[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

Preparation and Polymerization of Unsaturated Quaternary Ammonium Compounds. II. Halogenated Allyl Derivatives[1,2]

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In order to compare the physical properties and ion-exchange capacities of typical polymers prepared by polymerization of unsaturated halogenated quaternary ammonium salts with a typical non-halogenated polymer, several polymers of this type were prepared. As intermediates for these polymers several new unsaturated halogenated tertiary amines and quaternary ammonium salts were prepared and characterized. Polymerization of these salts resulted in the formation of water soluble polymers from those compounds containing only two unsaturated groups, and water insoluble polymers from those compounds containing more than two unsaturated groups. Comparison of the properties of typical members of the two types of polymers showed that the halogenated polymer has a higher coefficient of swelling and a higher ion-exchange capacity per unit weight than the non-halogenated polymer.

The first paper of this series[3] demonstrated that unsaturated quaternary ammonium salts, specifically the chlorides and bromides, would undergo peroxide-catalyzed polymerization. Compounds containing at least three unsaturated groups per molecule produced water insoluble polymers capable of undergoing ion-exchange reactions. It has since been demonstrated that those compounds containing only two allyl or substituted allyl groups per molecule invariably produced water-soluble polymers.

Conditions described in the first paper of this series for polymerizing these compounds resulted in brittle polymers of rather low tensile and mechanical strength. Even though, in general, the water insoluble polymers were infusible, the particles tended to disintegrate on repeated treatment with aqueous solutions. It was therefore highly desirable to improve these physical characteristics. This investigation employed the introduction of halogenated allyl groups into the quaternary ammonium compounds. In view of the fact that these groups contain the vinyl chloride entity, it appeared likely that polymers of more desirable physical properties would result from polymerization of compounds of this nature.

The results of these studies are recorded below in the experimental section and in the accompanying tables.

Experimental

Materials.—The diallylamine and dichloropropenes used in this work for the preparation of unsaturated tertiary amines were obtained from Shell Chemical Company. The diallylamine was used as received, but the 2,3-dichloropropene-1 was fractionated, recovering the fraction boiling in the range of 93–95°. The 1,3-dichloropropene-1 was fractionated to separate the *cis* and *trans* isomers. The *cis* isomer boiled in the range of 103.5–104.5°; the *trans* isomer, in the range of 112–113°.

The piperidine was obtained from Eastman Kodak Company, and the morpholine from Carbide and Carbon Chemical Company. Both were used without further purification. The allyl bromide was a product of the Dow Chemical Company and was used without fractionation. The *t*-butyl hydroperoxide was obtained as a 60% solution from Union Bay State Company.

Preparation of Halogenated Unsaturated Tertiary Amines.—Two general procedures were used for preparation of the unsaturated tertiary amines required for this work:

Method I.—The following preparation of diallyl 2-chloroallylamine will illustrate this method: 48.6 grams of diallylamine was mixed with 42.0 g. of sodium bicarbonate and sufficient water to produce a paste in a 500-ml. three-necked flask. After heating to 100°, 61.1 g. of 2,3-dichloropropene-1 was added dropwise, with stirring. Heating was continued for 5.5 hours. After cooling, the oily layer was separated, dried and fractionated under reduced pressure; yield 52 g.; b.p. 81–82° (19–20 mm.).

Method II.—The following preparation of tri-(2-chloroallyl)-amine will illustrate this method: a solution of 90.2 g. of 28% aqueous ammonia and 350 ml. of water was heated to 100° in a one-liter, three-necked flask. One hundred eleven grams of 2,3-dichloropropene-1 was added dropwise, with vigorous stirring. Heating was continued, with stirring, for 8 hours. After cooling, the heavy, oily layer which separated was removed, dried overnight over solid sodium hydroxide and fractionated under reduced pressure; yield 59 g.; b.p. 120–121.5° (9–10 mm.).

All amines prepared were fractionated through a 2 × 82 cm. heated column packed with Raschig rings. Electric heating mantles were used. Temperatures recorded are uncorrected. Pressures lower than atmospheric were determined by means of a Zimmerli gage.

Densities were determined by means of a calibrated 10-ml. Kimble specific gravity bottle equipped with a standard taper thermometer. Refractive indexes were found by use of an Abbe refractometer. The properties, analyses and yields of these compounds are summarized in Table I.

Preparation of Halogenated Quaternary Ammonium Salts.—Procedures similar to that described in the first paper of this series were employed for these preparations. Because of the pronounced hygroscopicity of these compounds, considerable speed and care in filtration and handling was found to be essential. In spite of extreme care in handling, N-allyl-N-*cis*-3-chloroallylmorpholinium bromide could not be obtained as a solid, but remained a viscous liquid of taffy-like consistency. All efforts to prepare a quaternary ammonium derivative by reaction of tri-(2-chloroallyl)-amine with allyl bromide failed.

The properties, analyses and yields of these compounds are summarized in Table II.

Polymerization Studies.—Procedures similar to those described previously were used in preparation of the polymers. Of the quaternary ammonium salts reported in Table II, only those two containing more than two unsaturated groups produced water-insoluble polymers. In order to compare the physical properties of a polymer prepared by polymerization of a halogenated quaternary ammonium salt with one prepared from a non-halogenated derivative, the following experiment was carried out. Ten grams of triallyl-2-chloroallylammonium bromide, 0.57 g. of water and 0.17 g. of *t*-butyl hydroperoxide (60%) were mixed and maintained at 30° for 10 days. At the end of this period, the soluble substances were leached out with water, leaving a granular resin. This resin was then washed repeatedly with distilled water to remove the last traces of the unreacted monomer. The final washings showed no test for the bromide ion when treated with silver nitrate. The polymer was dried under vacuum for 24 hours and weighed; yield 4.30 g.

A similar polymerization of tetraallylammonium bromide resulted in a yield of 6.55 g. of water-insoluble polymer.

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[2] This material was presented in part before the Meeting-in-miniature, Florida Section, American Chemical Society, Tampa, Florida, May, 1950.

[3] G. B. Butler and R. L. Bunch, THIS JOURNAL, **71**, 3120 (1949).

TABLE I

HALOGENATED UNSATURATED TERTIARY AMINES

Compound	Formula	B.p., °C.	Mm.	d^{25}_4	$n^{25}D$	Nitrogen, % Calcd.	Nitrogen, % Found	Yield, %
N-2-Chloroallylmorpholine	$C_7H_{12}ClNO$	99–101	26	1.0887	1.4796	8.67	8.49	88.7
N-*cis*-3-Chloroallylmorpholine	$C_7H_{12}ClNO$	109–110	26	1.0967	1.4866	8.67	8.61	71.0
N-2-Chloroallylpiperidine	$C_8H_{14}ClN$	70–71	10	0.9969	1.4767	8.78	8.74	71.0
Diallyl-2-chloroallylamine	$C_9H_{14}ClN$	81–82	19.5	.9394	1.4680	8.16	8.16	60.4
N-*trans*-3-Chloroallylmorpholine	$C_7H_{12}ClNO$	91–92	8.5	1.0973	1.4869	8.67	8.63	82.6
Tri-(2-chloroallyl)-amine	$C_9H_{12}Cl_3N$	120–121.5	9.3	1.1868	1.5036	5.82	5.89	73.5
Methyl-di-(*trans*-3-chloroallyl)-amine	$C_7H_{11}Cl_2N$	94–95	10	1.1069	1.4910	7.78	7.74	32.8
Allyl-di-(2-chloroallyl)-amine	$C_9H_{13}Cl_2N$	88.5	5.6	1.0692	1.4863	6.80	6.75	22.0
Diallyl-*trans*-3-chloroallylamine	$C_9H_{14}ClN$	66–67	3.9	0.9477	1.4748	8.16	8.11	54.0

TABLE II

HALOGENATED UNSATURATED QUATERNARY AMMONIUM HALIDES

Bromide	Formula	M.p., °C.	Bromine, % Calcd.	Bromine, % Found	Yield, %
N-Allyl-N-2-chloroallylmorpholinium	$C_{10}H_{17}BrClNO$	172	28.28	28.41	29.7
N-Allyl-N-2-chloroallylpiperidinium	$C_{11}H_{19}BrClN$	164	28.48	28.47	90.5
N-Allyl-N-*trans*-3-chloroallylmorpholinium	$C_{10}H_{17}BrClNO$	160–165	28.28	27.90	67.4
Triallyl-2-chloroallylammonium	$C_{12}H_{19}BrClN$	155–160	27.31	27.25	28.2
Butyldiallyl-*trans*-3-chloroallylammonium[a]	$C_{13}H_{23}Cl_2N$	146–149	13.42	13.38	85.5

[a] The compound prepared was the chloride. The reacting halide was *trans*-3-chloroallyl chloride. The reported analytical values are % chlorine.

Comparisons between the two polymers were made as follows: The volumes occupied by the total quantity of the resins were measured in the dry and wet forms. The ratio of wet volume to dry volume is expressed as "coefficient of swelling." The capacities of the polymers for ion exchange were determined by conversion of weighed samples of the bromide form to the hydroxyl form as described in the first paper of this series, and the resulting hydroxyl form of the polymers titrated with one normal hydrochloric acid, using a Beckman model H-2 *p*H meter equipped with Beckman 4990 glass electrode and Beckman 4970 calomel electrode. The instrument was standardized against a buffer solution immediately before each titration. The procedure[4] involved placing 22 ml. of the wet, settled polymer in a titration beaker equipped with stirrer and electrodes. Two hundred ml. of 0.01 *N* potassium chloride was added, and the stirrer started. After 3 min., the *p*H was recorded and 1 ml. of acid added immediately. After 3 min., the *p*H was recorded and an additional ml. of acid added. This routine of *p*H measurement and addition of acid was continued until the titration was complete. The capacities are expressed both as milliequivalents per ml. of wet resin and as milliequivalents per gram of the dry bromide form. The results of these determinations are shown in Table III.

TABLE III

PROPERTIES OF ION EXCHANGE POLYMERS

Ammonium bromide polymer		Triallyl-2-chloroallyl-	Tetrallyl-
Coefficient of swelling		1.83	1.17
Yield, %		43.0	65.5
Capacity	meq./ml.	0.405	0.450
	meq./g.	2.08	1.53
% of theoret. capacity		61.0	39.4
Dry bromide, form. per ml. wet, g.		0.195	0.289

Discussion of Results.—The results of this investigation indicate that the presence of a halogenated allyl group in a quaternary ammonium derivative tends to decrease the polymerization rate. This is substantiated by the fact that the coefficient of swelling of a triallyl-2-chloroallylammonium bromide polymer is considerably greater than that of a tetraallylammonium bromide polymer prepared under similar conditions, indicating a lower degree of cross-linking. The decreased yield of the chlorinated polymer also supports this argument. The fact that the ion-exchange capacity per gram of the halogenated polymer is greater than that of the non-halogenated polymer can best be explained on the basis of screening. A higher ratio of the ions associated with the quaternary nitrogen centers in the highly swollen polymer are available for exchange than in the more highly cross-linked tetraallyammonium polymer.

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(4) Private communication from National Aluminate Corporation, Chicago, Illinois.