

The Effect of Certain Groups on the Basic Properties  
of Polyquaternary Ammonium Hydroxides

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A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF  
THE UNIVERSITY OF FLORIDA  
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE  
DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA  
January, 1953

## TABLE OF CONTENTS

	Page
LIST OF TABLES.....	111
LIST OF ILLUSTRATIONS.....	iv
Section	
I. INTRODUCTION.....	1
A. Literature Review.....	1
B. Statement of the Problem.....	3
C. Source and Purification of Reactants.....	5
II. PREPARATION OF TERTIARY AMINES.....	7
A. General Discussion.....	7
B. Experimental.....	9
III. PREPARATION OF UNSATURATED QUATERNARY AMMONIUM HALIDES.....	15
A. General Discussion.....	15
B. Experimental.....	17
IV. POLYMERIZATION OF UNSATURATED QUATERNARY AMMONIUM HALIDES.....	29
A. General Discussion.....	29
B. Experimental.....	30
V. ION EXCHANGE CAPACITY OF RESINS.....	40
A. General Discussion.....	40
B. Experimental.....	42
VI. DISCUSSION OF RESULTS.....	58
VII. SUMMARY.....	58
BIBLIOGRAPHY.....	60
ACKNOWLEDGMENTS.....	61
BIOGRAPHICAL ITEMS.....	62
COMMITTEE REPORT.....	63

## LIST OF TABLES

Table	Page
I. Unsaturated Tertiary Amine and Tertiary Amine Hydrobromides .....	14
II. Unsaturated Quaternary Ammonium Bromides .....	27
III. Unsaturated Quaternary Ammonium Chlorides .....	28
IV. Data on Titration of Resins A-H .....	44
V. Data on Titration of Resins I-P .....	46
VI. Properties of Ion Exchange Resins .....	52

## LIST OF ILLUSTRATIONS

Graph	Page
I. Ion Exchange Capacity Titrations of Polymers A-D .....	48
II. Ion Exchange Capacity Titrations of Polymers E-H .....	49
III. Ion Exchange Capacity Titrations of Polymers I-L .....	50
IV. Ion Exchange Capacity Titrations of Polymers M-P .....	51

## I. INTRODUCTION

### A. Literature Review

The absence of information in the literature concerning the polymerization of unsaturated quaternary ammonium compounds to anion exchange resins of high basicity led Butler and Bunch (1) to investigate the polymerization of various unsaturated quaternary ammonium compounds with peroxide catalysts. Tertiary butyl hydroperoxide proved to be the most satisfactory catalyst in preparing polymers from unsaturated quaternary ammonium halides. Resins capable of operating in a pH range of 11 to 12, but having capacities no greater than 0.40 milliequivalents of anion per milliliter of wet resin, were synthesized in this study.

Butler and Ingley (2) have shown that the presence of a halogenated allyl group in a quaternary ammonium derivative tends to decrease the polymerization rate. This was substantiated by the fact that the coefficient of swelling of a triallyl-2-chloroallyl ammonium bromide polymer was considerably greater than that of a tetraallylammonium bromide polymer prepared under similar conditions, indicating a lower degree of cross-linking. The halogenated polymer had a higher ion-exchange capacity per unit weight and a lower ion-exchange capacity per unit volume than the non-halogenated polymer.

Investigation of unsaturated quaternary ammonium bromides containing the vinyloxyethyl group by Butler and this author (3) showed that the vinyloxyethyl group did not enter into the polymerization under the conditions used.

The work of Butler and Johnson (4) showed that the triple bond did not enter into the polymerization when quaternary ammonium compounds containing the propargyl group were tested.

Butler, Banch, and Ingley (5) have shown by titration that the polymers obtained by polymerization of unsaturated quaternary ammonium salts function as strongly basic ion exchange resins. Titration curves resembled a typical strong base-strong acid titration curve. Under the conditions of polymerization used in the work, the polymers showed a small amine capacity as the result of thermal decomposition of the quaternary ammonium salt. The hydroxide form of the polymers decomposed by a Hofmann degradation when heated. Polymers prepared by polymerization at low temperatures showed decreased swelling coefficients and correspondingly decreased capacities, probably as the result of screening. Polymers prepared by suspension polymerization showed an increase in capacity with decreasing swelling coefficient. The polymers prepared by bulk polymerization showed a definite relationship between the coefficient of swelling and the ion exchange capacity. The higher the coefficient of swelling, the more nearly the theoretical capacity of the resin is approached. These workers also found that the hydroxyl ions were replaced more rapidly than chloride ions under the conditions which they used. Although the initial anion concentration did not affect the ultimate capacity of the resin, the initial pH was higher.

### B. Statement of the Problem

In the work done by Butler and co-workers (1,2,3,4,5) no specific study of the basic properties of the polymers had been made by varying the substituent groups on the nitrogen atom. It was therefore decided to investigate the effect of certain groups on the basic properties of poly-quaternary ammonium hydroxides.

In order to conduct this investigation it was necessary to obtain various aliphatic or aromatic derivatives of ammonium bromide or chloride having a minimum functionality of six. The proposed procedure was to have three allyl groups in each compound and to vary the fourth group. Since there were only two such compounds which had been previously prepared, it was necessary to prepare several new compounds for this investigation.

In order to determine whether the butene-2 double bond enters into the polymerization of 1,4-bis(trialkylammonium)butene-2 dibromide compounds, quaternary ammonium salts containing two and four double bonds, in addition to the butene-2 double bond, and 1,4-bis(trialkylammonium)butane dibromide compounds containing two and four double bonds were prepared. Therefore, work was directed toward the synthesis of these new compounds.

It was also decided to attempt to produce resins of higher capacity than those prepared by Bunch (6) and Ingley (7). It can readily be seen that the lower the equivalent weight of a quaternary ammonium salt, the higher will be the theoretical exchange capacity (milliequivalents per gram) of the polymer produced from the salt. There are several ways of accomplishing this task of producing a lower equivalent weight. The polymer may be produced in the form of the chloride, or the molecular weight

of the quaternary ammonium salt may be lowered by use of low molecular weight substituent groups, such groups giving a minimum functionality of six, or a low molecular weight quaternary ammonium salt, without the minimum functionality needed to form a cross-linked polymer, may be copolymerized with a quaternary ammonium salt which has the necessary functionality to produce a cross-linked polymer. With these ideas in mind, investigation of several types of ion exchange resins produced from various 1,4-bis(trialkylammonium)butene-2 dihalides was undertaken. After a review of the literature, it was found that it would be necessary to synthesize several new compounds in order to carry this line of investigation to a successful conclusion.

### C. Source and Purification of Reactants

Diethyl amine, and 1,4-dichlorobutene-2 were obtained from Carbide and Carbon Chemicals Company. The tetrahydrofuran, ethylene bromohydrin, methyl bromide, methyl amine, and dimethyl amine were obtained from the Matheson Company. The allyl chloride was obtained from Shell Chemical Corporation. The beta-chloropropionitrile and the diallyl cyanamide, which was hydrolyzed to make the diallyl amine used in this research project, were obtained from American Cyanamid Company. Benzyl bromide was obtained from Columbia Organic Chemicals Company. The tertiary-butyl hydroperoxide was obtained as a 60% solution from the Lucidol Division, Novadel-Agene Corporation. All of the compounds mentioned above were utilized without further purification.

Allyl bromide was obtained from Dow Chemical Company and the fraction, boiling between 70.0-70.2<sup>o</sup>, was recovered for use.

The 1,4-dibromobutane used in this project was synthesized from tetrahydrofuran and 48% hydrobromic acid according to the procedure given by Cason and Rapoport (8) for making 1,5-dibromopentane. The dibromobutane recovered for use boiled at 82<sup>o</sup> under 14.5 mm.

1,4-Dibromobutene-2 was made according to the procedure of Prevost (9). The material boiled at 61-5<sup>o</sup> at 4.8 mm.

Bis(diallylamino)methane was synthesized by the procedure of Lewis (10). Material boiling at 80.0-80.2<sup>o</sup> at 4.2 mm. was recovered for use in experimental work.

Bis(dimethylamino)methane was produced in the same manner as bis(diallylamino)methane (10) with one change in procedure. The amine was not extracted with benzene since its boiling point was so close to that of benzene.

Instead, the product was merely separated from the water layer and dried over solid NaOH.

1,4-Bis(diethylamino)butene-2 and 1,4-bis(dimethylamino)butene-2 were both made by the procedure of Willstatter and Wirth (11). Better yields of these compounds were obtained by the use of 1,4-dichlorobutene-2 instead of 1,4-dibromobutene-2. The substitution of the dichloro compound was made after reading an article by Amundsen and co-workers (12), in which they had obtained larger yields than had been obtained by this author with the use of 1,4-dibromobutene-2.

It is of interest to note that 1,4-bis(diethylamino)butene-2 was also obtained by reacting 1,2-dichlorobutene-3 with diethyl amine in the same manner as mentioned by Willstatter and Wirth. The yield of the product was somewhat lower than that obtained using the 1,4-dichlorobutene-2, but nevertheless satisfactory.

Allyldimethyl amine was obtained by merely reacting allyl chloride with dimethyl amine. The product boiled at 62.3-63.0°.

Diallylmethyl amine was synthesized by the procedure of Partheil and von Broich (13). The amine boiled at 111°.

Triallylbenzylammonium bromide and tetraallylammonium bromide were made by the same procedure which Bunch used (14,15).

## II. PREPARATION OF TERTIARY AMINES

### A. General Discussion

It was necessary to synthesize both saturated and unsaturated tertiary amines as intermediates for the preparation of the unsaturated quaternary ammonium compounds. Two methods were used to synthesize the tertiary amines: a modification of the ammonium hydroxide synthesis reported by Butler and Benjamin (16); and the method described by Willstatter and Wirth (11). The latter method was modified as a result of work published by Amundsen and co-workers (12).

In preparing triallyl amine (previously reported), allyl chloride and a 28% aqueous ammonia solution were placed in an iron bomb which was immediately sealed and heated for a time at an elevated temperature. The bomb and contents were then cooled in ice and the amine layer separated. More amine was salted out of the water layer with NaOH. The combined amine layers were fractionated after drying over solid NaOH for at least 18 hours.

The 1,4-bis(dialkylamino)butene-2 and 1,4-bis(dialkylamino)butane compounds were prepared by adding the secondary amine dropwise to a benzene (dry) solution of either 1,4-dibromobutene-2, 1,4-dichlorobutene-2, or 1,4-dibromobutane contained in a three neck, round-bottom flask fitted with a water-cooled reflux condenser, mechanical stirrer and an addition funnel. The mixture was stirred at room temperature for at least 24 hours. The ratio of amine to halogen compound was two moles to one mole respectively. At the end of the period of stirring, an excess of concentrated sodium hydroxide solution was added. When the reaction mixture had separated into two layers, the amine layer was removed and the amine purified by fractional distillation.

In the second method, the procedure was slightly modified when the secondary amine was very volatile. In this case, the amine was dissolved in dry benzene and the halogen compound added dropwise. The rest of the procedure was identical.

A heated column 2 x 40 cm., packed with  $\frac{1}{2}$  inch Berl saddles was used for fractionation of the compounds. The pot was heated with a Glas-Col heating mantle. The distilling pot, head, and the part of the column which extended beyond the heating jacket were well insulated with glass wool. Ground glass joint equipment was used for both the preparation and purification of the amines. Temperatures recorded for the boiling points are uncorrected. All pressures were measured by means of a Zimmerli gauge.

The refractive indices were determined by means of an Abbé refractometer at 25° C. White light was used as the source of illumination. Constant temperature was maintained by circulating water through the refractometer from a constant temperature bath. Before taking a reading, sufficient time was allowed for the amine to acquire the same temperature as the lens of the instrument.

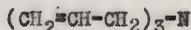
The specific gravities were determined at 25° C. with a calibrated 10 ml. Kimble specific gravity bottle, equipped with a standard taper thermometer. Freshly distilled portions of the compounds were used in both the specific gravity and refractive index determinations.

The nitrogen content of the amine was found by the Kjeldahl method. Mercuric oxide was used as a catalyst. The sodium hydroxide solution contained two parts sodium thiosulfate for each part of mercuric oxide.

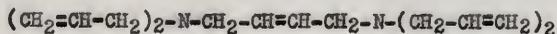
The properties, analyses and yields of these new tertiary amines are summarized in Table I. Individual details not covered in this general discussion can be found in the experimental part of this section.

## B. Experimental

Individual details not included in the general procedure are given in this section. All temperatures are in degrees centigrade, and its symbol is omitted in conformity with the present usage in scientific reports.

Synthesis of Triallyl amine.

Allyl chloride (490.2 ml., 6 moles) and 28% aqueous ammonia solution (540 ml., 8 moles  $\text{NH}_3$ ) were placed in an iron bomb equipped with a pressure gauge and stirrer. The bomb was placed in an oil bath at  $135^\circ$  and the contents stirred. The pressure rose to 220 lbs./in.<sup>2</sup> within 15 minutes. After a short time, the pressure decreased considerably and the bomb was heated at  $140-155^\circ$  for  $3\frac{1}{2}$  hours. When the bomb had cooled to room temperature, it was placed in an ice bath before opening. The oily layer was removed. The water layer was saturated with NaOH and the oily layer which formed was removed and combined with the original amine layer. Both were dried over solid NaOH for 18 hours before distillation. Some allyl amine and diallyl amine were obtained. The triallyl amine boiling between  $148-9^\circ$  was collected and weighed 131.3 g. The yield was 48%. Since triallyl amine has been reported previously, it was characterized by means of its physical constants.

Synthesis of 1,4-bis(diallylamino)butene-2.

This compound was prepared by two methods: (1) reaction of diallyl amine with 1,4-dibromobutene-2 and (2) reaction of diallyl amine with 1,4-dichlorobutene-2.

1. One-fourth mole (53.5 g.) of 1,4-dibromobutene-2 was dissolved in a minimum amount of dry benzene in a three neck flask equipped with mechanical stirrer, reflux condenser and addition funnel. Diallyl amine (60.6 g., 0.5 mole + 25% excess) was added dropwise with external cooling of the reaction flask. Stirring at room temperature was continued for 24 hours. A saturated solution of NaOH (100 g.) was added to the flask and the mixture was stirred overnight. The benzene layer was then removed and dried over solid sodium hydroxide for 144 hours. The benzene was removed and the amine distilled at  $92-3^{\circ}$  at 0.4 mm. was collected. The product weighed 23 g. The yield was 37.4%.

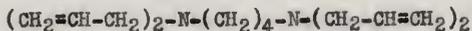
Analysis: Calcd. for  $C_{16}H_{26}N_2$ : N, 11.37. Found: N, 11.45.

Physical Constants:  $D_{25}^{25}$  0.8622;  $n_D^{25}$  1.4820; b.p.  $92-3^{\circ}$  at 0.4 mm.

$M_r_D$  calcd. 81.95;  $M_r_D$  found 81.47.

2. One mole (125 g.) of 1,4-dichlorobutene-2 was dissolved in 300 ml. of dry benzene in a three neck flask equipped with mechanical stirrer, reflux condenser, and addition funnel. Diallyl amine (194 g., 2 moles) was added dropwise. Stirring at room temperature was continued for 48 hours. A saturated solution of NaOH (200 g.) was added to the flask and the benzene layer then removed and dried over solid NaOH. The benzene was removed and the amine distilled at  $102^{\circ}$  under a pressure of 0.8 mm. The product weighed 167.7 g. The yield was 68%.

3. An attempt was made to make 1,4-bis(diallylamino)butene-2 by reacting 1,4-dibromobutene-2 with diallyl amine in the presence of a paste of sodium bicarbonate in water. A yield of 5.4% was obtained. This procedure was unsatisfactory under the conditions used.

Attempted Synthesis of 1,4-bis(diallylamino)butane.

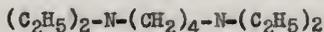
1. 1,4-Dibromobutane (54 g., 0.25 mole) was dissolved in 100 ml. of dry benzene and diallyl amine (48.6 g., 0.50 mole) was added dropwise with stirring. The reaction was stirred at room temperature for 36 hours. A saturated solution of sodium hydroxide (80 g.) was added to the flask. Three layers were obtained. The lower one was discarded, the top one dried over NaOH, and the middle one was distilled from solid NaOH. The top layer of the distillate thus obtained, was added to the top layer previously obtained. Both amine layers were dried over the solid NaOH for about 16 hours before distilling. After the benzene had been removed, two fractions were obtained, having the following physical properties: b.p. 77-9° at 11 mm.,  $n_D^{20}$  1.4690; and b.p. 79-80° at 11 mm.,  $n_D^{29}$  1.4712. Each fraction was only a few ml. in size. A sodium fusion was run on the second fraction. Nitrogen was present and halogen was absent. The refractive index of 1,4-dibromobutane was 1.5153 at 29°.

2. Four grams (0.0186 mole) of 1,4-dibromobutane and 7.23 g. (0.0744 mole) of diallyl amine were mixed in 20 ml. of dry benzene. This mixture was allowed to stand at room temperature for two days. The white crystals were filtered off and dried. The product weighed 5.7 g., giving a yield of 74.5% of the amine dihydrobromide.

Analysis: Calcd. for  $\text{C}_{16}\text{H}_{30}\text{N}_2\text{Br}_2$ : Br, 38.95. Found: Br, 38.70.

Physical Constants: m.p. 58°.

No material was isolated which could be considered as the 1,4-bis(diallylamino)butane; only the dihydrobromide of the amine was obtained.

Attempted Synthesis of 1,4-bis(diethylamino)butane.

1. 1,4-Dibromobutane (54 g., 0.25 mole) was dissolved in 100 ml. of dry benzene and diethyl amine (73.1 g., 1.00 mole) was added dropwise with stirring. The reaction mixture was stirred at room temperature for 12 hours and then was refluxed gently for  $1\frac{1}{2}$  hours. After the contents of the flask had cooled to room temperature, a concentrated solution of NaOH (80 g.) was added to the reaction mixture. Three layers were formed and the upper layer was separated and dried over solid NaOH for a short time and then it was distilled. The lower two layers were discarded. Only benzene and diethyl amine were obtained from the distillation of the dry upper layer. A very small amount of crystalline residue remained in the distilling pot.

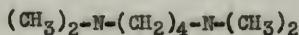
2. Four grams (0.0186 mole) of 1,4-dibromobutane and 5.44 g. (0.0744 mole) of diethyl amine were mixed in 20 ml. of dry benzene. This mixture was allowed to stand at room temperature for 24 hours. White crystals began to precipitate within half an hour after the two compounds were mixed. The white crystals were removed by filtration, dried, and weighed. A yield of 4.3 g. or 63.8% of 1,4-bis(diethylamino)butane dihydrobromide was obtained.

Analysis: Calcd. for  $C_{12}H_{30}N_2Br_2$ : Br, 44.13. Found: Br, 43.92.

Physical Constants: m.p.  $80^{\circ}$ .

No material was isolated which could be considered to be 1,4-bis(diethylamino)butane; only the dihydrobromide of the amine was obtained.

Attempted Synthesis of 1,4-bis(dimethylamino)butane.



Dimethyl amine (22.54 g., 0.5 mole) was poured from a cold trap into the reaction flask which contained 100 ml. of cool dry benzene. 1,4-Di-

bromobutane (54 g., 0.25 mole) was added dropwise with stirring. Crystals formed very shortly after the 1,4-dibromobutane had been added. After the ice bath was removed, the reaction proceeded smoothly with a very slight evolution of heat. The reaction was stirred at room temperature for about 18 hours. The reaction mixture was treated with a concentrated solution of NaOH (80 g.) and the upper layer which formed separated from the two lower layers. After the upper layer had dried over solid NaOH for a short period of time, it was distilled. Nothing was obtained from the distillation, except benzene.

TABLE I

UNSATURATED TERTIARY AMINE AND  
TERTIARY AMINE HYDROBROMIDES

COMPOUND	FORMULA	B.P. °C./mm.	$D_{25}^{25}$	$n_D^{25}$	ANALYSES		YIELD %
					CALCD.	FOUND	
1,4-Bis(diallylamino)butene-2	$C_{16}H_{26}N_2$	92-3/0.4	0.8622	1.4820	11.37	11.45	68.3
<hr/>							
COMPOUND	FORMULA	M.P. °C.	ANALYSES		YIELD		
			CALCD.	FOUND	FOUND	%	
1,4-Bis(diallylamino)butene dihydrobromide	$C_{16}H_{30}N_2Br_2$	58	38.95	38.70	38.70	74.5	
1,4-Bis(diethylamino)butene dihydrobromide	$C_{12}H_{30}N_2Br_2$	80	44.13	43.92	43.92	63.8	

### III. PREPARATION OF UNSATURATED QUATERNARY AMMONIUM HALIDES

#### A. General Discussion

The quaternary ammonium halides were synthesized by two methods: (1) by adding the alkyl, aryl, or substituted alkyl bromide dropwise with stirring to the tertiary amine, dissolved in a dry solvent; and (2) by adding the tertiary amine dropwise with stirring to the dihalobutene-2, dissolved in a dry solvent. The apparatus used was a round-bottom flask equipped with a mechanical stirrer, water cooled reflux condenser with  $\text{CaCl}_2$  tube attached, and an addition funnel. Acetophenone, acetone, methyl ethyl ketone, benzene, and hexanol-1 were the solvents used. Most of the reactions were stirred at room temperature for 24 hours. Some of the compounds precipitated out of the solvents very easily, but others had to be salted out with dry diisopropyl ether. All of the quaternary ammonium halides were washed with the ether and then placed in a vacuum desiccator to dry. Since the compounds obtained were quite hygroscopic, they were not recrystallized for analysis. The ether used for salting out purposes was first dried over calcium chloride and then the last traces of moisture were removed by placing the ether over sodium ribbon. The ether was filtered before use.

The bromide content of the quaternary ammonium salts (unpurified) was found by direct titration with a 0.1 normal solution of silver nitrate. Dichlorofluorescein was used as an indicator. The end-point was a sudden change from white to pink in the color of the silver bromide particles. Dextrin was used to prevent coagulation of the silver halide. A 50 ml. buret with 0.1 ml. graduations was used.

Three, 0.3 to 0.6 g. samples, of the quaternary ammonium halide were weighed by difference, into a 125 ml. Erlenmeyer flask. The halide was then

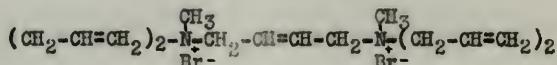
dissolved in about 20 ml. of distilled water and about 0.05 g. of dextrin and 3 drops of indicator were added. The solution was titrated in diffuse light. With several of the quaternary ammonium salts it was necessary to dry them in an Abderhalden drying pistol before analysis.

The quaternary ammonium salts were very soluble in water, low molecular weight alcohols, and ketones. The products were stored under anhydrous conditions to prevent absorption of moisture.

Individual details about the preparation of these salts are discussed in the experimental part of this section.



Attempted Synthesis of 1,4-bis(diallylmethylammonium)butene-2 dibromide.

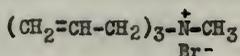


This compound was prepared by two methods: (1) reaction of methyl bromide with 1,4-bis(diallylamino)butene-2 and (2) reaction of diallylmethyl amine with 1,4-dibromobutene-2.

1. Methyl bromide (0.014 mole) which had been liquified was added to 1,4-bis(diallylamino)butene-2 (0.007 mole) and then the tube containing the two compounds was sealed and allowed to stand at room temperature for three days. At the end of this time the tube was opened. The product was in the form of a dark viscous liquid, containing very few crystals. Recrystallization was unsuccessful.

2. 1,4-Dibromobutene-2 (8 g., 0.0373 mole) was dissolved in 15 ml. of dry acetone and diallylmethyl amine (8.3 g., 0.0746 mole) added dropwise with stirring. A viscous liquid, accompanied by the evolution of heat, separated. The liquid soon became so viscous that another 15 ml. of acetone was added. After the mixture had stirred at room temperature for an hour, heat was applied so that the acetone refluxed gently. Since no solid was obtained, the viscous liquid was removed, washed with dry diisopropyl ether, and dried in a vacuum desiccator. Recrystallization was unsuccessful. No analysis could be obtained which corresponded to the calculated value.

Synthesis of triallylmethylammonium bromide.



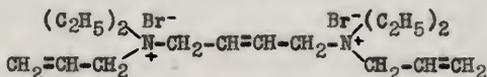
Triallyl amine (68.5 g., 0.5 mole) was dissolved in 190 ml. of dry acetone and methyl bromide was bubbled in slowly with cooling and stirring. When

some methyl bromide collected in the cold trap, which was connected, by means of rubber tubing, to the top of the reflux condenser, the passage of the bromide was discontinued and the reaction flask and contents allowed to warm up to room temperature. The reaction stood overnight at room temperature. The fine, white, hygroscopic solid was filtered, washed well with dry diisopropyl ether, and dried in a vacuum desiccator. One hundred six grams of product were obtained giving a yield of 91.5%.

Analysis: Calcd. for  $C_{10}H_{18}NBr$ : Br, 34.42. Found: Br, 34.44.

Physical Constants: m.p. 89-91°.

Synthesis of 1,4-bis(allyldiethylammonium)butene-2 dibromide.



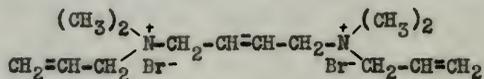
1,4-Bis(diethylamino)butene-2 (16 ml., 0.0686 mole) was dissolved in 30 ml. of dry acetone and allyl bromide (12 ml., 0.137 mole) was added dropwise with stirring. After about half an hour, the mixture warmed up to about 50° and crystals began to precipitate. Stirring was continued for an hour after the flask had cooled to room temperature. The white, slightly hygroscopic solid was removed, filtered, washed well with dry diisopropyl ether, and dried in a vacuum desiccator. The dry product weighed 27.0 g. The yield was 89.3%.

Analysis: Calcd. for  $C_{18}H_{36}N_2Br_2$ : Br, 36.29. Found: Br, 36.31.

Physical Constants: m.p. 172-3°.

It was necessary to dry this compound in the Abderhalden drying pistol before an analysis which corresponded to the calculated value was obtained.

Synthesis of 1,4-bis(allyldimethylammonium)butene-2 dibromide.

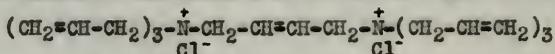


1,4-Bis(dimethylamino)butene-2 (46.4 g., 0.307 mole) was dissolved in 75 ml. of dry acetone and allyl bromide (75 g., 0.62 mole) was added dropwise, using a polymer kettle equipped with mechanical stirrer, reflux condenser, thermometer, and addition funnel. Toward the end of the reaction, there was such a large amount of solid formed that more dry acetone had to be added. The reaction continued at room temperature for an additional hour. The light yellow solid was removed and washed well with dry diisopropyl ether before drying in a vacuum desiccator. The dry solid weighed 109.3 g. The yield was 92.7%. The compound was recrystallized from both hexanol and amyl alcohol.

Analysis: Calcd. for  $\text{C}_{14}\text{H}_{28}\text{N}_2\text{Br}_2$ : Br, 41.60. Found: Br, 41.57.

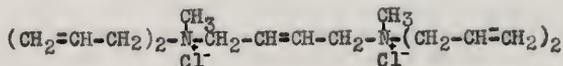
Physical Constants: m.p. 183-4°.

Attempted Synthesis of 1,4-bis(triallylammonium)butene-2 dichloride.



1,4-Dichlorobutene-2 (1.17 g., 0.0094 mole) and triallyl amine (2.57 g., 0.019 mole) were mixed in a test tube which was stoppered and allowed to stand at room temperature. At the end of two months there was approximately a 60% yield of dark-red, viscous liquid. Upon longer standing more liquid separated. Since the dibromide had been prepared no further work was done on this compound.

Attempted Synthesis of 1,4-bis(diallylmethylammonium)butene-2 di-  
chloride.

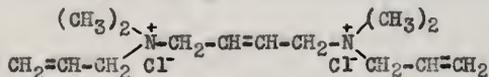


This compound was made by two methods: (1) the reaction of methyl chloride with 1,4-bis(diallylamino)butene-2 and (2) the reaction of 1,4-dichlorobutene-2 with diallylmethyl amine.

1. 1,4-Bis(diallylamino)butene-2 (1.72 g., 0.007 mole) and methyl chloride (0.71 g., 0.014 mole), both chilled, were mixed in a tube which was immediately sealed and allowed to stand at room temperature. Only a very small amount of viscous liquid separated -- even upon prolonged standing.

2. The diallylmethyl amine (1 g., 0.01 mole) and 1,4-dichlorobutene-2 (0.63 g., 0.005 mole) were mixed in a test tube which was immediately stoppered and allowed to stand at room temperature. A rather large quantity of viscous liquid separated. No purification or analysis was attempted. Since the dibromide had been obtained in good yield, investigation of this compound was not pursued further.

Attempted Synthesis of 1,4-bis(allyldimethylammonium)butene-2 dichloride.



This compound was made by two methods: (1) the reaction of 1,4-bis(dimethylamino)butene-2 with allyl chloride and (2) the reaction of diallylmethyl amine with 1,4-dichlorobutene-2.

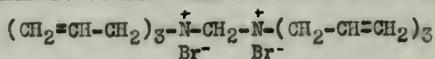
1. 1,4-Bis(dimethylamino)butene-2 (0.7 g., 0.005 mole) and allyl chloride (0.75 g., 0.01 mole) were mixed in a test tube which was immediately stoppered and allowed to stand at room temperature. Within a short period

of time, both solid and liquid separated. No purification or analysis was attempted.

2. Allyldimethyl amine (1 g., 0.0118 mole) and 1,4-dichlorobutene-2 (0.74 g., 0.006 mole) were mixed in a test tube which was immediately stoppered. After standing at room temperature for six hours, there was a 50% yield of a viscous liquid. No attempt was made to purify or analyze the compound.

Investigation of this compound was not pursued further.

Synthesis of bis(triallylammonium)methane dibromide.

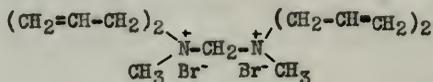


Bis(diallylamino)methane (8 ml., 0.0326 mole) was dissolved in 17 ml. of dry hexanol and the allyl bromide (5.7 ml., 0.065 mole) was added dropwise with stirring. Stirring at room temperature was continued overnight. The mixture was then heated gently for 3-4 hours, then cooled and removed from the flask. The product was salted out of the hexanol as a viscous liquid by use of dry diisopropyl ether. The viscous liquid was washed well with more ether and dried in a vacuum desiccator.

Analysis: Calcd. for  $\text{C}_{19}\text{H}_{32}\text{N}_2\text{Br}_2$ : Br, 35.65. Found: Br, 35.40.

No melting point was obtained since the compound was never obtained in crystalline form. It was necessary to dry this product in the Abderhalden drying pistol before an analysis corresponding to the calculated value was obtained.

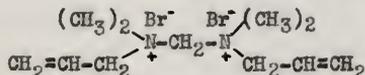
Attempted Synthesis of bis(diallylmethylammonium)methane dibromide.



Bis(diallylamino)methane (4 ml., 0.016 mole) and methyl bromide (1.8 ml., 0.032 mole), both cooled in dry ice and acetone, were mixed in a test tube, which was immediately stoppered and placed in an iron tube for a day at room temperature. The viscous liquid which formed was washed well with dry diisopropyl ether and then dried in an Abderhalden drying pistol.

The compound was not obtained in pure enough form for an analysis which would correspond to the calculated value. No melting point determination was made since the compound was not a solid.

Synthesis of bis(allyldimethylammonium)methane dibromide.

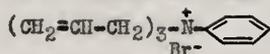


Bis(dimethylamino)methane (5.1 g., 0.05 mole) was dissolved in 20 ml. of dry benzene. Allyl bromide (12.1 g., 0.1 mole) was added slowly to the above solution with stirring. After a short period of stirring, some solid began to precipitate. Stirring was continued for several hours more. The solid was washed well with dry diisopropyl ether and placed in a vacuum desiccator to dry. Very shortly the solid became viscous and finally turned to liquid. This viscous liquid was well dried in an Abderhalden drying pistol.

Analysis: Calcd. for  $\text{C}_{11}\text{H}_{24}\text{N}_2\text{Br}_2$ : Br, 46.42. Found: Br, 46.85.

No melting point was obtained since the compound was never obtained in crystalline form.

Synthesis of triallylanilinium bromide.



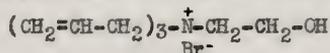
The compound was synthesized by two methods, differing only in the solvent used and the reaction time.



Analysis: Calcd. for  $C_{22}H_{34}N_4Cl_2$ : Cl, 16.67. Calcd. for  $C_{16}H_{28}N_2Cl_2$ : Cl, 22.21. Found: Cl, 22.25.

From the analysis obtained, it is evident that HCl split out of the  $\beta$ -chloropropionitrile to form the dihydrochloride of 1,4-bis(diallylamino)-butene-2.

Synthesis of Triallyl-2-hydroxyethylammonium bromide.

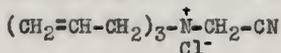


Triallyl amine (16 g., 0.12 mole) was dissolved in 25 ml. of dry acetone and the ethylene bromhydrin (14.6 g., 0.12 mole) was added dropwise with stirring. The stirring was continued at room temperature for several days. The reaction mixture was cooled in a beaker and dry diisopropyl ether added. A viscous liquid separated which would not solidify. The liquid was dried in a vacuum desiccator.

Analysis: Calcd. for  $C_{11}H_{20}NOBr$ : Br, 30.50. Found: Br, 30.10.

No melting point was obtained since the compound was not obtained in crystalline form.

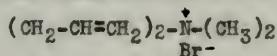
Attempted Synthesis of Triallylcyanomethylammonium chloride.



Triallyl amine (16 g., 0.12 mole) was dissolved in 20 ml. of acetonitrile and the chloroacetonitrile (8.9 g., 0.12 mole) was added dropwise with stirring. The reaction was stirred at room temperature for three days. The mixture was then poured into a beaker and the compound precipitated by the addition of dry diisopropyl ether. After several washings with more dry ether, the product was placed in the vacuum desiccator. After several days in the vacuum desiccator, the compound solidified. Attempts to recrystal-

lize the product from the following solvents were made: absolute ethanol, amyl alcohol, hexanol-1, methylethyl ketone, methylisobutyl ketone, ethylene dichloride, butyl cellosolve, and dioxane. Amyl alcohol was the only substance which gave any indication of possibly being a suitable recrystallizing solvent. Since no pure triallylcyanomethylammonium chloride could be obtained, no analysis or melting point data was secured.

Synthesis of diallyldimethylammonium bromide.



Diallylmethyl amine (11.1 g., 0.1 mole) was dissolved in 30 ml. of dry acetone and the methyl bromide was bubbled in slowly with cooling and stirring. When some methyl bromide collected in the cold trap, which was connected by means of rubber tubing to the top of the reflux condenser, the passage of the bromide was discontinued and the reaction flask and contents allowed to warm up to room temperature. The mixture was stirred overnight. During the course of the reaction, a viscous liquid formed which turned to a solid and then back to a viscous liquid. The reaction mixture was cooled in a beaker and dry diisopropyl ether added with vigorous stirring. A very hygroscopic solid precipitated. The solid was washed several times with more ether and was then dried in a vacuum desiccator. The product weighed 20.6 g. giving a 100% yield.

Analysis: Calcd. for  $\text{C}_8\text{H}_{16}\text{NBr}$ : Br, 38.68. Found: Br, 39.08.

No melting point was obtained because of the extreme hygroscopicity of the compound.

TABLE II

## UNSATURATED QUATERNARY AMMONIUM BROMIDES

Dibromide	Formula	M.P. °C.	Analyses Calcd.	% Br Found	Yield %
1,4-Bis(triallylammonium)butene-2	$C_{22}H_{36}N_2Br_2$	155-7	32.72	32.47	100.0
1,4-Bis(diallylmethylammonium)butene-2	$C_{18}H_{32}N_2Br_2$	(a)	36.63	(b)	(c)
1,4-Bis(allyldiethylammonium)butene-2	$C_{18}H_{36}N_2Br_2$	172-3	36.29	36.31	89.3
1,4-Bis(allyldimethylammonium)butene-2	$C_{14}H_{28}N_2Br_2$	183-4	41.60	41.57	92.7
Bis(triallylammonium)methane	$C_{19}H_{32}N_2Br_2$	(a)	35.65	35.40	(c)
Bis(diallylmethylammonium)methane	$C_{15}H_{28}N_2Br_2$	(a)	40.34	(b)	(c)
Bis(allyldimethylammonium)methane	$C_{11}H_{24}N_2Br_2$	(a)	46.42	46.85	(c)

Bromide	Formula	M.P. °C.	Analyses Calcd.	% Br Found	Yield %
Triallylmethylammonium	$C_{10}H_{18}NBr$	89-91	34.42	34.44	91.5
Triallylanilinium	$C_{15}H_{20}NBr$	(a)	27.17	(b)	(c)
Triallyl-2-hydroxyethylammonium	$C_{11}H_{20}NOBr$	(a)	30.50	30.10	(c)
Diallyldimethylammonium	$C_8H_{16}NBr$	(a)	38.68	39.08	100.0

(a)The compound was not obtained in crystalline form.

(b)The compound was not obtained in pure enough form for an analysis which would correspond to the calculated value.

(c)No yield was calculated because the compound was obtained in the form of a viscous liquid.

TABLE III  
UNSATURATED QUATERNARY AMMONIUM CHLORIDES

Dichloride	Formula	M.P. °C.	Analyses Calcd.	% Cl Found	Yield %
1,4-Bis(triallylammonium)butene-2	$C_{22}H_{36}N_2Cl_2$	(a)	17.75	(b)	60.0
1,4-Bis(diallylmethylammonium)butene-2	$C_{18}H_{32}N_2Cl_2$	(a)	20.42	(b)	(c)
1,4-Bis(allyldimethylammonium)butene-2	$C_{14}H_{28}N_2Cl_2$	(a)	24.02	(b)	(c)

Chloride	Formula	M.P. °C.	Analyses Calcd.	% Cl Found	Yield %
Triallylcyanomethylammonium	$C_{11}H_{17}NCl$	(a)	16.67	(b)	(c)

(a)The compound was not obtained in crystalline form.

(b)The compound was not obtained in pure enough form for an analysis which would correspond to the calculated value.

(c)No yield was calculated because the compound was obtained in the form of a viscous liquid.

#### IV. POLYMERIZATION OF UNSATURATED QUATERNARY AMMONIUM HALIDES

##### A. General Discussion

The general procedure followed in polymerizing the unsaturated quaternary ammonium compounds with t-butyl hydroperoxide was as follows: one gram of the halide, enough water to make a concentrated solution, and 0.012 g. of t-butyl hydroperoxide were mixed well and placed in an oven at 65° for an average time of 24 hours. This ratio of quaternary ammonium halide to catalyst was maintained in making larger quantities of the polymers. The polymer was removed and hot distilled water added. If the polymer failed to dissolve in the water, it was broken down to small insoluble particles. The resin was then washed with hot distilled water until the filtrate did not give a test for the halide ion. The polymer was dried in the oven at 65°. When the resin was dry, it was ground to 20-60 mesh material. Only polymers of this mesh size were used in the experimental work. The dry volume and settled wet volume were measured before the resin was placed in an ion exchange column (a glass tube 20 or 42 mm. in diameter, closed at one end by a 50 mesh stainless steel disk upon which the resin rested). A 4% solution of sodium hydroxide was passed through the resin bed until the acidified effluent was halogen free. The hydroxide form of the polymer was then washed free of excess sodium hydroxide and a 4% solution of potassium bromide was passed through the resin bed until the effluent was free of hydroxide ions. The bromide form of the polymer was then washed free of excess potassium bromide and dried at 65°. The dry polymer was screened and the 20-60 mesh material stored for future use. All of the water-insoluble resins were cycled once before storage.

Individual details are discussed in the experimental part of this section.

## B. Experimental

Polymer of 1,4-bis(triallylammonium)butene-2 dibromide.

Fourteen grams of 1,4-bis(triallylammonium)butene-2 dibromide, 0.168 g. of t-butyl hydroperoxide, and 1.03 g. of water were well mixed in a beaker and placed in an oven at 65° for 24 hours. The polymer was light tan and water insoluble. Twelve grams of the material was obtained. The yield was 86%. The 20-60 mesh resin weighed 6.1 g. and had a dry volume of 13.2 ml. and a settled wet volume of 18.2 ml. The swelling coefficient (wet volume divided by the dry volume) was 1.38. After one cycle, the 20-60 mesh material weighed 4.3 g.

Polymer of 1,4-bis(diallylmethylammonium)butene-2 dibromide.

One gram of 1,4-bis(diallylmethylammonium)butene-2 dibromide, 0.012 g. of t-butyl hydroperoxide, and 0.1 g. of water were well mixed in a beaker and placed in an oven at 65° for 12 hours. At the end of this time, 0.024 g. of catalyst was added and the mixture allowed to remain in the oven for an additional 24 hours. The polymer was light tan and water insoluble. The dry resin weighed 0.6 g. The yield was 60%.

Polymer of 1,4-bis(allyldiethylammonium)butene-2 dibromide.

One gram of 1,4-bis(allyldiethylammonium)butene-2 dibromide, 0.012 g. of t-butyl hydroperoxide, and 0.06 g. of water were well mixed in a beaker and placed in an oven at 65° for 18 hours. The polymer was a rather hard, tan-colored, water-soluble solid.

Copolymer of 1,4-bis(allyldiethylammonium)butene-2 dibromide and tetraallylammonium bromide.

Nine grams of 1,4-bis(allyldiethylammonium)butene-2 dibromide, 3 g. of tetraallylammonium bromide, 0.0144 g. of t-butyl hydroperoxide, and 0.42 g. of

water were well mixed in a beaker and placed in an oven at 65° for 22 hours. The copolymer was a tan, water-insoluble solid. Ten grams of the resin was obtained giving a yield of 83.3%. After grinding and sizing, 6.4 g. of 20-60 mesh polymer was obtained. This material had a dry volume of 10 ml. and a settled wet volume of 26 ml. The swelling coefficient was 2.6. After one cycle, the 20-60 mesh part of the resin weighed 5.8 g.

Copolymers of 1,4-bis(triallylammonium)butene-2 dibromide and 1,4-bis(allyldimethylammonium)butene-2 dibromide.

Four copolymers of these two salts were made. The molar ratio of the two components was varied (1 to 9; 2 to 8; 3 to 7; and 4 to 6).

1. 1,4-Bis(triallylammonium)butene-2 dibromide (0.49 g., 0.001 mole), 1,4-bis(allyldimethylammonium)butene-2 dibromide (3.469 g., 0.009 mole), and enough water to make a clear solution, were mixed well and then 0.048 g. of t-butyl hydroperoxide was stirred in. The mixture, in a beaker, was placed in an oven at 50° for 24 hours, then at 65° for 24 hours, and finally at 75° for 24 hours. The copolymer was a light-tan, water-insoluble solid. The dry resin weighed 3.4 g. giving a yield of 85%. The copolymer was ground to 20-60 mesh. This material weighed 3.2 g., and had a dry volume of 5.0 ml. and a settled wet volume of 13.0 ml. The swelling coefficient was 2.6. After one cycle, the weight of the 20-60 mesh material was 2.3 g.

2. 1,4-Bis(triallylammonium)butene-2 dibromide (7.33 g., 0.015 mole), and 1,4-bis(allyldimethylammonium)butene-2 dibromide (23 g., 0.06 mole), were mixed with enough water to give a clear solution. The t-butyl hydroperoxide (0.18 g.) was stirred in and the mixture placed in an oven at 50° for 24 hours, then at 65° for 24 hours, and finally at 75° for 24 hours.

The copolymer was a light-tan, water-insoluble solid. The dry resin weighed 15.4 g. The yield was 50.8%. The 20-60 mesh material weighed 13.9 g. and had a dry volume of 21 ml. and a settled wet volume of 72.8 ml. The swelling coefficient was 3.46. After one cycle, the amount of 20-60 mesh material obtained was 13.1 g. It should be noted here that the catalyst to quaternary ammonium salt ratio is one-half the usual value.

3. 1,4-Bis(triallylammonium)butene-2 dibromide (10.98 g., 0.0225 mole), and 1,4-bis(allyldimethylammonium)butene-2 dibromide (20.2 g., 0.0525 mole) were mixed with enough water to give a clear solution. The t-butyl hydroperoxide (0.18 g.) was stirred in and the mixture, in a beaker, placed in an oven at 50° for 24 hours, then at 65° for 24 hours, and finally at 75° for 24 hours. The polymer was a tan, water-insoluble solid. The dry resin weighed 15.8 g. The yield was 50.5%. The 20-60 mesh material weighed 15.4 g. and had a dry volume of 24 ml. and a settled wet volume of 75 ml. The swelling coefficient was 3.12. After one cycle, the amount of 20-60 mesh material obtained was 13.7 g. It should be noted here that the catalyst to quaternary ammonium salt ratio is one-half the usual value.

4. 1,4-Bis(triallylammonium)butene-2 dibromide (14.65 g., 0.030 mole) and 1,4-bis(allyldimethylammonium)butene-2 dibromide (17.3 g., 0.045 mole) were mixed with enough water to give a clear solution. The t-butyl hydroperoxide (0.18 g.) was stirred in and the mixture, in a beaker, placed in an oven at 50° for 24 hours, then at 65° for 24 hours, and finally at 75° for 24 hours. The copolymer was a tan, water-insoluble solid. The dry resin weighed 17.9 g. The yield was 55%. The 20-60 mesh material weighed 16.1 g. and had a dry volume of 25.5 ml. and a settled wet volume of 63.2 ml. The swelling coefficient was 2.48. After one cycle, the amount of 20-60

mesh material obtained was 13.8 g. It should be noted here that the catalyst to quaternary ammonium salt ratio is one-half the usual value.

Polymer of bis(triallylammonium)methane dibromide.

One gram of bis(triallylammonium)methane dibromide, in the form of a viscous liquid, was placed in a small beaker. The t-butyl hydroperoxide (0.012 g.) was stirred in and the mixture placed in the oven at 65° for 13 hours. The polymer was a dark-red, water-insoluble solid. The dry resin weighed 0.8 g. for a yield of 80%. More of the monomer was polymerized so that a total of 8.8 g. of 20-60 mesh material was obtained. This amount of the resin had a dry volume of 14.2 ml. and a settled wet volume of 49.2 ml. The swelling coefficient was 3.46. After one cycle, the amount of 20-60 mesh material obtained was 6.4 g.

Copolymer of bis(triallylammonium)methane dibromide and tetraallylammonium bromide.

Bis(triallylammonium)methane dibromide (4.5 g.), tetraallylammonium bromide (1.5 g.), and water (0.5 g.) were well mixed and then 0.072 g. of t-butyl hydroperoxide was stirred into the mixture. The material was placed in an oven at 100° for 48 hours and then at 65° for 48 hours. The copolymer was a dark-red, viscous, water-soluble liquid.

Copolymer of bis(triallylammonium)methane dibromide and bis(allyldimethylammonium)methane dibromide.

Bis(triallylammonium)methane dibromide (1.8 g.), bis(allyldimethylammonium)-methane dibromide (4.3 g.), and water (0.168 g.) were mixed well and then 0.084 g. of t-butyl hydroperoxide was stirred into the mixture. The solution was placed in an oven at 56° for 20 hours. Both quaternary ammonium bromides were viscous liquids which had been previously dried in an Abderhalden dry-

ing pistol. At the end of 20 hours of heating, the mixture was placed in a vacuum desiccator to remove as much of the water as possible. Another 0.084 g. of catalyst was added and the mixture replaced in the oven at 56° for several days. The copolymer was a dark, viscous, water-soluble liquid.

Polymer of bis(diallylmethylammonium)methane dibromide.

One gram of bis(diallylmethylammonium)methane dibromide and four drops of water were well mixed. One drop (0.012 g.) of t-butyl hydroperoxide was stirred in and the mixture placed in the oven for 24 hours at 56°. The polymer was a dark, partially water-insoluble, elastic solid. The weight of the dry resin was 0.09 g. The yield was 9%.

Polymer of triallylanilinium bromide.

One gram of triallylanilinium bromide, in the form of a viscous liquid, was placed in a beaker and 0.012 g. of t-butyl hydroperoxide was stirred in. The mixture was placed in an oven at 65° for 24 hours. At the end of this time, another 0.024 g. of catalyst was added. After about a week the polymer was found to be a dark, tar-like, partially water-soluble, viscous liquid.

Polymer of triallylcyanomethylammonium chloride.

One gram of triallylcyanomethylammonium chloride and 0.03 g. of water were mixed well in a beaker and 0.012 g. of t-butyl hydroperoxide was stirred in. The mixture was placed in an oven at 65° for two days, then the temperature was raised to 100° for two days. At the end of this time the polymer was a dark, hard, water-insoluble solid.

Polymer of triallylmethylammonium bromide.

Triallylmethylammonium bromide (19.8 g.) and 0.5 g. of water were well mixed

and 0.24 g. of t-butyl hydroperoxide was stirred in. The beaker containing the mixture was placed in an oven at 65° for 66 hours. The polymer was a light-tan, water-insoluble solid. The dry resin weighed 16.5 g. for a yield of 83.5%. The 20-60 mesh material weighed 14.7 g. and had a dry volume of 34 ml. and a settled wet volume of 52 ml. The swelling coefficient was 1.52. After one cycle, the amount of 20-60 mesh material obtained was 12.9 g.

Polymer of triallylbenzylammonium bromide.

Triallylbenzylammonium bromide (23.3 g.) and 1.27 g. of water were well mixed in a beaker and 0.29 g. of t-butyl hydroperoxide was stirred in. The mixture was placed in an oven at 65° for 48 hours. At the end of this time, a crust of crystals had formed over the top of the mixture. Another 0.29 g. of catalyst was stirred in and the mixture replaced in the oven for a week. The polymer was a tan, viscous, water-insoluble liquid.

Other conditions of polymerization were attempted. The catalyst to quaternary ammonium bromide ratio was doubled (0.024 g. to 1 g.), and the temperature of the polymerization was raised to 100°. The same tan, viscous water-insoluble liquid was obtained.

Polymer of diallyldimethylammonium bromide.

One gram of diallyldimethylammonium bromide and 0.024 g. of water were well mixed in a beaker and 0.012 g. of t-butyl hydroperoxide was stirred in. The mixture was placed in a 65° oven for four days. The polymer was a hard, light-tan, water-soluble solid.

Copolymers of triallylmethylammonium bromide and diallyldimethylammonium bromide.

Four copolymers of these two salts were synthesized. The molar ratio of the

two components was varied (1 to 9; 2 to 8; 1 to 1; and 4 to 1).

1. Triallylammmonium bromide (1.2 g., 0.005 mole), and diallyldimethylammmonium bromide (9.5 g., 0.045 mole) were mixed with 0.29 g. of water in a beaker. The t-butyl hydroperoxide (0.13 g.) was stirred in and the mixture was placed in an oven at 65° for approximately 64 hours. The copolymer was a cream-colored, water-insoluble solid. The dry resin weighed 7.8 g. The yield was 74.3%. The 20-60 mesh material weighed 6.1 g. and had a dry volume of 10.0 ml. and a settled wet volume of 104 ml. The swelling coefficient was 10.4.

2. Triallylammmonium bromide (3.5 g., 0.015 mole), and diallyldimethylammmonium bromide (12.4 g., 0.062 mole) were mixed with 0.29 g. of water in a beaker. The t-butyl hydroperoxide (0.15 g.) was stirred in and the mixture was placed in an oven at 65° for approximately 64 hours. The copolymer was a cream-colored, water-insoluble solid. The dry resin weighed 11.4 g. The yield was 71.7%. The 20-60 mesh material weighed 9.9 g. and had a dry volume of 13.9 ml. and a settled wet volume of 97 ml. The swelling coefficient was 6.97.

3. Triallylammmonium bromide (9.3 g., 0.04 mole), and diallyldimethylammmonium bromide (8.3 g., 0.04 mole) were mixed with 0.43 g. of water in a beaker. The t-butyl hydroperoxide (0.21 g.) was stirred in and the mixture was placed in an oven at 65° for approximately 64 hours. The copolymer was a light-tan, water-insoluble solid. The dry resin weighed 13.7 g. The yield was 78.0%. The 20-60 mesh material weighed 12.0 g. and had a dry volume of 17.1 ml. and a settled wet volume of 55.3 ml. The swelling coefficient was 3.22.

4. Triallylammmonium bromide (13.9 g., 0.06 mole), and diallyl-

dimethylammonium bromide (3.1 g., 0.015 mole) were mixed with 0.41 g. of water in a beaker. The t-butyl hydroperoxide (0.20 g.) was stirred in and the mixture was placed in an oven at 65° for approximately 64 hours. The copolymer was a light-tan, water-insoluble solid. The dry resin weighed 13.0 g. The yield was 76.5%. The 20-60 mesh material weighed 11.4 g. and had a dry volume of 17.0 ml. and a settled wet volume of 44.7 ml. The swelling coefficient was 2.62.

Copolymer of triallylbenzylammonium bromide and tetraallylammonium bromide.

Triallylbenzylammonium bromide (13.9 g.) and tetraallylammonium bromide (1.3 g.) were mixed well with 0.96 g. of water in a beaker. The t-butyl hydroperoxide (0.26 g.) was stirred in and the mixture was placed in an oven at 65° for 24 hours. At the end of this time, a small portion of the mixture was found to be water soluble, so an additional 2.6 g. of tetraallylammonium bromide, 0.58 g. of water, and 0.30 g. of t-butyl hydroperoxide were added and the mixture replaced in the oven for 80 hours. The copolymer was a brown, water-insoluble solid. The dry resin weighed 9.3 g. The yield was 61.0%. The 20-60 mesh material weighed 8.4 g. and had a dry volume of 11.0 ml. and a settled wet volume of 135 ml. The swelling coefficient was 12.3.

Copolymer of triallylmethylammonium bromide and tetraallylammonium bromide.

Triallylmethylammonium bromide (10.5 g.) and tetraallylammonium bromide (3.9 g.) were well mixed with 0.26 g. of water in a beaker. The t-butyl hydroperoxide (0.14 g.) was stirred in and the mixture was placed in an oven at 65° for 36 hours. The monomers had copolymerized within the first

30 minutes. The copolymer was a light-tan, water-insoluble solid. The dry resin weighed 12.0 g. The yield was 83.2%. The 20-60 mesh material weighed 11.6 g. and had a dry volume of 18.5 ml. and a settled wet volume of 37.8 ml. The swelling coefficient was 2.04.

Copolymer of diallyldimethylammonium bromide and tetraallylammonium bromide.

Diallyldimethylammonium bromide (7.7 g.) and tetraallylammonium bromide (3.2 g.) were well mixed with 0.73 g. of water in a beaker. The t-butyl hydroperoxide (0.13 g.) was stirred in and the mixture was placed in an oven at 65° for 48 hours. The copolymer was a cream-colored, water-insoluble solid. The dry resin weighed 9.2 g. The yield was 84.3%. The 20-60 mesh material weighed 8.6 g. and had a dry volume of 13.0 ml. and a settled wet volume of 33.5 ml. The swelling coefficient was 2.58.

Polymer of triallyl-2-hydroxyethylammonium bromide.

One gram of triallyl-2-hydroxyethylammonium bromide, in the form of a viscous liquid, was placed in a beaker and 0.012 g. of t-butyl hydroperoxide was stirred in. The mixture was placed in an oven at 65° for two days, then the temperature was raised to 100° for two days. Within the first hour, the mixture became dark red and quite viscous. After four days of heating the polymer was a dark, water-insoluble, elastic semi-solid.

Copolymer of triallyl-2-hydroxyethylammonium bromide and tetraallylammonium bromide.

Triallyl-2-hydroxyethylammonium bromide (3.93 g.) and tetraallylammonium bromide (1.3 g.) were mixed with 0.14 g. of water in a beaker. t-Butyl hydroperoxide (0.06 g.) was stirred in and the mixture placed in an oven at

65° for about three weeks. The copolymer was a dark, elastic, water-insoluble solid.

Copolymer of triallylanilinium bromide and tetraallylammonium bromide.

Triallylanilinium bromide (3.0 g.) and tetraallylammonium bromide (0.9 g.) were mixed with 0.1 g. of water in a beaker. t-Butyl hydroperoxide (0.048 g.) was stirred in and the mixture placed in an oven at 65° for about three weeks. The copolymer was a dark, viscous, partially water-soluble liquid.

Copolymer of triallylcyanomethylammonium chloride and tetraallylammonium bromide.

Triallylcyanomethylammonium chloride (3.2 g.) and tetraallylammonium bromide (1.3 g.) were mixed with 0.36 g. of water in a beaker. The t-butyl hydroperoxide (0.06 g.) was stirred in and the mixture placed in an oven at 65° for about three weeks. The copolymer was a dark, viscous, almost completely water-soluble liquid.

Polymer of tetraallylammonium bromide.

Tetraallylammonium bromide (11.1 g.) and 0.34 g. of water were well mixed in a beaker. t-Butyl hydroperoxide (0.13 g.) was stirred in and the mixture placed in an oven at 65° for 60 hours. The polymer was a tan, water-insoluble solid. The dry resin weighed 11.1 g. The yield was 100.0%. The 20-60 mesh material weighed 10.5 g. and had a dry volume of 19.2 ml. and a settled wet volume of 28.5 ml. The swelling coefficient was 1.48.

## V. ION EXCHANGE CAPACITY OF RESINS

### A. General Discussion

The method of obtaining the ion exchange capacities of resins has been previously described by Butler, Bunch, and Ingley (5). This method was used in this investigation with several modifications.

The general procedure used was as follows. All of the resins studied had been through one complete exchange cycle. The bromide form of the resin was thoroughly dried at 65° and then cooled in a desiccator before weighing out a 2.0000g. sample into a 400 ml. beaker. One hundred ml. of 4% NaOH solution was added to the resin. After about 24 hours the solution was filtered off and the resin washed at least four times with distilled water. Another 100 ml. of 4% NaOH solution was added to the resin. This process was continued until there were no more than 10 parts of Br<sup>-</sup> per million in the solution above the resin after the sodium hydroxide solution had stood over the resin for 24 hours. The concentration of bromide ion was estimated by comparison with a standard solution treated similarly with halogen free nitric acid and silver nitrate solution. When the bromide ion concentration reached the desired level of less than 10 parts per million, the hydroxide form of the resin was washed free of excess hydroxyl ions. Since the solution had to be filtered from the resin, it was necessary to use some distilled water to wash the resin from the funnel into the original beaker. The initial volume of water and resin was about 50 ml. The beaker containing the resin was placed in position for measurement of the pH. A mechanical stirrer and Beckman Model H-2 pH meter, equipped with Beckman #4990-75 glass electrode and Beckman #4970 calomel electrode, were placed in position for obtaining the pH during the titration

of the resin. In general, 100 ml. of a 0.1 N KBr solution was added to the beaker, and the time of addition observed. After 3 minutes, the pH was recorded and the first milliliter of acid added at once from the buret. A second 3 minute interval was allowed to pass, and the pH was determined again. This process of addition and measurement of pH was continued until the titration was completed. The results of the ion exchange capacity titrations carried out in this investigation are given in the experimental part of this section.

The hydrobromic acid used in these titrations was standardized against standard sodium hydroxide solution. Approximately 0.2 N acid was used. The 0.1 N potassium bromide solution was made by dilution of a 0.2 N solution prepared by weighing the salt and making up the solution in a volumetric flask.

A compilation of the properties of all ion exchange resins studied herein may be found in Table VI.

## B. Experimental

The resins, whose ion exchange capacities were determined, and the letter used to represent each resin in the graphs and tables, are given below. Also included is the end point of each titration.

<u>Monomer or Monomers</u>	<u>Letter</u>	<u>End Point of Titration (ml.)</u>
Triallylmethylammonium bromide	A	30.00
1,4-bis(triallylammonium)butene-2 dibromide	B	22.30
Bis(triallylammonium)methane dibromide	C	19.20
Tetraallylammonium bromide	D	18.90
Diallyldimethylammonium bromide (3 moles) Tetraallylammonium bromide (1 mole)	E	33.30
1,4-bis(allyldiethylammonium)butene-2 dibromide (2.04 moles) Tetraallylammonium bromide (1.16 moles)	F	30.50
Triallylmethylammonium bromide (3 moles) Tetraallylammonium bromide (1 mole)	G	27.30
Triallylbenzylammonium bromide (3 moles) Tetraallylammonium bromide (1 mole)	H	24.52
1,4-bis(triallylammonium)butene-2 dibromide (1 mole) 1,4-bis(allyldimethylammonium)butene-2 dibromide (9 moles)	I	38.40
1,4-bis(triallylammonium)butene-2 dibromide (2 moles) 1,4-bis(allyldimethylammonium)butene-2 dibromide (8 moles)	J	35.40
1,4-bis(triallylammonium)butene-2 dibromide (3 moles) 1,4-bis(allyldimethylammonium)butene-2 dibromide (7 moles)	K	33.57
1,4-bis(triallylammonium)butene-2 dibromide (4 moles) 1,4-bis(allyldimethylammonium)butene-2 dibromide (6 moles)	L	31.40
Triallylmethylammonium bromide (1 mole) Diallyldimethylammonium bromide (9 moles)	M	36.47
Triallylmethylammonium bromide (2 moles) Diallyldimethylammonium bromide (8 moles)	N	36.63
Triallylmethylammonium bromide (1 mole) Diallyldimethylammonium bromide (1 mole)	O	33.90

<u>Monomer or Monomers</u>	<u>Letter</u>	<u>End Point of Titra- tion (ml.)</u>
Triallylmethylammonium bromide (4 moles)	P	32.40
Diallyldimethylammonium bromide (1 mole)		

All of the resins, with the exception of M, were about 50 ml. in initial volume before 100 ml. of 0.1 N KBr solution was added and the titration with 0.2024 N HBr begun. In the case of M, the initial volume was about 75 ml. and 75 ml. of 0.133 N KBr solution was added.

The data obtained from the titration of the resins listed above are given on the following pages of this section. Graphs of these data follow.

TABLE IV  
DATA ON TITRATION OF RESINS A-H

Time in Min.	Vol. HBr	pH of							
		A	B	C	D	E	F	G	H
0	0	---	---	---	---	---	---	---	---
3	0	12.50	12.18	12.19	12.20	12.47	12.22	12.24	12.18
6	1	12.40	12.08	12.14	12.19	12.45	12.25	12.30	12.19
9	2	12.33	12.01	12.09	12.19	12.42	12.24	12.29	12.18
12	3	12.28	11.99	12.04	12.12	12.38	12.22	12.29	12.17
15	4	12.28	11.95	11.99	12.07	12.34	12.20	12.28	12.13
18	5	12.26	11.90	11.93	12.04	12.32	12.20	12.28	12.12
21	6	12.24	11.86	11.88	12.00	12.31	12.19	12.27	12.07
24	7	12.22	11.78	11.80	11.95	12.30	12.11	12.25	12.04
27	8	12.22	11.70	11.73	11.89	12.28	12.10	12.24	12.01
30	9	12.18	11.63	11.63	11.84	12.27	12.08	12.22	11.97
33	10	12.17	11.57	11.50	11.77	12.27	12.05	12.18	11.92
36	11	12.13	11.47	11.35	11.68	12.26	12.03	12.13	11.89
39	12	12.10	11.30	11.15	11.58	12.25	11.99	12.10	11.85
42	13	12.08	11.12	10.87	11.47	12.21	11.95	12.05	11.80
45	14	12.02	10.90	10.58	11.31	12.13	11.90	12.01	11.73
48	15	11.97	10.62	10.33	11.09	12.09	11.85	11.97	11.67
51	16	11.90	10.35	10.03	10.71	12.02	11.70	11.90	11.59
54	17	11.85	10.10	9.72	10.27	12.02	11.68	11.83	11.48
57	18	11.79	9.83	9.33	9.72	11.97	11.68	11.77	11.37
60	19	11.76	9.59	8.53	8.04	11.93	11.62	11.68	11.13
63	20	11.69	9.30	7.42	6.55	11.90	11.57	11.57	10.83
66	21	11.61	8.86	7.03	5.85	11.87	11.48	11.43	10.49

TABLE IV  
(cont'd)

Time in Min.	Vol. HBr	A	B	C	D	pH of			
						E	F	G	H
69	22	11.50	7.70	6.72	4.05	11.81	11.38	11.22	10.12
72	23	11.38	7.90	6.54	3.24	11.75	11.23	10.90	9.70
75	24	11.20	7.00	6.46	2.95	11.67	11.06	10.53	9.10
78	25	10.95	6.60	6.31	2.79	11.59	10.75	10.14	7.43
81	26	10.60	6.20	6.15	2.64	11.46	10.43	9.70	6.68
84	27	10.21	5.99	5.87	2.54	11.31	10.12	8.70	6.26
87	28	9.97	5.63	5.70		11.11	9.80	7.03	5.80
90	29	9.28	5.20	5.40		10.82	9.44	6.58	4.75
93	30	7.84	4.30	4.80		10.46	8.82	6.11	3.25
96	31	6.74	3.65	4.32		10.08	7.20	5.07	2.86
99	32	6.24	3.30	4.00		9.71	6.68	3.37	2.63
102	33	5.73	3.08	3.80		9.18	6.28	3.03	
105	34	4.00	2.98	3.54		7.50	5.98	2.88	
108	35	3.08		3.45		6.73	5.51	2.70	
111	36	2.73		3.28		6.32	3.89		
114	37			3.18		5.91	3.10		
117	38			3.03		5.12	2.80		
120	39			3.00		3.28	2.62		
123	40			2.93		2.91	2.50		
126	41			2.80		2.68			
129	42					2.53			
132	43					2.41			

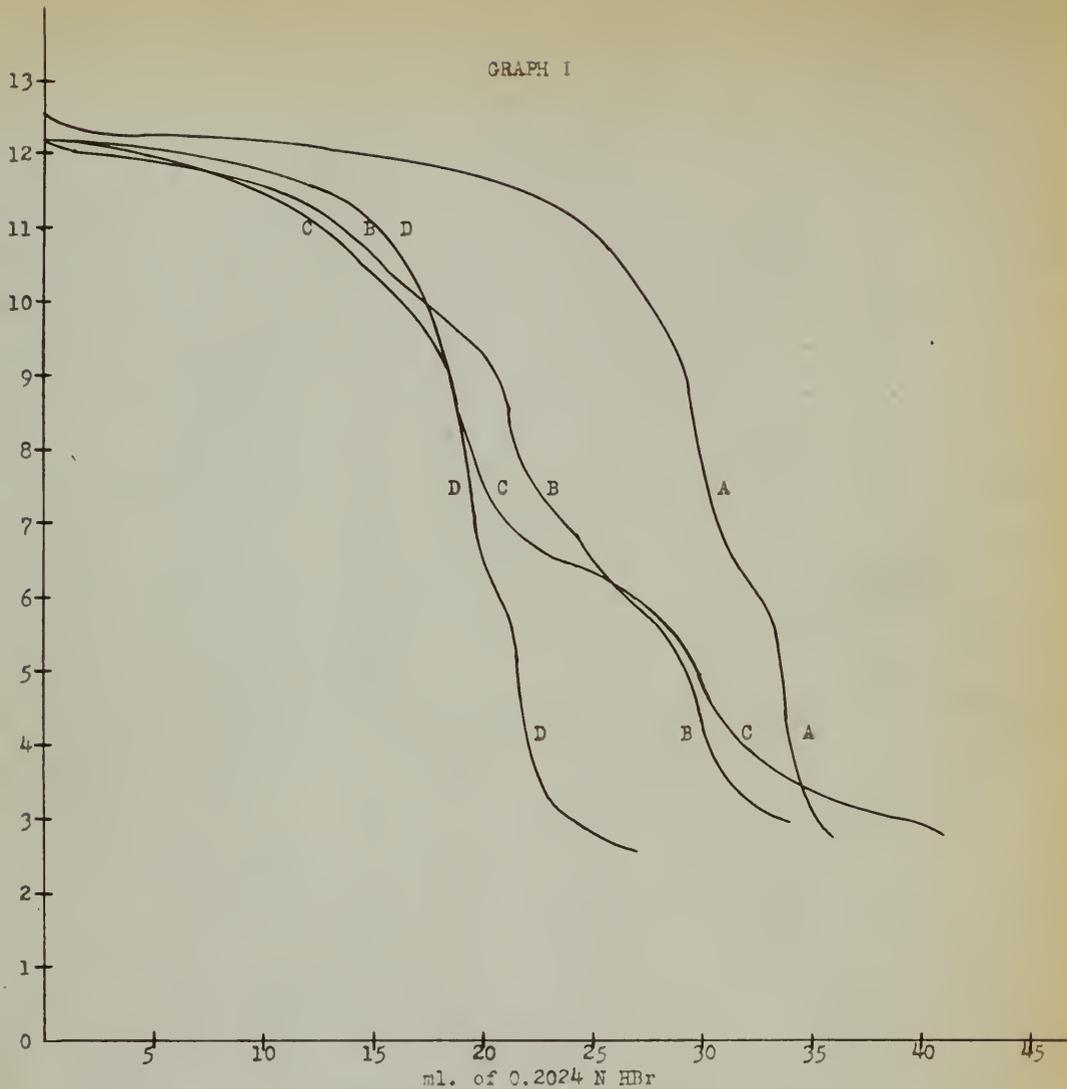
TABLE V.  
DATA ON TITRATION OF RESINS I-P

Time in Min.	Vol. HBr	I	J	K	L	pH of M	N	O	P
0	0	---	---	---	---	---	---	---	---
3	0	12.40	12.10	12.22	12.28	12.31	12.31	12.35	12.37
6	1	12.33	12.20	12.23	12.29	12.30	12.30	12.32	12.37
9	2	12.32	12.20	12.25	12.30	12.28	12.27	12.29	12.36
12	3	12.30	12.20	12.27	12.28	12.25	12.23	12.26	12.34
15	4	12.29	12.19	12.15	12.28	12.23	12.22	12.21	12.33
18	5	12.28	12.18	12.15	12.27	12.22	12.21	12.19	12.32
21	6	12.25	12.11	12.12	12.20	12.20	12.20	12.16	12.31
24	7	12.22	12.11	12.11	12.12	12.19	12.18	12.13	12.26
27	8	12.20	12.09	12.08	12.11	12.17	12.15	12.12	12.23
30	9	12.19	12.07	12.04	12.08	12.13	12.12	12.09	12.20
33	10	12.19	12.02	12.05	12.08	12.12	12.10	12.07	12.18
36	11	12.17	12.00	12.02	12.04	12.10	12.08	12.05	12.16
39	12	12.15	11.99	12.00	12.00	12.08	12.06	12.02	12.12
42	13	12.12	11.97	11.99	11.95	12.08	12.05	12.00	12.09
45	14	12.08	11.92	11.96	11.90	12.03	12.03	11.98	12.07
48	15	12.08	11.91	11.89	11.87	12.00	12.01	11.93	12.03
51	16	12.03	11.89	11.87	11.82	11.99	11.97	11.88	12.00
54	17	12.00	11.85	11.82	11.78	11.93	11.95	11.87	11.97
57	18	11.98	11.80	11.78	11.75	11.89	11.92	11.83	11.92
60	19	11.96	11.75	11.72	11.69	11.87	11.90	11.80	11.88
63	20	11.92	11.71	11.68	11.62	11.82	11.88	11.75	11.82
66	21	11.90	11.69	11.61	11.55	11.79	11.83	11.72	11.78

TABLE V.  
(cont'd.)

Time in Min.	Vol. HBr	pH of							
		I	J	K	L	M	N	O	P
69	22	11.87	11.62	11.53	11.48	11.73	11.78	11.67	11.72
72	23	11.82	11.53	11.43	11.35	11.68	11.73	11.59	11.65
75	24	11.80	11.47	11.32	11.21	11.62	11.69	11.53	11.53
78	25	11.75	11.38	11.18	11.02	11.57	11.62	11.44	11.43
81	26	11.70	11.25	10.99	10.78	11.49	11.57	11.32	11.37
84	27	11.67	11.11	10.72	10.43	11.39	11.49	11.18	11.20
87	28	11.52	10.85	10.42	10.10	11.28	11.41	10.99	10.98
90	29	11.41	10.59	10.15	9.70	11.13	11.30	10.68	10.58
93	30	11.31	10.29	9.88	9.30	10.90	11.12	10.32	10.10
96	31	11.18	10.00	9.58	8.58	10.60	10.90	9.93	9.57
99	32	10.96	9.73	9.25	7.20	10.28	10.62	9.55	8.69
102	33	10.65	9.43	8.78	6.61	9.97	10.25	9.08	6.79
105	34	10.30	9.08	7.60	6.38	9.64	9.89	7.72	6.23
108	35	9.95	8.40	6.91	5.97	9.30	9.52	6.72	5.57
111	36	9.60	7.20	6.58	5.40	8.61	9.02	6.26	3.44
114	37	9.22	6.78	6.33	4.00	7.15	7.53	5.83	2.92
117	38	8.35	6.48	6.11	3.29	6.56	6.72	5.07	2.68
120	39	7.00	6.20	5.32	2.99	6.23	6.26	3.18	
123	40	6.51	5.98	5.36	2.78	5.90	5.88	2.79	
126	41	6.20	5.60	3.82		5.43	5.23		
129	42	5.90	4.80	3.08		3.76	3.42		
132	43	5.50	3.30	2.78		3.02	2.92		
135	44	4.08	2.88			2.72	2.70		
138	45	3.05	2.68						
141	46	2.73							

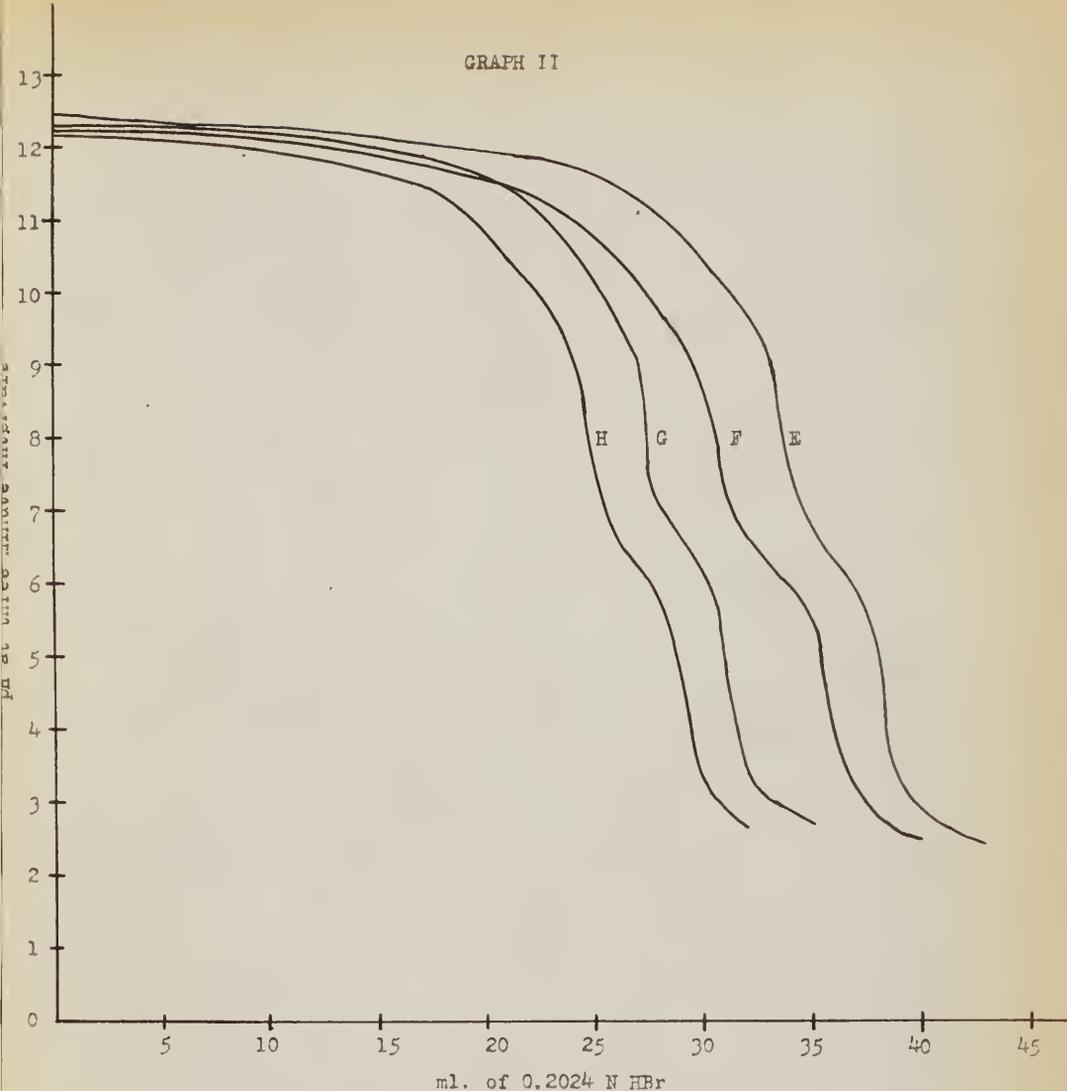
GRAPH I



Legend:

- A. Polymer of triallylmethylammonium bromide
- B. Polymer of 1,4 bis(triallylammonium)butene-2 dibromide
- C. Polymer of bis(triallylammonium)methane dibromide
- D. Polymer of tetraallylammonium bromide

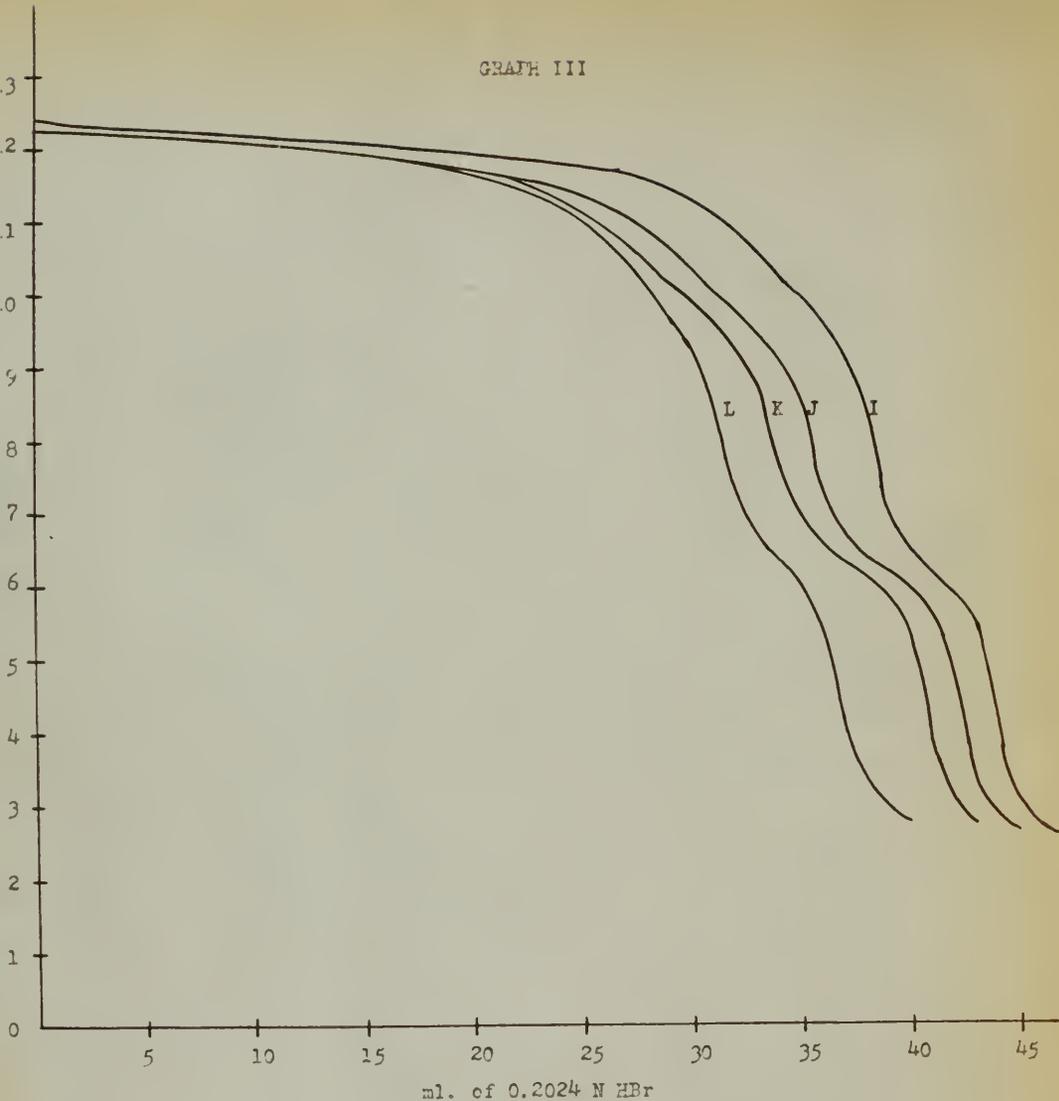
GRAPH II



Legend:

- E. Copolymer of diallyldimethylammonium bromide(3 moles) and tetraallylammonium bromide(1 mole).
- F. Copolymer of 1.4 bis(allyldiethylammonium)butene-2 dibromide(2.04 moles) and tetraallylammonium bromide(1.16 moles).
- G. Copolymer of triallylmethylammonium bromide(3 moles) and tetraallylammonium bromide(1 mole).
- H. Copolymer of triallylbenzylammonium bromide(3 moles) and tetraallylammonium bromide(1 mole).

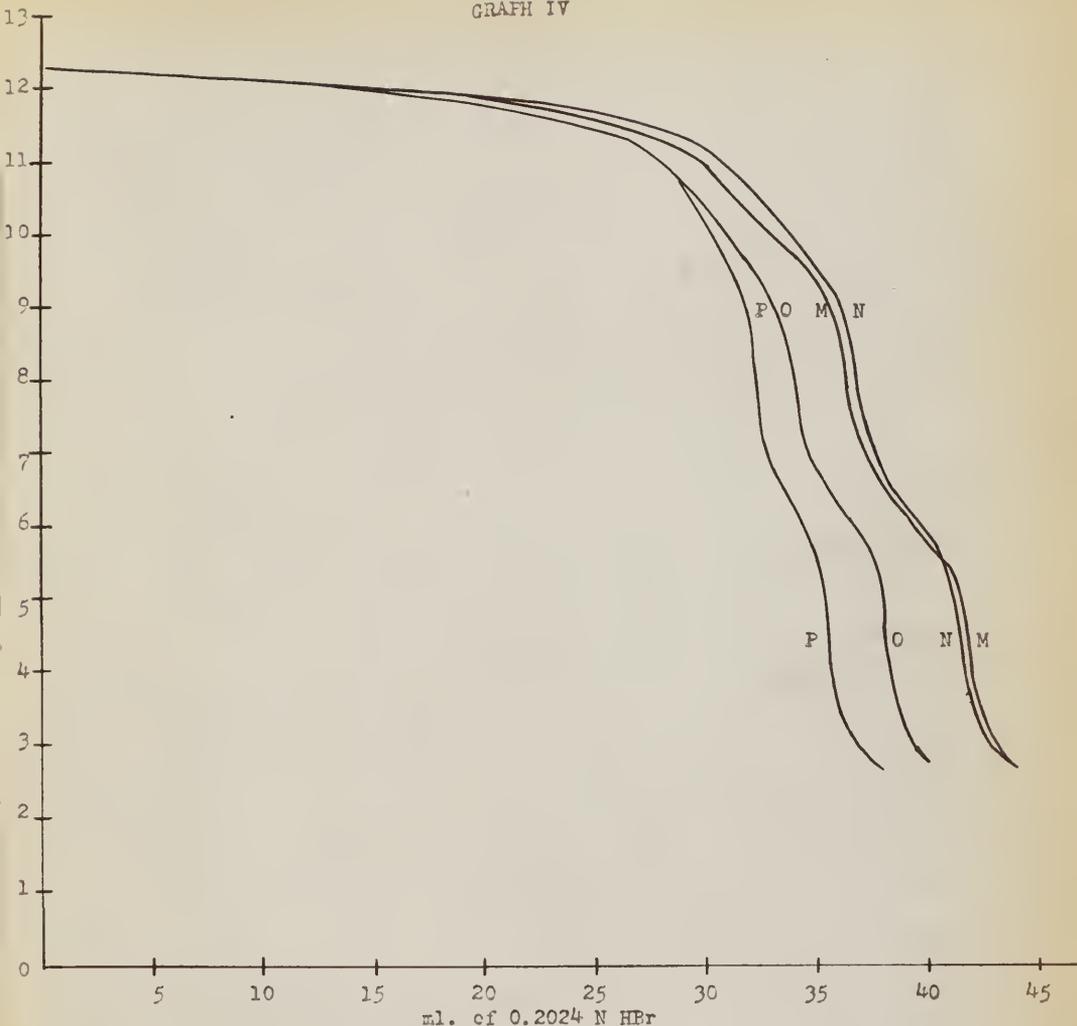
GRAPH III



Legend:

- I. Copolymer of 1,4 bis(triallylammonium)butene-2 dibromide(1 mole) and 1,4 bis(allyldimethylammonium)butene-2 dibromide(9 moles).
- J. Copolymer of 1,4 bis(triallylammonium)butene-2 dibromide(2 moles) and 1,4 bis(allyldimethylammonium)butene-2 dibromide(8 moles).
- K. Copolymer of 1,4 bis(triallylammonium)butene-2 dibromide(3 moles) and 1,4 bis(allyldimethylammonium)butene-2 dibromide(7 moles).
- L. Copolymer of 1,4 bis(triallylammonium)butene-2 dibromide(4 moles) and 1,4 bis(allyldimethylammonium)butene-2 dibromide(6 moles).

GRAPH IV



Legend:

- M. Copolymer of triallylmethylammonium bromide(1 mole) and diallyldimethylammonium bromide(9 moles).
- N. Copolymer of triallylmethylammonium bromide(2 moles) and diallyldimethylammonium bromide(8 moles).
- O. Copolymer of triallylmethylammonium bromide(1 mole) and diallyldimethylammonium bromide(1 mole).
- P. Copolymer of triallylmethylammonium bromide(4 moles) and diallyldimethylammonium bromide(1 mole).

TABLE VI

## PROPERTIES OF ION EXCHANGE RESINS

Resin*	Yield %	Swelling Coefficient	C a p a c i t y		Weight of Resin per ml. wet (Bromide form)		
			Theoretical mes./g.	Experimental mes./ml. mes./g. Theoretical			
A	83.5	1.52	4.31	0.87	3.04	70.5	0.28
B	86.0	1.38	4.09	0.76	2.26	55.4	0.33
C	80.0	3.46	4.46	0.35	1.94	43.5	0.18
D	100.0	1.48	3.38	0.71	1.92	49.5	0.37
E	84.3	2.58	4.56	0.87	3.37	73.9	0.26
F	83.3	2.60	4.36	0.76	3.09	71.0	0.25
G	83.2	2.04	4.20	0.85	2.76	65.7	0.31
H	61.0	12.3	3.38	0.15	2.48	73.4	0.06
I	85.0	2.60	5.07	0.96	3.89	76.7	0.25
J	50.8**	3.46	4.94	0.69	3.58	72.5	0.19
K	50.5**	3.12	4.81	0.70	3.40	70.7	0.21
L	55.0**	2.48	4.69	0.81	3.18	67.8	0.26
M	74.3	10.4	4.80	0.22	3.69	76.9	0.06
N	71.7	6.97	4.74	0.38	3.71	78.3	0.10
O	78.0	3.22	4.56	0.75	3.43	75.2	0.22
P	76.5	2.62	4.41	0.84	3.28	74.5	0.26

\* Refer to pages 42 and 43 for identification.

\*\*Catalyst to monomer ratio one-half of the value used in synthesizing the other resins.

## VI. DISCUSSION OF RESULTS

The procedure found best suited for preparing the 1,4-bis(dialkylamino)butene-2 compounds was that using 1,4-dichlorobutene-2 and the secondary amine in benzene solution. The yields of the one new amine and the other tertiary amines, previously reported, were considerably larger when 1,4-dichlorobutene-2 was used than when 1,4-dibromobutene-2 was used. The yield of the new tertiary amine was 68.3%.

The attempt to produce 1,4-bis(dialkylamino)butane compounds in order to ascertain whether the butene-2 double bond entered into the polymerization was unsuccessful. The dihydrobromides of the desired tertiary amines were obtained, but when these amines were liberated with sodium hydroxide, none of the amines were isolated.

Another method was used to show that the double bond in butene-2 did not take part in the polymerization when t-butyl hydroperoxide was used as a catalyst. It has been shown previously (1,2) that three allyl double bonds must be present in the quaternary ammonium salt before a cross-linked, water-insoluble polymer can be obtained. Using this information, several compounds were prepared, varying in number of allyl double bonds from two to four to six. It was found that a water-soluble polymer resulted when only two allyl double bonds were present in the molecule, in addition to the butene-2 double bond, while, on the other hand, when four or six allyl double bonds were present, a water-insoluble polymer resulted. The evidence obtained in this work shows that the butene-2 double bond does not take part in the polymerization when t-butyl hydroperoxide is used as a catalyst.

About half of the quaternary ammonium salts were obtained in solid form. The others were obtained in the form of viscous liquids, some of which could be dried enough to secure analyses which corresponded to the calculated values. Perhaps the incomplete polymerization of some of the quaternary ammonium compounds was caused by the impurities contained in these compounds. Purification was attempted in almost all cases, but some of the products seemed to resist purification. Hence, these compounds had to be used as obtained. Yields of the quaternary ammonium salts ranged from 60-100%.

The bis(trialkylammonium)methane dibromides did not polymerize to give very high yields. This fact may be attributed, in part at least, to the relative instability of the compounds. This is born out by curve C on Graph I. A high amine capacity is indicated. Lewis (17) reported the ease with which the bis(dialkylamino)methane compounds decompose. It was found that the quaternary ammonium bromides which contained four or more allyl double bonds, gave cross-linked, water-insoluble polymers. When only two double bonds were present, a water-soluble polymer resulted.

In general, the results of this investigation support those previously obtained (2,3,5) that the higher the coefficient of swelling, the nearer the experimental ion exchange capacity of the resin approaches the theoretical exchange capacity.

It was found, in this work, that lowered yields of the resins were obtained when the ratio of catalyst to quaternary ammonium salt was lower than 0.012 g. of catalyst to 1 g. of quaternary.

The resins obtained in this investigation were of much higher capacity than those obtained previously by Bunch (6) and Ingley (7). Several of the

resins had extremely large swelling coefficients, thereby lowering their capacity in milliequivalents per milliliter. With but two exceptions, the resins produced in this work all had ion exchange capacities above two milliequivalents per gram. The majority of the resins had capacities above 0.7 milliequivalents per milliliter. These values compare favorably with some of the commercially available strongly basic anion exchange resins. Of the resins investigated in this project, the one showing the highest capacity and one of the lowest swelling coefficients was a copolymer of 1,4-bis(triallylammonium)butene-2 dibromide (1 mole) and 1,4-bis(allyldimethylammonium)butene-2 dibromide (9 moles). This resin showed a capacity of 0.96 meq./ml. or 3.89 meq./g.

The effect of substitution of certain groups on the nitrogen center of the ion exchange resins has a definite effect upon the ratio of the theoretical capacity obtained experimentally. This effect can be observed in Graphs I-III. The substitution of one methyl group for one allyl group on the tetraallylammonium bromide monomer (curve D), produces a polymer (curve A) in which the experimentally determined capacity more nearly approaches the theoretical ion exchange capacity.

In the second graph, curve E shows a copolymer which results in a higher ratio of the theoretical capacity than the copolymer represented by curve F.

It can be easily seen, in Graph III, that the copolymer represented by curve I shows a higher ratio of the theoretical capacity than the copolymer corresponding to curve L.

This increase in ratio of the experimental capacity to the theoretical capacity is attributed to the increased basicity of the nitrogen center due

to the presence of groups with greater electron releasing properties. Since the allyl group can exhibit resonance forms, it will be less electron releasing than such groups as methyl or ethyl. Thus, it can easily be seen that the resins fall in the order which one would assume because of prior knowledge of the electronic properties of the various substituent groups.

In making these comparisons, pairs of resins were chosen which had approximately the same swelling coefficients. The ratio of the experimental capacity to the theoretical capacity of each resin was used in the comparison, rather than the theoretical capacity, since the latter is fixed immediately upon choice of the monomer or monomers.

The other curves could be compared, but it would be rather hazardous to attempt to draw any conclusion from such experimental work containing two variables (swelling coefficient and substituent group). The conclusions reached above, are those which the experimental work in this project has suggested.

In cycling the resins in ion exchange columns, it was apparent that the ease and rapidity of conversion to hydroxide or bromide was dependent upon the substituent groups. Resins containing a greater proportion of the stronger electron releasing groups could be more rapidly exchanged than those resins containing the weaker electron releasing groups. The exchange from the bromide form of the resin to the hydroxide form was slower than the exchange from hydroxide form to bromide form, as previously observed by Butler, Bunch, and Ingley (5). However, there was some modification in the separate rates. That is, with resins which contained the butene-2 group, the exchange from bromide to hydroxide was faster than

Ingle observed in the polymer of tetraallylammonium bromide, while the reverse exchange was slower than in the case of the polymer of tetraallylammonium bromide. In the case of resins containing the methyl group, the exchange from bromide to hydroxide was slower than in tetraallylammonium bromide polymer, with the reverse reaction being faster than in the polymer of tetraallylammonium bromide. Of course, for these observations to be completely valid, kinetic studies would have to be made. This variation in rates is attributed to the decreased basicity of the quaternary ammonium center in the case of the butene-2 derivatives and the increased basicity when such strongly electron releasing groups as methyl or ethyl are present.

## VII. SUMMARY

Fifteen new unsaturated quaternary ammonium halides were prepared. Eight of these new compounds were characterized. The identity of the remaining seven compounds was assumed on the basis of the means of preparation, since purification was not effected. The compounds were prepared by reaction of the appropriate tertiary amine and appropriate aliphatic or aromatic halide.

One new unsaturated tertiary amine was prepared as an intermediate. It was characterized and physical constants determined. It was obtained in largest yield by reacting diallyl amine and 1,4-dichlorobutene-2, neutralizing the hydrochloride formed with sodium hydroxide, separation and purification of the amine by distillation.

The unsaturated quaternary ammonium halides were polymerized by means of t-butyl hydroperoxide. Those compounds containing two allyl double bonds gave thermoplastic, water-soluble polymers, but those containing four or more allyl double bonds formed thermosetting, water-insoluble polymers. Compounds containing two allyl double bonds could be copolymerized with a compound containing three or four double bonds to form a water-insoluble copolymer. It was shown that the double bond of 1,4-diaminobutene-2 derivatives did not enter into the polymerization.

The substitution of certain groups on the nitrogen center of the ion exchange resins was found to have a very definite effect upon the rate of exchange of the various ions and upon the ratio of the experimental capacity to the theoretical capacity. This effect was found to be consistent with that which would be predicted on the basis of modern electronic interpretations. The change in the rate of exchange of the various ions and in

the ratio of the experimental capacity to the theoretical capacity is attributed to the variation in basicity of the quaternary ammonium center caused by substitution of groups of differing electrophilic properties.

Several anion exchange resins were prepared which compare favorably in pH range and capacity with those now available.

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#### ACKNOWLEDGMENTS

The author wishes to express his sincerest appreciation to Dr. G. B. Butler, who conceived this research project and under whose patient guidance this work was carried out. His suggestions and encouragement both in the carrying out of the research described and in the writing of the Dissertation, were unstintedly contributed.

The author desires to express thanks to his parents, Mr. and Mrs. W. L. Goette, and to his laboratory partner, Carl Michaelis, who generously helped by proof reading the manuscript. It is the wish of the author to give his sincerest thanks to Miss Emily Smith, who graciously typed the Dissertation.

To the members of the author's Supervisory Committee and to the other staff members of the Department of Chemistry and to his student associates the author wishes to express gratitude for their advice and suggestions.

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COMMITTEE REPORT

This dissertation was prepared under the direction of the Chairman of the candidate's Supervisory Committee and has been approved by all members of the committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council and was approved as partial fulfilment of the requirement for the degree of Doctor of Philosophy.

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