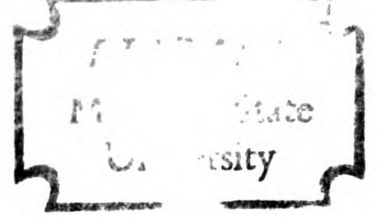
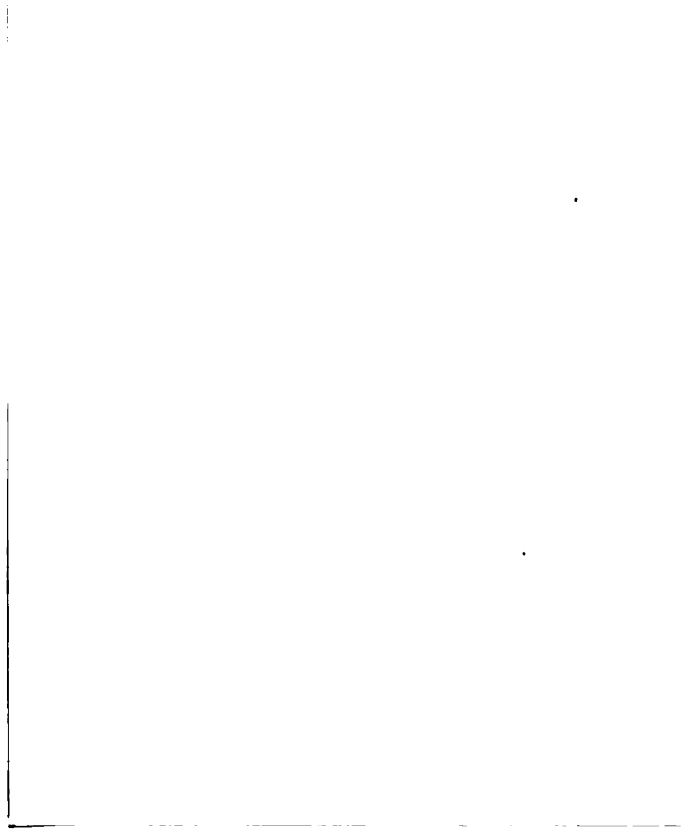


STUDIES ON POLY-(MALEIC ANHYDRIDE CO STYRENE)

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
Everett Geoffrey Meyer
1965





STUDIES ON POLY-(MALEIC ANHYDRIDE CO STYRENE)

by
Everett Geoffrey Meyer

AN ABSTRACT

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

MASTER OF SCIENCE

Department of Chemistry

1965

Approved Ralph L. Guille

ABSTRACT

Copolymers of maleic anhydride and styrene have been prepared with average molecular weights of the following orders of magnitude: 3000, 6000, 9000, 15,000, and 20,000. Polymerization conditions to produce copolymers in these various molecular weight ranges have been described. The lowest molecular weight poly-(maleic anhydride co styrene) was prepared in dimethoxymethane solvent using 0.8 percent benzoyl peroxide as the initiator.

The various copolymers were reacted with gaseous ammonia to yield the ammonium salt of the half amide of the dicarboxylic acid moieties. Total nitrogen content of the ammoniated copolymers was determined by the Kjeldahl method. Ammonium salt nitrogen was determined by a method employing high frequency titration. This method involved the displacement of ammonium ion from the ammonium salt linkages by a strong acid and evaluation of the carboxylate groups thus liberated by the strong acid titrant.

Anhydrous tetrahydrofuran was shown to be a suitable solvent in which to carry out ammoniation of the anhydride copolymers. The ammoniated copolymers were insoluble in tetrahydrofuran and insoluble in acetone. Acetone, a good solvent for the copolymers, was shown to be reactive with gaseous ammonia and yield ammoniated copolymers contaminated with light unstable, dark colored, acetone soluble materials.

Infrared spectra were determined on the various copolymers and their ammoniated derivatives. Analysis and comparison of these spectra indicated the presence of the anhydride linkage in the poly-(maleic anhydride co styrene) samples; and the presence of amide and carboxylate groups

in the ammoniated derivatives. Infrared spectra have been used to distinguish copolymer samples from their ammonia derivatives.

Several polymaleic anhydrides were prepared by the homopolymerization of maleic anhydride. These homopolymers were converted into the ammonium salt of the half amide of the dicarboxylic acid moiety. Homopolymaleic anhydride samples and their ammonia derivatives were then characterized by high frequency titration and nitrogen analysis.

10

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ACKNOWLEDGEMENT

I would like to thank Dr. Ralph Guile for his guidance, encouragement, and patience.

I wish to dedicate this thesis to my parents who also have been patient.

E. Geoffrey Meyer

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INTRODUCTION

This work is a continuation of the studies in this laboratory on the copolymers of maleic anhydride with styrene and their derivatives^{1,2}. Poly-(maleic anhydride co styrene) with an average molecular weight in the order of 50,000 had been reacted with ammonia to produce a nitrogen containing material of unknown structure that exhibited some anti-carcinogenic activity.

The work reported in this thesis was initiated to prepare copolymers of maleic anhydride with styrene of different but known average molecular weights and to convert these copolymers into their ammoniated derivatives. The structures of the ammoniated derivatives were to be studied and their number average molecular weights determined.

Some commercial samples of the poly-(maleic anhydride co styrene) were available from Sinclair Petrochemicals, Incorporated. These samples were advertized to be of relatively low molecular weights based on the property of relatively low solution viscosity. No information was obtainable relative to the method of preparation of these samples, the values of their number average molecular weights, or their structure and purity. The commercial samples were to be used as an immediate source of copolymer material for study and as comparison samples with any that were prepared in the laboratory.

Since the Michigan State Chemistry Department had recently acquired a Vapor Pressure Osmometer - Mechrolab Model 302, which can effectively be used to determine number average molecular weights in the order of 100 - 20,000 it was decided to measure the number average molecular weights of the commercial samples and to attempt to prepare poly-(maleic anhydride co styrene) with number average molecular

weight that would fall within the limits of measurement of the above mentioned instrument.

It was also a part of the problem to ammoniate the commercial samples and to determine the structure and molecular weight of these ammoniated derivatives.

The production of lower molecular weight copolymers and their ammoniated derivatives with average molecular weights in the order of 500 to 5000 was very desirable for several reasons. Low molecular weight polymers would in general be more soluble, more easily produced in the laboratory, more easily reacted and more compatible with biological systems.

Since some of the ammonia derivatives of the poly-(maleic anhydride co styrene) have been shown to be anti-carcinogenic a variation in molecular weight might effect the toxicity and effectiveness. It was hoped that low molecular weight polymers would prove less toxic and more effective.

Any samples of known structure and known molecular weight resulting from this investigation would be submitted for evaluation in certain anti-cancer screens.

Within the course of this work, it was found desirable to prepare and ammoniate polymaleic anhydride. This work also describes the results of the ammoniation of succinic anhydride as a model reaction for the investigation of the reaction of the maleic anhydride moiety in a copolymer.

HISTORICAL

Copolymers of maleic anhydride and styrene have been treated with ammonia under varying conditions to yield several products. Aqueous ammonia produces the mono- or diammonium salts of the poly-(maleic anhydride co styrene) 3,4,5,6. When heat was applied during the treatment with aqueous ammonia followed by heating the initial reaction product in vacuo the imide of poly-(maleic anhydride co styrene) was formed⁷.

Ammonium salts of poly-(maleic anhydride co styrene) were also prepared by dry blending equivalent amounts of ammonium carbonate or ammonium bicarbonate with the copolymer⁵.

When the copolymer was dissolved in an anhydrous medium and gaseous ammonia passed through the solution the amide of poly-(maleic anhydride co styrene) was formed⁸. It also has been reported that reacting the copolymer with gaseous ammonia in anhydrous tetrahydrofuran yielded the ammonium salt of the half amide⁴.

Poly-(maleic anhydride co styrene) dissolved in anhydrous acetone and reacted with gaseous ammonia under pressure quantitatively formed the imide⁹.

Orange colored amidated polymers were formed when the copolymer of maleic anhydride and styrene in acetone solution was treated with p-aminobenzoylacetanilide or benzoyl acetic acid p-aminoanilide¹⁰. Likewise, amidation products were the result of reacting poly-(maleic anhydride co styrene) with N-methylaurylamine or N-methyloctylamine¹¹.

While the copolymer of maleic anhydride and styrene has been prepared in this laboratory, little work has been

done on the reaction of these copolymers with gaseous ammonia and the characterization of these ammonia derivatives^{1,2}.

The synthesis of polymaleic anhydride was reported recently and a search of the literature revealed no published data on its reaction with gaseous ammonia¹².

Chrysomelidae

FART A

REAGENTS AND INSTRUMENTAL

James M. Smith, Jr., Secretary

REAGENTS

1. Benzene

Thiophene free benzene was dried over sodium metal and distilled; boiling range 80-81°C.

2. Acetone

The acetone was purified by washing with silver nitrate and sodium hydroxide. The acetone was then filtered and stored over calcium chloride. Finally it was distilled from potassium permanganate; boiling range 56-57°C.

3. Tetrahydrofuran

Tetrahydrofuran obtained from Eastman Chemicals was stored over potassium hydroxide, refluxed with lithium aluminum hydride, and distilled; boiling range 65-66°C.

4. Methanol

Absolute methanol was dried by refluxing with magnesium turnings and distilled; boiling point 64.5°C.

5. Chloroform

The chloroform was dried over calcium chloride, distilled, and stored over calcium chloride; boiling range 60-61°C.

6. Benzoyl peroxide

Eastman Kodak, Reagent grade.

7. Maleic anhydride

The maleic anhydride (Fisher Scientific Co., Reagent grade) was purified by distillation; melting point 53°C.

8. Ammonia

The Matheson Company, Anhydrous.

9. Succinic Anhydride

The succinic anhydride was purified by recrystallization from acetyl chloride; melting point 120°C.

10. Styrene

The styrene monomer (Dow Chemical Company) 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.

11. Dimethoxymethane

Eastman Organic Chemicals, Reagent grade.

12. Dioxane

Technical grade dioxane was refluxed with 1.8 N HCl under a flow of nitrogen gas and stored over KOH pellets. It was then refluxed with sodium metal and distilled from the sodium metal; boiling range 101-102°C.

INSTRUMENTAL

1. pH Meter

A Beckman H₂ pH meter, with glass-saturated calomel electrode pair.

2. Infrared Spectrophotometer

A Perkin-Elmer 237B Double Beam Recording Infrared Spectrophotometer.

3. Vapor Pressure Osmometer

A Mechrolab Vapor Pressure Osmometer - Model 302 was used. The operation temperature was 37°C. for all determinations. The K value for acetone solvent was determined with benzoic acid and found to be 375. The K value for water solvent was determined with potassium acid phthalate and found to be 132.

PART B

THE COPOLYMER OF MALEIC ANHYDRIDE AND STYRENE

1. The first part of the document is a list of names and titles, including "The Hon. Mr. Justice" and "The Hon. Mr. Justice".

PREPARATION OF THE COPOLYMER OF MALEIC ANHYDRIDE AND STYRENE

The copolymerization of maleic anhydride and styrene was carried out in a one liter, three neck, round bottom flask with ground glass joints. The flask was equipped with a mechanical stirrer, a reflux condenser, and a gas inlet tube. A 50:50 mole ratio of maleic anhydride and styrene was reacted in five hundred milliliters of the appropriate solvent. Benzoyl peroxide initiator was used at 0.5 weight percent, based on the total monomer weight. Since approximately 42 grams of copolymer were needed for studies 0.2 mole of each monomer was copolymerized. At 100 percent conversion, this would yield the required amount of copolymer.

The appropriate weighed amount of maleic anhydride was dissolved in refluxing solvent. When the maleic anhydride had dissolved completely, the styrene was introduced into the flask and allowed to mix with the maleic anhydride solution for a few minutes. After this the benzoyl peroxide initiator was added and the reaction allowed to proceed until a good yield of copolymer was evident as indicated by the amount of precipitation which had occurred.

Purified nitrogen was introduced into the flask by means of the gas inlet tube prior to the addition of the maleic anhydride and a constant flow of nitrogen gas was maintained through the reaction mixture during the entire procedure to insure a nitrogen atmosphere at all times. The reaction was carried out at the refluxing temperature of the solvents.

Upon completion of the polymerization, the copolymer was filtered by suction and washed four times with the same solvent in which it had been prepared. The copolymer was then dried in a desiccator under vacuum.

1. *Phragmites australis* (Cav.) Trin. ex Steud.

The dried copolymer was extracted with benzene in a Soxhlet extractor for at least 168 hours. After the extraction, the copolymer was again dried under vacuum in a desiccator. Analytical samples were further dried in vacuo in an Abderhalden drying pistol heated by refluxing acetone (B.P. 56.5°C.) for a period of 24 hours.

Poly-(maleic anhydride co styrene) was prepared in chloroform, dimethoxyethane, benzene¹³, and tetrahydrofuran¹³ by the above procedure.

The samples of poly-(maleic anhydride co styrene) which were acquired from Sinclair Petrochemicals, Incorporated, were subjected to Soxhlet extraction with benzene for at least 168 hours, followed by drying in vacuo in a desiccator. Samples for analysis were dried in vacuo in an Abderhalden drying pistol heated by refluxing acetone (B.P. 56.5°C.).

MOLECULAR WEIGHT OF POLY-(MALEIC ANHYDRIDE CO STYRENE)

Number average molecular weights for various samples of poly-(maleic anhydride co styrene) were determined using a Mechrolab Vapor Pressure Osmometer. The copolymer samples were dissolved in acetone for the determination. The results are listed in Table I and representative curves are shown in Figures 1 and 2.

Sample Calculation

$$\text{Number average molecular weight} = \frac{K}{\Delta R/c(c \rightarrow 0)}$$

K = calibration constant.
 ΔR = Resistance.
 c = Concentration (grams/liter).

Table I

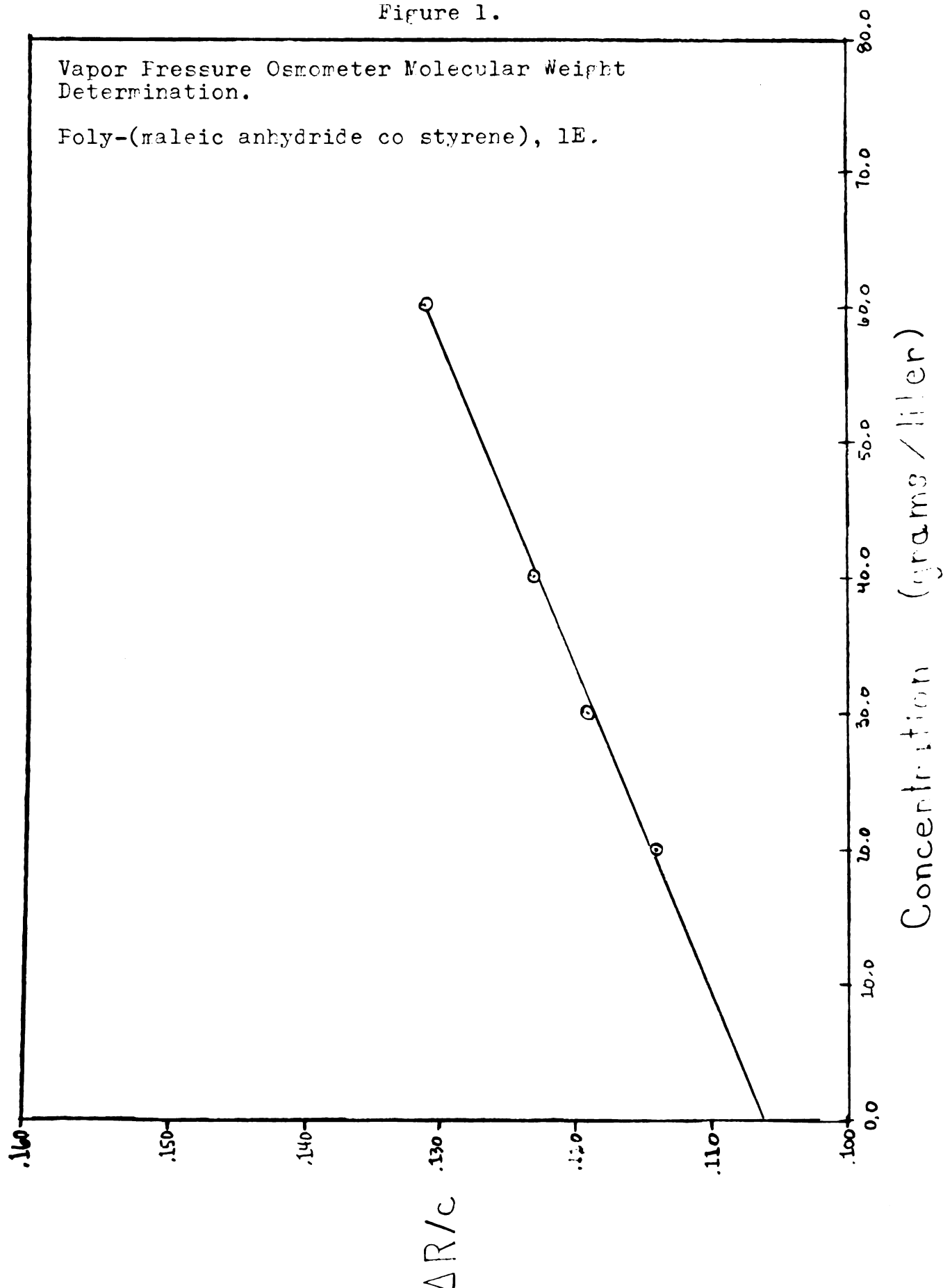
Molecular Weight of Poly-(maleic anhydride co styrene)

<u>Sample Number</u>	<u>Preparation Solvent</u>	<u>Molecular Weight</u>
1E*	Dimethoxymethane	3,540
2E	Benzene	20,400
3E	Chloroform	9,200
4E	Tetrahydrofuran	6,640
Sinclair Resin 2000A**		1,790
Sinclair Resin 3000A		2,100
Sinclair Resin 4000A		670
Sinclair Resin 5000A		23,400
Sinclair Resin 7000A		12,900

* The E designation indicates poly-(maleic anhydride co styrene).

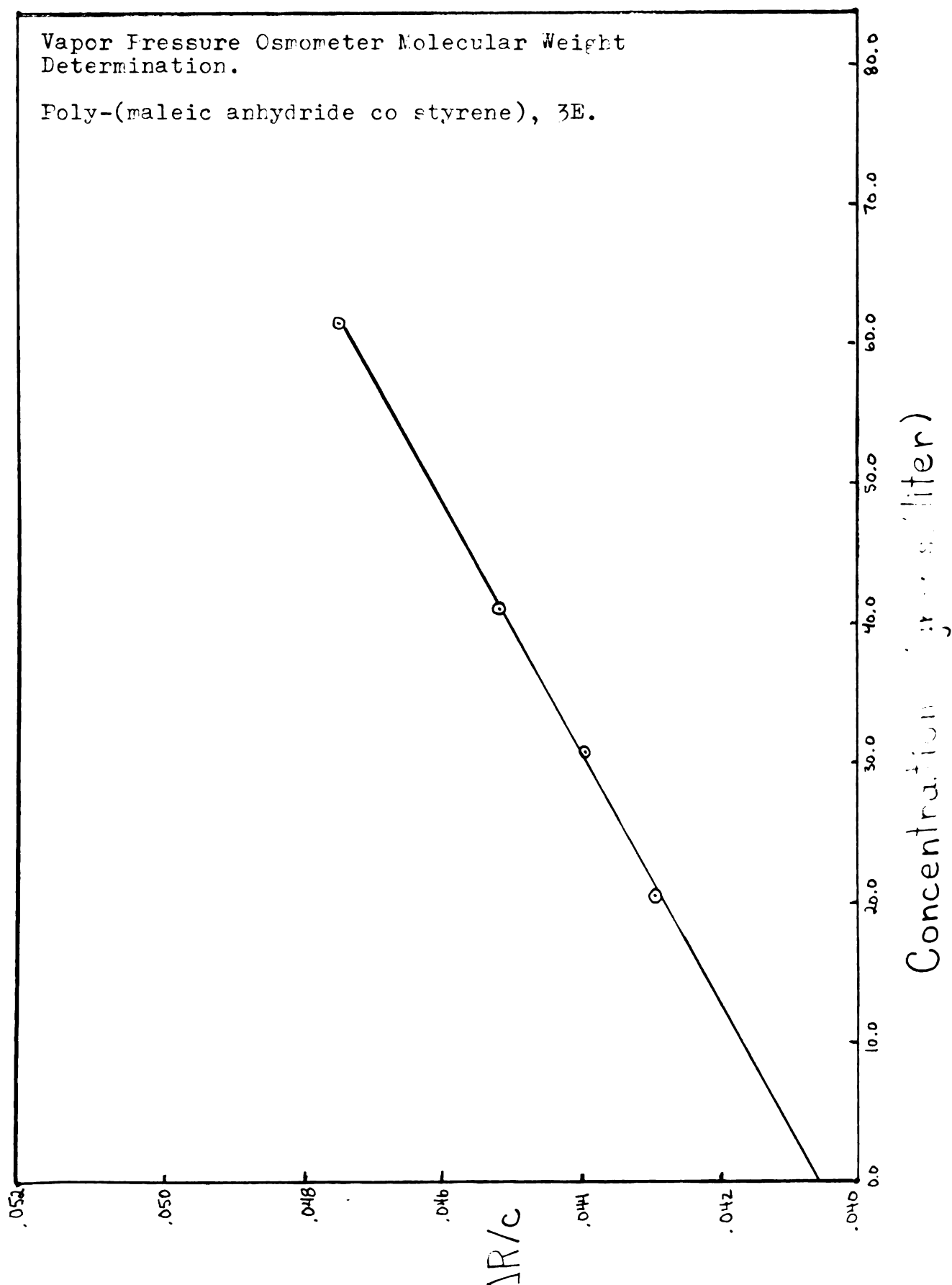
** The solvent and method of preparation of the Sinclair Resins was unknown.

Figure 1.



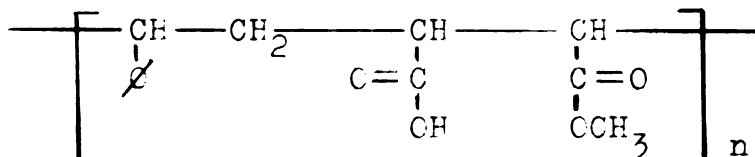
1. 2. 3. 4. 5. 6. 7. 8. 9. 10. 11. 12. 13. 14. 15. 16. 17. 18. 19. 20. 21. 22. 23. 24. 25. 26. 27. 28. 29. 30. 31. 32. 33. 34. 35. 36. 37. 38. 39. 40. 41. 42. 43. 44. 45. 46. 47. 48. 49. 50. 51. 52. 53. 54. 55. 56. 57. 58. 59. 60. 61. 62. 63. 64. 65. 66. 67. 68. 69. 70. 71. 72. 73. 74. 75. 76. 77. 78. 79. 80. 81. 82. 83. 84. 85. 86. 87. 88. 89. 90. 91. 92. 93. 94. 95. 96. 97. 98. 99. 100.

Figure 2.



HIGH FREQUENCY TITRATION OF POLY-(MALEIC ANHYDRIDE CO STYRENE)

Accurately weighed (± 0.0001 gram) samples of approximately 0.1 gram of poly-(maleic anhydride co styrene) were refluxed with absolute methanol until the copolymer dissolved. The following copolymer derivative was formed¹⁴:



Fifteen milliliters of 0.1000 N NaOH were added to the product in order to form the sodium salt of the half ester. This was then titrated with 0.1000 N HCl. The titration was followed with a pH meter and a high frequency titrimeter^{14,15}. The results are listed in Table II. Figure 3 shows a representative curve.

Calculation

EW = equivalent weight of maleic anhydride moiety.

NE = number of equivalents of carboxylate groups from titration.

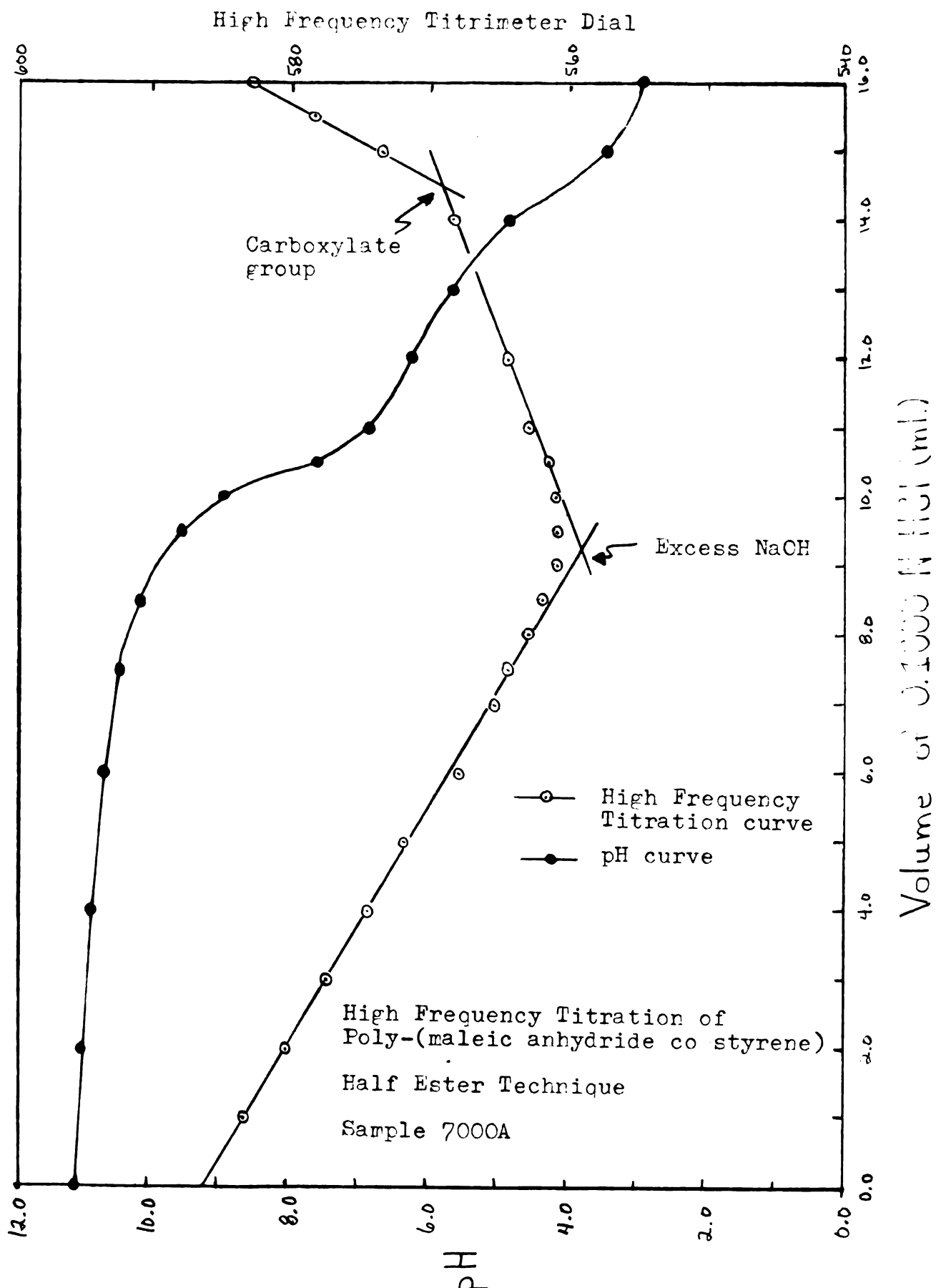
W = weight of sample in grams.

$\frac{(EW)(NE)}{(W)} \times 100$ = percent maleic anhydride moiety in the poly-(maleic anhydride co styrene).

Table II
Composition of Copolymer Samples

| <u>Sample
Number</u> | <u>Experimental Percent
Maleic Anhydride Moiety</u> | <u>Theoretical Percent
Maleic Anhydride Moiety</u> |
|--------------------------|---|--|
| 1E | 47.5 | 48.5 |
| 2E | 49.2 | 48.5 |
| 3E | 48.1 | 48.5 |
| 4E | 48.5 | 48.5 |
| 500CA | 52.1 | 48.5 |
| 700CA | 52.5 | 48.5 |

Figure 3.



INFRARED SPECTRUM

An infrared spectrum was recorded for a sample of poly-(maleic anhydride co styrene). A mineral oil mull sample was employed to record the 2000 cm^{-1} to 750 cm^{-1} range and a Fluorolube mull sample was used to record the 4000 cm^{-1} to 1250 cm^{-1} range. The instrument settings are placed beside the spectrum (Figure 4 and 5).

Figure 4.

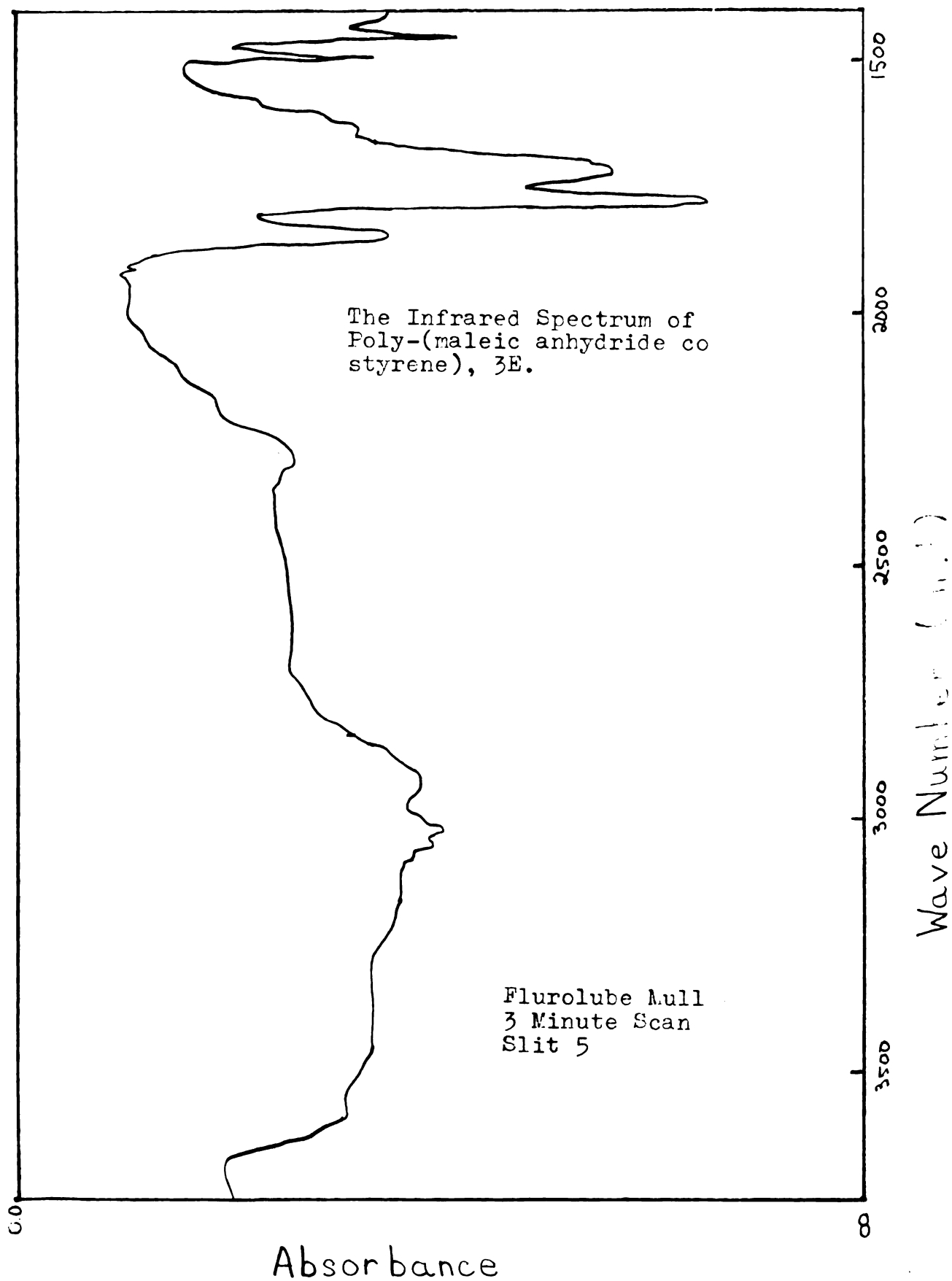
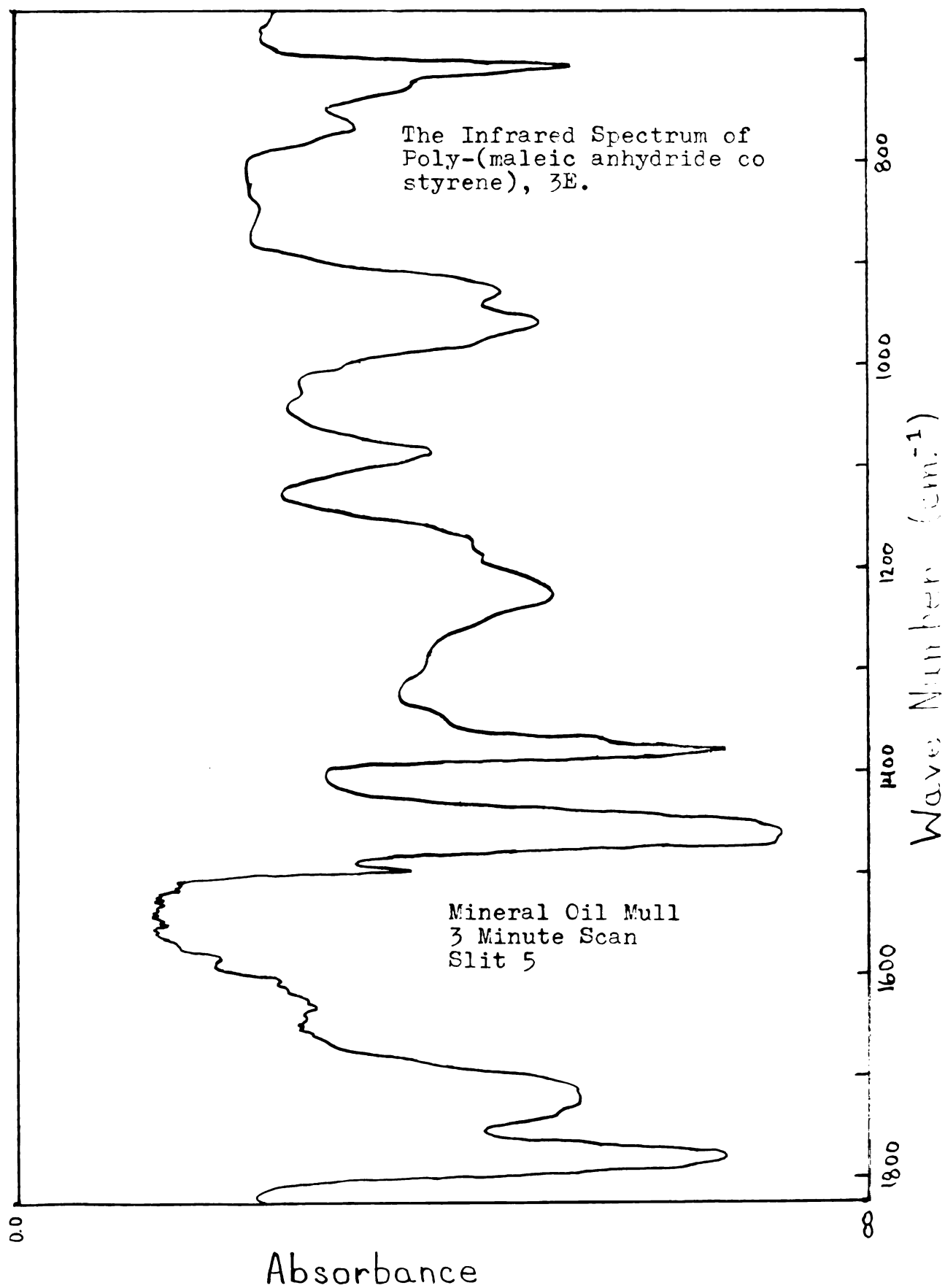


Figure 5.



PREPARATION OF LOW MOLECULAR WEIGHT
POLY-(MALEIC ANHYDRIDE CO STYRENE)

The copolymerizations of the maleic anhydride and styrene were carried out in ground glass 250 milliliter round bottom flasks. The flasks were equipped with magnetic stirrers, reflux condensers, and gas inlet tubes. Approximately 0.04 mole of each monomer was dissolved in about 100 milliliters of dimethoxymethane. After the monomers had dissolved, the initiator was introduced and the reaction allowed to run at the boiling temperature of dimethoxyethane (44°C.) for 24 hours.

The reactions were allowed to cool with constant stirring for 2 hours. After the cooling period, the copolymers were filtered with suction and washed several times with anhydrous benzene. They were finally dried in vacuo. After drying the copolymers were washed twice with hot anhydrous benzene and again dried in vacuo.

Benzoyl peroxide was used as the initiator in all these polymerizations with varying concentrations. The atmosphere in which the copolymerizations were run was pre-purified nitrogen. A summary of the various experiments and the conditions under which they were carried out is given in Table III.

The number average molecular weights of the poly-(maleic anhydride co styrene) were determined with a Mechrolab Vapor Pressure Osmometer. The determinations were made in acetone solvent. The results are given in Table III. Figure 6 shows a representative graph. A sample calculation of a molecular weight is given on page 11.

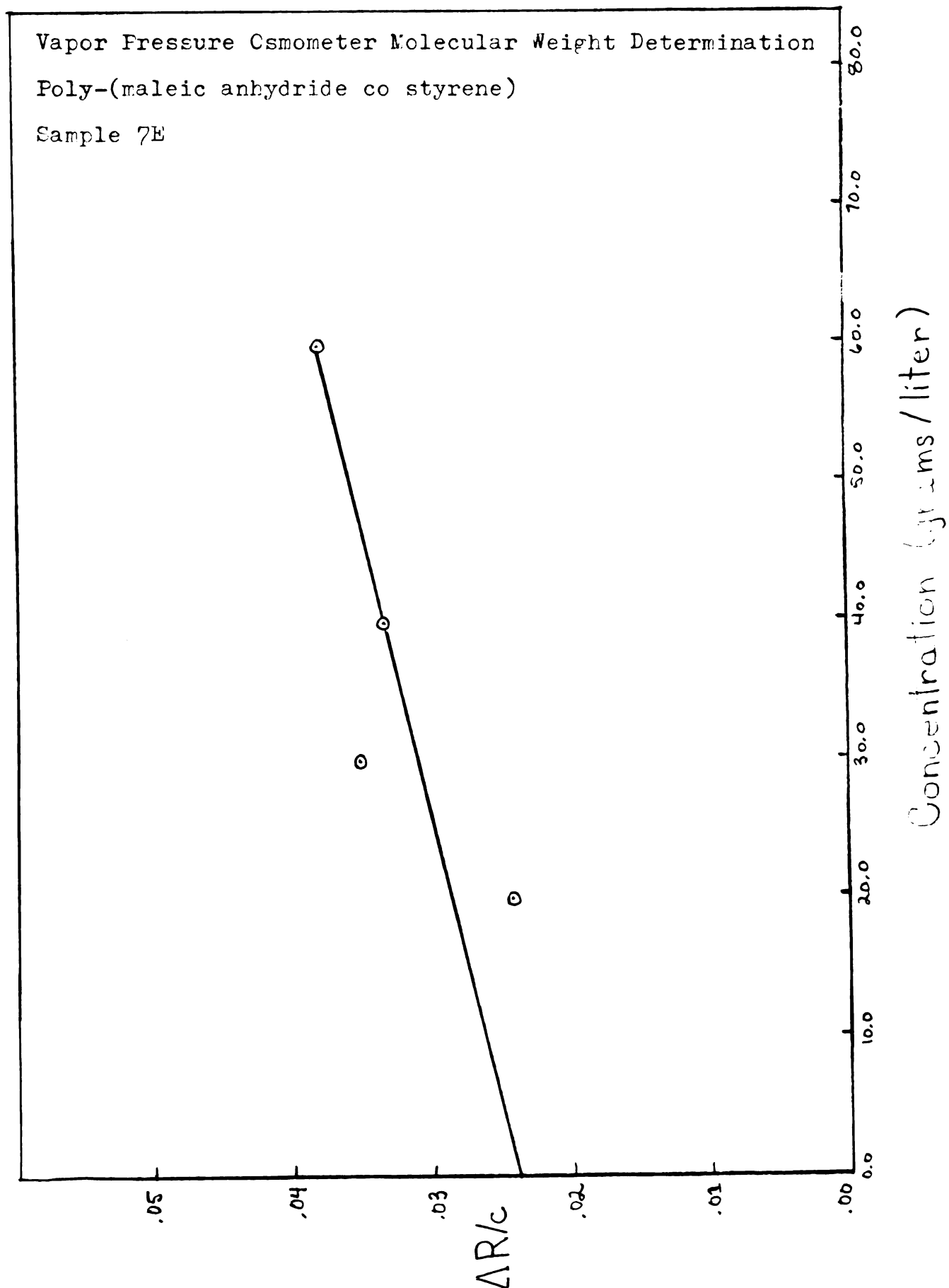
Table III

Experimental Conditions and Molecular Weight of
Low Molecular Weight Poly-(maleic anhydride co styrene)

| <u>Sample
Number</u> | <u>Percent Initiator
Based on Total
Monomer Weight</u> | <u>Molecular
Weight</u> |
|--------------------------|--|-----------------------------|
| 1E* | 0.4 | 3,540 |
| 5E | 0.8 | 2,880 |
| 6E | 1.3 | 18,750 |
| 7E | 1.6 | 15,600 |

* This copolymer was prepared under the procedure described on page 9 of this thesis.

Figure 6.



DISCUSSION

The purpose of this series of experiments was to determine, if possible, the optimum conditions under which a low molecular weight copolymer of maleic anhydride and styrene could be prepared. It was known from preceding work that a relatively low molecular weight copolymer of maleic anhydride and styrene could be prepared using dimethoxymethane as a solvent (See page 11 of this thesis). On this basis it was decided to use dimethoxymethane as solvent and vary the benzoyl peroxide initiator concentration.

It can be seen from Table III that the lowest molecular weight poly-(maleic anhydride co styrene) was obtained from the copolymerization utilizing 0.8 percent initiator concentration. The copolymer prepared with 0.4 percent benzoyl peroxide was also quite low. However, the two highest initiator concentrations yielded the highest molecular weight copolymers.

There are two factors which influence the molecular weight of the copolymer. One of these is the rate of initiation and the other factor is the rate of termination¹⁶. The faster termination takes place the lower the copolymer molecular weight will be. It appears that termination occurs fastest when the initiator concentration is between 0.4 and 0.8 percent.

On the other hand, when the initiator concentration is in the range of 1.3 to 1.6 percent the rate of termination has decreased. This is indicated by the considerably higher molecular weights found in this range. One reason for this behavior may be that the free radical is incorporated in the polymer bulk and is prevented from

reacting with other free radicals because of its restricted mobility. It does continue to react with monomer because there is a much higher concentration of monomer in the system.

PART C

SUCCINIC ANHYDRIDE

TREATMENT OF SUCCINIC ANHYDRIDE IN ACETONE WITH AMMONIA

The reaction was carried out in a 500 milliliter three neck flask with ground glass joints. The flask was equipped with a reflux condenser, a mechanical stirrer, and a gas inlet tube.

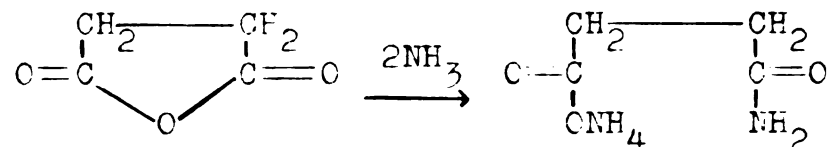
Three grams of succinic anhydride were dissolved in 300 milliliters of acetone*. After the succinic anhydride dissolved, anhydrous ammonia gas was passed into the solution for five hours.

The reaction was carried out at room temperature with continuous stirring and with no protection from light.

The white crystalline precipitate which resulted was filtered by suction and washed three times with acetone. The product was then dried in a vacuum desiccator.

After drying, the ammonia derivative of succinic anhydride was subjected to a Soxhlet extraction with acetone for 22 hours and again dried in vacuo. The product after extraction and drying remained white and crystalline.

The melting point of the extracted and dried ammonia treated succinic anhydride was 122.5°C. The product was assumed to be ammonium succinamate produced by the following reaction:



This assumption was later shown to be correct (See page 30).

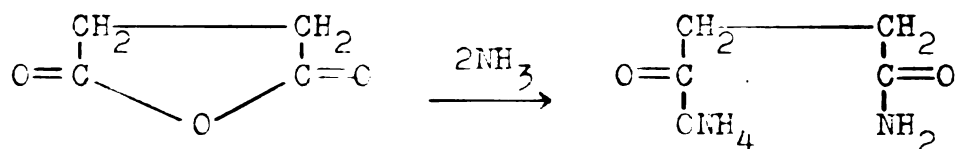
* The ammonia derivative of succinic anhydride prepared in acetone is sample 1G.

TREATMENT OF SUCCINIC ANHYDRIDE IN TETRAHYDROFURAN WITH AMMONIA

The procedure followed in this experiment was essentially the same as that for the treatment of succinic anhydride in acetone with ammonia. The solvent in this case was tetrahydrofuran* and this reaction and the product were protected from light at all times. The reaction was allowed to run for 4 hours.

After filtering by vacuum and washing with tetrahydrofuran three times the product was dried in vacuo and then extracted with tetrahydrofuran in a Soxhlet extractor for 26 hours. After extraction it was again dried in vacuo.

After extraction and drying the product was white and had a melting point of 122.5°C. The product was assumed to be ammonium succinamate formed by the following reaction:



This assumption was later proven to be correct (See page 30).

* The ammonia derivative of succinic anhydride prepared in tetrahydrofuran is sample 2G.

TOTAL NITROGEN ANALYSIS OF THE AMMONIA DERIVATIVES OF
SUCCINIC ANHYDRIDE

The Kjeldahl method was employed to determine the percent total nitrogen in an accurately weighed (± 0.0001 gram) sample of ammonium succinamate of approximately 0.1 gram¹⁷.

All attempts to determine ammonium nitrogen by titration of ammonia liberated from the ammonium salt by a strong base resulted in the hydrolysis of the amide and gave values for total nitrogen in the ammonium succinamate.

Calculations

EW = equivalent weight of nitrogen.

NE = number of equivalents of ammonia determined by titration.

W = weight in grams of the original sample.

$\frac{(EW)(NE)}{(W)} \times 100 = \text{percent total nitrogen in sample.}$

Table IV
Percent Total Nitrogen in Ammonium Succinamate
by the Kjeldahl Method

| <u>Sample
Number</u> | <u>Percent Total
Nitrogen</u> | <u>Theoretical
Percent Total
Nitrogen</u> |
|--------------------------|-----------------------------------|---|
| 1G | 19.8 | 20.9 |
| 2G | 18.4 | 20.9 |

SYNTHESIS OF SUCCINAMIC ACID FROM AMMONIA TREATED SUCCINIC ANHYDRIDE

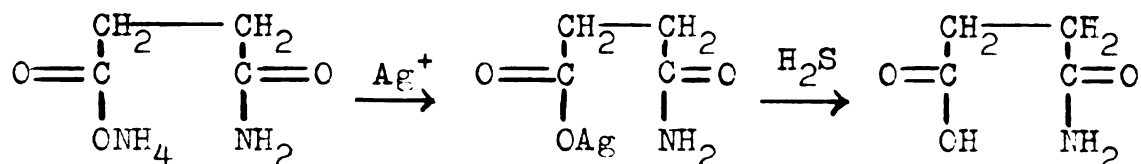
A sample of ammonia treated succinic anhydride was dissolved in distilled water. An excess of a 5 percent silver nitrate solution was added to the dissolved ammonia derivative of succinic anhydride and a white precipitate was immediately formed. The precipitate was filtered by suction, washed with distilled water three times, and dried in vacuo.

The dry white precipitate was treated with an aqueous solution of H_2S . The black-brown precipitate which was formed in the reaction was removed by suction filtration.

The filtrate was evaporated on a steam bath under vacuum. The colorless crystals remaining after all the water had evaporated were recrystallized three times from an acetone-ether mixture.

If the ammonia derivative of succinic anhydride were ammonium succinamate, the above procedure should yield succinamic acid as the final product¹⁸. The melting point of the recrystallized product was 156-157°C. which agrees with the known melting point of succinamic acid¹⁸.

The following reactions occurred in the above procedure:



HIGH FREQUENCY TITRATIONS OF AMMONIUM SUCCINATE

To prepare the ammonia treated succinic anhydride for high frequency titration an accurately weighed sample (± 0.0001 gram) of approximately 0.1 gram was dissolved in distilled water. This was then directly titrated with 0.1000 N HCl. The titration was followed with a high frequency titrimeter and a Beckman glass electrode pH meter. A titration curve is shown in Figure 7. The results are shown in Table V.

Calculations

EW = equivalent weight of nitrogen.

NE = number of equivalents of ammonium ion present as determined by the titration of the carboxylate group (Figure 7).

W = weight in grams of sample.

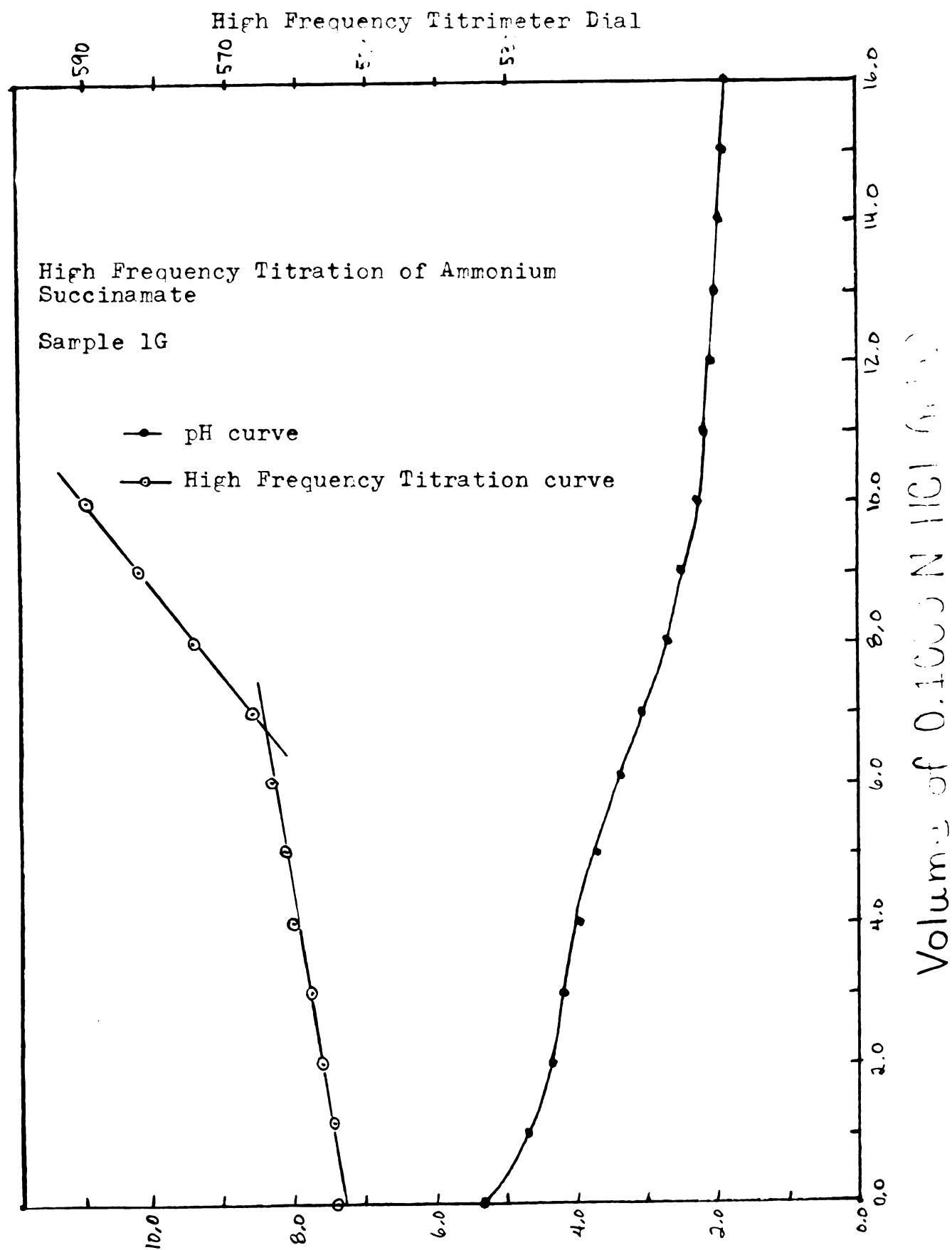
$\frac{(EW)(NE)}{(W)} \times 100$ = percent ammonium nitrogen as determined by high frequency titration.

Table V

Percent Ammonium Nitrogen in Ammonium Succinate by
High Frequency Titration

| <u>Sample
Number</u> | <u>Experimental Percent
Ammonium Nitrogen</u> | <u>Theoretical Percent
Ammonium Nitrogen</u> |
|--------------------------|---|--|
| 1G | 9.18 | 10.4 |
| 2G | 9.89 | 10.4 |

Figure 7.



COLCRIMETRIC DETERMINATION OF AMMONIUM NITROGEN IN
AMMONIA TREATED SUCCINIC ANHYDRIDE

A standard solution of ammonium chloride was prepared by quantitatively dissolving an appropriate weighed amount in ammonia free water to give a solution containing 6.4×10^{-6} equivalents of ammonium ion per liter.

The samples were prepared by dissolving an accurately weighed sample (± 0.0001 gram) of approximately 0.1 gram of ammonia treated succinic anhydride quantitatively in 100.0 milliliters of ammonia free water.

One milliliter of this solution was then diluted with ammonia free water to 50.0 milliliters and treated with 5.0 milliliters of Nessler's Reagent* (Prepared by the Kock and Meckin Method) and allowed to stand for 15 minutes. The same treatment was given to 50.0 milliliters of the standard solution¹⁷.

The transmittance of the solutions was then determined on a Bausch and Lomb Spectronic 20 Colorimeter at a wavelength of 500 microns¹⁹.

Calculations

If colorimeter experiments utilize matched cells, the same solvent, temperature, and wavelength for all samples and the standard solution, then the following relationship is true:

$$c = K \log 1/T$$

where c is some concentration term for the colored substance, K is a constant, and T is the transmittance.

* Kindly furnished by Dr. Hans Lillevik.

Since A is constant in all cases the following relationship is true¹⁷:

$$\frac{\log 1/T_s}{c_s} = \frac{\log 1/T_x}{c_x}$$

where subscript s refers to the standard solution and subscript x refers to the sample. Data and results are shown in Table VI.

The following is the method for calculating the percent ammonium nitrogen from transmittance:

c_x = equivalents/liter of ammonium nitrogen from transmittance.

EW = equivalent weight of nitrogen.

W = weight of sample in grams.

$$\frac{(EW)(c_x)(5.0)}{(W)} \times 100 = \text{percent ammonium nitrogen.}$$

Table VI

Percent Ammonium Nitrogen in Ammonium Succinamate
by Colorimetry

| <u>Sample
Number</u> | <u>Transmittance</u> | <u>Equivalents of
Ammonium Nitrogen
Per Liter</u> | <u>Experimental
Percent
Ammonium
Nitrogen</u> |
|--------------------------|----------------------|---|---|
| Standard | .526 | 6.4×10^{-6} | |
| 1G | .266 | 13.2×10^{-6} | 8.90 |
| 2G | .270 | 13.0×10^{-6} | 8.78 |

The theoretical percent ammonium nitrogen for ammonium succinamate is 10.4 percent.

INFRARED SPECTRA

Infrared spectra were recorded for samples of succinic anhydride and ammonium succinamate. A mineral oil mull sample was employed to record the 2000 cm.^{-1} to 750 cm.^{-1} range and a Fluorolube mull sample was used to record the 4000 cm.^{-1} to 1250 cm.^{-1} range. The instrument settings are placed beside the spectra (Figures 8 and 9).

Figure 8.

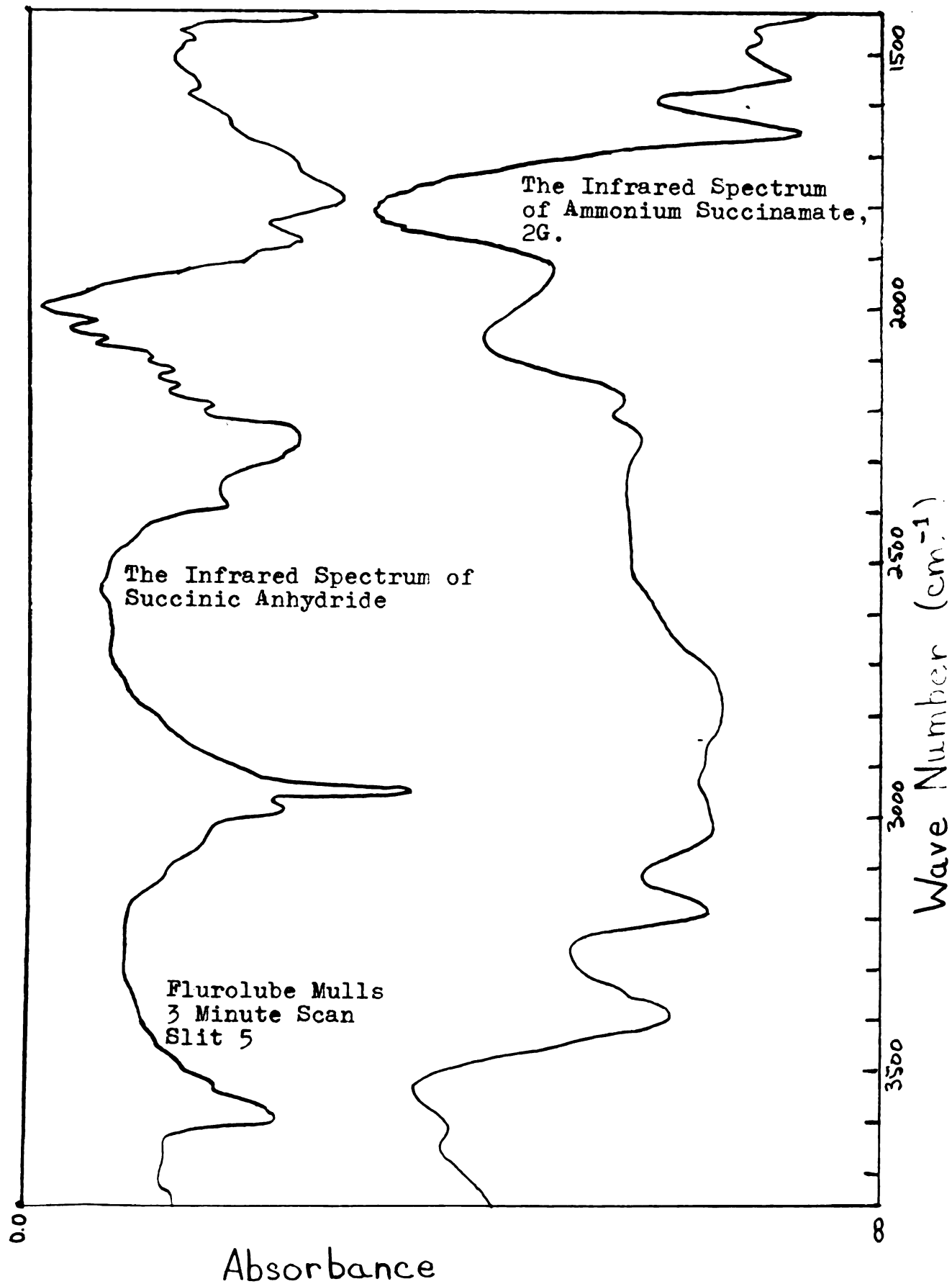
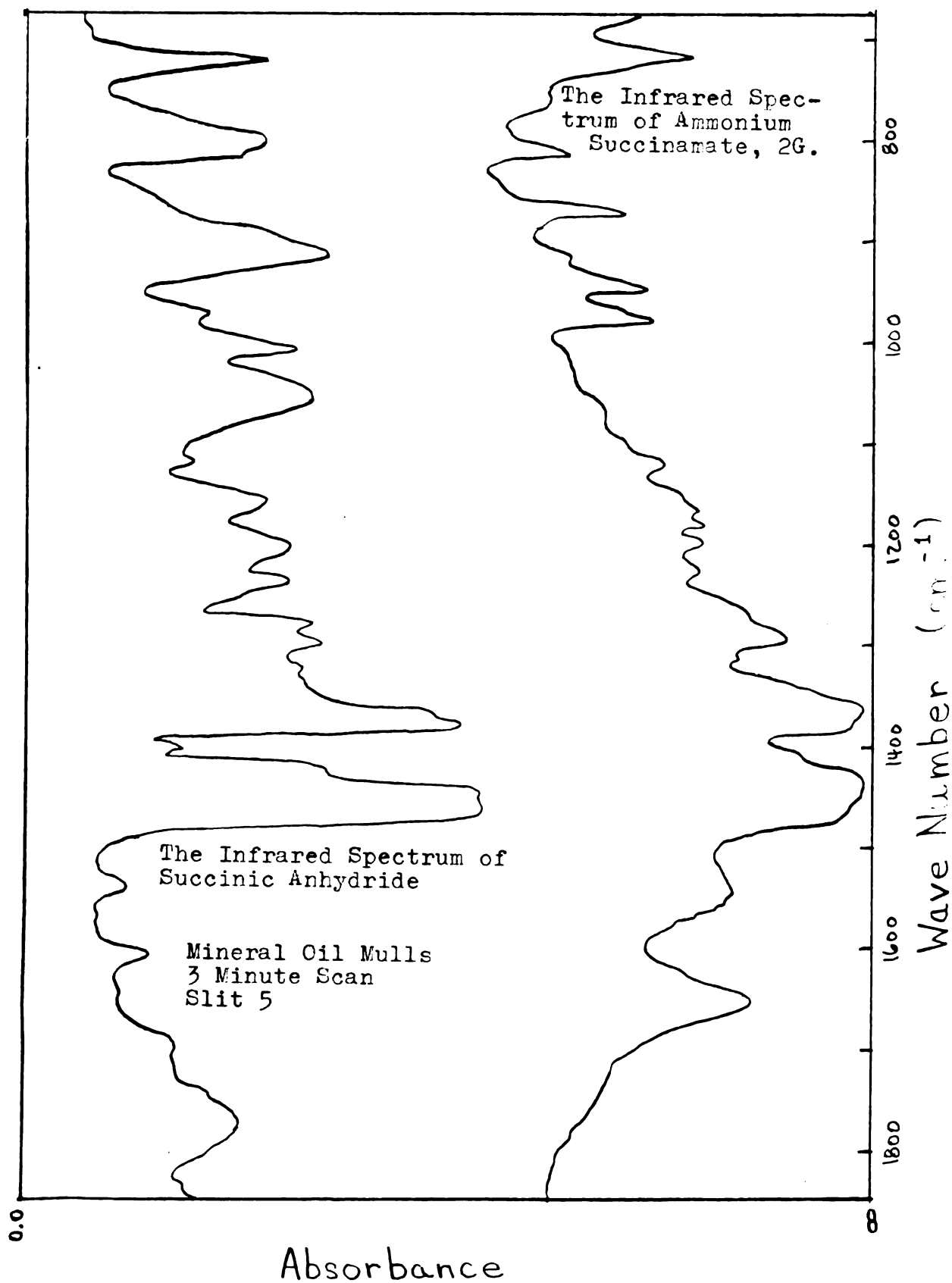


Figure 9.

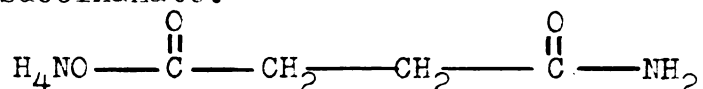


DISCUSSION

Reacting succinic anhydride with dilute aqueous ammonia yields ammonium succinamate from which it is possible to prepare succinamic acid¹⁸.

Since it was suspected that the product which resulted from reacting succinic anhydride and gaseous ammonia in an anhydrous medium was ammonium succinamate the preparation of succinamic acid from this product was attempted. The colorless crystals which resulted had a melting point of 156-157°C. The melting point of succinamic acid is 157°C.¹⁸.

It was concluded from this that the product which results from treating succinic anhydride with gaseous ammonia is ammonium succinamate.



Kjeldahl analysis for total nitrogen gave 19.8 percent nitrogen on the sample prepared in acetone and 18.4 percent nitrogen for the sample prepared in tetrahydrofuran. The theoretical percent total nitrogen is 20.9 percent (Table IV).

Colorimetric determination of percent ammonium nitrogen yielded 8.90 percent and 8.78 percent (Table VI). The theoretical percent ammonium nitrogen is 10.4 percent. The method is relatively straightforward with compounds which dissolve to form colorless solutions. However, some of the ammonia treated copolymers form solutions that vary from yellow to brown. This color would cause difficulties in applying a colorimetric method to the ammoniated copolymers.

The high frequency titration of the samples gave a curve with one break (Figure 7). If we assume that this

break is the titration of the carboxylate group then we can calculate the percent ammonium nitrogen. The percent ammonium nitrogen calculated from the high frequency titration curves is 9.18 percent and 9.89 percent. The theoretical percent ammonium nitrogen is 10.4 percent (Table V). From these results it can be seen that high frequency titration is an acceptable method for determining percent ammonium nitrogen in ammonia treated anhydrides.

PART D

AMMONIA TREATMENT OF THE COPOLYMERS OF
MALEIC ANHYDRIDE AND STYRENE

PREPARATION OF THE AMMONIA DERIVATIVES OF
POLY-(MALEIC ANHYDRIDE CO STYRENE)

A 10 percent (weight/volume) solution of poly-(maleic anhydride co styrene) in an anhydrous solvent was placed in a three neck round bottom flask fitted with a mechanical stirrer, a reflux condenser, and a gas inlet tube.

Anhydrous ammonia gas was passed into the solution with continuous stirring. In all cases the reaction was carried out at room temperature.

A summary of the various experiments and the conditions of each are given in Table VII.

Table VII
Experimental Conditions for the Ammonia Treatment of
Poly-(maleic anhydride co styrene)

| <u>Sample Number</u> | <u>Reactant</u> | <u>Protected From Light</u> | <u>Solvent</u> | <u>Reaction Time - Hours</u> |
|----------------------|-----------------|-----------------------------|-----------------|------------------------------|
| 1M* | Resin 7000A | No | Acetone | 48 |
| 3M | Resin 5000A | Yes | Acetone | 6 |
| 4M | Resin 7000A | Yes | Acetone | 6 |
| 5M | 1E | Yes | Acetone | 2 |
| 6M | 2E | Yes | Acetone | ½ |
| 7M | 3E | Yes | Tetrahydrofuran | 3 |
| 8M | 4E | No | Tetrahydrofuran | 4 |

In all experiments a white gelatinous precipitate resulted. This precipitate was separated from the solvent by centrifugation and decantation of the supernatant solvent. The precipitate was repeatedly washed in the centrifuge

* The designation M in the sample number indicates ammonia derivatives of poly-(maleic anhydride co styrene).

tube and separated from the wash solvent by centrifugation. The white gelatinous precipitate was then dried in vacuo. After drying it was subjected to Soxhlet extraction for 24 hours with the same kind of solvent in which it had been prepared. The extracted product was dried in vacuo.

In all the experiments the product recovered following centrifuging was a white gelatinous substance. However, the products prepared in acetone turned brown during vacuum drying. The darkest product was obtained from experiment 1M which was exposed to light.

The two experiments carried out in tetrahydrofuran yielded final products considerably lighter in color than any of those prepared in acetone. The reaction in tetrahydrofuran which was protected from light gave a perfectly white product while the experiment not protected from light yielded a substance which was slightly yellow. The latter was considerably lighter than any prepared in acetone.

Soxhlet extraction removed some of the colored substances from all the colored products but even after extraction considerable color remained.

THE EFFECT OF EXTRACTION ON THE NITROGEN CONTENT

Since Soxhlet extraction removed colored products from the ammonia derivatives of poly-(maleic anhydride co styrene), the effect of the extraction on the total nitrogen content of the unextracted derivatives was determined.

The percent total nitrogen was determined by the Kjeldahl method on an accurately weighed (± 0.0001 gram) sample of approximately 0.1 gram¹⁷.

The percent total nitrogen was determined on a sample before extraction, after extraction for 24 hours, and after extraction for 48 hours. The results are given in Table VIII.

Table VIII

The Effect of Extraction on the Nitrogen Content

| <u>Sample
Number</u> | <u>Percent Total
Nitrogen
Before Extraction</u> | <u>Percent Total
Nitrogen
After 24 Hours</u> | <u>Percent Total
Nitrogen
After 48 Hours</u> |
|--------------------------|---|--|--|
| 1M | 7.45 | 4.96 | 4.89 |
| 3M | 7.79 | 6.54 | 6.59 |
| 4M | 7.86 | 6.50 | 6.62 |

It can be seen from the results in Table VIII that extraction does remove some nitrogen-containing substances and the ammonia derivatives of poly-(maleic anhydride co styrene) reach a constant nitrogen content at least after Soxhlet extraction for 24 hours.

BY-PRODUCTS FROM AMMONIA TREATMENT OF ACETONE

Gaseous anhydrous ammonia was passed into acetone in an attempt to see if the colored products formed during the ammonia treatment of the copolymers were due to the acetone reacting with the ammonia.

Three hundred milliliters of acetone were placed in a ground glass, three neck, round bottom, 500 milliliter flask equipped with a reflux condensor, a mechanical stirrer, and a gas inlet tube. Gaseous anhydrous ammonia was passed through the acetone for 6 hours with constant stirring.

There was no observable reaction or change of color.

TOTAL NITROGEN DETERMINATION OF AMMONIA TREATED
COPOLYMERS OF MALEIC ANHYDRIDE AND STYRENE

The total percent nitrogen in the ammonia derivatives of poly-(maleic anhydride co styrene) was determined by the Kjeldahl method using an accurately weighed (± 0.0001 gram) sample of approximately 0.1 gram¹⁷. The results are shown in Table IX.

HIGH FREQUENCY TITRATIONS OF AMMONIA TREATED POLY-(MALEIC ANHYDRIDE CO STYRENE)

Previous experiments showed that high frequency titrations are a valid method for analyzing the percent ammonium nitrogen in the ammonium succinamate (See page 31 vide infra). Therefore, it was concluded that this method could be used to determine the percent ammonium nitrogen in the ammonia derivatives of poly-(maleic anhydride co styrene).

Accurately weighed (± 0.0001 gram) samples of approximately 0.1 grams of the ammonia derivatives were dissolved in distilled water. The dissolved samples were titrated directly with 0.1000 N HCl. The titration was followed with a high frequency titrimeter and a Beckman glass electrode pH meter. The method of calculation for percent ammonium nitrogen is given on page 31. A typical titration curve is shown in Figure 10. The results are given in Table IX.

Table IX

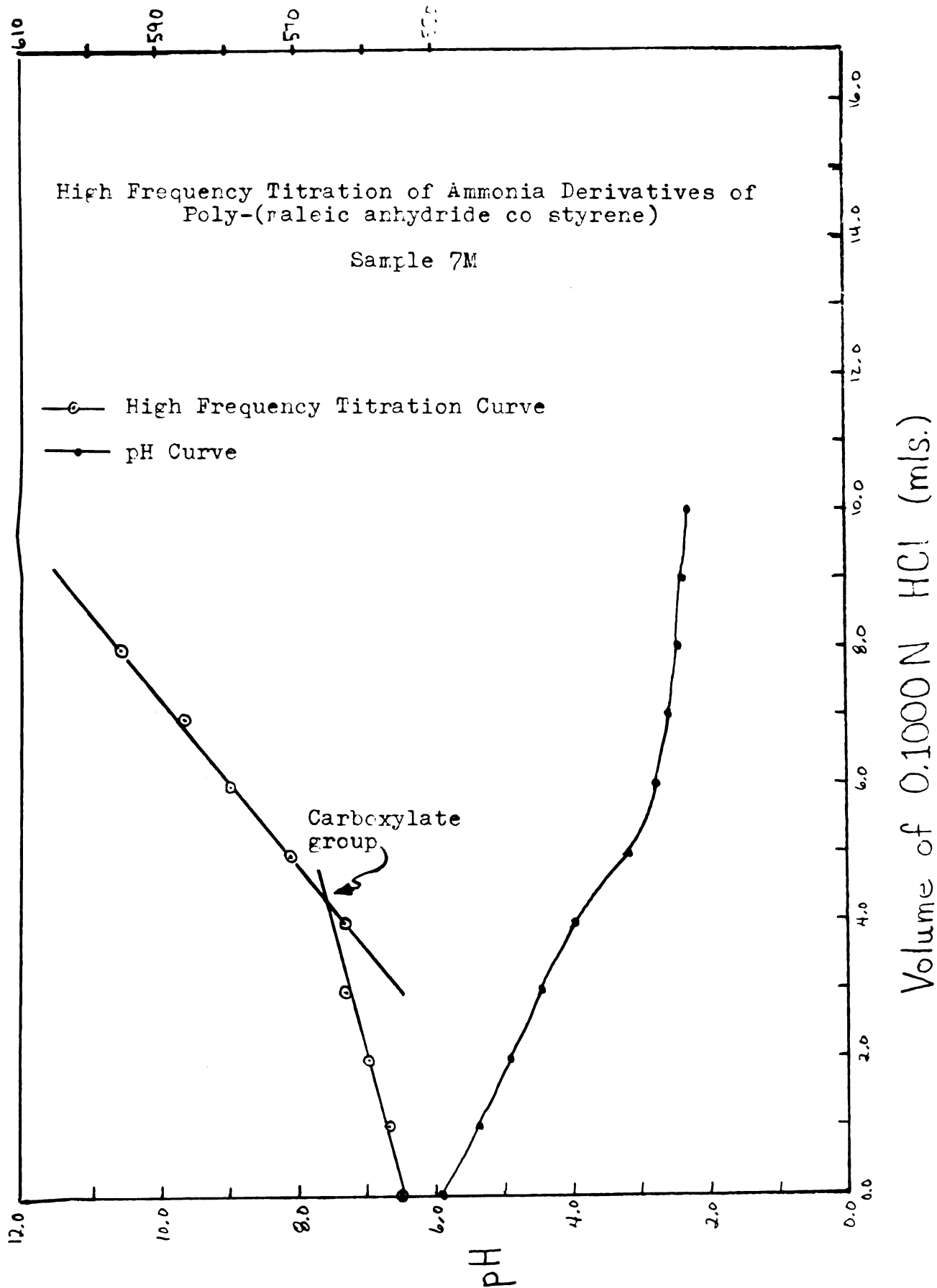
Percent Total Nitrogen and Percent Ammonium Nitrogen
in Ammonia Derivatives of Poly-(maleic anhydride co styrene)

| <u>Sample
Number</u> | <u>Percent
Total
Nitrogen</u> | <u>Theoretical
Percent Total
Nitrogen</u> | <u>Percent
Ammonium
Nitrogen</u> | <u>Theoretical
Percent Ammonium
Nitrogen</u> |
|--------------------------|---------------------------------------|---|--|--|
| 1M | 4.96 | 11.9 | 2.77 | 5.95 |
| 3M | 6.54 | 11.9 | 2.72 | 5.95 |
| 4M | 6.50 | 11.9 | 2.73 | 5.95 |
| 5M | 4.59 | 11.9 | 3.39 | 5.95 |
| 6M | 4.80 | 11.9 | 3.04 | 5.95 |
| 7M | 5.50 | 11.9 | 2.91 | 5.95 |
| 8M | 5.34 | 11.9 | 2.84 | 5.95 |

Figure 10.

High Frequency Titrimeter Dial

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MOLECULAR WEIGHTS OF THE AMMONIA DERIVATIVES OF
POLY-(MALEIC ANHYDRIDE CO STYRENE)

The molecular weights of the ammonia derivatives of poly-(maleic anhydride co styrene) were determined using a Mechrolab Vapor Pressure Osmometer. The determinations were carried out in water solution. A sample calculation of molecular weight is shown on page 11. A typical curve is shown in Figure 11 and the results are listed in Table X.

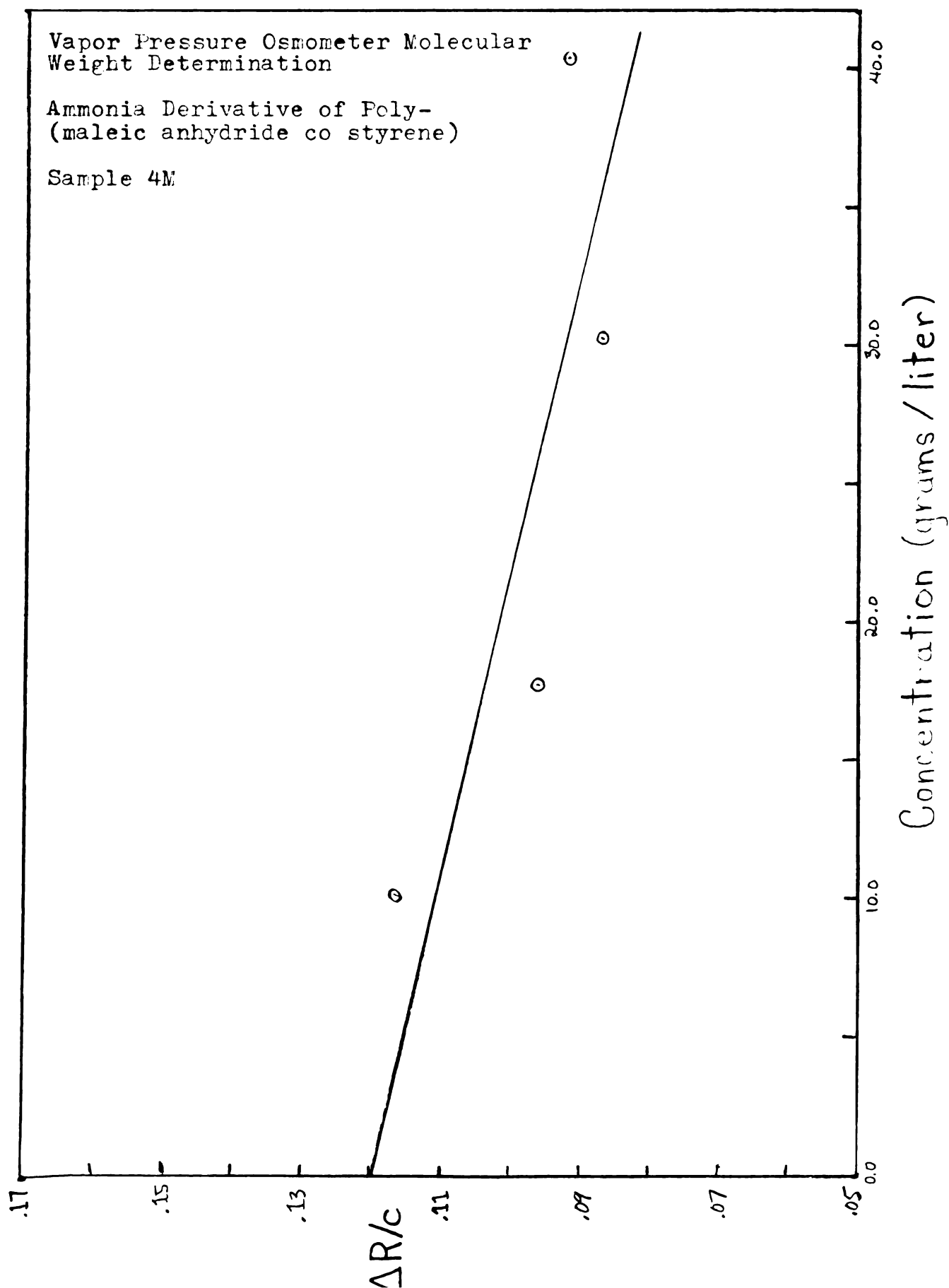
Table X

Molecular Weights of the Ammonia Derivatives of
Poly-(maleic anhydride co styrene)

| <u>Sample
Number</u> | <u>Number Average
Molecular Weight of
Ammonia Derivative</u> | <u>Number Average Molecular
Weight of Copolymer from Which
Ammonia Derivative Was Prepared</u> |
|--------------------------|--|--|
| 4M | 1,100 | 12,900 |
| 5M | 1,640 | 3,540 |
| 7M | 836 | 9,200 |
| 8M | 1,390 | 6,640 |

Figure 11.

49



INFRARED SPECTRA

Infrared spectra were recorded for the samples of the ammonia derivatives of the poly-(maleic anhydride co styrene). A mineral oil mull sample was employed to record the 2000 cm.^{-1} to 750 cm.^{-1} range and a Fluorolube mull sample was used to record the 4000 cm.^{-1} to 1250 cm.^{-1} range.

Since the infrared spectra for the ammonia derivatives of the copolymer were, qualitatively speaking, identical a representative spectrum is illustrated in Figures 12 and 13. The instrument settings are placed beside the spectra.

Figure 12.

51

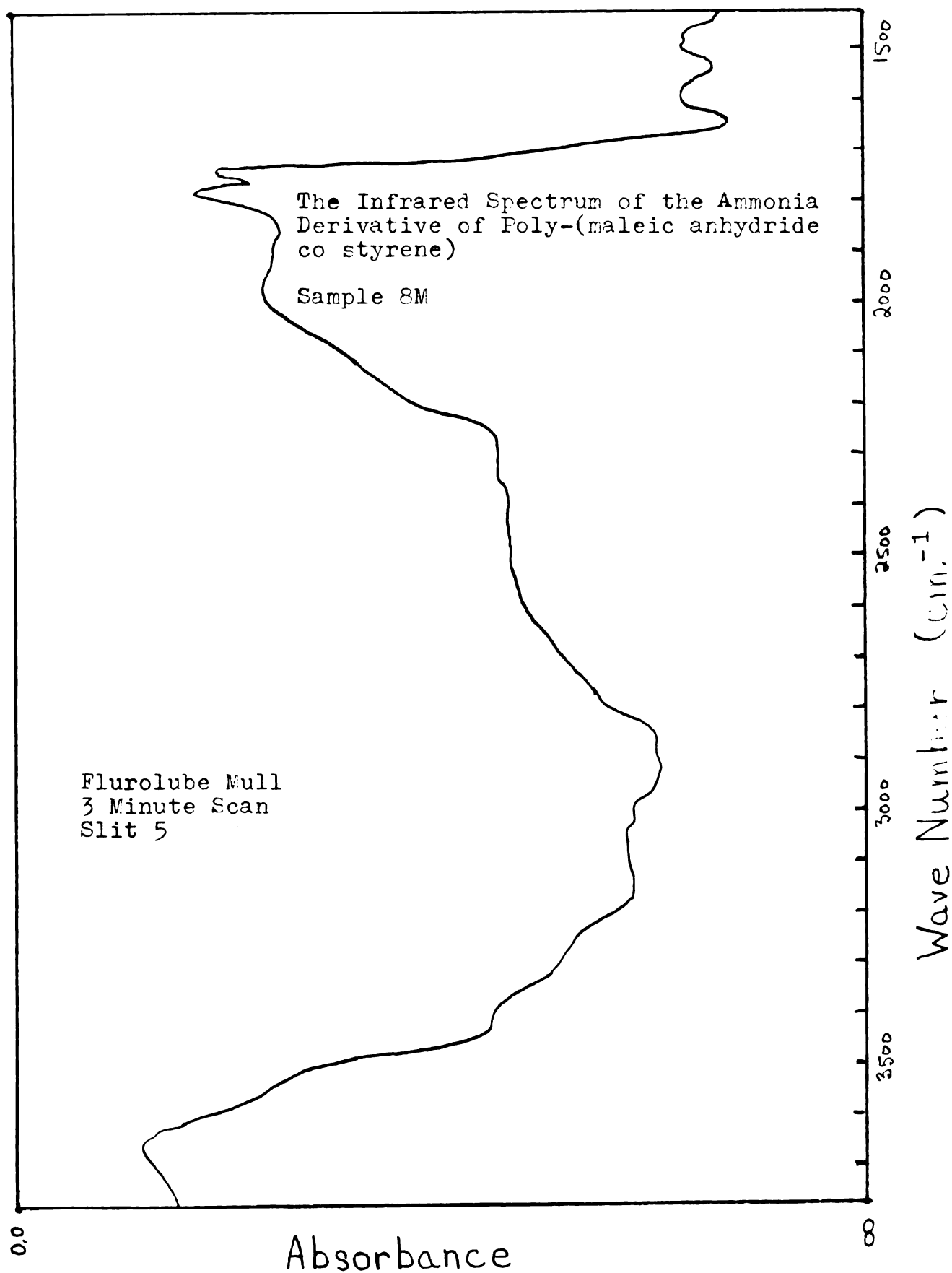
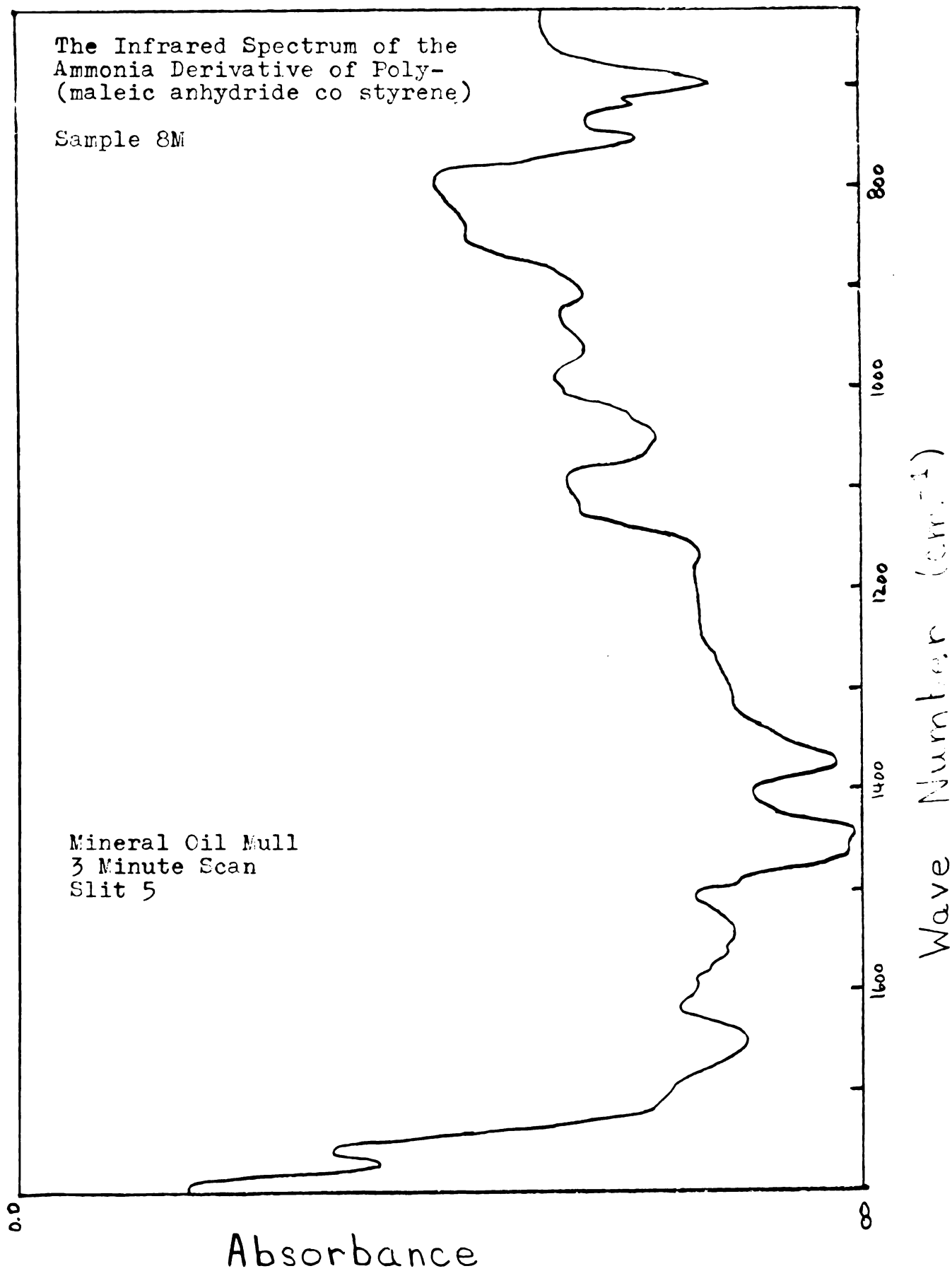
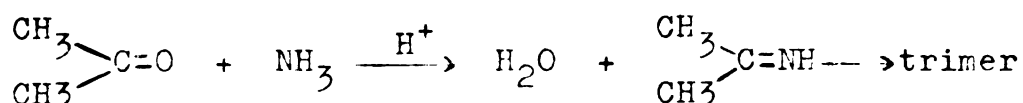


Figure 13.



DISCUSSION

The color which was formed when the poly-(maleic anhydride co styrene) was reacted with gaseous ammonia in acetone could be due to the reaction of the acetone with ammonia. Ammonia reacts with ketones to form imines, which are stable only in solution and form trimers or more complex molecules when their isolation is attempted²⁰.



The acid which is required to catalyze the formation of the imine could very well have come from acid impurities in the anhydride copolymer²¹.

The color is probably due to the formation of complex molecules which are formed when the solvent is removed by drying, since the color does not appear to any great degree until the ammonia derivative is dried. Since the color was more intense when the reaction was exposed to light, it leads one to believe that the formation of these colored products is enhanced by light.

The fact that ammonia derivatives prepared in tetrahydrofuran were white supports the argument that the formation of these colored substances is characteristic of a reaction involving acetone.

Since these colored by-products contain nitrogen if they originate from imines, it would be expected that the total nitrogen content of the ammonia derivative would decrease when some of the colored by-products are removed by Soxhlet extraction. This was found to be the case (See page 43).

Because this thesis was concerned primarily with developing a technique for preparing the ammonia derivatives

of poly-(maleic anhydride co styrene) and not investigating the reaction of acetone with ammonia to form imines and other complex molecules no further study on the composition of the colored matter was carried out.

A 100 percent reaction of the copolymer to form the half ammonium salt half amide would yield a product which would have a total nitrogen content of 11.9 percent. None of the poly-(maleic anhydride co styrene) which was treated with ammonia had 11.9 percent total nitrogen.

Apparently not all the anhydride rings in the copolymer are available for reaction with the ammonia at any given time. This would appear reasonable since the polymer chains are probably coiled in solution and some of the anhydride rings sterically protected from the ammonia. Once the gel precipitate begins to form one would expect that some of the anhydride rings in the copolymer would be shielded by adjacent polymer molecules.

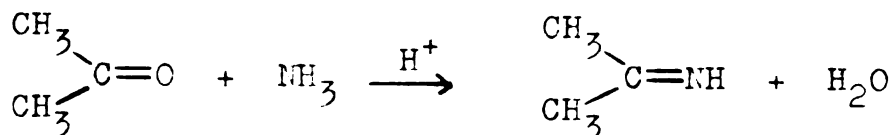
If all the anhydride rings were available for reaction with the ammonia a precipitate should form almost immediately because of the electrolytic properties of the ammonium salt part of the copolymer molecule. However, precipitation does not begin to occur until ammonia has been passed into the solution for at least 20 minutes.

There does appear to be some correlation between the length of time the copolymer is reacted with gaseous ammonia and the percent total nitrogen. It can be seen from Table VII and Table IX that the longer the gaseous ammonia **was** allowed to pass through the reaction mixture the higher the percent total nitrogen in the product. The exception to this was sample 1M. I would point out that this particular experiment was carried out while exposed to light

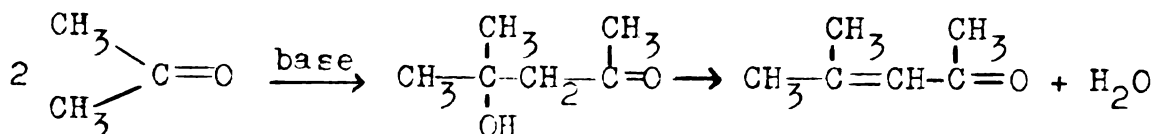
and a considerable amount of colored material was formed in the final product. The same copolymer (Resin 700CA) was reacted with ammonia while protected from light (Sample 4M). In this case the percent total nitrogen does correlate with time of reaction.

In samples 5M and 6M there was a greater percent of ammonium nitrogen than non ammonium nitrogen (Total nitrogen - ammonium nitrogen = non ammonium nitrogen). One explanation of this may be that some hydrolysis of the anhydride ring to form the dicarboxylic acid took place prior to the reaction with ammonia.

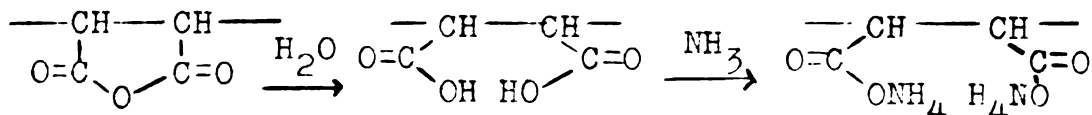
The water which hydrolyzed the anhydride ring could have come from two sources. The first possibility is the reaction of acetone with ammonia²⁰.



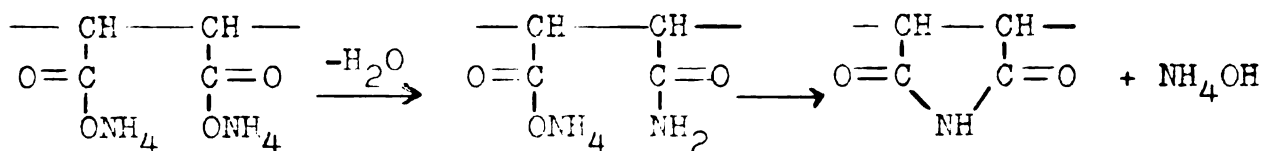
The second possible source of water would be from the condensation products of acetone²².



The dicarboxylic acid then could have reacted with ammonia to form the diammonium salt.

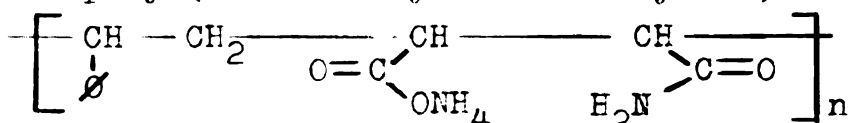


The percent ammonium nitrogen decreases as the reaction time increases. A possible explanation for this behavior would be the formation of the imide⁹.



Normally, however, these reactions to form the imide require much higher temperatures than were attained under the reaction conditions^{7,22}.

The reactions carried out in tetrahydrofuran yielded ammonia derivatives which had approximately twice as much percent total nitrogen as percent ammonium nitrogen. This would indicate that the product is the half ammonium salt half amide of poly-(maleic anhydride co styrene).



Since tetrahydrofuran is inert in the presence of gaseous ammonia the possibility of water forming by condensation reactions is eliminated.

The absence of the colored substances and the reasonable nitrogen analysis when the copolymer is reacted with gaseous ammonia in tetrahydrofuran indicates that the side reactions occurring in acetone have been eliminated by the use of tetrahydrofuran.

Molecular weights determined for the ammonia derivatives of the various samples of poly-(maleic anhydride co styrene) are considerably lower than the molecular weights of the original copolymers. The reason for this may be that fractionation occurs. Fractionation would occur if the formation of the ammonium salt takes place at the same rate regardless of the size of the molecule. If this is the case, the low molecular weight fraction would acquire a greater percentage of ionic character in a given time.

Thus the low molecular weight fraction would precipitate out first. Future work investigating the molecular weight of ammonia derivatives precipitated in a given time interval would be interesting (See Table X).

The interpretation of the infrared spectrum of poly-(maleic anhydride co styrene) has been discussed by Curtice⁶. The infrared spectrum of poly-(maleic anhydride co styrene) (See page 17 of this thesis.) was compared to the infrared spectra of the ammonia derivatives of the poly-(maleic anhydride co styrene) (See page 49)^{23,24,25}.

Three new bands were observed in the ammonia derivatives of the copolymer (Figures 12 and 13). A band at 1550 cm.^{-1} can be attributed to asymmetrical stretching of the carboxylate group. A strong absorption occurred at 1650 cm.^{-1} which was due to the C=O in the primary amide. This band is referred to as the Amide I band. The third band appeared at 3150 cm.^{-1} . This was a weak band and not readily observable in all the ammonia derivatives. This absorption is assigned to both the ammonium ion and primary amides.

A band at 1220 cm.^{-1} due to the cyclic anhydride in the poly-(maleic anhydride co styrene) was completely eliminated in the spectra of the ammonia derivatives of the copolymer. Two other bands which are due to cyclic anhydrides were observed in the spectra of the ammonia derivatives. These were at 1775 cm.^{-1} and 1850 cm.^{-1} . Since none of the copolymers treated with gaseous ammonia reacted 100 percent, it is to be expected that absorption due to the anhydride ring would be present in the infrared spectra of the ammonia derivatives.

The spectra of the ammonium succinamate (See page 35 and Figures 8 and 9) when compared to the spectrum of succinic anhydride (See page 35 and Figures 8 and 9) also revealed three new bands^{23,24,25}.

As in the case of the ammonia derivatives of the copolymer the bands occurred at 1650 cm.^{-1} , 1550 cm.^{-1} , and 3150 cm.^{-1} . These absorptions can be assigned to the primary amide, the carboxylate ion, and the primary amide or ammonium ion respectively. All the characteristic cyclic anhydride bands (1220 cm.^{-1} , 1775 cm.^{-1} , and 1850 cm.^{-1}) present in the spectrum of succinic anhydride were not observed in the spectrum of the ammonium succinamates.

Since imides absorb in the same region as cyclic anhydrides (1770 cm.^{-1} to 1775 cm.^{-1}) it was impossible to draw any conclusions concerning the formation of imides from the infrared spectra.

PART E

POLYMALEIC ANHYDRIDE

PREPARATION OF POLYMALEIC ANHYDRIDE

The preparation of polymaleic anhydride has been reported¹². The homopolymerization of maleic anhydride was carried out in a ground glass 250 milliliter round bottom flask equipped with a magnetic stirrer, a reflux condenser, and a gas inlet tube.

Approximately 0.5 moles of maleic anhydride was dissolved in 150 milliliters of benzene and the polymerization initiated with 5 percent benzoyl peroxide, based on the weight of the monomer. The polymerization reaction was continued for 64 hours under a continuous flow of prepurified nitrogen gas.

After 15 to 20 minutes the solution turned a dark red and then eventually almost black. The dark brown precipitate which resulted was filtered by suction, washed with benzene and then dried in vacuo.

The homopolymer was subjected to Soxhlet extraction for 72 hours and dried again in vacuo.

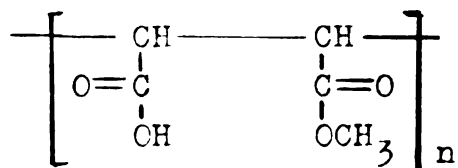
The polymerization was repeated with 150 milliliters of 1-4 dioxane as the solvent. A dark brown precipitate was formed in this case also.

After the Soxhlet extraction and drying the homopolymer prepared in benzene was light brown and the homopolymer prepared in dioxane was light pink.

Number average molecular weights determined with the Mechrolab Vapor Pressure Osmometer using acetone as a solvent showed that the polymaleic anhydride polymerized in benzene had a molecular weight of 1050. The homopolymer prepared in dioxane had a molecular weight of 691.

HIGH FREQUENCY TITRATION OF POLYMALEIC ANHYDRIDE

1 The percent maleic anhydride in polymaleic anhydride was determined by accurately weighing (± 0.0001 gram) a sample of approximately 0.1 gram. This sample was then refluxed in absolute methanol until all the homopolymer dissolved. The product formed by this esterification is¹⁴

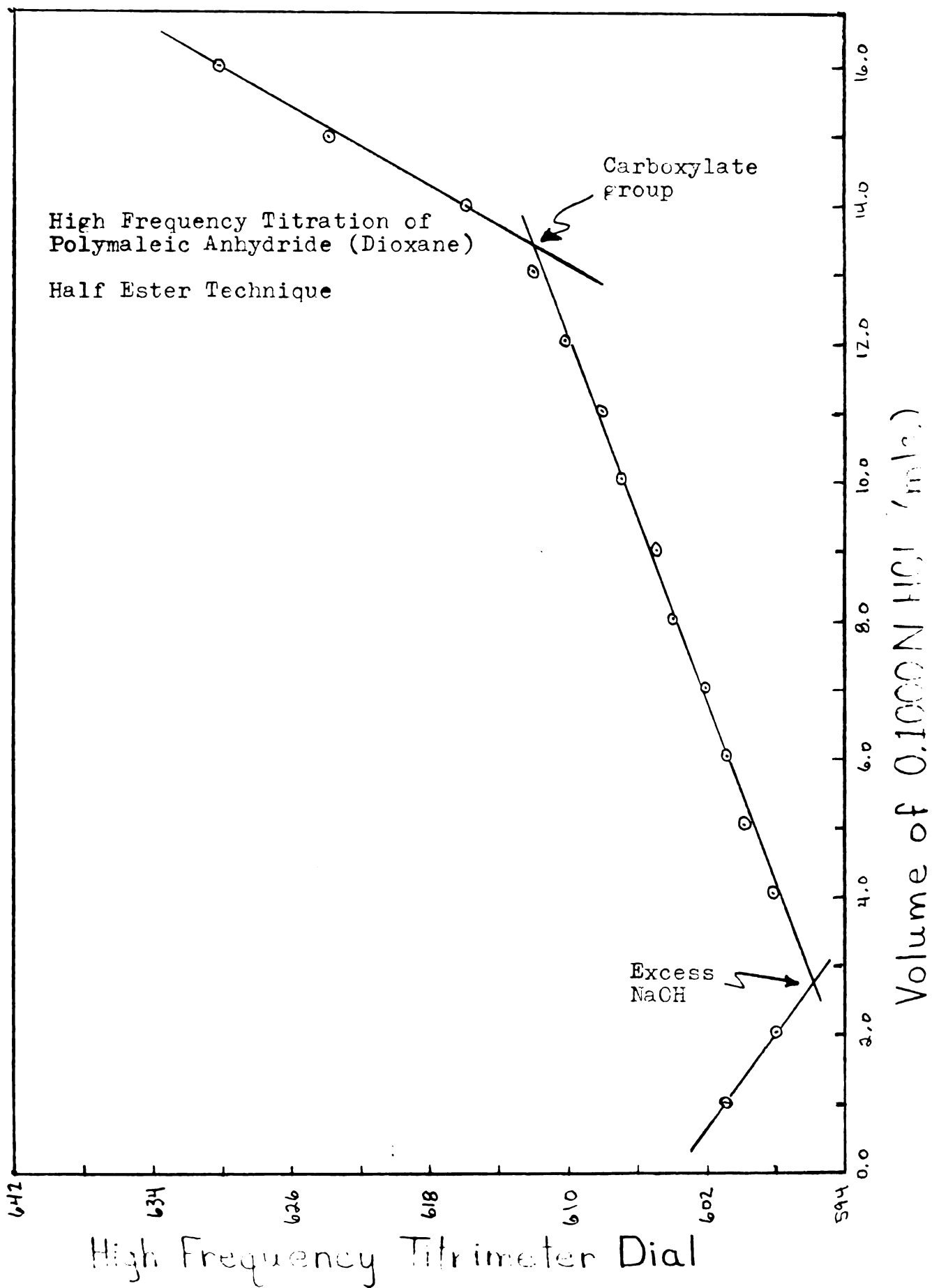


This was treated with 15.00 milliliters of 0.1000N NaOH and titrated with 0.1000N HCl. The titration was followed with a Beckman glass electrode pH meter and a high frequency titrimeter^{14,15}. Sample calculations are shown on page 14 and a typical titration curve is shown in Figure 14. The results are given in Table XI.

Table XI
The Percent Maleic Anhydride Moiety in
Polymaleic Anhydride

| <u>Sample</u> | <u>Preparation Solvent</u> | <u>Experimental Percent Maleic Anhydride</u> | <u>Theoretical Percent Maleic Anhydride</u> |
|----------------------|----------------------------|--|---|
| Polymaleic Anhydride | Dioxane | 96.5 | 100.0 |
| Polymaleic Anhydride | Benzene | 98.5 | 100.0 |

Figure 14.



AMMONIA DERIVATIVE OF POLYMALEIC ANHYDRIDE

The half amide half ammonium salt of the polymaleic acid was prepared by passing ammonia gas into a ten percent (weight/volume) solution of the polymaleic anhydride in tetrahydrofuran.

The reaction was carried out in a 250 milliliter ground glass, round bottom flask equipped with a magnetic stirrer, a reflux condenser, and a gas inlet tube. The reaction was carried out at room temperature with constant protection from light.

As soon as the ammonia gas was passed into the solution, a dark brown precipitate was formed. After 5 hours, the reaction was stopped and the chocolate brown precipitate was removed by centrifugation. The supernatant solvent was discarded and the precipitate was washed with tetrahydrofuran in the centrifuge tube three times. After the last washing and centrifugation, the precipitate was dried in vacuo. The precipitate was still chocolate brown after drying.

The dried product was then subjected to Soxhlet extraction with tetrahydrofuran for 72 hours. The tetrahydrofuran remained clear and colorless throughout the extraction. When the extraction was completed, the product was again dried under vacuum. The final dried product retained the chocolate brown color.

NITROGEN ANALYSIS OF THE AMMONIA DERIVATIVES OF POLYMALEIC ANHYDRIDE

The total nitrogen content of the ammonia derivatives of polymaleic anhydride was determined by the Kjeldahl method¹⁷.

The ammonium nitrogen was determined by dissolving an accurately weighed (± 0.0001 gram) sample of the ammonia derivative of approximately 0.1 gram in distilled water. The dissolved ammonia derivative was then directly titrated with 0.1000 N HCl. The titration was followed with a high frequency titrimeter and a pH meter. A typical curve is shown in Figure 15 and the results are given in Table XII. The method of calculation for the percent ammonium nitrogen is given on page 31.

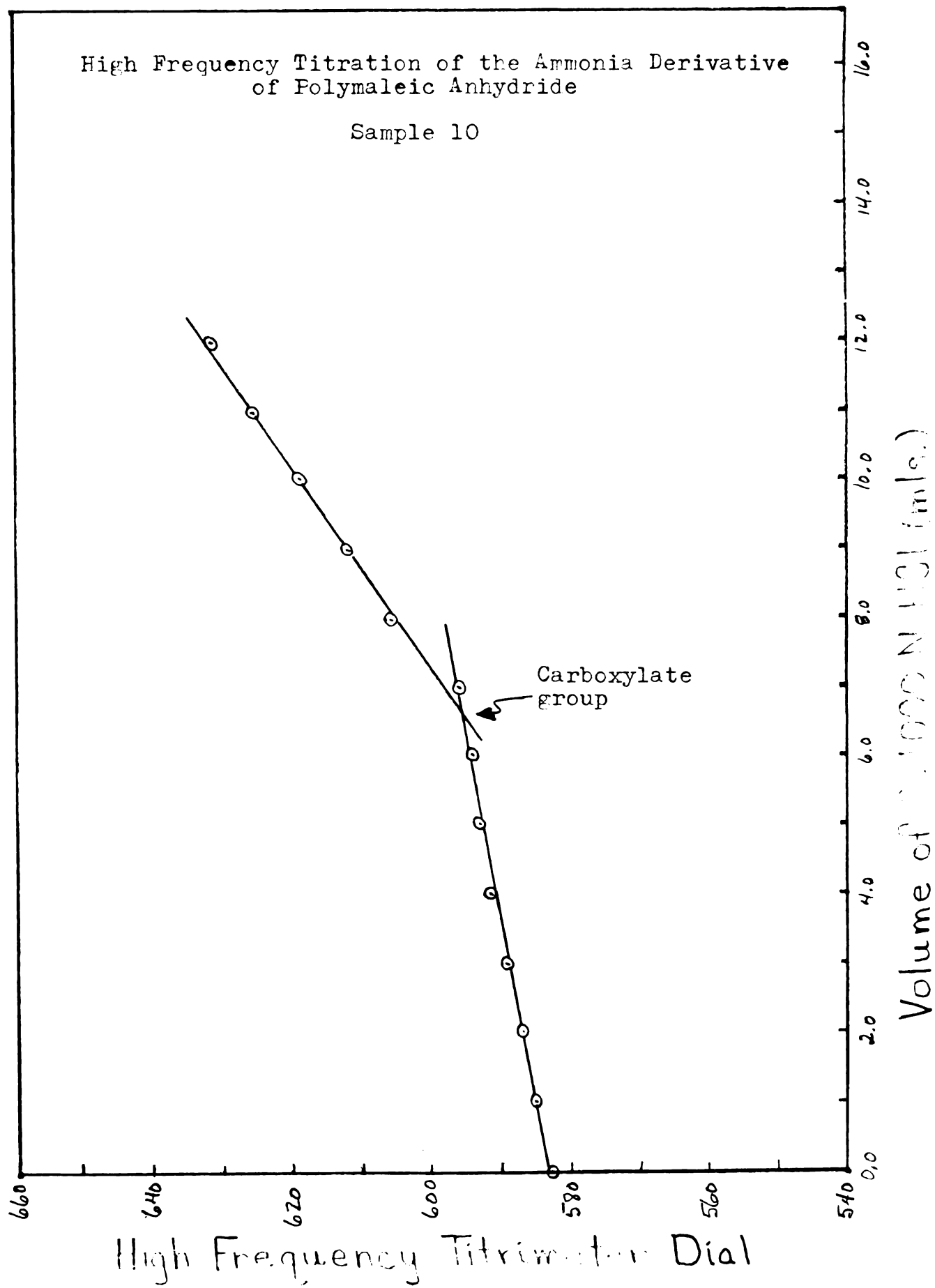
Table XII

Percent Total Nitrogen and Percent Ammonium Nitrogen
in the Ammonia Derivatives of Polymaleic Anhydride

| <u>Sample
Number</u> | <u>Percent
Total
Nitrogen</u> | <u>Theoretical
Percent Total
Nitrogen</u> | <u>Percent
Ammonium
Nitrogen</u> | <u>Theoretical
Percent Ammonium
Nitrogen</u> |
|--------------------------|---------------------------------------|---|--|--|
| 9* | 17.2 | 20.9 | 8.67 | 10.5 |
| 10* | 16.7 | 20.9 | 8.52 | 10.5 |

- * The sample number 9 designates the ammonia derivative of the homopolymer prepared in dioxane and 10 refers to the derivative of the homopolymer prepared in benzene.

Figure 15.



DISCUSSION

The preparation of a homopolymer of maleic anhydride has been reported¹². The polymerization of maleic anhydride was attempted and the products which resulted were found to have high enough molecular weights to show that the maleic anhydride did polymerize (See page 59).

The composition of the polymers was determined by high frequency titration and found to be ~100 percent maleic anhydride moiety (See Table XI).

The homopolymers of maleic anhydride which were prepared had relatively low molecular weights. This low molecular weight may reflect the reluctance of the maleic anhydride monomer to react with a free radical of similar structure^{26,27}.

The ammonia derivatives of the polymaleic anhydride were found to be half ammonium salts half amides (See Table XII). The theoretical percent total nitrogen for a complete reaction of the polymaleic anhydride with the gaseous ammonia is 20.9 percent. Neither of the two homopolymers which were reacted with gaseous ammonia reacted completely. The lower molecular weight homopolymer of maleic anhydride had a higher percentage of total nitrogen which may be due to greater accessibility of the anhydride ring in the lower molecular weight homopolymer.

PART F

CONCLUSIONS

CONCLUSIONS

1. Relatively low molecular weight poly-(maleic anhydride co styrene) can be prepared in dimethoxymethane solvent with 0.4 to 0.8 percent benzoyl peroxide initiator concentration.
2. The half amide half ammonium salt can be prepared from poly-(maleic anhydride co styrene) in anhydrous tetrahydrofuran by reacting the copolymer with gaseous ammonia.
3. High frequency titration is a valid method for the determination of ammonium nitrogen in the ammonia derivatives of the copolymer.
4. The ammonia derivatives of the copolymer can be characterized by infrared spectra.
5. Polymaleic anhydride can be prepared in dioxane or benzene using benzoyl peroxide initiator.
6. The half amide half ammonium salt can be prepared from polymaleic anhydride in anhydrous tetrahydrofuran by reacting the homopolymer with gaseous ammonia.

PART G

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