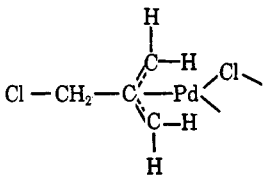

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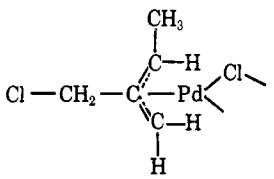

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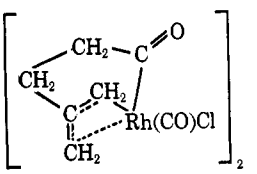


VI

anionic mechanism; that is, it occurs by incorporation of the monomer on a polarized metal$^{\delta+}$–C$^{\delta-}$ bond between the transition metal and the last polymerized unit.

This mechanism easily accounts for the formation of a copolymer between I and ethylene. Furthermore, it is to be considered that both $TiCl_3ARA$–$Al(i\text{-}Bu)_3$ and $Ti(CH_2Ph)_4$ are typical coordinated-anionic systems and are inactive for the oligomerization or polymerization of aliphatic vinylidene olefins such as isobutylene.

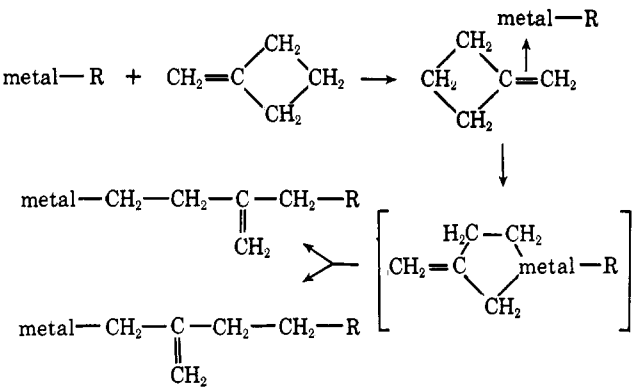
The formation of structural units of type II can be related to the analogous ring-opening reactions of I with $PdCl_2$ and $[Rh(CO)_2Cl]_2$ in which the organic moiety attributable to such units derives from the fission of I at the C_2–C_3 bond.

In the light of the above reactions the polymerization of I can tentatively be visualized as shown in Scheme I.

The strain of I is most probably the reason for the ring opening. Several analogous metal-promoted ring-opening reactions are reported in the literature.[10-12]

(10) J. Wrister, L. Brener, and R. Pettit, *J. Amer. Chem. Soc.*, **92**, 7499 (1970).
(11) K. G. Powell and F. J. McQuillin, *J. Chem. Soc. D*, 931 (1971).
(12) L. Cassar and J. Halpern, *ibid.*, 1089 (1970), and references therein.

SCHEME I



The above mechanism is consistent with the fact that the homopolymer of I from $TiCl_3ARA$–$Al(i\text{-}Bu)_3$ is amorphous. The lack of crystallinity in such a polymer could in fact be attributed to the presence of units II in head-to-head and head-to-tail arrangements. An irregular enchainment is foreseeable on the basis of the two above-represented modes of insertion of I into the metal$^{\delta+}$–C$^{\delta-}$ bond. On the other hand, the homopolymer of I from $TiCl_3ARA$–$Al(i\text{-}Bu)_3$ shows three bands in the region of methylene rocking vibrations (700–800 cm^{-1}) which could be assigned to sequences of four, three, and two CH_2 groups (Figure 1).

The presence of 1,4-isoprene and 1,4-pentadiene units in the polymers obtained either by $Ti(CH_2Ph)_4$ or by the $RhCl_3$–EtOH system could be attributed to one or both of the following factors: (a) isomerization of the II units by the catalyst or a species derived from it; (b) possible isomerization of I to 1,3-pentadiene and isoprene.

It has been shown in fact that $Ti(CH_2Ph)_4$[6] and rhodium compounds[13,14] can promote isomerization of α-olefins.

Acknowledgment. The financial support of the Consiglio Nazionale delle Ricerche is gratefully acknowledged.

(13) R. Cramer, *Accounts Chem. Res.*, **1**, 186 (1968).
(14) A. J. Hubert and H. Reimlinger, *Synthesis*, 405 (1970).

Synthesis and Characterization of Dibenzothiophene–Formaldehyde Copolymers

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IBM Research Laboratory, San Jose, California 95114. *Received December 8, 1971*

ABSTRACT: The structures of the polymeric products produced from a 1- to 24-hr condensation of paraformaldehyde with dibenzothiophene have been investigated by chemical and physical methods. It was shown that the polymers formed during the early stages of the condensation appear to have a linear structure with a degree of polymerization (DP) equivalent to *ca.* six repeat units. The polymers produced during the latter stages of the reaction (DP > 6) are branched and of different chemical composition than the early stage polymers. The polymer structures contain both methylene and oxymethylene bridges as well as hydroxymethyl end groups.

Under appropriate reaction conditions, formaldehyde condenses with a large number of organic compounds to yield derivatives ranging from simple methylol and methylated compounds to highly intractable resins.[1] The intermediates produced in many of these reactions have been identified and characterized, especially those low molecular weight products derived from pheolic condensations.[2-4] However,

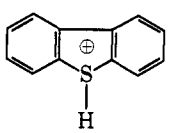
(1) J. F. Walker, "Formaldehyde," 3rd ed, Reinhold, New York, N. Y., 1969.
(2) D. Gould, "Phenolic Resins," Reinhold, New York, N. Y., 1959.
(3) R. Martin, "The Chemistry of Phenolic Resins," Wiley, New York, N. Y., 1958.
(4) N. Megson, "Phenolic Resin Chemistry," Butterworths, London, 1958.

the resinous products from these reactions have been poorly characterized, and considerable speculation exists concerning their molecular structures.[5,6]

Several reaction parameters are reported to affect the structure of formaldehyde condensation polymers. These are the reactant ratios, the type of solvent, the reaction temperature, the time, and the acid catalyst.[7] For example, the use of acetic acid as catalyst favors the formation of oxygen-free resins, whereas sulfuric and perchloric acids promote the formation of both methylene- and oxymethylene-linked resins.[8] An excess of formaldehyde, when used under reaction conditions favoring the formation of oxygen-rich resins, will also promote the formation of arylmethyl polyoxymethylene ethers.[7]

The kinetics of the acid catalyzed condensation of formaldehyde with aromatic hydrocarbons such as acenaphthalene in aqueous acetic acid solvent has been reported.[9] The reaction rate was found to be proportional to the concentration of the hydrocarbon and formaldehyde, respectively, but not to the catalyst concentration. The rate equation for the condensation was based on a preequilibrium reaction of formaldehyde with a proton to give the methylol cation, the rate-determining step being the reaction of acenaphthalene with methylol cation.

In this investigation, the acid-catalyzed condensation of paraformaldehyde with dibenzothiophene was investigated because of our interest in the polymerizability of aromatic heterocyclic compounds[10-18] and because polymers of this class had not been reported previously. The formation of methylene and oxymethylene linkages would be expected to take place predominantly at the 2 and 2,8 positions of dibenzothiophene because of the directive influence of the S atom on incoming electrophilic groups.[14] It is also possible that a sulfonium ion could be formed in the condensation



system because of the basicity of a sulfide group (C–S–C); *i.e.*, a sulfonium ion would be more stable than an oxonium ion, and two benzene rings could stabilize the sulfonium ion to some extent. If this sulfonium ion were present it might influence the rate of condensation.

In the early experiments in acetic acid or formic acid solvents, low molecular weight polymers precipitated after 4–6 hr. In later experiments it was found that the perchloric acid catalyzed condensation in *p*-dioxane solvent favored the formation of higher molecular weight polymers probably because the polymers did not precipitate out of solution for 24 hr. This permitted the reaction products to be investigated as a function of time and conversion.

(5) N. Megson, *J. Soc. Chem. Ind.*, **52**, 422T (1933).
(6) E. Pritchett, *Chem. Ind. (London)*, 295 (1949).
(7) R. Wegler, *Angew. Chem.*, **60**, 88 (1948).
(8) J. Yen, M. Davar, and A. Rembaum, *J. Macromol. Sci., Chem.*, **3**, 703 (1970).
(9) T. Tanigaki and M. Imoto, *Makromol. Chem.*, **43**, 222 (1963).
(10) W. Hewett and E. Gipstein, *J. Polym. Sci., Part B*, **6**, 565 (1968).
(11) E. Gipstein and W. Hewett, *Macromolecules*, **2**, 282 (1969).
(12) E. Gipstein, W. Hewett, and O. Need, *J. Polym. Sci., Part A*, **8**, 3285 (1970).
(13) E. Gipstein, W. Hewett, and O. Need, *J. Polym. Sci., Part B*, **9**, 671 (1971).
(14) H. Hartough and S. Meisel, "The Chemistry of Heterocyclic Compounds," Interscience, New York, N. Y., 1954.

Experimental Section

Condensation polymerizations were carried out in 3-l. convoluted flasks equipped with stirrer, water condenser, thermometer, and gas-inlet adapter. The heating rate and stirring speed were kept constant in all reactions. Reactions were carried out with 92.1 g (0.50 mol) of dibenzothiophene (Matheson Coleman and Bell (MCB), 99%) and 23.2 g (0.74 mol) of paraformaldehyde (MCB, 95%) dissolved in 1050 ml of *p*-dioxane. The mixture was heated to 90° under an argon atmosphere and 5 ml of perchloric acid (62–64%) was added. Aliquot samples of the reaction mixture were removed at regular time intervals up to 24 hr, at which time the reaction product began to precipitate slowly out of solution. If the reaction was continued longer, the proportion of insoluble product increased until the entire product was intractable. The reaction mixture was poured into a large excess of methyl alcohol to isolate the polymer. The polymer was washed first with hot water and then with ethyl alcohol followed by heating in chloroform. The chloroform-soluble fraction was precipitated with methyl alcohol (fraction S1). The chloroform-insoluble fraction was then heated in *p*-dioxane. The dioxane-soluble fraction was precipitated with methyl alcohol (fraction S2). The residue (fraction S3) was insoluble in all common organic solvents as well as in DMF, DMSO, hexamethylphosphoramide, and sulfuric acid. All the fractions were collected and dried 48–60 hr under vacuum and heat (71% conversion). The products were examined by gel permeation chromatography (GPC), nmr, infrared spectroscopy, vapor-phase osmometry, differential scanning calorimetry, and elemental analysis.

Discussion

Gel Permeation Chromatography. Molecular weight distribution and molecular weight averages (number and weight averages) were obtained with a modified Waters Associates GPC-200 chromatograph. The chromatograph was run under ambient conditions in THF solvent at a 1-ml/min flow rate. The Styrogel-packed fractionating columns had permeability limits of 10^3, 250, (two columns) and 60 Å (two columns) and exhibited excellent resolution, showing four distinct peaks for a low molecular weight polystyrene standard (Pressure Chemical PS-600). The chromatograph was interfaced with the laboratory automation system developed in this laboratory.[15,16] This system consisted of an IBM 1800 process-control computer with the supporting peripheral equipment, *i.e.*, input–output devices, analog to digital equipment, etc. This allows six samples to be run unattended. A run or a series of runs requires the following operations: (a) fill the sample loops (up to six sample loops) of the automatic sample injection system with a 0.1% solution in THF, (b) input the length of the run (number of hours) to the computer through data switches provided at the GPC console, and (c) start computer data collection by pressing a system interrupt switch also located on the GPC operating console.

At the end of the run, the data collected and stored by the computer can be processed and reduced to obtain normalized chromatograms and molecular weight averages (number, viscosity, weight, and *z* averages) by simply introducing integration parameters and Mark–Houwink constants of the calibration standard (polystyrene) and the sample.

Molecular Weight Distribution. Except for the highest molecular weight fraction (S2), the GPC chromatograms (molecular weight distribution) of the dibenzothiophene–formaldehyde copolymers exhibit multimodal characteristics with four distinct peaks. The retention volumes of these peaks appear to remain constant with increasing conversion

(15) J. Gladney, *J. Comput. Phys.*, **2**, 255 (1968).
(16) A. Ouano, *J. Polym. Sci., Part A*, **9**, 2179 (1971).

or molecular weight average as indicated in Figure 1. However, the relative peak heights (or relative concentration of the molecular species in the sample represented by the peak) appear to change considerably. A plot of the normalized height of these peaks as a function of polymerization time is shown in Figure 2. At higher conversions approaching 24 hr polymerization time, a new peak has developed in the chromatogram, shown in Figure 1, which represents the highest molecular weight fraction. The sharp and narrow peaks of the lower conversion polymers suggest distinct molecular species or mixtures of isomers. Peaks 1–4 have retention volumes equivalent to polystyrene with molecular weights of 800, 700, 550, and 300, respectively. This suggests that the compounds represented by peaks 1–4 have an effective molecular size in solution equivalent to that of a polystyrene octamer, heptamer, pentamer, and trimer, respectively.

Osmometry. Number-average molecular weights were determined independently by vapor-phase osmometry. Since the osmometric method is considered to give absolute number-average molecular weights, it can serve as a basis of comparison for molecular weights obtained by GPC. The osmometer used in this study was the Mechrolab vpo. Chloroform was used as the solvent at 37°. Benzil (M_w = 210.22) and squalene (M_w = 422.83) were used as calibration standards.

Molecular Weight Averages. Table I shows that for low conversion (<25%) the number-average molecular weights as determined by the vapor-phase osmometry method agree (within 10%) with those obtained by GPC. At higher conversion, however (exception S_1), the osmometry values are considerably higher than the GPC values. The discrepancy between GPC and osmometry values could be indicative of a change in the molecular structure of the polymer from a linear to a branched structure. This rationale is based on the fact that separation by GPC is based on the hydrodynamic volume of the polymer rather than molecular weight. Since a linear configuration will appear larger than that of a branched polymer with equivalent molecular weight, the GPC will consequently give lower apparent molecular weights for branched polymers when compared to linear polymers.

The polydispersivity index (M_w/M_n) for low conversions also appeared to remain constant at 1.25. At higher conversion, however, the polydispersivity appears to increase markedly with conversion. The large change in the polydispersivity is greater than that which would result from an increase in the molecular weight averages, *i.e.*, such as those predicted from asymmetric distribution without change in molecular structure. Therefore, this could be interpreted as additional evidence for branching in the polymer structure.

Elemental Analysis. Another source of information which gives an indication of the changing structure of the polymer with molecular weight is the atomic ratio of oxygen to sulfur in the polymer. At low conversion under the synthetic conditions used to prepare the polymers, the dibenzothiophene repeat units are connected by methylene bridges. Hence, most of the oxygen must come from methylol end groups.

TABLE I
MOLECULAR WEIGHT AVERAGES AND CONVERSIONS OF DBTF COPOLYMER

Sample identification	Reaction time, hr	Conversion, %	Molecular weight averages: Osmometry $\bar{M}_n$	GPC $\bar{M}_n$	GPC $\bar{M}_w$	GPC $\bar{M}_w/\bar{M}_n$
1-3	1	0.23		500	622	1.24
2-3	3	15.8	550	600	752	1.25
3-3	5	24.7	750	695	885	1.27
4-3	7	34.0	842	708	1074	1.52
5-3	10	43.8	950	786	1346	1.71
6-3	14	52.2	1070	861	1857	2.16
S_1-3	24		1047	1181	3063	2.59
S_2-3	24	71.4	1661	1380	4169	3.02
S_3-3	24	Insoluble fraction				

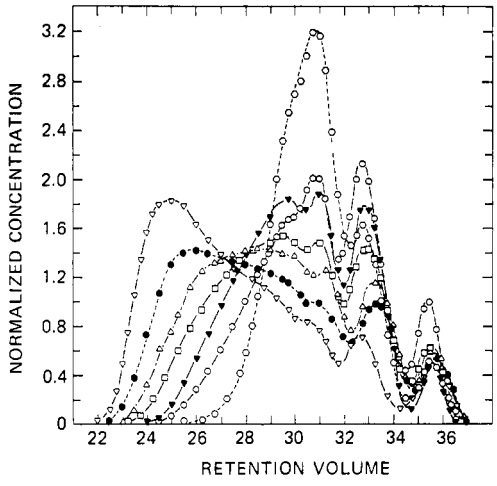


Figure 1. Normalized GPC chromatogram of dibenzothiophene at various conversions: (○) 0.23%, (○) 15.8%, (▼) 24.7%, (□) 34.0%, (Δ) 43.8%, (●) 52.2%, (▽) 71.4% (soluble fraction).

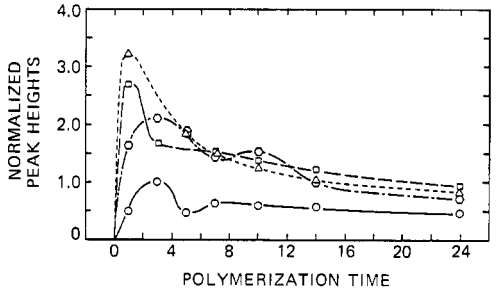


Figure 2. Normalized GPC peak heights as a function of polymerization time: (○) peak 1, (□) peak 2, (Δ) peak 3, (○) peak 4.

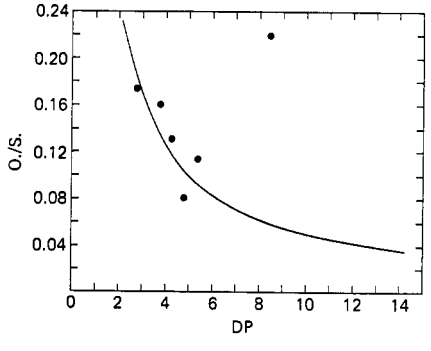


Figure 3. Oxygen to sulfur ratio *vs.* degree of polymerization.

A plot of the oxygen to sulfur ratio (O/S) *vs.* the degree of polymerization (DP) in Figure 3 shows a sharp increase in the O/S for DP > 6. Several repeat runs of the highest molecular weight sample (highest DP) showed a consistently higher O/S ratio; hence, the increase in the O/S ratio with DP is not an artifact but a real trend. As a reference curve, the O/S *vs.* DP plot of the dibenzothiophene–formaldehyde polymers with methylene bridges only and with a single methylol end group is plotted as a solid line in Figure 3. At low DP, the experimental O/S ratios agree closely with

TABLE II
MELTING POINTS OF HIGH MOLECULAR WEIGHT DBTF COPOLYMER

Sample identification	Mp, °C	Molecular weight osmometry
S_1-3	44	1074
S_2-3	51	1661
S_3-3	67	Insoluble

the reference curve but deviate sharply at DP's > 6. This behavior may be an indication of a change in the chemical composition of the polymer as well as a change in configuration, *i.e.*, methylol end groups (increased branching) and increasing number of oxymethylene bridges.

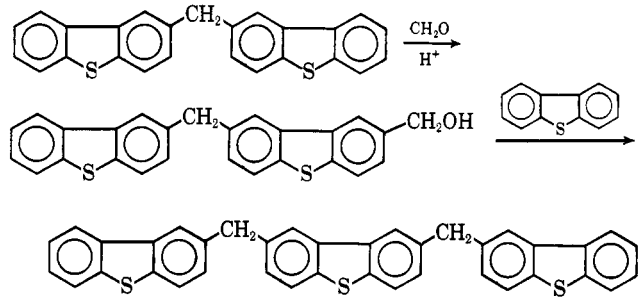
Melting Point. The melting points of the higher molecular weight samples (represented by the S samples) were obtained using the Du Pont TMA 900 differential thermal analyzer. The melting points were found to be dependent on molecular weight as shown in Table II. The dta measurements indicated that the polymers decomposed exothermally above 190°.

Nmr Spectroscopy. Nmr spectra obtained in $CDCl_3$ and CCl_4 with a Varian HA-100 spectrometer and tetramethylsilane as an internal standard were poorly resolved. Better resolution was obtained in *o*-dichlorobenzene at 140°; however, those broad spectra in the region from δ 5.40 to 3.6 indicative of $ArCH_2OCH_2Ar$, $Ar(CH_2O)_xAr$, and $ArCH_2Ar$ type structures[17] could not be sufficiently resolved to make quantitative assignments. Those assignments that could be made were at δ 6.7–8.2, a multiplet assigned to the aromatic protons, and at δ 1.45, a sharp singlet assigned to OH connected to $-CH_2-$. The presence of hydroxymethylene end groups was confirmed by an exchange reaction with D_2O, the OH absorption completely disappearing from the spectrum. A broad absorption occurring between δ 4.8 and 5.6 was observed to increase as the molecular weight of the polymer increased.

Infrared Spectroscopy. The infrared spectra were obtained with a Perkin-Elmer 521 grating spectrophotometer. The low molecular weight fractions, dissolved in THF, were spread as thin films on NaCl plates. Before the spectra were taken, the plates were dried under vacuum 48 hr to remove all traces of solvent. The spectra showed absorptions at 3400 (OH), 800 (trisubstituted benzene ring (in higher molecular weight samples)), and 725 and 750 cm^{-1} (disubstituted benzene ring), indicating that the structure of the polymer was becoming more branched with increasing molecular weight. The absorption band for C–O–C could not be confirmed because of strong aromatic absorption bands appearing in the same region.

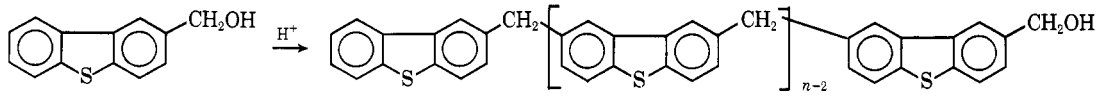
Mechanism and Structure. The low molecular weight polymers produced in formaldehyde condensation reactions have been broadly classified as belonging to several distinct types: (1) soluble resins in which the component polymer molecules have low molecular weights and have a linear or chain-like structure, (2) difficultly soluble resins that consist of moderately high molecular weight molecules in which the chains are branched, and (3) insoluble resins in which the component molecules are made up of a three-dimensional network consisting of cross-linked molecules. The latter classification is by no means absolute, and cross linkages may be few or nonexistent, the insolubility resulting from a large amount of polyoxymethylene in the polymer. It has also been suggested that the properties of the intractable resins result entirely from entanglement or irregular chains.[6] Our data seem to refute this latter view.

The formation of low molecular weight linear dibenzothiophene–formaldehyde polymers may be visualized to proceed *via* the 8,8′ nuclear positions being readily accessible for further attack and subsequent chain growth, *i.e.*, eq 1.



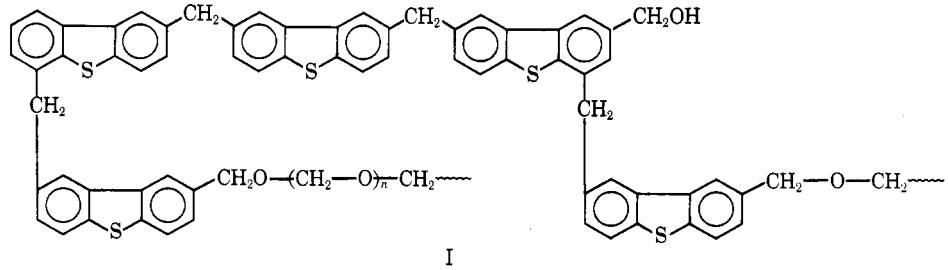
(1)

The process may be repeated, leading to higher oligomers. Alternatively, the process may also proceed by self-condensation of a 3-hydroxymethyldibenzothiophene formed *in situ* from dibenzothiophene and paraformaldehyde, the chain growth being finally terminated by reaction of the long-chain methylol compound with dibenzothiophene, *i.e.*, eq 2.



(2)

In the formation of the higher molecular weight fractions, other reactive sites on the dibenzothiophene nucleus are most likely utilized, producing methylene and oxymethylene links both ortho and para to the S atom,[18,19] thereby producing the branched structures visualized for this polymer, *i.e.* I.



I

(17) J. Woodbrey, H. Higginbottom, and H. Culbertson, *J. Polym. Sci., Part A*, 3, 1079 (1965).

(18) H. Gilman and A. Jacoby, *J. Org. Chem.*, 3, 108 (1938).

(19) G. M. Badger, "The Chemistry of Heterocyclic Compounds," Academic Press, New York, N. Y., 1961, 180 ff.

Continuing the reaction beyond this stage results in the formation of an insoluble and very large oxygen-rich macromolecule.

Conclusions

Based on the investigation of the polymeric products formed during the condensation of paraformaldehyde with dibenzothiophene, the following conclusions are made. (1) The conversion of dibenzothiophene to polymethylene dibenzothiophene was 71% in 24 hr. (2) The molecular weight of the polymer increases with increasing conversion. (3) The polymeric products formed during the early stage of the condensation appear to be composed of at least four oligomeric species having linear structures. (4) The polymeric products formed at the higher conversions appear to contain large amounts of branched, high molecular weight fractions in addition to low molecular weight fractions. (5) The low molecular weight polymer fractions contain methylene bridges and hydroxymethyl end groups. The higher molecular weight fractions contain, in addition to these groups, oxymethylene bridges.

Acknowledgments. The authors wish to acknowledge the assistance of the following individuals in obtaining the data given in this paper. The GPC analyses were carried out by Annie R. Gregges, the nmr analyses by Terry T. Horikawa, the ir analyses by George A. Shrout, the vpo analyses by James A. Carothers, and the dta analyses by Edward M. Barrall II and J. A. Logan.

Reactions of N,N,N′,N′-Tetramethyl-α,ω-diaminoalkanes with α,ω-Dihaloalkanes. I. 1–y Reactions[1]

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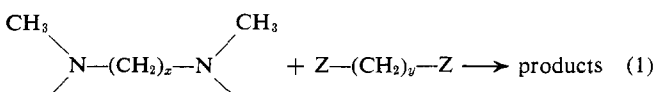
ABSTRACT: The reactions of N,N,N′,N′-tetramethyldiaminomethane with a number of α,ω-dihaloalkanes were investigated in dimethylformamide (DMF), DMF–methanol (1:1 by volume), and acetonitrile. The most important products of these reactions consisted of dimethylaminohaloalkanes, dimethylamine hydrohalides, cyclic and linear mono- and diammonium salts, as well as polyelectrolytes. The course of the reaction was influenced by the solvent. The reaction of tetramethyldiaminomethane with 1,4-dibromobutane yielded unexpectedly in DMF–methanol a linear diammonium compound containing two methoxy groups. A mechanism accounting for the reaction products is proposed and experimental evidence for the isolated compounds is presented.

A detailed study was carried out of the reactions of I with II in which x and y are integers and Z represents a halogen.



$$(CH_3)_2N-(CH_2)_x-N(CH_3)_2 + Z-(CH_2)_y-Z \longrightarrow \text{products} \quad (1)$$

I II

A large variety of products consisting mainly of mono-, di-, and polyammonium salts was obtained, depending on the reaction mechanism. The latter varied not only with the structure of reagents and the values of x and y, but also with the solvent medium. The most significant intermediate species formed during the course of reaction 1 were the dimethylaminohaloalkanes $(CH_3)_2N(CH_2)_yBr$. The chemical behavior of the latter was investigated by Marvel[3-7] and Knorr.[8] The reaction of N,N,N′,N′-tetramethyl-α,ω-diaminoalkanes with α,ω-dihaloalkanes (1) was also studied by Kern,[9] McElvain,[10] and Cadogan.[11]

Because of the considerable general interest in the synthesis of this type of compounds and in particular in the synthesis of polyelectrolytes in which the distances between positive nitrogens can be varied almost at will,[12] we have carried out a systematic study of reaction 1 using various combinations of x and y. In this paper a detailed account of the reaction of tetramethyldiaminomethane with a number of α,ω-dibromo- or diiodoalkanes, *i.e.*, the 1–y reaction, is presented, and some corrections to previously published data[13] are pointed out. The results of x–y reactions leading to low and high molecular weight ammonium compounds ($x \geq 2$) will be described in part II of this work.

Results and Discussion

Synthesis. The present study covers the reactions of tetramethyldiaminomethane with $Br(CH_2)_yBr$ (y = 1–8, 10, and 16) and $I(CH_2)_yI$ (y = 1, 4, and 5) in such solvents as dimethyl-

(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. NAS-7100.

(2) NRC–NASA Resident Research Associate.

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