THE COPOLYMERIZATION OF STYRENE AND ITACONIC ANHYDRIDE

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By

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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

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THE COPOLYMERIZATION OF STYRENE AND METHYLIC ACRYLATES

By

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AN ABSTRACT

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Year 1958

Approved _____

ABSTRACT

Styrene and itaconic anhydride were copolymerized in benzene and in tetrahydrofuran solvents with benzoyl peroxide or bis-azo-isobutyronitrile catalyst.

The rates of copolymerization of 1:1 mole ratio of styrene and itaconic anhydride were determined in the four systems, based on individual monomer concentrations and the amount of polymer formed. The rates were found to be first order with respect to either monomer concentration. The apparent first order rate constants were calculated for each system.

The composition of the copolymers were also determined, by the rate of disappearance of monomers, by elemental analysis of the copolymer, and by titration of the copolymer by both potentiometric and high frequency methods.

A number average molecular weight of 23,000 was found by the osmotic pressure method for a copolymer prepared in benzene solution. Weight average molecular weights were obtained by the light scattering method, for a copolymer prepared in benzene solution the weight average molecular weight was 156,000, and for two copolymers prepared in tetrahydrofuran the weight average molecular weights were 50,000.

TABLE OF CONTENTS

TABLE OF CONTENTS - Continued

INTRODUCTION

I. PURPOSE AND SCOPE

The study of styrene and itaconic anhydride copolymerization has been a continuing project in this laboratory (1,2). Earlier investigations have shown the copolymer to be of an alternating monomer unit structure similar to that found with styrene-maleic anhydride copolymer (3,4,5). The purpose of this work was to determine the nature of the copolymerization reaction by means of analysis of monomer concentrations throughout the reaction in conjunction with analysis of the copolymers formed. In addition, measurements of molecular weight of the copolymers were made to determine the influence of the solvent and catalyst on the reaction.

II. REAGENTS

1. Itaconic anhydride

The itaconic anhydride monomer was prepared (6) from itaconic acid (Chas. Pfizer & Company, 99% assay). After recrystallization from chloroform the product melted at 68-69° C.

2. Styrene

The styrene monomer was distilled to remove the inhibitor, the sample was free of polymer, as indicated by the absence of a precipitate on the addition of methanol.

3. Benzene

Thiophene free benzene was dried over sodium metal.

4. Tetrahydrofuran

The tetrahydrofuran was purified (7) and dried by distillation from lithium aluminum hydride; boiling range 65-66°C.

5. Methanol

The methanol was dried (8) by reaction with magnesium turnings (10 grams for 300 ml of methanol), under reflux conditions for four hours. The dry methanol was distilled, boiling point 64.0° C.

6. Acetone

The acetone solvent was dried by distillation from potassium carbonate. In addition to distillation the acetone to be used for light scattering determinations was filtered repeatedly through a fine sintered glass filter.

7. Collodion

Baker, USP grade.

I. QUANTITATIVE DETERMINATION OF MONOMERS, STYRENE AND ITACONIC ANHYDRIDE

A. Determination of Itaconic Anhydride, Methods Based on Unsaturation

Since itaconic anhydride is an unsaturated cyclic anhydride, methods for its quantitative determination could be based upon reactions of the ethylenic unsaturation or of the anhydride group. Both methods were examined experimentally.

There are many methods available for determining ethylenic unsaturation, including halogen addition (9-13), catalytic hydrogenation (14), addition of dinitrogen tetroxide (15), reaction with perbenzoic acid (16,17), reaction with ozone (18), and reaction with mercuric acetate (19-21). The methods of halogen addition and reaction with mercuric acetate were chosen for further investigation, based on speed of analysis and equipment available.

1. Mercuric acetate method.

Martin (21) has described a method for the rapid estimation of olefins by means of their reaction with mercuric acetate in alcohol solution.

$$R\text{-}CH=CH\text{-}R' + (CH_3COO)_2Hg + CH_3OH \longrightarrow$$

$$R\text{-}\underset{\displaystyle OCH_3}{\underset{|}{CH}}\text{-}\underset{\displaystyle HgOOCCH_3}{\underset{|}{CH}}\text{-}R' + CH_3COOH$$

The reaction was carried out in excess mercuric acetate. The amount of mercuric acetate in excess of that necessary to react with the

ethylenic unsaturation was converted to mercuric chloride by adding sodium chloride before titration of the liberated acetic acid. Methanol was reported to be the best solvent for the reaction and was employed for these determinations. In the case of itaconic anhydride the methanol solvent forms the monomethyl ester instantaneously at room temperature (22), making it necessary to first neutralize the monomethyl ester of itaconic acid before proceeding with the mercuric acetate reaction.

Procedure: An accurately weighed (approximately 0.3 gm.) sample was dissolved in 15 ml. of benzene, 25 ml. of carbon tetrachloride and 30 ml. of methanol. The acid was then neutralized with standard sodium hydroxide to a phenolphthalein end point. After 4 grams of mercuric acetate had been added the solution was allowed to stand for one-half hour; 75 ml. of saturated sodium chloride solution were added and the sample titrated with standard sodium hydroxide solution to a phenolphthalein end point. The percent of itaconic acid and anhydride were calculated as follows:

a. By direct titration of the acid.

$$\text{Percent itaconic acid} = \frac{(\text{ml. NaOH})(\text{N. of NaOH})}{(\text{sample weight})} \; 6.5$$

$$\text{Percent itaconic anhydride} = \frac{(\text{ml. NaOH})(\text{N. of NaOH})}{(\text{sample weight})} \; 11.2$$

b. By titration of acetic acid liberated from the mercuric acetate reaction.

$$\text{Percent itaconic anhydride} = \frac{(\text{ml. NaOH})(\text{N. of NaOH})}{(\text{sample weight})} \quad 11.2$$

TABLE I

ITACONIC ANHYDRIDE DETERMINATION BY MERCURIC ACETATE METHOD

Sample	Percent Itaconic Anhydride	
	Titration of Unsaturation	Titration of Acid Function
1. Itaconic acid	92.43	97.86
2. Itaconic anhydride, sample 1	27.68	100.7
3. Itaconic anhydride, sample 2	20.39	101.3

2. Catalyzed bromination.

The bromination of ethylenic unsaturation can be catalyzed by mercuric sulfate (13), providing a general method by which the unsaturation in a variety of compounds can be determined.

Procedure: Into an evacuated flask were added an accurately weighed (approximately 0.4 gm.) sample of itaconic anhydride, 10 ml. acetic anhydride, 5 ml. 6 N. hydrochloric acid and 10 ml. of water. After standing for some time 50.0 ml. of 0.1 N. bromide-bromate reagent were added along with 20 ml. of 2 N. mercuric sulfate solution. After standing for one-half hour 15 ml. of 15% potassium iodide solution were added and the mixture was titrated with sodium thiosulfate. Starch solution was

used as an indicator. The percent of itaconic anhydride was calculated as follows:

$$\text{Percent itaconic anhydride} = \frac{(\text{blank titer} - \text{sample titer})(\text{N. of } Na_2S_2O_3)}{(\text{sample weight})} 5.6$$

Results: One analysis by this procedure gave a value for itaconic anhydride of 66.53%.

3. Direct bromination.

Still a third method for quantitative determination of ethylenic unsaturation, which has been used for styrene (10), is the direct bromination by a solution of bromine in acetic acid.

Procedures:

a. An accurately weighed (approximately 0.4 gm.) sample of itaconic anhydride was dissolved in benzene and then directly titrated with bromine in acetic acid solution. The orange color of excess bromine indicates the end point. The percent of itaconic anhydride was calculated as follows:

$$\text{Percent itaconic anhydride} = \frac{(\text{ml. Br})(\text{N. of Br})}{(\text{sample weight})} 5.6$$

b. An excess amount of bromine reagent was added to an accurately weighed (approximately 0.4 gm.) sample of itaconic anhydride, which had been dissolved in benzene. This mixture was allowed to stand in a cool dark place and then potassium iodide solution was added. The liberated iodine was titrated with standard sodium

thiosulfate, using starch solution as an indicator. The percent of itaconic anhydride was calculated as follows:

$$\text{Percent itaconic anhydride} = \frac{(\text{blank titer} - \text{sample titer})(\text{N. of } Na_2S_2O_3)}{(\text{sample weight})} 5.6$$

Result: The direct titration, procedure (a), gave a value for pure itaconic anhydride of 0.8%, while the back titrations of excess bromine, procedure (b), gave a value for pure itaconic anhydride of 5.3%.

B. Determination of Itaconic Anhydride, Methods Based on Acid Function

The other reactive center in itaconic anhydride upon which quantitative reactions can be based is the anhydride group. In addition to the usual methods for determining anhydrides, by direct titration with base or back titration of excess base, it is possible to titrate the monoester of itaconic anhydride with standard base. Siegel and Moran (22) have reported that the monoester is formed instantaneously and quantitatively at room temperature from a primary alcohol and a cyclic anhydride.

1. Back titrations of excess base.

Procedure: An accurately weighed (approximately 0.2 gm.) sample of itaconic anhydride was dissolved in acetone. To this solution were added 30.0 ml. of 0.1430 N sodium hydroxide and the solution was heated on a steam bath to boil off the acetone. The solution was then cooled and the excess sodium hydroxide was titrated with

standard hydrochloric acid solution, to a phenolphthalein end point. The percent of itaconic anhydride was calculated as follows:

$$\text{Percent itaconic anhydride} = \frac{(\text{ml. NaOH})(\text{N. of NaOH}) - (\text{ml. HCl})(\text{N. of HCl})}{(\text{sample weight})} 5.6$$

Result: This procedure gave a value for pure itaconic anhydride of 93.30%.

2. Direct titration of acid function.

Procedure: An accurately weighed sample of itaconic anhydride (approximately 0.2 gm.) was dissolved in benzene, 25 ml. of distilled water were added, and the sample was heated on a steam bath, for 20 minutes. The dibasic itaconic acid formed was then neutralized, to a phenolphthalein end point with standard sodium hydroxide. The percent of itaconic anhydride was calculated as follows:

$$\text{Percent itaconic anhydride} = \frac{(\text{ml. NaOH})(\text{N. of NaOH})}{(\text{sample weight})} 5.6$$

TABLE II

ITACONIC ANHYDRIDE DETERMINATIONS FROM DIRECT TITRATION OF THE ACID FUNCTION

Sample	Percent Itaconic Anhydride
Itaconic acid	99.70
Itaconic anhydride, sample 1	93.40
Itaconic anhydride, sample 2	98.74
Itaconic anhydride, sample 3	98.52

3. Titration of monomethyl ester.

As has been mentioned, cyclic anhydrides can be determined by titrating the monomethyl ester of the dibasic acid with base.

Procedure: An accurately weighed sample of itaconic anhydride, (approximately 0.4 gm.), was dissolved in absolute methanol and then neutralized with standard alcoholic potassium hydroxide solution to a phenolphthalein end point. The percent of itaconic anhydride was then calculated as follows:

$$\text{Percent itaconic anhydride} = \frac{(\text{ml. KOH})(\text{N. of KOH})}{(\text{sample weight})} \quad 11.2$$

TABLE III

ITACONIC ANHYDRIDE DETERMINATION BY TITRATION OF MONOMETHYL ESTER

Sample	Percent Itaconic Anhydride
Itaconic acid	98.96
Itaconic anhydride, sample 1	99.98
Itaconic anhydride, sample 2	100.63
Itaconic anhydride, sample 3	100.32

TABLE IV

SUMMARY OF VALUES OBTAINED FOR ITACONIC ANHYDRIDE BY VARIOUS METHODS OF DETERMINATION

	Percent Itaconic Anhydride
1. Unsaturation determination	
a. mercuric acetate	27.7
b. catalyzed bromination	66.5
c. direct bromine titration	0.8
d. back titration of excess bromine	5.3
2. Titration of acid function	
a. back titration of excess base	93.30
b. direct titration	98.55
c. direct titration of the monomethyl ester	100.31

C. Determination of Styrene

Quantitative methods for the determination of styrene are best based on the ethylenic unsaturation. Methods for determining ethylenic unsaturation have been reviewed by Stone (9), and specific methods for styrene by Luce (23). A direct bromination method has been used by Uhrig and Levin (10), while Bartlett and Nozaki (13) have described a catalyzed bromination of a more general application. The mercuric acetate reaction (19-21) has also been widely used for analysis of styrene.

1. Mercuric acetate method.

The procedure used was essentially the same as already has been described in Section I, A-1, except that it was unnecessary to neutralize the acid before carrying out the titration.

Procedure: An accurately weighed sample of styrene, (approximately 0.3 gm) was dissolved in 15 ml. benzene, 25 ml. of carbon tetrachloride and 30 ml. of methanol. After adding 4 grams of mercuric acetate the solution was allowed to stand for one-half hour; 75 ml. of saturated sodium chloride solution were added and the sample titrated with standard sodium hydroxide solution to a phenolphthalein end point. The percent styrene was calculated as follows:

$$\text{Percent styrene} = \frac{(\text{ml. NaOH})(\text{N. of NaOH})}{(\text{sample weight})} 10.4$$

Result: The mercuric acetate method for the determination of styrene gave a value of 95.02%.

2. Direct bromination.

The direct bromination with bromine in acetic acid reagent was also tried for the analysis of unsaturation in styrene.

Procedures: The procedures used were exactly as have been described in Section I, A-1, for itaconic anhydride analysis. Both procedures were used (a) direct titration to the color of excess bromine and (b) back titration of excess bromine, iodometrically. The percent styrene was calculated as follows:

(a) Direct titration:

$$\text{Percent styrene} = \frac{(\text{ml. Br})\ (\text{N. of Br})}{(\text{sample weight})}\ 5.2$$

(b) Back titration of excess bromine:

$$\text{Percent styrene} = \frac{(\text{blank titer} - \text{sample titer})\ (\text{N. of } Na_2S_2O_3)}{(\text{sample weight})}\ 5.2$$

Results: Experiments on pure styrene using procedure (a), gave values of 98.1%, while procedure (b), gave values of 99.5%.

TABLE V

SUMMARY OF VALUES OBTAINED FOR STYRENE BY VARIOUS METHODS OF DETERMINATION

Sample	Percent Styrene
1. Mercuric acetate	95.0
2. Direct bromine titration	98.1
3. Back titration of excess bromine	99.5

D. Determination of Styrene and Itaconic Anhydride in Mixtures

For mixtures of styrene and itaconic anhydride monomers it is apparent that the following general methods of obtaining separate analysis of each component are applicable:

1. Specific determination of anhydride group and total amount of ethylenic unsaturation.

2. Determination of anhydride group and selective unsaturation determination for styrene.
3. Selective unsaturation determination for each monomer, itaconic anhydride and styrene.
4. Selective unsaturation determination for styrene or itaconic anhydride, and total amount of ethylenic unsaturation.

Examination of methods used for the quantitative determination of itaconic anhydride and styrene, in the preceding section, indicate that methods for total unsaturation were unreliable for itaconic anhydride. Furthermore, there was no method available for selective unsaturation determination of itaconic anhydride. These considerations eliminate proposals 1, 3 and 4. However, a specific method for determining styrene is available by direct titration with bromine, and itaconic anhydride can be determined without interference by titration of the acid function. These methods were tried in the following experiments for mixtures in both benzene and tetrahydrofuran solutions.

It was found that the orange color of excess bromine was not visible in tetrahydrofuran solutions, because of a yellow color which developed on addition of the bromine solution. For this reason no determination of styrene was made in tetrahydrofuran, but the concentration of styrene in reactions carried out in tetrahydrofuran was determined by difference from the total polymer weight.

TABLE VI

ANALYSIS OF MIXTURES OF STYRENE AND ITACONIC ANHYDRIDE

Mixture	Known amount Added	Amount Found
1. Benzene solution		
Styrene	0.0359 gm/ml.	0.0363 gm/ml.
Itaconic anhydride	0.0423 gm/ml.	0.0413 gm/ml.
2. Tetrahydrofuran and xylene solution		
Itaconic anhydride	0.00635 gm/ml.	0.00655 gm/ml.

II. COPOLYMERIZATION OF STYRENE AND ITACONIC ANHYDRIDE, RATE OF REACTION STUDIES

Copolymerizations of styrene and itaconic anhydride, present as monomers in a 1:1 mole ratio, were carried out in two solvents, benzene and tetrahydrofuran, using two catalysts, benzoyl peroxide and bis-azo-isobutyronitrile. The rate of each copolymerization was followed by analyzing samples, which were removed at definite time intervals, for the amount of polymer formed and, wherever possible, for the amount of each monomer remaining in solution. Several of the four copolymerizations were duplicated as a check on the reproducibility of results. Based on the assumption that the monomer which disappears from solution appears only as polymer, comparisons were made of the percent polymerization determined from the amount of polymer formed with the percent polymerization determined from the disappearance of monomers. The compositions of the copolymers were also determined from analysis of the copolymers, as described in the following Section III, and these compositions were compared with those determined by the disappearance of the monomers.

A. Procedure

The copolymerizations were carried out in all glass equipment, under a nitrogen atmosphere, and with a vacuum sampling device, a technique widely employed in this laboratory for sampling polymerization reactions and described by Garrett, Quile *et al.* (1,4,24). In this particular case the polymerizations were carried out in a 1,000 ml.

three-necked round-bottomed flask with ground glass joints fitted with stirrer, condenser with calcium chloride tube at the top, nitrogen inlet, thermometer, and vacuum sampling device. The flask was heated by an oil bath on an electric hot plate. The polymerizations were carried out at reflux temperature, 80° C for benzene and 65° C for tetrahydrofuran.

The weighed amount of itaconic anhydride and the measured amount of solvent were placed in the flask, nitrogen was passed over the solution, stirring was started, and the itaconic anhydride was dissolved by heating the solvent to reflux. Stirring, heating and the stream of nitrogen were continued throughout the reaction. As soon as the solution was clear and at reflux temperature the weighed amount of styrene and catalyst were added, in that order, and the time of catalyst addition was recorded as zero time. A sample was taken immediately using the sampling device and then at appropriate intervals. Further reaction in the samples was arrested by chilling. In the case where benzene was the solvent and bis-azo-isobutyronitrile the catalyst the samples were plunged directly into a dry ice and acetone bath.

The determinations of styrene and itaconic anhydride concentrations were run as indicated in Section I-D on aliquots of clear benzene solution after separating the polymer in a centrifuge. The copolymerizations made in tetrahydrofuran solvent could not be analyzed for styrene as noted in Section I-D so in these cases the styrene concentration was obtained by difference. Since the polymer precipitates from benzene,

it was separated by filtering on a Gooch crucible, washed, dried, and weighed. However, the polymer had to be precipitated from tetrahydrofuran solution by a nonsolvent. Xylene was found to be a satisfactory precipitant and was used for this purpose. A slight trace of water was also required to facilitate this precipitation. After adding a measured amount of xylene the sample was centrifuged and treated in a similar manner as described above for samples obtained from copolymerizations in benzene solvent.

The final copolymer samples were separated from tetrahydrofuran by the addition of anhydrous ether to the reaction mixture. This gave a much finer precipitate, but avoided the use of even traces of water in the procedure. Copolymer samples were exhaustively extracted with benzene in a Soxhlet extractor to remove last traces of monomer before analysis.

B. Copolymerizations and Results

The amounts of materials used in the four copolymerizations are summarized in Table VII and the results of these polymerizations are tabulated and plotted in Tables VIII through XII and Figures 1 through 12.

The calculations used to obtain values from experimental data for the tables are outlined below along with sample calculations.

The following symbols were used throughout this section:

M_1 = molar concentration of styrene at any time, t.

M_2 = molar concentration of itaconic anhydride at any time, t.

M_1^0 = initial molar concentration of styrene.

M_2^0 = initial molar concentration of itaconic anhydride.

N_2 = mole fraction of itaconic anhydride in the copolymer.

I. A. = itaconic anhydride

THF = tetrahydrofuran

BzO_2 = benzoyl peroxide

bis-azo = bis-azo-isobutyronitrile

1. Percent polymerization from the weight of copolymer formed from benzene solution:

$$\text{Percent polymerization} = \frac{(\text{wt. of polymer})}{(\text{wt. of sample})} \quad 13.2$$

Sample calculation:

$$\text{Percent polymerization} = \frac{(1.3142 \text{ gm})}{(25.5004 \text{ gm.})} \, 13.2 = 68.2\%$$

2. Percent polymerization from the weight of copolymer formed from tetrahydrofuran solution:

$$\text{Percent polymerization} = \frac{(\text{wt. of polymer})}{(\text{wt. of sample})} \quad 13.4$$

Sample calculation:

$$\text{Percent polymerization} = \frac{(0.0507)}{(4.5036)} \, 13.4 = 15.0\%$$

3. Molar concentration of styrene, M_1 for a 5 ml. aliquot in benzene solution:

$$M_1 = \frac{(\text{ml. Br}) \, (\text{N. of Br})}{10}$$

Sample calculation:

$$M_1 = \frac{(4.67) \, (0.685)}{10} = 0.318$$

4. Molar concentration of itaconic anhydride, M_2, for a 5 ml. aliquot in benzene solution:

$$M_2 = \frac{(\text{ml. NaOH})\ (\text{N. of NaOH})}{10}$$

Sample calculation:

$$M_2 = \frac{(23.10)\ (0.1319)}{10} = 0.304$$

5. Molar concentration of itaconic anhydride, M_2, in tetrahydrofuran solution:

A twenty ml. aliquot was taken of the clear layer after a measured amount of xylene was added to precipitate the copolymer.

$$M_2 = \frac{(\text{ml. NaOH})\ (\text{N. of NaOH})}{40} \frac{(\text{ml. sample})+(\text{ml. xylene})}{(\text{ml. sample})}$$

Sample calculation:

$$M_2 = \frac{(17.15)\ (0.1339)}{40} \frac{19.71 + 75.00}{19.71} = 0.275$$

6. Molar concentration of styrene, M_1, in tetrahydrofuran solution, from difference of polymer formation and disappearance of itaconic anhydride:

$$M_1 = \frac{(\text{wt. of polymer/wt. of sample})\ 0.925 - 112M_2}{104}$$

Sample calculation:

$$M_1 = \frac{\frac{(0.0507)}{(4.5035)}\ (9.25) - 112(0.275)}{104}$$

$$M_1 = 0.270$$

7. Percent polymerization, from the rate of disappearance of monomers:

Percent polymerization = [104 ($M_1^\circ - M_1$) + 112 ($M_2^\circ - M_2$)] 1.442

Sample calculation:

Percent polymerization = [104 (0.332 - 0.231) + 112 ---

(0.313 - 0.185)] 1.442

Percent polymerization = 36.0%

8. Mole fraction of itaconic anhydride in the copolymer, N_2:

$$N_2 = \frac{(M_2^\circ - M_2)}{(M_1^\circ - M_1) + (M_2^\circ - M_2)}$$

Sample calculation:

$$N_2 = \frac{(0.313 - 0.087)}{(0.332 - 0.130) + (0.313 - 0.087)} = 0.528$$

TABLE VII

SUMMARY OF COPOLYMERIZATIONS

Amount of Monomers			Solvent		Catalyst		Initial
Styrene gms.	I. A. gms.	Total Wt. Percent Monomers	Kind	Amt. ml.	Kind	Amt. gm.	Density of Reaction Mixture Calcd.
24.20	26.10	7.56	benzene	700.0	BzO_2	0.232	0.916
17.30	18.60	7.56	benzene	500.0	bis-aso	0.113	0.916
24.20	26.10	7.48	THF	700.0	BzO_2	0.232	0.925
24.20	26.10	7.48	THF	700	bis-aso	0.159	0.925

Symbols used in above table and throughout this section:

I.A. = itaconic anhydride

THF = tetrahydrofuran

BzO_2 = benzoyl peroxide

bis-aso = bis-aso-isobutyronitrile

TABLE VIII

RATE OF DISAPPEARANCE OF MONOMERS AND COMPOSITION OF COPOLYMER
(In 1:1 Styrene:itaconic anhydride copolymerization
in benzene solvent by benzoyl peroxide catalyst.)

	Time Minutes	M_1 Molar conc. of Styrene	M_2 Molar conc. of I.A.	N_2 Mole fraction I.A. in the copolymer
a.	0	0.332	0.313	-
	60	0.231	0.185	0.550
	120	0.130	0.087	0.523
	180	0.106	0.048	0.534
	240	0.082	0.029	0.510
	360	0.010	0.016	0.511
	600	-	0.008	-
	780	-	0.006	-
b.	duplicate polymerization			
	0	0.330	0.310	-
	15	0.318	0.304	
	30	0.205	0.254	0.576
	60	0.221	0.176	0.550
	150	0.065	0.060	0.521
	240	0.056	0.029	0.510
	362	-	0.016	-

TABLE IX

RATE OF POLYMER FORMATION
(In 1:1 Styrene:Itaconic Anhydride Copolymerisation in Benzene Solvent by Benzoyl Peroxide Catalyst)

	Time Minutes	Percent Polymerisation From Weight of Copolymer	Percent Polymerisation From Disappearance of Monomers
a.	0	0.2	-
	60	36.5	36.8
	120	68.2	66.9
	180	77.8	76.9
	240	86.3	83.5
	360	90.5	96.5
	600	92.8	-
	780	93.7	-
b. duplicate polymerisation			
	0	0.1	-
	15	5.2	2.8
	30	15.6	15.8
	60	38.2	38.0
	150	75.3	80.5
	240	86.2	-
	362	100.2	-

Figure 1

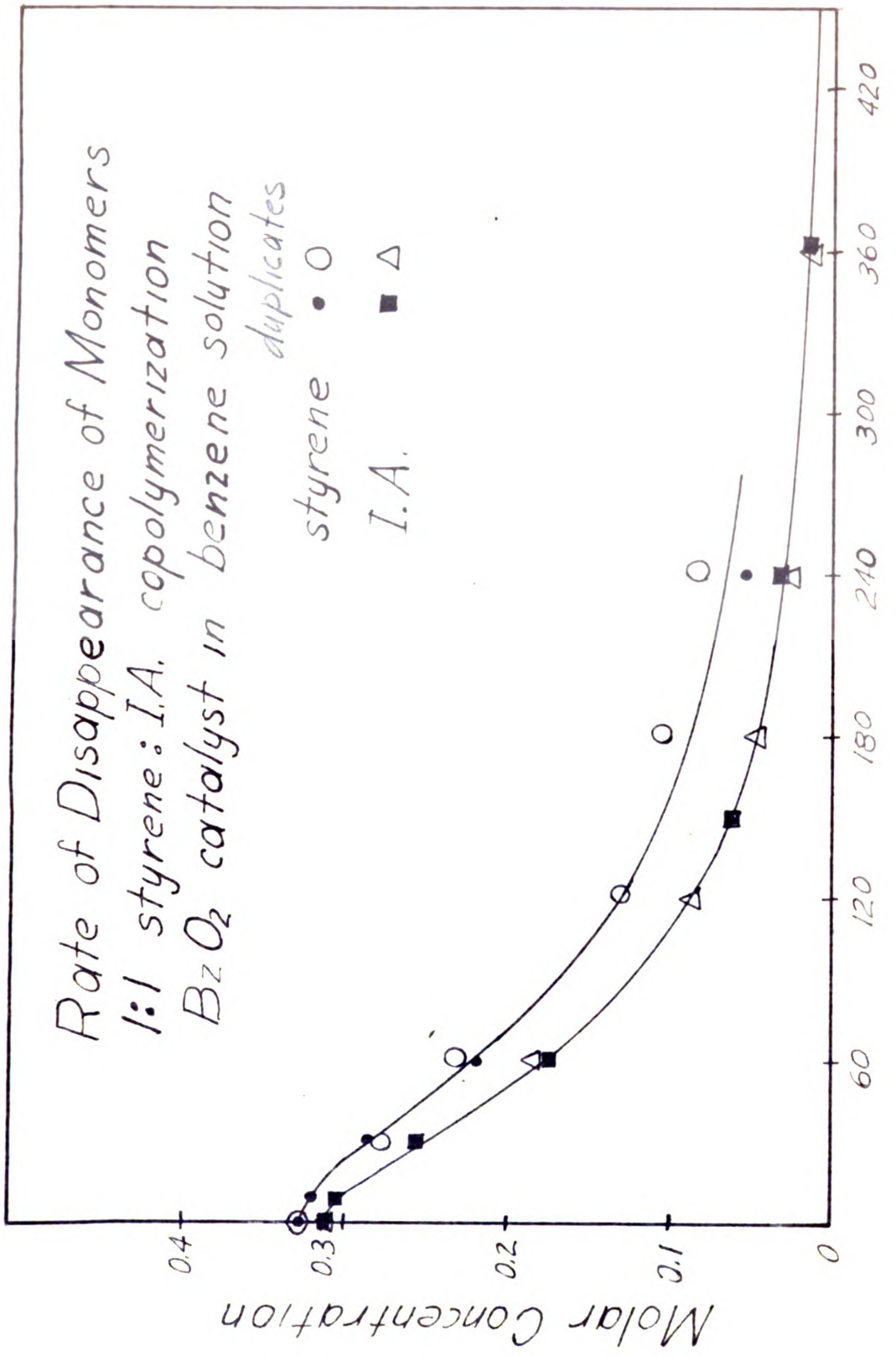

Rate of Disappearance of Monomers
1:1 styrene : I.A. copolymerization
$Bz O_2$ catalyst in benzene solution
duplicates
styrene • ○
I.A. ■ △
Molar Concentration
0.4
0.3
0.2
0.1
0
60
120
180
240
300
360
420
Time (minutes)

Figure 2

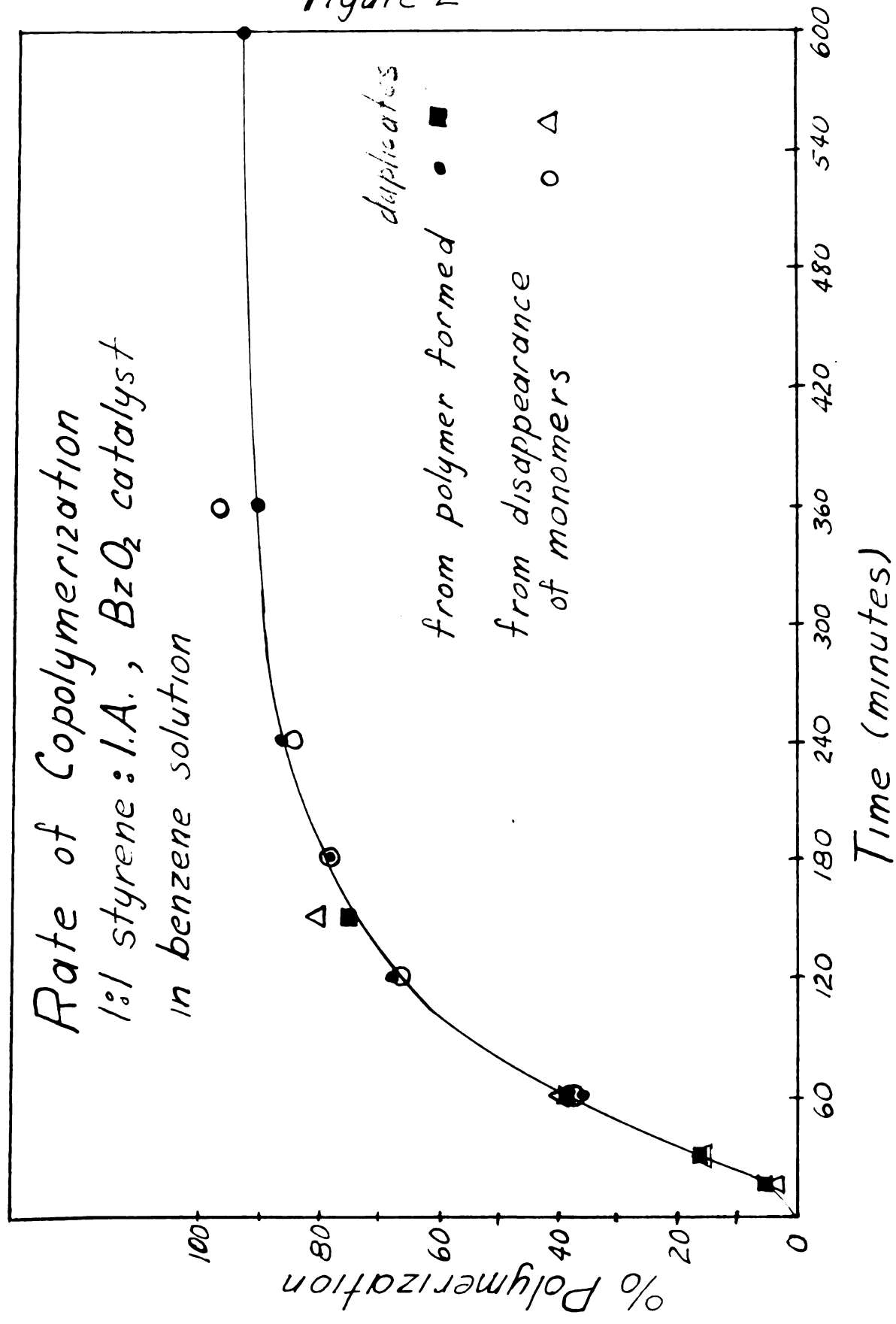

Rate of Copolymerization
1:1 styrene : I.A., BzO_2 catalyst
in benzene solution
duplicates
from polymer formed • ■
from disappearance of monomers ○ △
% Polymerization
0
20
40
60
80
100
60
120
180
240
300
360
420
480
540
600
Time (minutes)

Figure 3

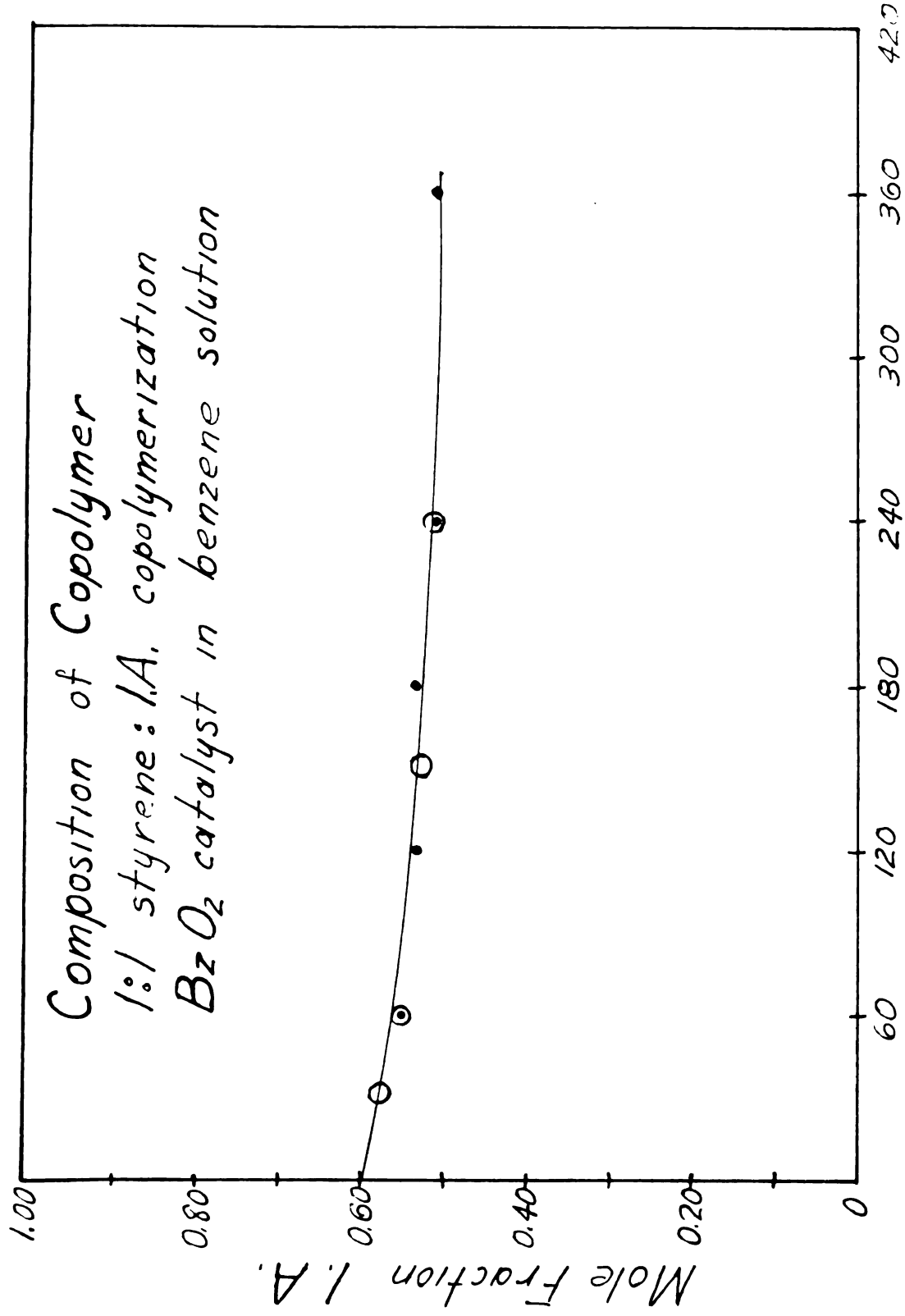

Composition of Copolymer
1:1 styrene : I.A. copolymerization
Bz O2 catalyst in benzene solution
Mole Fraction I.A.
1.00
0.80
0.60
0.40
0.20
0
60
120
180
240
300
360
420
Time (minutes)

TABLE X

RATE OF DISAPPEARANCE OF MONOMERS, COMPOSITION OF THE COPOLYMER AND RATE OF POLYMERIZATION
(1:1 Styrene:Itaconic Anhydride Copolymerization in Benzene Solvent with Bis-azo-isobutyronitrile Catalyst.)

Time Minutes	M_1 Molar Conc. of Styrene	M_2 Molar Conc. of I.A.	Percent Polymerization from Wt. of Copolymer	N_2 Mole Fraction I.A. in the Copolymer
0	0.321	0.309	1.5	-
7	-	0.298	5.7	-
15	0.291	0.269	11.0	0.57
30	0.231	0.208	29.7	0.53
45	0.175	0.160	45.2	0.50
60	0.146	0.124	56.0	0.51
100	0.103	0.069	71.4	0.53

Figure 4

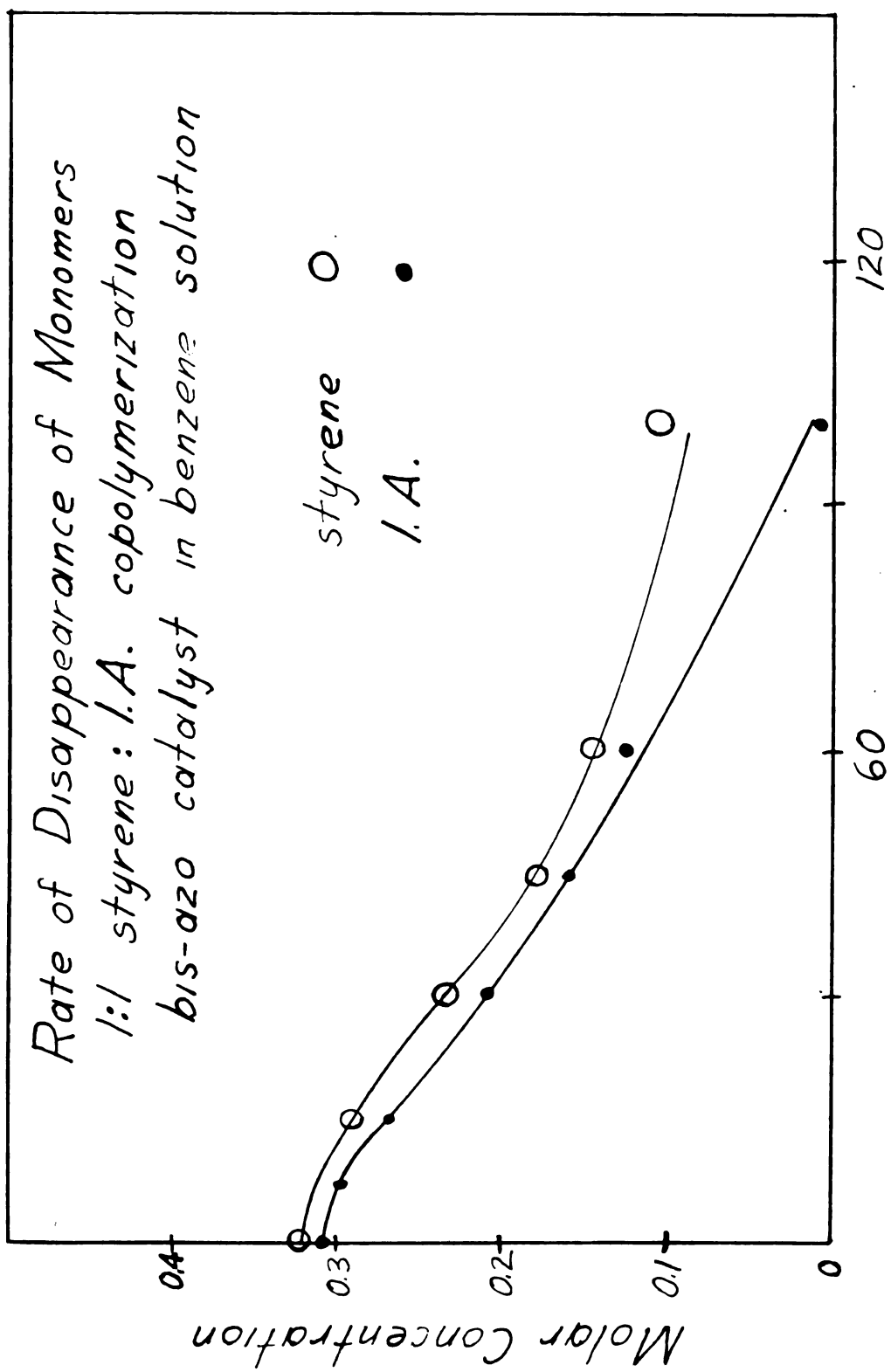

Rate of Disappearance of Monomers
1:1 styrene : I.A. copolymerization
bis-azo catalyst in benzene solution
styrene O
I.A. ●
Molar Concentration
0.4
0.3
0.2
0.1
0
60
120
Time (minutes)

Figure 5

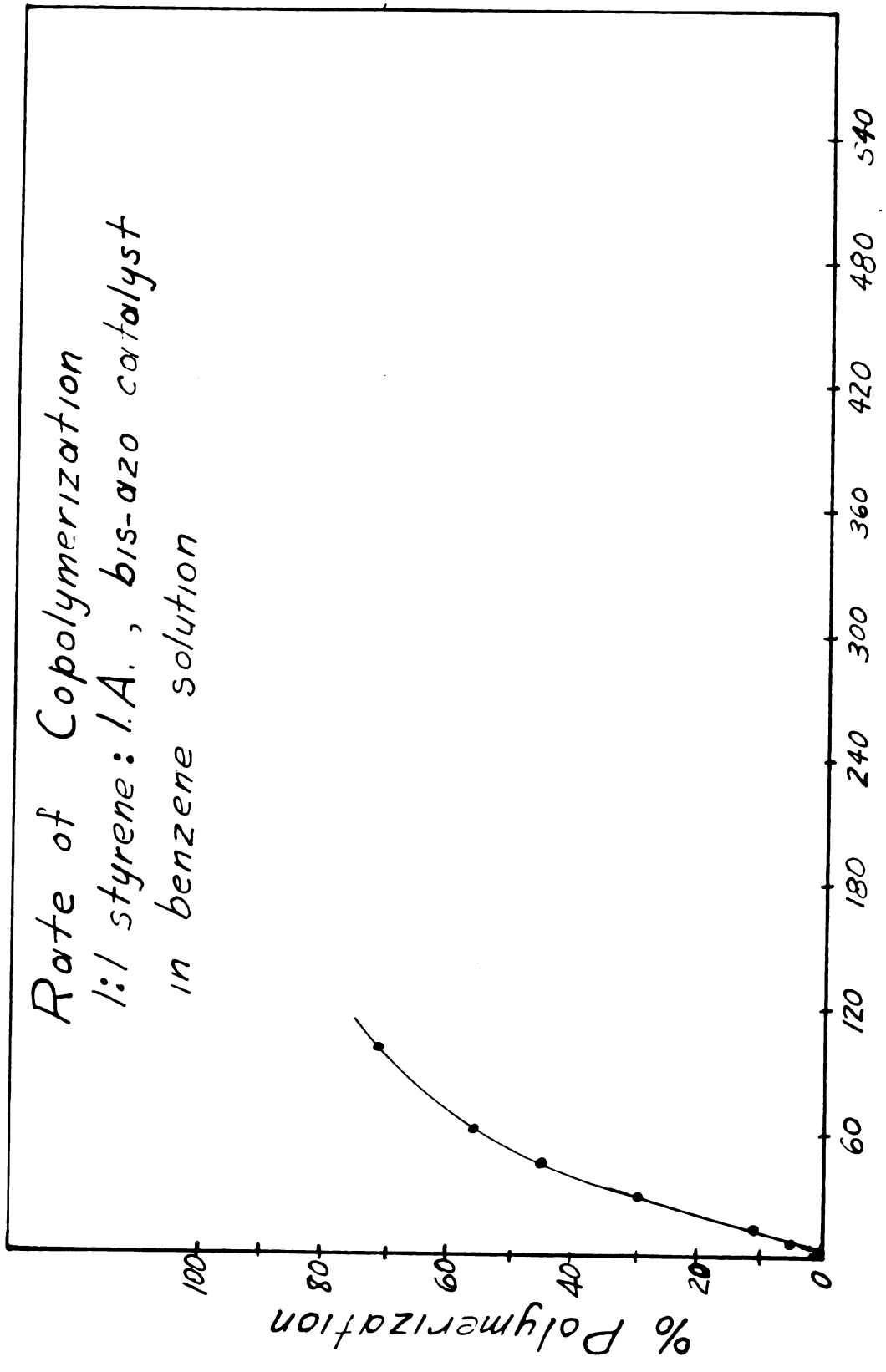

Rate of Copolymerization
1:1 styrene : I.A. , bis-azo catalyst
in benzene solution
% Polymerization
0
20
40
60
80
100
Time (minutes)
60
120
180
240
300
360
420
480
540

Figure 6

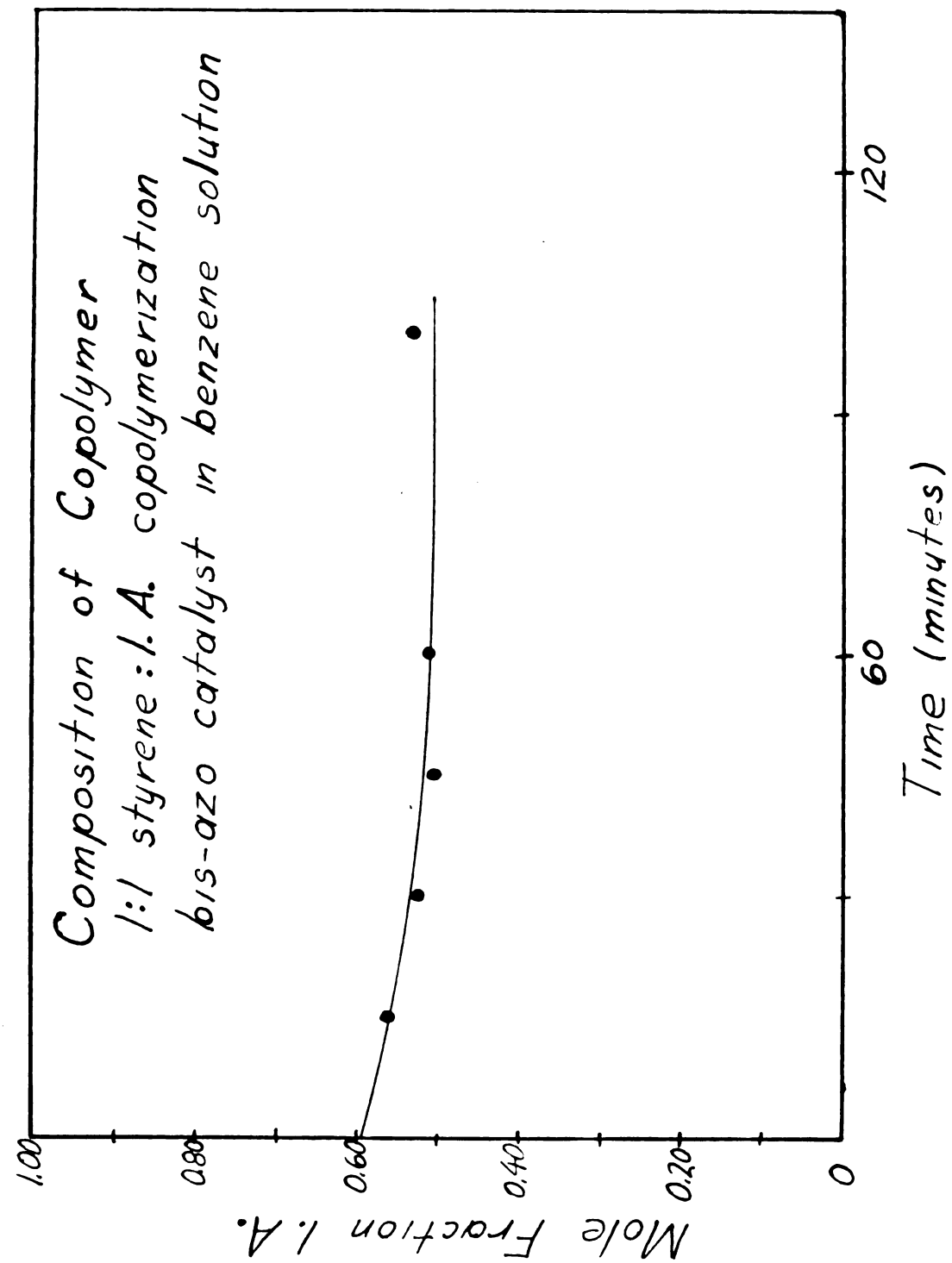

Composition of Copolymer
1:1 styrene : 1. A. copolymerization
bis-azo catalyst in benzene solution
Mole Fraction 1. A.
1.00
0.80
0.60
0.40
0.20
0
60
120
Time (minutes)

TABLE XI

RATE OF DISAPPEARANCE OF MONOMERS, COMPOSITION OF THE COPOLYMER, AND RATE OF POLYMERIZATION
(1:1 Styrene:Itaconic Anhydride Copolymerization in Tetrahydrofuran Solvent with Benzoyl Peroxide Catalyst.)

Time Minutes	M_1 Molar Conc. of Styrene	M_2 Molar Conc. of I. A.	Percent Polymerization From Wt. of Copolymer	N_2 Mole Fraction I.A. in the Copolymer
a. 0	0.321	0.321	0.1	-
240	0.269	0.285	13.6	0.410
360	0.258	0.265	18.6	0.470
540	0.231	0.246	25.6	0.455
720	0.217	0.226	30.9	0.477
b. duplicate experiment				
0	0.321	0.316	0.5	-
60	0.306	0.311	3.9	0.400
240	0.270	0.275	15.0	0.475
480	0.246	0.244	23.8	0.506
720	0.228	0.228	29.1	0.500
940	0.210	0.224	32.4	0.466
1285	0.192	0.216	35.9	0.449
1500	0.198	0.198	38.2	0.500
1740	-	0.190	40.4	-
2040	-	0.183	42.8	-

Figure 7

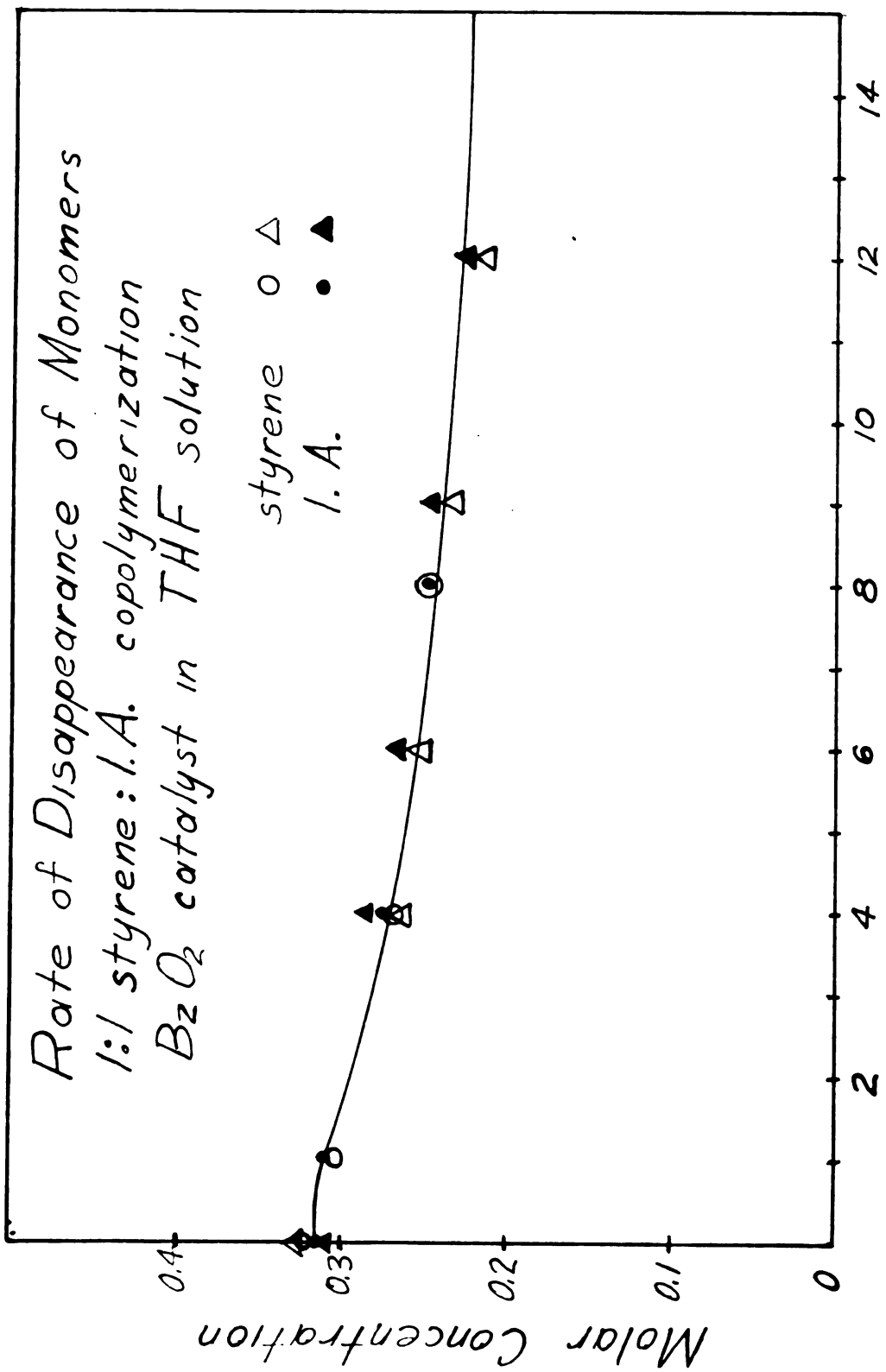

Rate of Disappearance of Monomers
1:1 styrene : I.A. copolymerization
Bz_2O_2 catalyst in THF solution
styrene ○ △
I.A. ● ▲
Molar Concentration
0.4
0.3
0.2
0.1
0
2
4
6
8
10
12
14
Time (hours)

Figure 8

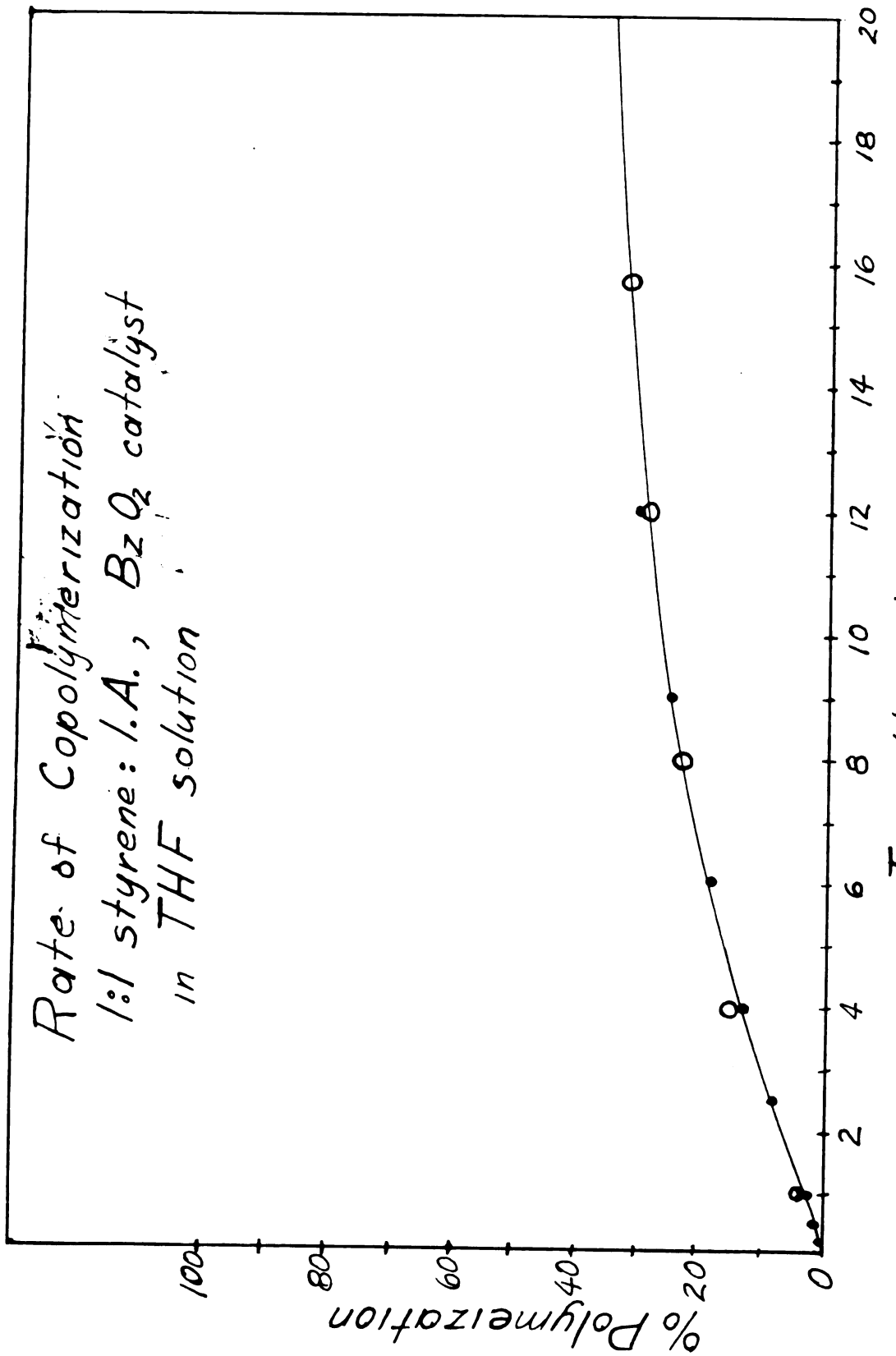

Rate of Copolymerization
1:1 styrene: I.A., Bz_2O_2 catalyst
in THF solution
% Polymerization
Time (hours)
0
20
40
60
80
100
2
4
6
8
10
12
14
16
18
20

Figure 9

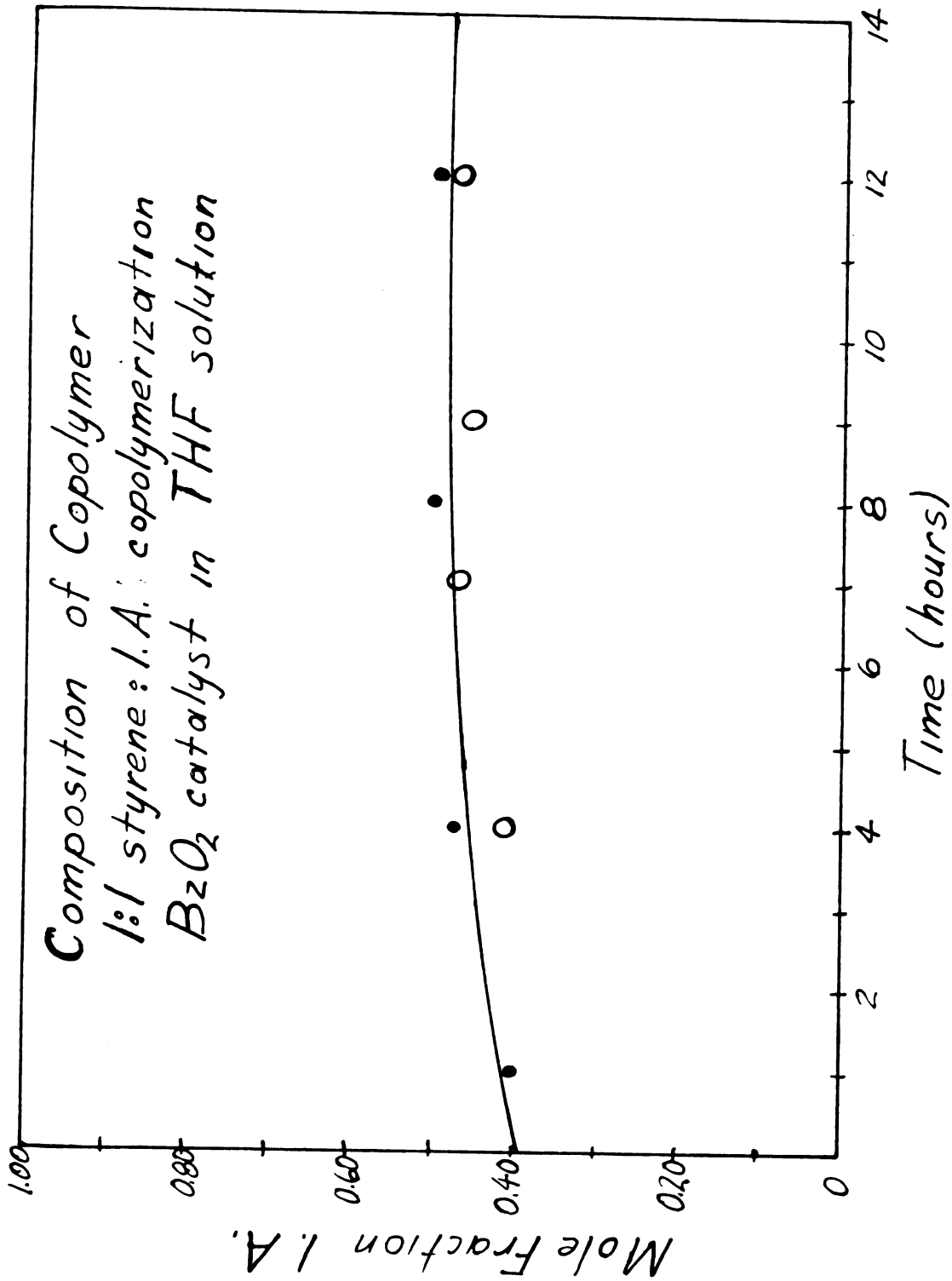

Composition of Copolymer
1:1 styrene : I.A. copolymerization
BzO_2 catalyst in THF solution
Mole Fraction I.A.
1.00
0.80
0.60
0.40
0.20
0
2
4
6
8
10
12
14
Time (hours)

TABLE XII

RATE OF DISAPPEARANCE OF MONOMERS, COMPOSITION OF THE COPOLYMER, AND RATE OF POLYMERIZATION
(1:1 Styrene:Itaconic Anhydride Copolymerization in Tetrahydrofuran Solvent with Bis-azo-isobutyronitrile Catalyst.)

Time Minutes	M_1 Molar Conc. of Styrene	M_2 Molar Conc. of I.A.	Percent Polymerization From Wt. of Copolymer	N_2 Mole Fraction I.A. in the Copolymer
0	0.321	0.321	-	-
35	0.319	0.318	0.6	0.500
60	0.310	0.312	3.0	0.460
150	0.279	0.284	12.2	0.468
240	0.266	0.262	17.7	0.517
420	0.231	0.230	28.1	0.502
600	0.206	0.211	35.1	0.489
840	0.187	0.189	41.3	0.496
1341	0.157	0.166	49.8	0.486
1680	0.140	0.154	54.0	0.480

Figure 10

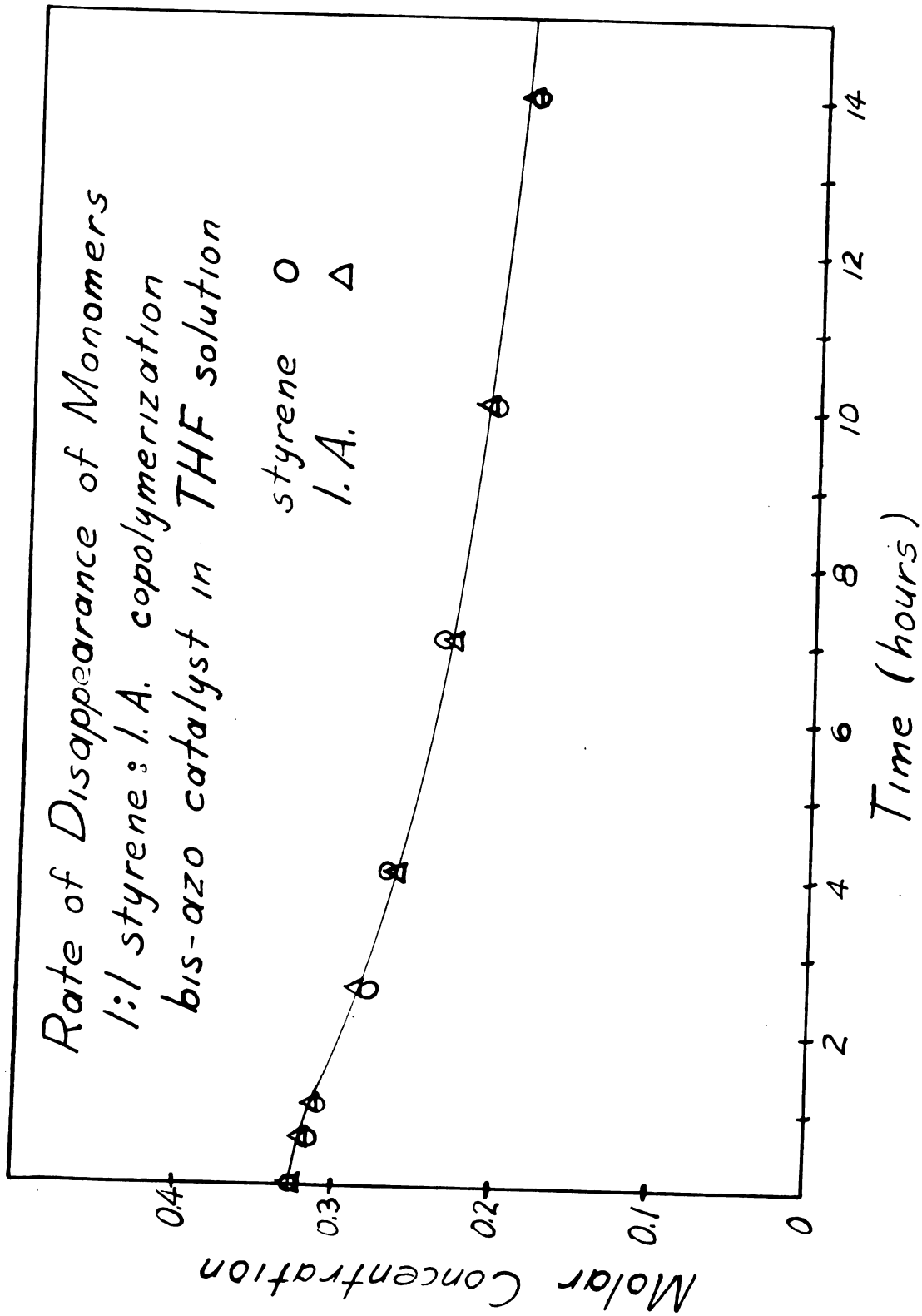

Rate of Disappearance of Monomers
1:1 styrene : I.A. copolymerization
bis-azo catalyst in THF solution
styrene O
I.A. Δ
Molar Concentration
0.4
0.3
0.2
0.1
0
2
4
6
8
10
12
14
Time (hours)

Figure 11

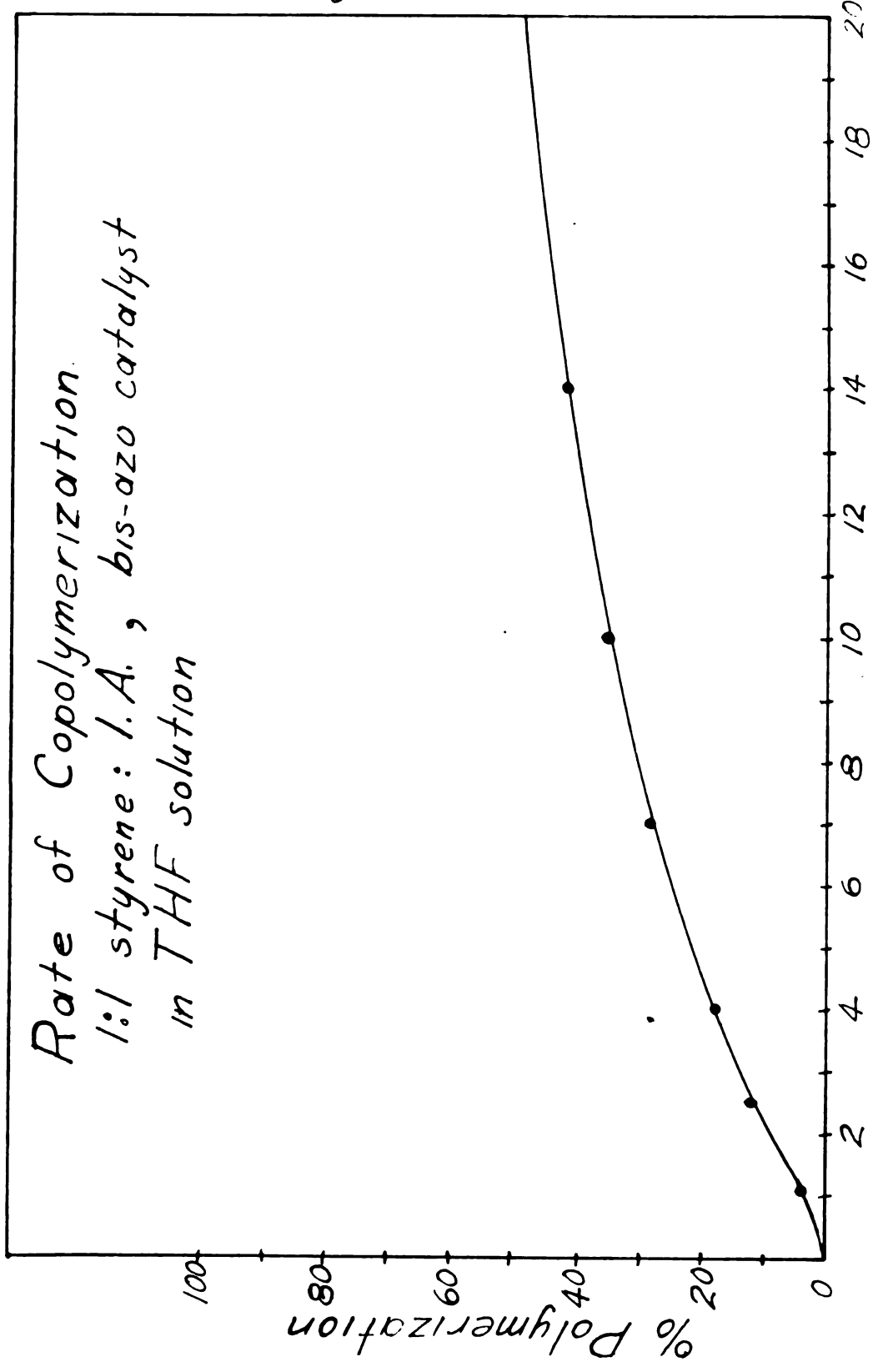
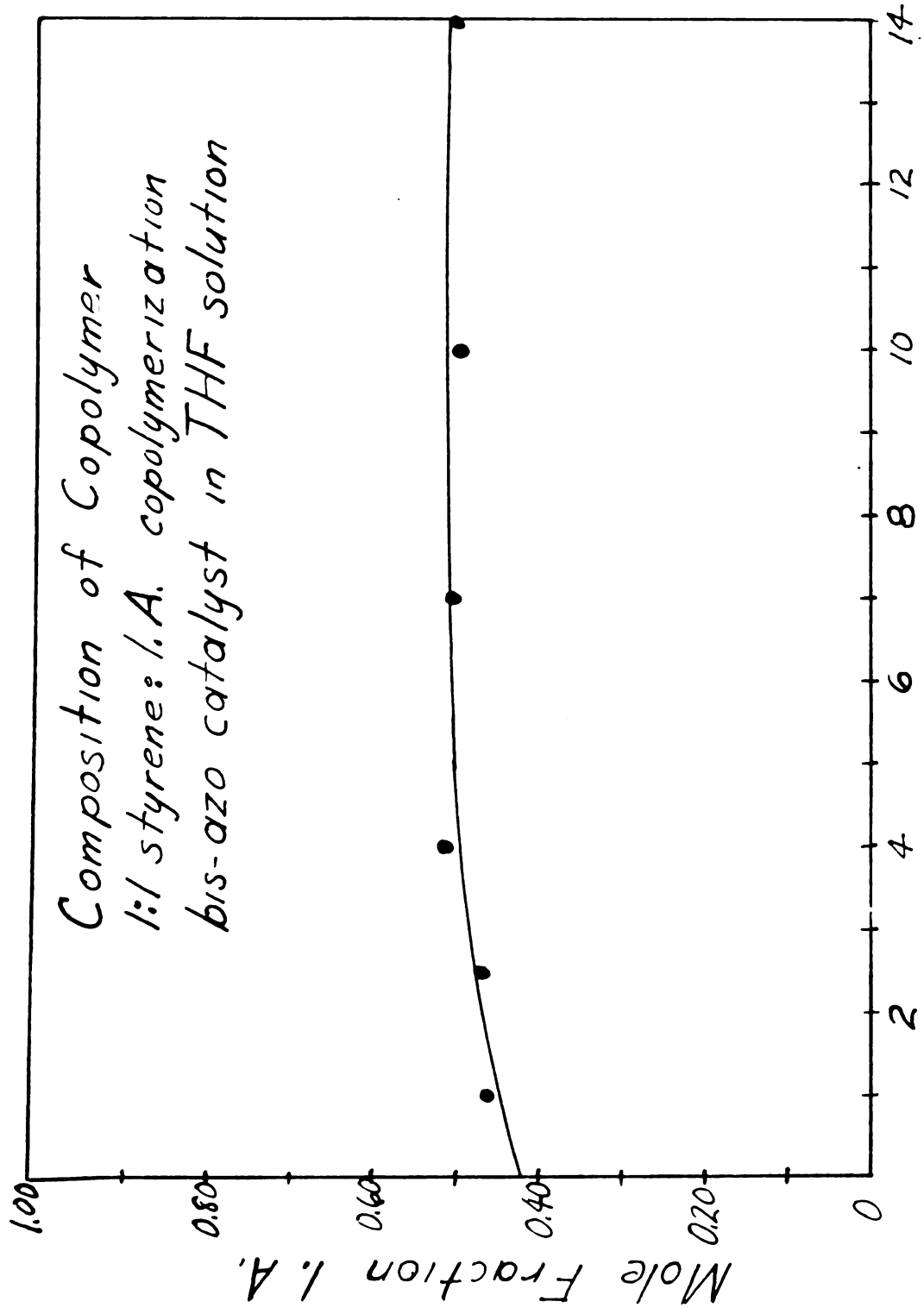

Rate of Copolymerization
1:1 styrene: I.A. , bis-azo catalyst
in THF solution
% Polymerization
0
20
40
60
80
100
2
4
6
8
10
12
14
16
18
20
Time (hours)

Figure 12


Composition of Copolymer
1:1 styrene: I.A. copolymerization
bis-azo catalyst in THF solution
Mole Fraction I.A.
1.00
0.80
0.60
0.40
0.20
0
2
4
6
8
10
12
14
Time (hours)

C. Order of Reaction with Respect to Styrene and Itaconic Anhydride Concentrations

The rate expression for copolymerization of styrene and itaconic anhydride has been proposed to be (1):

$$\text{Rate} = k' [M^*]^1$$

where M^* is a complex of 1:1 styrene and itaconic anhydride. If this is the case then the rate of polymerization would be expected also to be first order with respect to either styrene or itaconic anhydride concentration. The first order rate expression when integrated is:

$$\log [M^*] = \log [M_0^*] - \frac{k}{2.3} t$$

Graphs of the log of styrene concentration, M_1, and log of itaconic anhydride concentration, M_2, are shown in Figures 13-20 for each solvent and catalyst system.

Figure 13

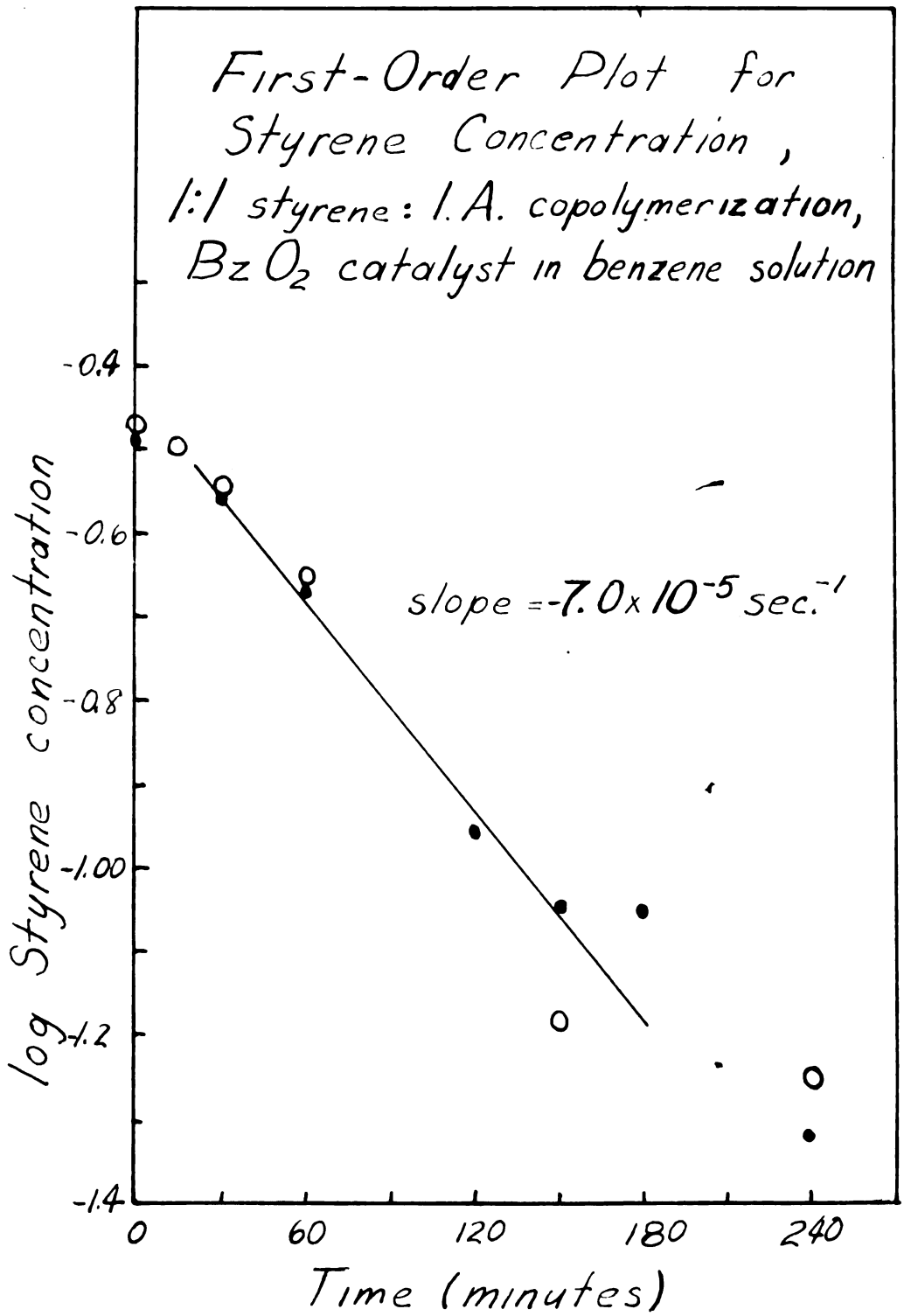

First-Order Plot for Styrene Concentration, 1:1 styrene: I.A. copolymerization, $Bz O_2$ catalyst in benzene solution
slope = -7.0×10^{-5} sec.$^{-1}$
log Styrene concentration
-0.4
-0.6
-0.8
-1.00
-1.2
-1.4
0
60
120
180
240
Time (minutes)

Figure 14

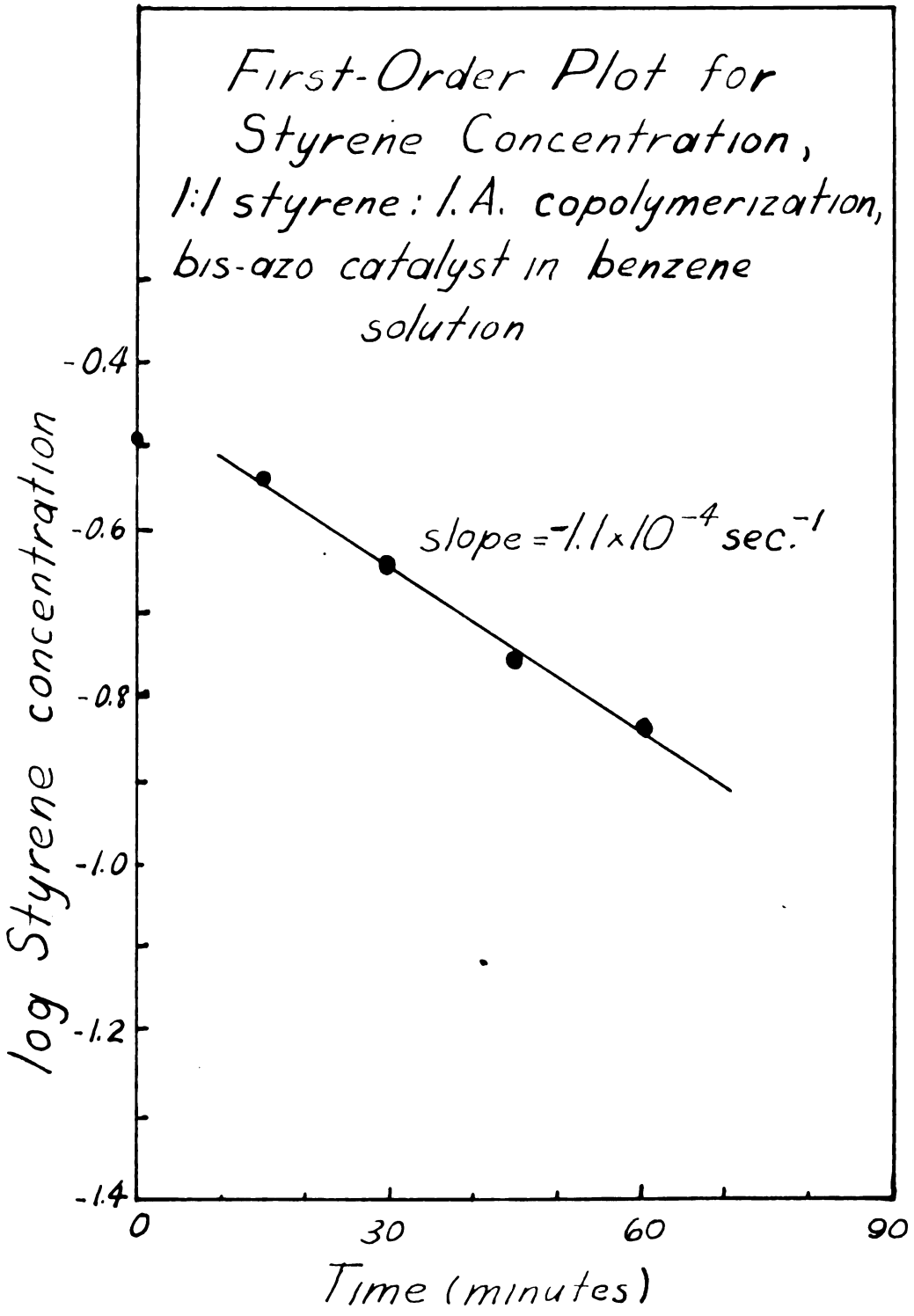

First-Order Plot for Styrene Concentration, 1:1 styrene : I.A. copolymerization, bis-azo catalyst in benzene solution
slope = -1.1×10^{-4} sec.$^{-1}$
log Styrene concentration
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
0
30
60
90
Time (minutes)

Figure 15

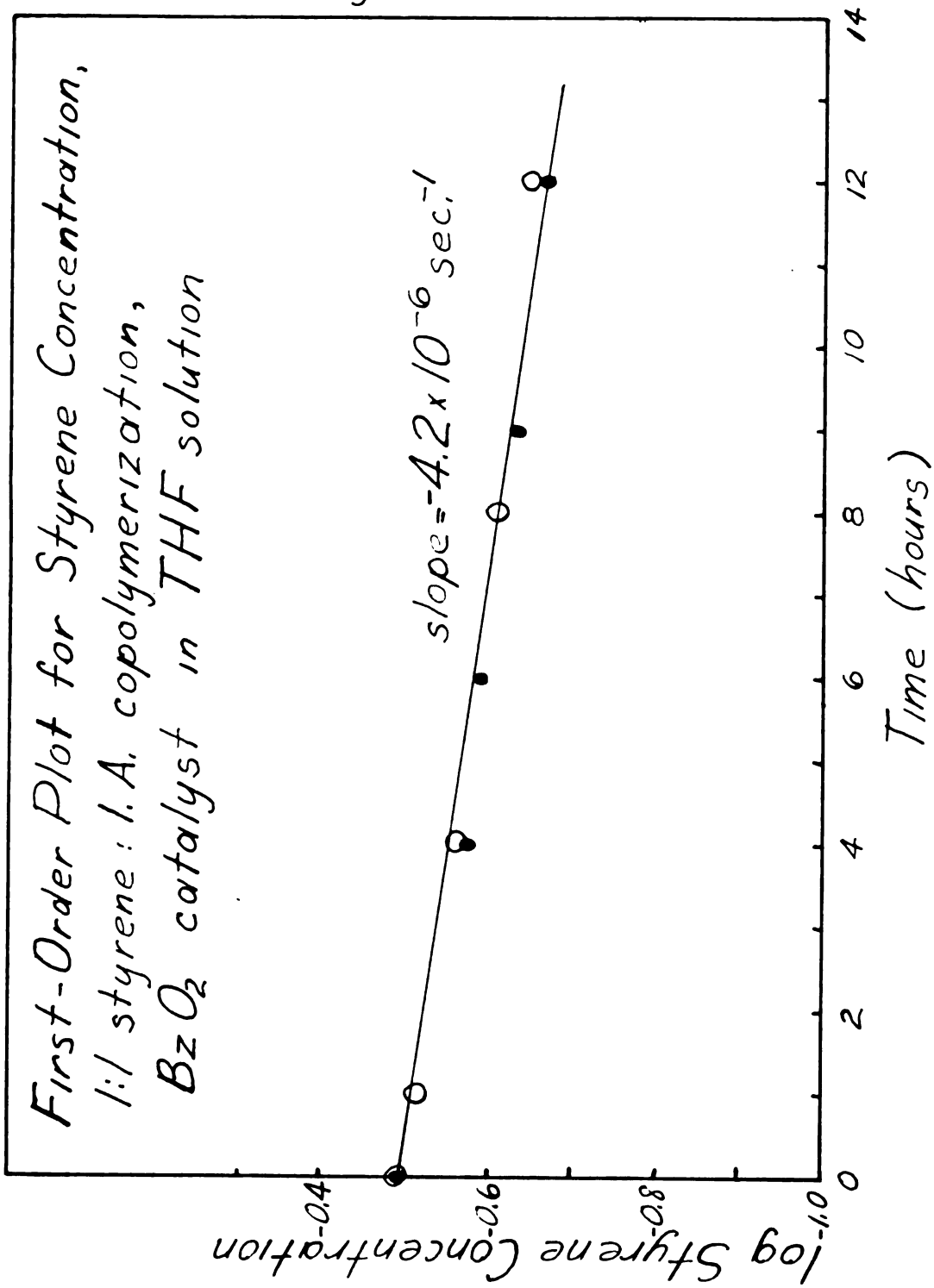

First-Order Plot for Styrene Concentration,
1:1 styrene : I.A. copolymerization,
BzO_2 catalyst in THF solution
slope = -4.2×10^{-6} sec.$^{-1}$
log Styrene Concentration
-0.4
-0.6
-0.8
-1.0
0
2
4
6
8
10
12
14
Time (hours)

Figure 16

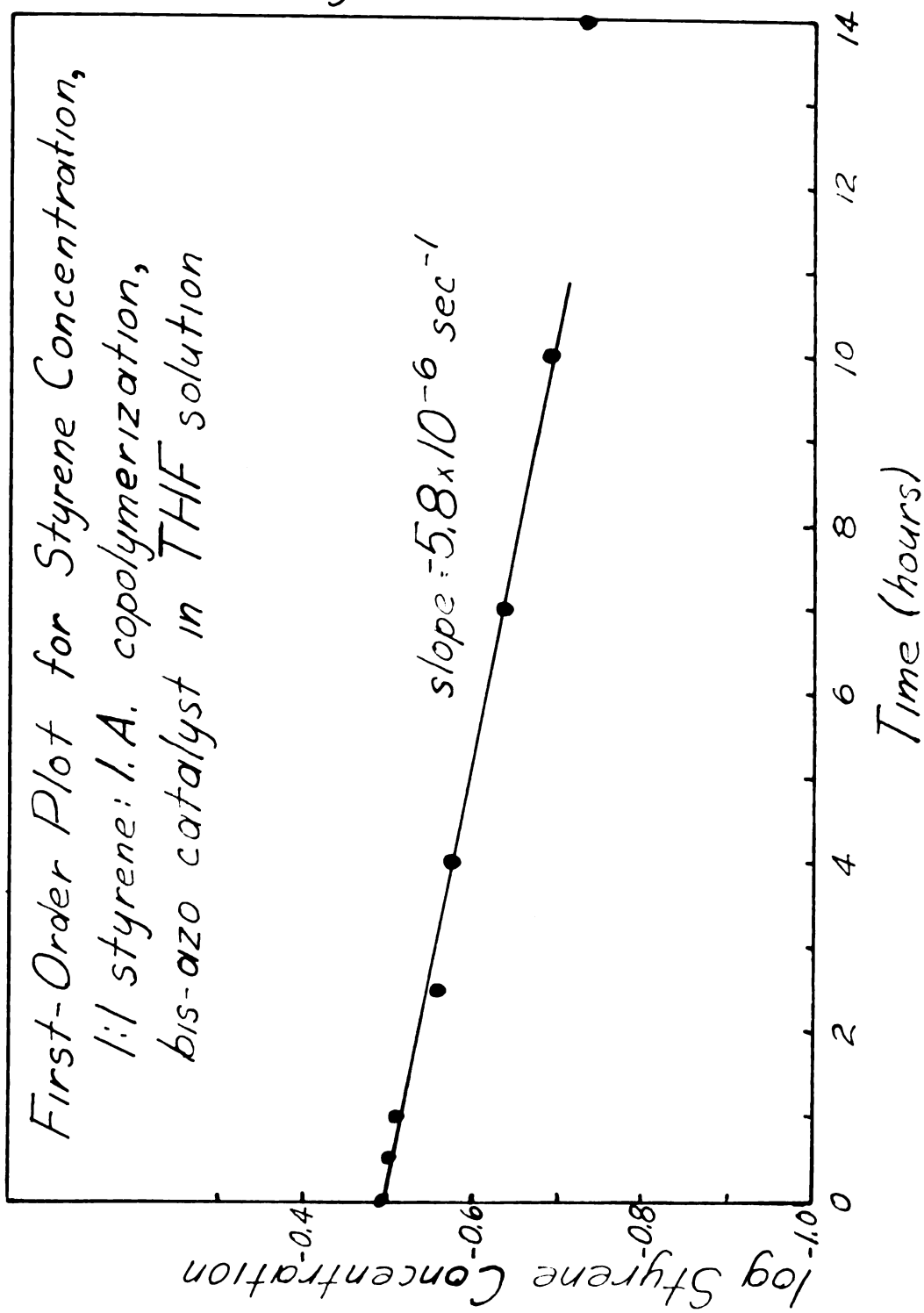

First-Order Plot for Styrene Concentration,
1:1 styrene: I.A. copolymerization,
bis-azo catalyst in THF solution
slope = -5.8 x 10⁻⁶ sec⁻¹
log Styrene Concentration
Time (hours)
-0.4
-0.6
-0.8
-1.0
0
2
4
6
8
10
12
14

Figure 17

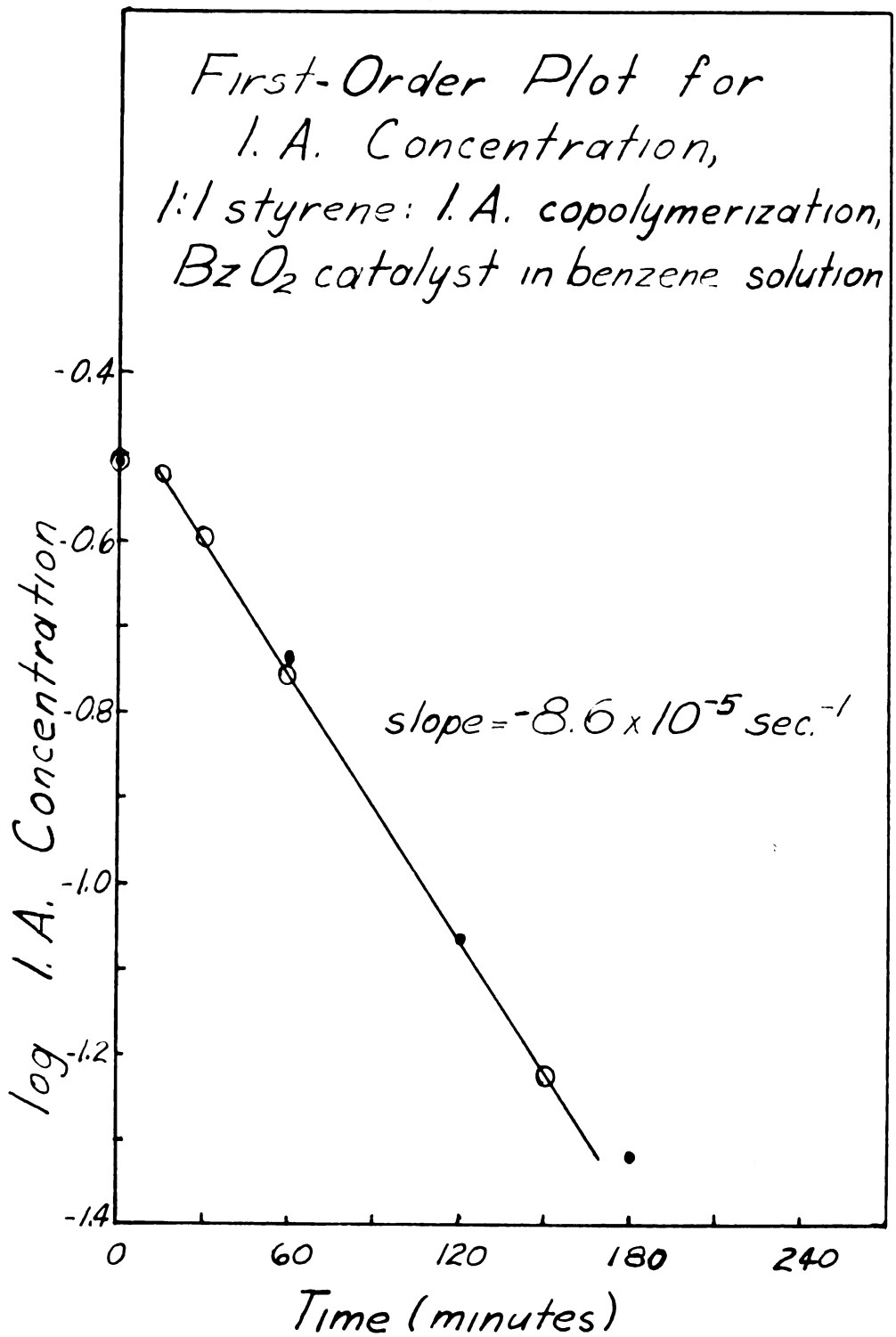

First-Order Plot for
I. A. Concentration,
1:1 styrene: I. A. copolymerization,
$Bz O_2$ catalyst in benzene solution
slope = -8.6×10^{-5} sec.$^{-1}$
log I. A. Concentration
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
0
60
120
180
240
Time (minutes)

Figure 18

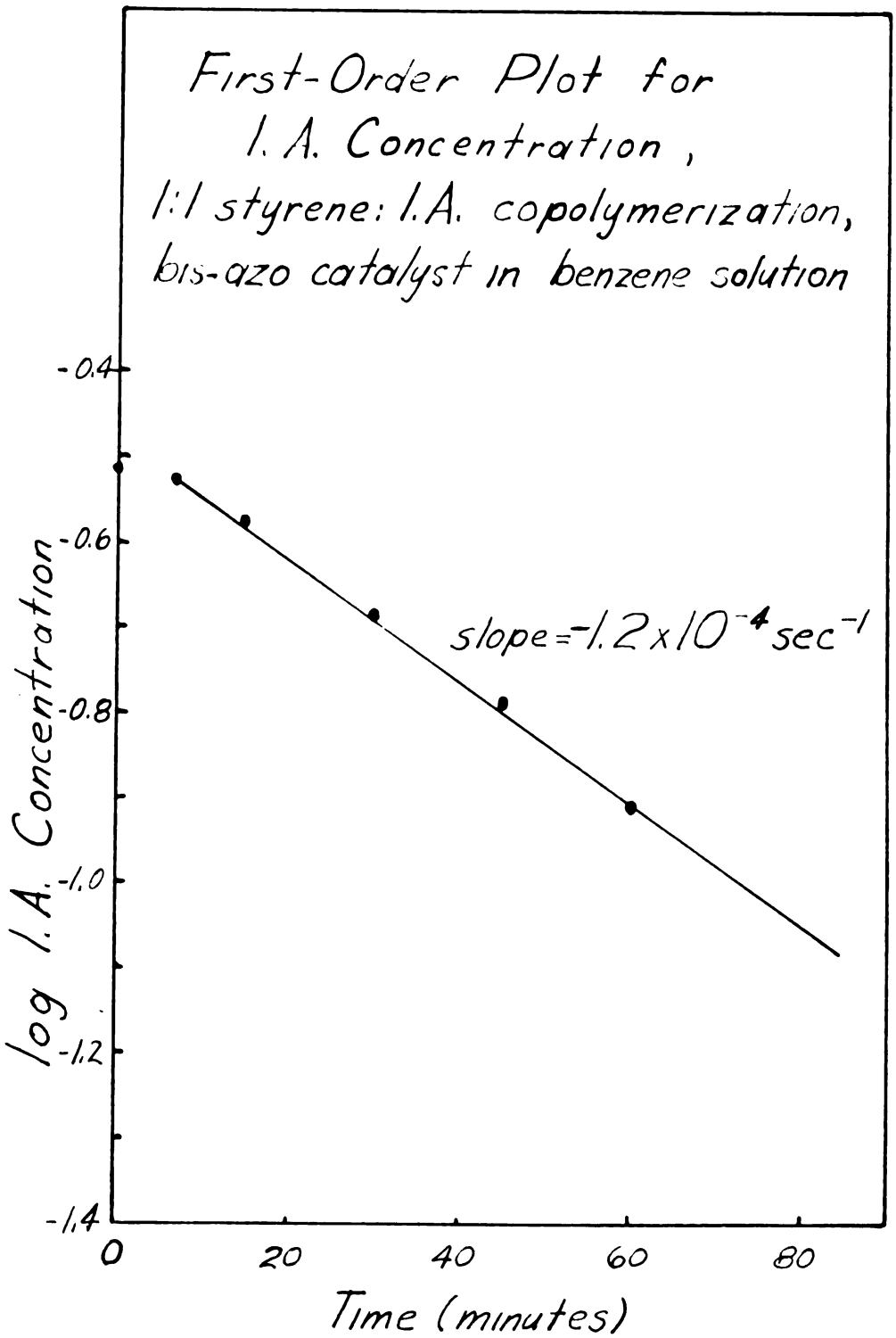

First-Order Plot for
I. A. Concentration,
1:1 styrene: I.A. copolymerization,
bis-azo catalyst in benzene solution
slope = -1.2 x 10⁻⁴ sec⁻¹
log I.A. Concentration
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
0
20
40
60
80
Time (minutes)

Figure 19

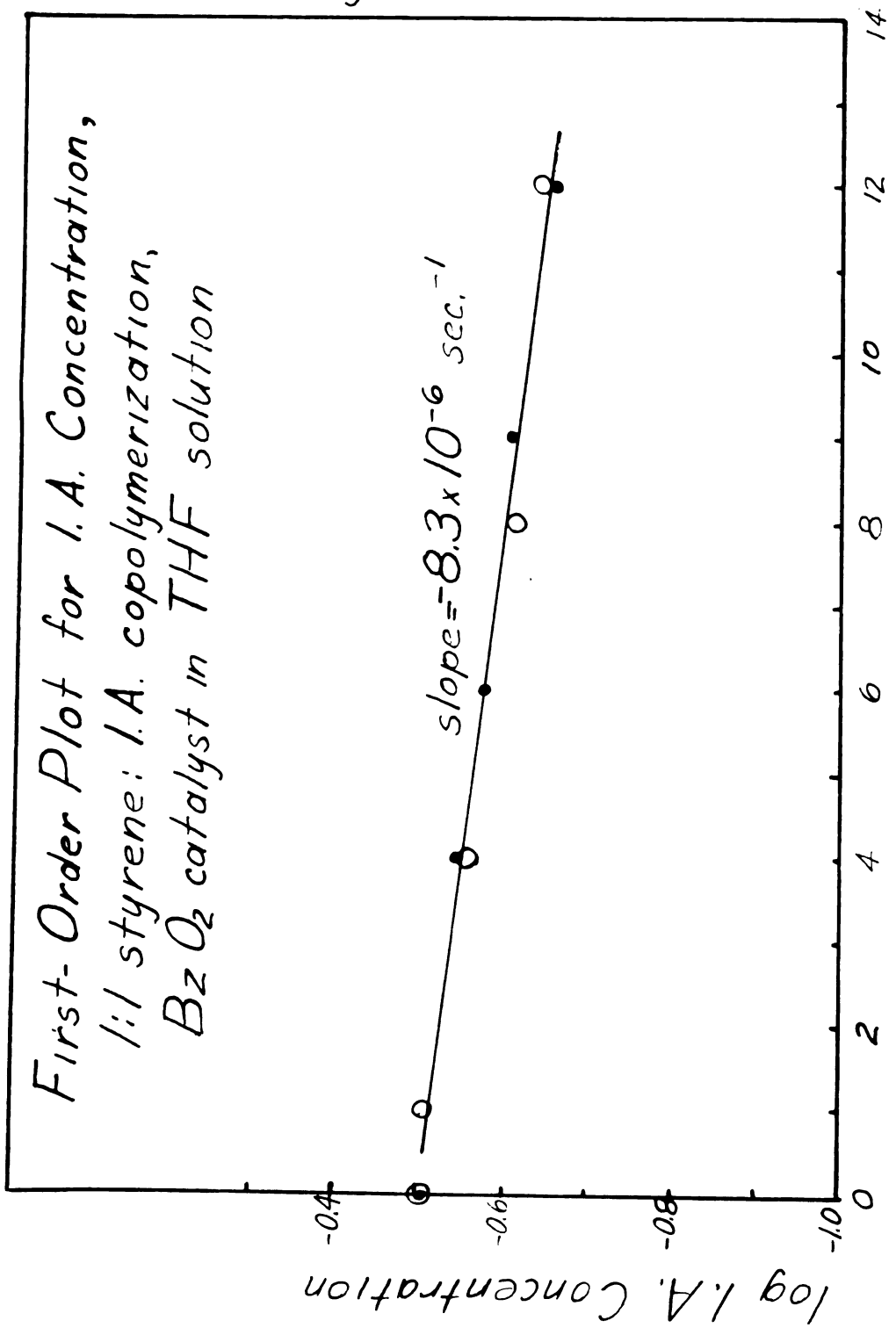
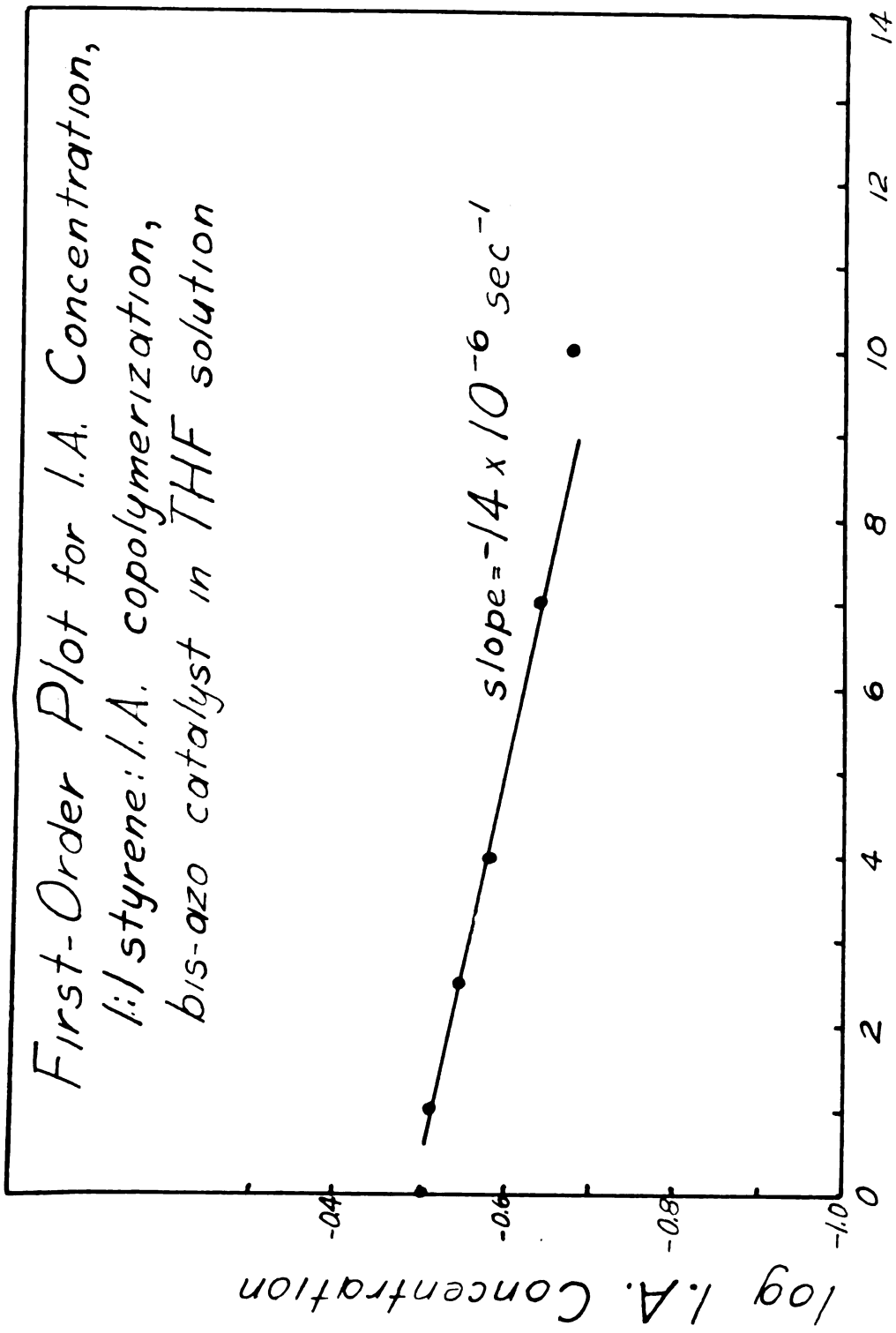

First-Order Plot for I.A. Concentration,
1:1 styrene: I.A. copolymerization,
Bz_2O_2 catalyst in THF solution
slope = -8.3×10^{-6} sec.$^{-1}$
log I.A. Concentration
Time (hours)
-0.4
-0.6
-0.8
-1.0
0
2
4
6
8
10
12
14

Figure 20


First-Order Plot for I.A. Concentration,
1:1 styrene: I.A. copolymerization,
bis-azo catalyst in THF solution
slope = -14 x 10^-6 sec^-1
log I.A. Concentration
Time (hours)
-0.4
-0.6
-0.8
-1.0
0
2
4
6
8
10
12
14

D. Overall Rate of Copolymerization

The overall rate of copolymerization can be expressed, if the simplifying assumption is made that the rate of initiation, R_i, is independent of the reaction medium and the concentration of the two monomers, by the following rate equation (25,26):

$$\frac{-d\{[M_1]+[M_2]\}}{dt} =$$

$$\frac{\left\{r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2\right\}\left(\frac{R_i^{\frac{1}{2}}}{\delta_i}\right)}{\left\{r_1^2[M_1]^2 + 2\left(\phi r_1 r_2 \frac{\delta_2}{\delta_1}\right)[M_1][M_2] + \left(r_2\frac{\delta_2}{\delta_1}\right)^2[M_2]^2\right\}^{\frac{1}{2}}}$$

where $\delta_1 = \frac{(2k_{t11})^{\frac{1}{2}}}{k_{11}}$ $\qquad \delta_2 = \frac{(2k_{t22})^{\frac{1}{2}}}{k_{22}}$

$\phi = \frac{k_{t12}}{2k_{t11}^{\frac{1}{2}}\, k_{t22}^{\frac{1}{2}}}$ $\qquad r_1 = k_{11}/k_{12}$ $\qquad r_2 = k_{22}/k_{21}$

k_{11}, k_{12}, k_{22} and k_{21} = propogation rate constants

The symbol ϕ is known as the cross termination constant because it is a ratio of the termination constant between unlike monomer radicals to the product of the termination constants between like monomer radicals. De Bette (27) has integrated this equation. When the constant ϕ is large, i.e., a very strongly alternating copolymer, the integrated equation is:

$$\ln \frac{[(b_1[M_1])^{\frac{1}{2}} + (b_2[M_2])^{\frac{1}{2}}]}{[(b_1[M_1])^{\frac{1}{2}} - (b_2[M_2])^{\frac{1}{2}}]} =$$

$$\left\{\frac{R_i^{\frac{1}{2}} b_1 b_2}{2a_1 a_2 (\phi-1)}\right\} t + \ln \frac{[(b_1[M_1]_o)^{\frac{1}{2}} + (b_2[M_2]_o)^{\frac{1}{2}}]}{[(b_1[M_1]_o)^{\frac{1}{2}} - (b_2[M_2]_o)^{\frac{1}{2}}]}$$

where $b_1 = r_1 - 1$

$b_2 = r_2 - 1$

$a_1 = r_1 \delta_1$

$a_2 = r_2 \delta_2$

This is a linear function of time with respect to the factor involving both monomer concentrations, M_1 and M_2, and the monomer reactivity ratios, r_1 and r_2. The slope of this line is a function of the rate of initiation and the cross termination constant ϕ. Since the reactivity ratios are known for the copolymerization of styrene and itaconic anhydride (2,28), from work previously done in this laboratory, in both benzene and tetrahydrofuran solvents, the rate of polymerization can be evaluated from the integrated equation. The values for benzene solvent are shown in Table XIII and Figure 21. The values for tetrahydrofuran solvent are shown in Table XIV and Figure 22.

TABLE XIII

OVERALL RATE OF COPOLYMERIZATION
(From DeBetta Integrated Equation of 1:1 Styrene: Itaconic Anhydride in Benzene Solvent.)
$r_1 = 0.015$; $r_2 = 0.80$

Time Minutes	$\frac{[(b_1[M_1])^{\frac{1}{2}} + (b_2[M_2])^{\frac{1}{2}}]}{[(b_1[M_1])^{\frac{1}{2}} - [b_2[M_2])^{\frac{1}{2}}]}$	
1. Benzoyl peroxide catalyst		(duplicate)
0	2.60	2.57
15	-	-
30	-	2.48
60	2.40	2.39
120	2.29	-
150	-	2.16
180	1.98	-
240	2.06	2.03
360	1.83	-
2. Bis-azo-isobutyronitrile catalyst		
0	2.60	
7	-	
15	2.52	
30	2.54	
45	2.51	
60	2.42	
100	2.16	

Figure 21

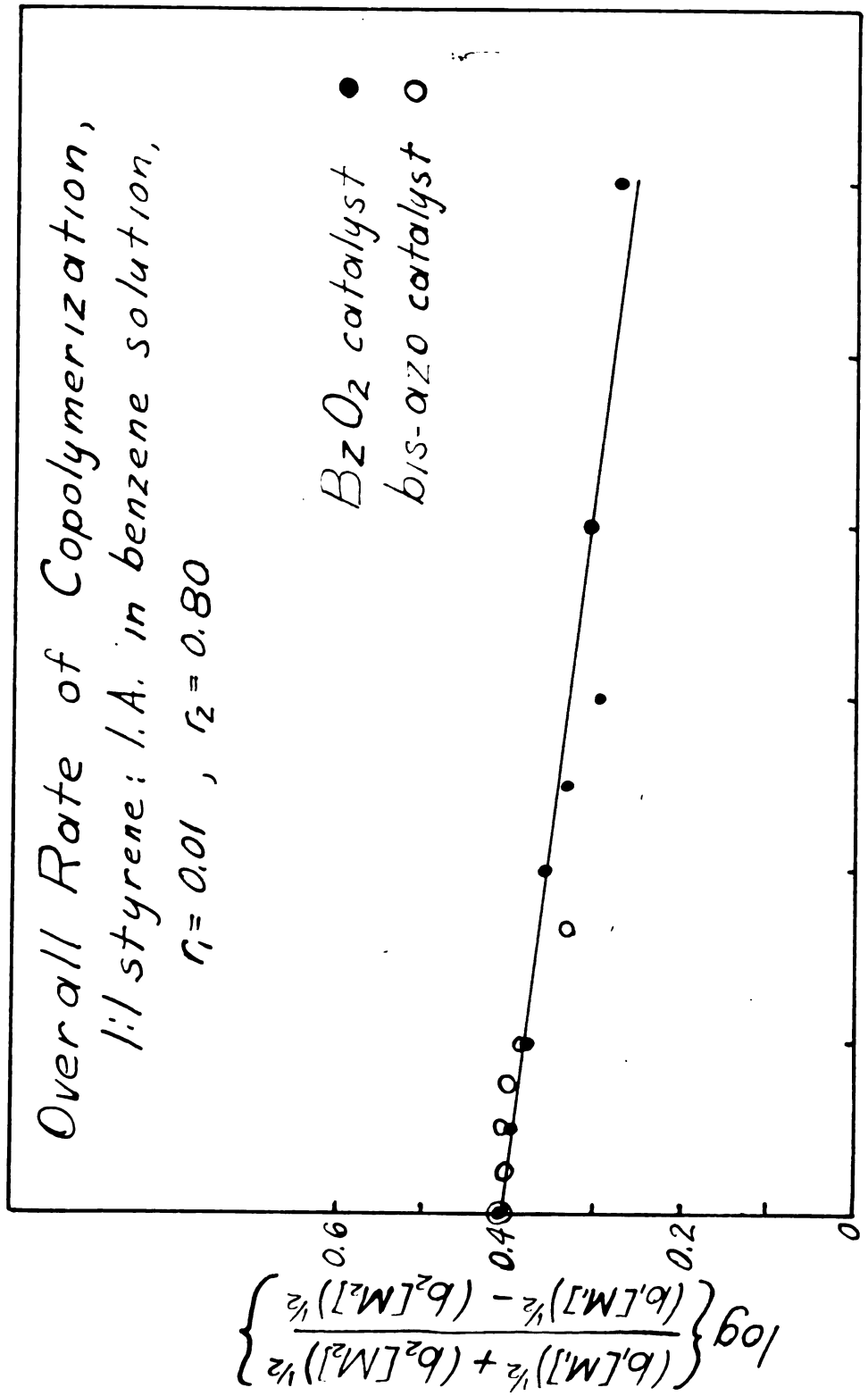
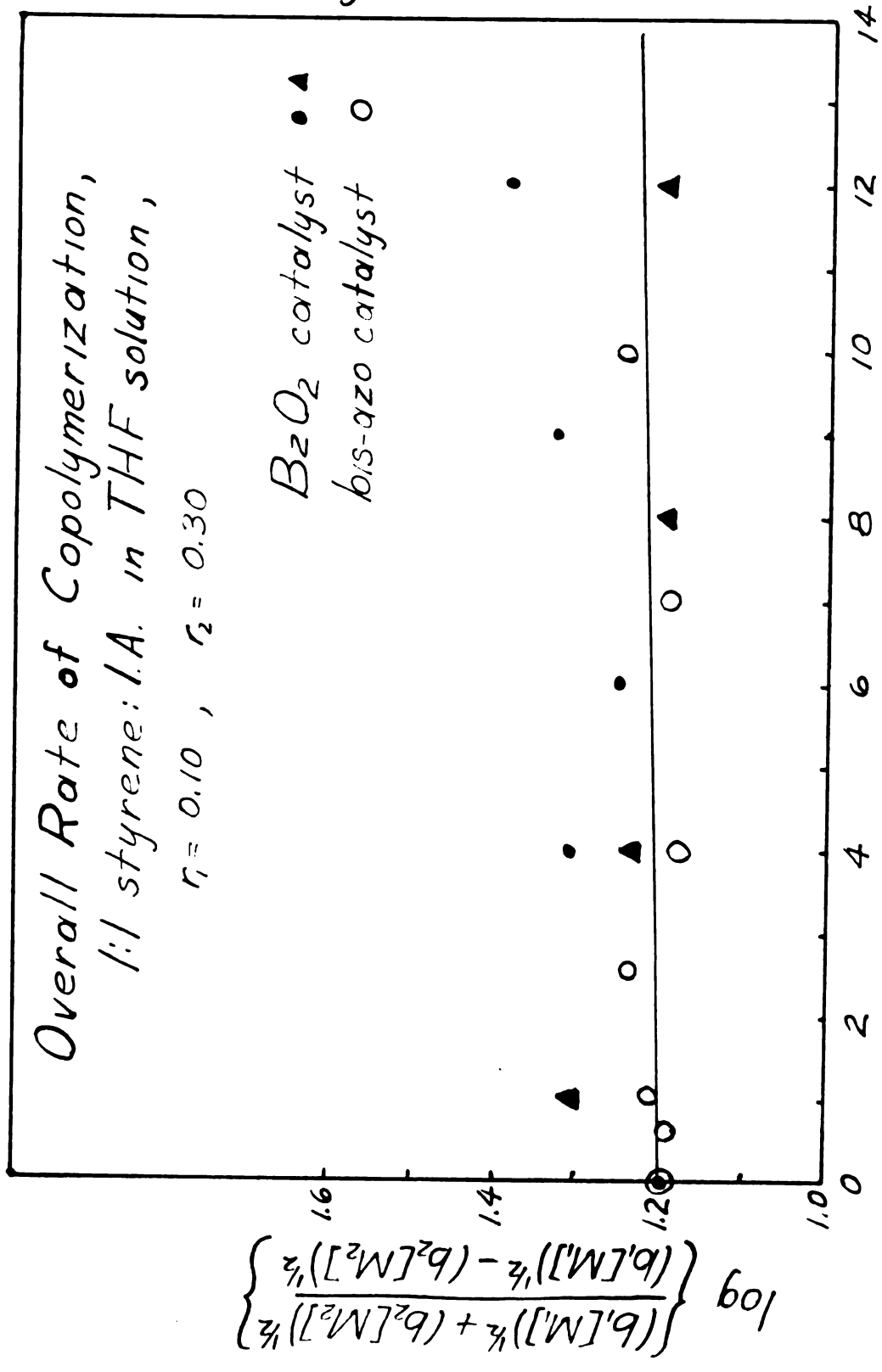

Overall Rate of Copolymerization,
1:1 styrene: I.A. in benzene solution,
$r_1 = 0.01$, $r_2 = 0.80$
BzO_2 catalyst ●
bis-azo catalyst ○
$\log \left\{ \frac{(b_1[M_1])^{1/2} + (b_2[M_2])^{1/2}}{(b_1[M_1])^{1/2} - (b_2[M_2])^{1/2}} \right\}$
0.6
0.4
0.2
0
0
60
120
180
240
300
360
Time (minutes)

TABLE XIV

OVERALL RATE OF COPOLYMERIZATION
(From DeBotts Integrated Equation, of 1:1 Styrene: Itaconic Anhydride in Tetrahydrofuran Solvent.)
$r_1 = 0.1 \qquad r_2 = 0.3$

Time Minutes	$\frac{[(b_1[M_1])^{\frac{1}{2}} + (b_2[M_2])^{\frac{1}{2}}]}{[(b_1[M_1])^{\frac{1}{2}} - (b_2[M_2])^{\frac{1}{2}}]}$	
1. Benzoyl peroxide catalyst		duplicate experiment
0	15.8	15.9
60	-	20.2
240	20.4	17.2
360	17.9	-
480	-	15.7
540	21.2	-
720	24.4	15.8
2. Bis-azo-isobutyronitrile catalyst		
0	15.8	
35	15.5	
60	16.3	
150	17.2	
240	15.0	
420	15.6	
600	17.7	
840	16.4	

Figure 22


Overall Rate of Copolymerization,
1:1 styrene: I.A. in THF solution,
$r_1 = 0.10$, $r_2 = 0.30$
B_2O_2 catalyst
bis-azo catalyst
$\log \left\{ \frac{(b_1[M_1])^{1/2} + (b_2[M_2])^{1/2}}{(b_1[M_1])^{1/2} - (b_2[M_2])^{1/2}} \right\}$
Time (hours)
1.0
1.2
1.4
1.6
0
2
4
6
8
10
12
14

III. ANALYSIS OF STYRENE-ITACONIC ANHYDRIDE COPOLYMER COMPOSITIONS

Samples of the styrene-itaconic anhydride copolymers prepared in experiments described in Section II-B were analyzed to determine their composition. The copolymers were first purified by exhaustive extraction with benzene in a Soxhlet extractor and then dried under vacuum in a drying pistol, at the temperature of refluxing benzene. The carbon analysis was obtained on each sample and each sample was titrated potentiometrically (1,29) and also with a high frequency titrimeter (29a,29b).

A. Elemental Analysis of Copolymers

The analyses of percent carbon in the copolymer samples were carried out by Micro-Tech Laboratories, Skokie, Illinois, see Table XV.

B. Potentiometric and High Frequency Titration of Styrene-Itaconic Anhydride Copolymers

The copolymer samples were also analyzed by titration of the acid function of the itaconic anhydride unit. The titrations were followed potentiometrically (1,29) and with the high frequency titrimeter. Hydrogen ion concentration was measured on a Beckman pH meter, equipped with glass reference and saturated calomel electrodes. The high frequency readings were measured on a titrimeter which has been assembled by Dr. Timnick (29a). Both readings were taken simultaneously and the best value of the end point as determined by consideration of both methods was used.

TABLE XV

COMPOSITION OF STYRENE-ITACONIC ANHYDRIDE COPOLYMERS FROM CARBON ANALYSIS

Copolymer Sample Prepn. Solvent	Catalyst	Extraction	Percent Polym.	Percent Carbon	N_2 Mole Fract. I.A.
Benzene	BzO_2	yes	93.7	69.41	0.574
Benzene	BzO_2	no	93.7	67.64	0.619
Benzene	BzO_2	yes	100.2	69.74	0.564
Benzene	BzO_2	no	100.2	68.91	0.588
Benzene	bis-aso	yes	11.0	69.52	0.570
Benzene	bis-aso	yes	71.4	69.09	0.581
Benzene	bis-aso	no	71.4	67.94	0.614
THF	BzO_2	yes	18.6	68.10	0.608
THF	BzO_2	yes	31.0	71.19	0.526
THF	BzO_2	yes	42.8	72.00	0.505
THF	bis-aso	yes	12.2	70.01	0.557
THF	bis-aso	yes	54.0	70.45	0.546
THF	bis-aso	no	54.0	68.30	0.604

Symbols: THF = tetrahydrofuran

BzO_2 = benzoyl peroxide

bis-aso = bis-aso-isobutyronitrile

I.A. = itaconic anhydride

Calculation of N_2, mole fraction of itaconic anhydride in the copolymer:

$$N_2 = \frac{9600 - 104\ (\text{percent C})}{3600 + 8\ (\text{percent C})}$$

The copolymer samples were titrated in two ways.

1. Aqueous procedure.

An accurately weighed sample (approximately 0.2 gram), was dissolved in acetone. After this 25.00 ml. of standardized sodium hydroxide was added and the solution was heated to drive off the acetone. When the odor of acetone was gone, the solution was titrated with standardized hydrochloric acid. Although this is a titration of the dibasic acid function, the most accurate analyses were obtained by considering the equivalents of acid required for only one carboxyl group. The break due to excess base is often displaced or nonexistent in the aqueous titration.

2. Half ester procedure.

An accurately weighed sample, (approximately 0.2 gram), was dissolved in absolute methanol. The monomethyl ester is formed immediately at room temperature. The solution was titrated with standardized hydrochloric acid after adding 25.00 ml. of standardized sodium hydroxide.

Calculations:

$$\text{Percent itaconic anhydride, by weight} = \frac{(\text{ml. HCl})(\text{N of HCl})}{(\text{sample weight})} \quad 11.2$$

$$M_2 = \frac{13\ (\text{percent I. A.})}{1100 - (\text{percent I. A.})}$$

A summary of the results obtained by the various titration methods used for the analysis of copolymer samples is given in Table XVI. Typical potentiometric titration curves are shown in Figures 23, 25, and 27, and typical high frequency titration curves are shown in Figures 24, 26, and 28.

A comparison of the three methods of copolymer composition determination is listed in Table XVIa.

TABLE XVI

COMPOSITION OF STYRENE-ITACONIC ANHYDRIDE COPOLYMERS DETERMINED BY POTENTIOMETRIC AND HIGH FREQUENCY TITRATIONS

Copolymer Sample Preparation				N_2 Mole Fraction of Itaconic Anhydride	
Solvent	Catalyst	Extraction	Percent Polymerization	Aqueous Procedure	Half Ester Procedure
Benzene	BzO_2	yes	93.7	0.576	0.575
Benzene	BzO_2	yes	100.2	0.561	0.565
Benzene	bis-aso	yes	11.0	0.572	-
Benzene	bis-aso	yes	71.4	0.502	0.505
THF	BzO_2	yes	18.6	0.605	-
THF	BzO_2	yes	31.0	0.524	0.525
THF	BzO_2	yes	42.8	0.508	0.505
THF	bis-aso	yes	12.2	0.561	-
THF	bis-aso	yes	54.0	0.546	0.545
Benzene	BzO_2	no	93.7	0.542	-
Benzene	BzO_2	no	100.2	0.516	-
Benzene	bis-aso	no	71.4	0.538	-
THF	bis-aso	no	54.0	0.482	-

Symbols:

THF = tetrahydrofuran

BzO_2 = benzoyl peroxide

Bis-aso = bis-aso-isobutyronitrile

Figure 23

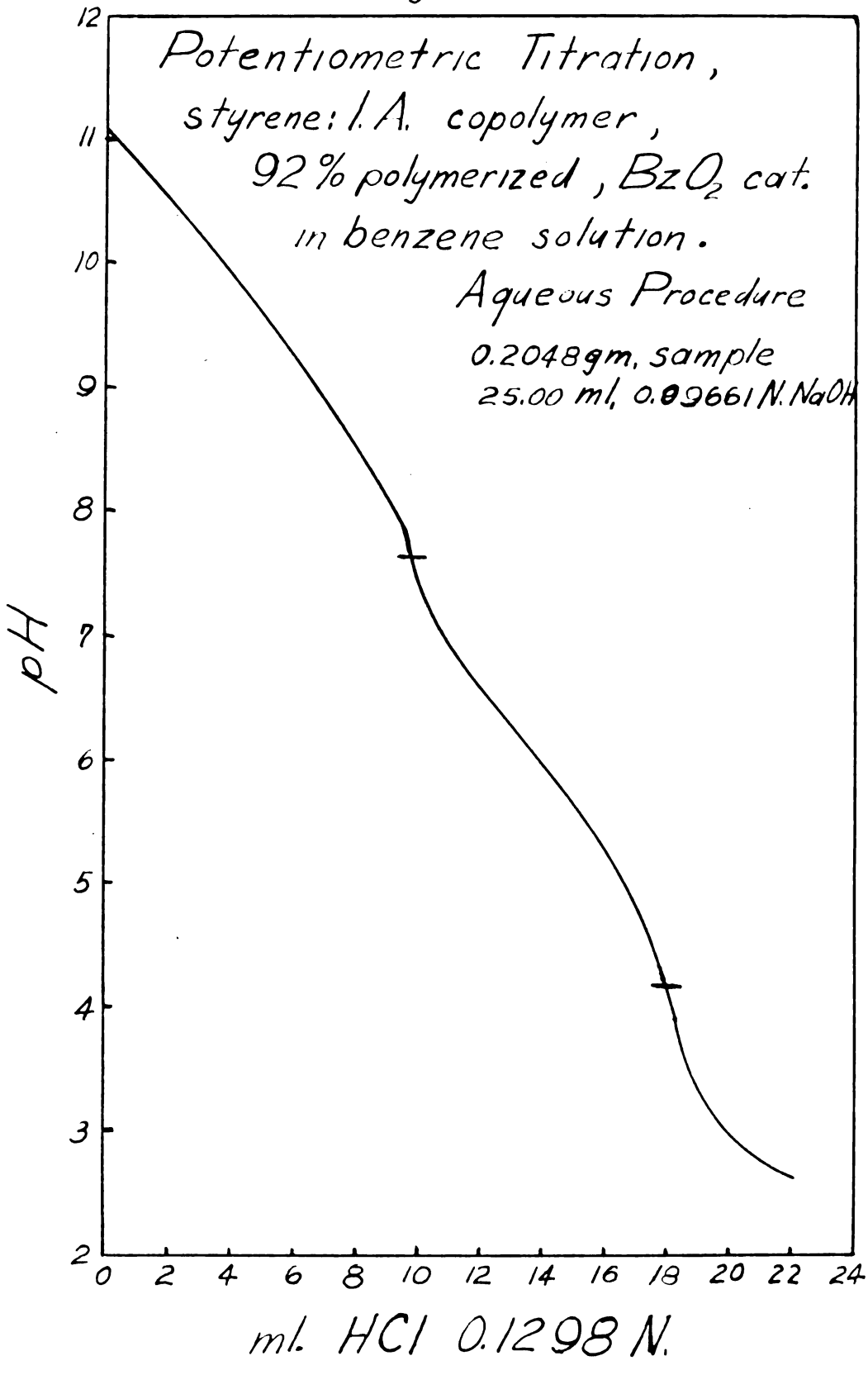

Potentiometric Titration,
styrene: I.A. copolymer,
92% polymerized, BzO_2 cat.
in benzene solution.
Aqueous Procedure
0.2048 gm. sample
25.00 ml. 0.09661 N. NaOH
pH
12
11
10
9
8
7
6
5
4
3
2
0 2 4 6 8 10 12 14 16 18 20 22 24
ml. HCl 0.1298 N.

Figure 24

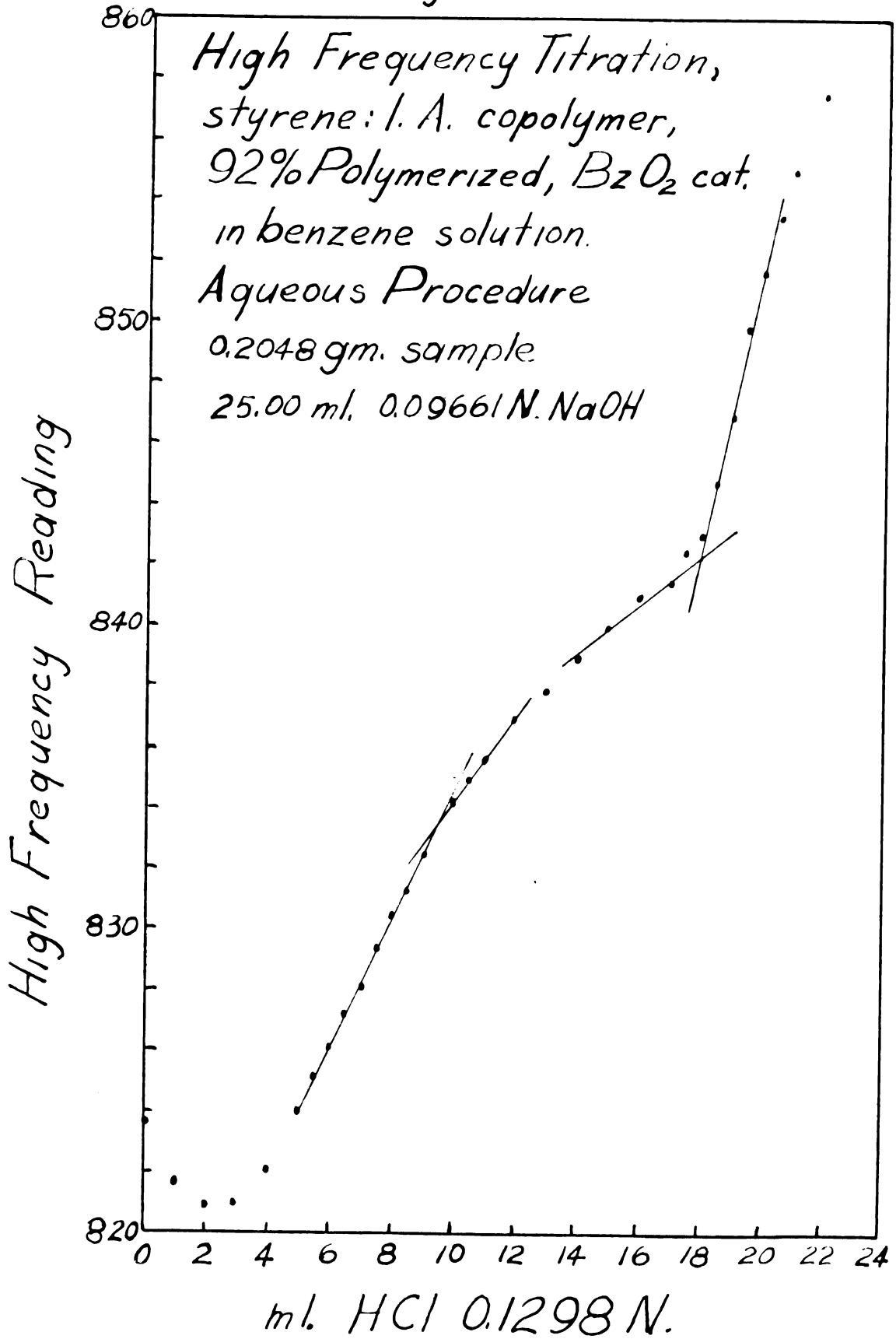

High Frequency Titration,
styrene: I. A. copolymer,
92% Polymerized, Bz_2O_2 cat.
in benzene solution.
Aqueous Procedure
0.2048 gm. sample
25.00 ml. 0.09661 N. NaOH
High Frequency Reading
860
850
840
830
820
0
2
4
6
8
10
12
14
16
18
20
22
24
ml. HCl 0.1298 N.

Figure 25

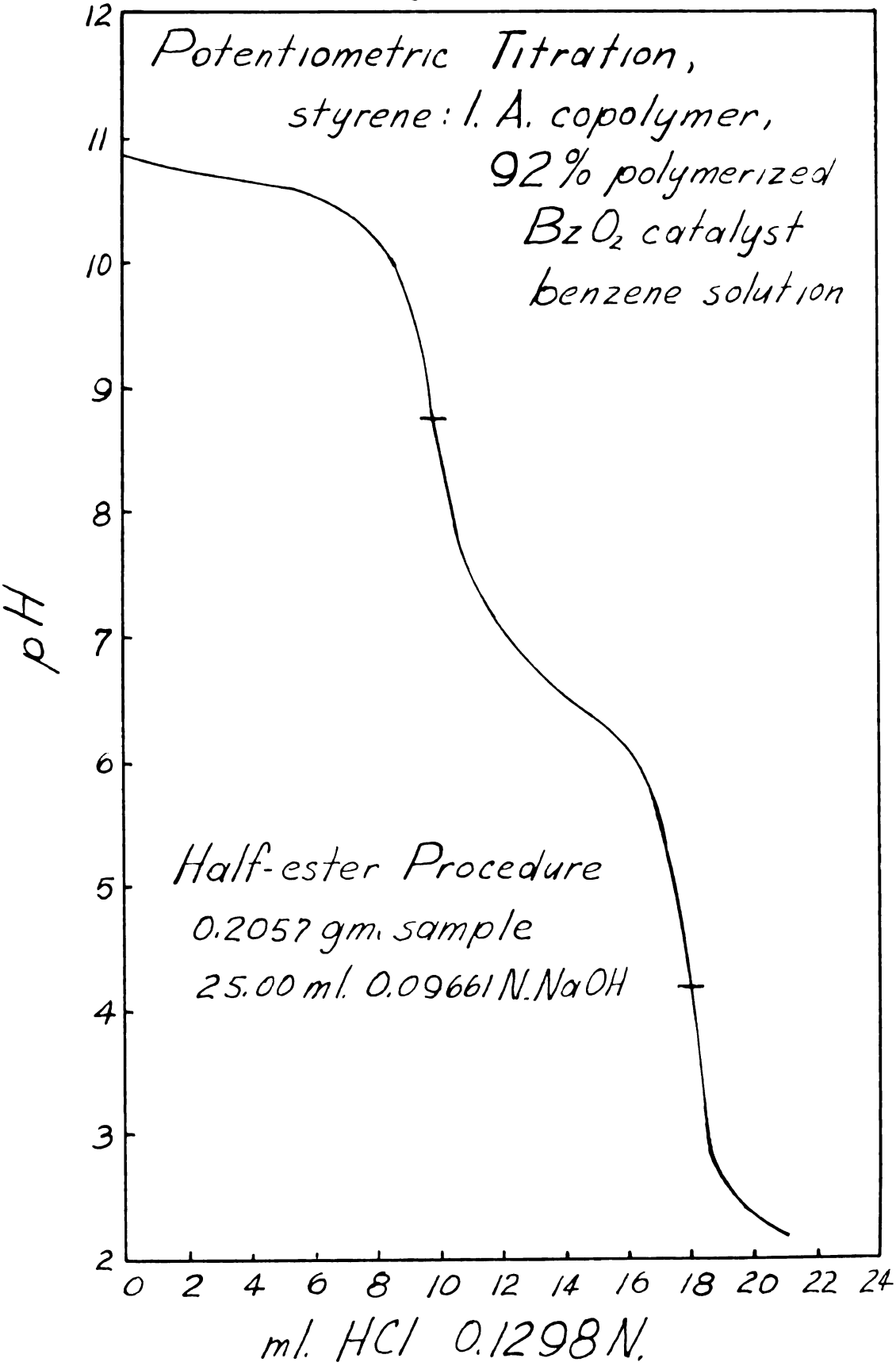

Potentiometric Titration,
styrene : I. A. copolymer,
92% polymerized
Bz_2O_2 catalyst
benzene solution
Half-ester Procedure
0.2057 gm. sample
25.00 ml. 0.09661 N. NaOH
pH
12
11
10
9
8
7
6
5
4
3
2
0 2 4 6 8 10 12 14 16 18 20 22 24
ml. HCl 0.1298 N.

Figure 26

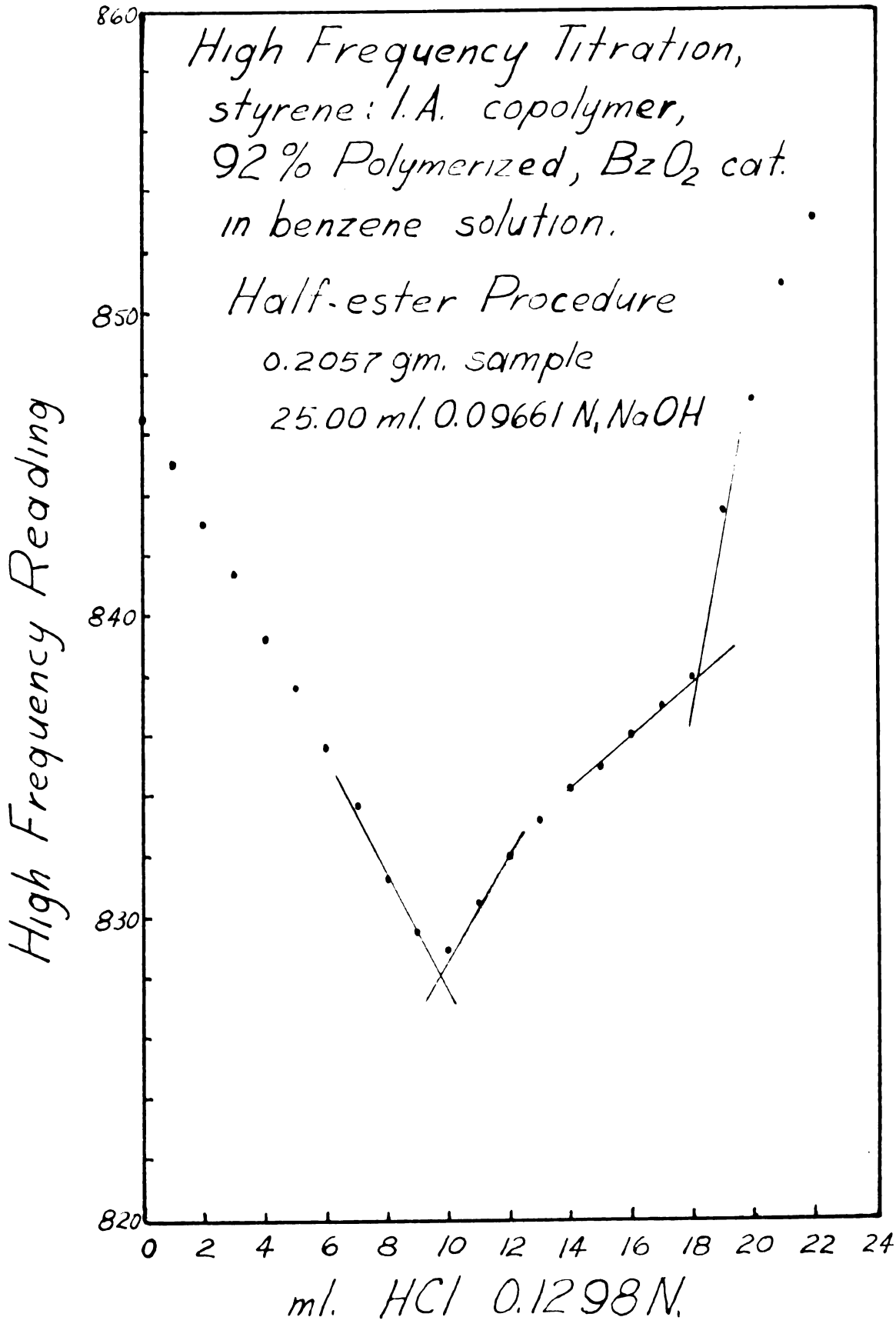

High Frequency Titration,
styrene : I.A. copolymer,
92% Polymerized, Bz_2O_2 cat.
in benzene solution.
Half-ester Procedure
0.2057 gm. sample
25.00 ml. 0.09661 N. NaOH
High Frequency Reading
860
850
840
830
820
0 2 4 6 8 10 12 14 16 18 20 22 24
ml. HCl 0.1298 N.

Figure 27

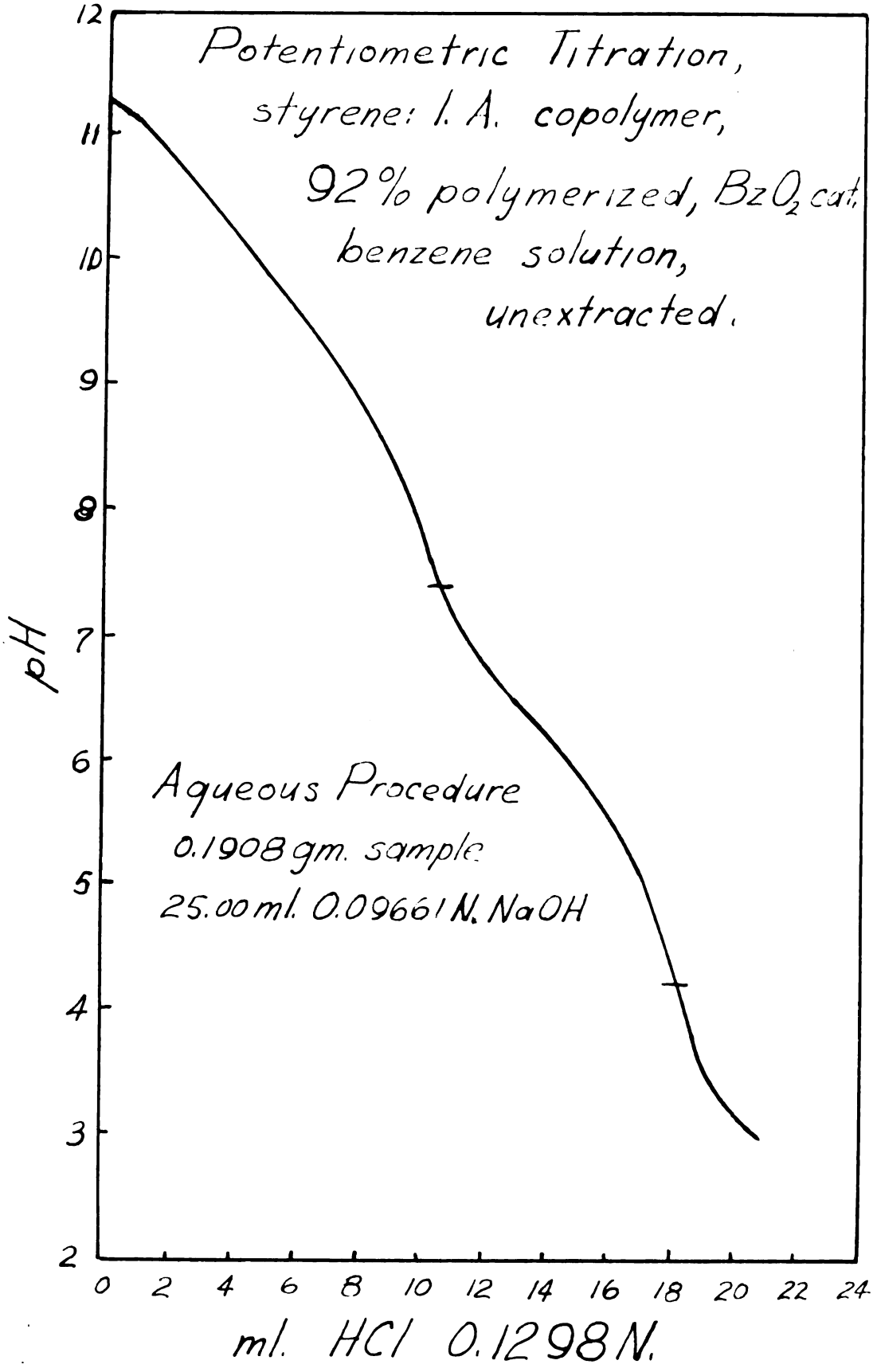

Potentiometric Titration,
styrene: I. A. copolymer,
92% polymerized, BzO_2 cat.
benzene solution,
unextracted.
Aqueous Procedure
0.1908 gm. sample
25.00 ml. 0.09661 N. NaOH
pH
12
11
10
9
8
7
6
5
4
3
2
0 2 4 6 8 10 12 14 16 18 20 22 24
ml. HCl 0.1298 N.

Figure 28

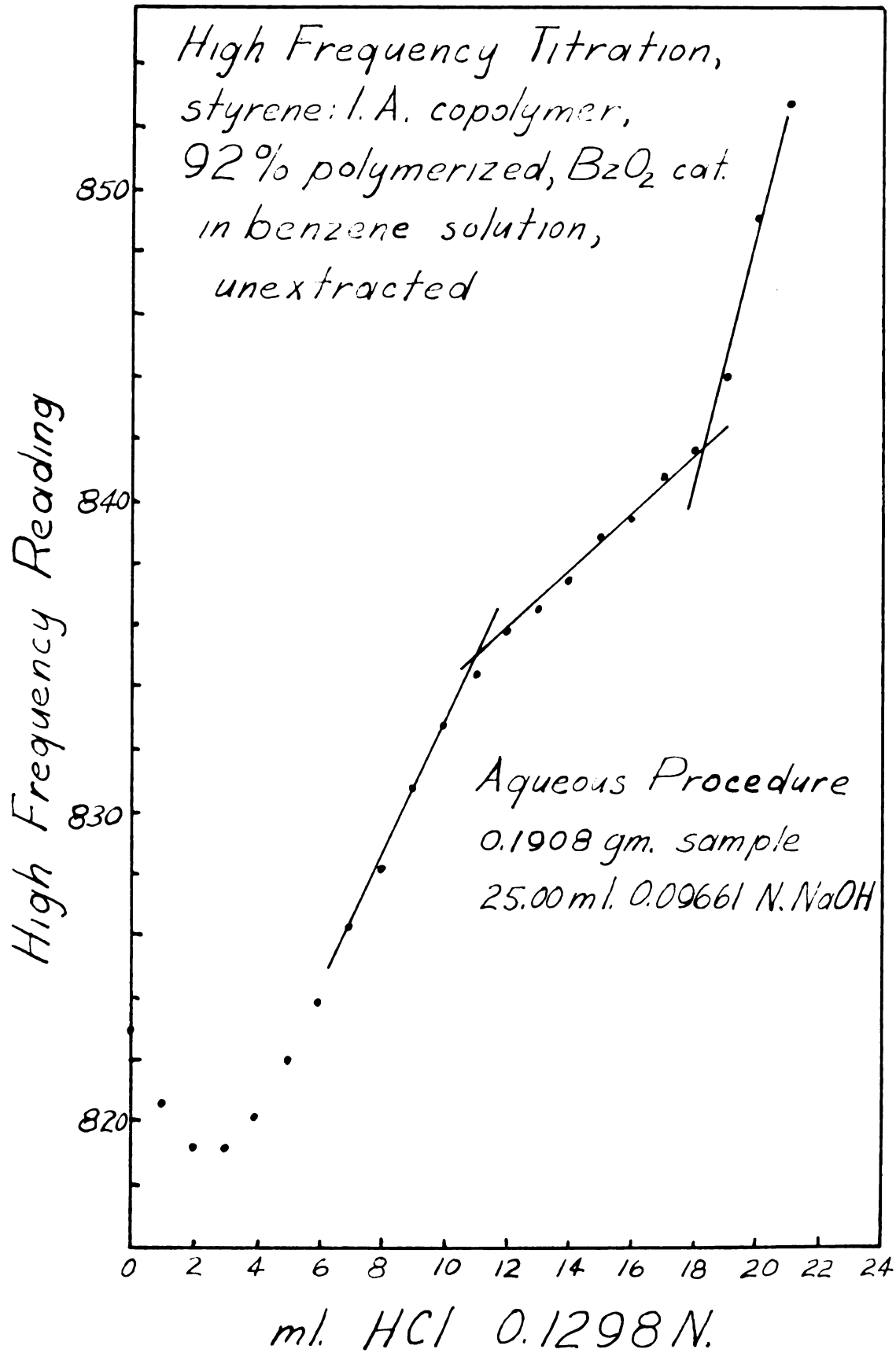

High Frequency Titration,
styrene: I. A. copolymer,
92% polymerized, Bz_2O_2 cat.
in benzene solution,
unextracted
Aqueous Procedure
0.1908 gm. sample
25.00 ml. 0.09661 N. NaOH
High Frequency Reading
850
840
830
820
0
2
4
6
8
10
12
14
16
18
20
22
24
ml. HCl 0.1298 N.

TABLE XVIa

COMPARISON OF METHODS OF ANALYSIS OF COPOLYMER COMPOSITION

Copolymer Sample				N_a Mole Fraction of I. A.		
Solvent	Catalyst	Extraction	Percent Polymerization	Carbon Anal.	Titration	Disappearance of Monomers
Benzene	BzO_2	yes	93.7	0.574	0.576	0.500
Benzene	BzO_2	no	93.7	0.619	0.542	0.500
Benzene	BzO_2	yes	100.2	0.564	0.563	0.500
Benzene	BzO_2	no	100.2	0.583	0.516	0.500
Benzene	bis-azo	yes	11.0	0.570	0.572	0.570
Benzene	bis-azo	yes	71.4	0.561	0.582	0.500
Benzene	bis-azo	no	71.4	0.614	0.538	0.500
THF	BzO_2	yes	18.6	0.608	0.605	0.470
THF	BzO_2	yes	31.0	0.526	0.524	0.477
THF	BzO_2	yes	42.8	0.505	0.508	0.500
THF	bis-azo	yes	12.2	0.557	0.561	0.463
THF	bis-azo	yes	54.0	0.546	0.546	0.480
THF	bis-azo	no	54.0	0.604	0.482	0.430

IV. MOLECULAR WEIGHT OF STYRENE-ITACONIC ANHYDRIDE COPOLYMERS

The molecular weight of a polymer can be measured by any of the following methods (25,39).

a) Sedimentation

b) End group determination

c) Viscosity

d) Cryoscopic properties

e) Osmotic pressure

f) Light scattering

Osmotic pressure, cryoscopic properties and end group determinations all measure properties of the number of particles in solution, hence, a number average molecular weight is obtained:

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i M_i} = \frac{\sum N_i M_i}{\sum N_i}$$

N_i = number of molecules
M_i = molecular weight

Light scattering from a polymer solution, on the other hand, is dependent upon the mass of each particle in solution, hence, a weight average molecular weight is obtained:

$$\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

The viscosity of a polymer solution is a more complicated function of size, shape and number of polymer particles in solution, hence a viscosity average molecular weight is obtained:

$$\bar{M}_v = \frac{\sum (N_i M_i^{(a+1)})}{\sum N_i M_i^{a}}^{1/a}$$

a = a constant

Because an unfractionated polymer sample contains many different molecular weight species, each of the above averages will have a different value. The ratio of the average molecular weight is an indication of the breadth of the distribution of molecular weights. In general the averages are in the order $\bar{M}_w > \bar{M}_v > \bar{M}_n$.

The molecular weights of three copolymers of styrene-itaconic anhydride, were measured in acetone solutions by osmotic pressure and light scattering methods.

A. Molecular Weight of Styrene-Itaconic Anhydride Copolymer by a Osmotic Pressure Method

1. The Osmometer.

The osmometer used was the symmetrical cell block type, described by Fuoss and Mead (30-32). The cell consists of two stainless steel blocks, each of which has carefully machined semicircular ridges with a vertical channel extending from the bottom port to the top port. The membrane was clamped between the two blocks. The outer ridge of each block was slightly higher than the supporting ridges so that the membrane was clamped tight to serve as a gasket. Pins were provided to insure proper alignment of the blocks. A jacket was provided for circulating water through each block to maintain the solution at a constant temperature. However, this was found to be inadequate

temperature control. Therefore, the measurements were made in an air conditioned constant temperature room with the osmometer insulated by packing it in a cardboard box with cheese cloth.

The upper ports lead to glass capillary tubing, which were connected with ground glass joints. The level of liquid was measured in the capillary tubing by means of a cathetometer. Osmotic pressure measurements were made by the static elevation method (33), i.e., the solvent was allowed to diffuse through the membrane until the liquid head was constant and just balanced the osmotic pressure. This method of measurement was used in preference to the dynamic method (31,34).

The lower parts, of each block, were connected to a filling tube through two needle valves. This arrangement allowed filling and draining the cell chambers from the bottom. Both solvent and solution cells were rinsed several times to assure correct concentration and absence of air bubbles.

2. Membranes.

The selection and preparation of the semipermeable membrane to be used for osmotic pressure measurements is most important, as success in preparing a truly semipermeable membrane determines the success of the measurement. Many materials have been used (30) among which are collodion, cellulose, gelatin, rubber sheet, parchment paper, metallic foil and porous glass. Cellulose membranes prepared by denitrating collodion were used for these measurements. Cellulose film was too hard in acetone solution and did not form a tight seal. The procedure (35) used to prepare the membranes follows.

U. S. P. Collodion was used for casting the films. Fifty ml. of collodion were poured into a brass ring, 16 cm. in diameter, which was floating on a clean surface of mercury. A glass jar was placed over the film while drying to avoid bubble formation by rapid evaporation of the solvent. After drying, the collodion films were soaked away from the ring in distilled water, the final bits of mercury were washed away and rough edges cut off the film.

The denitrating reagent was prepared as follows:

100 ml. concentrated ammonia (15 N.)

800 ml. distilled water

100 ml. ethanol

This solution was saturated with hydrogen sulfide by bubbling the gas through the solution. Several films were formed, washed in distilled water, and placed in the denitrating reagent for two hours, with intermittent turning and stirring. After removal from the denitrating reagent the films were washed several times in distilled water followed by successive washings in 50-50 water-ethanol, ethanol, 50-50 ethanol-acetone and finally acetone. The films were kept under acetone and never allowed to dry out.

3. Measurement of osmotic pressure.

a) Styrene-itaconic anhydride copolymer prepared in benzene solvent with benzoyl peroxide catalyst.

The osmotic pressures of acetone solutions of the copolymers of styrene-itaconic anhydride obtained from polymerization in benzene

solvent with benzoyl peroxide catalyst were measured at three concentrations. The results of duplicate measurements at each concentration are shown in Figure 29 where the measured height difference, h, is plotted against time of standing in the osmometer. The osmotic pressure is:

$$w = h \times d$$

where,

w, is the osmotic pressure (gm/cm^2) and d is the density of acetone,

$d = 0.785$ at $25^\circ C$ ($gm/cc.$)

The osmotic pressure is related to the number average molecular weight by the equation:

$$\frac{\pi}{C} = \frac{RT}{M_n} + Bc$$

where

c = concentration of the polymer solution

R = gas constant

T = absolute temperature

B = a constant

From this equation it can be seen that a plot of π/C against C should give a straight line of slope B, and furthermore that at the intercept, (i.e., infinite dilution):

$$\left[\frac{\pi}{C}\right]_0 = \frac{RT}{M_n}$$

The plot of π/C against C is shown in Figure 30, and the calculations are tabulated in Table XVII.

Figure 29

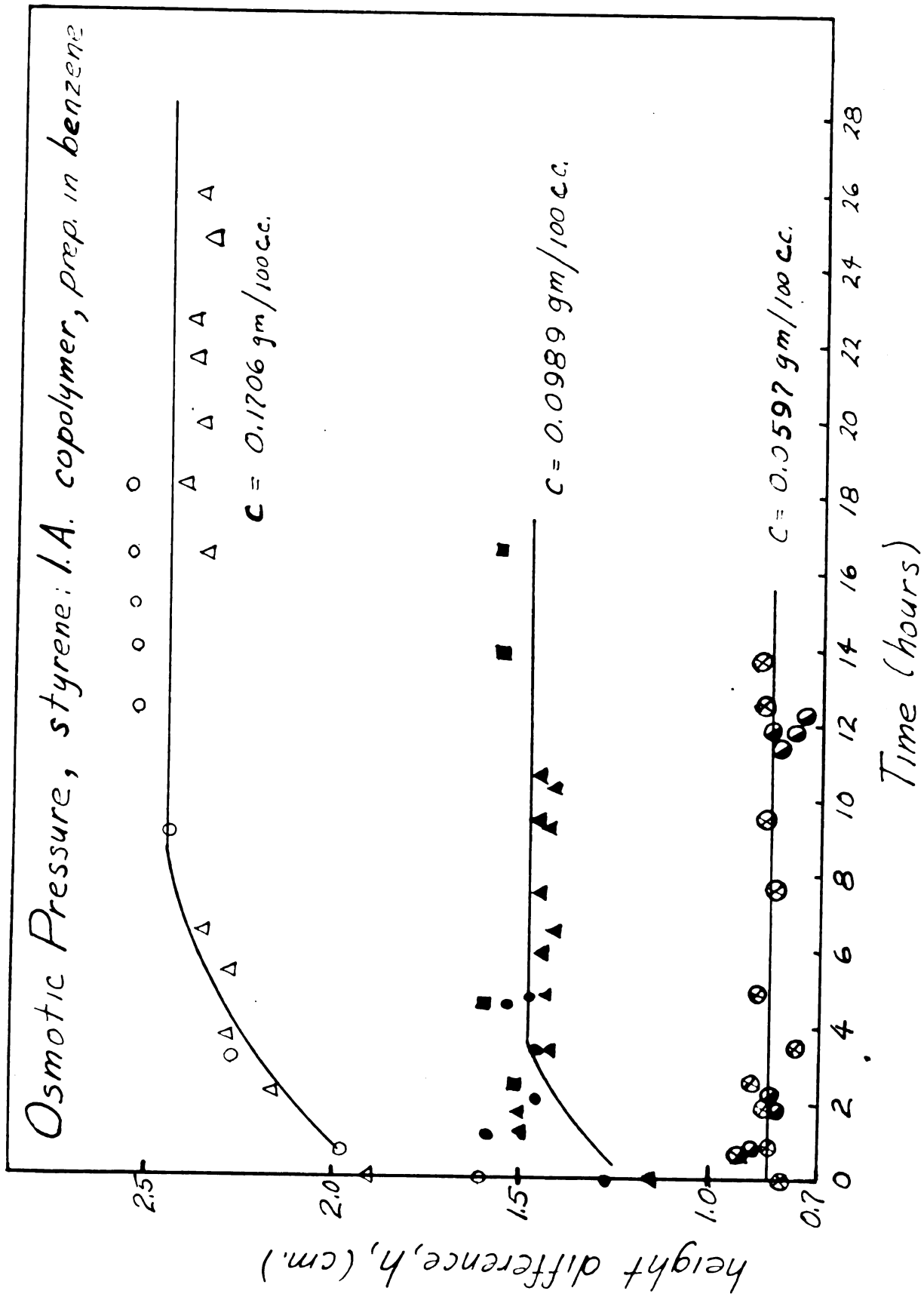

Osmotic Pressure, styrene: I.A. copolymer, prep in benzene
c = 0.1706 gm/100 c.c.
c = 0.0989 gm/100 c.c.
c = 0.0597 gm/100 c.c.
height difference, h, (cm.)
Time (hours)
2.5
2.0
1.5
1.0
0.7
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28

Figure 30

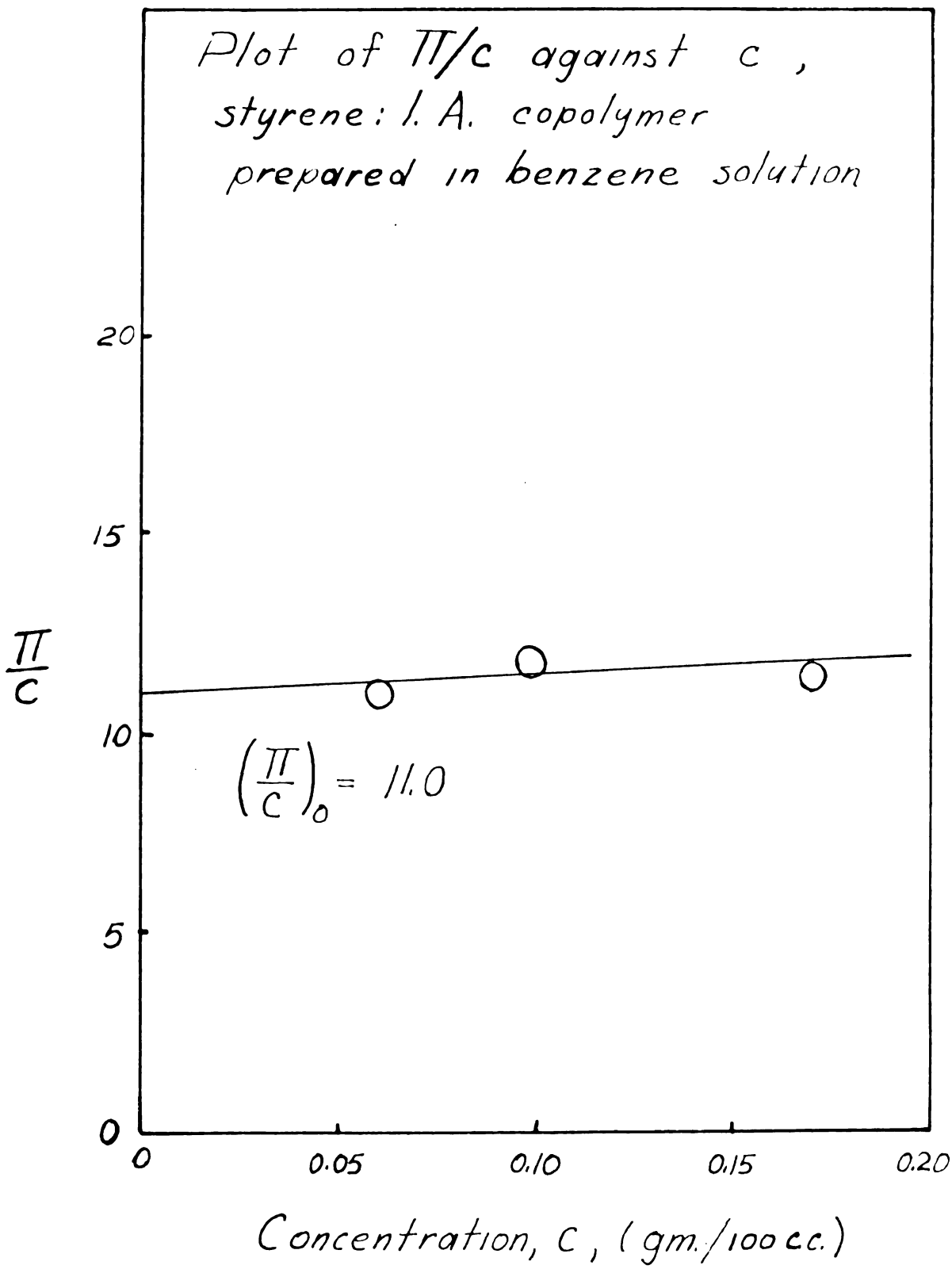

Plot of π/c against c ,
styrene : I. A. copolymer
prepared in benzene solution
π/c
20
15
10
5
0
(π/c)₀ = 11.0
0
0.05
0.10
0.15
0.20
Concentration, c , (gm./100 c.c.)

TABLE XVII

CALCULATION OF $\bar{M}_n$ FOR COPOLYMER OF STYRENE-ITACONIC ANHYDRIDE PREPARED FROM BENZENE SOLVENT WITH BENZOYL PEROXIDE CATALYST

C gm./100 cc.	h cm.	π	π/C
0.1706	2.45	1.92	11.3
0.0989	1.48	1.16	11.7
0.0597	0.83	0.65	10.9

Calculation of $\bar{M}_n$:

$$\left[\frac{\pi}{C}\right]_o = 11.0 = \frac{RT}{\bar{M}_n}$$

$R = 8.479 \times 10^4$ cm.-gm./$^\circ$K/mole

$T = 298^\circ$K

$\bar{M}_n = 23{,}000$

b) Styrene-itaconic anhydride copolymer prepared in tetrahydrofuran solvent with benzoyl peroxide catalyst.

The osmotic pressure of an acetone solution of the copolymer of styrene-itaconic anhydride prepared in tetrahydrofuran solution with benzoyl peroxide catalyst was measured. The results of three measurements are shown in Figure 31 where the measured height difference, h, is plotted against time of standing in the osmometer. No calculation of molecular weight was made because the height difference never reached a constant maximum but increased for a time and then decreased.

B. Molecular Weight of Styrene-Itaconic Anhydride Copolymers by a Light Scattering Method

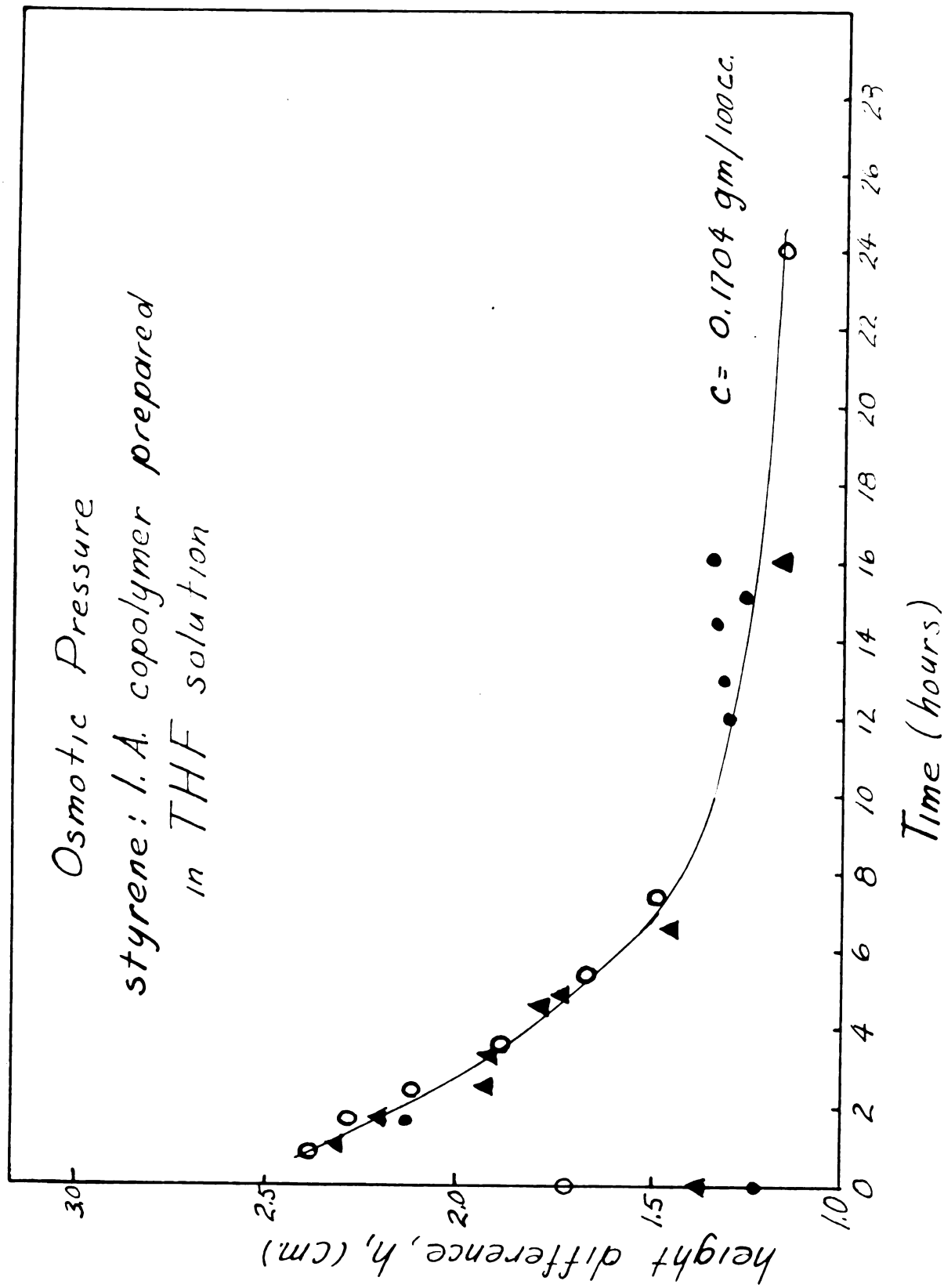
The use of light scattering from dilute solutions of polymers has been adapted to the determination of their molecular weight (36,37,38). The average molecular weight obtained is a weight average and will ordinarily have a different value than the number average found by osmotic pressure measurements for unfractionated samples. The light scattering of styrene-itaconic anhydride copolymers was measured in acetone.

1. The Light Scattering Photometer.

A Brice-Phoenix light scattering photometer (39) was used to measure the amount of light scattered by acetone solution of three styrene and itaconic anhydride copolymers. The essential components of the photometer are:

a) mercury arc lamp

Figure 31


Osmotic Pressure
styrene: I.A. copolymer prepared
in THF solution
c = 0.1704 gm/100cc.
Height difference, h, (cm.)
Time (hours)
1.0
1.5
2.0
2.5
3.0
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28

b) filters, to adjust intensity and to provide monochromatic light either 4358Å, blue, or 5460Å, green.

c) a light tight dark box containing 1) sample cell, 2) photometer, mounted on a calibrated turn-table.

d) recording galvanometer.

The sample cell was semi-circular in shape, to allow light to pass out at any angle without refraction. The turn-table mounting of the photometer permitted the measurement of scattered light at 0°, 45°, 90°, and 135° from the incident light beam or at any desired angle.

2. Procedure for making measurements.

The amount of light, scattered at angles of 0°, 45°, 90° and 135° from the incident beam was measured for six concentrations of each copolymer sample in acetone solution in the following manner.

An acetone stock solution of known concentration (approximately 1%) of the copolymer sample to be measured, was prepared. A weighed quantity of purified and filtered acetone was placed in the sample cell and the scattered light was measured at the several angles mentioned. Increments of stock solution were added, with vigorous stirring, by a magnetic stirrer, weighing before and after each set of light scattering measurements to account for vaporization loss of acetone. With each additional increment of stock solution the scattered light was measured at the several angles mentioned above. The stock solution additions were made by hypodermic syringe, equipped with a filter, two layers of ordinary extra-fine filter paper were used as filtering medium.

3. Outline of calculation of molecular weight from light scattering measurements.

a) The limiting equation.

The limiting equation relating the turbidity, τ_s, of a polymer in solution and the weight average molecular weight, $\bar{M}_w$, is:

$$\left[\frac{Hc}{\tau_s}\right]_o = \frac{1}{\bar{M}_w}\left(\frac{1}{P(\theta)}\right)$$

where:

c = concentration of polymer (gm./ml.)

$\frac{1}{P(\theta)}$ = correction factor from the dissymmetry measurement, $[Z_{45}]_o$.

$H = \frac{32\pi^3 n_o^2 (dn/dc)^2}{3\lambda^4 N_o}$

n_o = refractive index of the solvent as the wave length used for the measurement.

(dn/dc) = increment of change of refractive index for change of polymer concentration.

λ = wave length of light (cm.)

N_o = Avogadro's number

$\tau_s = \tau - \tau_o$

τ = turbidity at 90° of the polymer solution

τ_o = turbidity at 90° of acetone solvent

From the limiting equation it can be seen that a plot of H_c/τ_s values for each concentration of polymer against concentration of the

polymer can be extrapolated to zero concentration to find $[\eta_c/\tau_s]_o$. The value of the weight average molecular weight, $\overline{M}_w$, can then be calculated. The graphs of η_c/τ_s against c for each of the three copolymers measured are shown in Figure 32 and tabulated in Tables XIX, XX, and XXI.

b) Refractive index of acetone, n_o.

The index of refraction of blue mercury light, 4358.35 A^o, in acetone at 25° was found from a plot of refractive index at four wave lengths (41,42), at 19.4° C. From the same source Δn was given as 53 x 10^{-6}/degree C.

$$n \begin{matrix} 19.4^oC \\ 4358A^o \end{matrix} = 1.36725$$

$$n \begin{matrix} 25^oC \\ 4358A^o \end{matrix} = n_o = 1.36523$$

c) Determination of dn/dc.

The incremental change of refractive index of the copolymer solution for incremental change in copolymer concentration was measured on the three acetone stock solutions. A Brice-Phoenix differential refractometer (4C) was used, five readings were averaged for each determination. The calculation of dn/dc from the observed readings are shown below:

$$\frac{dn}{dc} = \frac{k\Delta d}{\Delta c}$$

Δc = concentration of polymer in solution gm./ml.

$k = 9.5300 \times 10^{-6}$ (a constant)

$\Delta d = (d_2 - d_1) - (d_2^\circ - d_1^\circ)_0$

d_1 and d_2 = readings at 0° and 100° for the polymer solution

d_2° and d_1° = readings at 0° and 100° for the solvent solution

Acetone solvent gave a value for $(d_2^\circ - d_1^\circ)$ of 1.30, this was used for all three samples. The values of dn/dc obtained are tabulated in Table XVIII.

d) Calculation of the value of the constant H.

The value of the constant H can be calculated for acetone solutions of styrene-itaconic anhydride copolymer using the equation:

$$H = \frac{32\pi^3 n_0^2 (dn/dc)^2}{3 \lambda^4 N_0}$$

when $n_0 = 1.36528$

$dn/dc = 0.19032$ ml./gm.

$\lambda = 4358.35 \times 10^{-8}$ cm.

$N_0 = 6.023 \times 10^{23}$ $mole^{-1}$

then $H = 1.0275 \times 10^{-5}$ $\frac{(ml.)^2}{gm.} \frac{mole}{cm.^4}$

e) Calculation of, τ_s, the turbidity values.

The turbidities, τ, at each concentration of the copolymer in acetone solution were calculated with this equation:

$$\tau = \frac{i_{90}^\circ}{I_0^\circ} \times \frac{I_0^\circ}{I_0} \times t$$

i_{90}° = intensity of 90° scattered light

TABLE XVIII

DETERMINATION OF dn/dc VALUE OF STYRENE-ITACONIC ANHYDRIDE COPOLYMERS

Styrene:I. A. Copolymer Preparation Solvent	Catalyst	d_2-d_1	C	dn/dc
Benzene	BzO_2	208.5	1.0372×10^{-3}	0.19038
THF	BzO_2	204.5	1.0144×10^{-3}	0.19090
THF	bis-azo	236.0	1.1792×10^{-3}	0.18968

Average value of dn/dc = 0.19032 ml./gm.

i°_{o} = intensity of 0° light, no solute

I°_{o} = intensity of incident light initially, no cell

I_{o} = intensity of incident light for each reading, no cell

$t = \left[\frac{I^{\circ}_{o}}{I_{o}}\right]_{c=0}$ 1.03468 x 10^{-5}

$\tau_{s} = \tau - \tau_{o}$

τ_{s} = turbidity of the solute at 90°

τ_{o} = turbidity of acetone solvent at 90°

The values of τ_{s} are tabulated for each of the three copolymers measured in Tables XIX, XX, and XXI.

f) Determination of the correction factor, (1/P6), from dissymmetry value, $[Z]_{45}^{\circ}$

The intensity of light scattered at angles of 45° and 135° from a polymer solution are related to the shape and size of the polymer molecules in solution. The value for dissymmetry Z_{45} was calculated from this equation:

$$Z_{45} = \frac{i_{45}-(i_{45})_{o}}{i_{135}-(i_{135})_{o}}$$

where

i_{45} = intensity of scattered light at 45° for the polymer solution

$(i_{45})_{o}$ = intensity of scattered light at 45° for the acetone solvent

i_{135} = intensity of scattered light at 135° for the polymer solution

$(i_{135})_{o}$ = intensity of scattered light at 135° for the acetone solvent.

TABLE XIX

TURBIDITY AND DISSYMMETRY VALUES
(Styrene-Itaconic Anhydride Copolymer Prepared in Benzene Solvent with Benzoyl Peroxide Catalyst)

C gm./100 ml.	τ_s	Hc/τ_s	Z_{45}
0.026383	4.0413×10^{-4}	0.6708×10^{-5}	1.14
0.043711	7.0573×10^{-4}	0.7092×10^{-5}	1.15
0.063165	9.1691×10^{-4}	0.7397×10^{-5}	1.13
0.083005	12.0256×10^{-4}	0.7519×10^{-5}	1.15
0.10936	14.9557×10^{-4}	0.7513×10^{-5}	1.19
0.14356	18.7505×10^{-4}	0.7367×10^{-5}	1.17

TABLE XX

TURBIDITY AND DISSYMMETRY VALUES
(Styrene-Itaconic Anhydride Copolymer Prepared in Tetrahydrofuran Solvent with Benzoyl Peroxide Catalyst)

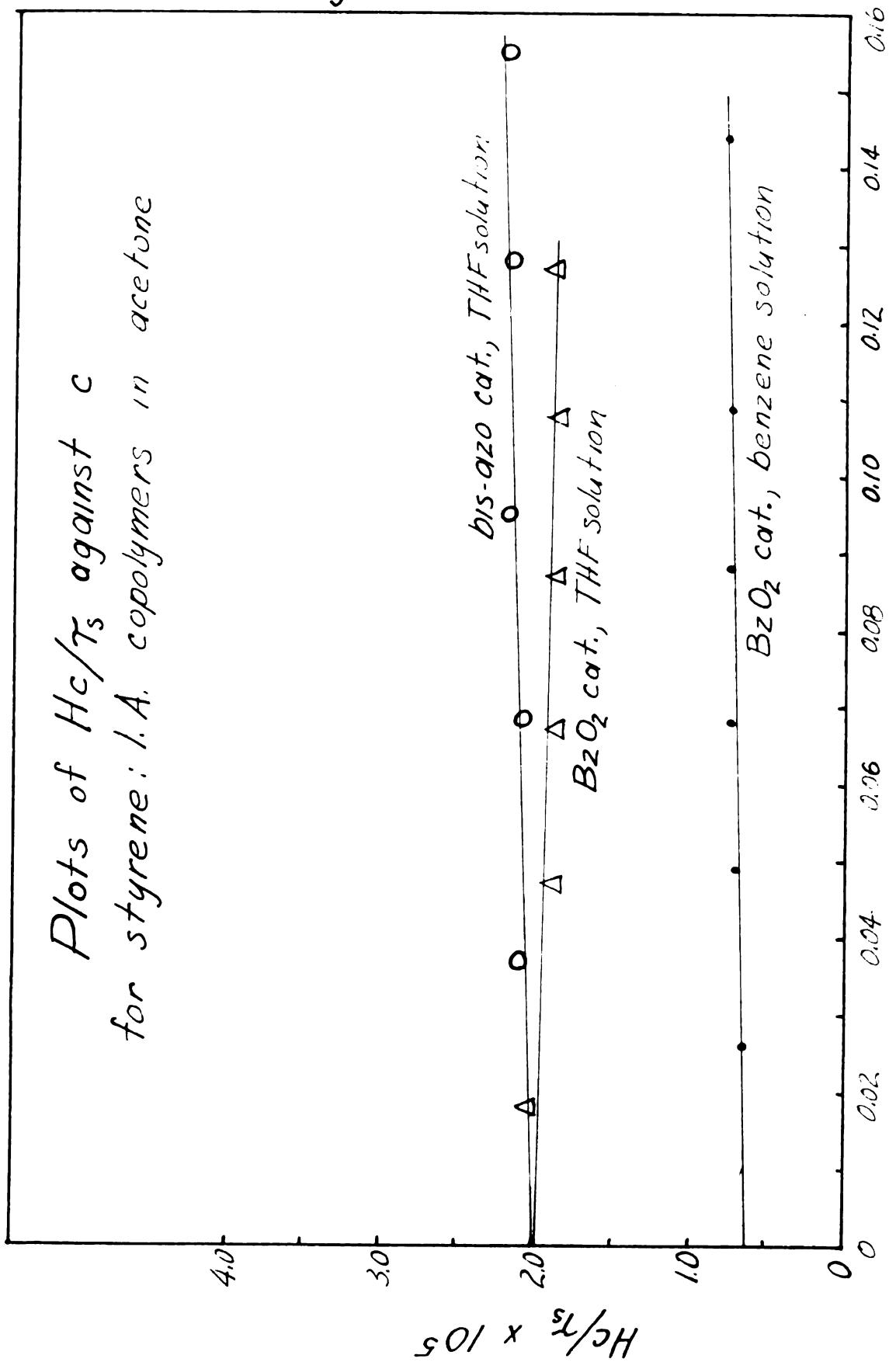
C gm./100 ml.	τ_s	Kc/τ_s	Z_{45}
0.017350	0.8729×10^{-4}	2.0986×10^{-5}	2.40
0.047273	2.5020×10^{-4}	1.8813×10^{-5}	2.81
0.066466	3.6967×10^{-4}	1.8174×10^{-5}	2.76
0.086740	4.7838×10^{-4}	1.8631×10^{-5}	2.80
0.107851	5.9702×10^{-4}	1.8561×10^{-5}	2.70
0.126427	6.8252×10^{-4}	1.9039×10^{-5}	2.82

TABLE XXI

TURBIDITY AND DISSYMMETRY VALUES
(Styrene-Itaconic Anhydride Copolymer Prepared in Tetrahydrofuran Solvent with Bis-azo-isobutyronitrile Catalyst)

C gm./100 ml.	τ_s	Ke/τ_s	Z_{45}
0.036975	1.8150×10^{-4}	2.0933×10^{-5}	2.34
0.063301	3.4128×10^{-4}	2.0564×10^{-5}	2.44
0.095197	4.4719×10^{-4}	2.1873×10^{-5}	2.39
0.128033	6.0706×10^{-4}	2.1679×10^{-5}	2.52
0.155881	7.2770×10^{-4}	2.1911×10^{-5}	2.54
0.176098	9.0161×10^{-4}	2.0068×10^{-5}	2.59

Figure 32


Plots of Hc/τs against c
for styrene : I.A. copolymers in acetone
bis-azo cat., THF solution
Bz O2 cat., THF solution
Bz O2 cat., benzene solution
Hc/τs x 10^5
4.0
3.0
2.0
1.0
0
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
Concentration, c, (gm./100 c.c.)

A plot of Z_{45} values against concentration, C, of the polymer should approximate a straight line which can be extrapolated to zero concentration to give $[Z]_{45}$, the intrinsic dissymmetry. The plots of Z_{45} against C for the three polymers measured are shown in Figure 33. Assuming that the polymer molecules are polydisperse coils a value of $1/P(\theta)$ can be found from published graphs of $[Z]_{45}$ against $1/P(\theta)$ (37,43).

4. Molecular weight calculations.

a) Styrene-itaconic anhydride copolymer sample prepared in benzene solvent with benzoyl peroxide catalyst molecular weight calculations

$$\left[\frac{H_c}{\tau_s}\right]_o = 0.640 \times 10^{-5}$$

$$\left[\frac{H_c}{\tau_s}\right]_o = \frac{1}{\bar{M}_w}$$

$$\bar{M}_w = 156{,}000$$

Assuming polydisperse coils

$$[Z]_{45} = 1.10$$

$$P^{-1}(\theta) = 1.07$$

$$\left[\frac{H_c}{\tau_s}\right]_o = \frac{1}{\bar{M}_w}\left(\frac{1}{P(\theta)}\right)$$

$\bar{M}_w$ = 167,000, corrected for dissymmetry

b) Styrene-itaconic anhydride copolymer prepared in tetrahydrofuran solvent with benzoyl peroxide catalyst, molecular weight calculation.

$$\left[\frac{\eta_{sp}}{C}\right]_{\theta} = 2.00 \times 10^{-5} = \frac{1}{\bar{M}_w}$$

$\bar{M}_w$ = 50,000

$[\eta]_{\theta}$ = 2.70

$\left(1/P(\theta)\right)$ = 2.86

$$\left[\frac{\eta_{sp}}{C}\right]_{\theta} = \frac{1}{\bar{M}_w}\left(\frac{1}{P(\theta)}\right)$$

$\bar{M}_w$ = 143,000, corrected for disymmetry.

e) Styrene-itaconic anhydride copolymer prepared in tetrahydrofuran solvent with bis-azo-isobutyronitrile catalyst molecular weight calculation.

$$\left[\frac{\eta_{sp}}{C}\right]_{\theta} = 2.00 \times 10^{-5} = \frac{1}{\bar{M}_w}$$

$\bar{M}_w$ = 50,000

$[\eta]_{\theta}$ = 2.27

$\left(1/P(\theta)\right)$ = 2.20

$$\left[\frac{\eta_{sp}}{C}\right]_{\theta} = \frac{1}{\bar{M}_w}\left(\frac{1}{P(\theta)}\right)$$

$\bar{M}_w$ = 110,000, corrected for disymmetry

Figure 33

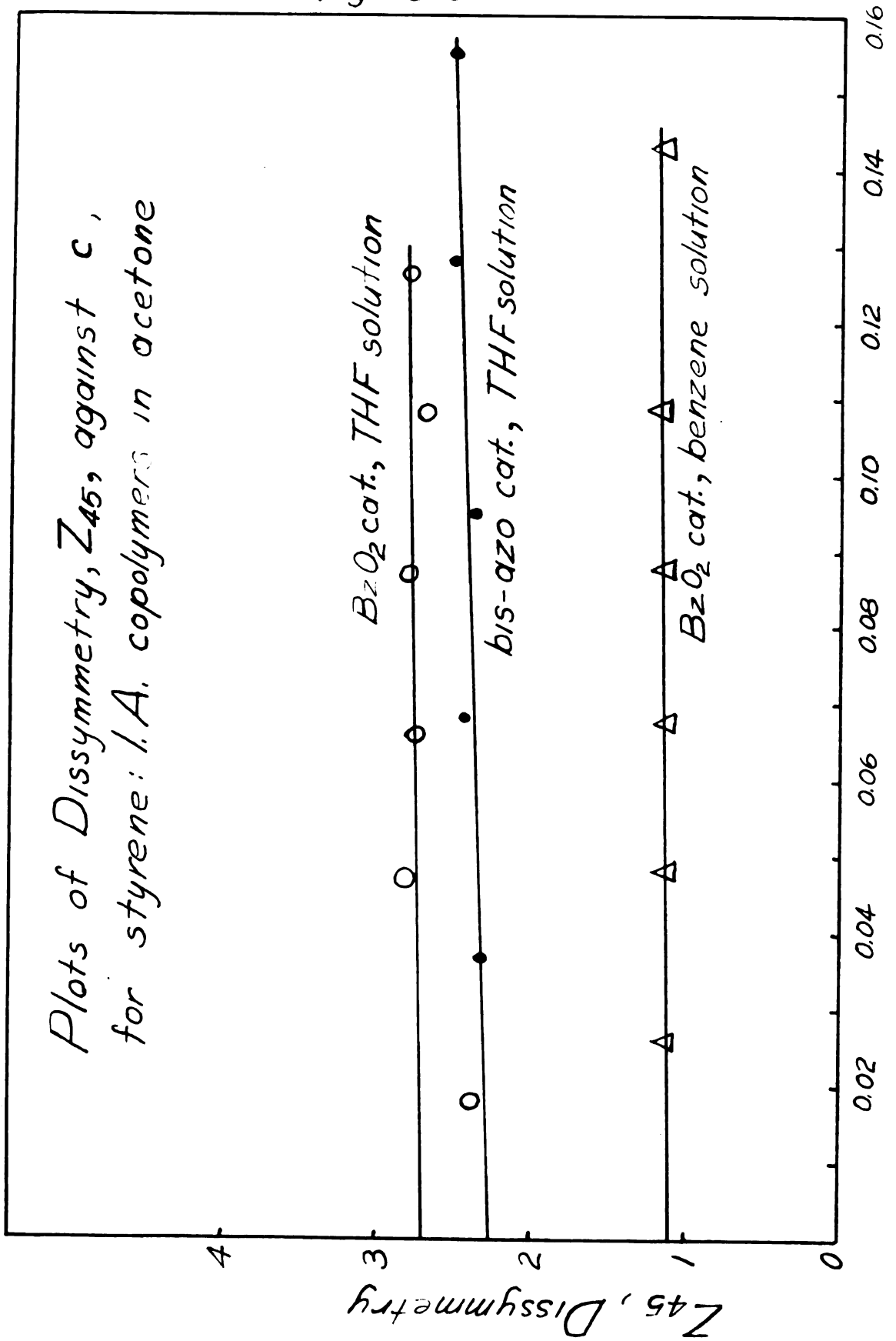

Plots of Dissymmetry, Z_{45}, against c, for styrene : I.A. copolymers in acetone
$Bz O_2$ cat., THF solution
bis-azo cat., THF solution
$Bz O_2$ cat., benzene solution
Z_{45}, Dissymmetry
Concentration, c, (gm/100cc.)
0
1
2
3
4
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16

TABLE XXII

WEIGHT AVERAGE MOLECULAR WEIGHTS OF STYRENE-ITACONIC ANHYDRIDE COPOLYMERS FROM LIGHT SCATTERING METHOD

Styrene I. A. Copolymer Preparation		$\bar{M}_{w_0}$ from 90° Turbidity	$\bar{M}_w$ Corrected for Dissymmetry
Solvent	Catalyst		
Benzene	BzO_2	156,000	167,000
THF	BzO_2	50,000	113,000
THF	bis-aso	50,000	110,000

DISCUSSION

I. QUANTITATIVE DETERMINATION OF ITACONIC ANHYDRIDE AND STYRENE MONOMERS

Methods for the determination of itaconic anhydride monomer could be based on reactions of either the ethylenic unsaturation or the acid anhydride function. Both reactions were investigated experimentally for the purpose of determining itaconic anhydride and styrene concentrations in solutions containing both of these monomers, so that the rate of their copolymerization could be determined from the rate of disappearance of the individual monomers.

The mercuric acetate reaction is a rapid procedure for the determination of certain unsaturated compounds. It has been commonly used for styrene analysis and it was reported by Martin (21) to occur only to a slight extent with the diethyl ester of itaconic acid. It was found that the monoethyl ester reacted to the extent of 27% while itaconic acid reacted to the extent of 92%.

Thus the mercuric acetate method was considered unsatisfactory for the analysis of mixtures of itaconic anhydride and styrene because of the partial reaction with the itaconic anhydride ethylenic unsaturation, which rules out its use for the specific determination of styrene and for the determination of total amount of unsaturation.

The catalyzed bromination method for determination of unsaturation was also found unsatisfactory for itaconic anhydride monomer because of partial bromine addition. However the direct titration of the

double bond with a solution of bromine and acetic acid gave only slight addition of bromine to itaconic anhydride.

The method for determination of itaconic anhydride, with which styrene would not interfere, is the titration of the acid anhydride function. The methods available were three: a) direct titration with base, b) back titration of a added excess of base, or c) titration of the monomethyl ester in methanol. The direct titration of the acid in water solution was chosen as accurate and rapid. This procedure was used to determine itaconic anhydride concentration independent of the presence of styrene monomer. It was of course necessary to separate all the polymer from the copolymer solution before the direct titration could be used on a copolymerization system.

Chemical methods for analysis of styrene must be based on its ethylenic unsaturation. The methods often used for styrene determination, catalyzed bromination and mercuric acetate reaction were not satisfactory for mixtures of itaconic anhydride and styrene for the reasons noted above. The direct bromination procedure did give quantitative analysis of styrene in benzene solutions and was used for the determination of styrene concentration without interference from itaconic anhydride. Unfortunately, tetrahydrofuran is an unsatisfactory solvent for the determination, because a yellow color, formed on first addition of bromine, masked the end point. Uhrig and Lewin (10) have reported that some solvents were unsatisfactory for the method because the end point became indefinite.

II. COPOLYMERIZATION OF STYRENE AND ITACONIC ANHYDRIDE, RATE STUDIES

Four systems were used for the copolymerization of a 1:1 mole ratio of styrene and itaconic anhydride. They were combinations of two solvents and two catalysts.

The two solvents differed in that the copolymer was insoluble in benzene, whereas the copolymer was soluble in tetrahydrofuran.

The two catalysts used were benzoyl peroxide and bis-azo-isobutyronitrile. Benzoyl peroxide is a commonly used polymerization initiator and it is known to undergo an induced decomposition (44-46). Therefore, its decomposition is not a simple first order reaction but may be affected by change of solvent. The decomposition of bis-azo-isobutyronitrile does proceed by a simple cleavage into two free radicals (44,47,48) and its decomposition is independent of solvent change. The copolymerizations were first carried out with benzoyl peroxide. To assure conditions of equal concentration of free radicals in both benzene and tetrahydrofuran solvents the copolymerizations were also run with bis-azo-isobutyronitrile as catalyst.

The composition of the copolymer formed from a mixture of two monomers has been extensively studied and a copolymer composition equation has been formulated (49,50):

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left(\frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \right)$$

where $[M_1]$ and $[M_2]$ are the concentrations of monomers $[M_1]$ and $[M_2]$ in the reaction mixture and $d[M_1]$ and $d[M_2]$ are the concentrations of the monomers in an increment of copolymer. The constants r_1 and r_2 are the monomer reactivity ratios and represent the ratio of reactivity of a free radical formed from one monomer with the corresponding monomer, compared to the reactivity of the free radical with the other monomer.

Wall (51) has suggested for an ideal copolymerization that the reactivity of the monomers is independent of the nature of the free radicals. In this ideal case the monomer reactivity ratios would be the reciprocal of one another and the value of their product, r_1r_2, would be equal to one. However, the usual value found for r_1r_2 is less than one. In extreme cases, in which alternation must occur, the value of r_1r_2 approaches zero. Thus the critical product r_1r_2 may be taken as a measure of the tendency for the monomers to alternate upon entering the copolymer.

The reactivity ratios of styrene, M_1, and itaconic anhydride, M_2, have been determined, from copolymerizations previously carried out in this laboratory (1,2,20). The values found for polymerizations in benzene solvent were:

$$r_1 = 0.01$$

$$r_2 = 0.80$$

$$r_1r_2 = 0.008$$

The values found for polymerizations in tetrahydrofuran solvent were:

$r_1 = 0.10$

$r_2 = 0.30$

$r_1 r_2 = 0.03$

The value of the product, $r_1 r_2$, in both cases indicates a strong tendency of the monomers to alternate in the copolymer. Furthermore, the alternating tendency is stronger in benzene than in tetrahydrofuran.

The nature of the alternating tendency in copolymer formation has been studied. Lewis, Mayo and Hulse (52) suggested some dipole interaction or compound formation between the monomers. Others (13,26,55,54) have shown that the tendency towards alternation is polar in origin. The Alfrey-Price equation (55,56) has been derived on the basis of permanent charges arising from the polarization of radicals and double bonds and assuming that the charge is the same for both the radical and the monomer.

In the specific case of styrene and maleic anhydride there was speculation as to whether or not the copolymerization might proceed <u>via</u> a complex of the two monomers, which would be the reacting species, adding to the growing chain (50). Garrett and Guile (4,57) have shown that this is possible in the case of styrene and maleic anhydride copolymerization and Curtice (1) has found evidence that styrene and itaconic anhydride may copolymerize in a similar fashion. Curtice has shown from the rate of copolymer formation that the reaction was first order with respect to an assumed reactant of a 1:1 complex of styrene and itaconic anhydride.

For the four copolymerizations systems studied first order dependence was found with respect to either styrene or itaconic anhydride concentration, as shown in Figures 13-20. Reaction rate constants were calculated from the slopes of these lines and they are listed in Table XXIII.

The rate constants were nearly equal, whether based on the disappearance of styrene or itaconic anhydride monomer, in each of the four systems. The concentration of a 1:1 complex of styrene and itaconic anhydride could be represented by the concentration of either monomer, and therefore the close approximation of first order dependence with respect to either monomer would indicate that the copolymerization of styrene and itaconic anhydride might proceed <u>via</u> the 1:1 complex of the monomers.

The values of the rate constants, Table XXIII, and relative rates of copolymer formation, Figure 3b, both show that the copolymerization of styrene and itaconic anhydride was faster in benzene, from which it was precipitated, than in tetrahydrofuran, in which it remained in solution. The rate constant, with either benzoyl peroxide or bis-azoisobutyronitrile as catalyst, was twenty times greater for benzene than for tetrahydrofuran solvent.

The large difference in rate of polymerization in the two solvents was probably the result of a large difference in the termination rate constant, k_t, in the two solvents. Considering the case of only one monomer, M, the rate of polymerization, R_p, is determined from the following rate expression (25):

TABLE XXIII

FIRST ORDER REACTION RATE CONSTANTS
(1:1 Styrene:Itaconic Anhydride Copolymerization)

Copolymerization System		k ($Sec.^{-1}$)	
Solvent	Catalyst	From Styrene Concentration	From I. A. Concentration
Benzene	BzO_2	1.6×10^{-4}	2.0×10^{-4}
Benzene	bis-azo	2.6×10^{-4}	2.7×10^{-4}
THF	BzO_2	9.6×10^{-6}	8.3×10^{-6}
THF	bis-azo	13.0×10^{-6}	14.0×10^{-6}

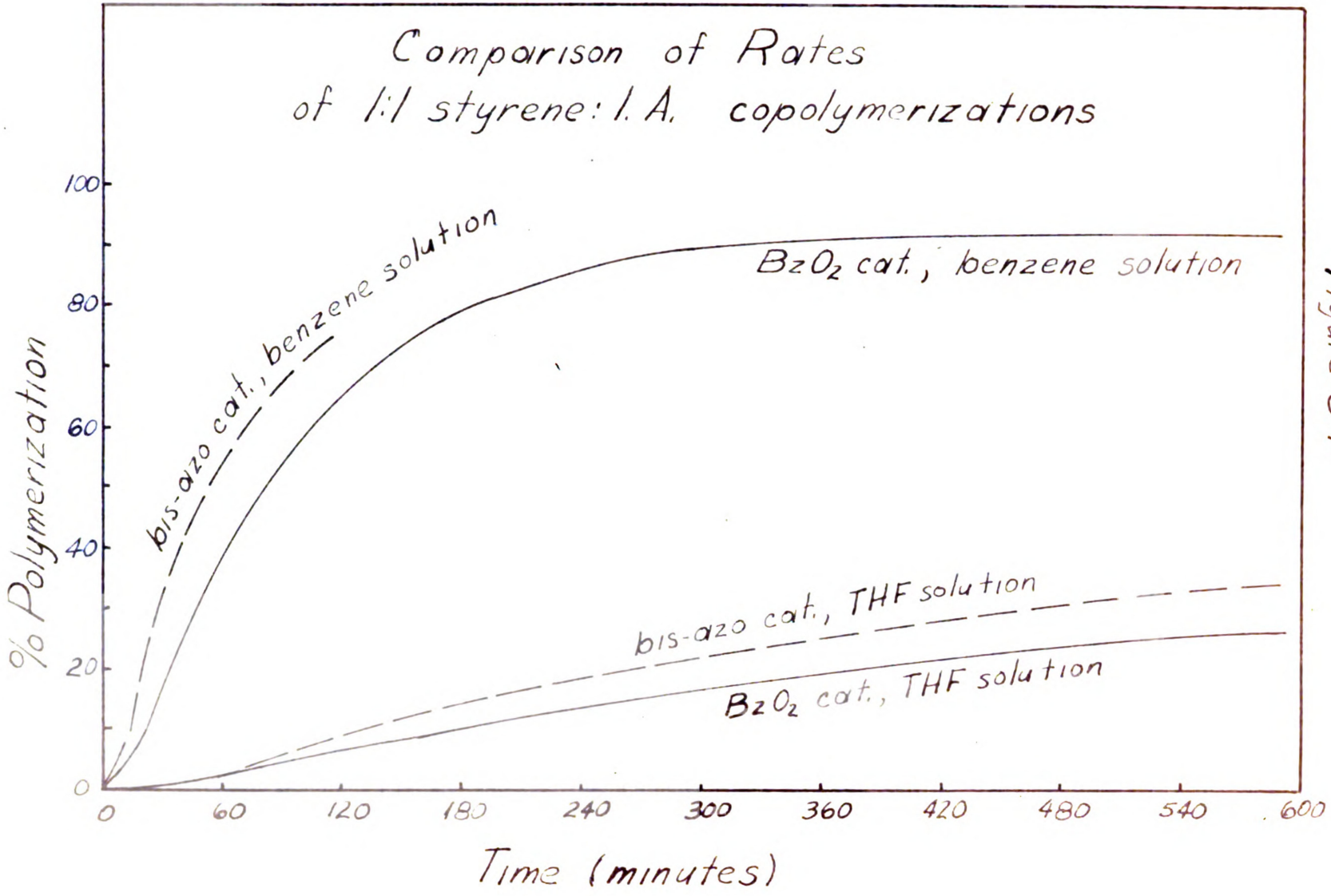

Comparison of Rates
of 1:1 styrene: I. A. copolymerizations
% Polymerization
100
80
60
40
20
0
0
60
120
180
240
300
360
420
480
540
600
Time (minutes)
bis-azo cat., benzene solution
Bz_2O_2 cat., benzene solution
bis-azo cat., THF solution
Bz_2O_2 cat., THF solution

Figure 34

$$R_p = \frac{k_p(R_i)^{\frac{1}{2}}}{k_t^{\frac{1}{2}}} \quad [1]$$

A copolymerisation can be considered analagous to a homopolymerisation, in regard to the dependence of the rate of polymerisation on the various rate constants. An increase in rate would occur if either the rate of initiation, R_i, or the rate constant of propagation, k_p, were increased. An increase in rate would also occur if the rate constant of termination, k_t, was decreased. Faster rates of polymerisation have been observed for acrylonitrile (58) and methyl methacrylate (59) in solvents from which the polymers precipitated than in solvents in which the polymers were soluble. In both cases it was shown that the rate constant of the termination reaction was decreased in the precipitating medium by occlusion of growing chain radicals in the precipitated polymer.

The rate constants were found to be one and one-half times greater with bis-azo-isobutyronitrile than with benzoyl peroxide catalyst in both benzene and tetrahydrofuran solution. This indicates very little participation of either benzene or tetrahydrofuran in the decomposition of the benzoyl peroxide catalyst.

The rates of disappearance of monomers were also plotted according to the integrated rate expression, given by DeBetts (27), for the four copolymerisation systems studied, Figures 21 and 22. The points fall on the predicted straight line for copolymerisation in benzene solvent, using the previously determined values of r_1 and r_2, for copolymerisation

of styrene and itaconic anhydride in this solvent. However, the points are scattered for copolymerisation in tetrahydrofuran solvent using the previously determined values of r_1 and r_2, for copolymerization of styrene and itaconic anhydride in tetrahydrofuran.

The initial copolymer composition which would be predicted from the values of r_1 and r_2 for polymerisations in benzene of 1:1 mole ratio of styrene and itaconic anhydride is 0.64 mole fraction of itaconic anhydride. The composition found by extrapolation of the plot of copolymer composition against time, Figures 3 and 6, to zero time was 0.60 mole fraction of itaconic anhydride. The initial copolymer composition predicted from the values of r_1 and r_2, previously determined for tetrahydrofuran solvent is 0.54 mole fraction itaconic anhydride. Whereas the composition found by extrapolation to zero time, Figures 9 and 12, was 0.40 mole fraction of itaconic anhydride. The previously determined values of r_1 and r_2 for styrene and itaconic anhydride copolymerisation in tetrahydrofuran solution did not predict the initial copolymer composition found in this study from the rate of disappearance of the monomers. Values of r_1 and r_2 were estimated based on the assumption that an azeotropic composition occurs at 0.4 mole fraction itaconic anhydride. In this case the copolymer composition equation reduces to:

$$3r_1 - 2r_2 = 1$$

It was further assumed that the degree of alternation was the same as shown from the previous values of r_1 and r_2 so that:

$$r_1 r_2 = 0.03$$

When these equations were solved simultaneously the following values were found:

$$r_1 = 0.38$$

$$r_2 = 0.08$$

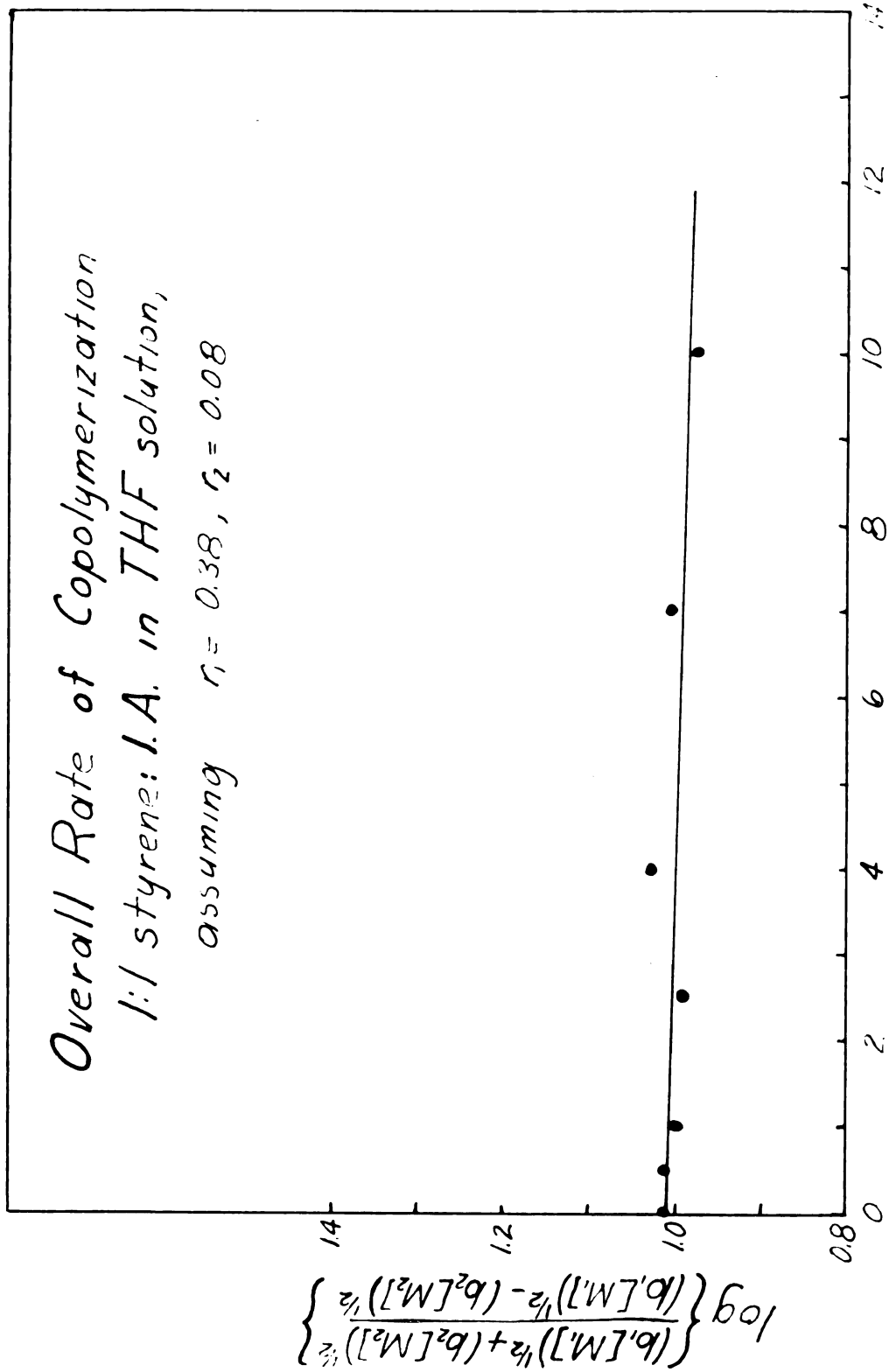
Using these estimated values for r_1 and r_2 the rate of disappearance of the monomers was evaluated from the Mayo-Lewis integrated rate equation. These values are shown in Table XXIV and plotted in Figure 35. The points fall nearer to a straight line than those shown in Figure 22.

TABLE XXIV

OVERALL RATE OF COPOLYMERIZATION OF STYRENE AND ITACONIC ANHYDRIDE
(Assuming $r_1 = 0.38$ and $r_2 = 0.08$ in Tetrahydrofuran Solvent
With Bis-azo-isobutyronitrile Catalyst)

Time Minutes	$\frac{(b_1[M_1])^{\frac{1}{2}} + (b_2[M_2])^{\frac{1}{2}}}{(b_1[M_1])^{\frac{1}{2}} - [b_2[M_2])^{\frac{1}{2}}}$
0	10.3
35	10.4
60	10.0
150	9.8
240	10.7
420	10.2
600	9.5

Figure 35


Overall Rate of Copolymerization
1:1 styrene: I.A. in THF solution,
assuming $r_1 = 0.38$, $r_2 = 0.08$
$\log \left\{ \frac{(b_1[M_1])^{1/2} + (b_2[M_2])^{1/2}}{(b_1[M_1])^{1/2} - (b_2[M_2])^{1/2}} \right\}$
0.8
1.0
1.2
1.4
0
2
4
6
8
10
12
Time (hours)

III. COMPOSITION OF STYRENE-ITACONIC ANHYDRIDE COPOLYMERS

The composition of copolymer samples was determined after first extracting the samples exhaustively with benzene in a Soxhlet extractor. This was done to free the samples of any residual monomers. The agreement between the composition found from titration methods and that found from elemental analysis was good for extracted samples. A difference was noted, however, between the composition of unextracted samples determined by the titration methods and that calculated from elemental analysis. Moreover, the composition of the copolymer predicted from the rate of disappearance of monomers was also quite different from that calculated from elemental analysis of the copolymer.

Some of the reasons why this difference in copolymer composition may have occurred are:

a) Not all of the copolymer was precipitated from the solvent.

b) The copolymer preferentially adsorbed one of the monomers as it was precipitated.

c) A fraction of the polymer was soluble in benzene and was removed in the Soxhlet extraction.

d) Traces of impurities such as monomers, affected the accuracy of titration values.

Because elemental analysis of the crude sample gave a higher fraction of itaconic anhydride than the extracted samples, it was assumed that itaconic anhydride monomer was adsorbed on the copolymer

during the precipitation. Any adsorbed itaconic anhydride may not be removed by benzene extraction, since it may have polymerized to polyitaconic anhydride during the extraction which was carried out for long periods of time at 80° C.

Traces of monomers such as itaconic anhydride have previously been observed, in this laboratory, to affect the results and accuracy of the titration methods employed (29), in determining the composition of styrene-itaconic anhydride copolymer. It was not surprising then, to find differences between the composition found from titration methods and that calculated from elemental analysis of an unextracted copolymer sample.

IV. MOLECULAR WEIGHT OF STYRENE-ITACONIC ANHYDRIDE COPOLYMERS

The number average molecular weight of polymers has been commonly determined by means of osmotic pressure measurements. This method was employed with some success to determine the molecular weight of a styrene-itaconic anhydride copolymer which had been prepared in benzene solvent with benzoyl peroxide catalyst. The number average molecular weight found was 23,000. However, the osmotic pressure of the copolymer prepared in tetrahydrofuran solvent did not attain a constant equilibrium value. The difference in height between the two liquid levels, Figure 31, decreased after reaching a high value in a short time. This would indicate that the membrane was permeable to the copolymer sample. Since the same membrane was used for measurements of both copolymer samples the decrease in height with time would suggest that the copolymer prepared in tetrahydrofuran solvent was of lower molecular weight than that prepared in benzene solvent.

The problem of osmotic membranes, which are permeable to polymer molecules, places a limitation on the measurements of molecular weight by means of osmotic pressure and has been the subject of some recent studies (60-62). The difficulties are greater for unfractionated polymer samples of less than 20,000 number average molecular weight. If the copolymer from tetrahydrofuran solvent is of low molecular weight, possibly some other cryoscopic method could be used in a future study to determine the number average molecular weight.

Measurements of light scattering of polymer solutions have been adapted for the determination of the weight average molecular weight. The method becomes more reliable for high molecular weight polymers, in contrast to the osmotic pressure method, because of the form of the limiting equation. In addition, information can be obtained, from measurements of scattered light at all angles, concerning the size and shape of molecules in solution.

The weight average molecular weights found from 90° scattered light, uncorrected for dissymmetry, Table XXII, were three times larger for the sample prepared in benzene solvent than for the two samples prepared in tetrahydrofuran solvent. The degree of polymerization, $\bar{P}$, can be expressed by (25):

$$\bar{P} = \frac{\text{Rate of Propagation}}{\text{Rate of Termination}}$$

A decrease in the rate of termination would be expected to increase the average degree of polymerization. herefore, the fact that the molecular weight is higher for copolymers prepared in benzene solvent, from which they were precipitated, than for the copolymers prepared in tetrahydrofuran solvent, in which they were soluble, supports the previous evidence of a corresponding increase in the rate of copolymerization in benzene solvent due to a decrease in the rate constant of termination in a precipitating medium.

The chain transfer reaction would also affect the degree of polymerization in the presence of a solvent. The change in average degree of polymerization, $\bar{P}_o$, without chain transfer, is expressed as follows (25):

$$\frac{1}{P} = \frac{1}{P_0} + C\frac{S}{M}$$

Where C is the chain transfer constant, S is the solvent concentration, and M is the monomer concentration.

The chain transfer constant has not been reported for any monomer in tetrahydrofuran, however, it has been reported (63) that both toluene and dioxane have larger chain transfer constants than benzene for both styrene and methyl methacrylate monomers. Therefore, it would be expected that tetrahydrofuran might also have a larger chain transfer constant than benzene. An increase in the chain transfer constant would cause a decrease in the average molecular weight, as was found on changing the solvent from benzene to tetrahydrofuran.

The values of the dissymmetry factor, $[Z]_{45}$, found from the measurement of angular scattered light were larger than expected for low molecular weight polymers. The high $[Z]_{45}$ values could be caused by a rod-like structure of the low molecular weight samples, or minute dust contamination of the solutions. A chain of alternating styrene and itaconic anhydride monomer units is likely to be much stiffer than a polystyrene chain and could possibly be rod-like in solution. Polydisperse coils were assumed to be the shape of the copolymer molecules to obtain the values of the correction factor, $P^{-1}(\theta)$. Further measurements are required before a definite conclusion can be drawn. Furthermore, the presence of very minute dust particles is a source of error in light scattering measurements which has often been difficult to

remove. The presence of dust particles would be expected to affect the dissymmetry value of the lower molecular weight samples more than the higher molecular weight samples. For these reasons, the uncorrected values of the weight average molecular weight are considered to be the more accurate estimate.

CONCLUSIONS

CONCLUSIONS

1. Itaconic anhydride concentration can be determined in the presence of styrene by direct titration with base.

2. Styrene concentration can be determined in the presence of itaconic anhydride by direct titration with bromine in acetic acid, when both monomers are in benzene solution. The method is unsatisfactory to determine styrene concentration in tetrahydrofuran solutions of the two monomers.

3. The rate of copolymerization of 1:1 mole ratio of styrene and itaconic anhydride approximates first order dependence with respect to the concentration of either monomer. The apparent first order rate constants found in four systems are:

System		
Solvent	Catalyst	k ($Sec.^{-1}$)
Benzene	benzoyl peroxide	1.8×10^{-4}
Benzene	bis-azo-isobutyronitrile	2.6×10^{-4}
Tetrahydrofuran	benzoyl peroxide	9.0×10^{-6}
Tetrahydrofuran	bis-azo-isobutyronitrile	13.5×10^{-6}

4. The number average molecular weight, $\overline{M}_n$, of an unfractionated sample of styrene-itaconic anhydride copolymer, prepared with benzoyl peroxide catalyst in benzene solution, was found to be 23,000, by the osmotic pressure method.

5. The weight average molecular weights, $\bar{M}_w$, of three unfractionated samples of styrene-itaconic anhydride copolymers, prepared in different systems, were measured by the light scattering method. The values of $\bar{M}_w$ are:

Copolymer Preparation System		
Solvent	Catalyst	$\bar{M}_w$
Benzene	benzoyl peroxide	156,000
Tetrahydrofuran	benzoyl peroxide	50,000
Tetrahydrofuran	bis-azo-isobutyronitrile	50,000

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LITERATURE CITED

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