CHEMICAL STUDIES OF THE COPOLYMER OF STYRENE AND MALEIC ANHYDRIDE

Thesis for the Degree of M. S.

MICHIGAN STATE COLLEGE

Robert Emmett Byrne, Jr.

1949

This is to certify that the

thesis entitled

CHEMICAL STUDIES OF THE COPOLYMER OF STYRENE AND MALEIC ANHYDRIDE

presented by

Robert Emmett Byrne, Jr.

has been accepted towards fulfillment of the requirements for

M.S. degree in Chemistry

Ralph L Shriner
Major professor

Date March 16, 1949

M-795

CHEMICAL STUDIES OF THE COPOLYMER OF STYRENE AND MALEIC ANHYDRIDE

by

ROBERT EMMETT BYRNE, JR.

A THESIS

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

MASTER OF SCIENCE

Department of Chemistry

1949

ACKNOWLEDGMENT

The author wishes to express his appreciation to Ralph L. Guile for his guidance and encouragement and to Kenneth G. Stone and Robert M. Herbst for their helpful suggestions and criticism.

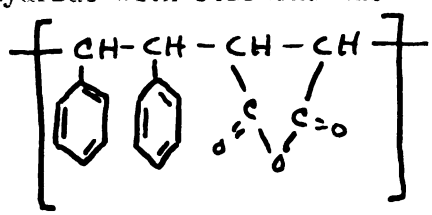
TABLE OF CONTENTS

INTRODUCTION

The literature is almost entirely lacking in any study of the chemical properties of the copolymer of styrene and maleic anhydride. As a part of a continuing investigation in this laboratory[1] the study herein described was initiated in an attempt to elucidate some of the chemical reactions of the copolymer. Since many linear polymers of high molecular weight exhibit reactivity dependent upon functional groups present in the polymer, this particular copolymer was investigated as to reactions typical of acid anhydrides. The hydrolyzed form of the copolymer was investigated as to the properties of an acid. In most cases attempts were made to use standard analytical methods in identifying products.

HISTORICAL

One of the first studies of the copolymerization of maleic anhydride and styrene, as well as other ethylenic hydrocarbons, is reported by Wagner-Jauregg[2]. He proposed that the structural unit of the reaction product of maleic anhydride with stilbene was



in which the two components were combined in equimolar proportion. It was also stated that benzalfluorene gave a product in which the ratio of monomer units was 1:1 even though the initial concentration of the reacting monomers was varied. The addition of styrene to diethylmaleate, on the other hand, was found to yield a product in which the ratio of styrene to ester was 5:1. This was further substantiated by Alfrey and Merz[3] and Mayo and his co-workers[4] who state that "for styrene-diethylmaleate, polymer compositions lay very close to polystyrene." The relative unreactivity of diethylmaleate compared to maleic anhydride is explained by Alfrey who assumes that while the ethylenic bond in the anhydride is relatively exposed, the bond in diethylmaleate is protected from reaction by the presence of bulky carboethoxy groups. Similar unreactive character is exhibited to a somewhat lesser degree by diethylchloromaleate.

Derivatives of the copolymer which are described in the literature [5,6,7,8,9,10,11,12] are limited largely to the monosodium salt and the monoammonium salt. Directions for the preparation of a "partially esterified" copolymer are given in a U. S. patent[6] and a German patent[12]. Some esters of the copolymer have been prepared[5,7,8] by the copolymerization of styrene with diallyl and divinyl esters of maleic acid. These,

however, do not correspond to esters which have been prepared by the author. They represent another approach to the study of the derivatives of the copolymer. It is interesting to note that the copolymerization of styrene with the esters of fumaric acid is easily accomplished[4].

EXPERIMENTAL

REAGENTS:

Styrene: The inhibited Dow Chemical Company product was purified by vacuum distillation and the fraction having an index of refraction of 1.544 at 20°C was used. In some cases it was stored for several weeks at 5°C before being used.

Maleic Anhydride: Eastman Kodak maleic anhydride was used. Several quantities of copolymer were prepared using anhydride which had been purified by distillation and no differences were noted in the resulting products.

Benzoyl Peroxide: Eastman Kodak benzoyl peroxide was used without purification.

Normal Amyl Alcohol: Normal amyl alcohol was purified by distillation collecting the fraction 135-136°C at 746mm pressure.

Normal Butyl Alcohol: Normal butyl alcohol was purified by distillation collecting the fraction 116-117.5°C at 758mm pressure.

Other Reagents: Commercially available C. P. grades were used.

PREPARATION OF THE COPOLYMER[10]

The reaction vessel was a one liter three-neck, round bottom flask with standard taper ground glass joints. It was fitted with a mechanical stirrer, a gas inlet tube and an addition tube in which were placed a thermometer and a reflux condenser. Twenty-six grams of styrene (0.25 mole), 24.5g of maleic anhydride (0.25 mole) and 0.25g of benzoyl peroxide (0.2 mole percent) were placed in the flask with 700ml of benzene. The mixture was stirred until dissolution was complete. The reaction

was carried out in a nitrogen atmosphere. The nitrogen used was first bubbled through alkaline pyrogallol to remove traces of oxygen which might inhibit the copolymerization and then introduced below the surface of the reaction mixture. Heating was accomplished with an electric heating mantle to bring the benzene to reflux(80°C). Reflux was maintained for two hours and the mixture was allowed to cool with stirring. The copolymer was collected by filtration and washed six times with small portions of benzene to remove polystyrene. The copolymer was air dried overnight(12 hours) and then dried at 90°C for several days. Micro carbon-hydrogen determinations were made on the dry copolymer and the percent carbon was found to be 72.11, 70.01, 71.38 and 71.20. The values for hydrogen were 5.59, 5.07, 4.81 and 5.03 percent. The calculated percentage based on a structural unit containing one molecule of styrene to one molecule of maleic anhydride is 71.3 for carbon and 4.98 for hydrogen.

DETERMINATION OF THE PERCENT ANHYDRIDE IN THE COPOLYMER[13]

A weighed sample of the copolymer was dissolved in acetone and the solution was heated to about 25°C. Methyl alcohol was added in twice the amount theoretically necessary to form the half ester of the copolymer. This sample was titrated with approximately 0.1N NaOH in methyl alcohol using phenolphthalein as the indicator. A second weighed sample of the copolymer was dissolved in acetone, heated to about 25°C and titrated to the phenolphthalein end-point with approximately 0.1N aqueous NaOH. The mole percent anhydride was calculated to be 91.2.

Sample calculation using 1.0g samples:

$$\text{Mole \% anhydride} = \frac{2(\text{meq aq. base}_{\text{Sample 1}} - \text{meq alc. base}_{\text{Sample 2}})}{\text{meq aq. base}_{\text{Sample 1}}} \times 100$$

$$= \frac{2(9.80\text{meq} - 5.33\text{meq})}{9.80\text{meq}} \times 100$$

$$= 91.2\%$$

MOLECULAR WEIGHT DETERMINATION[14]

Weighed samples of the copolymer were dissolved in acetone and the resulting solution diluted to 100ml in a volumetric flask. These were cooled to 20°C ± 0.1 in a constant temperature water bath. Viscosity measurements were made at the temperature of the bath with a Cannon-Fenske Ostwald viscosimeter. The time of efflux was measured with an electric timer. The relative viscosity, η_r, was determined by comparing the time of efflux of the pure solvent with that of the copolymer solution

$$\eta_r = \frac{\text{time of efflux of the solution}}{\text{time of efflux of the solvent}}$$

Specific viscosity, η_{sp}, was calculated from the relationship, $\eta_{sp} = \eta_r - 1$. Concentration was expressed in grams of solute per 100ml of solution and the values were calculated for η_{sp}/C. A graph of η_{sp}/C versus C appears below. The average weight of the copolymer was found to be of the order of 36,300. (See page 25 for a discussion of this method.)

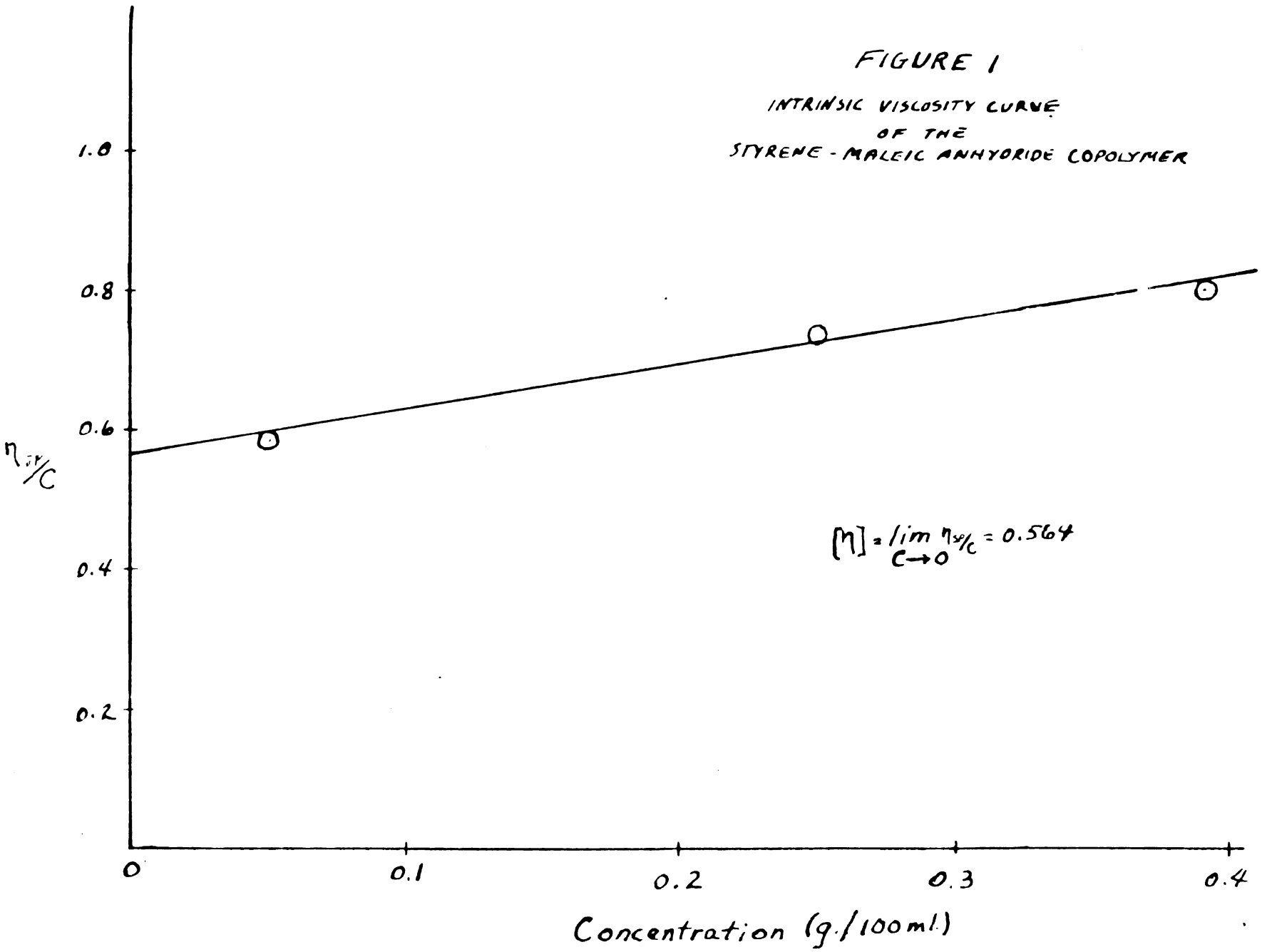
VISCOSITY DATA

Grams of copolymer per 100ml	0.0517	0.2543	0.3912
Time of efflux in secs.	36.7	43.7	46.8
η_r	1.0302	1.197	1.314
η_{sp}	0.0302	0.197	0.314
η_{sp}/C	0.535	0.738	0.804

Time of efflux of acetone 35.6 seconds

FIGURE 1

INTRINSIC VISCOSITY CURVE
OF THE
STYRENE - MALEIC ANHYDRIDE COPOLYMER



SOLUBILITY OF THE COPOLYMER

Solubility determinations on the copolymer were made in a qualitative way to ascertain which solvents might logically be employed in the various preparations. It was found that the copolymer was easily soluble in acetone and methyl ethyl ketone; this was true of all the various forms of the copolymer and its derivatives except for the basic salts. Solubility of the acid and anhydride forms of the copolymer was noted in basic solvents such as pyridine and aqueous alkali. The solution in aqueous alkali is undoubtedly due to the formation of the salts of the copolymer which are soluble in water. Some slight solubility of both the anhydride and acid forms of the copolymer in alcohols, dioxane and water was apparent. The acid form of the copolymer was appreciably soluble in water if moist, but was difficultly soluble when dry.

In dealing with macromolecules of this type, insolubility is a problem. Often lack of reaction is confused with lack of solubility. A polymer is said to be soluble in a given solvent if it swells after several hours contact and goes into solution completely in a day.

PREPARATION OF SALTS FROM THE COPOLYMER[11]

In the course of other preparations it appeared necessary to prepare salts of the copolymer. The sodium salt was prepared by treating the copolymer with a calculated amount of aqueous NaOH based on a 1:1 styrene-maleic anhydride structural unit. It was isolated by pouring the dilute aqueous solution of the copolymer salt into a relatively large volume of acetone in which the sodium salt was insoluble. Vigorous stirring was necessary to prevent the formation of lumps of the salt in acetone. The ammonium salt was prepared by dissolving the copolymer, 5g, in an excess, 100ml, concentrated NH_4OH. It was isolated by evaporating the resulting solution to dryness. A Kjeldahl analysis for nitrogen gave 5.62 and 5.37 percent compared to the value of 11.02 percent based on the structural unit containing two ammonium ions. The result, therefore, of the treatment with excess ammonium hydroxide was the monoammonium salt.

PREPARATION OF THE FREE ACID FORM OF THE COPOLYMER

The free acid form of the copolymer was prepared in two ways:

Preparation A: The sodium or ammonium salt of the copolymer in water was neutralized with reagent HCl in a Waring blendor. The resulting material was washed extensively with water until no test for the Cl^- ion was obtained from the washings. The product was finely divided and was suitable for use without grinding. When the material was prepared using a mechanical stirrer, lumps formed during the neutralization and grinding was required before it could be used in subsequent reactions. Material prepared in this manner was also very difficult to dry.

Preparation B: A dilute (approx. 5%) solution of the copolymer in acetone was added slowly to a relatively large volume of water in a Waring blendor. The acid copolymer was washed with water to remove excess acetone.

Analysis of products:

Method a: Carbon-hydrogen determinations were carried out on the products from preparations A and B. Percentages of carbon found on the products from A were 65.92, 63.81 and 65.69. Hydrogen percentages on the same product were 5.47, 4.62 and 5.76. The product from B showed 64.66 and 63.96 percent carbon and 7.30 and 4.37 percent hydrogen. The calculated values based on a 1:1 styrene-maleic acid structural unit are 65.45 percent carbon and 5.45 percent hydrogen.

Method b: Determinations of the percent acid in the hydrolyzed copolymer were made. Weighed samples of the copolymer were dissolved in a measured excess of aqueous alkali. The excess base was titrated with standard HCl using phenolphthalein as the indicator. The percent acid copolymer was calculated on the basis of the 1:1 structural unit. The values obtained were 46.3 and 48.6 percent.

ESTERIFICATION WITH METHYL ALCOHOL

The preparation of the methyl ester of the copolymer was attempted in several ways:

Preparation A: In a 500ml three-neck, round bottom flask with ground glass standard taper joints fitted with a condenser, mechanical stirrer and a gas inlet tube below the surface of the liquid were placed 20g of the copolymer and 250ml of absolute methyl alcohol. The alcohol was heated to reflux while stirring and anhydrous HCl was allowed to flow through the system. After four hours of refluxing, a mass of polymer separated and 100 ml of absolute methyl alcohol was added to effect dissolution. The polymer again separated after several minutes. The mixture was cooled and the polymer mass collected and dried at 100°C for 13 hours. The alcoholic solution in which the reaction had been carried out was evaporated to dryness and no residue remained.

Preparation B: In a 500ml three-neck flask with ground glass standard taper joints fitted with a mechanical stirrer, dropping funnel with a gas inlet tube and a fractionating head were placed 5g of the copolymer and 100ml of absolute methyl alcohol. Stirring was started; anhydrous HCl was passed into the system and solution occurred rapidly. Distillate was collected from the fractionating head and the volume was kept constant by the addition of absolute methyl alcohol through the dropping funnel. After four hours at reflux, a polymer mass separated. Enough dioxane-1,4 was added to dissolve the precipitate. Dioxane and absolute methyl alcohol were mixed in equal proportions and the mixture was added dropwise to keep the volume constant. Refluxing was continued for 24 hours. The solution was evaporated to dryness under vacuum. The solid product was

dried in a vacuum oven at 70°C. Carbon-hydrogen determinations were made on the dry product. It was found to contain 66.49, 66.45, and 66.34 percent carbon and 6.07, 6.98 and 6.09 percent hydrogen. The calculated values based on the completely esterified 1:1 structural unit are 67.74 percent carbon and 6.45 percent hydrogen.

Preparation C: The copolymer, 5g, was dissolved in a large excess, 250ml, of absolute methyl alcohol and refluxed for four hours after going into solution. A solid was isolated by evaporating the solution to dryness. It was allowed to dry overnight at 100°C. A carbon-hydrogen analysis on the dry product showed 65.51, 63.89 and 65.30 percent carbon and 7.84, 4.73 and 5.00 percent hydrogen. The calculated values as stated above are 67.74 percent carbon and 6.45 percent hydrogen.

Preparation D: The copolymer, 4g, which had been dried overnight under vacuum was dissolved in 100ml of absolute methyl alcohol. The absolute alcohol was prepared by adding metallic sodium to commercial absolute methyl alcohol and distilling the anhydrous alcohol directly into the reaction vessel. Solution of the copolymer required about ten hours during which time the mixture was stirred and heated to about 50°C. The reaction mixture was protected from moisture with calcium chloride. The product was isolated by evaporating the solution to dryness under vacuum. The solid product was then dried overnight in a vacuum oven at 70°C. Carbon-hydrogen determinations on the product showed 67.81 and 67.53 percent carbon and 6.70 and 6.79 percent hydrogen. Calculated values are 67.74 percent carbon and 6.45 percent hydrogen.

ESTERIFICATION WITH ETHYL ALCOHOL

The preparation of the ethyl ester of the copolymer was attempted in two ways:

Preparation A: Four grams of the copolymer were dissolved in 100ml of absolute ethyl alcohol which were distilled directly into the reaction vessel from 200ml of absolute ethyl alcohol treated with 10g of sodium. The reaction mixture was protected from moisture. Solution of the copolymer was complete in 14 hours, being aided by continuous stirring and heating to about 50°C. A solid product was isolated by evaporating the alcohol solution under vacuum. The product was then dried at 70°C in a vacuum oven. Carbon-hydrogen determinations were made on the dry product and the percentages were 66.50 and 66.01 for carbon and 8.69 and 7.98 for hydrogen. The calculated values based on the completely esterified 1:1 structural unit are 67.13 percent carbon and 6.99 percent hydrogen.

Preparation B: Five grams of the acid copolymer were dissolved in 100ml of purified dioxane[22] (redistilled from sodium). Excess thionyl chloride, 20ml, was added dropwise to the solution which was protected from moisture. After solution was complete an excess of absolute ethyl alcohol (200ml) was added. A solid product was isolated by evaporating the solution under vacuum. It was dried for several hours in the vacuum oven at 70°C. Carbon-hydrogen determinations on the dry product showed 66.53 and 66.74 percent carbon and 7.07 and 7.35 percent hydrogen. The calculated values as previously given are 67.13 percent carbon and 6.99 percent hydrogen.

ESTERIFICATION WITH NORMAL BUTYL ALCOHOL

In a 500ml three-neck, round bottom flask with ground glass standard taper joints fitted with a mechanical stirrer, a fractionating head and a dropping funnel with a gas inlet tube were placed 5g of the copolymer and 100ml of redistilled n-butyl alcohol. Stirring, heating and the flow of anhydrous HCl through the system were begun and solution was rapid. Normal butyl alcohol was added dropwise and the volume was kept constant by distilling off solvent. The mixture was refluxed for 24 hours. Vacuum distillation was used to isolate the product which was then dried at 70°C in the vacuum oven. Carbon-hydrogen determinations on the dry product showed it to contain 66.79 and 66.87 percent carbon and 5.44 and 6.32 percent hydrogen. The values calculated on the basis of the completely esterified 1:1 structural unit are 74.53 percent carbon and 8.70 percent hydrogen.

ESTERIFICATION WITH NORMAL AMYL ALCOHOL

Preparation A: The copolymer, 1g, was dissolved in 100 ml of redistilled n-amyl alcohol. The solution was heated near its boiling point (about 110°C) for two hours after dissolution was complete. The product was not isolated but was subjected to saponification in the alcohol solution. (See page 21)

Preparation B: In a 500ml three-neck, round bottom flask with ground glass standard taper joints fitted with a mechanical stirrer, a fractionating head and a dropping funnel with a gas inlet tube were placed 5g of copolymer and 200ml of redistilled amyl alcohol. Stirring and heating were begun and when dissolution was complete (about twenty minutes) a stream of anhydrous hydrogen chloride was allowed to pass through the system. Reflux was maintained and the volume of solution kept constant for 24 hours by balancing distillation rate with the dropwise addition of alcohol. The solution was evaporated to dryness under vacuum. The product was dried in a vacuum oven at 85°C overnight. The material from this preparation was quite charred and was not subjected to carbon-hydrogen analysis. (For saponification see page 21)

REACTION WITH THIONYL CHLORIDE

Preparation A: In a 500ml round bottom flask with ground glass standard taper joints fitted with a condenser were placed 10g of the acid form of the copolymer and 75ml of thionyl chloride. The mixture was refluxed for 24 hours and some swelling occurred in the copolymer. Excess thionyl chloride was removed under vacuum and the copolymer derivative stored in a dessicator over NaOH pellets. The acid chloride was decomposed in a Parr bomb with sodium peroxide and potassium nitrate according to the method of Lemp and Broderson[16]. An analysis for chlorine was made using the Volhard technique[17]. The product was found to contain 4.89 and 2.25 percent chlorine. The calculated value based on the 1:1 structural unit containing two chlorine atoms per unit is 28.74 percent.

Preparation B: The acid copolymer, 1g, was dissolved in 100ml of dioxane-1,4 in a 500ml round bottom flask with ground glass standard taper joint. Twenty ml. of thionyl chloride was added dropwise. The reaction mixture was allowed to stand for six hours. Excess thionyl chloride and solvent were removed under vacuum, and the product was dried over NaOH pellets. A Parr bomb-Volhard chloride analysis showed 10.48 and 11.21 percent chlorine.

Another preparation of the acid chloride was made using the same technique. It was used in the preparation of the ethyl ester (see page 13).

PREPARATION OF THE AMIDE OF THE COPOLYMER

Preparation A: The ammonium salt was prepared as previously described. It was subjected to baking at temperatures of from 120-135°C for periods ranging up to 25 days in attempts to rearrange the salt to the amide. Considerable charring was noted even at the shorter periods and lower temperatures. Hydrolysis of the products with cold aqueous NaOH gave a test for ammonia[15] in all cases. The acidified solution yielded a product which gave no indication of nitrogen by the Lassaigne[16] test.

Preparation B: The product of the treatment of the copolymer with methyl alcohol described in preparation A of that section was allowed to react with 30ml of liquid ammonia. A high pressure bomb was used as the reaction vessel and 8g of the partially esterified material were used. The temperature was raised to 120°C corresponding to a pressure of 550 pounds per square inch. The bomb was allowed to cool overnight, the reaction products removed and the resulting polymer was dried at 100°C for 24 hours to eliminate excess ammonia. A qualitative test for nitrogen, the Lassaigne test, on the product was positive. Treatment with aqueous alkali in the cold indicated the presence of ammonia. The acidified alkaline solution from the above test yielded a polymeric material which contained no nitrogen as indicated by the Lassaigne test.

Preparation C: The partially esterified material from preparation A of the esterification with methyl alcohol was treated with concentrated NH_4OH for three days. After evaporating the solution to dryness, the copolymer derivative was dried at 100°C overnight. A Kjeldahl analysis on the product showed 1.85 percent nitrogen. The calculated value is 12.84 percent nitrogen based on a 1:1 structural unit containing two ammonium ions.

REACTION WITH HYDRAZINE

The partially esterified material prepared with methyl alcohol as described in preparation A was allowed to react with hydrazine hydrate. Methyl alcohol was used as the solvent and 1.5g of the esterified material and 0.5g of hydrazine hydrate were used. Very little solution of the ester occurred and the mixture was allowed to go to dryness slowly on the steam bath. The resulting product was slightly soluble in water. A Kjeldahl analysis showed 8.40, 5.35, and 5.62 percent nitrogen. The calculated value is 22.58 percent nitrogen for a 1:1 styrene-maleic acid unit containing two hydrazide groups.

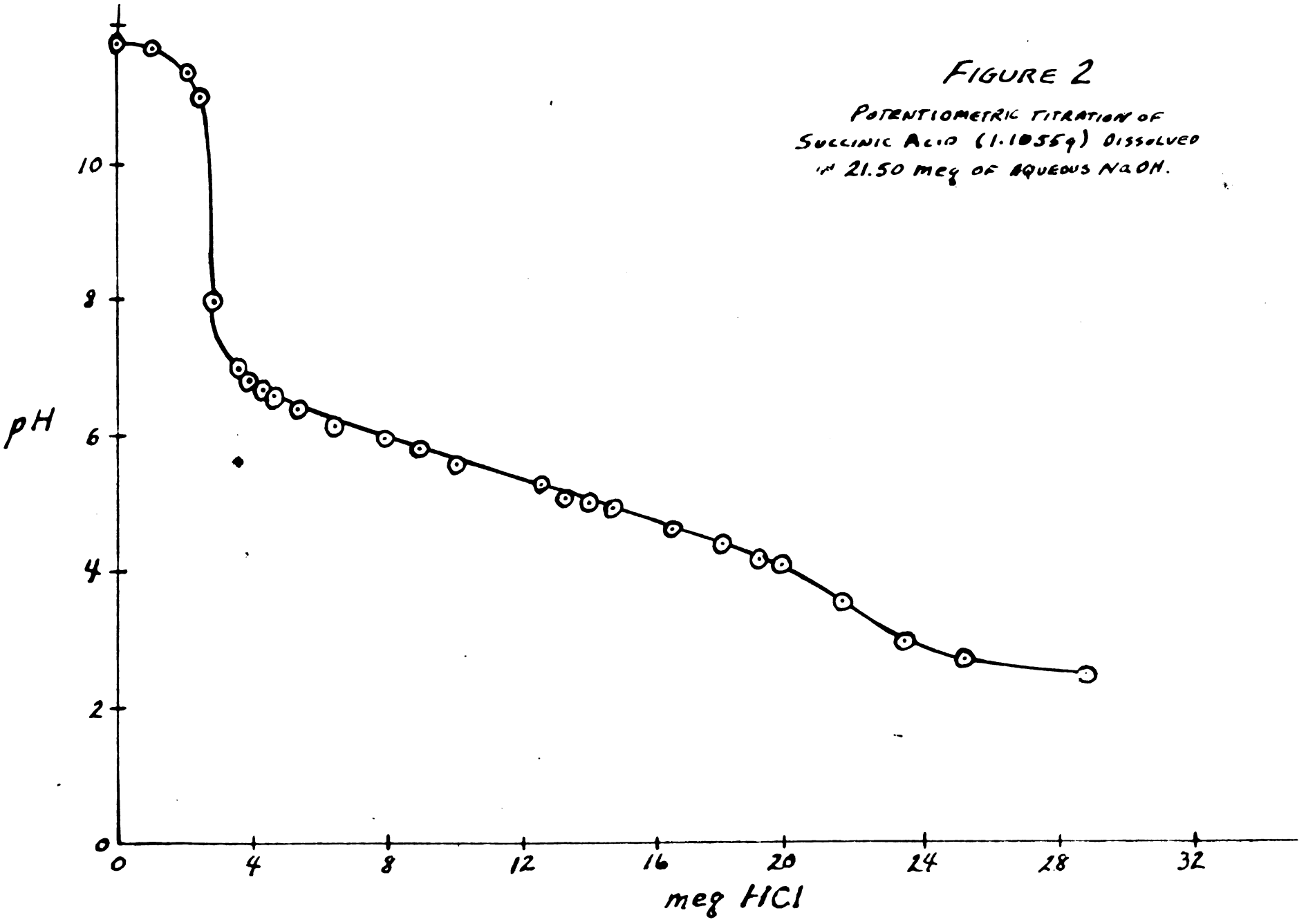


FIGURE 2

POTENTIOMETRIC TITRATION OF SUCCINIC ACID (1.1056g) DISSOLVED IN 21.50 meq OF AQUEOUS NaOH.

POTENTIOMETRIC TITRATIONS

I. A potentiometric titration was made on succinic acid dissolved in aqueous alkali. The acid, 1.1055g, was dissolved in 200ml of water to which had been added 21.50 meq. of NaOH. The pH meter used was the Cenco Model 20965 with external standard glass electrode. Standard hydrochloric acid was added from a buret and pH measurements were made at intervals.

DATA:

meq HCl	pH	meq HCl	pH
0	11.78	9.00	5.80
1.08	11.71	10.08	5.59
2.16	11.35	12.60	5.27
2.52	11.00	13.32	5.08
2.88	7.97	14.04	4.99
3.06	7.49	14.76	4.92
3.24	7.26	16.57	4.60
3.60	6.99	18.00	4.40
3.96	6.81	19.09	4.15
4.36	6.69	19.80	4.08
4.68	6.60	21.60	3.52
5.40	6.37	23.40	2.97
6.48	6.13	25.20	2.70
7.92	5.94	28.80	2.48

II. A weighed sample of the copolymer, 0.6230g, was dissolved in 50ml. of 0.4626N NaOH (23.13 meq.) by refluxing. The solution was diluted to 200ml. and standard hydrochloric acid was added. The pH of the solution was measured at intervals with a Cenco pH meter using an external

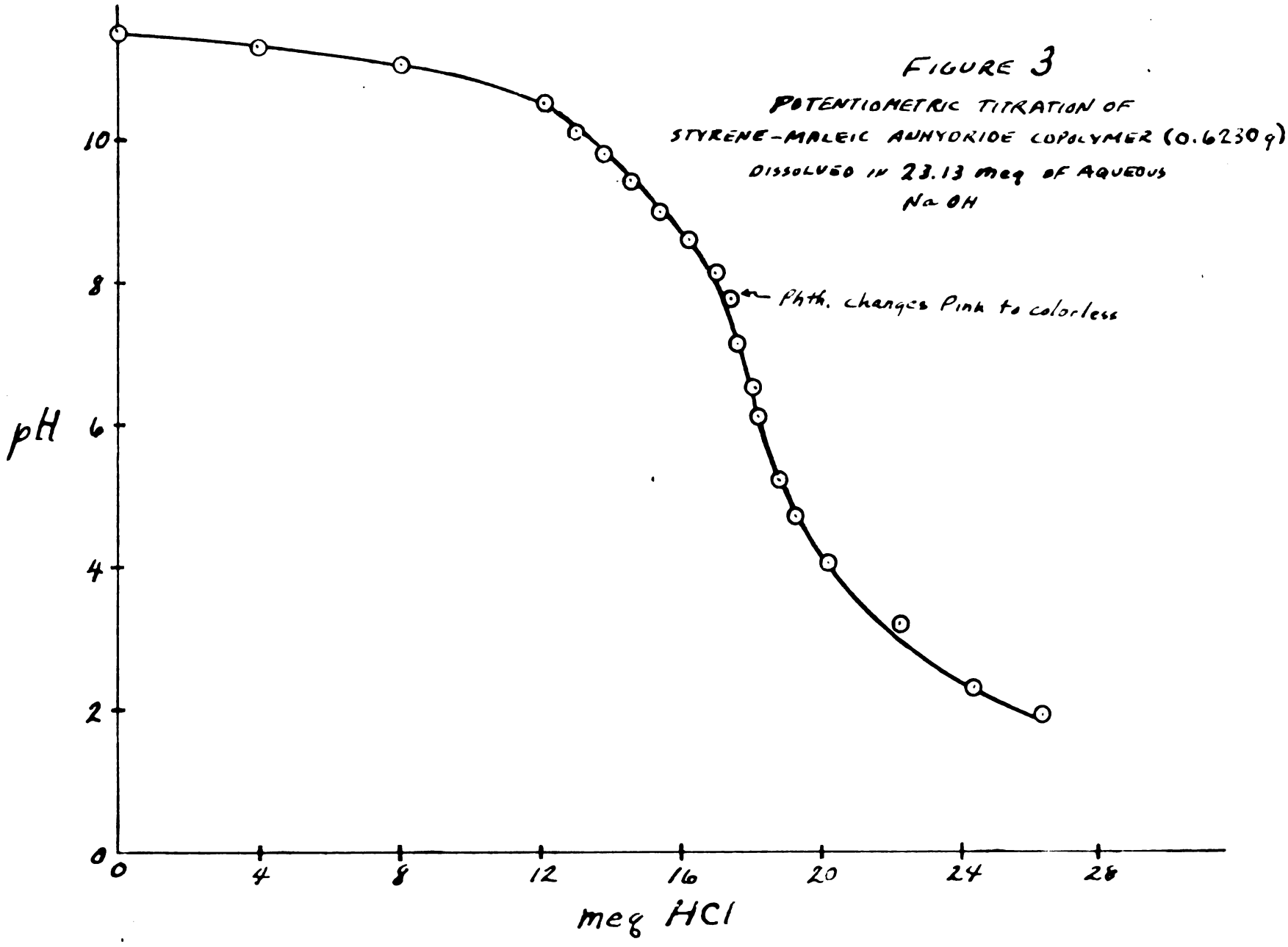


FIGURE 3

POTENTIOMETRIC TITRATION OF STYRENE-MALEIC ANHYDRIDE COPOLYMER (0.6230 g) DISSOLVED IN 23.13 meq OF AQUEOUS NaOH

standard glass electrode.

DATA:

meq. HCl	pH	meq. HCl	pH
0	11.52	17.89	7.14
2.02	11.47	17.79	7.03
4.04	11.32	17.99	6.58
6.07	11.24	18.20	6.16
8.09	11.17	18.40	5.89
10.11	11.01	18.60	5.48
12.13	10.51	18.80	5.27
12.94	10.12	19.21	4.75
13.75	9.82	19.61	4.43
14.56	9.41	20.22	4.09
15.37	9.00	21.23	3.73
16.18	8.61	22.24	3.23
16.58	8.43	23.25	2.60
16.98	8.13	24.26	2.30
17.35	7.78	26.29	1.95

SAPONIFICATION OF ESTERIFIED MATERIALS

Saponification of the esters was accomplished in the same alcohol from which they were prepared. The alcoholic solution was neutralized and a measured excess of the alcoholic base was added. The mixture was refluxed for from 12 to 48 hours. Excess base was titrated with 0.1N HCl to the phenolphthalein end-point. Percent esterification was calculated from the amount of alkali consumed based on the theoretically completely esterified 1:1 structural unit.

Calculations were made using the formula

$$\text{Percent esterification} = \frac{(\text{meq. base consumed})\ (\text{meq. wt. of ester})}{\text{Sample weight}} \times 100$$

A copolymer sample completely esterified by ethyl alcohol would have a molecular weight of 276 per unit and a sample calculation on one ethyl alcohol esterified product follows:

$$\text{Percent esterification} = \frac{(0.311)\ (0.133)}{1.0114} \times 100$$

$$= 10.1\%$$

The percent esterification was also approximated from the carbon-hydrogen analyses using the formula

$$\text{Percent ester} = \frac{(\%C \text{ found in ester} - \%C \text{ calc for acid})}{(\%C \text{ calc for ester} - \%C \text{ calc for acid})} \times 100$$

The accuracy of this empirical method was checked and was found to

vary by less than 1% in the case of the ethyl ester. A complete ethyl ester of the hydrolyzed copolymer should contain 67.13 percent carbon and the hydrolyzed copolymer (free acid form) should contain 65.45 percent carbon. A sample calculation for the ethyl ester from Preparation A (page 13) follows:

$$\% \text{ ester} = \frac{(66.26-65.45)}{(67.13-65.45)} \times 100$$

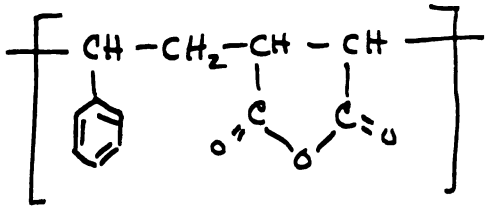
$$= 43.3\%$$

TABLE I

Ester	% esterification (by saponification)	% esterification (by C-H analysis)
Methyl		
Prep A	2.6	-
Prep B	-	42.8
Prep C	3.6	0
Prep D	-	99.1
Ethyl		
Prep A	10.1	43.3
Prep B	-	70.7
Butyl	-	15.2
Amyl		
Prep A	6.4	-
Prep B	15.1	-

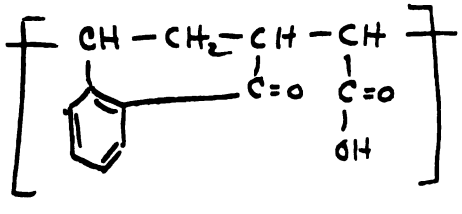
DISCUSSION

It was originally assumed that the structural unit of the copolymer of styrene and maleic anhydride was



(1)

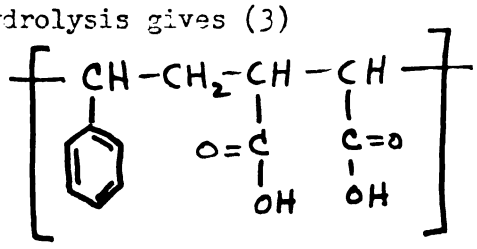
which would agree with the work of Wagner-Jauregg[2]. Apparently the composition of the copolymer is a 1:1 molar ratio of the reacting monomers[1,2]. Preliminary work on the problem of chemical reactivity of the copolymer, however, cast doubt on the accuracy of this assumption. The copolymer did not behave as the anhydride of a typical dibasic acid. It could not be titrated to indicate both carboxyl groups and derivatives appeared not to form under the usual conditions. It seemed that either the ratio of styrene to maleic anhydride units in the copolymer was not 1:1 or that formulation (1) was in error; it appeared that some other structure might better describe the experimental results obtained. Both Garrett[1] and the author noted the inability to neutralize the sodium salt of the copolymer to the extent expected on the basis of two carboxyl groups per unit. For this reason the structure



(2)

was postulated to explain these facts more satisfactorily. Assuming that structure (2) was correct, the copolymer and its hydrolysis product should be identical. It also should be possible to detect the presence of carbonyl groups in the copolymer. It was shown by carbon-hydrogen analysis

and a qualitative test for carbonyl groups based on the method of Duke[19] that structure (2) does not apply. While other formulations are, of course, possible, results of these determinations correspond to structure (1) which upon hydrolysis gives (3)



(3)

Structures (1) and (3) are those used as the bases for calculations.

The method of Siegel and Koran[13] for the determination of anhydrides of dibasic acids in the presence of the acid was employed to help prove that the copolymer contained primarily anhydride linkages when prepared as described. While there is some doubt as to the applicability of this method to the copolymer, results obtained were those anticipated. It was shown that the copolymer contained about 91% anhydride which upon hydrolysis yielded a copolymer which had only 50% of the expected acid groups. This can be explained if it is possible to neutralize only one-half of the carboxyl groups in the hydrolyzed copolymer, or if one carboxyl per unit is in some way rendered inactive by reaction with some other portion of the molecule. Since no satisfactory explanation of the latter is possible at present, the former is assumed to be the case. It appears that some sort of steric hindrance prevents the second carboxyl from reacting. Thus a hydrolyzed copolymer which contained carboxyl groups resulting from a 100% conversion of anhydride groups would give on titration the indication of only 50% of the carboxyl groups actually present.

It has been reported by Bruckner and Kovacs[20] that maleic anhydride and compounds similar to styrene will undergo a Diels-Alder type conden-

sation under the influence of heat and in the absence of a catalyst which leads to the formation of compounds of low molecular weight. If Diels-Alder type compounds were formed during copolymerization, they would partially account for the relative unreactivity exhibited by the copolymer. For this reason the average molecular weight of the copolymer has been determined. The basic formula of Flory[21] and Houwink[21]

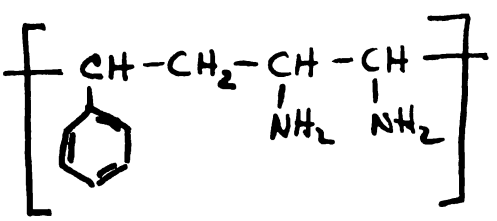
$$[\eta] = KM^{a}$$

was employed using the constants determined by Carter, Scott and Magat[14]. Carter et al, from their study of a series of rubbers, found that K was 5.02×10^{-4} and that the exponent a was 0.667 giving the equation the form

$$[\eta] = 5.02 \times 10^{-4} M^{0.667}$$

An average molecular weight of 36,300 was obtained for the copolymer using these values with the intrinsic viscosity obtained by the graphical method. The intrinsic viscosity, $[\eta]$, was obtained by extrapolating the curve to the zero ordinate. This value corresponds to the value of η_{sp}/C at infinite dilution. Since no value for K or the exponent a has been determined for the styrene-maleic anhydride copolymer, these values of Carter et al were used arbitrarily. However, a molecular weight has been obtained which is reproducible and should be valuable in helping to characterize the copolymer. It also serves the purpose of indicating that the material being investigated was indeed polymeric and of relatively high molecular weight.

The original problem was to be an attempt to prepare the corresponding polyamine



(4)

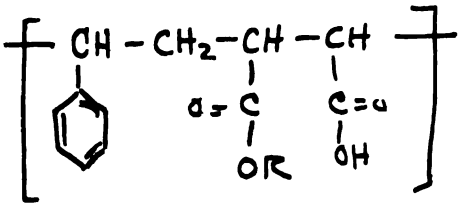
from the copolymer. It was hoped to accomplish this through the rearrangement of the amide. It was, therefore, necessary to prepare the free acid form of the copolymer. This preparation, as shown in the Experimental, could be accomplished in either of two ways. The most suitable method was the precipitation of the acid form from an acetone solution with water. Material prepared in this way was easily dried and was in a workable state.

The acid form of the copolymer was used to prepare an ammonium salt, but it was found that the salt could be prepared as well from the copolymer itself. The ammonium salt contained slightly less than 50% of the calculated amount of nitrogen based on the 1:1 structural unit containing two ammonium ions, and, hence, was probably the monoammonium salt. Attempts were made to rearrange the ammonium salt to the amide by the elimination of water or ammonia by heat. Heating the ammonium salt even at temperatures which caused the copolymer to char did not result in significant amide formation. This conclusion was based on the Lassaigne test for nitrogen on the product after it had been subjected to hydrolysis with cold aqueous NaOH. In the light of later results, it would seem that a quantitative determination of nitrogen in this product should have been carried out.

The preparation of the amide of carboxylic acids through the acid chloride is a standard procedure in preparative organic chemistry. In this connection, an attempt was made to treat the acid copolymer with an excess of thionyl chloride[15] to obtain the acid chloride. The free acid form was insoluble in the thionyl chloride and this attempt produced a material which contained only 4% chlorine while the calculated value is 28.74 percent based on the 1:1 structural unit containing two chlorine

atoms per unit. An effort was made to circumvent the lack of reaction due to solubility difficulties by treating a dioxane solution of the copolymer with thionyl chloride. A material was obtained which contained about 11 percent chlorine. This corresponds to about 40 percent acid chloride formation. A product prepared in the same way was treated with absolute ethyl alcohol and yielded an ester which was 70 percent esterified.

Anhydrides of dibasic acids when dissolved in alcohols yield the half ester. This fact has been observed by Siegal and Moran[13] and others. It, therefore, seemed reasonable that if the copolymer were dissolved in absolute alcohols, the half ester of the copolymer



(5)

would be formed. The ester represented by formulation (5) corresponds to a 50 percent esterification of the copolymer containing alternating units of styrene and maleic acid.

At the beginning of this investigation, attempts to study reactions or products prepared in this manner resulted in failure. The treatment of these materials with ammonia to form amides and treatment with hydrazine to form hydrazides did not give the expected results. However, it is now apparent that while the reactions were not 100 percent complete, some significant formation of the desired products was realized. Saponification of the esters prepared early in this investigation always indicated very low esterification. It has since been shown that the saponification of these esters is at best unreliable.

While it is true that at first little esterification was accomplished

by the dissolution of the copolymer in alcohols, it later became apparent that the difficulty was due to the presence of traces of water. When the esterification was attempted by dissolving the copolymer in alcohols in systems protected from moisture and using reagents free of water, a material was obtained which was more than 50 percent esterified. Treatment of the copolymer with anhydrous methyl alcohol yielded a product which was shown to be about 99% esterified. This might be explained by the fact that the reaction was carried out under anhydrous conditions and that during the preparation the mixture was heated at 50°C over a period of 10 hours. A 70 percent esterification of the copolymer was accomplished by treatment of its dioxane solution with thionyl chloride and the subsequent addition of anhydrous ethyl alcohol. The high percent esterification in both cases was probably due to the anhydrous conditions.

The esterification of the copolymer was attempted with absolute methyl alcohol using gaseous HCl as the catalyst. Methyl alcohol and dioxane (1:1) was added in quantities necessary to keep the polymer in solution. The mixture was refluxed for 24 hours removing a portion of the distillate to keep the water concentration at a minimum. Carbon-hydrogen determinations on the product showed that there was about 50% esterification. From this we conclude that while it is possible to esterify the copolymer, the process is not spontaneous unless the water concentration is essentially zero. It is apparent that traces of water prevent esterification, probably in a manner similar to that observed in the preparation of esters of the simple acids.

The product of the attempt to prepare the n-butyl ester of the copolymer using forced conditions; i.e., using gaseous HCl, etc. showed about 15 percent esterification based on carbon-hydrogen determinations.

It appears that some effect is exerted by the size of the alcohol employed in esterification. The butyl ester as prepared was formed to only one-third the extent of the methyl ester by the same method.

It was apparent in the preparation of the amyl ester by the same technique that the reaction temperature with amyl alcohol as the solvent was too high. There was considerable charring in the product isolated and the highest temperature employed was 130°C. No charring was noted in the preparation of the butyl ester where the highest temperature attained was 100°C. It would seem desirable, therefore, to use a solvent carrier which would enable an esterification reaction to proceed at a temperature not greater than 100°C. It is possible that pyridine would be useful as a solvent in esterifications since it dissolves the copolymer, but its use was not investigated.

Some potentiometric titration curves of the copolymer and succinic acid were determined. It was hoped that there might be some correlation between the two. It can be seen from figures 2 and 3, however, that the effect of the substitution of the styrene nucleus in the molecule changes the characteristics of one of the carboxyls in the structural unit. This was, indeed, apparent from the standpoint of chemical reactivity. The pH at which the major break in the titration curve occurs is considerably different, indicating the alteration of the properties of one carboxyl group. It can also be seen from figure 3 that phenolphthalein indicator changes color at pH 7.8 which should make it a suitable indicator for the titration of the copolymer if no other effect influences its color change. The use of this indicator was questioned by Garrett in the titration[1] of the reacting copolymerization mixture of styrene and maleic anhydride.

It has been mentioned previously that the saponification of esterified products was attempted in this investigation. This was done in an effort to establish a quick and dependable method for the identification of reaction products. It can be seen from the data (page 22) that there is little correlation between the results of calculations of percent esterification from saponification and from carbon-hydrogen percentages. In fact, the percent esterification increases from methyl to amyl when determined from saponification data while it decreases when determined by carbon-hydrogen analyses. It must be concluded, therefore, that the usual saponification techniques for esters do not constitute an accurate method for use with esters of the copolymer of styrene and maleic anhydride. In addition to the apparent inaccuracy, a lack of reproducibility of results was also noted. It is possible that this is due, in part, to the inability to obtain products in the same physical state. It is also possible that at least some of the inconsistency noted may be due to the indicator used. If this is the case, it should be pointed out that a method for the saponification of these copolymer esters might be worked out using another indicator.

One of the greatest difficulties encountered in this investigation was the problem of solubility of the copolymer and resulting reaction products. Acetone was found to be the best solvent, but its reactivity toward many reagents prohibits its use. It is probable, as stated before, that pyridine would make a useful solvent for reaction where acetone can not be used. The pyridine employed, however, would have to be carefully dried. Small amounts of water will cause the polymeric materials to separate from any but the basic solvents and interfere in such reactions as esterification.

There are several logical outgrowths of the work which has been done in this investigation. Since one of the greatest difficulties in this study was a lack of solubility of the copolymer, it might be possible to prepare copolymers of lower molecular weight and hence increase their solubility and use in future studies. These probably could not be prepared by the technique used in this work, but possibly could be prepared by other means of synthesis. If, for example, a product could be obtained containing one styrene unit and one unit of maleic anhydride, it would allow a detailed study of chemical reactivity without involving the same solubility difficulty. Even though solubility was the paramount obstacle in this study, important data could be obtained regarding reactivity which would apply to the high molecular weight polymers.

It also seems probable that a thorough study of the saponification of the copolymer esters would present an interesting problem. While it has been shown that the usual techniques do not apply, it is possible that the use of another indicator or different reaction conditions would produce better results. Another extension of this problem would be the preparation of such derivatives of the copolymer as the amide or the hydrazide. The results obtained by this author while promising are inconclusive.

A study of derivatives which would better lend themselves to analysis also seems in order. An example is the ester which might be prepared from the copolymer with a halogen substituted alcohol. Such an ester could easily be analyzed for halogen and would greatly facilitate the study of the copolymer derivatives. The esters might be further studied by an indirect approach. For example, the dibutyl ester might be prepared by the copolymerization of styrene with dibutylmaleate. Some work has been

done along these lines, but it seems quite inadequate.

Another problem which seems pertinent to this investigation is the study of a series of copolymers of maleic anhydride with other materials containing acid groups. It would be interesting to compare the reactivity of a copolymer with two carboxyls per unit separated by a hydrocarbon group (i.e., the copolymer used in this study) with a copolymer in which there were three, four or more carboxyl groups separated by the same nucleus or merely with a copolymer containing a continuous chain of pendant carboxyl groups.

CONCLUSIONS

1. Esters can be prepared from the styrene-maleic anhydride copolymer by dissolving it in absolute alcohols under anhydrous conditions.
2. Esters can be prepared from the styrene-maleic anhydride copolymer using the appropriate alcohol with anhydrous hydrogen chloride as a catalyst.
3. The usual saponification technique as an analytical procedure is not applicable to esters of the copolymer of styrene-maleic anhydride.
4. Additional evidence has been presented to support a 1:1 structure of the styrene-maleic anhydride copolymer.
5. The styrene-maleic anhydride copolymer prepared as described is a macromolecule having an average molecular weight of the order of 36,000.
6. One-half of the carboxyl groups of the hydrolyzed strene-maleic anhydride copolymer are more reactive than the other. An ammonium salt and an acid chloride involving one-half of the carboxyls have been prepared.

LITERATURE CITED

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

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

3. Alfrey, T., and Merz, E., Polymer Bull., 1, 86 (1945).

4. Lewis, F., Walling, C., Cummings, W., Briggs, E., and Mayo, F., J. Am. Chem. Soc., 70, 1519 (1948).

5. Zemba, J., and Coleman, G., U. S. 2,311,615, C. A., 37, 4501 (1943).

6. Gerhart, H., and Bauer, W., U. S. 2,320,714, C. A. 37, 6769 (1943).

7. Britton, E., Coleman, G., and Zemba, J., U. S. 2,331, 263, C. A. 38, 1305 (1944).

8. Neher, H., Ger. 745,301, C. A. 40, 497 (1946).

9. Stoops, W., and Staff, C., U. S. 2,375,960, C. A. 39, 4263 (1945).

10. D'Alelio, G., "Experimental Plastics and Synthetic Resins" Wiley, 1948, p. 113.

11. Guile, R., and Huston, R., "A Revised Laboratory Manual of Synthetic Plastics and resinous Materials", 1944, p. 94.

12. Voss, A., and Dickhauser, E., U. S. 2,047,398.

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

14. Carter, W., Scott, R., and Magat, M., ibid., 68, 1480 (1946).

15. Shriner, R., and Fuson, R., "Identification of Organic Compounds", Wiley, 1940, p. 71.

16. Ibid., p. 113.

17. Lemp, J., and Broderson, H., J. Am. Chem. Soc., 39, 2069 (1917).

18. Willard, H., and Furman, N., "Elementary Quantitative Analysis", D. Van Nostrand, 1940, p. 135.

19. Duke, F., Ind. Eng. Chem., Anal. Ed., 16, 110 (1944).

20. Bruckner, V., and Kovacs, J., J. Org. Chem., 13, 641 (1948).

21. Houwink, R., J. Prakt. Chem., 197, 15 (1940); Flory, P., J. Am. Chem. Soc., 65, 372 (1943).

22. Fieser, L., "Experiments in Organic Chemistry", Heath, 1941, p. 368.

T547 216925
B995 Byrne