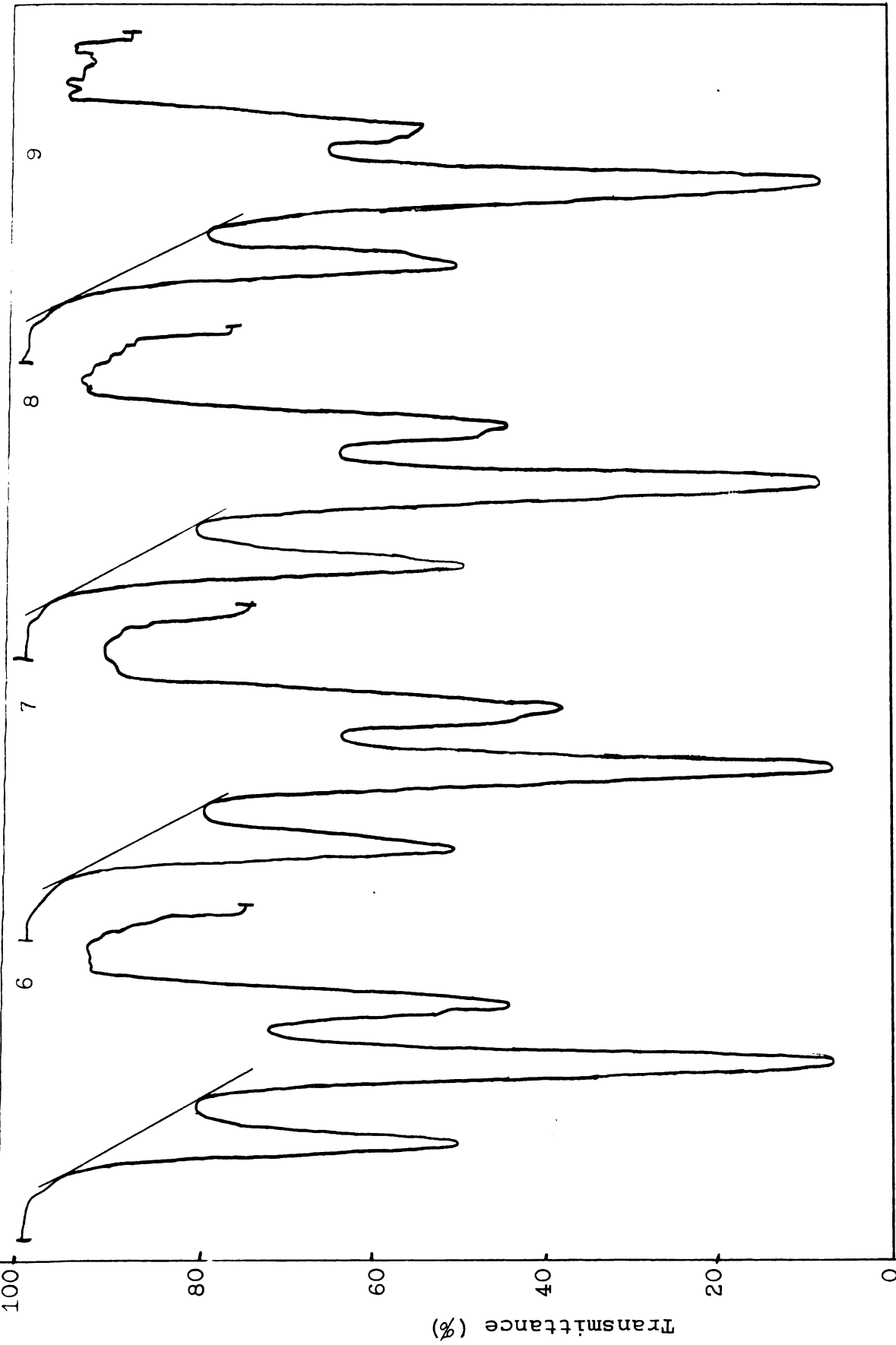
Figure VI. Infra-red carbonyl absorbances of copolymers obtained from copolymeri-zation of itaconic anhydride and methyl methacrylate in benzene (Experiments 6-9 in Table 2).

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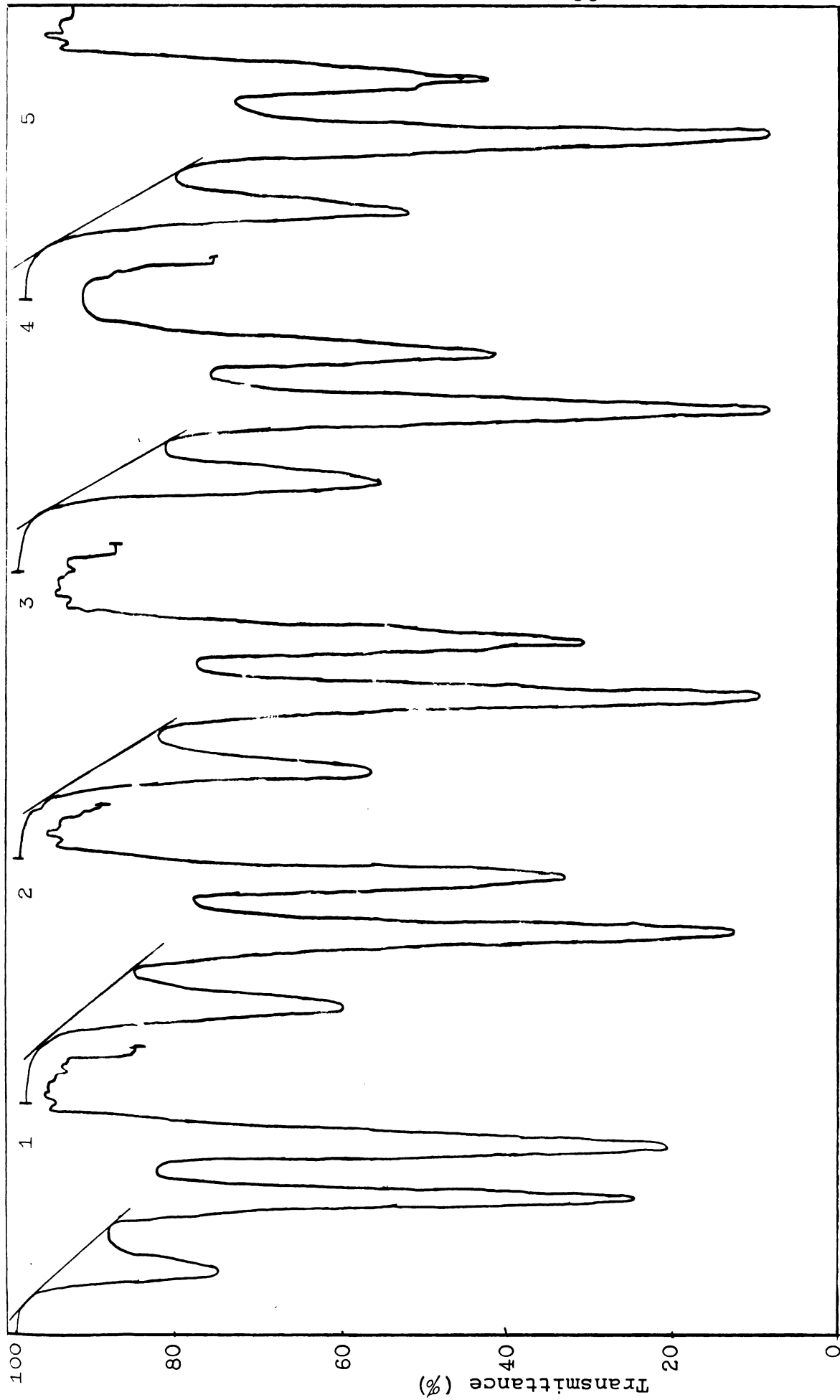Table 2. Reactivity Ratio Data for Itaconic Anhydride-Methyl Methacrylate
Copolymerization

Experiment Number	M_1 Grams	M_1 Mole Fractions	Yield Grams	Conversion Percent	Peak Area Sq. cm.	Itaconic Anhydride Moiety Percent	m_1 Mole Fraction
1	1.12	0.1	0.220	2.17	1.7	40	0.373
2	2.24	0.2	0.205	2.00	2.5	64	0.614
3	3.36	0.3	0.390	3.76	2.7	70	0.675
4	4.48	0.4	0.255	2.43	2.9	76	0.738
5	5.60	0.5	0.280	2.64	3.0	79	0.770
6	6.72	0.6	0.265	2.47	3.1	82	0.802
7	7.84	0.7	0.190	1.75	3.3	88	0.867
8	8.96	0.8	0.265	2.41	3.4	91	0.900
9	10.08	0.9	0.160	1.44	3.5	94	0.933

M_1 = Initial mole fraction of itaconic anhydride in reaction mixture.

m_1 = Mole fraction of itaconic anhydride in copolymer.
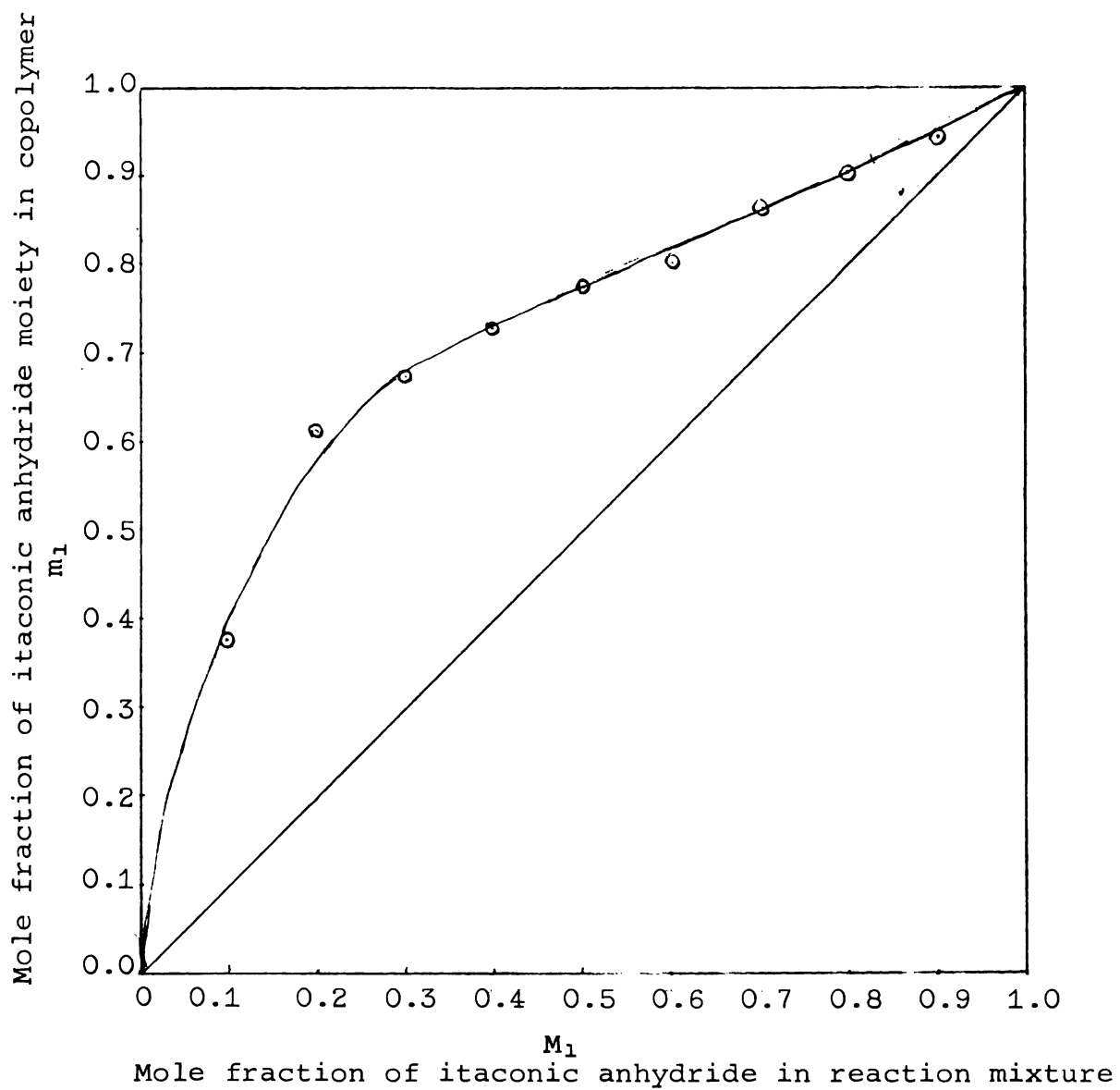
Figure VII. Copolymer composition curve of itaconic
            anhydride-methyl methacrylate co-
            polymerization.

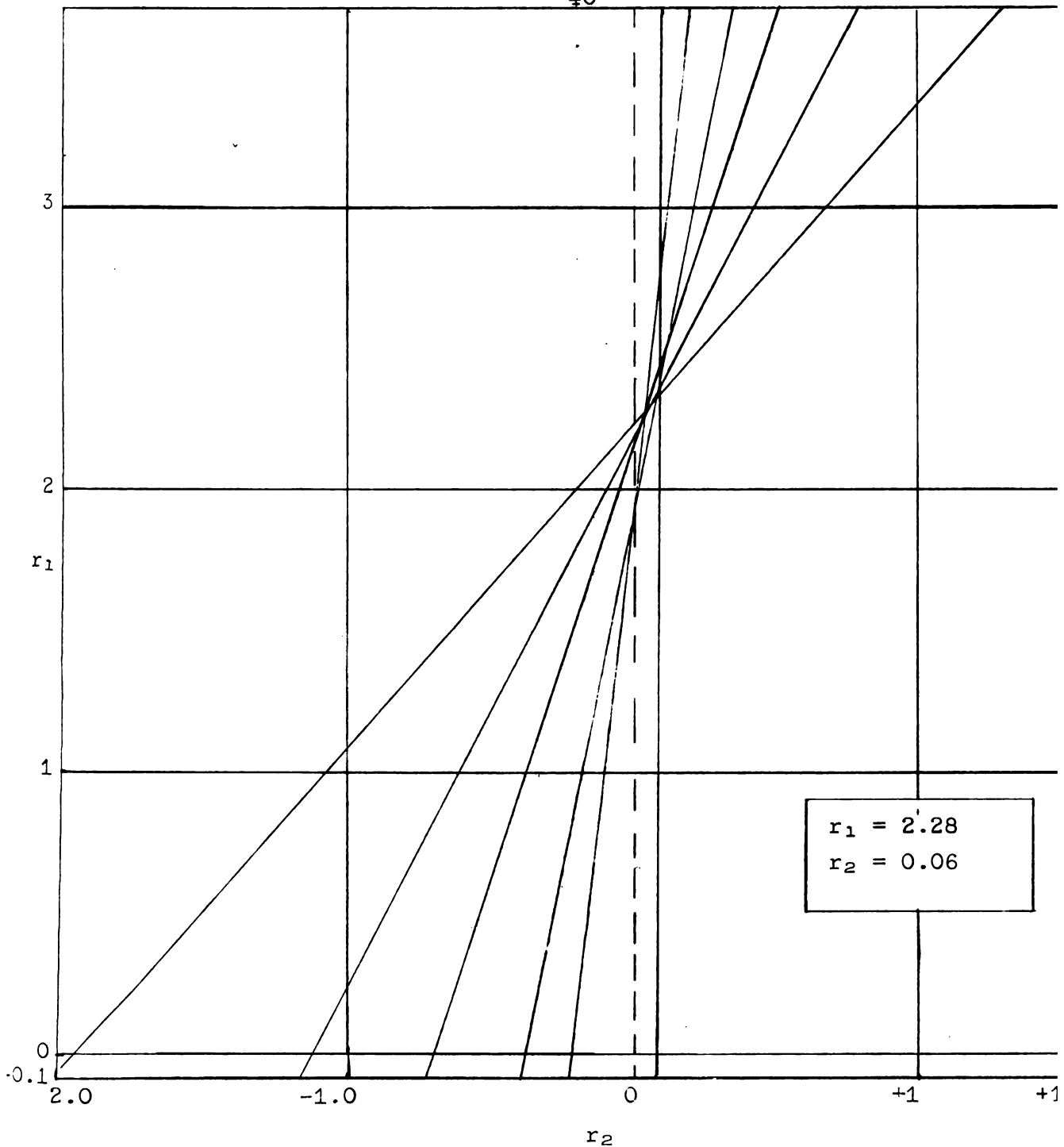Figure VIII.   Graphical solution of copolymerization equation
for itaconic anhydride-methyl methacrylate co-
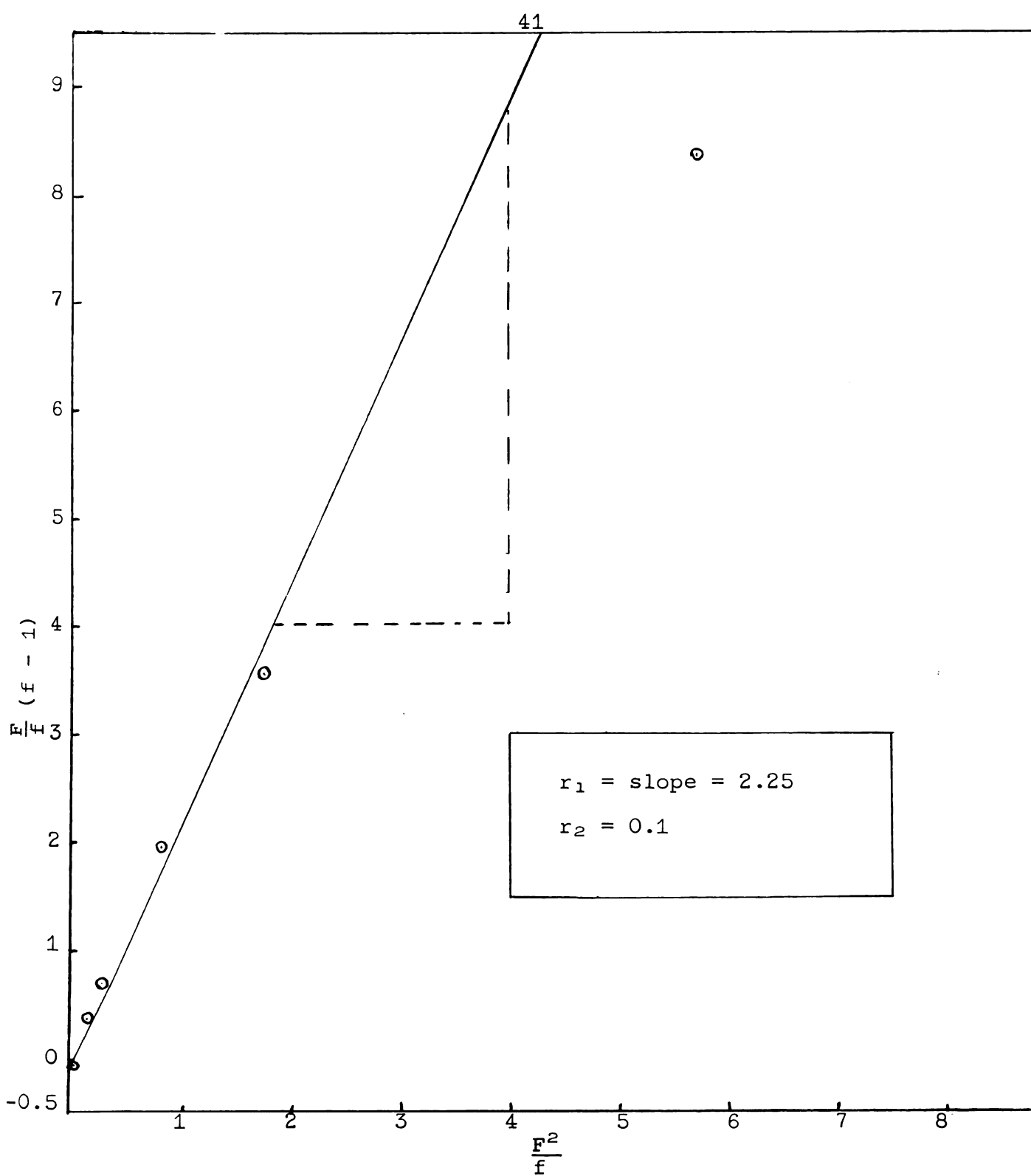polymers (Intersection method).

Figure IX. Graphical solution of copolymerization equation for itaconic anhydride-methyl methacrylate (Fineman and Ross method).

II - Copolymerization of Itaconic Anhydride
and 4-Methoxystyrene

Itaconic anhydride was copolymerized with 4-methoxy-styrene in benzene, using 2,2'-azobisisobutyronitrile as initiator. The copolymers were analyzed by infra-red spectro-photometry method, following the changes in the anhydride peak at 1865 cm^{-1}. A standard curve was plotted using mixtures of polyitaconic anhydride and p-sec. butylanisole (a model compound for 4-methoxystyrene), at different ratios. Figure X shows the spectrum of p-sec. butylanisole. The spectra of mixtures of 0.5% of these two are shown in Figure XI. Figure XII shows the standard curve obtained by plotting percent of polyitaconic anhydride in the mixture against peak areas of anhydride peak at 1865 cm^{-1}. The infra-red spectra of the copolymers obtained from different copolymerization experiments are shown in Figures XIII and XIV. By measuring the areas of the anhydride peak of the spectra of the various copolymer samples and comparing the areas with the standard curve, itaconic moiety percents were obtained for each co-polymer. Table 3 shows the data from which the reactivity ratios were calculated. A copolymer composition graph was drawn plotting m_1 against M_1 (Figure XV). The composition graph shows an azeotrope where initial composition of reaction mixture and composition of the copolymer is equal. The co-polymerization equation was graphically solved (by the inter-section method), for r_1, r_2 values (Figure XVI). Also, the graphical method of Fineman and Ross was utilized to determine the reactivity ratios (Figure XVII).
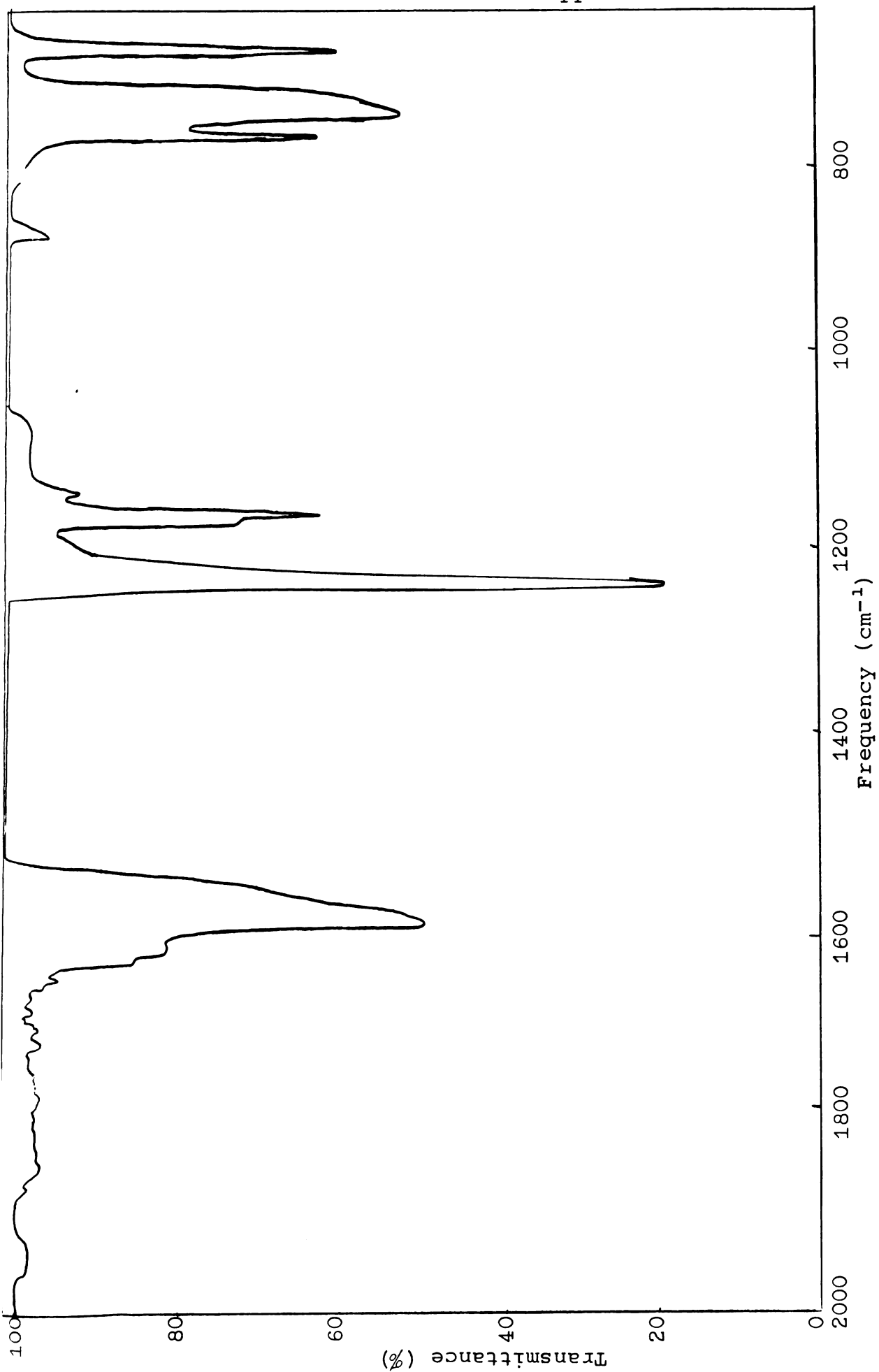
Figure X.   Infra-red spectrum of p-sec. butyl anisole (0.5% solution).
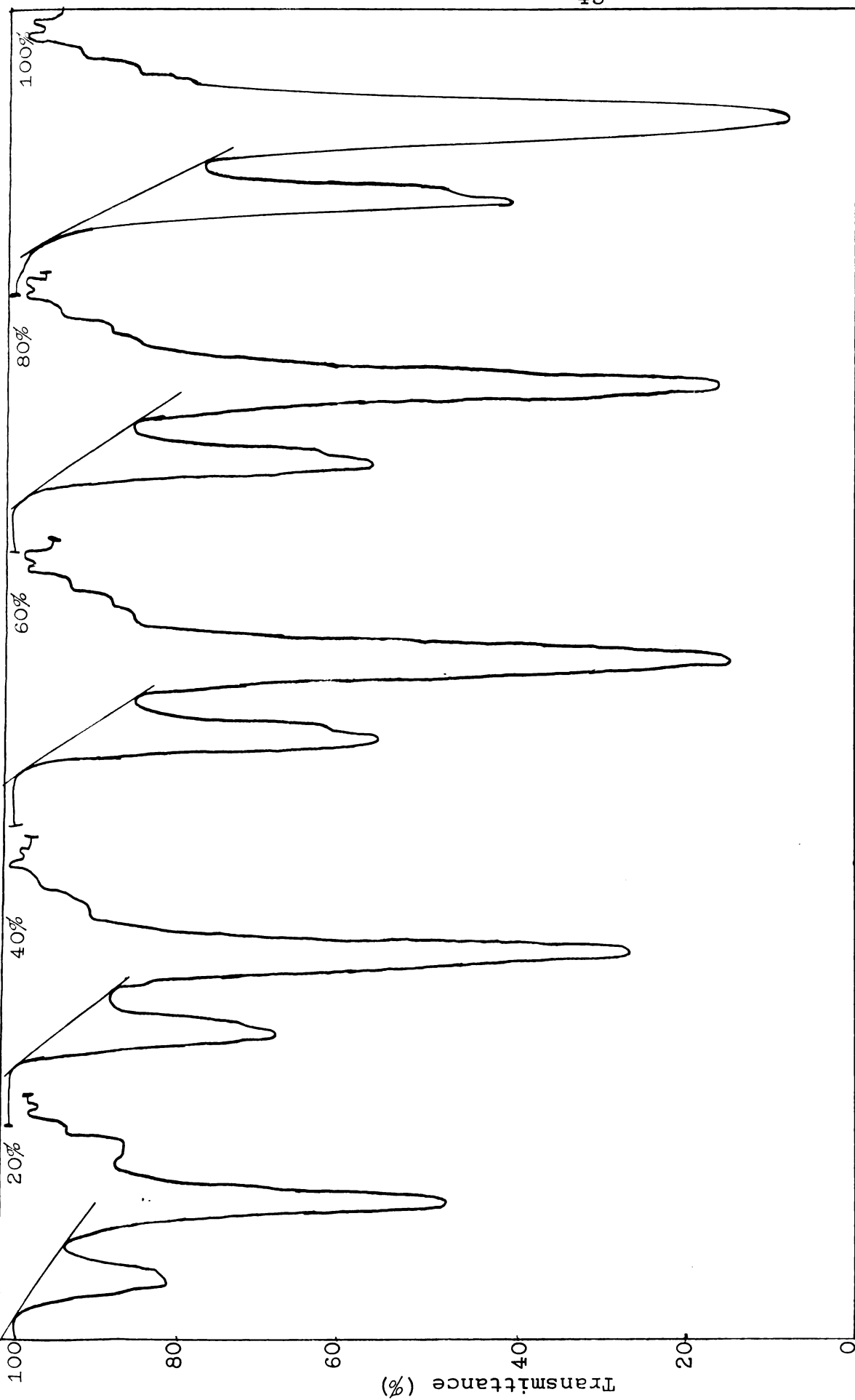
Figure XI.   Infra-red spectra of carbonyl absorbances of mixtures of polyitaconic anhydride and p-sec. butyl anisole.
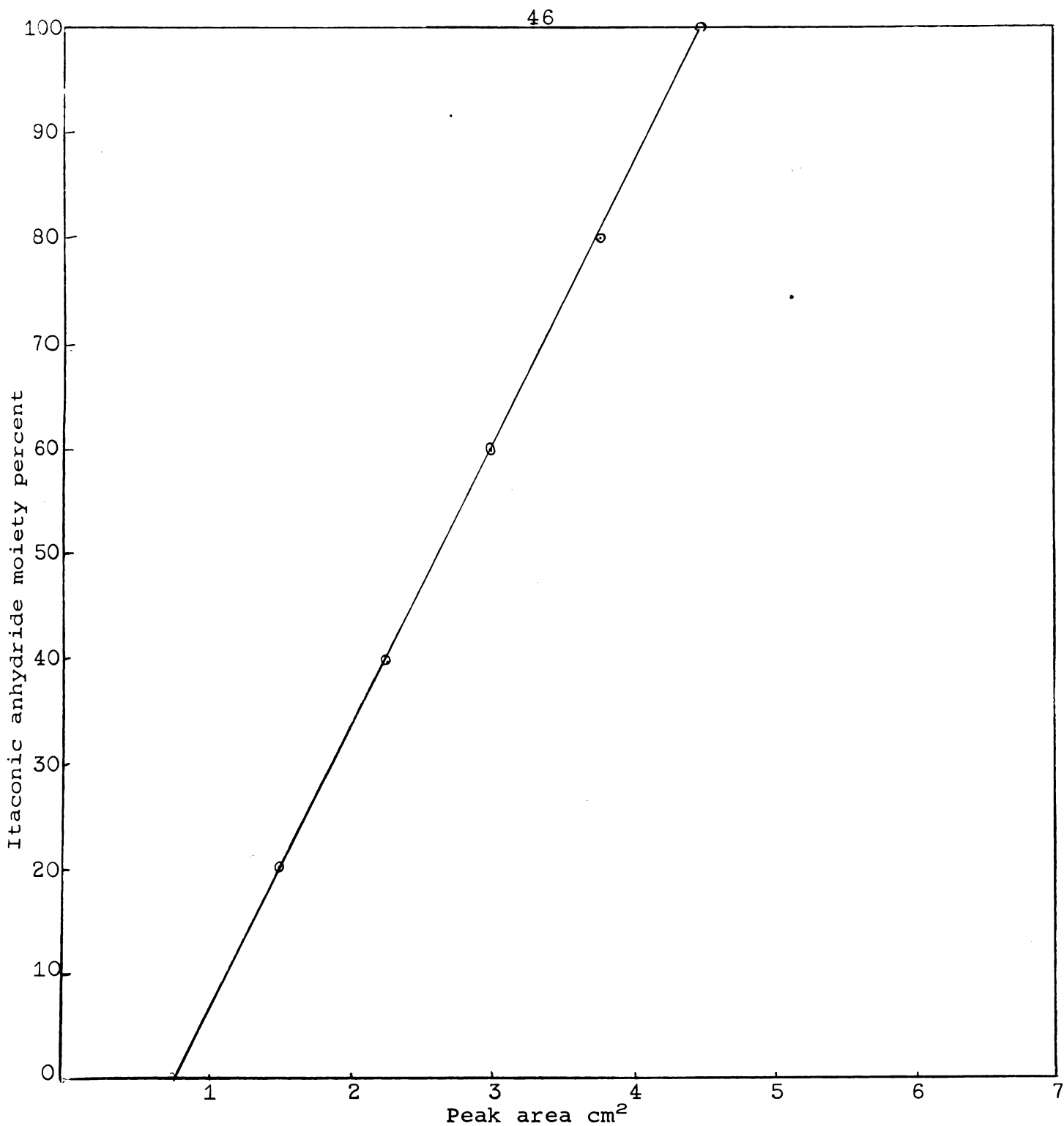
Figure XII. A graph of the area of anhydride peak at 1865 cm^{-1} against itaconic anhydride moiety content in mixtures of polyitaconic anhydride and p-sec. butyl anisole.
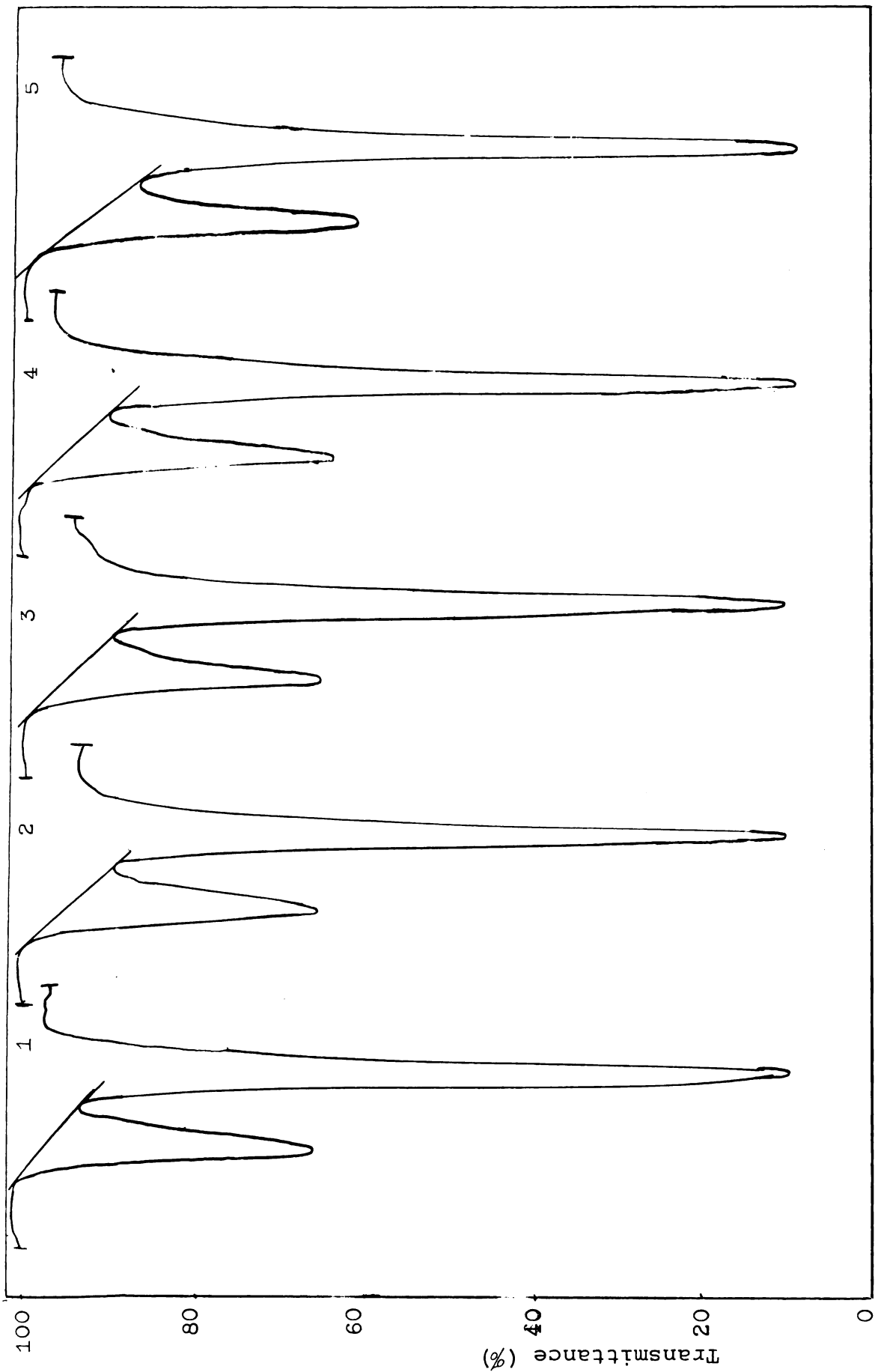
Figure XIII. Infra-red carbonyl absorbances of copolymers obtained from co-polymerization of itaconic anhydride and 4-methoxystyrene in benzene (Experiments 1-5 in Table 3).
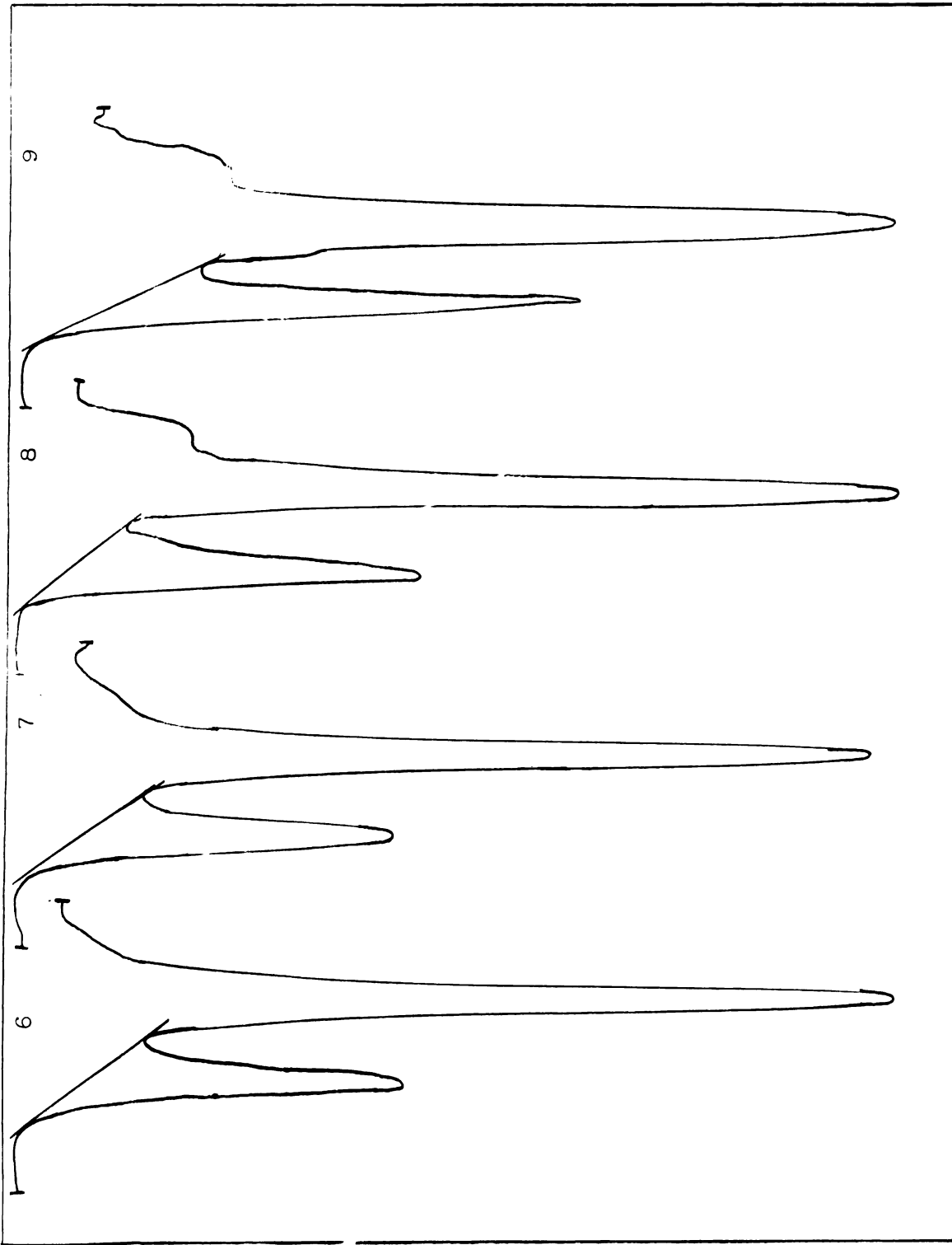
Figure XIV. Infra-red carbonyl absorbances of copolymers obtained from copolymerization of itaconic anhydride and 4-methoxy-styrene in benzene (Experiments 6-9 in Table 3).

Table 3. Reactivity Ratio Data for Itaconic Anhydride-4-Methoxystyrene Copolymerization

Experiment Number	M_1		Yield Gram	Con-version Percent	Carbon Percent	m_1	Peak Area Sq. cm.	Itaconic Anhydride Moiety %	m_1
	Grams	Mole							
1	1.12	0.1	0.524	3.95	68.81	0.485	2.4	43.5	0.479
2	2.24	0.2	0.876	6.76	68.07	0.515	2.5	46.5	0.509
3	3.36	0.3	0.820	6.43	67.50	0.530	2.6	49.0	0.535
4	4.48	0.4	0.965	7.70	----	----	2.7	52.0	0.564
5	5.60	0.5	0.978	7.95	66.60	0.560	2.8	54.5	0.590
6	6.72	0.6	0.724	5.99	65.60	0.590	2.9	57.0	0.613
7	7.84	0.7	0.595	5.02	65.10	0.618	3.0	60.0	0.643
8	8.96	0.8	0.457	3.92	65.00	0.623	3.1	62.0	0.661
9	10.08	0.9	0.360	3.15	60.10	0.759	3.5	73.0	0.764

M_1 = Initial mole fraction of itaconic anhydride in the reaction mixture.

m_1 = Mole fraction of itaconic anhydride moiety in copolymer.
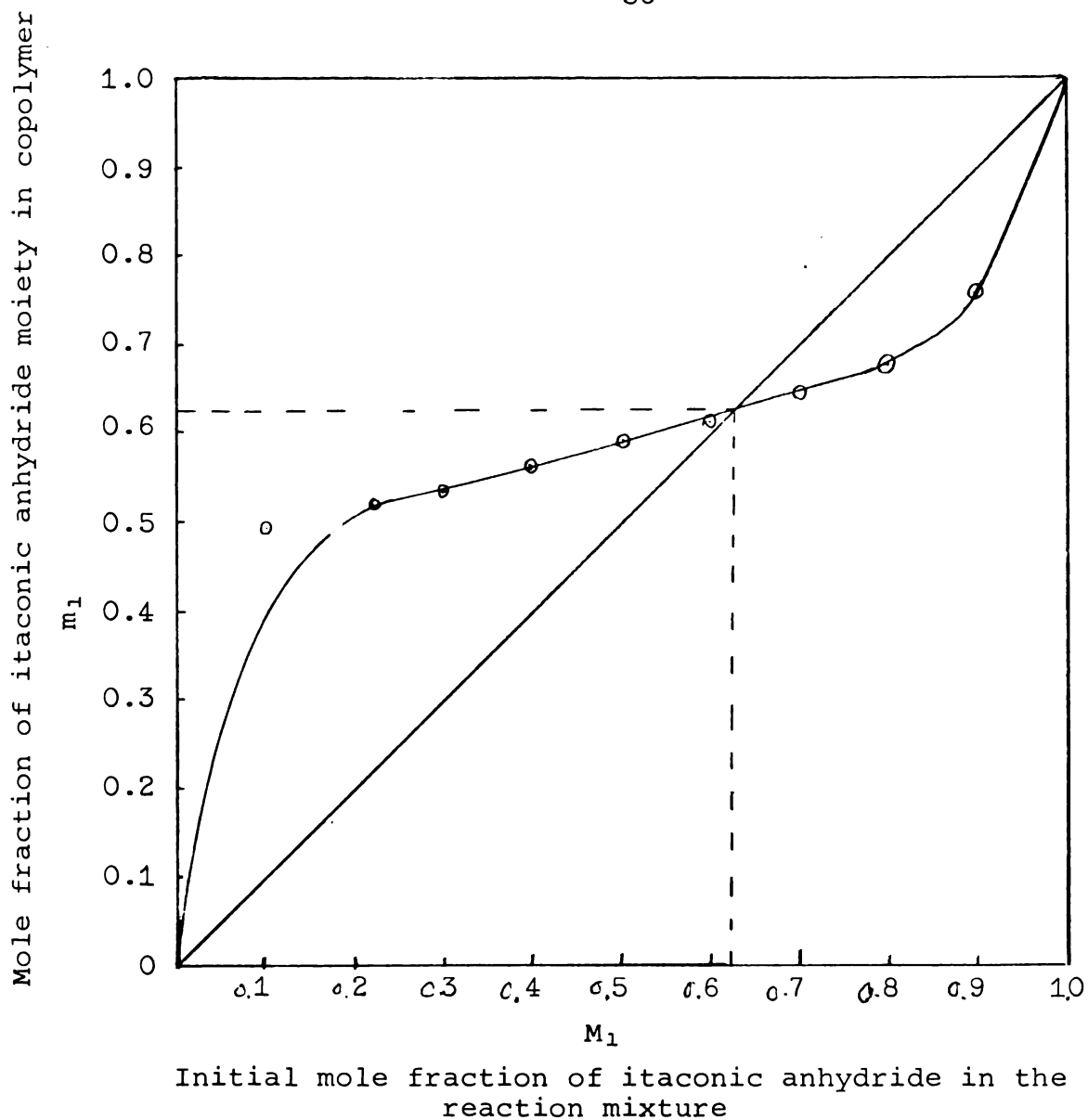
Figure XV. Copolymer composition graph for itaconic anhydride-4-methoxy-styrene copolymerization.

r₁ = 0.52
r₂ = 0.03

Figure XVI. Graphical solution of the copolymerization equation for itaconic anhydride-4-methoxystyrene copolymers (Intersection method).

Figure XVII. Graphical solution of copolymerization equation for itaconic anhydride-4-methoxystyrene copolymers (Fineman and Ross method).

III – Reactivity Ratios of Itaconic Anhydride
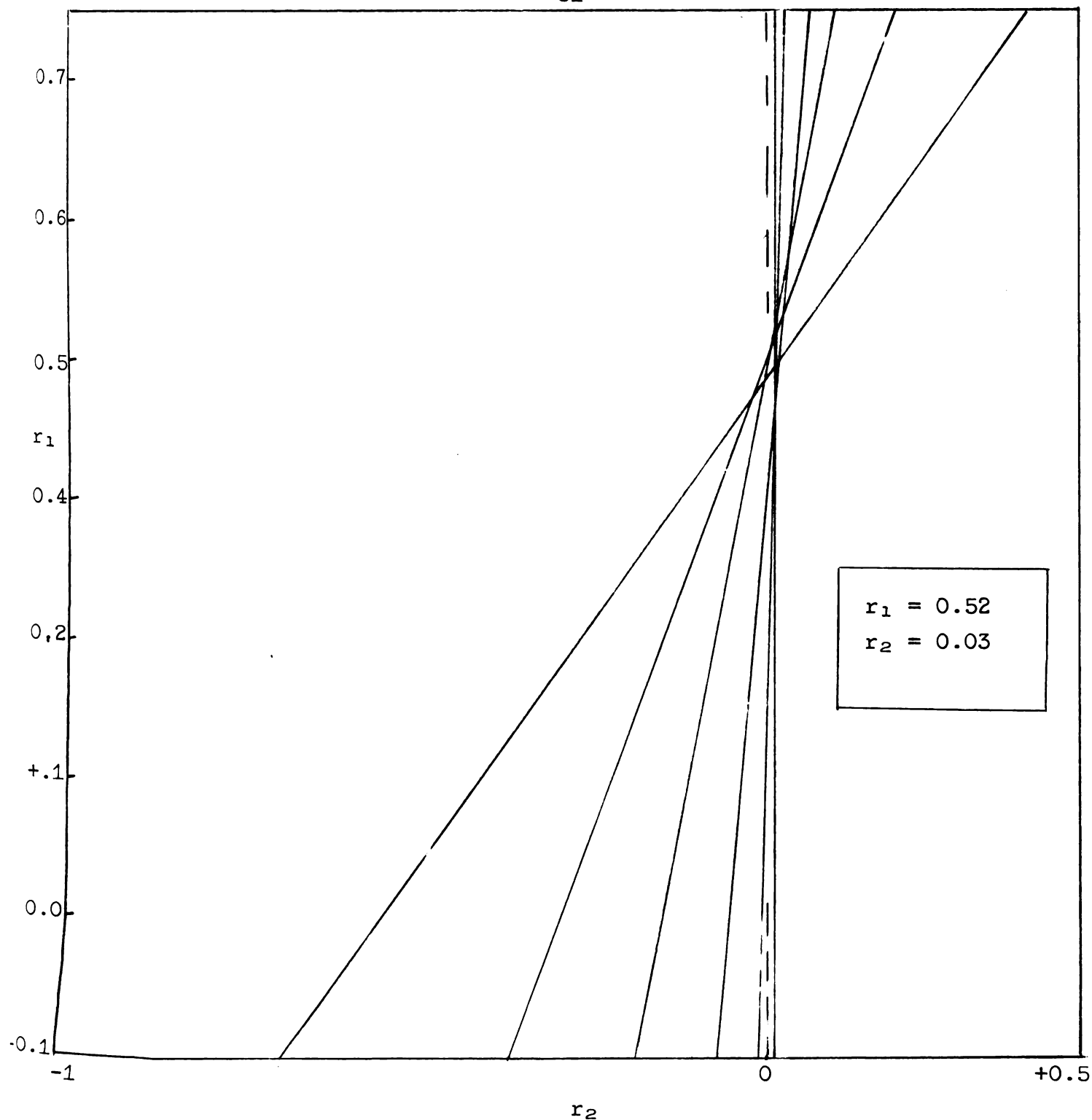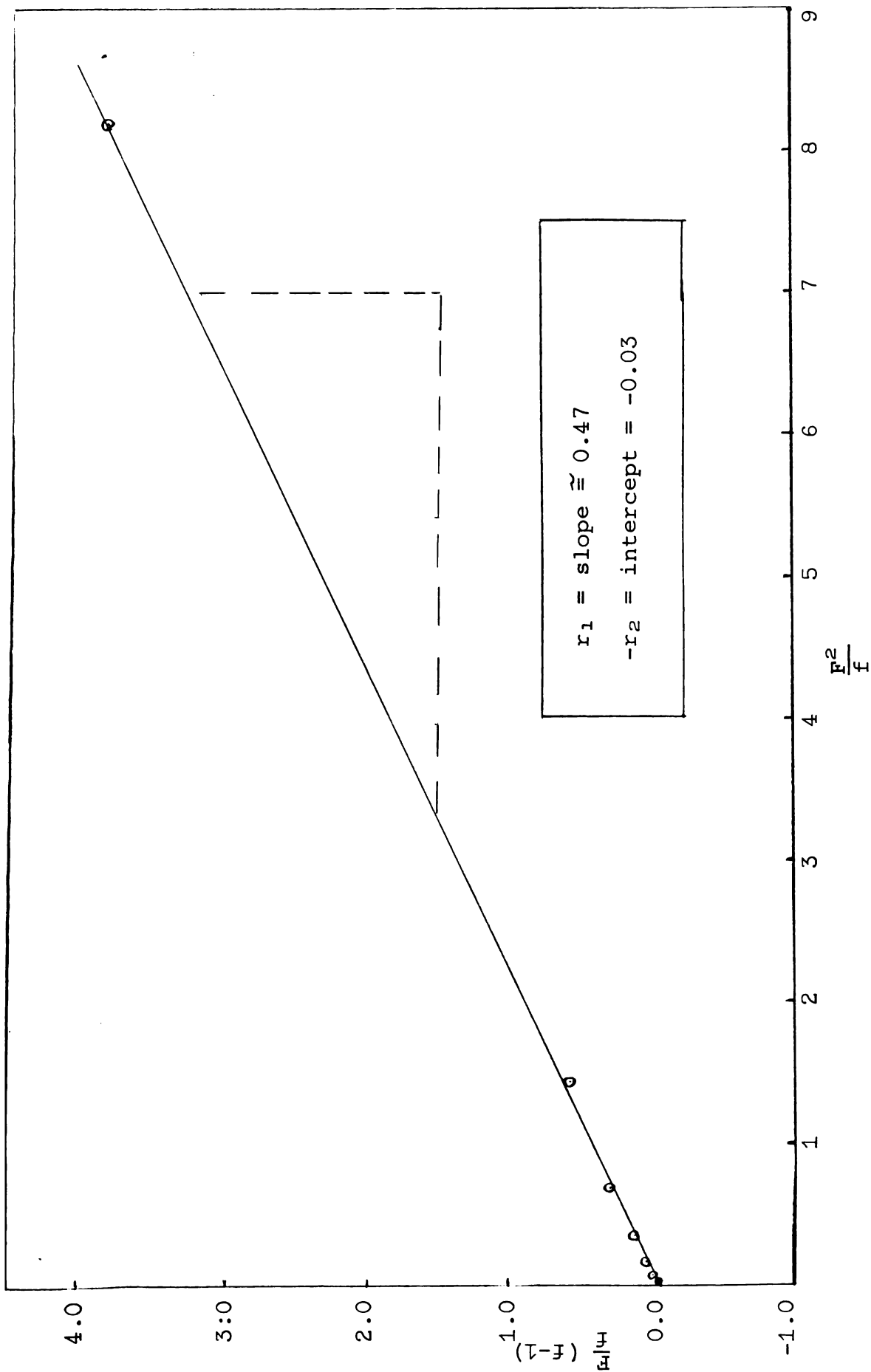and Styrene

A series of eight copolymers of itaconic anhydride and styrene (benzoyl peroxide, initiator), prepared in this laboratory (21), were analyzed by infra-red. A 0.5% solution of polyitaconic anhydride (benzoyl peroxide, initiator), was prepared and diluted with the solvent (acetonitrile) to obtain a series of solutions which were 20%, 40%, 60%, and 80% of the initial concentration. Infra-red spectra of the solutions were obtained, and anhydride peak areas (at 1865 cm^{-1}) were measured. Plotting the measured areas against the percentage of anhydride, assuming the initial solution to be 100%, a standard curve was constructed.

Itaconic anhydride styrene copolymers were dissolved in acetonitrile to form a 0.5% solution, and the infra-red spectra of these solutions were obtained. The peak areas of the itaconic anhydride moieties in the copolymers were measured and from the standard curve the percentages of itaconic anhydride moiety were determined. Mole fraction of itaconic anhydride moiety were calculated from these weight percentages. Infra-red spectra of different concentration of polyitaconic anhydride are shown in Figure XVIII. Figure XIX shows the standard curve obtained from the spectra and Figures XX and XXI show the infra-red spectra of the series of copolymers. The data from which the reactivity ratios were calculated are given in Table 4. A copolymer composition graph was made by plotting mole fraction of anhydride moiety in the copolymers (m_1) against the initial mole fraction of itaconic

anhydride in the reaction mixture (M_1) (Figure XXII).
Graphical solutions of copolymerization equations by inter-
section method and the Fineman and Ross method are shown in
Figures XXIII and XXIV, respectively.
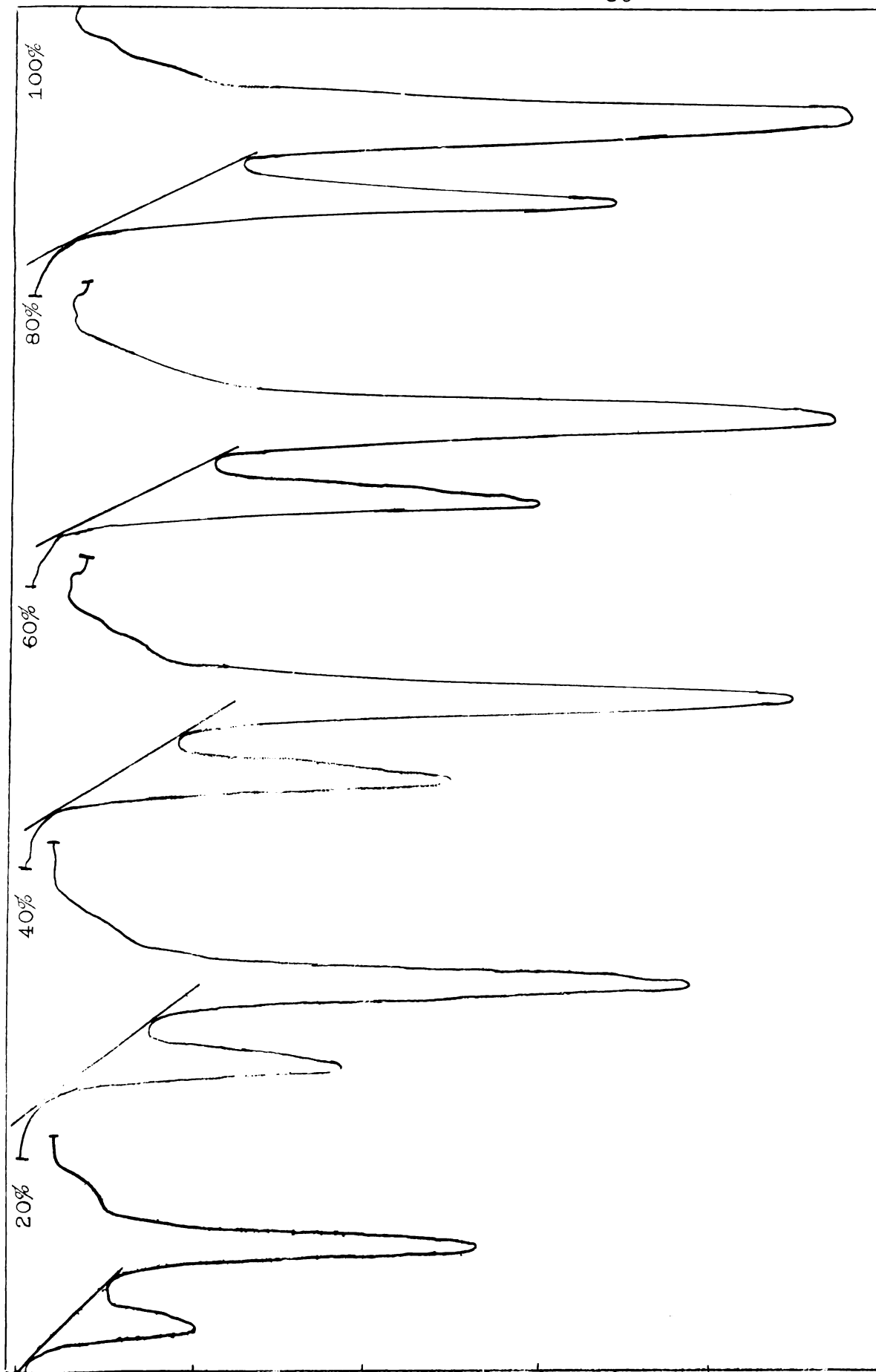
Figure XVIII. Infra-red spectra of polyitaconic anhydride (Initiated with benzoyl peroxide) solution with different concentrations.
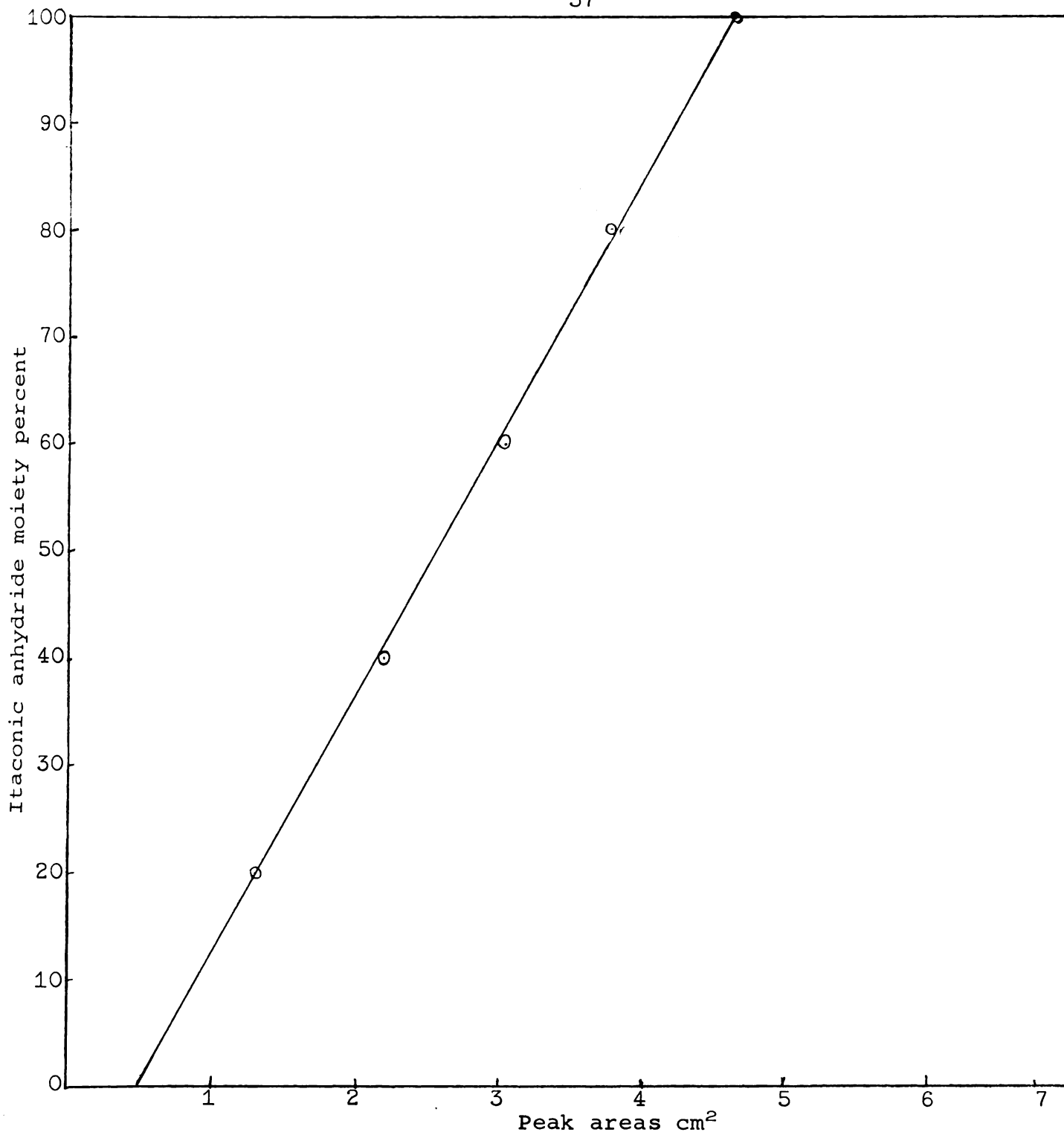
Figure XIX. A graph of the areas of anhydride peak at 1865 cm^{-1} versus the itaconic anhydride moiety percent.
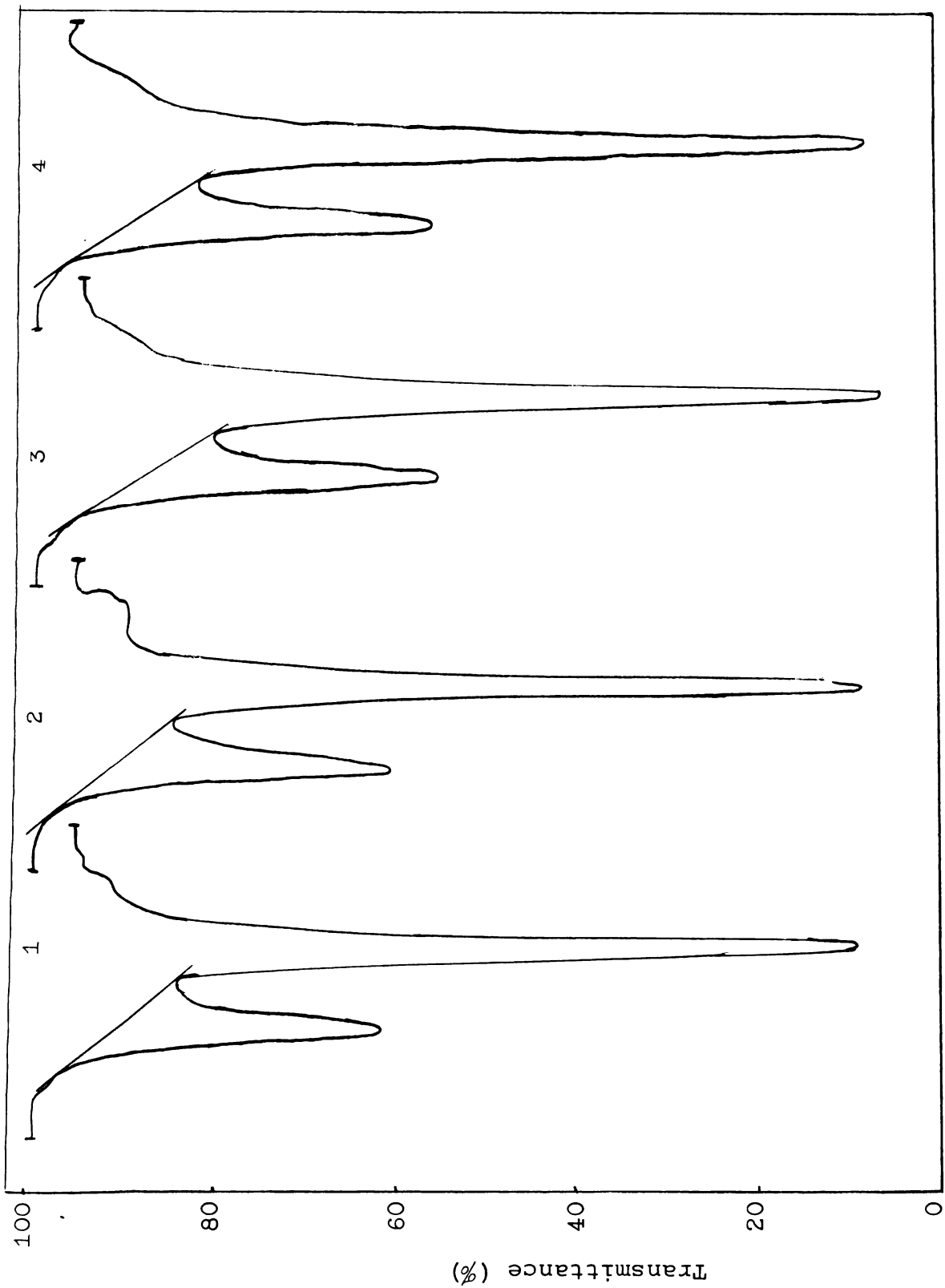
Figure XX. Infra-red spectra of itaconic anhydride-styrene copolymers (Experiments 1-4 in Table 4).
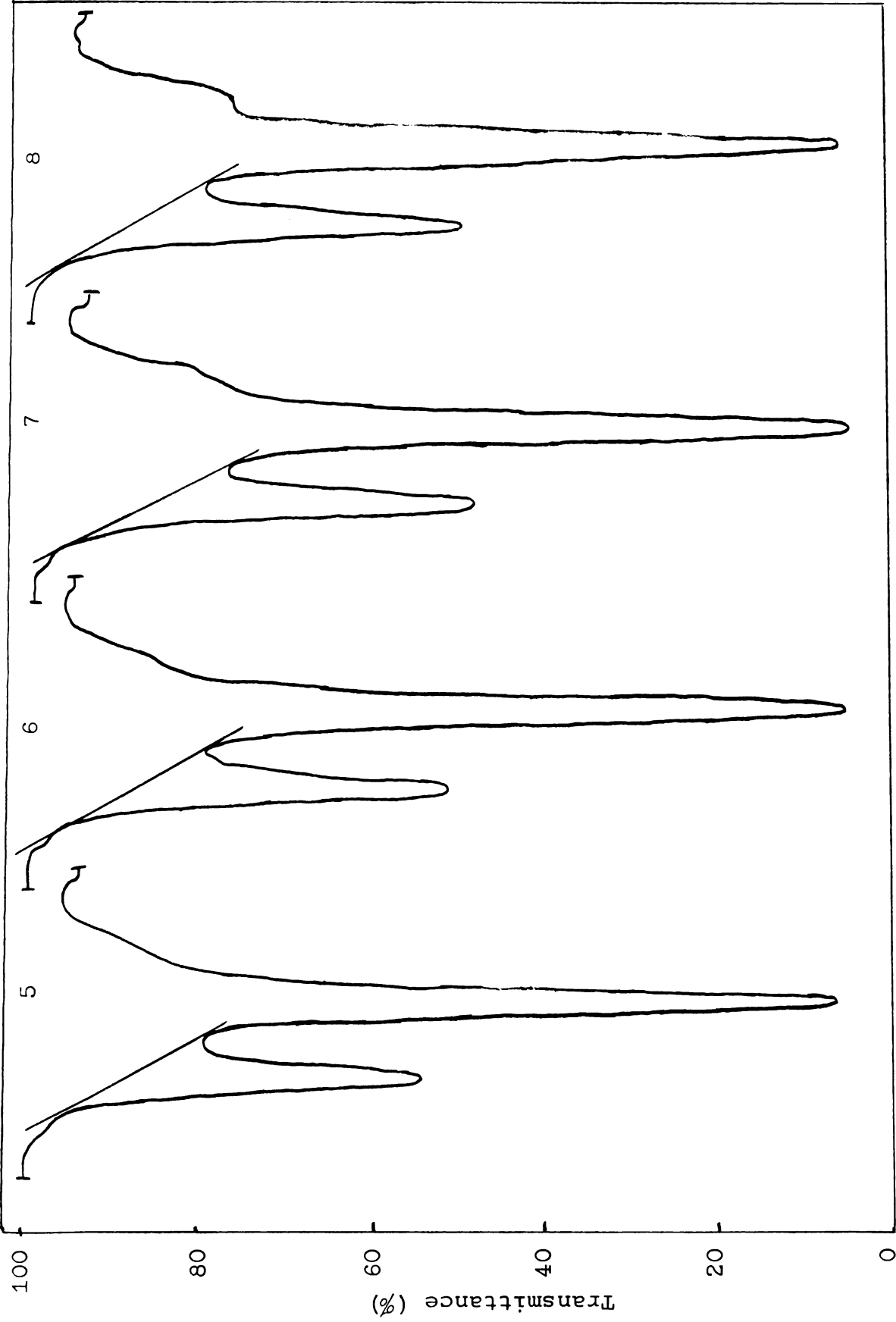
Figure XXI. Infra-red spectra of itaconic anhydride-styrene copolymers
(Experiments 5-8 in Table 4).

Table 4. Reactivity Ratio Data for Itaconic Anhydride-Styrene Copolymerization

Experiment Number	M₁[a]		Yield[a] Grams	Conversion Percent[a]	Carbon[a] Percent	m₁[a]	Peak Area Sq. cm.	Itaconic Anhydride Moiety %	m₁
	Grams	Mole Fraction							
1	1.12	0.1	0.250	2.40	73.00	0.480	2.6	49.5	0.476
2	2.24	0.2	0.450	4.29	71.61	0.520	2.7	52.0	0.500
3	3.36	0.3	0.725	6.70	70.23	0.550	2.8	54.5	0.527
4	4.48	0.4	0.560	5.22	69.72	0.565	2.9	56.5	0.547
5	6.72	0.6	0.610	5.6	67.83	0.615	3.1	61.5	0.597
6	7.84	0.7	0.535	4.88	66.31	0.650	3.3	66.0	0.643
7	8.96	0.8	0.761	6.80	65.32	0.700	3.4	68.0	0.664
8	10.08	0.9	0.555	5.00	61.60	0.78	3.5	71.0	0.694

[a]These parts of data were obtained from copolymerization experiments carried out by M. M. Sharabash in this laboratory (21).
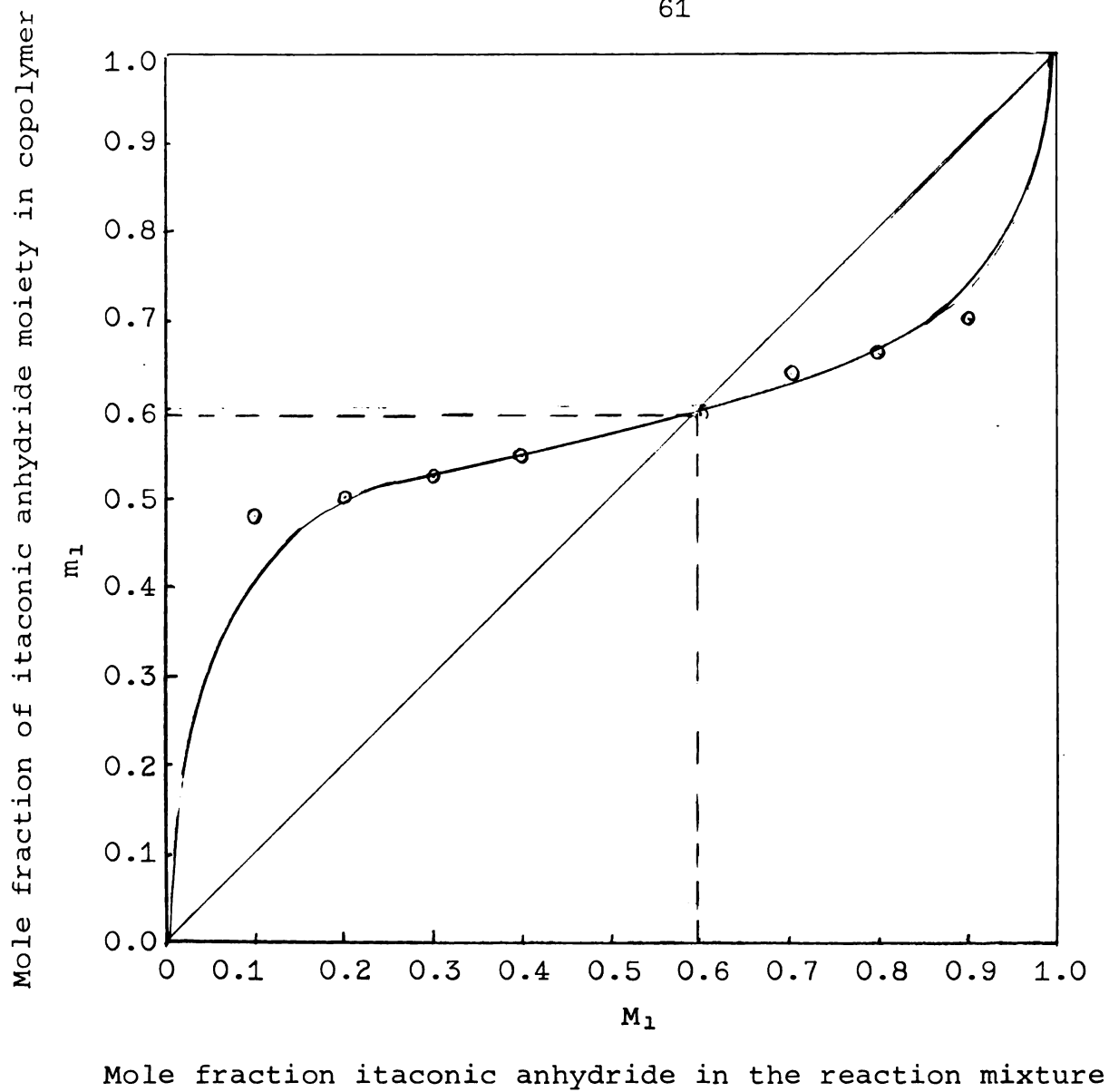
Figure XXII. Copolymer composition graph of itaconic anhydride styrene co-polymers.
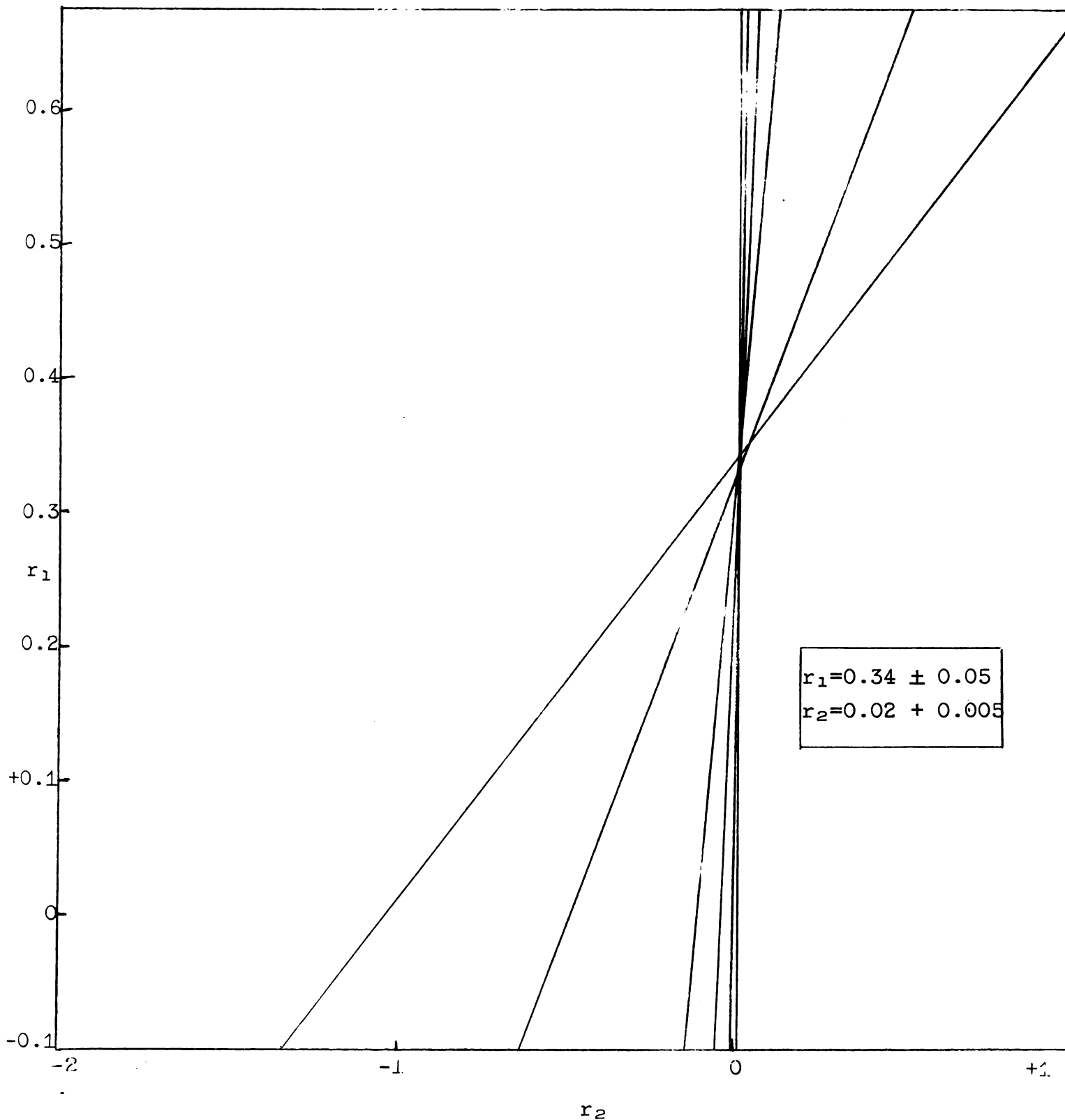
Figure XXIII. Graphical solution of copolymerization equation for r_1, r_2 values in copolymerization of itaconic anhydride-styrene (Intersection method).
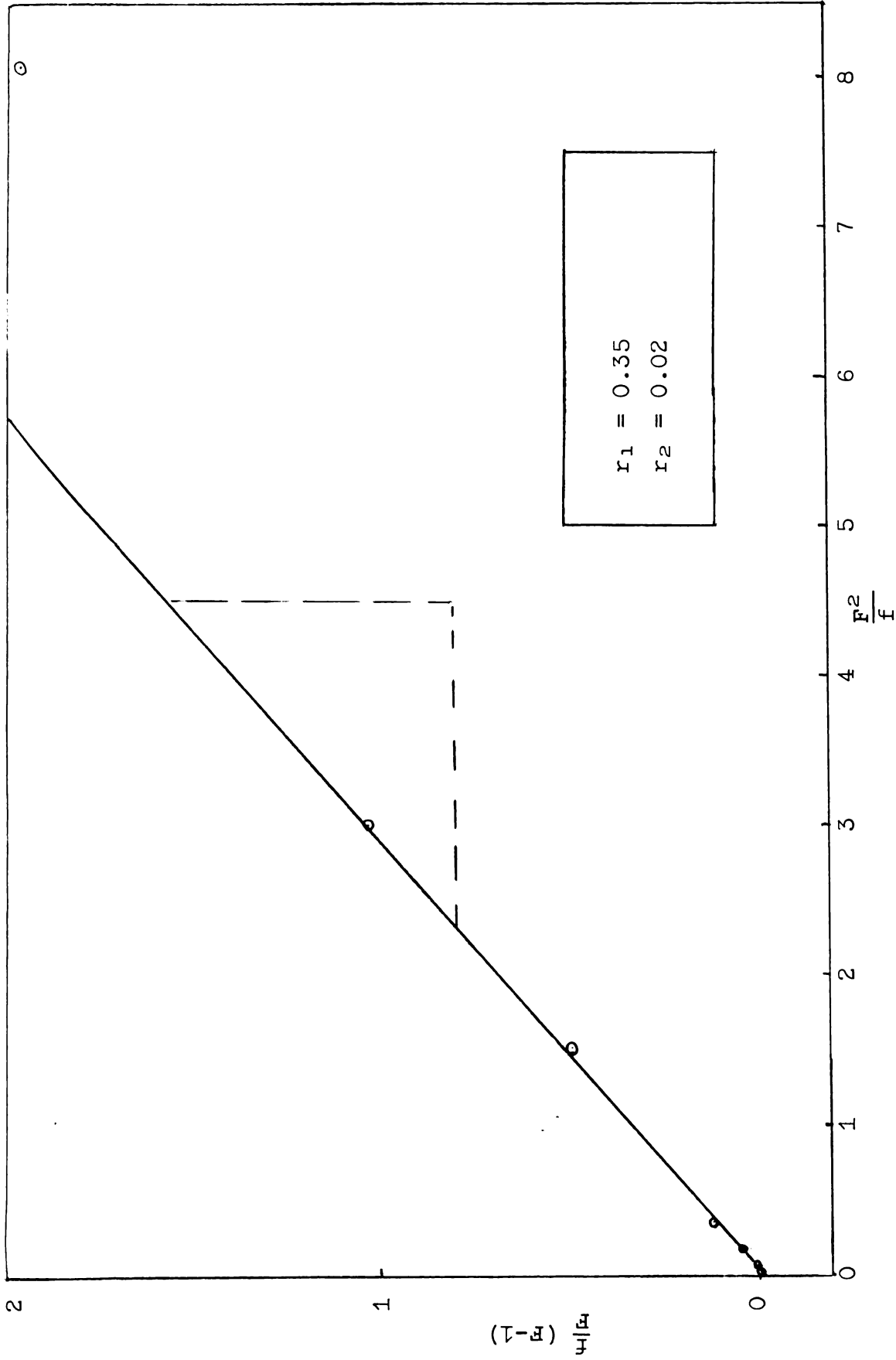
Figure XXIV. Graphical solution of copolymerization equation for itaconic anhydride-styrene copolymers (Fineman and Ross method).

$r_1 = 0.35$

$r_2 = 0.02$

$\frac{F}{f}(F-1)$

$\frac{F^2}{f}$

DISCUSSION

I - Interpretation of r_1, r_2 Ratios

A. <u>Itaconic Anhydride-Methyl Methacrylate</u>
   <u>Copolymerization</u>

Investigation of the copolymerization of this binary system resulted in $r_1 = 2.25$, $r_2 = 0.1$ (in this work subscript 1 refers to itaconic anhydride). The value of r_1 shows that itaconic anhydride radical is about two and one-half times more reactive toward its own monomer than it is toward methyl methacrylate. The r_2 value indicates that the reactivity of methyl methacrylate radical toward itaconic anhydride is almost twenty times greater than that for methyl methacrylate. The product of r_1 x r_2 is 0.225 which indicates a tendency for the monomer moieties to alternate in the copolymer chain. The copolymerization does not form an azeotrope since one of the ratios (r_1) is larger than unity and the other is smaller.

To confirm the accuracy of the obtained values, a series of calculations were carried out using available literature data and the Q-e scheme proposed by Alfrey and Price (42). Q and e values for itaconic anhydride are reported to be 2.5 and 0.88 and for methyl methacrylate 0.74 and 0.4, respectively (43). Substituting these values in the Alfrey and Price equation:

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

$$r_1 = \frac{2.5}{0.74}\, e^{-0.88(0.88\underset{5}{.}40)} = 2.42$$

$$r_2 = \frac{Q_2}{Q_1} \exp\left[-e_2(e_2-e_1)\right]$$

$$r_2 = \frac{0.74}{2.5}\, e^{-0.4(-.48)} = 0.36$$

(1)

There is some agreement between these calculated r_1 and r_2 values and the experimental values, but the calculated value of r_2 is much larger than that obtained experimentally. This kind of inconsistency is common when only one system is considered, for the Q-e scheme is quite empirical and Q-e values for a monomer, calculated from different systems of co-polymerization vary considerably. To remove this discrepancy and find the factor by which the calculated r_1, r_2 ratios differ from the experimental ones, a combination of three binary systems are employed when the data is available as follows:

$$r_{12} = \frac{Q_1}{Q_2} \ e^{-e_1(e_1-e_2)}$$

$$r_{21} = \frac{Q_2}{Q_1} \ e^{-e_2(e_2-e_1)}$$

$$r_{23} = \frac{Q_2}{Q_3} \ e^{-e_2(e_2-e_3)}$$

$$r_{32} = \frac{Q_3}{Q_1} \ e^{-e_3(e_3-e_2)} \tag{2}$$

$$r_{13} = \frac{Q_1}{Q_3} \ e^{-e_1(e_1-e_3)}$$

$$r_{31} = \frac{Q_3}{Q_1} \ e^{-e_3(e_3-e_1)}$$

From these equations, equation (3) follows directly

$$r_{12}r_{23}r_{31} = r_{13}r_{32}r_{21} \tag{3}$$

where r_{12} is the reactivity ratio of the monomer 1 in co-polymerization with monomer 2, and so on. The above relation is often in error and therefore the factor H. has been employed as a correction for values calculated using equation (3).

$$\frac{r_{12}r_{23}r_{31}}{r_{13}r_{32}r_{21}} = H \tag{4}$$

Considering three binary systems of methyl methacrylate (1), styrene (2), and itaconic anhydride (3), reactivity ratios for the three systems are as follows:

$$
\begin{aligned}
r_{12} &= 0.46 \\
r_{21} &= 0.52 \\
r_{23} &= 0.02 \\
r_{32} &= 0.35
\end{aligned}
$$

(44)

$$
\begin{aligned}
(c) \quad r_{13} &= 0.36 \\
r_{31} &= 2.42
\end{aligned}
$$
Calculated by means of Q-e scheme

therefore, substituting the values in (4)

$$
H = \frac{0.46 \times 0.02 \times 2.42}{0.36 \times 0.35 \times 0.52} = \frac{0.022264}{0.06136} = 0.36
$$

The ratio of calculated values then should differ from the experimental ones by this ratio

$$
\frac{r_{13}(c)}{r_{31}(c)} \times H = \frac{r_{13}}{r_{31}} \ (\text{exp.})
$$

$$
\frac{0.36}{2.42} \times 0.36 = \frac{0.129}{2.42}
$$

which are in agreement with the experimental ratio of $\frac{0.1}{2.25}$.

B. Itaconic Anhydride-4-Methoxystyrene Copolymerization

Reactivity ratio values for this system were calculated by the intersection and by the Fineman and Ross methods. The results were found to be as follows:

$r_1 = 0.52$

$r_2 = 0.03$

Intersection Method

$r_1 = 0.47$

$r_2 = 0.03$

Fineman and Ross Method

Since the point of intersection was an area and not a single point, and the author did not have ready access to the mathematical evaluation of the point of intersection, by the method of least squares, the values which were obtained from the Fineman and Ross method were considered to be the more reliable. A value of $r_1 = 0.47$ indicates that itaconic anhydride radical is two times more reactive with 4-methoxystyrene than with itaconic anhydride monomer. The value of $r_2 = 0.03$ indicates that 4-methoxystyrene radical is 33 times more reactive with itaconic anhydride monomer than it is with its own monomer. The product of r_1, $r_2 = 0.014$ indicates a high degree of alternation of units in the polymer chain. The composition graph (Figure XVI) shows an azeotrope at a composition $M_1 = m_1 = 0.625$, where the initial mole fraction of itaconic anhydride in the reaction mixture is equal to the mole fraction of itaconic anhydride moiety in the copolymer. Calculation of the azeotropic concentrations by means of the copolymerization equation (14) gives a good basis of confirmation for the values obtained in this work.

$$\frac{m_1}{m_2} = \frac{M_1}{M_2} \frac{r_1M_1 + M_2}{r_2M_2 + M_1}$$

since $M_1 = m_1$ and $M_2 = m_2$ at azeotrope point

$$1 = \frac{r_1M_1 + M_2}{r_2M_2 + M_1}$$

hence

$$\frac{M_2}{M_1} = \frac{r_1 - 1}{r_2 - 1}$$

substituting the values of r_1 and r_2

$$\frac{M_2}{M_1} = \frac{0.47 - 1}{0.03 - 1} = \frac{0.53}{0.87} = 0.546$$

since $M_1 + M_2 = 1$

M_1 by calculation is found to be 0.645 which differs by only 2% from the azeotropic point obtained. Although this does not prove the validity of the data and the results presented in this work, it is slightly better than the usual results that appear in the literature when comparisons are made between experimental and calculated azeotropic values obtained by different workers.

The approximate reactivity ratios for this system can be predicted from the Alfrey and Price Q-e scheme and are in agreement with the experimental values, if the previously mentioned corrections are applied as follows. Substituting the reported values of Q and e for 4-methoxystyrene, and itaconic anhydride (45):

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

$$r_1 = \frac{2.5}{1.36} \exp [-0.88(0.88 + 1.11)] = 0.315$$

$$r_2 = \frac{1.36}{2.5} \exp [1.11(-1.11-0.88)] \cong 0.06$$

$$\frac{r_1}{r_2} = \frac{0.315}{0.06}$$

The appropriate correction according to Mayo (46) is made by considering the three binary systems of copolymerization of methyl methacrylate (1), 4-methoxystyrene (2) and itaconic anhydride (3). The reactivity ratios of the systems (2,3 and 1,3) are those reported in this work and that of 1,2 by Walling (47).

$r_{12} = 0.32$

$r_{21} = 0.29$

$$\frac{r_{12} \times r_{23} \times r_{31}}{r_{13} \times r_{21} \times r_{32}} = H = \frac{0.32 \times 0.06 \times 2.25}{0.1 \times 0.29 \times 0.315} = 0.47$$

$r_{23} = 0.06$

$r_{32} = 0.31$

$r_{13} = 0.10$

$r_{31} = 2.25$

when the above calculated r_1, r_2 ratio for the copolymerization of itaconic anhydride with 4-methoxystyrene is multiplied by this factor

$$\frac{r_2}{r_1} = \frac{0.06}{0.315} \times 0.47 = \frac{0.030}{0.315}$$

This value is in reasonable agreement with the experimental ratio ($\frac{r_2}{r_1} = \frac{0.03}{0.47}$) found in this work.

C. Copolymerization Reactivity Ratios of Itaconic Anhydride and Styrene

In the case of itaconic anhydride styrene, the reactivity ratios obtained by the Fineman and Ross method are identical with those obtained by the intersection method. As indicated in Figure XXIII, $r_1 = 0.34 \pm 0.05$ and $r_2 = 0.02 \pm 0.005$ were obtained from the method of intersection and as shown in Figure XXIV, values $r_1 = 0.35$ and $r_2 = 0.02$ were obtained

from Fineman and Ross method of graphical solution. The value of r_1 indicated that itaconic anhydride radical is three times as active toward styrene monomer as it is toward itaconic anhydride monomer. The value of r_2 shows the greater reactivity (almost 50 times) of the styrene radical for the unlike monomer. From the fact that the product of $r_1 r_2 = 0.007$, one can readily conclude that the copolymer is highly alternating. The copolymer composition graph (Figure XXII) indicates an azeotrope at 0.59 mole percent itaconic anhydride. Calculation of this point for the itaconic anhydride-styrene system according to Wall, gives a very similar result

$$\frac{M_2}{M_1} = \frac{r_1 - 1}{r_2 - 1}$$

$$\frac{M_2}{M_1} = \frac{0.35 - 1}{0.02 - 1} = 0.66$$

Since $M_1 + M_2 = 1$

$$M_1 = 0.602$$

II - General Discussion

A. Application of Copolymerization Equations

The copolymerization equation as derived, is based on several assumptions (46). One of these is that $\frac{[M_1]}{[M_2]}$ represents the relative concentrations of monomers at the site of reaction. This may not be exactly applicable if the polymer precipitates as it forms, which is the case in the systems presented in this work. However, it has been found (44) that the monomer reactivity ratios for styrene-methyl methacrylate are the same whether the reaction is carried out in homogeneous solution or under conditions where the polymer precipitates as formed. On the other hand, Mayo and Walling have reported (48) inconsistencies and irreproducibilities accompanying the results of the system vinyl acetate —vinyl chloride when the reaction is heterogeneous. The copolymerization equation was used in this work despite the above mentioned inconsistencies, since there was no alternative.

B. The Effect of Ring Substitution in the
   Reactivity of Styrene Type Monomers

The reactivity ratios for the copolymerization of the binary system of styrene-4-methoxystyrene have been reported to be $r_1 = 1.16$, and $r_2 = 0.82$ (47). This indicates that styrene type radicals tend to react with their own monomer rather than monomeric 4-methoxystyrene, while 4-methoxystyrene type radicals tend to add to styrene molecules rather than 4-methoxystyrene. Therefore a copolymer of styrene with 4-methoxystyrene usually contains more styrene than 4-methoxystyrene moieties. This was exactly the result found in both

the copolymerization of itaconic anhydride with 4-methoxy-
styrene and with styrene. Since the styrene radical is more
reactive than the 4-methoxystyrene radical more styrene
moieties appear in a copolymer of itaconic anhydride and
styrene than 4-methoxystyrene moieties in a copolymer of
itaconic anhydride and 4-methoxystyrene if the initial molar
concentrations of comonomers are equal. The azeotropic
values for the two systems are in agreement with this concept.
The itaconic anhydride-styrene system forms an azeotrope
containing 0.41 mole of styrene, while the itaconic anhydride-
4-methoxystyrene system forms an azeotrope containing about
0.375 mole of 4-methoxystyrene. Axford (49) has investigated
the velocity constants in the polymerizations of styrene and
4-methoxystyrene. Comparison of his results indicate that
toward a given monomer the radical of the 4-methoxystyrene
is less reactive than the styrene radical. The difference in
reactivity, he suggested, are due to mesomeric stabilization
of the radical with a para substituent. Walling and Mayo (50)
have employed the Hammet (1) relationship

$$\log \frac{k}{k_o} = 6 \rho \qquad (1)$$

to explain the effect of substituents on the styrene molecule.
In the above equation k and k_o are rate constants for the
reaction of the side chain of the substituted and unsubstituted
benzene, 6 is a parameter for each substituent and ρ is a
parameter depending only upon the reaction (here free radical
reaction). Walling and Mayo applied this to copolymerization

of styrene with various substituted styrenes. They plotted
the logarithms of relative reactivities of substituted
styrene against the Hammett σ values for the substituents.
They found that the system obeyed equation (1) quite exactly.
They also calculated the slope of the curve and found ρ to
be 0.51. This indicates that the more active electron
donor substituent is, the lower the reactivity at the site
of the reaction becomes. The results obtained in this work
seem to indicate that itaconic anhydride radical, which is
less stabilized by resonance, is more reactive than the
styrene radical and therefore enters the copolymer more
readily. By the same token itaconic anhydride has an even
higher reactivity in the case of its copolymerization with
4-methoxystyrene. This phenomenon does not correlate with
the general thermodynamic concept of the formation of more
stable radicals. Walling and Mayo (50) have approached this
problem by employing electron accepting and donating proper-
ties of a conjugated carbonyl system and an aromatic ring
system. They considered a transition state in which an
electron had been donated from the double bond of styrene or
the substituted styrene to the conjugated carbonyl radical.
In the case of itaconic anhydride the structure of the tran-
sition state may be illustrated as:
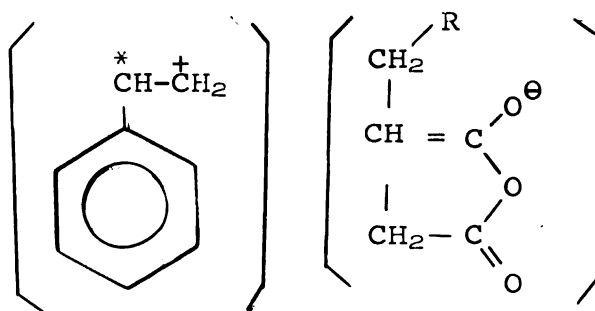
The resulting structure for itaconic anhydride will be an enolate ion which is relatively stable. This also may account for increased reactivity of the electron donor substituted styrene toward conjugated carbonyl radicals, since the substituted styrene ion radical has a number of additional structures. A similar approach has been taken by Bartlett and Nozaki in the copolymerization of maleic anhydride and allyl acetate (51). Walling and Mayo furthermore have suggested that the attack of the styrene radical on conjugated carbonyl monomers often results in a thermodynamically stable transition state. This transition state may be an addition complex of the monomer which then forms a complex radical that participates in the copolymerization. They proved the formation of such addition complexes by spectroscopy in the ultra violet region of the spectrum. In this laboratory the formation of complexes from maleic anhydride and para substituted styrenes has been investigated (52). Following the above discussion one could conclude that the cause of differences in reactivities of styrene and 4-methoxystyrene might be the result of some type of complex or adduct formation. A 1:1 adduct which polymerizes might also account for the alternating copolymer.

C. Infra-red Quantitative Analysis

This quantitative method of analysis proved to be convenient, simple and accurate for all systems studied. It was very useful for the itaconic anhydride-methyl methacrylate

system, since the carbon contents of the two monomer units were so close that elemental analysis could not be employed. In the case of the itaconic anhydride-4-methoxystyrene system, a model compound was used. The model compound, p-sec. butyl anisole gave the anticipated absorbances of polymethoxystyrene in the area of interest (at 1865 cm^{-1}). This is probably due to the styrene moiety in the copolymer having a similar structure in respect to the attachment of groups at the carbon α to the phenyl ring. A series of experiments in the infra-analysis of copolymers of polyvinylacetate with itaconic anhydride have been carried out in this laboratory using sec-butyl acetate as a model for the polyvinyl acetate (53). Infra-red analysis and elemental analysis for a series of copolymers of itaconic anhydride with 4-methoxystyrene gave comparable results (see Table 3). Since polystyrene was insoluble in the solvent (acetonitrile) which dissolves polyitaconic anhydride and no suitable common solvent useful in infra-red analysis could be found, it was decided to carry out the analysis of samples by means of a calibration curve constructed by measurement of anhydride peak areas of only polyitaconic anhydride solution at different concentrations. This might have been inaccurate if polystyrene or styrene moieties in the copolymer had had an absorbance in the same region as the anhydride. However, it is known that the only possible absorbances of polystyrene are very weak summation bands (overtones and combinations) of the C-H out of plane

deformation frequencies in the range of 2000-1650 cm^{-1} (506.06 μ). When the solutions used are dilute (in this work 0.5%), these bands are negligible. Calculation of composition of the series of the itaconic anhydride-styrene copolymers based on a calibration curve drawn by plotting the areas of anhydride peaks of standard solutions vs their anhydride content, gave results in agreement with those obtained by elemental analysis (Table 4).

SUMMARY

1. Binary copolymerizations of itaconic anhydride with six comonomers (vinyl pyrrolidine, 4-methoxystyrene, 2-chlorostyrene, 3-chlorostyrene, styrene, and divinyl ether) were carried out in tetrahydrofuran using 2,2'-azodiiso-butyronitrile as an initiator.

2. The reaction parameters were determined for the co-polymerization of itaconic anhydride M_1 with methyl methacry-late M_2 in benzene.

3. The reaction parameters were determined for the co-polymerization of itaconic anhydride M_1 with 4-methoxystyrene M_2 in benzene.

4. Quantitative infra-red analysis has been used to determine the anhydride moiety and thus copolymer composition of samples of itaconic anhydride co styrene, itaconic an-hydride co 4-methoxystyrene and itaconic anhydride co methyl methacrylate.

5. It has been demonstrated that a model compound can be used in place of the non-anhydride containing homopolymer to construct reference graphs useful for analysis of the compo-sition of itaconic anhydride copolymers.

6. It has been demonstrated that polyitaconic anhydride can be used to construct reference graphs useful for analysis of the composition of itaconic anhydride copolymers if there is no interference in the anhydride peak region at 1865 cm^{-1} by the comonomer unit.

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