STUDIES ON THE COPOLYMER OF STYRENE AND ITACONIC ANHYDRIDE

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
Gerald Melbourne Curtice
1955

STUDIES ON THE COPOLYMER
OF STYRENE AND ITACONIC ANHYDRIDE

by

GERALD MELBOURNE CURTICE

A THESIS

Submitted to the School of Graduate Studies of Michigan
State University of Agriculture and Applied Science
in partial fulfillment of the requirements for
the degree of

MASTER OF SCIENCE

Department of Chemistry

1955

ACKNOWLEDGEMENT

The author wishes to express his appreciation to Dr. Ralph Guile for his faithful interest, guidance, and constant encouragement.

He is also greatly indebted to Archer-Daniels-Midland Co., Minneapolis, Minnesota, for financial support which made it possible for him to complete this investigation.

TABLE OF CONTENTS

INTRODUCTION

Since in recent years this laboratory has carried on a study of the copolymer of styrene and maleic anhydride[1,2], an investigation of the styrene-itaconic anhydride copolymer appeared to be desireable. This study is concerned primarily with the preparation and properties of the copolymer of styrene and itaconic anhydride, but also includes a comparison of the properties of a new poly-(itaconic anhydride co styrene) with the already investigated poly-(maleic anhydride co styrene).

HISTORICAL

Styrene has been shown to be a useful monomer in many copolymerizations[2a,2b,2c]. Itaconic anhydride also has been used in various copolymerization recipes[3] with castor oil esters[3a], methyl linoleate[3b], fatty acids and polyamines[3c], and a mixture of styrene and maleic acid[9]. Reports and patents 4,5,6,7,8,9 indicate itaconic acid has been polymerized and copolymerized by several methods. The literature contains a report[10] and many patents [11-27] on the copolymerization of many various esters of itaconic acid with several comonomers in binary and ternary systems. This method of producing copolymer polyesters is quite different from the preparation of polyesters by the method of addition described in this thesis. Similar but quite different products often result when polymer derivatives are prepared by chemical reactions of the copolymers as compared to copolymerization of monomers chosen to yield the same derived copolymer.

A United States patent[3] indicates that styrene and itaconic anhydride have been copolymerized in water with a persulfate catalyst, but the work described in this study utilizes a different method of polymerization, i.e., solution polymerization with an organic peroxide catalyst. The previously referred to patent was primarily concerned with the effect of various polyelectrolytes when used in fertilizer and soil conditioning compositions. An extensive search of the literature revealed that no comprehensive study of the copolymerization of itaconic anhydride and styrene has been made.

EXPERIMENTAL

REAGENTS

Name	Manufacturer	Grade	Physical Constants	Purification
Benzene	----------	CP Thiophene free	BP 80°C	Stored over sodium
Maleic anhydride	Matheson, Coleman and Bell	Reagent	MP 53-55°C	None
Styrene	Dow Chemical Co.	Inhibited with t-butylcatechol	BP 54-58°, 31-33mm	Vacuum distillation under nitrogen. Fraction used n_D^{22} 1.5449
Itaconic anhydride	Smith Organic Chemicals	Reagent	MP 68°C	None
Benzoyl peroxide	Eastman Kodak	Reagent	MP 105-106°C d	None
Ethyl alcohol	----------	Absolute	78.5°C	Distilled from alcohol sodium mixture
Ethylene glycol	Matheson, Coleman and Bell	Reagent	BP 195-197°C	None
Normal butyl alcohol	----------	CP	BP 116-118°C	Dried over anhydrous sodium sulfate
2-Octanol	Eastman Kodak	Reagent ketone free	BP 178-180°C	None
2-methyl-1-butanol	Eastman Kodak	Synthetic reagent	BP 126-128°C	None
Ethylenediamine	Matheson, Coleman and Bell	CP 98-100%	BP 117°C	None
Ethylamine	Eastman Kodak	Reagent anhydrous	BP 16.5°C	None

PREPARATION OF THE COPOLYMERS OF STYRENE AND ITACONIC ANHYDRIDE

The method used for the copolymerizations of styrene and itaconin anhydride was similar to that used by Garrett[1]. The reaction was carried out in a one liter three neck, round bottom flask with standard taper ground glass joints. It was fitted with a reflux condenser, a gas inlet tube and a mechanical stirrer. In this reaction vessel styrene and itaconic anhydride were copolymerized using a 0.466 mole of total monomers and varying the relative monomer ratios. The appropriate amount of itaconic anhydride, accurately weighed, was placed in seven hundred milliliters of benzene. The mixture was stirred with heating at the reflux temperature of benzene (80°C) to dissolve the itaconic anhydride. Nitrogen was introduced beneath the surface of the benzene by means of the gas inlet tube. The nitrogen was allowed to bubble during the dissolution of the itaconic anhydride and kept bubbling throughout the reaction so that a nitrogen atmosphere was maintained at all times. The resulting solution of itaconic anhydride in benzene was hazy as the anhydride is very slightly soluble. No longer than thirty minutes was allowed for solution to take place. An accurately weighed amount of styrene based on the amount of itaconic anhydride to result in 0.466 mole of total monomers was added simultaneously with 0.233g benzoyl peroxide. The time was recorded. At intervals during the six or more hours reaction time samples were removed through the gas inlet tube by means of a vacuum sampling device. When the reaction appeared to be complete, heating was discontinued and the reaction mixture was allowed to cool with stirring for one hour. The copolymer was collected by filtering on a Buchner funnel and was washed about five times with hot benzene. It was air dried overnight and dried at 90°C for four hours. Copolymerizations with monomer ratios of the following were carried out: 1:1, 1:2, 2:1, 1:3, and 3:1, styrene to itaconic anhydride.

Two portions of the copolymer resulting from using a monomer ratio of 1:1 were subjected to Soxhlet extraction for 240 hours, one with benzene and the other with ether. The copolymers from the reactions with other monomer ratios were extracted similarly but with benzene only. After extraction each was air dried overnight and finally dried in a drying pistol heated by refluxing ethyl alcohol and under a vacuum of five millimeters of mercury for six hours. Carbon-hydrogen determinations were made on the dry copolymers. The results of Soxhlet extractions on Preparation I (1:1 mole ratio of reactants) are given in Table I. The data and analysis of the copolymers from all preparations are tabulated in Table II.

TABLE I

ANALYSIS OF THE POLYMER FROM PREPARATION I AFTER EXTRACTIONS WITH ETHER AND WITH BENZENE

Preparation Number	Reactant Ratio	Extraction Medium	Percent Carbon	Percent Hydrogen
I	1:1	Ether	69.88	5.53
		Benzene	69.62	5.55

TABLE II

PREPARATION OF THE COPOLYMERS OF STYRENE AND ITACONIC ANHYDRIDE

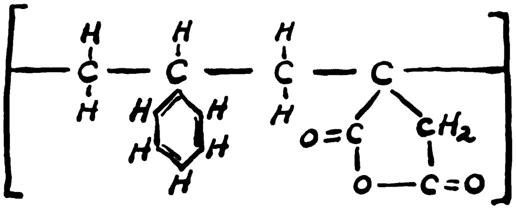
(Code: S. = styrene, I. A. = itaconic anhydride)

Preparation No.	Reactant ratio	Percent polymerization determined by precipitated polymer	Copolymer analysis				Copolymer composition calculated	
			Theoretical (Based on reactant ratio)		Actual		Mole percent S:I. A.	Mole ratio S:I. A.
			C	H	C	H		
I	1:1	56.4	72.25	5.55	69.55 69.69	5.52 5.57	43:57	0.77:1
II	1:2	23.2	65.90	4.87	60.42 61.14	5.63 5.34	20:80	0.25:1
III	2:1	43.6	78.70	6.25	71.31	5.68	48:52	0.91:1
IV	1:3	63.9	62.72	4.54	63.71 63.81	5.44 5.60	28:72	0.39:1
V	3:1	37.6	82.07	6.60	71.01	6.11	47:53	0.88:1

COPOLYMERIZATION RATE

The copolymerization rate was studied using a 0.466 mole of total monomers and a monomer ratio of 1:1. The reaction was carried out in a one liter three neck, round bottom flask with standard taper ground glass joints. The flask was fitted with a reflux condenser, a gas inlet tube and a mechanical stirrer. The reaction mixture was protected from moisture by a calcium chloride tube. The flask was charged with seven hundred milliliters (615.2g) of benzene and 26.1g of itaconic anhydride (0.233 mole). To dissolve the itaconic anhydride the mixture was heated at the reflux temperature of benzene (80°C) with stirring. The reaction mixture was kept under a nitrogen atmosphere. Thirty minutes was allowed for solution to take place. Styrene, 24.2g, (0.233 mole) and 0.233g benzoyl peroxide (0.00096 mole) were then added and the time recorded. Immediately a sample was removed through the gas inlet tube by means of a vacuum sampling device. Several samples were removed in this manner throughout the reaction. These samples were withdrawn into tared flasks and immediately chilled. The copolymer was obtained by filtering through weighed Gooch crucibles and washing with five portions of hot benzene. Crucibles and copolymer were dried at 90°C for twenty hours. They were then cooled and weighed.

The percent polymerization was calculated from the weight of precipitated polymer and the results are collected in Table III and plotted in Figure I. Considering the "reactant" to be a unit comprised of styrene and itaconic anhydride,e.g.,



and utilizing the data in Table III, the molar concentration of the "reactant" was calculated for any given time in seconds. These values as well as the logarithms are collected in Table IV. The data in Table IV was plotted in Figure II with the logarithm of the molar concentration of "reactant" as the ordinate and the time as the abscissa. Methods of calculation are included in the respective tables.

TABLE III

PERCENT POLYMERIZATION AS DETERMINED BY AMOUNT OF PRECIPITATED POLYMER

Sample	Time in minutes	Sample weight,g	Polymer Weight,g	Percent Polymerization
A	1	33.12	0.069	2.57
B	5	38.25	0.092	3.18
C	19	23.09	0.099	5.67
D	38	28.37	0.256	11.94
E	184	27.92	1.265	59.97
F	233	7.10	0.358	66.73
G	330	7.35	0.424	76.35
H	540	7.64	0.494	85.60
I	1320	8.53	0.594	92.16

Total Weight of Reaction Mixture: 665.73g

Total Weight of Monomers: 50.3g

Percent Monomers in Mixture: 7.55%

Weight of Monomers in Sample = Weight of Sample x Percent Monomers in Mixture.

Percent Polymerization = Weight of Polymer / Weight of Monomers in Sample.

FIGURE I

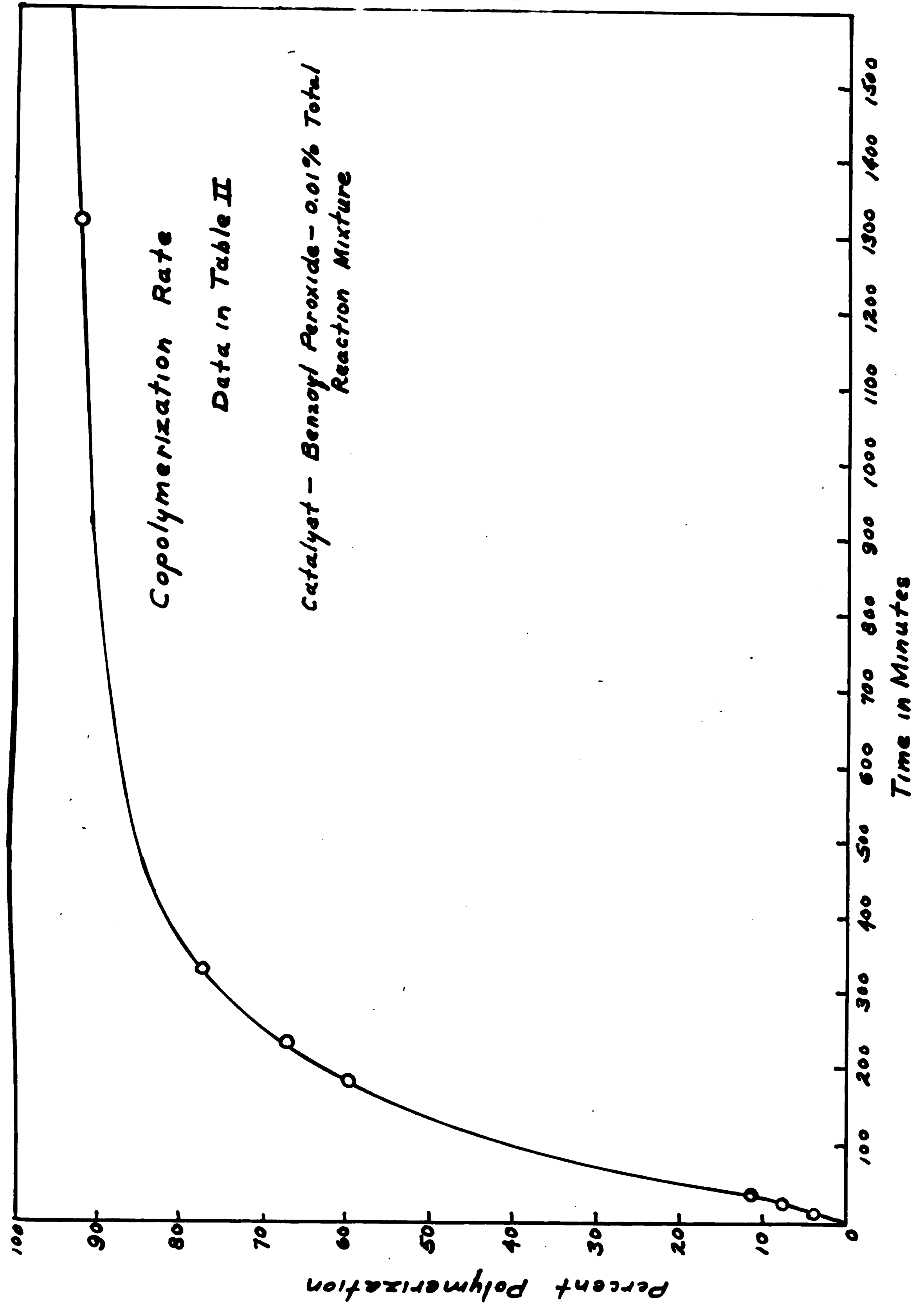

Copolymerization Rate
Data in Table II
Catalyst - Benzoyl Peroxide - 0.01% Total Reaction Mixture
Percent Polymerization
0
10
20
30
40
50
60
70
80
90
100
Time in Minutes
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500

TABLE IV

EVALUATION OF REACTION RATE CONSTANT

Sample	Time, seconds	Mole of reactant	Molar concentration of "reactant"	log ("reactant")
–	0	0.2323	0.3318	-.4792
A	60	(See Note)		
B	300	0.2249	0.3215	-.4928
C	1,140	0.2193	0.3128	-.5047
D	2,280	0.2048	0.2925	-.5339
E	11,040	0.0932	0.0137	-.8633
F	13,980	0.0774	0.0110	-.9586
G	19,800	0.0552	0.0079	-1.1024
H	32,400	0.0335	0.0047	-1.3279
I	79,200	0.0182	0.0026	-1.5850

Molecular weight styrene-itaconic anhydride unit =216.22

Initial weight of monomers = 50.3

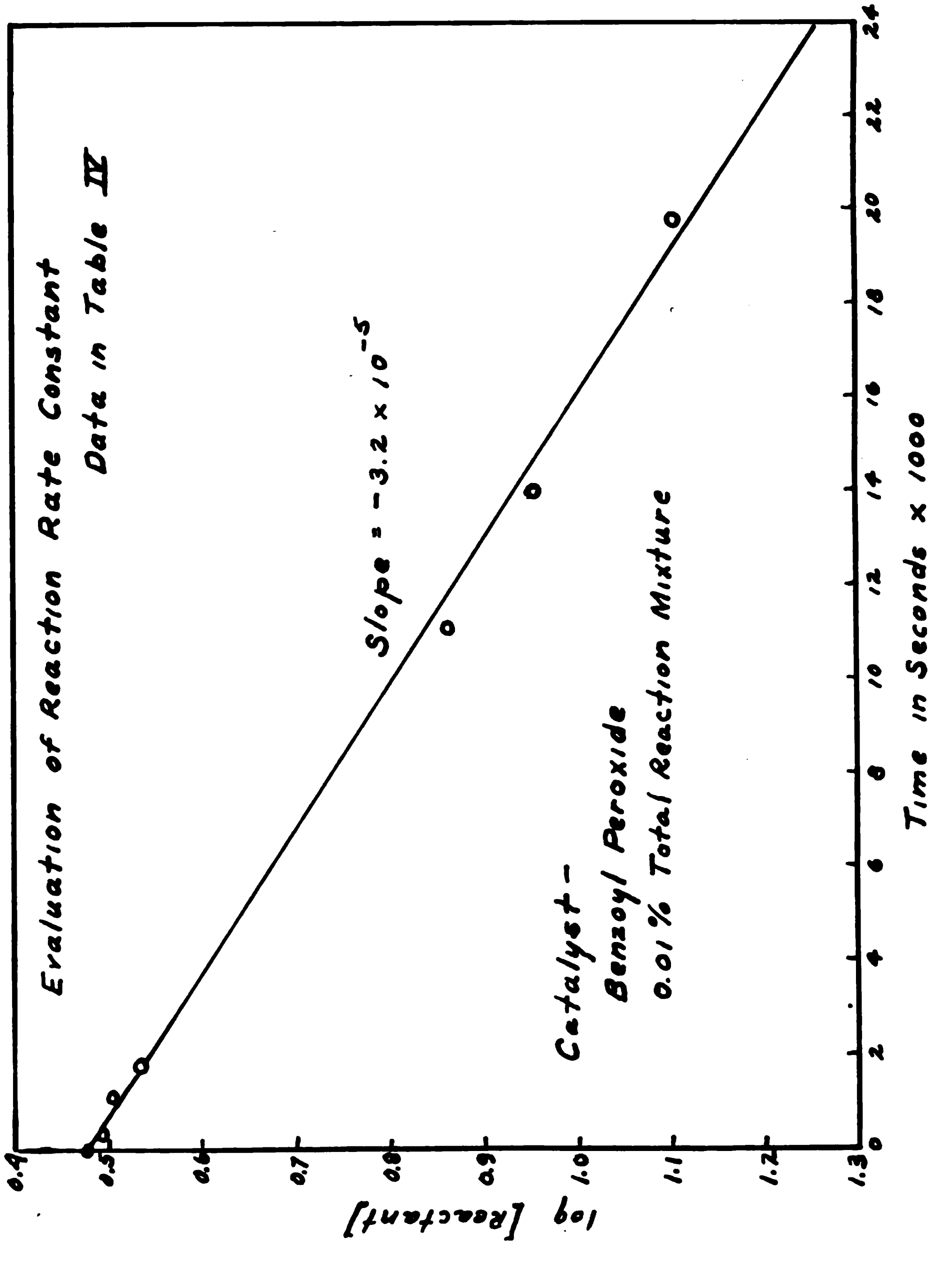
100% - % polymerization = % "reactant"

% "reactant" • initial weight / 216.22 = moles of "reactant"

Moles of "reactant" / 0.7 liter = molar concentration of "reactant"

Note: Sample A was found to be itaconic anhydride by melting point determination and was not included in consideration of the data.

FIGURE II


Evaluation of Reaction Rate Constant
Data in Table IV
Slope = −3.2 x 10⁻⁵
Catalyst –
Benzoyl Peroxide
0.01 % Total Reaction Mixture
Time in Seconds x 1000
0
2
4
6
8
10
12
14
16
18
20
22
24
log [Reactant]
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3

EVALUATION OF MONOMER REACTIVITY RATIOS

The evaluation of monomer reactivity ratios was accomplished using the same method for carrying out the polymerization in the previous preparation but stopping the reaction at about four percent polymerization. A solution comprising 0.233 mole of total monomers, 307.6g of benzene, and 0.1166g benzoyl peroxide was placed in a five hundred milliliter round bottom, three neck flask. The flask was fitted with a reflux condenser, stirrer, and a gas inlet tube, all with ground glass joints. The reaction was carried out under a nitrogen atmosphere. It was kept at the reflux temperature of benzene, 80°C by means of a heating mantle. When the percent polymerization was considered to be approximately four percent, as determined visually by amount of precipitation, the contents of the flask were transferred to a large test tube immersed in a dry ice-acetone bath. The copolymer was isolated by vacuum filtration and was washed with several portions of hot benzene. The residue was air dried overnight and at 90°C for two hours, then weighed to calculate the approximate percent polymerization. The copolymer was then subjected to Soxhlet extraction with benzene for 240 hours. It was dried in air for four hours and at 90°C for twelve hours. Carbon-hydrogen analysis gave the mole percent of itaconic anhydride in the copolymer.

(See Table V). Figure III is a graph of the composition of the increment of copolymer formed (ordinate) against the composition of the monomer mixture from which it is produced (abscissa).

Substitution in the equation

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

for M_1, M_2, m_1, and m_2 which are the monomer concentrations and the molar concentrations of the monomers in the resulting copolymer respectively was made for the seven reactions. In the resulting equations for straight lines values of r_1 (-0.1 to 0.5) were substituted to give values of r_2. A sample calculation is given in Table V. The values of r_2 versus r_1 were plotted as shown in Figure IV.

The analysis of the copolymers from six of the seven reactions for carbon and hydrogen indicated a finite percent of ash to be present. The arc spectra for the copolymers, copper and mercury (since mercury seal stirrers were used) were made. By identification of the persisting lines of the copolymers' spectra from the copper standard the ash was evaluated as silicon. It is probable that glass ground from the stirring assemblies found its way into the reaction flask. The percentage carbon and hydrogen were then calculated to an ash free basis. These values are shown in Table V.

TABLE V

COPOLYMER COMPOSITION BASED ON ELEMENTAL ANALYSIS FOR USE IN DETERMINING REACTIVITY RATIOS

Experiment Number	Monomer mole percent itaconic anhydride	Reaction time, minutes	Percent polymerization	Percent Carbon	Copolymer mole percent itaconic anhydride
A	10	13	1.65	70.97	53.5
B	20	13	3.04	67.43	62.6
C	25	14	4.98	66.10	66.0
D	40	14	4.48	66.25	65.5
E	50	12	4.15	55.88	92.5
F	60	9	3.68	60.64	80.2
G	75	11	4.83	55.78	92.9

Sample calculation for r_1-r_2 plot:

Experiment number: A

Equation:

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

Substitution:

$$r_2 = \frac{9}{1}\left[\frac{53.5}{46.5}\left(1 + \frac{9}{1} r_1\right) - 1\right]$$

$$r_2 = 9\left[(1.15 + 10.35r_1) - 1\right]$$

$r_1 = 0.1$ then $r_2 = 10.6$

$r_1 = 0.0$ then $r_2 = 1.3$

$r_1 = -0.1$ then $r_2 = 7.9$

FIGURE III

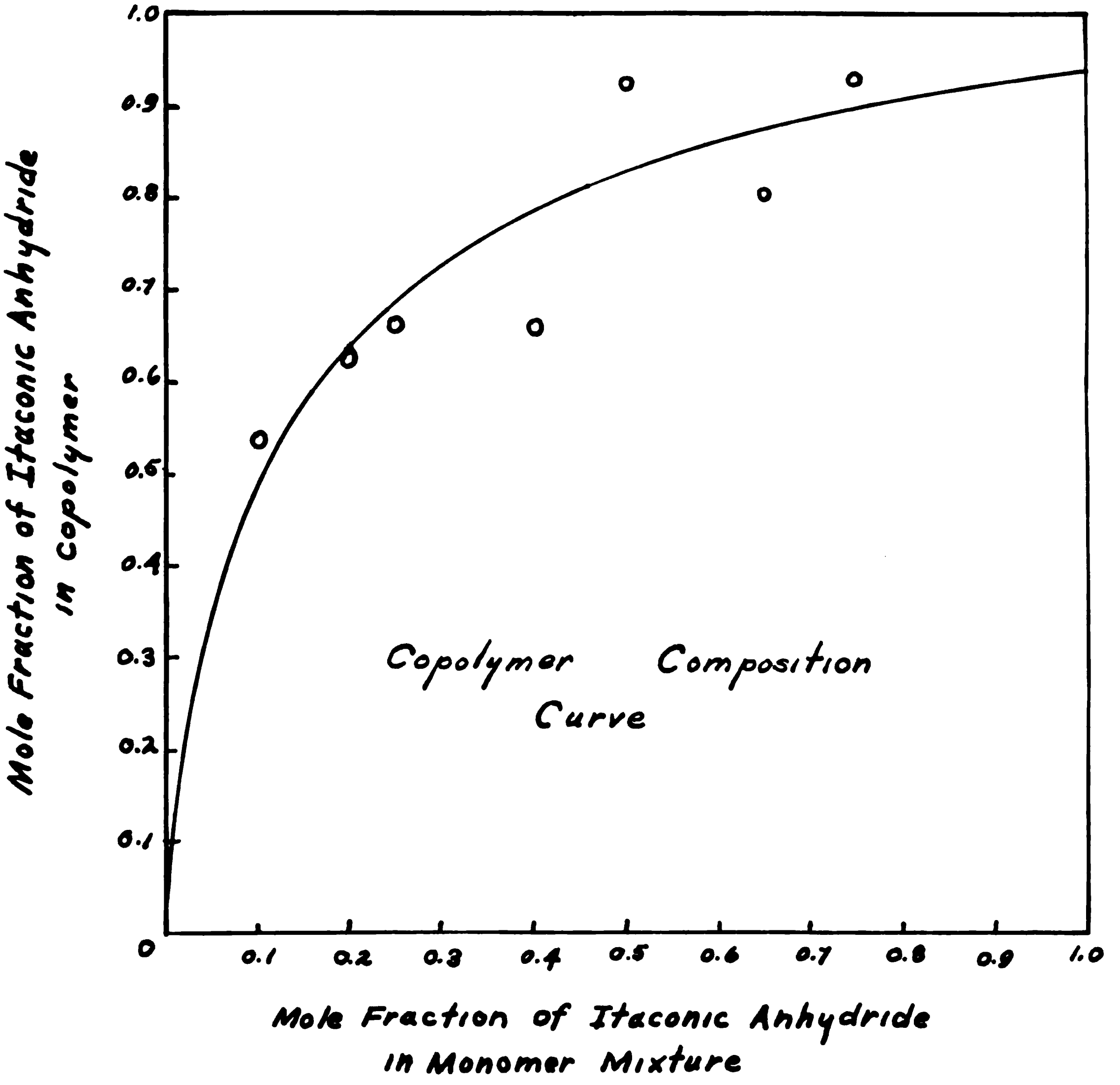
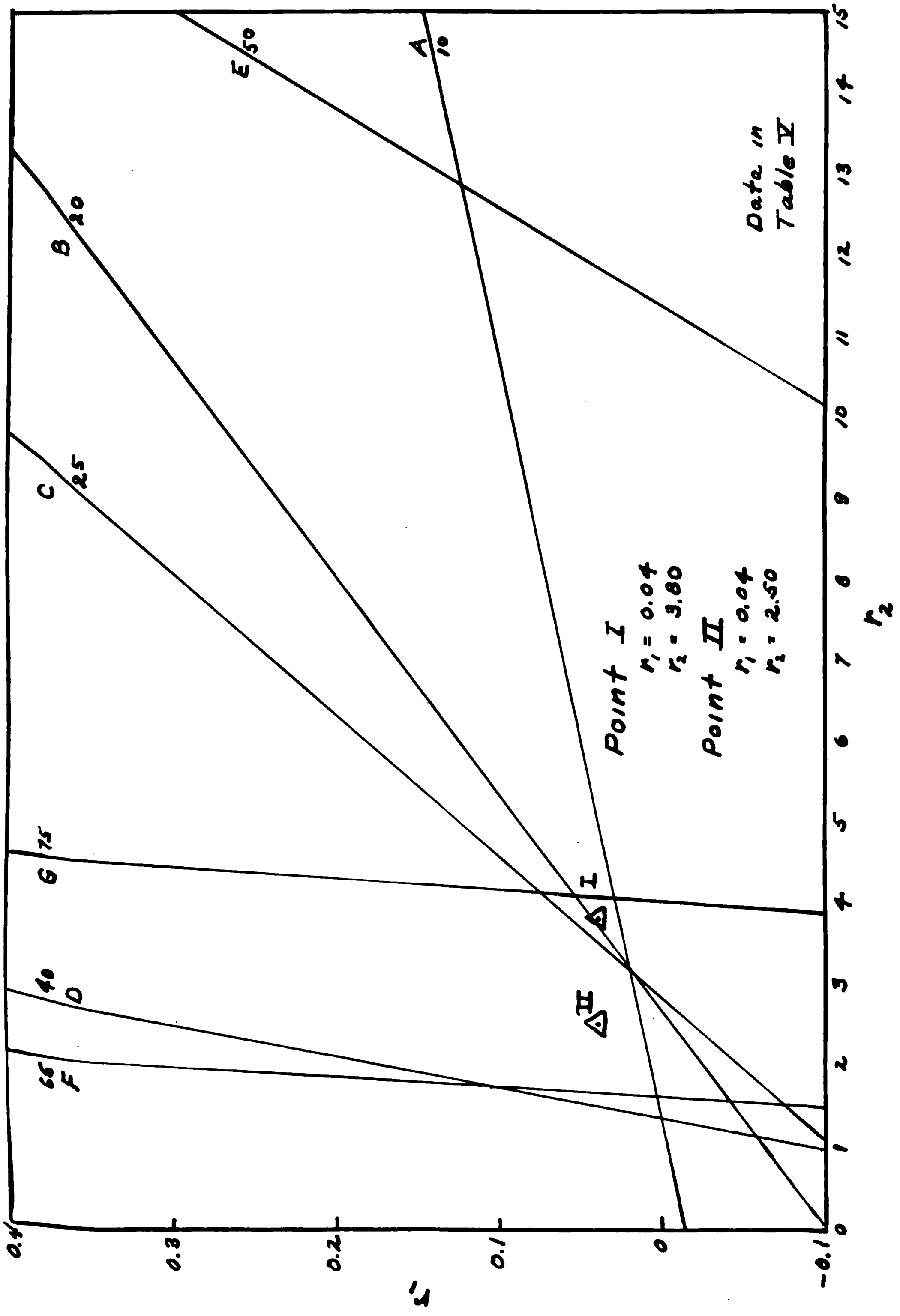

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Mole Fraction of Itaconic Anhydride in Copolymer
Copolymer Composition Curve
Mole Fraction of Itaconic Anhydride in Monomer Mixture

FIGURE IV

REACTIVITY RATIOS — r_1 Versus r_2 Plot



PREPARATION OF THE FREE ACID AND THE AMMONIUM SALT

Free Acid:

A dilute solution of poly - $\overline{57}:\overline{43}$ (itaconic anhydride co styrene) in acetone (approximately six percent) was added to a large volume of water. The water was vigorously agitated throughout the addition. A milky white suspension resulted. Two drops of concentrated hydrochloric acid precipitated the acid form of the copolymer. It was filtered and washed with water until the test for the chloride ion was negative. The product was dried at $105^{\circ}C$ for four hours. Carbon-hydrogen analysis showed 64.35 and 64.42 percent carbon. The percent hydrogen was 5.67 and 5.80. The calculated percentages are 64.60 for carbon and 5.94 for hydrogen.

Ammonium Salt:

About six grams of poly - $\overline{57}:\overline{43}$ (itaconic anhydride co styrene) was dissolved in 100ml of concentrated ammonium hydroxide. The ammonium salt was isolated by evaporating to dryness. Kjeldahl analysis for nitrogen indicated 6.90 and 6.97 percent. The theoretical percent calculated on two ammonium ions per unit is 10.43 and for the monoammonium salt is 5.39.

REACTION WITH ETHYL ALCOHOL

Four grams of the poly - $\overline{57}:\overline{43}$ (itaconic anhydride co styrene) (Preparation I) were placed in a 500ml three neck flask fitted with a reflux condenser and a mechanical stirrer. One hundred milliliters of absolute ethyl alcohol were distilled directly into the reaction flask from two hundred milliliters of absolute ethyl alcohol and ten grams of freshly cut sodium. The reaction was protected from moisture by calcium chloride. The mixture was heated at 50°C for twenty hours. The temperature was increased to 67°C and the copolymer dissolved in one hour. The solution was kept at 67°C for two additional hours. The solution was evaporated under vacuum while immersed in a water bath. The resulting polyester was subjected to carbon-hydrogen analysis. The percent carbon was found to be 66.98 and the percent hydrogen 6.75. The theoretical percentages based on half esterification of the styrene-itaconic anhydride copolymer are 66.95 for carbon and 6.83 for hydrogen.

REACTION WITH NORMAL BUTYL ALCOHOL

In a five hundred milliliter three neck round bottom flask with ground glass joints were placed 3.55g of poly-$\overline{57}$: $\overline{43}$. (itaconic anhydride co styrene) (Preparation I) and 30ml of n-butyl alcohol dried over anhydrous sodium sulfate. The flask was fitted with a moisture trap condenser, stirrer, and thermometer. The mixture was heated to 112°C and solution took place in twenty minutes. The temperature was increased to 119.5°C and the n-butyl alcohol collected in the moisture trap was removed and an equivalent amount of fresh n-butyl alcohol was added to the reaction flask keeping the volume approximately constant for nine hours. After nine hours distillation was continued until the product was almost to dryness. The residual n-butyl alcohol was removed by distillation under a vacuum. The brittle product was washed with several portions of ether and was air dried for two hours. The product was finally dried at 90°C for five hours. Carbon-hydrogen analysis showed the ester to contain 68.81 and 68.92 percent carbon. The percent hydrogen was 7.26 and 7.54. The theoretical percentages based on half esterification are 68.59 for carbon and 7.54 for hydrogen.

REACTION WITH 2-METHYL-1-BUTANOL

Two grams of poly - $\overline{57}:\overline{43}$ (itaconic anhydride co styrene) (Preparation I) were placed in a flask with 6.9g of 2-methyl-1-butanol. The flask was fitted with a stirrer, reflux condenser, and a thermometer. The mixture was heated at 125°C. The copolymer dissolved in one hour. After 36 hours at 127°C the solution was transferred to a 250ml flask fitted with a vacuum take off and reduced to dryness using a water bath. The residue was found to be soluble in acetone. Carbon-hydrogen analysis of the product indicated 69.83 and 69.95 percent carbon. The percent hydrogen found was 8.46 and 8.63. The percent carbon based on half esterification of the copolymer is theoretically 69.36 percent carbon and 7.85 for hydrogen.

REACTION WITH ETHYLENE GLYCOL

In a 500ml three neck flask fitted with a reflux condenser and a moisture trap. stirrer, and a thermometer were placed 5g of poly - $\overline{57}:\overline{43}$ (itaconic anhydride co styrene) (Preparation I) and 60g ethylene glycol. In heating the mixture to 170°C the solution began to gel. Gelling was further advanced after ten minutes, and another 30g of ethylene glycol were added. The excess ethylene glycol was distilled off after one hour. The residue was removed from the flask with difficulty and heated on a hot plate at 200°C until it was completely dry (about two hours). Carbon-hydrogen analysis on the resulting acetone insoluble product gave 61.38 and 61.54 percent carbon. The percent hydrogen was 6.44 and 6.52. The theoretical percent carbon and hydrogen based on half esterification is 62.9 for carbon and 6.43 for hydrogen.

POTENTIOMETRIC TITRATIONS OF THE COPOLYMER OF ITACONIC ANHYDRIDE AND STYRENE

The powdery, benzene extracted material from each of the five copolymerization reactions was weighed on tared watch glasses and washed into 400ml beakers with acetone. About 50ml of acetone was used in each case. Standard sodium hydroxide was added slowly with constant stirring to the acetone solution. In a few cases a turbid solution resulted. The solution samples were boiled on a hot plate to drive off the acetone. When the acetone odor disappeared the solution became transparent in those samples where turbidity was present. The solution samples were potentiometrically titrated with standard acid using a line operated constant reading pH meter with a glass electrode. The solutions were agitated during titration with magnetic stirrers. Data and comments for the titrations are given in Tables VI to X.

The data was obtained by observing the pH at milliliter and half milliliter increments of acid. These tables contain only the information concerned with the pertinent portions of the titrations. When the change in pH was constant with the addition of hydrochloric acid, data for inclusion in this thesis was chosen to present only a few points. In the areas where the pH changes vary, the entire data is given. In the tables blank spaces are left to represent

missing data. The corresponding pH versus milliliter acid graphs follow the respective data. Table XI gives the theoretical milliequivalents and the observed milliequivalents of the copolymer titrated for the five copolymers.

TABLE VI

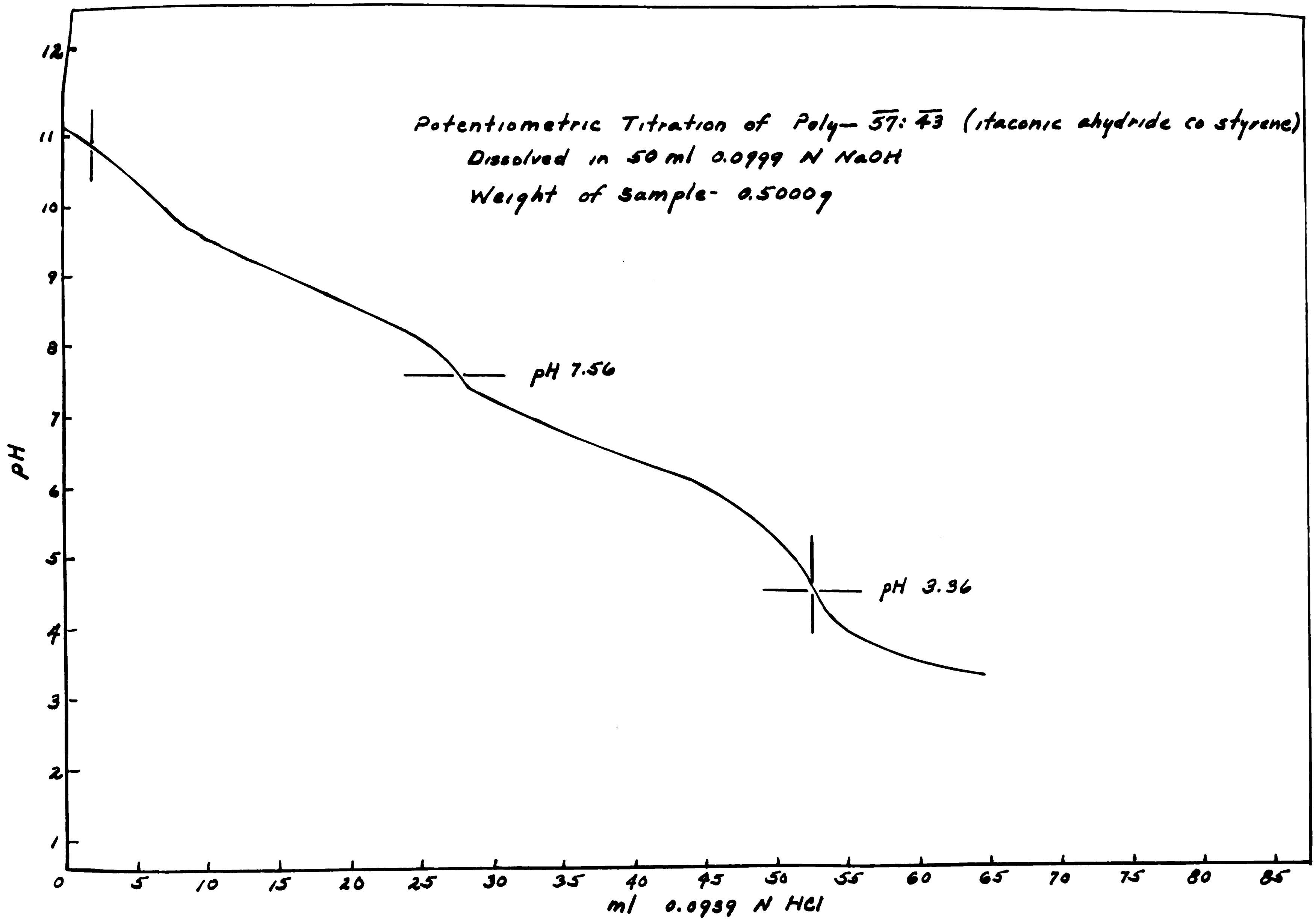
POTENTIOMETRIC TITRATION OF STYRENE-ITACONIC ANHYDRIDE COPOLYMER (PREPARATION I)

A 0.5000g sample of the copolymer from Preparation I, poly - $\overline{57}:\overline{43}$ (itaconic anhydride co styrene), was dissolved in 50ml of acetone. Fifty milliliters of 0.0999N NaOH was added slowly with stirring. The acetone was boiled off on a hot plate. The solution was titrated with 0.0939N HCl using a Cenco Titration pH Meter.

ml 0.0939N HCl	pH	Remarks
0.0	11.18	Solution clear.
—	—	
4.0	10.52	
—	—	
16.0	8.98	
20.0	8.60	
—	—	
25.0	8.09	
26.0	7.95	
26.5	7.88	
27.0	7.75	
27.5	7.65	
29.0	7.31	
30.0	7.21	
31.0	7.11	

ml 0.0939N Hcl	pH	Remarks
——	——	
40.0	6.39	
——	——	
44.5	6.01	Drop creates cloudiness, clears on stirring.
45.0	5.95	
——	——	
48.0	5.51	
——	——	
49.0	5.35	Cloudiness persisting longer.
49.5	5.26	Solution definitely cloudy.
50.0	5.19	
51.0	5.00	
——	——	
52.0	4.78	Solution opaque.
52.5	4.56	
53.0	4.38	
53.5	4.20	
54.0	4.09	
55.0	3.90	
61.0	3.46	
——	——	
71.0	3.20	

FIGURE V



Potentiometric Titration of Poly- $\overline{57}:\overline{43}$ (itaconic ahydride co styrene)
Dissolved in 50 ml 0.0999 N NaOH
Weight of Sample- 0.5000g

TABLE VII

POTENTIOMETRIC TITRATION OF STYRENE-ITACONIC ANHYDRIDE COPOLYMER (PREPARATION II)

A 0.5000g sample of the copolymer from Preparation II, poly - $\overline{80}:\overline{20}$ (itaconic anhydride co styrene), was dissolved in 50ml of acetone. Seventy-five milliliters of 0.0924N NaOH was added slowly with stirring. The acetone was boiled off on a hot plate. The solution was titrated with 0.0976N HCl using a Beckman constant reading pH meter.

ml0.0976N HCl	pH	Remarks
0.0	11.80	Solution clear.
——	——	
5.0	11.64	
——	——	
10.5	11.25	
——	——	
12.0	11.17	
——	——	
14.0	11.02	
15.0	10.97	
15.5	10.92	
——	——	
18.0	10.84	Meter adjusted.
——	——	

ml 0.0976N HCl	pH	Remarks
20.0	10.61	
——	——	
23.5	10.21	Meter adjusted.
——	——	
27.0	9.87	
——	——	
29.0	9.68	
——	——	
31.0	9.51	
——	——	
34.5	9.12	Meter checked.
——	——	
38.0	8.76	
——	——	
42.0	8.30	
——	——	
43.0	8.16	
44.0	8.02	
45.0	7.90	
45.5	7.80	
46.0	7.70	
46.5	7.60	
47.0	7.54	
47.5	7.45	

ml 0.0976N HCl	pH	Remarks
48.0	7.35	
——	——	
49.0	7.19	Meter adjusted.
——	——	
55.0	6.40	
——	——	
60.0	5.90	
——	——	
65.0	5.36	
——	——	
70.0	4.82	
——	——	
75.0	4.31	
——	——	
76.0	4.20	
76.5	4.12	
77.0	4.08	
77.5	4.00	
78.0	3.94	
——	——	
79.0	3.76	
79.5	3.69	
80.0	3.58	
——	——	

ml 0.0976N HCl	pH	Remarks
81.0	3.41	Drop creates cloudiness, clears on stirring.
81.5	3.32	
82.0	3.24	
82.5	3.14	Cloudiness remains.
83.0	3.02	Solution opaque.
—	—	
84.0	2.86	
85.0	2.72	
—	—	
90.0	2.36	

FIGURE VI

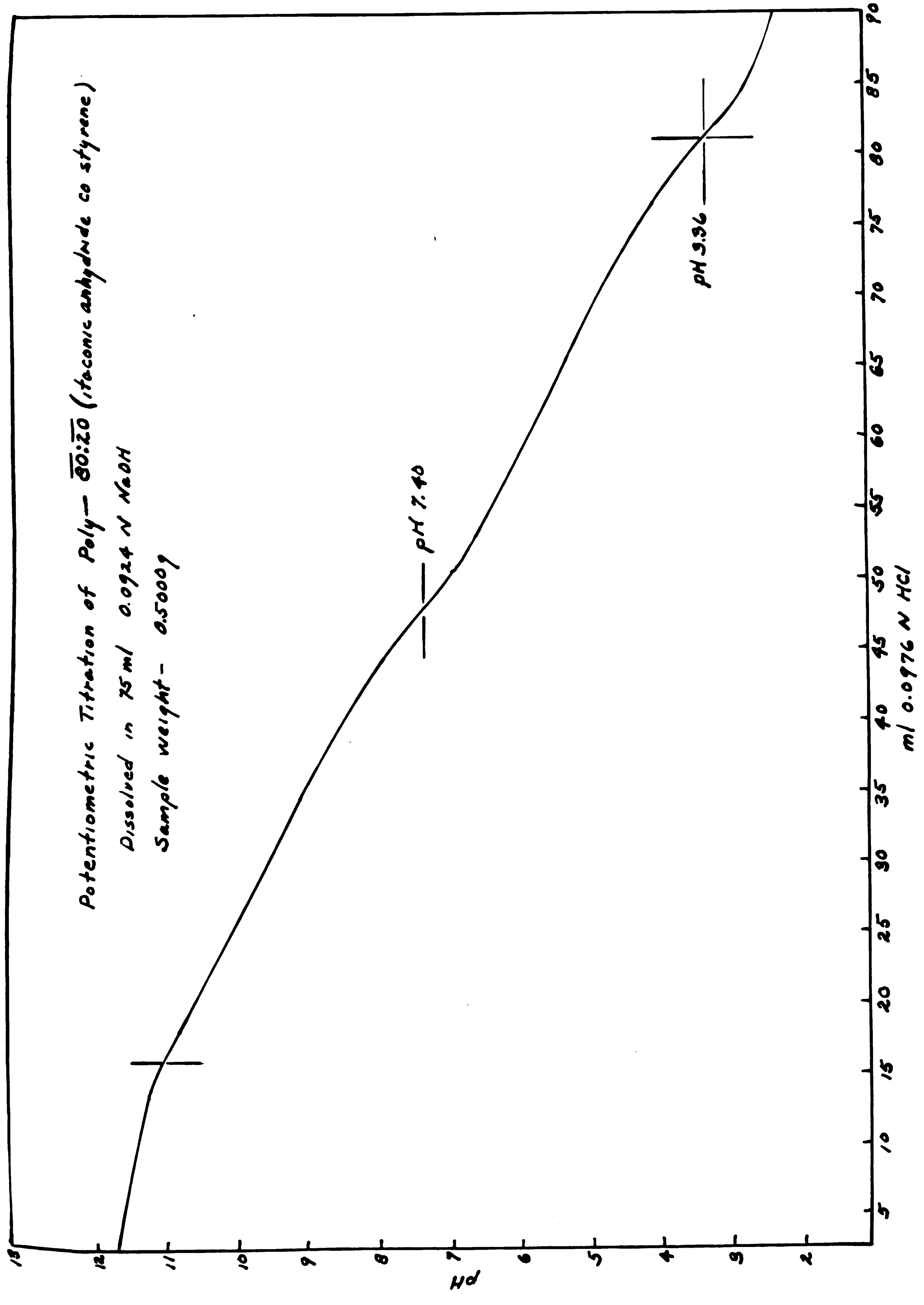

Potentiometric Titration of Poly— $\overline{80}:\overline{20}$ (itaconic anhydride co styrene)
Dissolved in 75 ml 0.0924 N NaOH
Sample weight— 0.5000g
pH 7.40
pH 3.36
pH
13
12
11
10
9
8
7
6
5
4
3
2
ml 0.0976 N HCl
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90

TABLE VIII

POTENTIOMETRIC TITRATION OF STYRENE-ITACONIC ANHYDRIDE COPOLYMER (PREPARATION III)

A 0.5000g sample of the copolymer from Preparation III, poly - $\overline{52}:\overline{48}$. (itaconic anhydride co styrene), was dissolved in 50ml of acetone. Seventy-five milliliters of 0.0924N NaOH was added slowly with stirring. The acetone was boiled off on a hot plate. The solution was titrated with 0.0976N HCl using a Beckman constant reading pH meter.

ml 0.0976N HCl	pH	Remarks
0.0	11.82	Solution clear.
——	——	
5.0	11.65	
——	——	
10.0	11.58	
——	——	
15.0	11.39	
16.0	11.33	
17.0	11.28	
18.0	11.21	
19.0	11.14	
——	——	
20.0	11.08	
——	——	

ml 0.0976N HCl	pH	Remarks
25.0	10.53	
—	—	
30.0	10.01	
—	—	
35.0	9.53	
—	—	
40.0	9.08	
—	—	
45.0	8.53	
—	—	
47.0	8.28	
48.0	8.13	
48.6	8.06	Meter adjusted.
49.0	8.00	
50.0	7.83	
50.5	7.74	
51.0	7.65	
—	—	
53.0	7.28	
—	—	
54.0	7.10	
—	—	
55.0	6.96	Meter adjusted
—	—	

ml 0.0976N HCl	pH	Remarks
60.0	6.44	
—	—	
64.0	6.08	Meter checked.
—	—	
70.0	5.54	
—	—	
72.0	5.28	
—	—	
74.0	5.00	
75.0	4.83	
75.5	4.73	
76.0	4.62	
77.0	4.36	
77.5	4.20	
78.0	4.03	
78.5	3.85	
79.0	3.70	Cloudiness appearing.
79.5	3.53	
80.0	3.42	Meter checked.
80.5	3.30	Solution opaque.
—	—	
82.0	3.04	
—	—	
84.0	2.83	

ml 0.0976N HCl	pH	Remarks
—	—	
90.0	2.50	
—	—	
95.0	2.32	Meter checked.

FIGURE VII

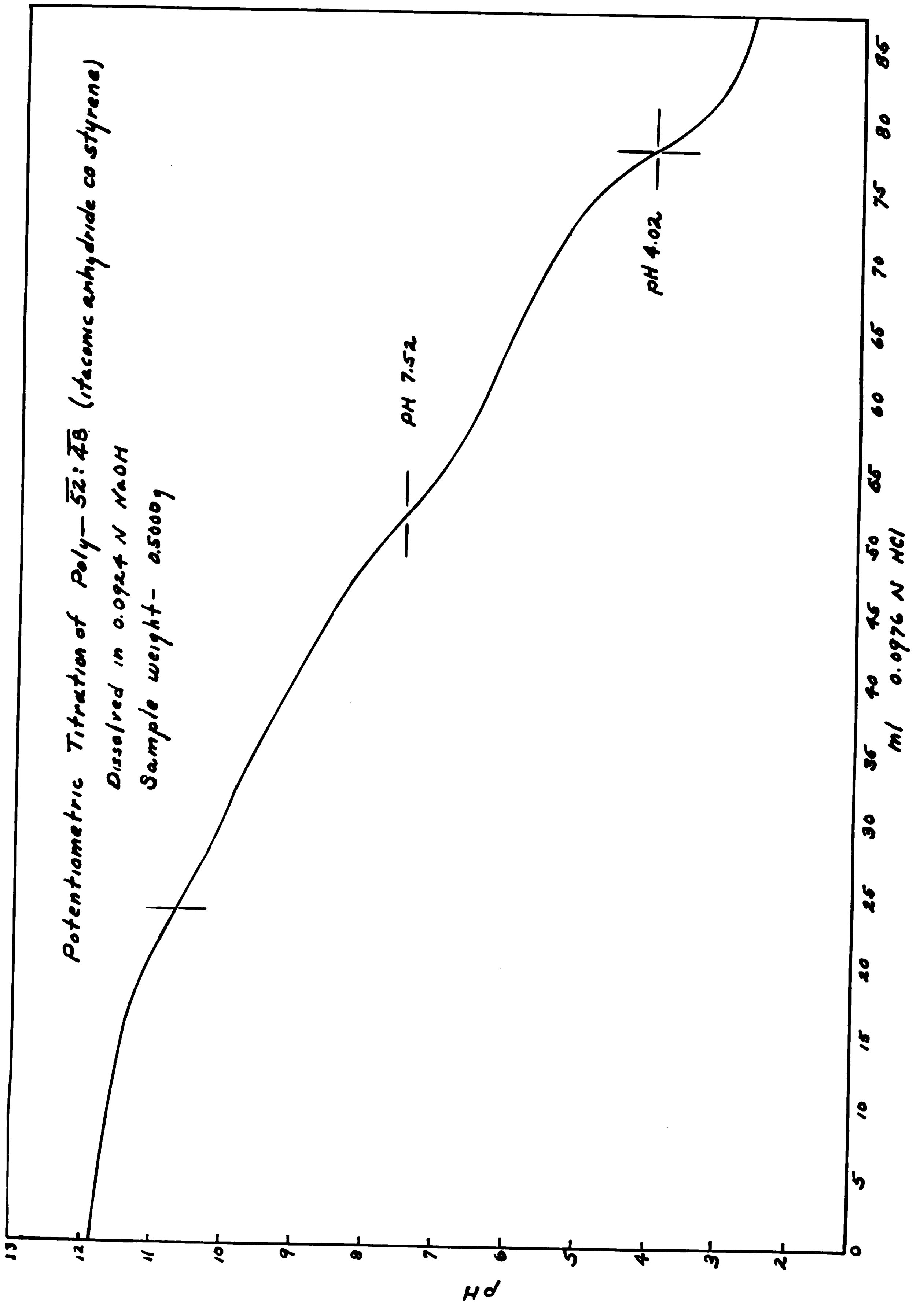

Potentiometric Titration of Poly — 52:48 (itaconic anhydride co styrene)
Dissolved in 0.0924 N NaOH
Sample weight — 0.5000g
pH 7.52
pH 4.02
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
ml 0.0976 N HCl
2
3
4
5
6
7
8
9
10
11
12
13
pH

TABLE IX

POTENTIOMETRIC TITRATION OF STYRENE-ITACONIC ANHYDRIDE COPOLYMER (PREPARATION IV)

A 0.5000g sample of the copolymer from Preparation IV, poly - $\overline{72}:\overline{28}$. (itaconic anhydride co styrene), was dissolved in 50ml of acetone. One hundred milliliters of 0.0924N NaOH was added slowly with stirring. The acetone was boiled off on a hot plate. The solution was titrated with 0.0976N HCl using a Beckman constant reading pH meter.

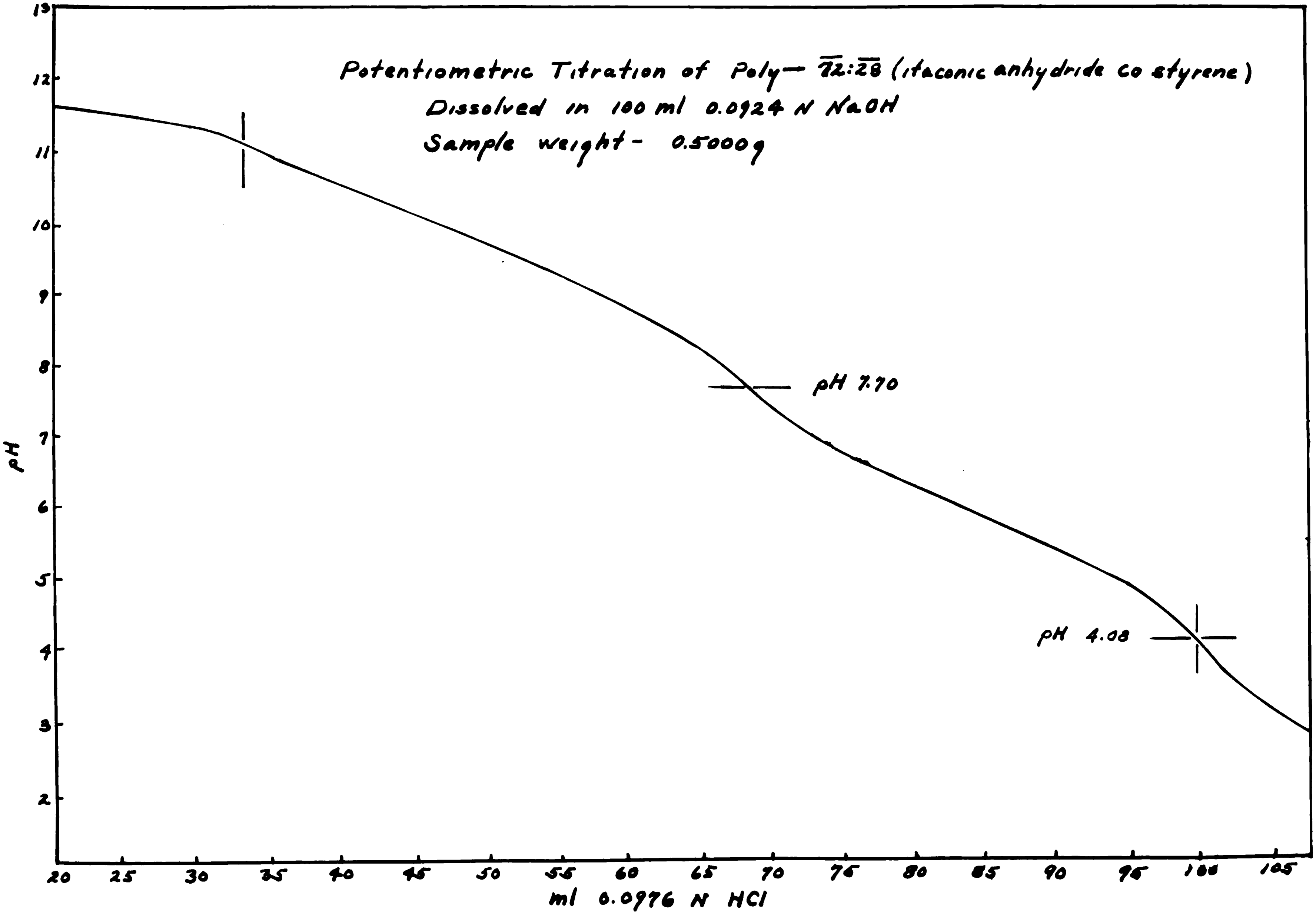
ml 0.0976N HCl	pH	Remarks
0.0	12.6	Solution clear.
——	——	
10.0	11.86	
——	——	
20.0	11.66	Meter adjusted.
——	——	
25.0	11.46	
26.0	11.42	
——	——	
27.0	11.36	
28.0	11.32	
——	——	
29.0	11.38	

ml 0.0976N HCl	pH	Remarks
30.0	11.33	
31.0	11.26	
—	—	
32.0	11.20	
—	—	
35.5	10.90	Meter adjusted.
—	—	
40.0	10.54	
—	—	
45.0	10.14	Meter adjusted.
—	—	
50.5	9.7	Meter checked.
—	—	
55.0	9.32	
60.0	8.83	
—	—	
65.0	8.27	Meter adjusted.
66.0	8.14	
66.5	8.06	
67.0	7.97	
67.5	7.89	
68.0	7.81	
—	—	
69.0	7.64	

ml 0.0976N HCl	pH	Remarks
70.0	7.45	
——	——	
71.0	7.28	
——	——	
72.0	7.13	
73.0	6.97	
——	——	
74.0	6.85	
75.0	6.73	
——	——	
80.0	6.32	
——	——	
85.0	5.90	
——	——	
90.5	5.40	Meter checked.
——	——	
95.0	4.93	
——	——	
97.0	4.68	
98.0	4.56	
——	——	
99.0	4.32	
99.5	4.20	
100.0	4.08	

ml 0.0976N HCl	pH	Remarks
102.0	3.63	Drop creates cloudiness, clears on stirring.
103.5	3.38	
104.0	3.31	Solution definitely cloudy.
105.0	3.16	Solution opaque.
109.0	2.67	
116.0	2.30	

FIGURE VIII



Potentiometric Titration of Poly— $\overline{72}:\overline{28}$ (itaconic anhydride co styrene)
Dissolved in 100 ml 0.0924 N NaOH
Sample weight - 0.5000g

TABLE X

POTENTIOMETRIC TITRATION OF STYRENE-ITACONIC ANHYDRIDE COPOLYMER (PREPARATION V)

A 0.5000g sample of the copolymer from Preparation V, poly - $\overline{53}:\overline{47}$ (itaconic anhydride co styrene), was dissolved in 25ml of acetone. Seventy-five milliliters of 0.0924N NaOH was added slowly with stirring. The acetone was boiled off on a hot plate. The solution was titrated with 0.0976N HCl using a Beckman constant reading pH meter.

ml 0.0976N HCl	pH	Remarks
0.0	12.03	Solution clear.
——	——	
5.0	11.90	
——	——	
10.0	11.72	
——	——	
15.0	11.50	
——	——	
16.0	11.42	
17.0	11.37	
17.5	11.34	Meter adjusted.
18.0	11.32	
19.0	11.27	
20.0	11.18	

ml 0.0976N HCl	pH	Remarks
——	——	
21.0	11.05	
——	——	
25.0	10.53	Meter adjusted.
——	——	
30.0	9.95	
——	——	
38.0	9.18	Meter adjusted.
——	——	
43.0	8.66	
——	——	
47.0	8.21	
48.0	8.06	
48.5	7.98	
49.0	7.89	
49.5	7.81	
50.0	7.71	Meter checked.
51.0	7.50	
51.5	7.42	
52.0	7.33	
——	——	
53.0	7.12	
54.0	7.00	
——	——	
59.0	6.44	Meter checked.

ml 0.0976N HCl	pH	Remarks
—	—	
65.0	5.88	
—	—	
69.0	5.47	Meter checked.
—	—	
75.0	4.54	Drop creates cloudiness, clears on stirring.
—	—	
76.0	4.33	
77.0	4.10	
78.0	3.73	Solution opaque.
—	—	
79.0	3.35	
—	—	
86.0	2.48	Meter checked.
—	—	
100.0	1.87	

FIGURE IX

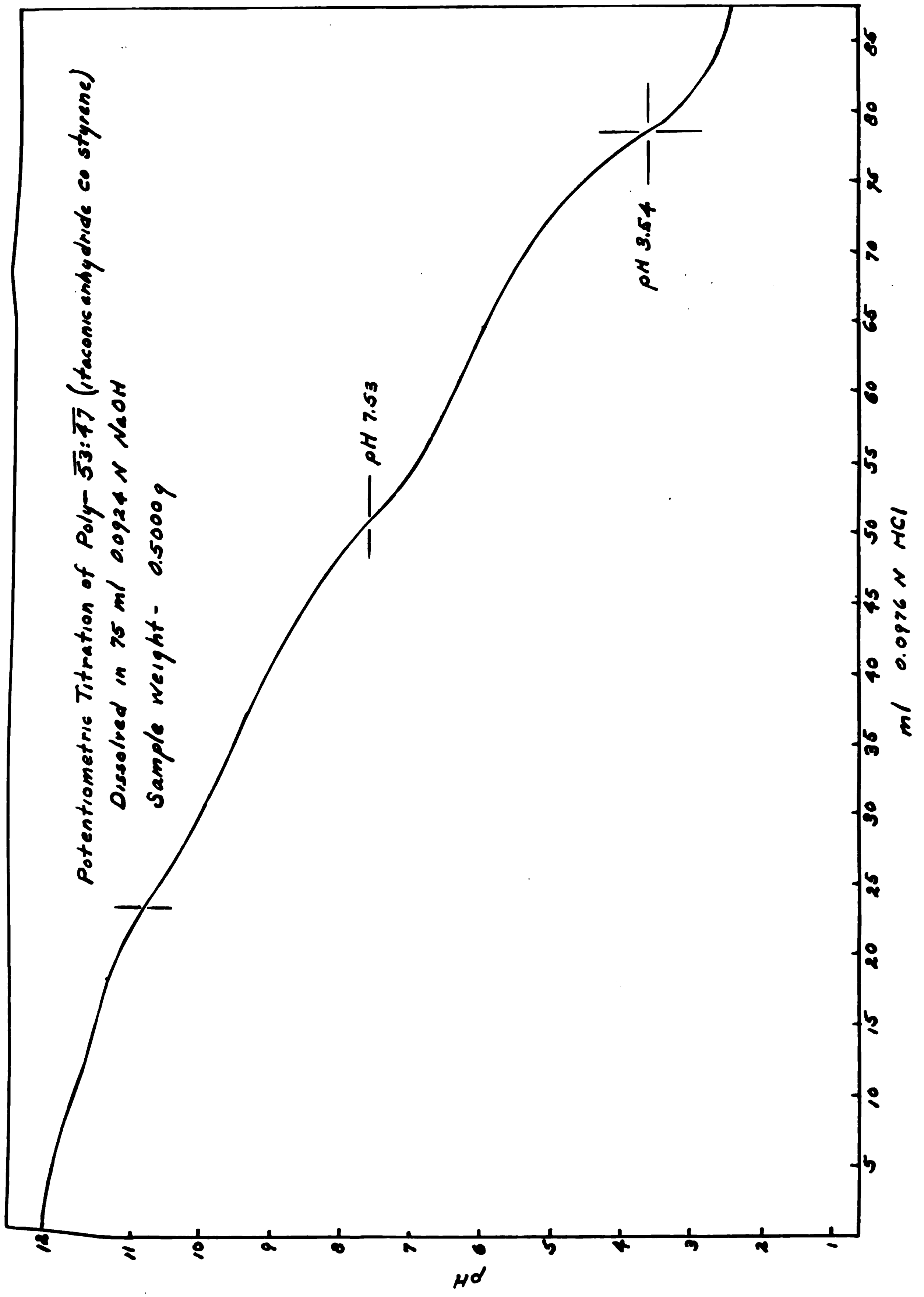

Potentiometric Titration of Poly- 53:47 (itaconic anhydride co styrene)
Dissolved in 75 ml 0.0924 N NaOH
Sample Weight - 0.5000 g
pH 7.53
pH 3.54
ml 0.0976 N HCl
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
pH
1
2
3
4
5
6
7
8
9
10
11
12

TABLE XI

TABULATION OF OBSERVED AND THEORETICAL NEUTRALIZATIONS IN THE POTENTIOMETRIC TITRATIONS

Titration No.	Copolymer Preparation No.	Theoretical copolymer meq.	Neutralization of excess NaOH, meq. observed	Complete neutralization, meq. observed	Observed copolymer meq. titrated
1	I	5.18	0.199	4.94	4.75
2	II	7.12	1.50	7.93	6.43
3	III	4.82	2.29	7.59	5.30
4	IV	6.58	3.27	9.75	6.48
5	V	4.93	2.24	7.72	5.48

CALCULATION OF THEORETICAL MILLIEQUIVALENTS:

(1) Weight of itaconic anhydride in unit = (molecular weight itaconic anhydride x mole percent itaconic anhydride) x 2

(2) Weight of styrene in unit = (molecular weight styrene x mole percent styrene) x 2

(3) Line (1) plus line (2) = unit weight

(4) Weight of itaconic anhydride = (sample weight x weight of itaconic anhydride in Unit) / unit weight

(5) Milliequivalents of itaconic anhydride = weight of itaconic anhydride / milliequivalent weight of itaconic anhydride

TABLE XII

SOLUBILITY

	Alkali	Pyridine	Acetone	Others
Copolymers				
Preparation I	S	S	S	Soluble in nitrobenzene. Insoluble in carbon tetrachloride, benzene, toluene, and ether.
Preparation II	S	S	S	
Preparation III	S	S	S	
Preparation IV	S	S	S	
Preparation V	S	S	S	
Polyitaconic anhydride	S	S	S	Soluble in water. Insoluble in nitrobenzene and nitromethane.
Ethyl ester	S	S	S	Insoluble in ethyl and amyl acetate.
n-butyl ester	S	S	S	-------
glycyl ester	I	I	I	Insoluble in ethyl and amyl acetate.
2-methyl-1-butyl ester	S	S	S	-------

The solubility was tried using a 0.5g sample in 5ml of solvent. If the sample dissolved completely it was referred to as soluble (S), if not then as insoluble (I).

PREPARATION OF COPOLYMER OF STYRENE AND MALEIC ANHYDRIDE

This preparation was carried out as described by Garrett[1] with the exception that the nitrogen was not washed with alkaline pyrogallol. A 1:1 molar ratio of reactants of 0.233 mole of maleic anhydride (23.0g) to 0.233 mole of styrene (24.2g) was copolymerized in 615.2g of benzene with 0.233g (.00096 mole) benzoyl peroxide. Copolymerization was carried out in a nitrogen atmosphere with continuous stirring. The copolymer was filtered on a Buchner funnel after an eight hour reaction time. It was washed several times with hot benzene and subsequently benzene extracted in a Soxhlet extractor for one hundred and twenty hours, after which it was air dried for four hours and finally dried at 90°C for ten hours.

REACTION OF ETHYLENEDIAMINE WITH STYRENE-MALEIC ANHYDRIDE COPOLYMER

Four grams of the copolymer of styrene and maleic anhydride were placed in a 500ml flask fitted with a reflux condenser and stirrer. To this was added 50ml of dry acetone and the mixture was heated with stirring until the copolymer was dissolved. A small amount of acetone in which was dissolved 1.19g ethylenediamine (0.0198 mole) was then added. Immediately a white film formed over the solution in the flask. In five minutes a gelatinous material was formed throughout. The acetone was partially removed with an aspirator and then the product was washed several times in acetone and finally dried in air. The product was yellow in color and insoluble in acetone. A Kjeldahl analysis on the product showed 3.95 and 4.11 percent nitrogen. The calculated value is 10.68 percent nitrogen based on a 1:1 structural unit containing one amide linkage.

REACTION OF ETHYLAMINE WITH STYRENE-MALEIC ANHYDRIDE COPOLYMER

Four grams of the copolymer of styrene and maleic anhydride were dissolved in 50ml of dry acetone with agitation in a 500ml flask fitted with reflux condenser and stirrer. Ethylamine, 0.894g (0.0198 mole) was added. Almost immediately a gelatinous material was formed around the agitator. The reaction was allowed to proceed for one hour. The resulting mixture was poured into several hundred milliliters of cold distilled water to form a soft stringy mass suspended in the water. This was filtered and the residue was washed with cold water. The solid was placed in distilled water and heated. The residue dissolved forming a viscous solution. The solution was evaporated to dryness. The product was soluble in acetone. A Kjeldahl analysis on the product showed 2.43 and 2.35 percent nitrogen. The calculated value is 5.36 percent nitrogen based on a 1:1 structural unit containing one amide linkage.

HOMOPOLYMERIZATION OF ITACONIC ANHYDRIDE

Five hundred milliliters of benzene and 52.19g itaconic anhydride (0.466mole) were placed in a one liter flask fitted with a reflux condenser, nitrogen inlet tube and a mechanical stirrer. The mixture was heated at the reflux temperature of benzene. The itaconic anhydride did not completely dissolve in thirty minutes. Nitrogen was bubbled beneath the surface of the benzene throughout the solution and reaction time. Benzoyl peroxide, 0.233g, was added. Nine hours were allowed for reaction to take place. The reaction mixture was filtered on a Buchner and washed with several portions of hot benzene. The white product collected was air dried. The yield was 11.0g, or a 21 percent polymerization. Carbon and hydrogen analysis showed 50.39 and 50.59 percent carbon. The percent hydrogen was 4.10 and 4.38. The theoretical percentages for polyitaconic anhydride are 53.57 for carbon and 3.57 for hydrogen. It appears there has been about forty one percent hydrolysis of the polymer. This would account for the difference in the actual and theoretical percentages of carbon and hydrogen.

The solubility of the polymer was tested in benzene, acetone, carbon tetrachloride, toluene, water, and alkali. It was found to be soluble in the acetone, alkali and water.

INFRARED SPECTRA

Infrared spectra were obtained for maleic anhydride, itaconic anhydride, styrene, the five copolymers of styrene and itaconic anhydride, and the poly-(styrene co maleic anhydride.

In addition infrared spectra were obtained for poly-itaconic anhydride, polystyrene, and the ethylene glycyl, ethyl, 2-methyl-1-butyl, and n-butyl esters of poly- 57 : 43. (itaconic anhydride co styrene). Also spectra of the free acid, ammonium salt, reaction products with ethylamine and ethylenediamine were made.

All of the above spectra were obtained as mulls with the exception of styrene which was run pure between salt plates. The instrument used in all cases was the Perkin-Elmer double beam recording spectrophotometer. The full spectra included in this work were reduced by means of a pantograph. The instrument settings are placed beside the respective spectra (Figures X — XX).

FIGURE X

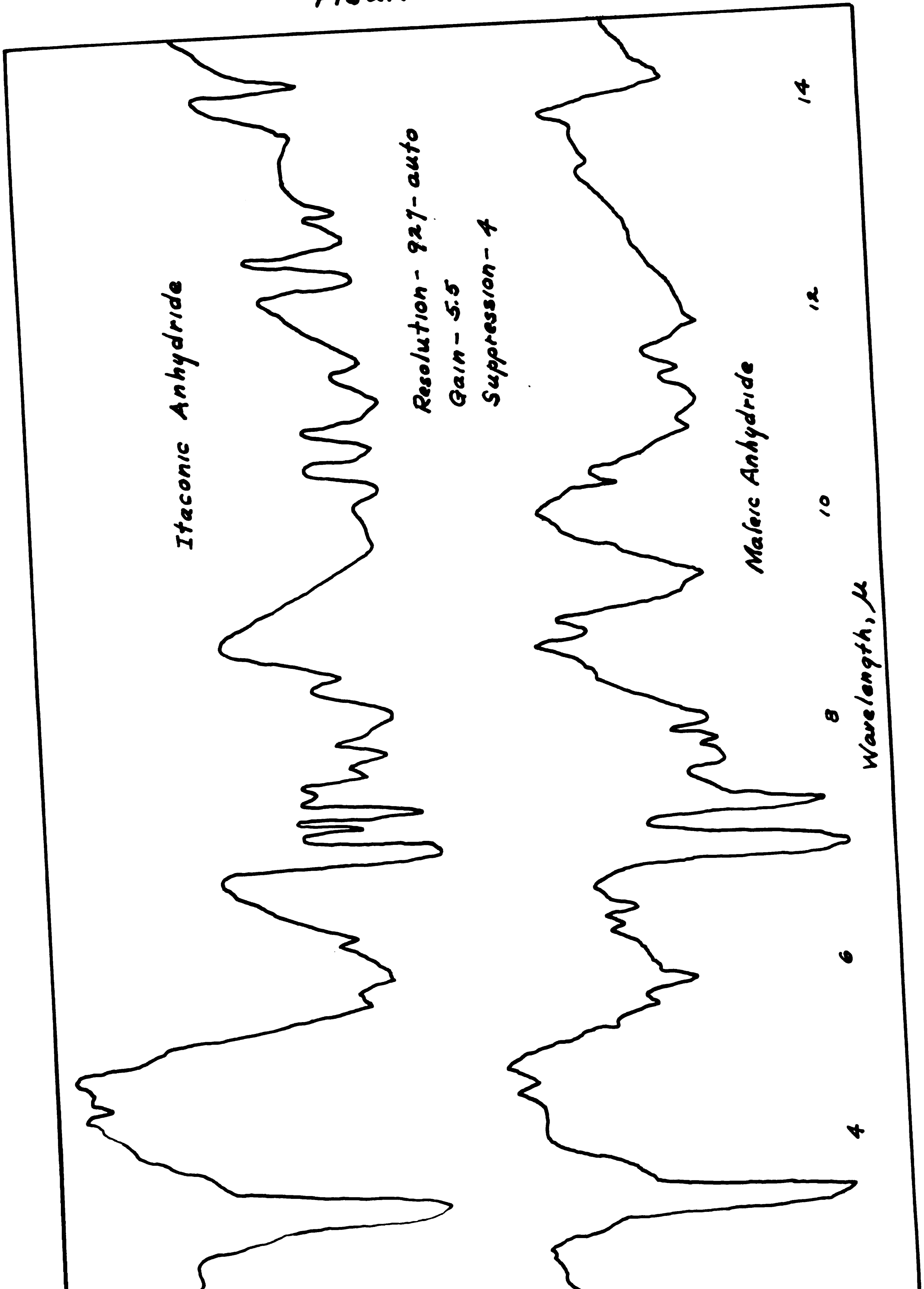

Itaconic Anhydride
Resolution - 927 - auto
Gain - 5.5
Suppression - 4
Maleic Anhydride
Wavelength, μ
2
4
6
8
10
12
14

FIGURE XI

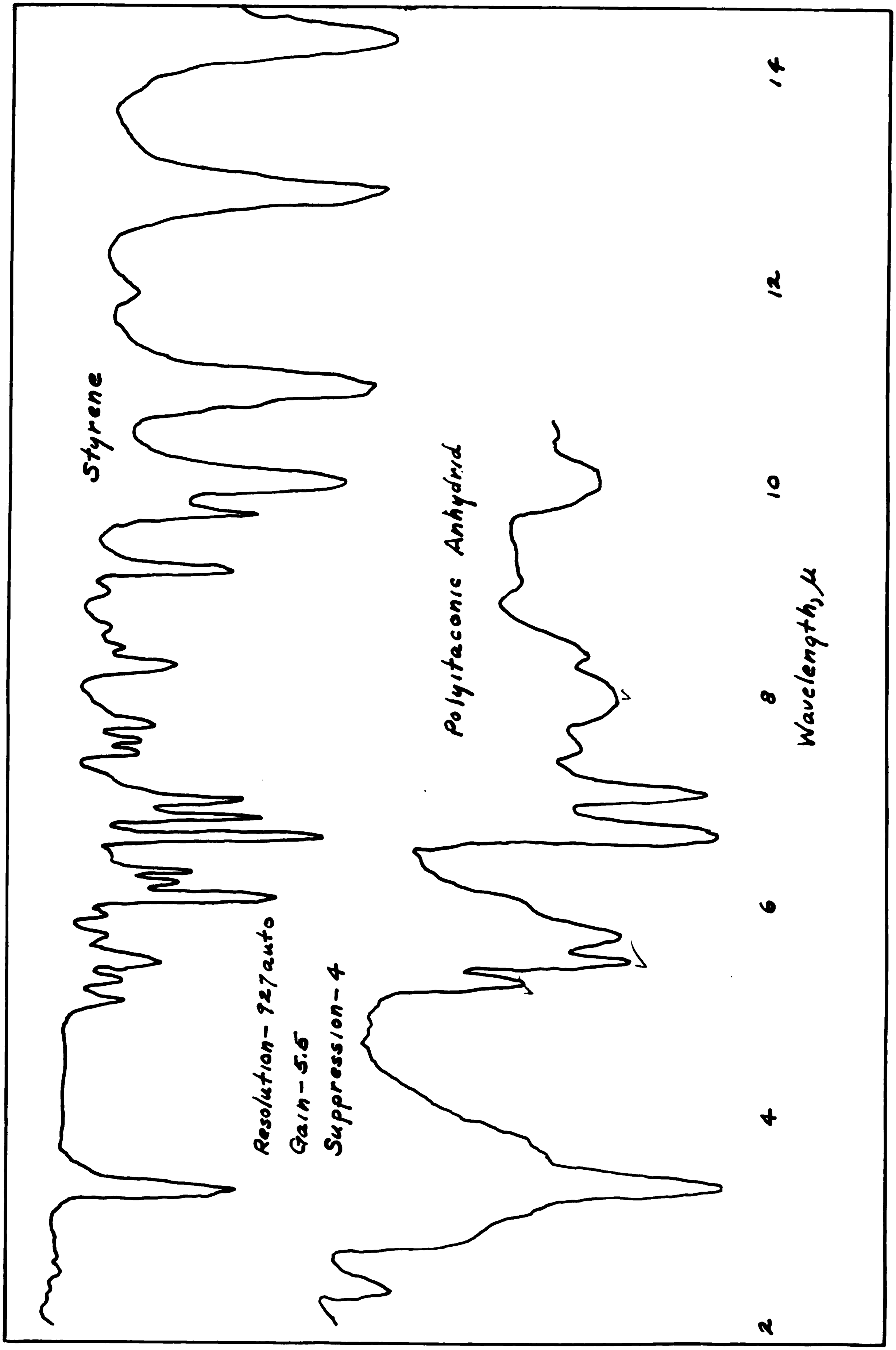

Styrene
Polyitaconic Anhydrid
Resolution- 927auto
Gain- 5.5
Suppression- 4
2
4
6
8
10
12
14
Wavelength, μ

FIGURE XII

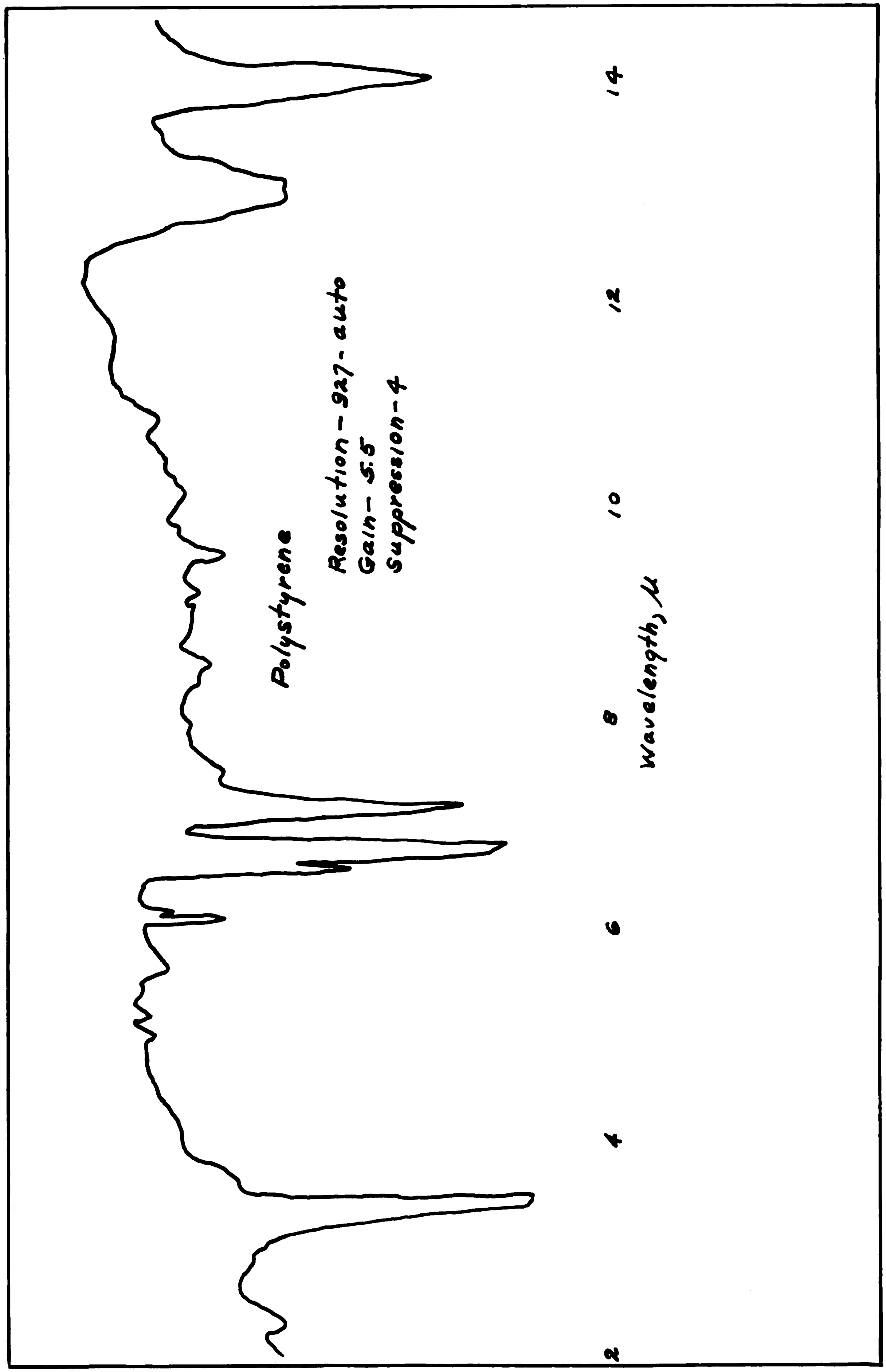

Polystyrene
Resolution - 927 - auto
Gain - 5.5
Suppression - 4
Wavelength, μ
2
4
6
8
10
12
14

FIGURE XIII

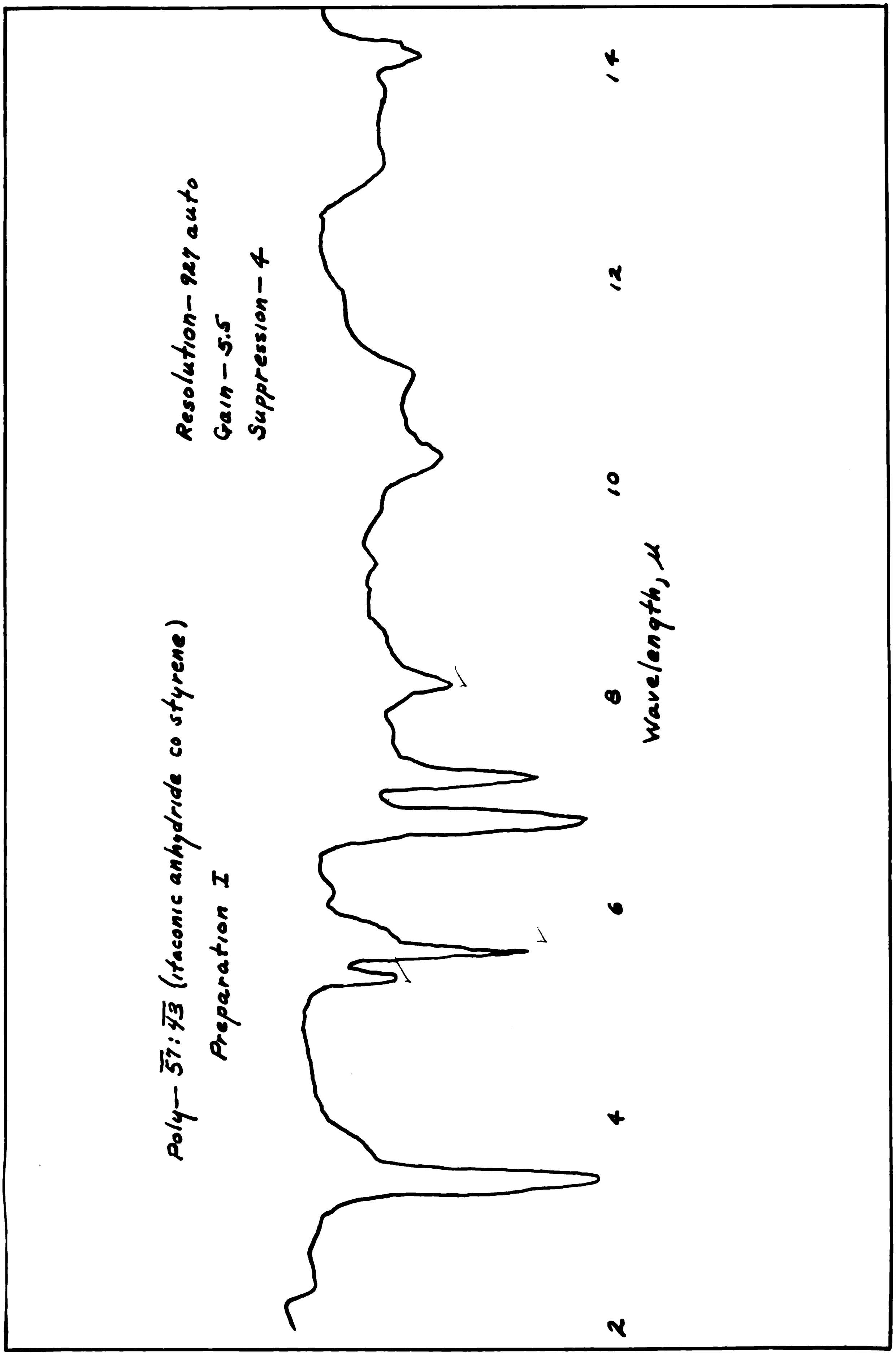

Poly – $\overline{57}:\overline{43}$ (itaconic anhydride co styrene)
Preparation I
Resolution – 927 auto
Gain – 5.5
Suppression – 4
2
4
6
8
10
12
14
Wavelength, μ

FIGURE XIV

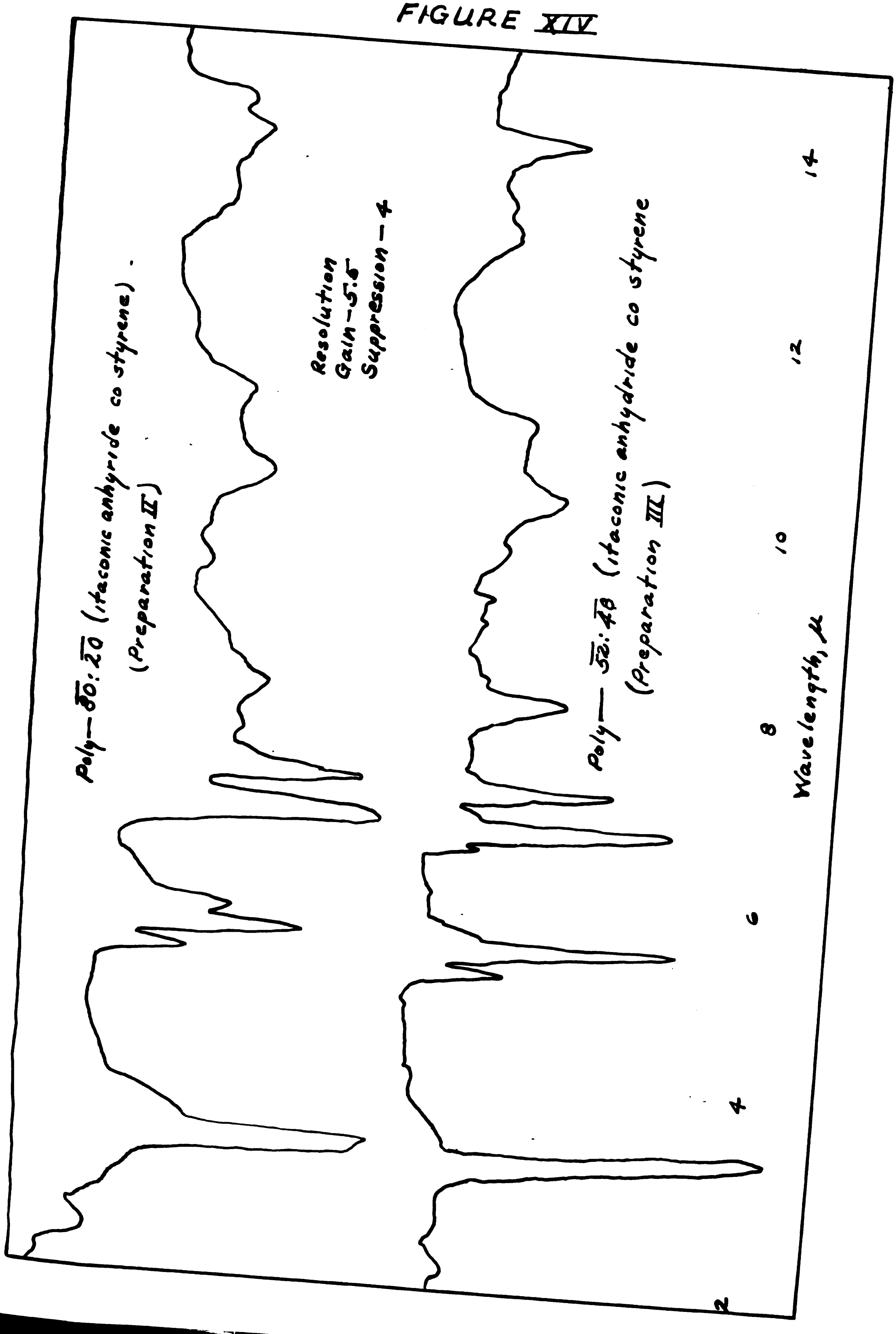

Poly—$\overline{80}$:$\overline{20}$ (itaconic anhydride co styrene).
(Preparation II)
Resolution
Gain—5.5
Suppression—4
Poly—$\overline{52}$:$\overline{48}$ (itaconic anhydride co styrene)
(Preparation III)
2
4
6
8
10
12
14
Wavelength, μ

FIGURE XV

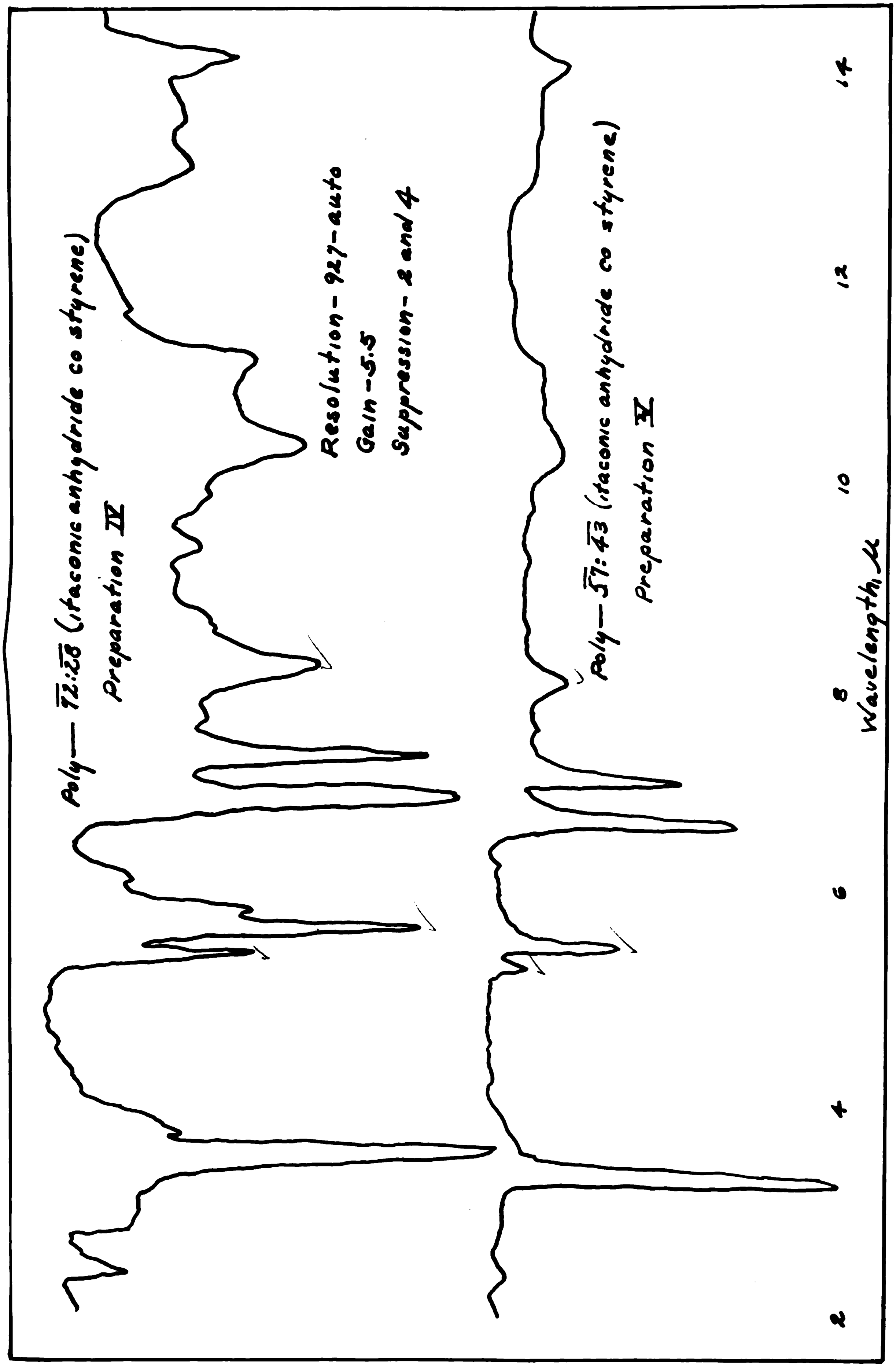

Poly— $\overline{72}:\overline{28}$ (itaconic anhydride co styrene)
Preparation IV
Resolution - 927-auto
Gain - 5.5
Suppression - 2 and 4
Poly— $\overline{57}:\overline{43}$ (itaconic anhydride co styrene)
Preparation V
2
4
6
8
10
12
14
Wavelength, μ

FIGURE XVI

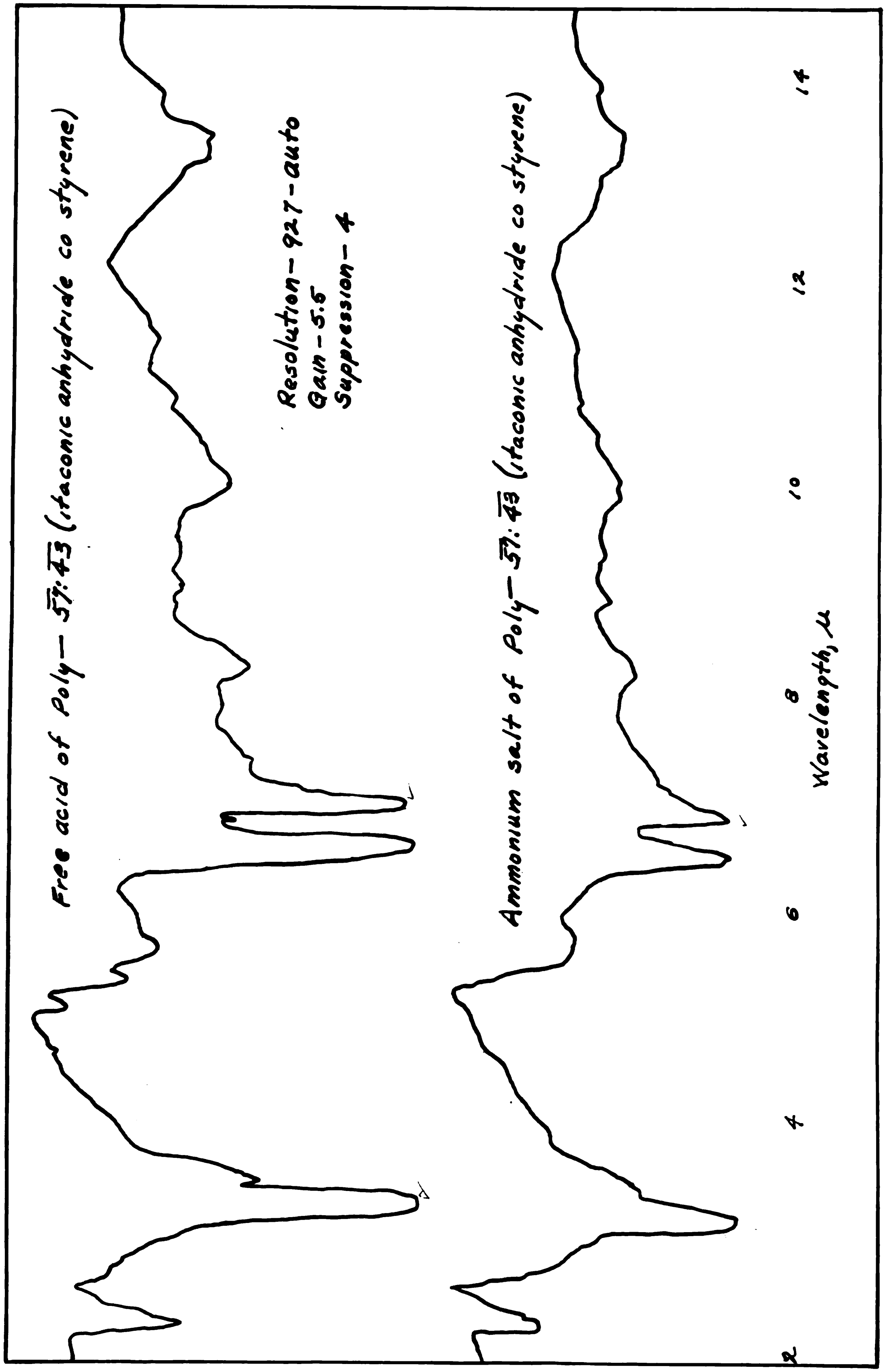

Free acid of Poly— 57:43 (itaconic anhydride co styrene)
Resolution— 927-auto
Gain — 5.5
Suppression— 4
Ammonium salt of Poly— 57:43 (itaconic anhydride co styrene)
2
4
6
8
10
12
14
Wavelength, μ

FIGURE XVII

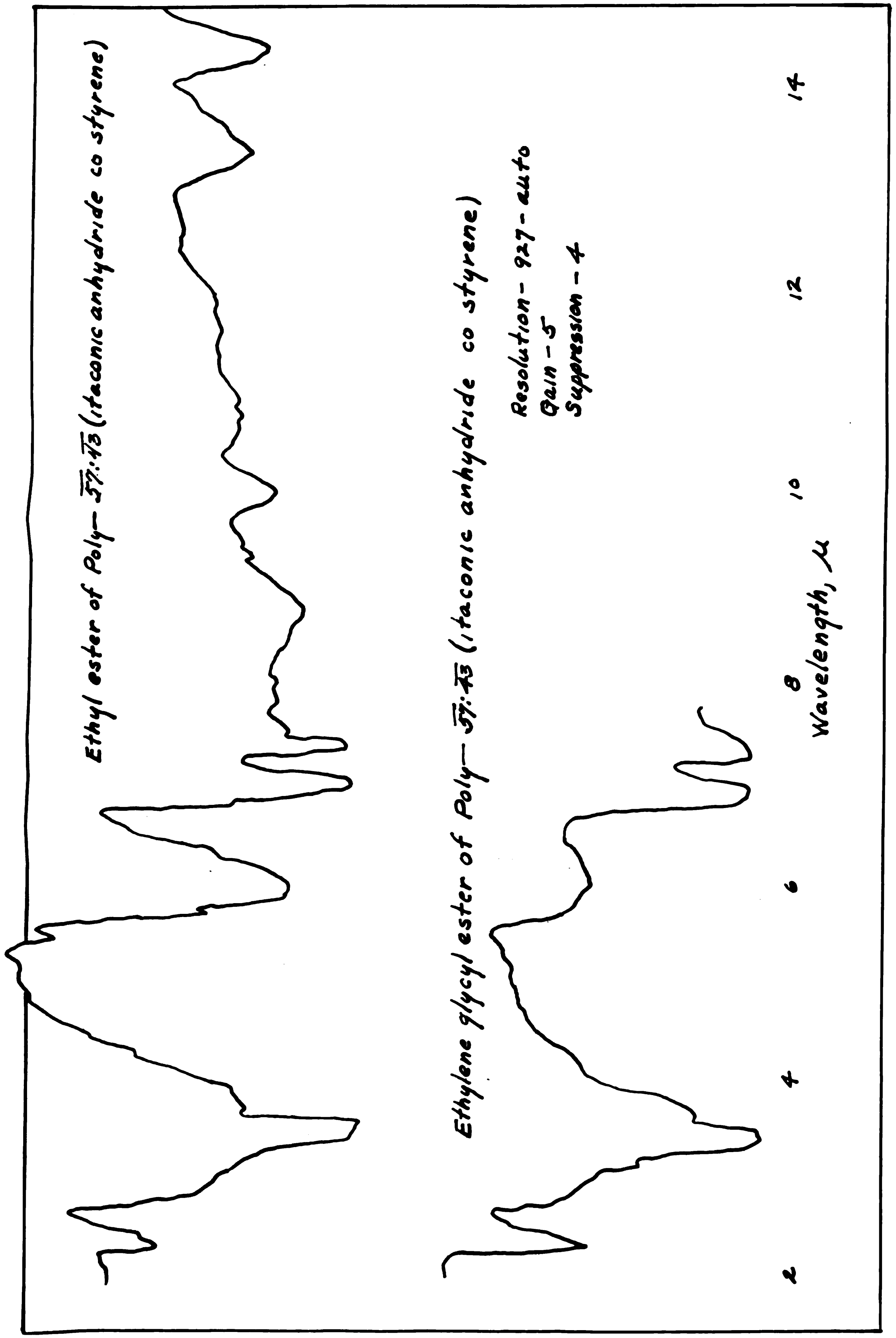

Ethyl ester of Poly— 57:43 (itaconic anhydride co styrene)
Ethylene glycyl ester of Poly— 57:43 (itaconic anhydride co styrene)
Resolution - 927 - auto
Gain - 5
Suppression - 4
2
4
6
8
10
12
14
Wavelength, μ

FIGURE XVIII

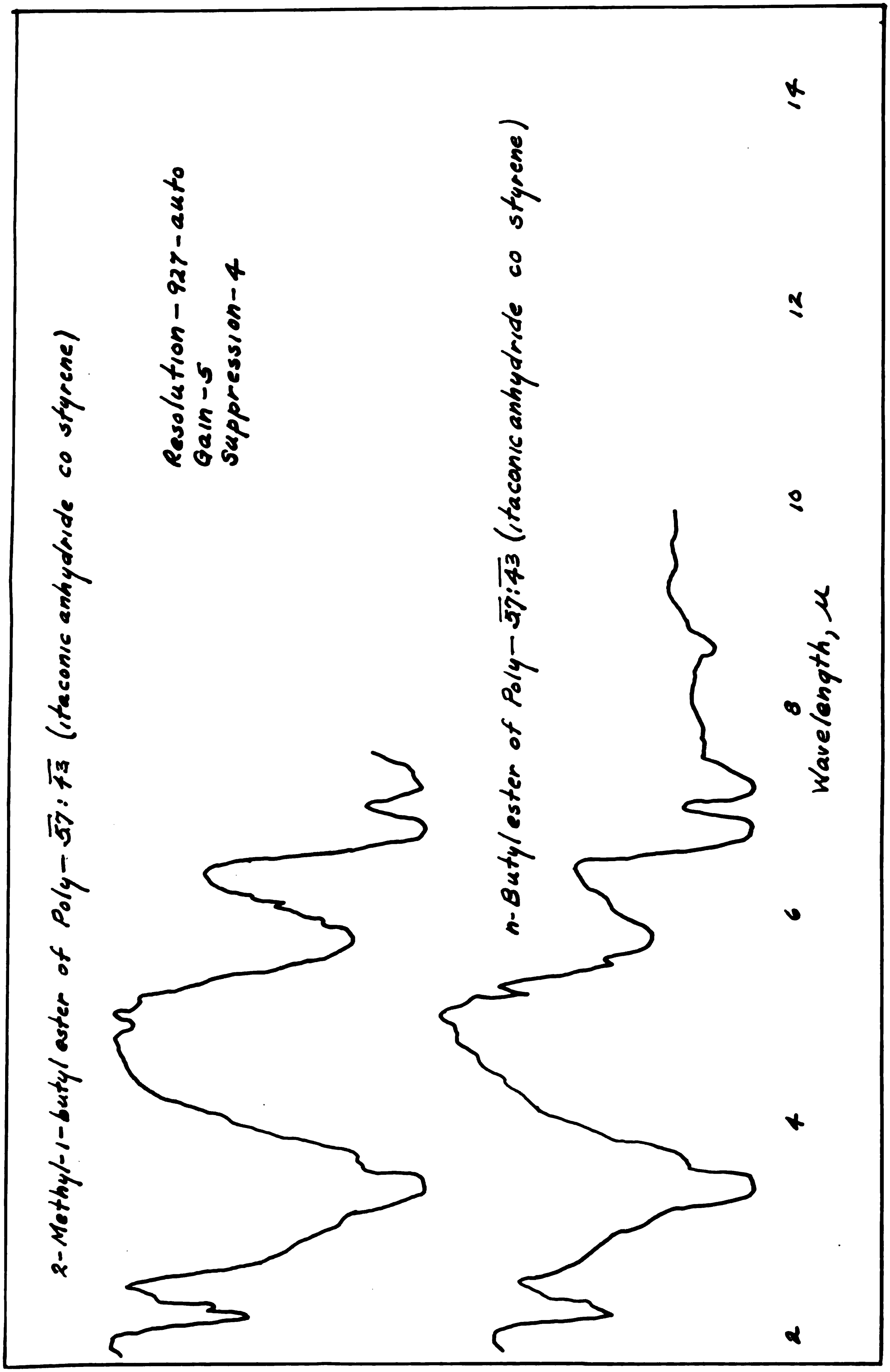


FIGURE XIX

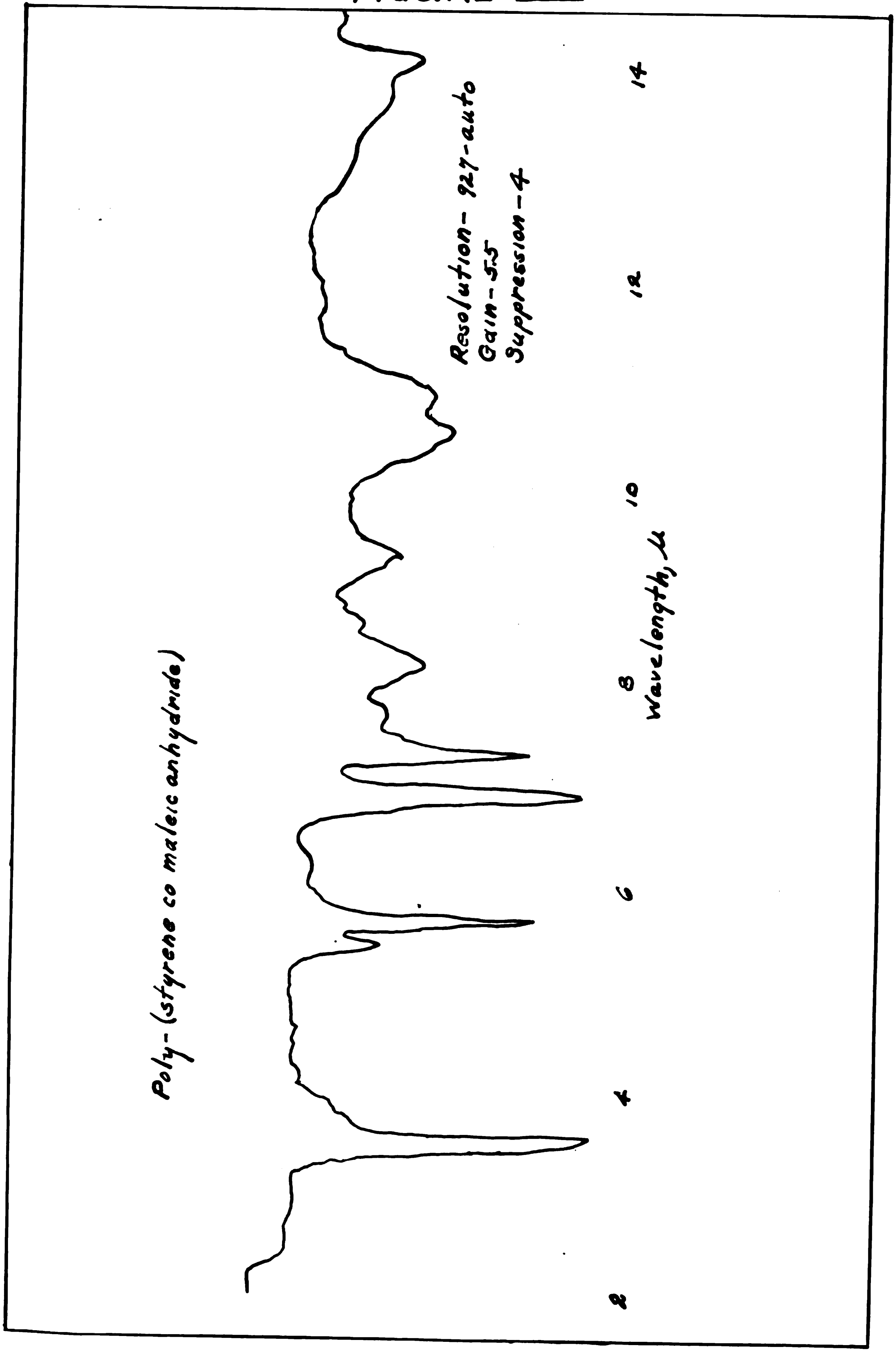
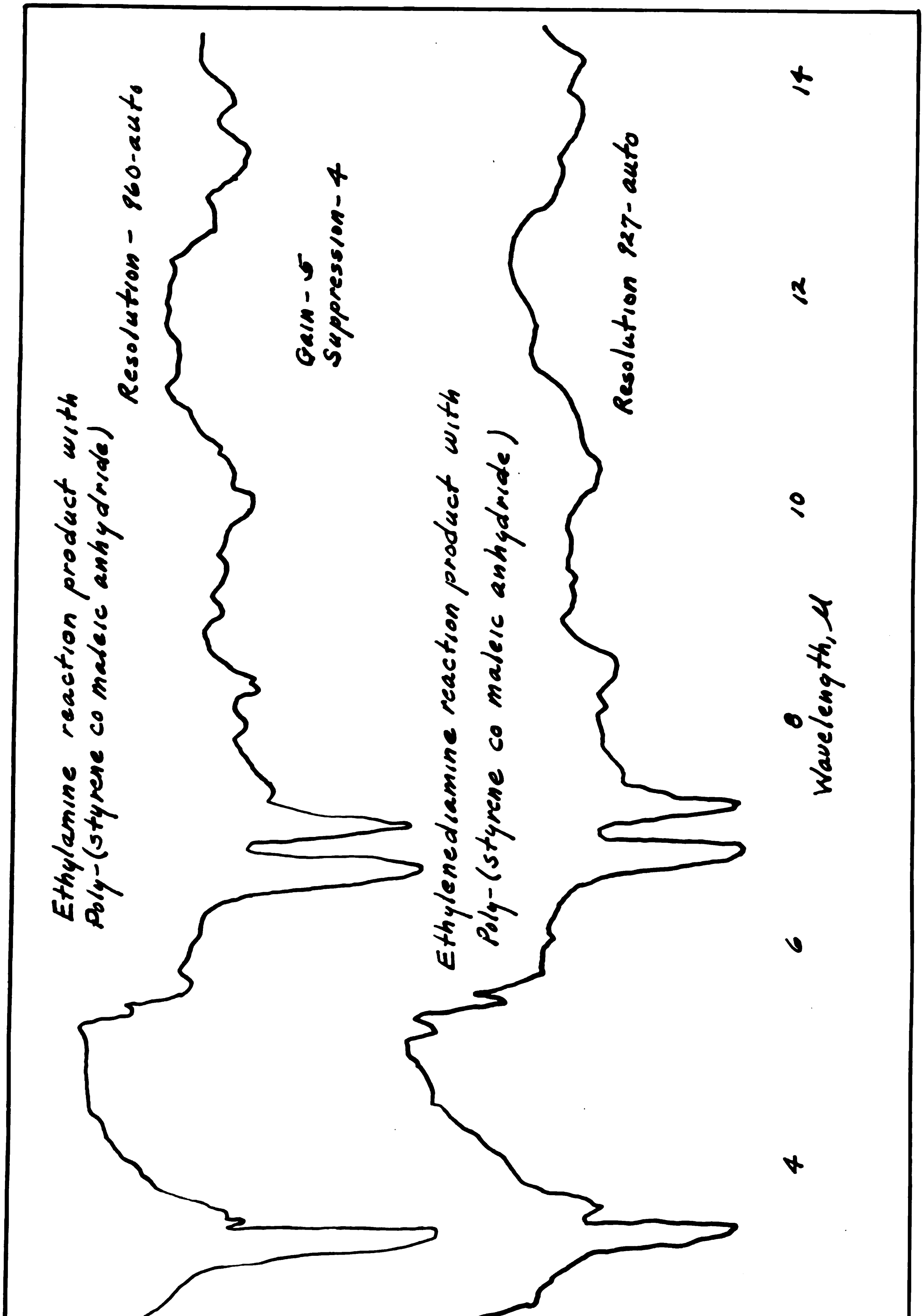
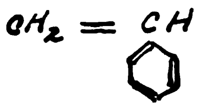
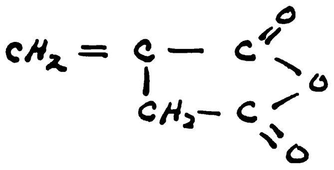

Poly-(styrene co maleic anhydride)
Resolution- 927-auto
Gain-5.5
Suppression-4
2
4
6
8
10
12
14
Wavelength, µ

FIGURE XX


Ethylamine reaction product with
Poly-(styrene co maleic anhydride)
Resolution - 960-auto
Gain - 5
Suppression - 4
Ethylenediamine reaction product with
Poly-(styrene co maleic anhydride)
Resolution 927-auto
2
4
6
8
10
12
14
Wavelength, μ

DISCUSSION

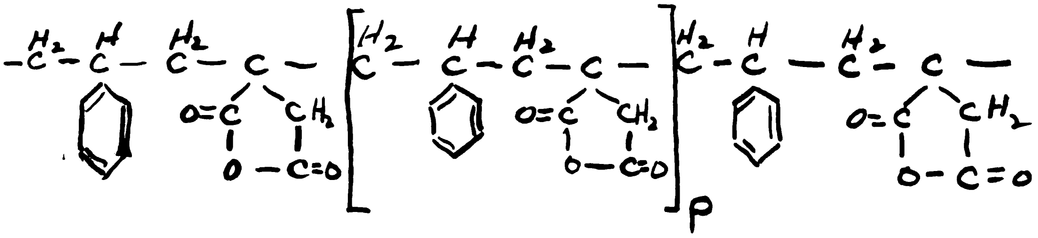
Industrially, styrene  is primarily produced by the catalytic dehydration of ethylbenzene, which is obtained by the catalytic addition of ethylene to benzene using aluminum chloride.



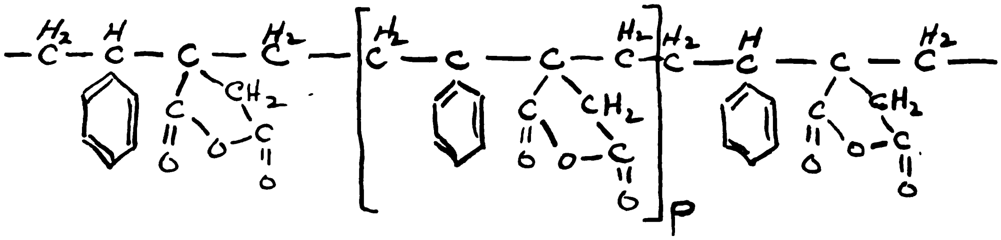
Itaconic anhydride, with the structural formula may be formed by treatment of the acid with a dehydrating agent, e. g., thionyl chloride[28], phosphorus pentoxide[28a], acetyl chloride[28b], or acetic anhydride[28c]. Itaconic acid is chiefly produced by the submerged culture fermentation of a glucose media by "Aspergillus terreus". In the laboratory itaconic anhydride is prepared by the rapid distillation of citric acid[29].

Monomer units may combine in the polymerization reaction in either a regular fashion or a random fashion. The two regular arrangements as applied to the styrene-itaconic anhydride copolymer are:

"head to tail"



"head to head" or "tail to tail"



where CH_2 in the chain is defined as the head. The random is a case of ideality in which the chance of an x unit to follow a y unit is the same as a y to follow a y unit. The styrene-butadiene system behaves approximately in this manner[30]. The alternating type in which the copolymer is very close to 1:1 in composition is characteristic of the system maleic anhydride-isopropenyl acetate[30a]. There was insufficient data to characterize the structure of poly-(itaconic anhydride co styrene). Further work is indicated in this direction. The methods usually used in elucidating structural problems are the synthesis of dimers, trimers or tetramers, and the degradation of polymers.

It was found in this work that the composition of the copolymer of styrene and itaconic anhydride was not 1:1 when using that ratio of reactants. By elemental analysis of Preparation I (reactant ratio 1:1) the copolymer composition was shown to be 57 mole percent itaconic anhydride units or a 0.77:1 ratio styrene units to itaconic anhydride units. The assumption that this copolymer would consist of a molecule with styrene and itaconic anhydride present mole for mole was an extension of the proposal by Wagner-Jauregg[31] on the structural unit of the reaction product of maleic anhydride and stilbene. In later work by Wall[32], Alfrey and Lavin[33], and Garrett[1] it was shown that the composition of poly-(maleic anhydride co styrene) approached the 1:1 basis, but did not attain it.

Preparation II (reactant ratio 1:2, styrene to itaconic anhydride) was also examined by elemental analysis and the results indicated 80 mole percent itaconic anhydride based on the percent carbon in the copolymer. The styrene-itaconic anhydride ratio in this case was 0.25:1. These results were in order with the results in Preparation I, in that in the latter the percent hydrogen was also lower indicating more itaconic anhydride units than 50 percent. In Preparation II the hydrogen percentage indicated a copolymer unit with less itaconic anhydride than expected. Consideration of these results indicated that some hydrolysis probably took place in the reaction since a lower percent carbon and a higher percent hydrogen is coincident with a definite amount of hydrolysis. This follows from the fact that the acid form has a lower and a higher percent carbon and hydrogen respectively than the anhydride form. In addition it was indicated by elemental analysis that the composition of this copolymer was similar to that of Preparation I in respect to the relative unit structure. The copolymer contained more itaconic anhydride units than the 1:2 molar ratio of the monomers predicted.

In preparations III and V (reactant ratios 2:1 and 3:1, styrene to itaconic anhydride) elemental analysis showed lower carbon and hydrogen predicting higher percentages of itaconic anhydride in the resulting copolymers than the initial monomer mixtures. These results could be expected from the observations made on the copolymerizations involving the 1:1 and 1:2 reactant ratios. There appeared to be a pattern in the four copolymerization reactions described. Each product contained more itaconic anhydride residues than the monomer ratio would have predicted.

This pattern was reversed in the reaction which yielded Preparation IV in which the reactants were in the proportion of a 1:3 styrene to itaconic anhydride. Elemental analysis of this copolymer showed it to contain a greater percentage of styrene than the initial monomer mixture.

By observation of the data in Table II on the preparation reactions , it was qualitatively apparent that itaconic anhydride was the more reactive monomer since the copolymer composition was generally richer in itaconic anhydride units than the monomer ratio predicted.

The kinetics of this copolymerization reaction is probably very complicated since both monomers will polymerize by themselves as well as react with each other. Also growing polymer molecules can react with the monomers as well as each other. Further complications arise from the fact that it is not known how many reactions take place before precipitation occurs. Thus an accurate evaluation of the rate constant is not theoretically possible at present. It was interesting however to attempt to treat the data, after several necessary assumptions, in the usual fashion for evaluating a rate constant and relative reaction order.

If we assume that the copolymer composition is mole for mole styrene and itaconic anhydride units, and the "reactant" to be a unit comprised of styrene and itaconic anhydride, we can assume a first order reaction with respect to the "reactant", from kinetic theory:

$$\frac{dx}{dt} = k(a-x) \qquad (2)$$

is the rate expression. This equation integrates to:

$$\ln a/(a-x) = kt \qquad (3)$$

where a is the initial concentration of "reactant" and x is the decrease in concentration of "reactant" (amount of precipitated polymer) in time t. A plot of ln(a-x) versus t should be linear with a slope of -k, where k is the rate constant. The rate constant k may be evaluated from this slope by:

$$k = -2.303\,(\text{slope}) \qquad (4)$$

The data in Table IV was plotted in Figure II with the logarithm of the molar concentration of "reactant" against the time in seconds. The plot gave a reasonably straight line indicating the reaction rate to be first order with respect to styrene or itaconic anhydride. The slope of the line was -3.2×10^{-5} and therefore from equation (4) the reaction rate constant k is 7.4×10^{-5} sec.$^{-1}$. This is not to be considered as an accurate rate constant, but a hypothetical approximation. Since the copolymer composition from a 1:1 ratio of reactants produced a copolymer which approached a 1:1 composition, kinetic treatment of the data obtained was possible after we first made the assumption that the copolymer consisted of a 1:1 unit. No completely adequate rate expression could be derived on the basis of elemental analysis of the precipitating polymer. To have made an adequate rate expression possible, it would have been necessary to have had a quantitative method for determining the amount of styrene and itaconic anhydride, each in the presence of the other.

The experiment designed for evaluating the monomer reactivity ratios was similar to the preparation reaction procedure with the exception that polymerization was not allowed to proceed to as great an extent. This was essential for the determination of the reactivity ratios. In the preparation reactions (Table II) the copolymer composition was an average over the entire polymerization range, and therefore did not represent the initial copolymer composition arising from the monomer ratio involved. The reactivity ratios were determined from a consideration of the composition of the copolymers formed from monomer compositions at low percent total polymerization and at the same degree of polymerization.

The theoretical considerations necessary for a discussion on monomer reactivity ratios can readily be obtained from several good sources[34,35]. The copolymer composition equation is written as:

$$\frac{m_1}{m_2} = \left(\frac{M_1}{M_2}\right)\frac{r_1 M_1 + M_2}{r_2 M_2 + M_1} \qquad (5)$$

which is valid for the composition of the initial copolymer formed at monomer concentrations M_1 and M_2. The differential form is valid at any degree of polymerization. The value m_1/m_2 is the ratio of the molar concentrations of the

two monomers in the resulting copolymer. The reactivity ratios r_1 and r_2 are the relative reactivities of the monomers for addition to the same and unlike growing radicals.

There are several accepted methods for the determination of the relative monomer reactivity ratios after a series of runs is made, with each run utilizing a different monomer feed ratio. The method used in this work was introduced by Mayo and Lewis[36]. It has its origin in the fact that equation (5) may be written as:

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

This equation then expresses r_2 as a linear function of r_1 and for each set of values for M_1, M_2, m_1, and m_2 a straight line is obtained when plotting r_2 versus r_1. Theoretically several different runs would yield straight lines intersecting at a single point which would be the r_1 and r_2 values for the system. Actually, however, the lines will generally define an area and the best point within this area is taken as r_2 and r_1. An area rather than a single point of intersection is the result of errors involved in the determination.

Substitution in equation (1) for the seven reactions and subsequent plotting of r_2 versus r_1 was shown in Figure

IV. The r_1 - r_2 values obtained from such a series of experiments suffered in exactness since the reactions were difficult to stop at the same degree of polymerization. Also the evaluation was dependent on the importance of the intersections involved. The more nearly perpendicular the intersecting lines, the more importance that could be assigned to that intersection. Further, the actual location of the r_1—r_2 point within the area of intersections was a matter of judgement left to the observer.

Four of the lines in Figure IV intersected in a fairly small area. In this area a point was placed representing the r_1 - r_2 values, this was point I where r_1 was 0.04 and r_2 was 3.80. Six lines were used similarly to describe another set of r_1 - r_2 values at point II where r_1 was 0.04 and r_2 was 2.50. Line E was disregarded since it fell so far from the group of intersections. The choice of point II used 85 percent of the experimental data. Assignment of r_1 - r_2 at point I neglected 42 percent of the data. The relative difference in the r_2 values of these two points was not great. The area of intersection, a measure of the errors involved, was large in the case of point II and small for point I. These were the errors in elementary analysis and the analysis of impure polymers. The r_1 - r_2 values at point II appeared more valid than those at point I. The errors from elementary analysis should be equivalent in all experiments. Those errors introduced by analysis of impure polymers would be of greater importance. No solvent was found to be selective for polyitaconic anhydride and not the copolymer. Therefore contamination of the copolymer with polyitaconic anhydride was possible. The composition curve (Figure III) was the best representative curve that could be drawn for the data. It was noted that in the area where the experimental points had the greatest deviation the values of r_1 changed slightly with changes in r_2, but r_2 changed greatly with values of r_1. This probably accounted for the large variation in r_2 values. The r_1 - r_2 plot (Figure IV) showed the extreme spread of r_2 values possible by interpretation of the experimental data. Consequently a choice of r_2 which was an average of more representative values was of greater validity.

On the basis of monomer reactivity, if r_1 was less than unity and r_2 was greater than unity, then itaconic anhydride would be more reactive than styrene with both types of growing free radicals. The results obtained in the preparation reactions (Table II) were consistent with this evaluation. Only in the reaction where the concentration of itaconic anhydride was extremely high with respect to the other monomer was there a less percentage of itaconic anhydride in the polymer than expected. The latter reaction was not consistent with the other preparations.

In view of the many variables encountered in even the simplest polymerization reaction, all experiments to be considered valid should be at least duplicated.

Fordyce and Ham[4] evaluated the monomer reactivity ratios for styrene and itaconic acid as 0.301 and 0.201 respectively. The system was a solution in dioxane using benzoyl peroxide as the catalyst. The system was closed after sweeping out with nitrogen.

Analysis of the product from the hydrolysis of poly-$\overline{57}$: $\overline{43}$. (itaconic anhydride co styrene) (page 21) showed it to be the complete free acid form. The ammonium salt, however, contained slightly over the amount of nitrogen expected in the monoammonium salt. This indicated that one carboxyl in the itaconic acid portion of the unit was different than the other.

The addition reactions of poly- $\overline{57}$: $\overline{43}$ (itaconic anhydride co styrene) with ethyl, n-butyl and 2-methyl-1-butyl alcohols yielded the half esters as determined by elemental analysis. This was in accord with the work of Siegal and Moran[37], who observed that anhydrides of dibasic acids when dissolved in alcohols quantitatively yielded the half esters. Since these results, however, indicated a slightly greater percentage of carbon than would be present in the half ester, some diester may have formed. The theoretical percent carbon in the half esterified copolymer was calculated on the basis of the carbon content of the original copolymer. The addition reaction with ethylene glycol did not yield the half ester since the product showed less carbon than the amount necessary. Since all of the above esters were soluble in acetone with the exception of the glycyl ester, this ester was probably a partial net polymer.

Potentiometric titration curves of the several copolymers of styrene and itaconic anhydride were determined. The curves were reproduced in Figures V to IX. The first vertical line on each curve represented the neutralization point of the excess standard alkali added. The exact point of the neutralization was difficult to assign since acidity in the buffered region is relatively independent of concentration when titrating a weak acid. A point of inflection apparently existed around pH 7.50 in all the curves, this point was indicated by a horizontal line. Theoretically this is the stoichiometric point of the neutralization of a carboxyl. This carboxyl appeared to be quite weak. The second inflection point was described by a vertical and a horizontal line. The titration of this carboxyl was quite sharp. The titrations showed that both carboxyls could be titrated.

Observing Table IX, a comparison of observed and theoretical titration data, it appeared that a more thorough potentiometric titration study of poly- (itaconic anhydride co styrene) should be made. Complete correlation of the observed milliequivalents of copolymer with the theoretical was not obtained, however the two values were of the same order in all cases. No pattern of differences could be noticed in the series of titrations. This was due to the fact that each involved an entirely different compound. It appeared probable that the method of calculating the theoretical values was subject to as much or more error than the experimental determination. The method used here was based on the elemental analysis and the calculation of a theoretical unit weight. This unit weight (equivalent weight) was variable depending on the composition of the polymer.

Nitrogen analysis of the reaction products from ethylenediamine and ethylamine with the copolymer of styrene and maleic anhydride definitely indicated that the reactions were incomplete. The reaction with ethylenediamine was probably stopped by net polymer formation so that the full formation of amide linkages on two different chains did not occur. It must be noted that this reaction was quite fast even for the amount of amide linkages formed. Percentage wise there was more reaction in the case with ethylamine. The product could represent half amide formation or by further elimination of water the imide could have been formed. The nitrogen analysis showed the reaction product to have less nitrogen than that necessary for either the half amide or imide. The infrared spectra (described on page 83) indicated that amide linkages were present. This was true of the reaction product with ethylenediamine and ethylamine.

Most of the infrared spectra obtained were made as mulls and the Nujol bands at 3.43, 3.49, 7.26 and 13.89µ were readily identified. The bands for carbonyl groups as a class are the most stable in position, 5.45µ - 6.50µ. In the region 5 - 7µ these are the strongest in the spectrum[38]. This was found to be true in the compounds investigated, the two absorption bands for the anhydride linkage, 5.38 and 5.62µ, were reasonably constant. In addition the 0.2µ separation between these two bands[38] was approximately constant in each case. The shift to higher frequencies for the carbonyl containing anhydrides followed the correlation that this shift was due to ring strain in the five membered ring. The band at 8.32µ in the spectra of itaconic anhydride and polyitaconic anhydride and that at 8.18µ in the copolymer's spectra were attributed to the C - O - C stretching vibration. The band was shifted in the copolymer which was probably due to hinderance to stretching by the phenyl groups in the proximity of the five membered anhydride ring[39]. There was yet another band which has been attributed to the anhydride linkage, the band 10.34µ arising from the C - O stretching vibration. There was some doubt as to the validity of this assignment. This band could be due to the C - C stretching vibration in the copolymer since it could be enhanced in the polymer due to the increased number of this type bond.

In the copolymer two definite absorption bands were attributed to the structure contribution of the styrene portion of the recurring unit. These occurred in the region

9.2 - 13.34μ and also about 14μ. Specifically the former was found at 9.32μ resulting from the C - C stretching vibration in the monosubstituted benzene. The absorption was fairly weak in the copolymer which was probably due to the relatively small amount of phenyl contribution to the total structure of the polymer. Through the correlation from open chain vibrations[39] in long chain molecules with methylene groups along the chain a strong band was observed in the region of 14μ. In this case it was found at 14.2μ. This band arises from a rocking mode of the CH_2 group.

The positions of the bands observed in the copolymers from Preparations II-V were essentially the same as in Preparation I. The band at 14.2μ shifted to higher and lower wavelengths with no correlation in the relative amounts of the contributing structures. This shift was not great, amounting to only 0.05μ.

In comparing the absorption bands of the copolymers of styrene-itaconic anhydride and styrene-maleic anhydride, it was noted there were few differences in their spectra. No absolutely new bands could be identified. However, shifts were noted from 10.34μ to 10.48μ and 9.32μ to 9.28μ.

The absorptions characteristic to esters arise from $C = O$ and $C - O -$ linkages. These appear approximately in the regions 5.73 to 5.80μ and 7.68 to 10.0μ. The spectra of the esterification products (page 64) had a common band at a about 5.8 - 5.9μ. This absorption had shifted from the normal region of ester $C = O$ and it was probably due to the unbalanced nature of the groups adjacent to the carbonyl carbon. The second absorption was found at 8.65μ in both the ethyl and n-butyl esters. The spectra for the other two esters were not carried out past 7.7μ since almost total absorption was observed in the longer wavelength region.

Absorption bands found in the styrene-maleic anhydride copolymer-amine reaction products were 3.94μ and 5.88μ. The former corresponded to the secondary amide N-H stretching mode. The second was probably due to a similar amide C=O absorption. The latter was found at a slightly lower wavelength than expected.

An excellent region for the identification of carbolylic acids lies in the range 3.71 - 4.0μ. The bands in this region are often weak and in the acids of high molecular weight the detection is difficult[39]. The separation of these bands from the absorptions of the C - H stretching vibrations was great enough to prevent any confusion. The absorption of the free acid of Preparation I was found at 3.67μ. Also in this acid spectrum the band at 7.68μ could be correlated with the C - O stretching vibrations or OH deformation vibrations. It can be seen in Figure XVI that there was no difference in the spectra of the free acid and the ammonium salt.

Generally, the spectra gave no quantitative evaluation of the linkages involved in the poly-(itaconic anhydride co styrene) polymers. Enough of the characteristic linkages were present to give sufficient absorption so that a qualitative identification was possible. It follows that the spectra of these compounds might be run quantitatively in solution so that a correlation of the spectra and the amount of itaconic anhydride or its derivatives present could be made.

CONCLUSIONS

1. Styrene and itaconic anhydride can be copolymerized in benzene solution using benzoyl peroxide as a catalyst.
2. The copolymerization rate of styrene and itaconic anhydride in the system described (1:1 molar ratio of reactants and 0.01% catalyst), as a first approximation, is first order with respect to styrene or itaconic anhydride and proceeds with an apparent rate constant in the order of 7.4×10^{-5} sec^{-1}.
3. In the system as described for the preparation of the styrene-itaconic anhydride copolymer the r_1 (styrene) value is 0.04 and the r_2 (itaconic anhydride) value is 2.50.
4. Esters can be prepared from the poly-$\overline{57}$:$\overline{43}$ (itaconic anhydride co styrene) by dissolving it in absolute alcohols under anhydrous conditions.
5. Both carboxyl groups in the styrene-itaconic anhydride copolymer can be titrated.
6. Amines will partially react with the styrene-maleic anhydride copolymer to form the amides.
7. The copolymer of styrene and itaconic anhydride can be characterized by infrared spectra analysis.

LITERATURE CITED

1. Garrett, E. R., Thesis, M. S., Michigan State College (1948)

2. Byrne, R. E., Thesis, M. S., Michigan State College (1949)

2a. Lecher, H., U. S. 1,780,873

2b. Norrish, R. G. W., and Brookman, E. F., Proc. Roy. Soc. London, A163, 205 (1937)

2c. Boundy, R. H., and Boyer, R. F., "Styrene, Its Polymers, Copolymers and Derivatives", A. C. S. Monograph, Reinhold Publishing Corp.

3. Mowry, D. T., and Hedrick, R. M., U. S. 2,625,471

3a. Minter, H. F., U. S. 2,462,209

3b. Teeter, H. M., Kini, U. S., Myren, R. A., Cowan, J. C. J. Am. Oil Chem. Soc. 26 660 (1949)

3c. Teeter, H. M., and Cowan, J. C., U. S. 2,641,593

4. Fordyce, R. G., and Ham, G. E., J. Am. Chem. Soc., 69, 581 (1947)

5. Dickey, J. B., and Coover, H. W., U. S. 2,533,207

6. D'Alelio, G. F., U. S. 2,531,408

7. Lippincott, S. B., and Mikeska, L. A., U. S. 2,542,542

8. Exner, J. and Bohdanecky, M., Chem. Listy. 48, 483 (1954), C. A., 48, 1615 (1954)

9. Wildish, M. F., Hefferline, J. E., and Rippey, H. F., U. S. 2,667,462

10. Stobbe, H., and Lippold, A., J. Prackt. Chem. 90, 336 (1914), C. A., 9, 209^4 (1915)

11. Hope, E., British 264,550

12. D'Alelio, G. F., U. S. 2,279,881
U. S. 2,279,882
U. S. 2,279,883
U. S. 2,279,884
U. S. 2,279,885
U. S. 2,298,039
U. S. 2,310,731
U. S. 2,366,495
U. S. 2,378,194
U. S. 2,431,373
U. S. 2,437,508
U. S. 2,441,799
U. S. 2,445,764
U. S. 2,583,325
U. S. 2,582,327
U. S. 2,583,326

13. Feagin, R. C., and Prange, C. H., U. S. 2,318,845

14. Wolfe, W. D., U. S. 2,393,007

15. Strain, F., U. S. 2,392,621

16. U. S. Rubber Co., British 2,428,788

17. British Thompson-Huston Co., British 587,445

18. Montclair Research Corp., British 642,414

19. Harris, R. R., U. S. 2,529,214

20. Weaver, W. I., U. S. 2,549,732

21. Rheineck, A. E., U. S. 2,536,658

22. Tawney, P. O., U. S. 2,556,989
U. S. 2,569,959
U. S. 2,569,960
U. S. 2,643,991

23. Barnes, F. W., and Arundale, E., U. S. 2,619,477

24. Giammaria, J. J., U. S. 2,616,849

25. Agnew, R. J., U. S. 2,595,625
U. S. 2,584,315

26. Feagin, R. C., and Bandel, D., U. S. 2,603,625

27. Tutwiler, T. S., U. S. 2,637,698

28. Meyer, H., Monatsh., 22 422(1901)

28a. Bakunin, Gazz. chim. ital., 30 361 (1900)

28b. Anschütz and Petri, Ber., 13 1539 (1880)

28c. Fittig and Boch, Ann., 331 174 (1904)

29. Shriner, R. L., Ford, S. G., and Roll, L. J., "Organic Synthesis", Collective Vol. II, John Wiley Co., 1943, p. 368

30. Lewis, F. M., Walling, C., Cummings, W., Briggs, E. R., and Wenisch, W. J., J. Am. Chem. Soc. 70, 1527, (1948)

30a. deWilde, M. C. and Smets, G., J. Polymer Sci., 5, 253 (1950)

31. Wagner-Jauregg, T., Ber., 63B, 3213 (1930)

32. Wall, F. T., J. Am. Chem. Soc., 66, 2050 (1944)

33. Alfrey, T., and Lavin, E., J. Am. Chem. Soc. 67, 2044 (1955)

34. Alfrey, T., Bohrer, J., and Mark, H., "High Polymers", Vol. III, Interscience, 1952, pp. 8 - 31.

35. Flory, P. J., "Principles of Polymer Chemistry", Cornell University Press, 1953, pp. 178 - 203.

36. Mayo, F. R., and Lewis, F. M., J. Am. Chem. Soc., 66, 1594 (1944)

37. Siegal, E., and Moran, M., J. Am. Chem. Soc., 69, 1457 (1947)

38. Randall, H. M., Fuson, N., Fowler, R. G., and Danyl, J. R., "Infrared Determination of Organic Structures", D. vanNostrand, Inc. 1949

39. Bellamy, L. W., "Infrared Spectra of Complex Molecules", Methuen, London, 1953

STUDIES ON THE COPOLYMER
OF STYRENE AND ITACONIC ANHYDRIDE

by

GERALD MELBOURNE CURTICE

AN ABSTRACT

Submitted to the School of Graduate Studies of Michigan
State University of Agriculture and Applied Science
in partial fulfillment of the requirements for
the degree of

MASTER OF SCIENCE

Department of Chemistry

1955

Approved______________________________________

ABSTRACT

Gerald Melbourne Curtice

This thesis reports that styrene and itaconic anhydride were caused to copolymerize in a benzene solution using benzoyl peroxide as a catalyst. Several copolymers were prepared using different monomer ratios.

The rate of the copolymerization of styrene and itaconic anhydride in benzene (0.01% catalyst) was studied. It was found to be first order with an apparent rate constant in the order of 7.4×10^{-5} $\sec^{-1}$.

An evaluation of the monomer reactivity ratios was made. The r_1 (styrene) value was 0.04 and the r_2 (itaconic anhydride) value was 2.50.

In addition various esters of poly-$\overline{57}:\overline{43}$ (itaconic anhydride co styrene) were prepared, and the poly-(itaconic anhydride co styrene) polymers were potentiometrically titrated.

Poly-(maleic anhydride co styrene) was reacted with amines to yield the partial amides. Infrared spectra were obtained for all the compounds prepared.

Curtice, Gerald Melbourne
Studies on the copolymer of styrene and itaconic anhydride

Curtice, Gerald Melbourne
Studies on the copolymer of styrene and itaconic anhydride

JUN 3 '58 DROUGAS