Reactions of *N,N,N′,N′*-Tetramethyl-α,ω-diaminoalkanes with α,ω-Dihaloalkanes. II. *x*-*y* Reactions[1,2]

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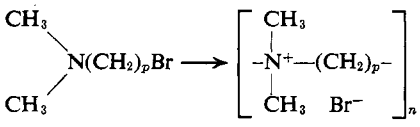
ABSTRACT: The reactions of *N,N,N′,N′*-tetramethyl-1,2-diaminoethane, -1,3-diaminopropane, -1,4-diaminobutane, and -1,6-diaminohexane with a number of α,ω-dibromoalkanes were investigated in solution. The main products of these reactions consisted of cyclic diammonium compounds (1:1 addition), linear diammonium compounds (1:2 addition), and ionene polymers (polyaddition). The conditions under which these products are formed as well as the information described in part I permit one to conclude that the reactions of tetramethyldiaminoethane with dibromobutane and of tetramethyldiaminopropane with dibromopropane yield ionene polymers with the highest known density of positive charges in a polymer backbone. The reaction of tetramethyldiaminobutane with dibromomethane in DMF–methanol (1:1 by volume) yielded unexpectedly tetramethyldiaminobutane dihydrobromide, indicating participation of methanol in the reaction. Elucidation of these results as well as experimental evidence for the isolated products is presented.

Polymers containing anionic or cationic substituents have been known for a long time and are at present the subject of intensive study.[4] However, the literature contains only a few scattered investigations concerning the preparation and properties of polymers with positively charged atoms in the polymeric backbone.[5–8] This type of polymer, for which the name ionene was suggested,[5] was synthesized by Lehman, Thompson, and Marvel,[6] using the following method.

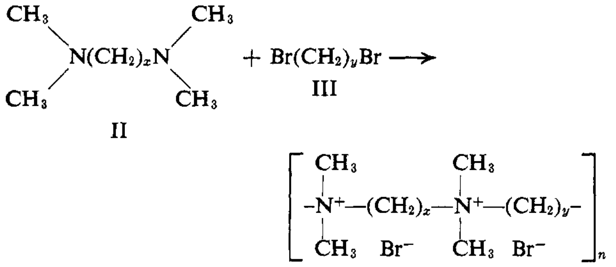


I

(1)

However, this reaction has severe limitations, since polymerization occurs only when $p = 3$ or $p \geq 7$, and even at these values of p only symmetrical ionenes can be formed.

Kern and Brenneisen[7] prepared unsymmetrical ionene polymers by means of the reaction



II III

(2)

IV, *x*-*y* ionene bromide

where x and y are the numbers of CH_2 groups in the diamine and the dibromide, respectively. This reaction permits the synthesis of a variety of polymers in which the distance between positive nitrogen atoms can be changed almost at will. Kern's work was interrupted, resulting in the fact that very little knowledge exists of reaction 2.

The academic interest in ionene polymers stems from the fact that no systematic study of the reactions of tetramethyldiaminoalkanes (II) with dihaloalkanes (III) or of the properties of ionene polymers has been carried out before, and hence conditions for formation of polyelectrolytes and the effect of cationic links in a macromolecular chain on the physical properties are not known.

Ionene polymers are also of practical importance, since ammonium groups impart fungicidal, bacteriocidal, and other properties.[9] In addition, polymers containing cationic centers form very interesting polysalts, for which a variety of uses have been listed.[10] The presence of cationic centers in membranes also increases their permeability, and hence a number of applications may be envisioned in this area.

Furthermore, positive polyelectrolytes form electrically conducting tetracyanoquinodimethane salts. The highest electronic conductivity of aliphatic ionene TCNQ complexes is of the order of 10^{-2} ohm^{-1} cm^{-1}, and this value varies characteristically when the distances between the positive charges are increased.[10b] Since ionenes of high positive charge concentration could lead to organic materials of high conductivity, and also since this type of polymer is of considerable general interest, we have carried out a detailed study of reactions of tetramethyldiaminoalkanes (II) with dihaloalkanes (III), using various combinations of x and y. It has been found that these reactions yield cyclic, linear or polymeric ammonium salts.

In part I of this series, we have reported the results of the reactions of tetramethyldiaminomethane ($x = 1$) with a number of dihaloalkanes, namely, the 1-y reactions. It has been shown that low molecular weight ionenes can be obtained by the 1-y reactions with $y = 3$ or with $y \geq 7$. In this paper a detailed account is presented of the reactions of tetra-

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(1) This paper represents one phase of research performed by the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration, Contract No. NAS7-100.

(2) Part I: H. Noguchi and A. Rembaum, *Macromolecules*, **5**, 253 (1972).

(3) NRC-NASA Resident Research Associate.

(4) Symposium on the Effect of Ions on the Bulk Properties of Polymers, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

(5) A. Rembaum, *J. Macromol. Sci., Chem.*, 3, 87 (1969).

(6) M. R. Lehman, D. D. Thompson, and C. S. Marvel, *J. Amer. Chem. Soc.*, **55**, 1977 (1933).

(7) W. Kern and E. Brenneisen, *J. Prakt. Chem.*, **159**, 14 (1941).

(8) A. A. Berlin, L. V. Zherebtsova, and Ye. F. Razvodovskii, *Polym. Sci., USSR*, **6**, 67 (1964); A. A. Berlin and E. F. Razvodovskii, *J. Polym. Sci., Part C*, No. **16**, 369 (1967).

(9) R. W. Preston, R. Hohf, and O. Trippel, *Quart. Bull. Northwestern Univ. Med. School*, 30, 138 (1956); E. T. Kimura, P. R. Young, and D. M. Ebert, *Toxic Appl. Pharm.*, **1**, 560 (1959); E. T. Kimura, P. R. Young, and G. H. Barlow, *Proc. Soc. Exp. Biol. Med.*, **111**, 37 (1962).

(10) (a) H. J. Bixler, R. A. Cross, and L. T. Markley, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Preprints of the Division of Organic Coatings and Plastics Chemistry, p 144; see also A. S. Michaels, *Ind. Eng. Chem.*, 57 (10), 32 (1965); (b) V. Hadek, H. Noguchi, and A. Rembaum, *Macromolecules*, **4**, 494 (1971).

TABLE I
SYNTHESIS OF IONENE POLYMERS[a]

	Time,	Yield, %		[η] (100 ml/g)		Calcd for Ionene Polymer, %					Found, %						
x-*y*	hr	I	II	I	II	C	H	N	Br (ionic)	Fraction	C	H	N	Br (ionic)	Br (total)	Fraction	Br (ionic)
2-4	165	79.9	8.8	0.065	0.029	36.16	7.28	8.43	48.12	I	34.69	7.34	8.09	44.10	47.73	II	44.42
2-6	187	59.0	25.6	0.089	0.050	40.02	7.84	7.75	44.37	I	38.62	7.85	7.41	42.53	42.78	II	41.29
3-3	168	88.0	15.2	0.086	0.025	36.16	7.28	8.43	48.12	I	35.31	7.43	8.22	47.05	47.28		
3-4	263	0	98.8		0.154	38.17	7.57	8.09	46.17	II	36.06	7.72	8.34	47.96	48.21		
3-6	120	4.3	87.5	0.064	0.341	41.73	8.08	7.44	42.71	I	40.67	8.15	7.25	41.64	41.69	II	37.26
4-3	120	0	92.0		0.123	38.17	7.57	8.09	46.17	II	40.01	8.13	6.42		44.99		
4-4	193	80.7	16.9	0.070	0.023				44.37	I				44.37		II	42.65
6-3	168	0.6	87.2		0.246	41.73	8.08	7.49	42.71	II	42.23	8.53	7.19	41.52	41.90		
6-4	168	92.8	7.0	0.167	0.049				41.16	I				38.78			
6-5	168	7.5	77.6	0.402	0.482				39.73	II				37.01			
6-6	168	92.8	5.2	0.299	0.087	46.16	8.72	6.73	38.39	I	45.94	8.66	6.81	38.07	38.04		
6-8	168	0	90.2		0.451				35.97	II				35.30			
6-10	168	0	77.3		0.600				33.83	II				32.90			
6-16[b]	1102	0	92.4		0.157	56.12	10.14	5.03	28.72	II	56.18	9.88	5.08	28.08	28.55		

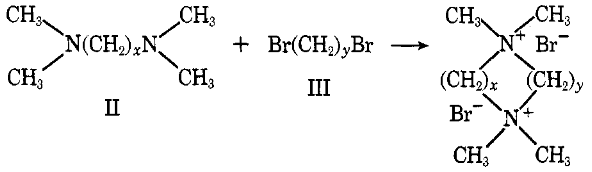
[a] Reaction conditions: *N*,*N*,*N'*,*N'*-tetramethyl-α,ω-diaminoalkane, 0.100 mol; α,ω-dibromoalkane, 0.100 mol; DMF–methanol (1:1), 65 ml; room temperature (*ca.* 22°). [b] Reaction conditions: *N*,*N*,*N'*,*N'*-tetramethyl-1,6-diaminohexane, 0.0150 mol; 1,16-dibromohexadecane, 0.0150 mol; tetrahydrofuran–benzene–methanol (1:1:1), 35 ml; room temperature.

methyldiaminoalkanes with dibromoalkanes, namely, the *x*-*y* reactions, which lead to relatively high molecular weight polyelectrolytes when carried out under well-defined conditions.

Results

Synthesis of Low Molecular Weight Compounds. The present study covers the reactions of II (x = 2, 3, 4, and 6) with III (y = 1, 6, 8, 10, and 16) carried out at room temperature in DMF–methanol solutions (1:1 by volume). The results of these reactions, most of which have not been investigated before, are described below.

The 2-1, 2-2, and 2-3 and 3-2 reactions yielded cyclic diammonium salts (Va, Vb, and Vc in (3)). The result of the 2-2 reaction is consistent with that of Cadogan.[11] On the other hand, our result of the 2-3 reaction as well as that of McElvain and Bannister[12a] shows that no polymers are formed, in contradiction to previous findings.[7]

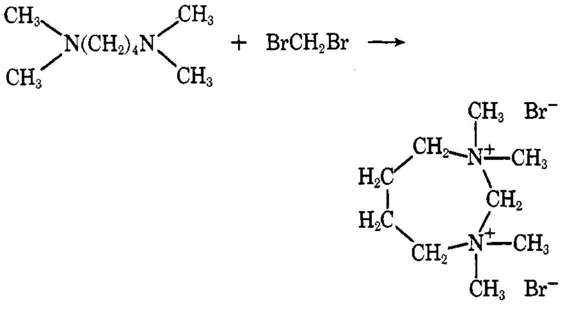


Va, $x = 2; y = 1$
b, $x = 2; y = 2$
c, $x = 2; y = 3$
$x = 3; y = 2$

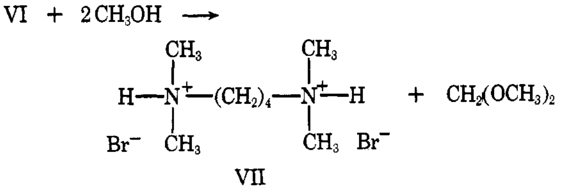
The isolation of pure products from the 3-1 reaction carried out in DMF–methanol was not successful. However, the same reaction in acetonitrile yielded a white powdery material containing a considerable amount of neutral bromine. This result, together with the nmr spectrum in D_2O (see Experimental Section), leads to the conclusion that the 3-1 reaction product consists mainly of trimethylenebis(bromomethyldimethylammonium bromide).

The 4-1 reaction, whether carried out in DMF–methanol or methanol alone, yielded tetramethyldiaminobutane dihydrobromide (VII). The latter has characteristic ir absorption bands in the region of 2400–2800 cm^{-1} due to the N^+–H stretching vibration. Its structure was ascertained by an independent synthesis, chemical analysis, and nmr and ir spectroscopy (see Experimental Section). The synthetic specimen was prepared by treating tetramethyldiaminobutane with hydrobromic acid, and its nmr and ir spectra were found to be identical with those of the 4-1 reaction product.

In order to explain the formation of VII, the following mechanism is postulated



VI



$$\text{VI} + 2\,CH_3OH \longrightarrow H\text{—}\overset{CH_3}{\underset{Br^-\ \ CH_3}{N^+}}\text{—}(CH_2)_4\text{—}\overset{CH_3}{\underset{CH_3\ \ Br^-}{N^+}}\text{—}H + CH_2(OCH_3)_2 \quad (5)$$

VII

$$\text{VI} + H_2O \longrightarrow \text{VII} + CH_2O \quad (6)$$

In order to obtain additional evidence for this mechanism, the 4-1 reaction was carried out in DMF or acetonitrile in the absence of methanol. The isolated crystalline compound decomposed in moist air to produce formaldehyde. Upon recrystallization from methanol, only tetramethyldiaminobutane dihydrobromide (VII) was obtained. The instability of the intermediate VI is primarily due to electrostatic repulsion between two positive nitrogen atoms in close vicinity and these results are, therefore, consistent with the postulated mechanism.

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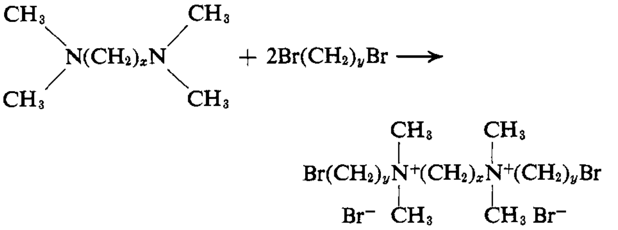
(11) J. I. G. Cadogan, *J. Chem. Soc.*, 2971 (1955).

(12) (a) S. M. McElvain and L. W. Bannister, *J. Amer. Chem. Soc.*, **76**, 1126 (1954); (b) G. Faust and W. Fiedler, *J. Prakt. Chem.*, **21**, 113 (1963).

The 4-2, 6-1, and 6-2 reactions gave the disalts VIIIa, VIIIb, and VIIIc, respectively and were independent of the solvent and the ratio of the reactant.



$$(CH_3)_2N(CH_2)_xN(CH_3)_2 + 2Br(CH_2)_yBr \longrightarrow Br(CH_2)_y\overset{CH_3}{\underset{Br^-\ CH_3}{N^+}}(CH_2)_x\overset{CH_3}{\underset{CH_3\ Br^-}{N^+}}(CH_2)_yBr \quad (7)$$

VIIIa, $x = 4;\ y = 2$
b, $x = 6;\ y = 1$
c, $x = 6;\ y = 2$

Synthesis of Polyelectrolytes. The remaining x-y reactions yielded ionene polymers. The results are summarized in Table I, in which the intrinsic viscosity $[\eta]$ measured in 0.4 M KBr aqueous solution is recorded. Two fractions were examined. Fraction I is the material filtered off from the mixture at the end of the reaction. Fraction II is the material isolated from the mother liquor.

The elemental analysis (Table I) is in disagreement with the theoretical values. This is particularly true for low molecular weight polymers (low intrinsic viscosity) and is due to the presence of dimethylamino or CH_2Br end groups as well as to the highly hygroscopic nature of the polymers.

In order to determine the intrinsic viscosity $[\eta]$ of ionene polymers, it was necessary to find the relation between the specific viscosity with concentration of salt (KBr).

Figure 1 shows the increase of specific viscosity determined in aqueous solutions with decreasing salt concentration for 6-6 and 3-3 ionene bromides. It also explains the choice of 0.4 M KBr concentration for the determination of intrinsic viscosity. At concentrations of KBr of 0.3–0.5 M, the specific viscosity is relatively constant; therefore, no further chain contraction occurs and the behavior of polyelectrolytes approximates that of uncharged polymers.[13a] Figure 1 also shows that the specific viscosity of a low molecular weight diammonium model compound (VIIIc) remains constant as the salt concentration changes, in contrast to ionene polymers.

In general, the intrinsic viscosity of the fraction obtained in a higher yield is greater than that of the fraction obtained in lower yield and increases with the values of x or y. It should be noted that by the use of sufficient amount of precipitant the polymer may be obtained in practically quantitative yields without fractionation.

The rate of polyelectrolyte formation depends primarily on concentration of reactants, temperature, time, and dielectric constant of the medium.[13b] The effect of concentration is illustrated in Figure 2, in which the increase of the relative viscosity measured in an evacuated viscometer is recorded as a function of time. The rate is considerably faster and the molecular weight higher at 0.730 molar concentration $[M]$ of each reactant than at $[M]$ = 0.186.

Molecular Weight. The molecular weight of 3-4 and 6-6 ionene bromides was determined by the light-scattering technique[14] and may be calculated from

$$[\eta](3{,}4Br) = (2.94 \times 10^{-4})M^{0.61} \quad (8)$$

$$[\eta](6{,}6Br) = (6.22 \times 10^{-4})M^{0.58} \quad (9)$$

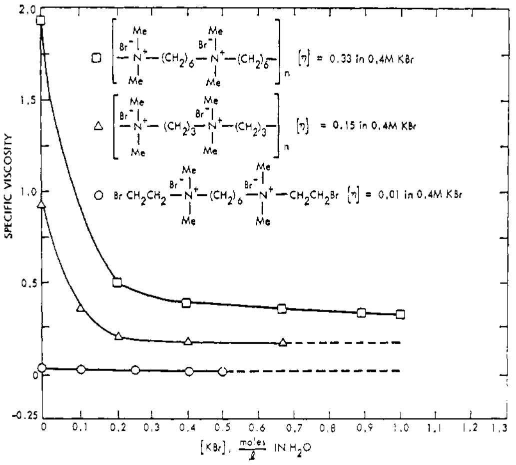


Figure 1. Specific viscosity as a function of KBr concentration (concentration of sample 1 g/100 ml, temperature 25°C).

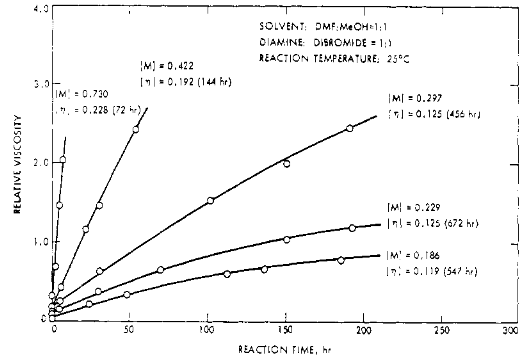


Figure 2. Relative viscosity *vs.* reaction time as a function of concentration ($x = 6, y = 6$).

Thus the intrinsic viscosity of 6-6 Br of 0.33 dl/g (Figure 1) corresponds to a weight-average molecular weight of 50,000. The weight-average molecular weight of 3-4 ionene bromide corresponding to $[\eta]$ = 0.154 dl/g (Table I) is equal to 29,000. The molecular weights of the ionenes listed in Table I can be increased[13b] by using longer reaction times or higher concentrations of reactants.

Solubility. Polymers with low x and y values exhibited limited solubility in methanol. The limited solubility is reflected in the high yields of fraction I (for $x = 2, y = 4, x = 2, y = 6$, and $x = 3, y = 3$, see Table I, column 3). 3-4 and 4-3 ionene polymers were highly soluble in methanol. Symmetrical ionenes ($x = y$) were found to be less soluble than the unsymmetrical polymers ($x \neq y$), indicating a higher crystallinity or packing in the former. Both kinds, however, yielded very distinct X-ray diffraction patterns (Figure 3). All examined ionene polymers listed in Table I were found to be soluble in water and methanol and insoluble in common organic solvents, irrespective of the values of x or y and of the intrinsic viscosity.

Nuclear Magnetic Resonance. Figures 4a, 4b, and 4c show the nmr spectra and the structures of the 2-1, 2-2, and 2-3 reaction products, respectively. The N^+–CH_3 proton resonance occurs at τ 6.32, 6.54, and 6.67, the τ value increasing with increasing ring size. Similarly, the N^+–CH_2CH_2–N^+ proton resonance occurs at τ 5.42, 5.97, and 5.95, respectively, the τ value being maximum for the six-membered ring. The same type of result has been obtained in the case of cyclic monoammonium salts.[2] The peak at τ 4.51 of the 2-1 reaction product can be assigned to the N^+–CH_2–N^+ resonance

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(13) (a) C. Tanford "Physical Chemistry of Macromolecules," Wiley, New York, N. Y., 1961, p 505; (b) A. Rembaum, H. Rile and R. Somoano, *Polym. Lett.*, 8, 457 (1970).

(14) D. Casson and A. Rembaum, *Macromolecules*, 5, 75 (1972).

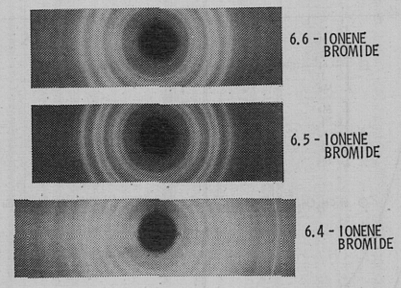

Figure 3. X-Ray powder diffraction diagrams of ionene polymers.

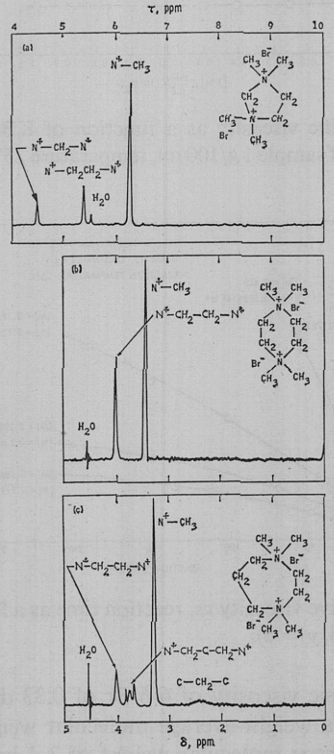

Figure 4. Nmr spectra in D_2O of (a) 2-1 reaction product, (b) 2-2 reaction product, and (c) 2-3 or 3-2 reaction product.

(Figure 4a). The C–CH_2–C and N^+–CH_2–C–CH_2–N^+ proton resonances of the 2-3 reaction product yield a singlet at τ 7.55 and a triplet at τ 6.20 (J = 5.1 Hz), respectively. The nmr spectrum of the 3-2 reaction product was identical with that of the 2-3 reaction product.

In Figure 5 the nmr spectra of the 4-2 (Figure 5b) and 6-2 reaction products (Figure 5c) are compared with that of (2-bromoethyl)trimethylammonium bromide (Figure 5a). In Figure 6 the nmr spectrum of the 6-1 reaction product (Figure 6b) is compared with that of bromomethyltrimethylammonium bromide (Figure 6a). The similarity of the spectra yields evidence for structures VIIIa, VIIIb, and VIIIc. It *should be noted that the* N^+–CH_2–*Br proton resonance gives a* singlet at τ *ca.* 4.8, which is close to the τ value of the N^+–CH_2–N^+ proton resonance (see Table II), while the N^+–CH_2CH_2–Br proton resonance a singlet at τ *ca.* 6.2 is close to the τ value of the N^+–CH_2–CH_2–N^+ proton resonance (see Table III). These facts indicate that the electric field effect of the bromine atom is about the same as that of the ammonium group.

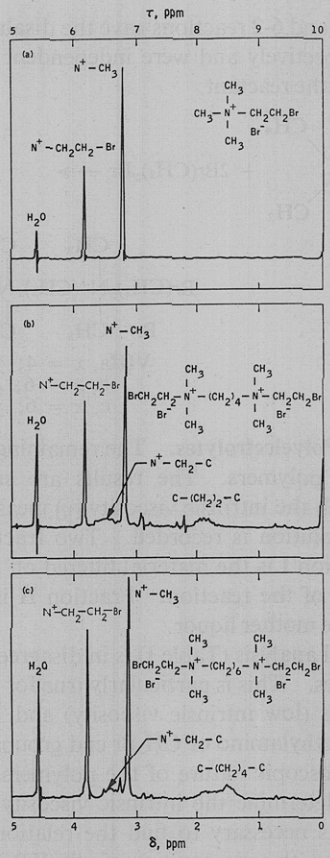

Figure 5. Nmr spectra in D_2O *of* (a) (2-bromoethyl)trimethylammonium bromide, (b) 4-2 reaction product, and (c) 6-2 reaction product.

Table II

τ Values for the N^+–CH_2–N^+ and N^+–CH_2–Br Proton Resonances

Compound	$\tau_{N^+-CH_2-N^+}$ (singlet)	$\tau_{N^+-CH_2-Br}$ (singlet)
2-1 cyclic disalt (Va)	4.51	
$(CH_3)_3N^+CH_2Br$, Br^-		4.77
6-1 linear disalt (VIIIb)		4.80

Table III

τ Values for the N^+–CH_2CH_2–N^+ and N^+–CH_2CH_2–Br Proton Resonances

Compound	$\tau_{N^+-CH_2CH_2-N^+}$ (singlet)	$\tau_{N^+-CH_2CH_2-Br}$ (singlet)
2-1 cyclic disalt (Va)	5.42	
2-2 cyclic disalt (Vb)	5.97	
2-3 cyclic disalt (Vc)	5.93	
$(CH_3)_3N^+CH_2CH_2N^+(CH_3)_3$, $2Br^-$	5.93	
2-4 ionene bromide	5.94	
2-6 ionene bromide	6.02	
$(CH_3)_3N^+CH_2CH_2Br$, Br^-		6.16
4-2 linear disalt (VIIIa)		6.18
6-2 linear disalt (VIIIc)		6.20

Evidence for the similarity of the electric field effect is obtained by comparison of τ values for the N^+–CH_3 resonances of two series of model compounds (Figure 7). The shifts in τ values of the B series of compounds polymethylenebis(trimethylammonium halides) parallels the shifts in τ values for the A series (ω-bromoalkyltrimethylammonium bromides).

The nmr spectra of ionene polymers agreed with their postulated structure. Also, the nmr spectrum of an *x-y ionene* was substantially the same as that of an *y-x* ionene. Figure 8

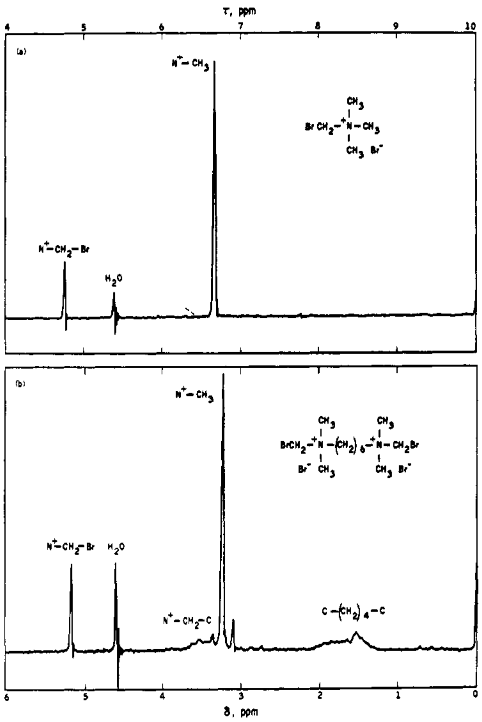

Figure 6. Nmr spectra in D_2O of (a) bromomethyltrimethylammonium bromide and (b) 6-1 reaction product.

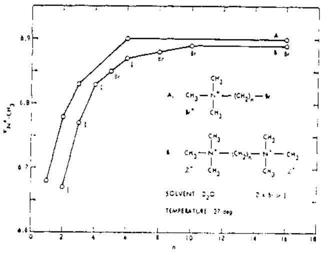

Figure 7. τ values for the N^+-CH_3 proton magnetic resonance of polymethylenebis(trimethylammonium halides) (a) and ω-bromoalkyltrimethylammonium bromides (b) as a function of the number of methylene groups.

shows the variation of the τ values for the N^+-CH_3 proton resonance of 3-y, 4-y, and 6-y ionenes as a function of y. The τ value increases with increasing x or y. When x is 6, the τ value increases with y and reaches the maximum value at y of about 6, indicating that the shielding effect of methylene groups on the positive nitrogen atoms is no more effective beyond y = 6. These τ values were independent of the intrinsic viscosity of the polymers. Thus the decrease of the τ value at y = 16 could perhaps be attributed to some conformational effect of the polymer chain. Similar effects and increases of τ values with the increase in the number of CH_2 groups were reported in part I of this paper.[2]

The N^+-CH_2-CH_2-N^+ proton resonance of 2-4 and 2-6 ionenes occurs as a singlet at almost the same τ values as those of low molecular weight compounds (see Table III).

Solvent Effect. Except for the 1-y and 4-1, the types of products of the x-y reactions seem to be independent of the solvent (see the results of 2-3, 4-2, and 6-16 reactions). The reaction rate increased in the following order: methanol < DMF-methanol (1:1) < acetonitrile < DMF < dimethyl sulfoxide. The same order of reaction rate has been found for the Menschutkin reaction of monofunctional compounds.[15] Out of several solvents, chloroform was found particularly favorable for the formation of 6-16 ionene bromide (Table IV), possibly because of coordination of chloroform with ammonium groups[16] or because of increased solubility.

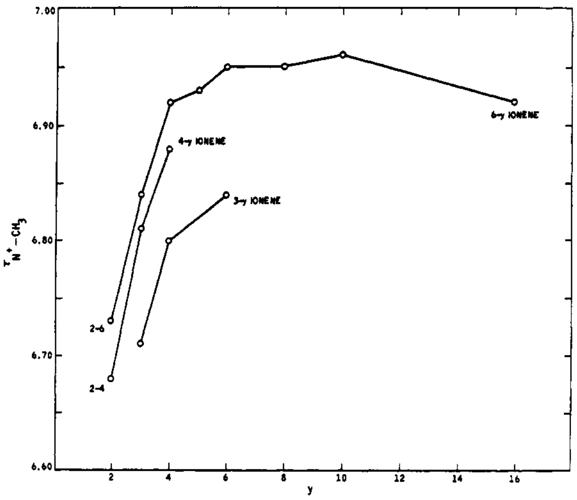

Figure 8. τ values for the N^+-CH_3 proton magnetic resonance of 3-y, 4-y, and 6-y ionene bromides as a function of y.

TABLE IV
SYNTHESIS OF 6-16 IONENES[a]

Solvent	Time, hr	Yield, g[b]	[η] in 0.4 M KBr (100 ml/g)
Benzene	308	1.86	0.117
CH_2Cl_2	190	2.82	0.053
$CHCl_3$	265	2.69	0.309
CCl_4[c]	215	1.26	0.064
$ClCH_2CH_2Cl$	190	2.78	0.082

[a] Reaction conditions: tetramethyldiaminohexane, 0.861 g (0.0500 mol); 1,16-dibromohexadecane, 1.921 g (0.0500 mol); solvent, 16 ml; reaction temperature, 25.0°. [b] Total yield in grams. All the products were collected by evaporating the reaction mixture to dryness. The residue was washed thoroughly with benzene to remove the dibromide and dried *in vacuo* at room temperature. [c] Tetramethyldiaminohexane reacts with carbon tetrachloride to form a white solid which was not identified.

Discussion and Conclusions

The results of part I and the present study have yielded (a) data on a number of new compounds, (b) an insight into the mechanism of reaction, (c) information on the stability of ring structures containing the dimethylammonium groups, and (d) information concerning the synthesis and properties of a novel class of polyelectrolytes.

Figure 9 summarizes the results of reaction 2, in which x and y varied from 1 to 6. Examination of all the data and of Figure 9 leads to the following conclusions.

(1) The first step in all x-y reactions is the addition of a ditertiary amine to the dihalide through quaternization of a

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(15) M. S. Newman, Ed., "Steric Effects in Organic Chemistry," Wiley, New York, N. Y., 1956, p 70.

(16) (a) W. Steinkopf and H. Teichmann, *J. Prakt. Chem.*, **127**, 337 (1930); (b) the NMR-EPR Staff of Varian Associates, "NMR and EPR Spectroscopy," Pergamon Press, Elmsford, N. Y., 1960, p 40.

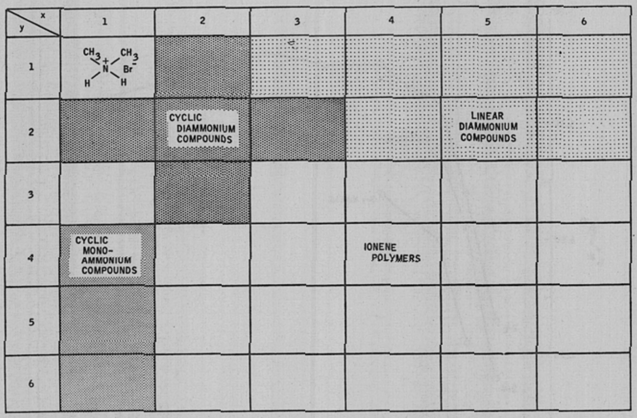
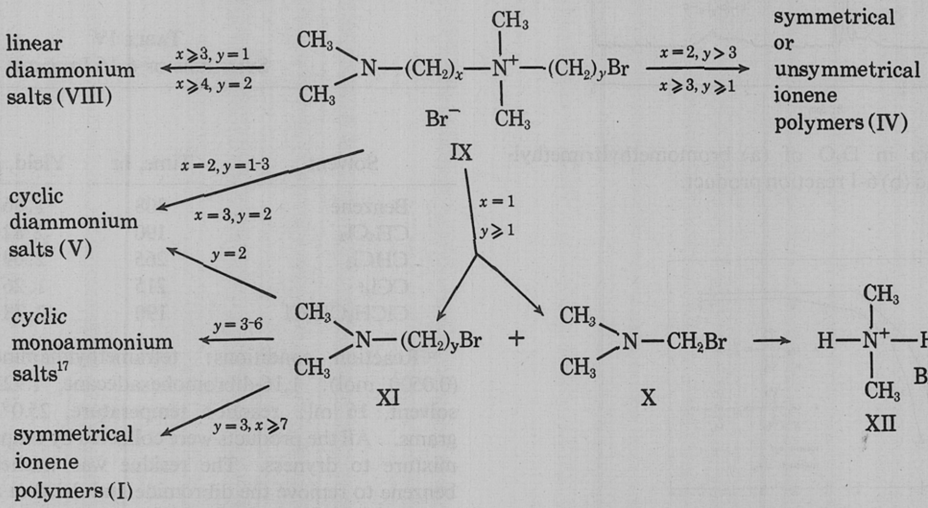


Figure 9. Summary of results of *x-y* reactions.

nitrogen atom to form an intermediate species (IX). The latter splits in the 1-*y* reactions to yield X and XI (Figure 9, *column* 1). In the 1-1 reaction, X and XI are identical and the sole end product is dimethylamine hydrobromide (XII). In the 1-2 reaction, a 1:1 *addition of* XI *takes place; therefore,* the final product is a stable six-membered cyclic diammonium salt. In the 2-1 reaction, cyclization of IX occurs without bond scission, leading to a five-membered diammonium salt. In the 1-3 reaction a mixture of a cyclic four-membered monoammonium compound and a low molecular weight polymer was probably obtained.[17] In the absence of cyclization and with specific values of *x* and *y*, intermediate IX leads to relatively high molecular weight polyelectrolytes.



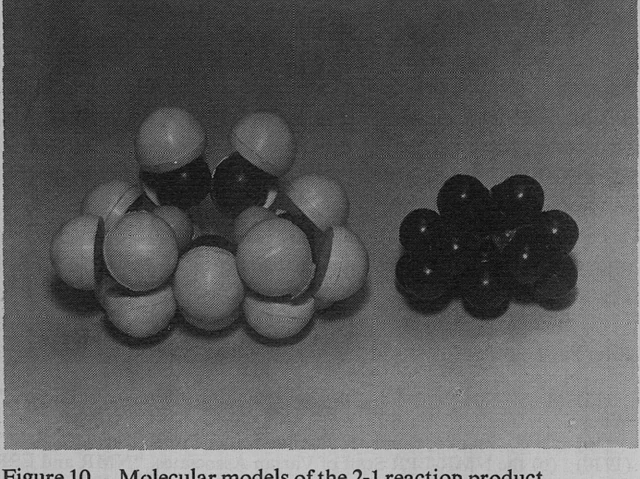


Figure 10. Molecular models of the 2-1 reaction product.

(2) The formation of cyclic structures is governed by the fact that *only five-, six-, or seven-membered rings* are stable when the positive nitrogens are separated by two or three methylenes.[17] The five-membered 2-1 reaction product (see the molecular models in Figure 10) is the only stable diammonium salt containing the $-\overset{|}{\underset{|}{N^+}}-CH_2-\overset{|}{\underset{|}{N^+}}-$ group. In this case less strain is imposed on the valence angles than in the corresponding six- or seven-membered structures. Molecular models and examination of eq 5 and 6 substantiate this conclusion; *e.g.*, the 4-1 reaction product yields a seven-membered cyclic structure (VI) in which the electrostatic re*pulsion of* N^+ *in close vicinity* results in chain scission. A similar chain scission has been reported[16a] for a six-membered cyclic structure containing the $-\overset{|}{\underset{|}{N^+}}-CH_2-\overset{|}{\underset{|}{N^+}}-$ group.

(3) In the *x*-1 and *x*-2 reactions (rows 1 and 2, Figure 9), cyclic structures are formed when the geometrical configuration of the reactants or of their intermediates is favorable for *the formation of five-, six-, or seven-membered rings.* If this is not the case, linear diammonium salts (VIII) are produced. The 6-2 and 2-6 reactions yield a diammonium salt and a polymer, *respectively, indicating that the dimethylamino* end groups are perhaps more reactive than the alkyl bromide end groups.

(4) In several cases, cyclic structures were formed at the exclusion of any other products (*e.g.*, 2-1, 2-2, and 2-3 reactions). Attempts to polymerize five- and six-membered ring structures using temperatures of 90–100° at different concentrations (0.1–4 *M*) were not successful. Furthermore, no cyclic structures could be isolated from *x-y* ($x \geqslant 3$, $y \geqslant 3$) reactions carried out at high dilution, and these reactions yielded only ionene polymers (Figure 9). Examination of nmr spectra with polymerization time also indicated absence of cyclic structures. It is therefore concluded that this step-growth reaction does not appear to be a ring formation *vs.* a chain *polymerization system, and the reaction path* which leads to ring structures, at least under the present experimental conditions, occurs with the exclusion of the polymerization process.

The polymerization of XI (where $y = 3$) is of particular interest, since, in the absence of dimethylamine hydrobromide or dimethylaminobromomethane, it yields relatively

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[17] See part I.

TABLE V
SYNTHESIS OF (ω-BROMOALKYL)TRIMETHYLAMMONIUM BROMIDES[a]

n	$N(CH_3)_3$, mol	$Br(CH_2)_nBr$, mol	Benzene, ml	Time, days	Yield,[b] %	Br⁻, % Calcd	Br⁻, % Found[c]	$\tau_{N^+CH_3}$
3	0.185	0.200	100	9	96	30.62	30.72	6.83
6	0.140	0.200	100	9	100	26.36	26.21	6.90
10	0.0964	0.100	50	10	95	22.25	22.16	6.89
16	0.0611	0.0500	130	25	94.1	18.02	18.11	6.90

[a] Reaction temperature, room temperature (*ca.* 22°). [b] Calculated based on trimethylamine ($n = 3$, 6, and 10) or on dibromide ($n = 16$). [c] Recrystallized prior to analysis from isopropyl alcohol ($n = 3$) or acetone ($n = 6$, 10, and 16).

high molecular weight polymers of high charge density. The investigation of this system will be reported separately.

Experimental Section

Reagents. The purification of dibromides was described previously.[2] Tetramethyldiaminoalkanes were dried over Drierite and distilled under atmospheric or reduced pressure. All the solvents were reagent or spectroscopic grade and were used without further purification.

Intrinsic Viscosity. The intrinsic viscosity of ionene polymers (with the exception of 6-16 ionene) was measured in an Ubbelohde viscometer at 25.0 ± 0.01°, using a 0.4 *M* KBr aqueous solution as solvent. The intrinsic viscosity of 6-16 ionene was measured similarly, using a 0.4 *M* KBr solution in a 2:1 mixture (by volume) of methanol and water as solvent.

All the other measurements were carried out as described before.[2]

Bromomethyltrimethylammonium Bromide. Using 50 ml of benzene as solvent, 34.78 g (0.200 mol) of dibromomethane was allowed to react with 11.8 g (0.200 mol) of anhydrous trimethylamine for 240 hr at room temperature. The precipitated crystal was filtered, washed with benzene, and dried *in vacuo* at 40°: yield 36.95 g (79.5%). It was recrystallized from absolute ethanol: nmr τ 4.77 (s, 2.0, 2 H,[18] N^+–CH_2–Br), 6.68 (s, 9.0, 9 H, N^+–CH_3).

Anal. Calcd for $C_4H_{11}Br_2N$: C, 20.62; H, 4.76; Br(ionic), 34.30; Br(total), 68.60; N, 6.01. Found: C, 20.72; H, 4.74; Br(ionic), 34.12; Br(total), 68.48; N, 6.07.

(2-Bromoethyl)trimethylammonium Bromide. This compound was synthesized in the same manner as the preceeding one, using 1,2-dibromoethane instead of dibromomethane, and 100 ml of benzene as solvent. The crystal formed was isolated as above: yield 25.00 g (50.7%). It was recrystallized from 99% ethanol: nmr τ 6.16 (s, 4.0, 4 H, N^+–CH_2CH_2–Br), 6.78 (s, 9.0, 9 H, N^+–CH_3).

Anal. Calcd for $C_5H_{13}Br_2N$: C, 24.32; H, 5.31; Br(ionic), 32.35; Br(total), 64.70; N, 5.67. Found: C, 24.36; H, 5.26; Br(ionic), 32.30; Br(total), 64.71; N, 5.69.

The preparation of other (ω-bromoalkyl)trimethylammonium bromides is summarized in Table V.

Tetramethyldiaminobutane Dihydrobromide. Pure tetramethyldiaminobutane weighing 8.15 g (0.0565 mol) was added to 10.04 g (0.0595 mol) of 47.9% hydrobromic acid with stirring. The mixture was cooled initially with ice water to keep the reaction temperature below 25°. After standing for 20 hr at room temperature, it was poured into 2 l. of acetone with stirring. The precipitate was filtered, washed thoroughly with acetone, and dried *in vacuo* at room temperature: yield 7.84 g (86.2% based on the diamine). It was recrystallized from methanol. The ir and nmr spectra were identical with those of the 4-1 reaction product in DMF–methanol or in methanol.

Anal. Calcd for $C_8H_{22}Br_2N_2$: C, 31.39; H, 7.24; Br(ionic), 52.22; N, 9.15. Found: C, 31.48; H, 7.21; Br(ionic), 52.22; N, 9.15.

Independent Synthesis of the 6-2 Reaction Product.[12b] **Hexamethylenebis((2-hydroxyethyl)dimethylammonium bromide).** In 50 ml of DMF–methanol (1:1), 17.83 g (0.200 mol) of dimethylaminoethanol was treated with 24.40 g (0.100 mol) of 1,6-dibromohexane for 24 hr at room temperature. The crystals formed were filtered, washed with the solvent three times and then with acetone, and dried *in vacuo* at 40°: yield 35.54 g (84.2%). The filtrate was poured into 1.5 l. of acetone with stirring to give more product. It was filtered, washed with acetone, and dried as before: yield 0.84 g (2.0%). The main fraction was recrystallized from methanol.

Anal. Calcd for $C_{14}H_{34}Br_2N_2O_2$: C, 39.82; H, 8.06; Br(ionic), 37.85; N, 6.63. Found: C, 40.01; H, 8.15; Br(ionic), 37.78; N, 6.68.

Bromination of Hydroxy Groups of Hexamethylenebis((2-hydroxyethyl)dimethylammonium bromide). In 12.55 g (0.075 mol) of 48.1% HBr was dissolved 7.63 g (0.018 mol) of hexamethylenebis((2-hydroxyethyl)dimethylammonium bromide) prepared as above. The mixture was refluxed for 20 hr. After cooling to room temperature, it was poured into 1.4 l. of acetone with stirring. The precipitate was filtered, washed thoroughly with acetone, and dried *in vacuo* at room temperature: yield 8.35 g. Its nmr spectrum was substantially the same as that of the starting dihydroxy compound, except for the presence of a singlet peak at τ 6.19 which is consistent with the N^+–CH_2CH_2–Br proton resonance peak of the 6-2 reaction product.

Anal. Calcd for $C_{14}H_{34}Br_2N_2O_2$ (hexamethylenebis((2-hydroxyethyl)dimethylammonium bromide)): Br(ionic), 37.85. Calcd for $C_{14}H_{32}Br_4N_2$ (hexamethylenebis((2-bromoethyl)dimethylammonium bromide)): Br(ionic), 29.16. Found: Br(ionic), 37.46.

2-1 Reaction in DMF–Methanol (1:1). Using 130 ml of DMF–methanol as solvent, 23.24 g (0.200 mol) of tetramethyldiaminoethane was allowed to react with 34.77 g (0.200 mol) of dibromomethane for 48 hr at room temperature. The crystalline precipitate (needles) was filtered, washed with a small amount of the solvent (three times) and then with acetone, and dried *in vacuo* at 40°: yield 28.0 g (48.2%). It was recrystallized from methanol: mp 159.5–160° dec; nmr τ 4.51 (s, 2.0, 2 H, N^+–CH_2–N^+), 5.42 (s, 4.0, 4 H, N^+–CH_2CH_2–N^+), 6.32 (s, 12.0, 12 H, N^+–CH_3).

Anal. Calcd for $C_7H_{18}Br_2N_2$ (tetrahydro-1,1,3,3-tetramethylimidazolium dibromide): C, 28.99; H, 6.26; Br(ionic), 55.10; N, 9.66. Found: C, 28.96; H, 6.20; Br(ionic), 55.15; N, 9.60.

The filtrate was poured into a large excess of acetone. The precipitate was filtered, washed with acetone, and dried as before: yield 4.25 g (7.3%).

Anal. Calcd for $C_7H_{18}Br_2N_2$: Br(ionic), 55.10. Found: Br (ionic), 54.67.

2-2 Reaction in DMF–Methanol (1:1). In 65 ml of DMF–methanol, 11.62 g (0.100 mol) of tetramethyldiaminoethane was allowed to react with 18.79 g (0.100 mol) of 1,2-dibromoethane for 168 hr at room temperature. The precipitated crystal was isolated as above: yield 21.58 g (71.0%). It was recrystallized from a 2:1 mixture (by volume) of methanol and water: mp 314–315° dec[17] (lit.[19] 370°); nmr τ 5.97 (s, 8.0, 8 H, N^+–CH_2CH_2–N^+), 6.54 (s, 12.0, 12 H, N^+–CH_3).

Anal. Calcd for $C_8H_{20}Br_2N_2$ (1,1,4,4-tetramethylpiperazinium dibromide): C, 31.60; H, 6.63; Br(ionic), 52.56; N, 9.21. Found: C, 31.63; H, 6.63; Br(ionic), 52.60; N, 9.25.

2-3 Reaction in DMF–Methanol (1:1). This reaction was carried out for 168 hr under the same conditions as for the 2-1 reaction. The precipitated crystal was isolated as before: yield 46.8 g (73.6%). It was recrystallized from 89% ethanol: mp 262–262.5° dec (lit.[12a]

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[18] Result of integration shown by a relative value followed by the number of protons in the molecule.

[19] F. G. Mann and A. Senior, *J. Chem. Soc.*, 4476 (1954).

286–286.5°); nmr τ 5.95 (s, 4.0, 4 H, N^+–CH_2CH_2–N^+), 6.20 (t, J = 5.1 Hz, 4.0, 4 H, N^+–CH_2–C), 6.67 (s, 12.0, 12 H, N^+–CH_3), 7.55 (br s, 1.9, 2 H, C–CH_2–C).

Anal. Calcd for $C_9H_{22}Br_2N_2$ (hexahydro-1,1,4,4-tetramethyl-1,4-diazepinium dibromide): C, 33.98; H, 6.97; Br(ionic), 50.24; N, 8.81. Found: C, 34.09; H, 6.92; Br(ionic), 50.16; N, 8.97.

3-1 Reaction in Acetonitrile. Using 65 ml of acetonitrile, 13.03 g (0.100 mol) of tetramethyldiaminopropane was allowed to react with 17.39 g (0.100 mol) of dibromomethane for 90 hr at room temperature. The precipitated solid material was filtered, washed three times with a small amount of acetonitrile and then with acetone, and dried *in vacuo* at room temperature: yield 7.00 g; nmr τ 4.70 (s, N^+–CH_2–Br), 6.34 (t, J = 7.8 Hz, N^+–CH_2–C), 6.64 (s, N^+–CH_3), 6.77 (s, N^+–CH_3), 7.0–8.0 (diffuse m, C–CH_2–C). The presence of two N^+–CH_3 resonance peaks suggests that this product is a mixture of at least two compounds.

Anal. Calcd for $C_8H_{20}Br_2N_2$ (V): C, 31.60; H, 6.63, Br (ionic), 52.56; N, 9.21. Calcd for $C_9H_{22}Br_4N_2$ (trimethylenebis-(bromomethyldimethylammonium bromide)): C, 22.62; H, 4.64; Br(ionic), 33.44; Br(total), 66.88; N, 5.86. Found: C, 25.72; H, 5.40; Br(ionic), 36.73; Br(total), 62.10; N, 6.67.

3-2 Reaction in DMF–Methanol (1:1). This reaction was carried out in the same manner as the 2-2 reaction. The crystals formed were isolated as before: yield 45.30 g (71.1%). It was recrystallized from 89% ethanol: mp 263–264° dec (lit.[12a] 286–286.5°); nmr τ 5.95 (s, 4.0, 4 H, N^+–CH_2CH_2–N^+), 6.20 (t, J = 5.1 Hz, 4.1, 4 H, N^+–CH_2–C), 6.68 (s, 11.9, 12 H, N^+–CH_3), 7.55 (br s, 2.0, 2 H, C–CH_2–C).

Anal. Calcd for $C_9H_{22}Br_2N_2$ (hexahydro-1,1,4,4-tetramethyl-1,4-diazepinium dibromide): C, 33.98; H, 6.97; Br(ionic), 50.24; N, 8.81. Found: C, 34.07; H, 7.11; Br(ionic), 50.31; N, 8.90.

A small amount of the same but slightly impure product was isolated from the filtrate when it was treated as in the 2-1 reaction, yield 0.92 g (1.4%).

Anal. Calcd for $C_9H_{22}Br_2N_2$: Br(ionic), 50.24. Found: Br (ionic), 48.60.

4-1 Reaction. (a) In DMF–Methanol (1:1). In 130 ml of the solvent, 28.85 g (0.200 mol) of tetramethyldiaminobutane was allowed to react with 34.77 g (0.200 mol) of dibromomethane for 48 hr at room temperature. The precipitated crystal was filtered, washed with a small amount of the solvent (three times) and then with acetone, and dried *in vacuo* at room temperature: yield 11.0 g (18.0%). It was recrystallized from methanol: mp 257–258° dec; nmr τ 6.77 (t, J = 7 Hz, 3.9, 4 H, N^+–CH_2–C), 7.09 (s, 12.0, 12 H, N^+–CH_3), 8.18 (quintet, J = 4.0 Hz, 4.0, 4 H, C–$(CH_2)_2$–C).

Anal. Calcd for $C_8H_{22}Br_2N_2$ (tetramethyldiaminobutane dihydrobromide): C, 31.37; H, 7.25; Br(ionic), 52.22; N, 9.15. Found: C, 31.36; H, 7.20; Br(ionic), 52.23; N, 9.11.

More of the same product was obtained when the filtrate was poured into a large excess of acetone. It was filtered, washed with acetone, and dried as before, yield 5.45 g (8.9%).

Anal. Calcd for $C_8H_{22}Br_2N_2$: Br(ionic), 52.22. Found: Br (ionic), 49.37.

(b) In Methanol. This reaction was carried out at room temperature for 48 hr in a manner similar to the preceding one, but using half the amount of starting materials. The homogeneous mixture was evaporated to dryness and the residue was triturated in 1 l. of acetone. The solid product was filtered, washed with acetone, and dried *in vaco* at 40°, yield 4.00 g (13.1%). It was recrystallized from methanol; nmr same as (a).

Anal. Calcd for $C_8H_{22}Br_2N_2$ (tetramethyldiaminobutane dihydrobromide): Br(ionic), 52.22. Found: Br(ionic), 52.04.

(c) In DMF. The 4-1 reaction in DMF was carried out under the same conditions as in (b). The crystal formed was filtered, washed with a small amount of DMF (three times) and then with benzene, with the exclusion of moisture, and dried *in vacuo* at room temperature, yield 8.64 g (27.2% based on structure VI).

Anal. Calcd for $C_9H_{22}Br_2N_2$ (VI): Br(ionic), 50.24. Found: Br(ionic), 49.17.

Upon exposure to moist air, this product decomposed to produce formaldehyde. It was recrystallized from methanol. The nmr spectrum agreed with that of tetramethyldiaminobutane dihydrobromide.

Anal. Calcd for $C_8H_{22}Br_2N_2$ (tetramethyldiaminobutane dihydrobromide): Br(ionic), 52.22. Found: Br(ionic), 52.10.

The filtrate was poured into 1.5 l. of benzene with stirring. The precipitate was filtered, washed with benzene, and dried as before, yield 14.23 g (45% on the same assumption as above). It contained 44.11% ionic bromine and produced formaldehyde in the moist air. It was recrystallized from methanol.

Anal. Calcd for $C_8H_{22}Br_2N_2$ (tetramethyldiaminobutane dihydrobromide): Br(ionic), 52.22. Found: Br(ionic), 51.88.

(d) In Acetonitrile. The 4-1 reaction in acetonitrile was carried out in the same manner as in (c), and it proceeded similarly. With the exclusion of moisture, the crystals formed were filtered, washed with a small amount of acetonitrile (three times) and then with benzene, and dried *in vacuo* at room temperature, yield 9.10 g (28.6% based on structure VI).

Anal. Calcd for $C_9H_{22}Br_2N_2$ (VI): Br(ionic), 50.24. Found: Br(ionic), 47.89.

Upon exposure to moist air, this product decomposed to produce formaldehyde. It was recrystallized from methanol. The nmr spectrum agreed with that of tetramethyldiaminobutane dihydrobromide.

Anal. Calcd for $C_8H_{22}Br_2N_2$ (tetramethyldiaminobutane dihydrobromide): Br(ionic), 52.22. Found: Br(ionic), 51.97.

The filtrate was treated as in (c), yield 14.22 g (45% based on structure VI). It contained 44.17% ionic bromine and produced formaldehyde in moist air. It was recrystallized from methanol.

Anal. Calcd for $C_8H_{22}Br_2N_2$ (tetramethyldiaminobutane dihydrobromide): Br(ionic), 52.22. Found: Br(ionic), 51.81.

4-2 Reaction. (a) In DMF–Methanol (1:1). In 65 ml of the solvent 14.43 g (0.100 mol) of tetramethyldiaminobutane was allowed to react with 37.57 g (0.200 mol) of 1,2-dibromoethane for 8 hr at room temperature. The colorless, homogeneous mixture was poured into a large excess of acetone with stirring. The precipitate was filtered, washed with acetone, and dried *in vacuo* at room temperature: yield 1.36 g (2.6%); mp 194–195° dec; nmr τ 6.18 (s, 7.6, 8 H, N^+–CH_2CH_2–Br), 6.50 (diffuse t, 4.0, 4 H, N^+–CH_2–C), 6.83 (s, 12.1, 12 H, N^+–CH_3), 8.10 (quintet, J = 4.0 Hz, 4.2, 4 H, C–$(CH_2)_2$–C).

Anal. Calcd for $C_{12}H_{28}Br_4N_2$ (tetramethylenebis((2-bromoethyl)-dimethylammonium bromide)): C, 27.72; H, 5.43; Br(ionic), 30.73; Br(total), 61.46; N, 5.39. Found: C, 27.87; H, 5.47; Br(ionic), 30.76; Br(total), 61.35; N, 5.40.

(b) In Methanol. The 4-2 reaction in methanol was carried out under the same conditions as in (a). After 24 hr of reaction at room temperature, the slightly yellowish, homogeneous mixture was evaporated by means of a rotary evaporator to about half its volume. The residual solution was poured into 1.2 l. of acetone with stirring. The precipitate was treated as in (a), yield 0.25 g (0.5%).

Anal. Calcd for $C_{12}H_{28}Br_4N_2$ (tetramethylenebis((2-bromoethyl)-dimethylammonium bromide)): Br(ionic), 30.73. Found: Br (ionic), 31.49.

(c) In Acetonitrile. This reaction was carried out for 7 hr at room temperature under the same conditions as in (a). The mixture became reddish. The brownish precipitate was filtered, washed with a small amount of acetonitrile three times and then with acetone, and dried as before, yield 3.88 g (7.5%).

Anal. Calcd for $C_{12}H_{28}Br_4N_2$ (tetramethylenebis((2-bromoethyl)-dimethylammonium bromide)): Br(ionic), 30.73. Found: Br (ionic), 33.04.

No appreciable amount of product was obtained from the filtrate when it was poured into a large excess of acetone.

(d) In DMF. The 4-2 reaction in DMF was carried out for 7 hr at room temperature under the same conditions as in (a), and it proceeded in a manner similar to (c). The orange crystals formed were isolated as in (c), yield 10.11 g (19.5%). It was recrystallized from 95% ethanol (pale yellow).

Anal. Calcd for $C_{12}H_{28}Br_4N_2$ (tetramethylenebis((2-bromoethyl)-dimethylammonium bromide)): Br(ionic), 30.73. Found: Br (ionic), 31.24.

No appreciable amount of solid product was obtained from the filtrate when it was poured in a large excess of acetone with stirring. The nmr spectra of the products of (b), (c), and (d) were identical to that of (a).

6-1 Reaction in DMF–Methanol (1:1). In 65 ml of DMF–methanol, 17.23 g (0.100 mol) of tetramethyldiaminohexane was allowed to react with 17.39 g (0.100 mol) of dibromomethane for 192 hr at room temperature. The crystals formed were filtered, washed with a small amount of the solvent (three times) and then with acetone, and dried *in vacuo* at 40°: yield 9.60 g (36.9% based on the dibromide). It was recrystallized from methanol: mp 152–152.5° (effervescence); nmr τ 4.80 (s, 4.0, 4 H, N^+–CH_2–Br), 6.44 (t, J = 6.0 Hz, 3.5, 4 H, N^+–CH_2–C), 6.74 (s, 11.9, 12 H, N^+–CH_3), 8.44 (tallest peak of the diffuse multiplet at τ 7.8–8.8, 8.7, 8 H, C–$(CH_2)_4$–C).

Anal. Calcd for $C_{12}H_{28}Br_4N_2$ (hexamethylenebis(bromomethyldimethylammonium bromide)): C, 27.72; H, 5.43; Br(ionic), 30.73; Br(total), 61.46; N, 5.39. Found: C, 27.64; H, 5.51; Br(ionic), 30.66; Br(total), 61.38; N, 5.36.

The filtrate was poured into a large excess of acetone with stirring. The precipitate was filtered, washed with acetone, and dried as before, yield 4.65 g (17.9%).

Anal. Calcd for $C_{12}H_{28}Br_4N_2$: Br(ionic), 30.73. Found: Br (ionic), 35.22.

6-2 Reaction in DMF–Methanol (1:1). Using 130 ml of methanol as solvent, 34.46 g (0.200 mol) of tetramethyldiaminohexane was allowed to react with 37.57 g (0.200 mol) of 1,2-dibromomethane for 48 hr at room temperature. The precipitated crystal was filtered, washed with a small amount of the solvent and then with acetone, and dried *in vacuo* at 40°: yield 12.35 g (22.5% based on the dibromide). It was recrystallized from methanol: mp 224.5–226.5° dec; nmr τ 6.20 (s, 8.0, 8 H, N^+–CH_2CH_2–Br), 6.56 (t, J = 6 Hz, 3.1, 4 H, N^+–CH_2–C), 6.85 (s, 11.3, 12 H, N^+–CH_3), 8.47 (strongest peak of the multiplet at 7.8–8.8, 8.1, 8 H, C–$(CH_2)_4$–C).

Anal. Calcd for $C_{14}H_{32}Br_4N_2$ (hexamethylenebis((2-bromoethyl)-dimethylammonium bromide)): C, 30.68; H, 5.89; Br(ionic), 29.16; Br(total), 58.32; N, 5.11. Found: C, 30.86; H, 5.99; Br(ionic), 29.15; Br(total), 58.23; N, 5.25.

The filtrate was treated as in the 6-1 reaction, yield 11.16 g (20.4%).

Anal. Calcd for $C_{14}H_{32}Br_4N_2$: Br(ionic), 29.16. Found: Br (ionic), 34.50.

Ionene Polymers. The *x-y* reactions yielding ionene polymers were carried out in the following way. A solution of a tetramethyldiaminoalkane was mixed thoroughly with a solution of a dibromoalkane and the mixture was left at room temperature (*ca.* 22°). The molar ratio of the diamine to the dibromide was in all cases 1:1. After a given time, the precipitated polymer was filtered; washed quickly with a small amount of the solvent, then with benzene, and finally with acetone; and dried under high vacuum at 40° (fraction I). The filtrate was poured into a large excess of acetone with stirring. The precipitated polymer was filtered, washed first with benzene and then with acetone, and dried as before (fraction II).

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Radiation-Induced Solid-State Polymerization of Derivatives of Methacrylic Acid. VIII. Postirradiation Polymerization of Barium Methacrylate

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ABSTRACT: The kinetics of polymerization of crystalline barium methacrylate monohydrate have been investigated in the temperature range 20–110° after γ irradiation at −78 and −196°. The initial rate was proportional to the radiation dose up to 4 Mrads and increased continuously with the polymerization temperature (E_a = 132 kJ/mol). The "limiting" polymer yields did not increase proportionately with dose or temperature. Esr spectra of the D_2O salt showed that at least 75% of the initiating radicals in the monohydrate are formed by addition of H atoms from the water of crystallization to the C═C bond. The polymerization rate was about double after irradiation at −78° compared with −196°, and esr studies showed a proportionate difference in concentrations of trapped radicals; G(radicals) = 8.8 ± 0.5 at −78° compared with 4.7 ± 0.5 at −196°. Less than 2% polymer was obtained from the crystalline anhydrate even after high radiation doses and prolonged heating up to 200°, although esr spectra indicated the formation of propagating radicals.

Barium methacrylate may be prepared as the monohydrate by crystallization from aqueous solution or as the anhydrate by crystallization from methanol or dehydration of the monohydrate. Lando and Morawetz (1964)[1] first reported polymerization of the monohydrate on heating after γ irradiation at −78°. They reported the hydrated salt to be a dihydrate, but Bowden and O'Donnell (1969),[2] who investigated the dehydration reaction, showed that it was the monohydrate, $Ba^{2+}(CH_2{=}C(CH_3)COO^-)_2 \cdot H_2O$.

Polymerization occurs sufficiently below the decomposition temperature of about 230° for there to be little likelihood of polymerization occurring in a "liquid drop" due to local melting caused by the exothermic heat of reaction.[3] It proceeds by a free-radical mechanism,[4] and esr spectra show well-resolved

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[1] J. B. Lando and H. Morawetz, *J. Polym. Sci., Part C*, No. 4, 789 (1964).

[2] M. J. Bowden and J. H. O'Donnell, *J. Phys. Chem.*, 73, 2871 (1969).

[3] G. Hardy, K. Nyitray, G. Kovacs, N. Fedorova, and J. Varga, Proceedings of the Tihany Symposium on Radiation Chemistry, Hungarian Academy of Sciences, Budapest, 1966, p 205.

[4] M. J. Bowden and J. H. O'Donnell, *Macromolecules*, 1, 499 (1968).