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Structural Investigations of
Organosilylethylenediamine Polymers

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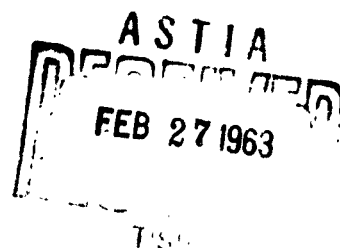
Preface

The work described in this report is a continuation of that outlined in the Technical Report of June, 1962 (Reactions of Methylchlorosilanes and SiCl_4 with N,N'-Bis-(trimethylsilyl) ethylenediamine) and the subsequent publications listed in the bibliography herein. This report has been prepared for publication in the Journal of Inorganic Chemistry.

The Project Director wishes to express to Dr. Dieter Kummer, formerly of the Inorganic Institute of the University of Münster, his appreciation for carrying to fruition many good research projects during his seventeen months' stay in this country. This will be the final ONR report from his pen.

E. G. Rochow

December 21, 1962



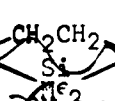
ORGANO SILYLETHYLENEDIAMINE COMPOUNDS III

Structural Investigations on Organosilylethylenediamine Polymers

by

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Abstract


 The polymers which are formed by the reaction of ethylenediamine and dimethyldichlorosilane are investigated by NMR methods. It is shown that these polymers consist of a mixture of linear and cyclic units, ~~of the type~~ $\text{--SiMe}_2\text{NHCH}_2\text{CH}_2\text{NH--}$ and $\text{--SiMe}_2\text{--N--}$  --N-- in a ratio of about 1/2. By heating the polymers to about 300°C ~~or~~ by reaction with Me_3SiCl , polymers of the pure cyclic species are obtained. By reaction with ethylenediamine,  polymers with a higher ratio of the linear component are formed. It is not possible to obtain a pure linear polymer even by reaction with an excess of ethylene diamine.

In the previous paper ^(1a,b) of this series the preparation of a

1. a. D. Kummer and E. G. Rochow, Z. Anorg. allg. Chem. (in press)

b. D. Kummer and J. D. Baldeschwieler, J. Phys. Chem. (in press) Paper II in this series.

number of monomeric organosilylethylenediamine compounds and a detailed investigation of their NMR spectra were described. It was shown that the spectra of these compounds contain a wealth of structural information which

is of particular use in the determination of the structures of more complex molecules of this type. In the present paper these investigations are extended to the polymeric materials which are formed by the reaction of ethylene diamine and dimethyldichlorosilane.

Polymers of this type were obtained for the first time some years ago by R. N. Minné and E. G. Rochow^(2,3) and independently by F. A. Henglein

2) R. Minné and E. G. Rochow, J. Am. Chem. Soc. 82, 5625 (1960)

3) R. Minné and E. G. Rochow, J. Am. Chem. Soc. 82, 5628 (1960)

and K. Lienhard^(4,5), when they investigated the reaction of ethylene diamine

4) F. A. Henglein and K. Lienhard, Makromol. Chem. 32, 218 (1959)

5) K. Lienhard, Dissertation, Technische Hochschule Karlsruhe (1959)

and Me_2SiCl_2 .

Two different polymers were reported. Based on chemical analysis and on the quantities of starting materials and products, the respective formulas were given as $\left[-\text{SiMe}_2\text{NHCH}_2\text{CH}_2\text{NH}- \right]_n^{(2)}$ and $\left[-\text{SiMe}_2\text{NCH}_2\text{CH}_2\text{NSiMe}_2- \right]_n^{(3,4,5)}$

Repetition of the reactions according to the information given in the cited papers^(2, 4) produced two polymeric materials: Polymer I in xylene⁽²⁾ and Polymer II in benzene⁽⁴⁾. Both polymers were slightly yellow viscous oils with molecular weights from ca. 1500 (I) to ca. 2400 (II). Unexpectedly, however, there were no remarkable differences in their chemical composition. The analytical data are shown in Table I together with the values calculated for the pure silylamine and silazane polymers. It is obvious from this table that neither of the pure compositions given above had been obtained. Instead, a

mixture of both must be present in Polymers I and II, the ratio of silylamine/silazane units being nearly equal in the two cases.

Further and more detailed information on the structure of these polymers can be derived from NMR investigations. The proton resonance spectra of the two polymers are very similar; they include three strong sharp peaks at 9.97; 9.91; 9.87 τ , a complex multiplet centered at 7.37 τ , a broadened peak at 7.03 τ and a very broad peak centered at 9.24 τ . The signals at 7.03 and 7.37 τ of Polymer II are shown in Fig. 1. The assignment of these features can easily be achieved by a comparison with the proton resonance spectra of the monomeric silylethylenediamine compounds.^(1a,b) The proton chemical shifts of the two polymers and of two monomeric silylamines which are expected to show the greatest structural similarity to the possible structural units of the polymers are given in Table 2. It is easily recognized that the peaks at 9.97-9.87 τ and can be assigned to SiMe groups, the peak at 9.24 τ to NH protons, the peak at 7.37 τ to CH₂ protons of the linear =NCH₂CH₂N= group, and the peak at 7.03 τ to the CH₂ protons of a five-membered ring system, the 1,3-diaza-2-silacyclopentane group. A series of compounds of this type had been investigated earlier and it was shown that the CH₂ proton resonances of this five-membered ring are characteristically about 0.30 ppm downfield from the CH₂ proton resonances in the linear silylethylenediamine compounds^(1b).

The presence of these five-membered rings as structural units of the polymers also is supported by IR investigations. It has been shown that the IR spectra of the 1,3-diaza-2-silacyclopentanes have a characteristic sharp absorption at 1340 cm⁻¹, which does not appear in the IR spectra of the linear silylethylenediamine.^(1,4,5) The IR spectra of both polymers contain the sharp peak at 1340 cm⁻¹.

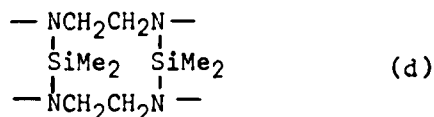
Further structural information can be derived from the CH₂ spectrum at 7.37 τ . In general, three possibilities can be expected for the linear

ethylene diamine group, $\equiv\text{SiNHCH}_2\text{CH}_2\text{NHSi}\equiv$ (a), $(\equiv\text{Si})_2\text{NCH}_2\text{CH}_2\text{NHSi}\equiv$ (b), and $(\equiv\text{Si})_2\text{NCH}_2\text{CH}_2\text{N}(\text{Si}\equiv)_2$ (c). The presence of an ethylene diamine group with a free NH_2 group at one end can be excluded from spectroscopic evidence. (No NH_2 frequencies at $3300\text{--}3400\text{ cm}^{-1}$ and $1540\text{--}1570\text{ cm}^{-1}$ in the IR spectra). A decision between these possibilities easily can be made for Polymer II in favor of group (a). It will, therefore, be discussed first. The CH_2 spectrum of this polymer consists of an asymmetrical "triplet" structure (Fig. 1) of the type which also was observed for the respective resonances of $\text{Me}_3\text{SiNHCH}_2\text{CH}_2\text{NHSiMe}_3$, $\text{RNHCH}_2\text{CH}_2\text{NHR}$, where R is a 1,3-diaza-2-sila-cyclopentane group^(1b), and a number of organic compounds of the type $\text{R}_1\text{NHCH}_2\text{CH}_2\text{NHR}_2$ ($\text{R}_1=\text{R}_2$)⁽⁶⁾.

6) a. G. Dudek and R. H. Holm, J. Am. Chem. Soc. **83**, 2099 (1961)

b. G. Dudek, R. H. Holm and J. D. Baldeschwieler (unpublished results)

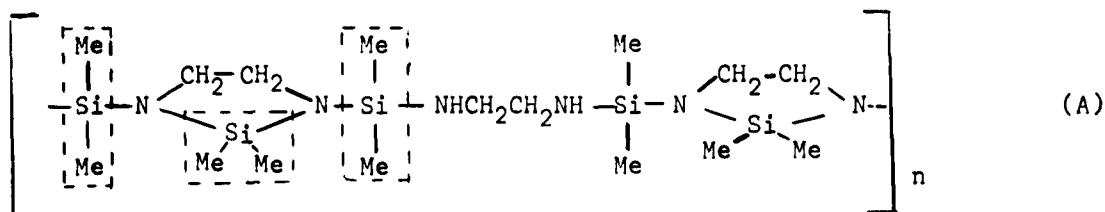
The presence of (b) and (c) groups in the polymer cannot be excluded completely by this argument in view of the broad and not very well resolved spectrum, but since the CH_2 signals of (b) and (c) are very different from that of (a),^(1b) the observation of a pure $\text{RNHCH}_2\text{CH}_2\text{NHR}$ signal indicates that only small amounts (if any) of (b) and (c) could be present. The best argument in favor of (a) and against appreciable amounts of (b), (c) and the cross-linked type



is provided by the relative intensities of the proton signals which will be discussed later.

It is, then, evident that the bulk of Polymer II consists of a framework of $\text{---NHCH}_2\text{CH}_2\text{NH---}$ and $\text{---N} \begin{array}{c} \text{CH}_2\text{---CH}_2\text{---} \\ \diagdown \quad \diagup \\ \text{Si} \\ \diagup \quad \diagdown \\ \text{Me} \quad \text{Me} \end{array} \text{N---}$ groups, which are connected by

$\text{—SiMe}_2\text{—}$ units. The ratio of these two groups in the polymer is given by the relative intensities of the linear and cyclic CH_2 signals, which is 1.00:2.26. Taking these results the approximate building unit of Polymer II can be given according to



This formula is in good agreement with the microanalytical findings. The values calculated for a ratio of 1.00:2.26 are listed in Table I.

Further proof is given by relative intensity arguments. It can be seen from (A) that the ratio of CH_2 protons to SiCH_3 protons in a ring unit is 1:3, while it is 2:3 for the particular linear group proposed in (A). Moreover the $\text{NH}:\text{CH}_2$ proton ratio of this group is 1:2. The relative intensities calculated according to this proposition for Polymer II are compared in Table 3 with the measured relative intensities.

At the same time this method provides the best evidence against appreciable amounts of the linear species (b) and (c), which have a $\text{CH}_2:\text{NH}:\text{SiCH}_3$ proton ratio of 4.1:9 (b) and 1:0.3 (c), respectively. Their presence would be reflected both in decreased NH and increased SiCH_3 signal intensities. In the case of the cross-linked type (d) this would only be true if the CH_2 proton resonance of this ten membered ring system would coincide with that of the linear groups. Unfortunately no compounds of this type and consequently no chemical shifts of such protons are known. By comparison one would suggest, however, that the chemical shift would be in the region of the linear CH_2 resonance rather than in that of the five-membered rings.

The limit for these considerations is set by the accuracy of the determination of relative intensities. For this reason the presence of smaller

amounts of these different groups in the polymers cannot be excluded.

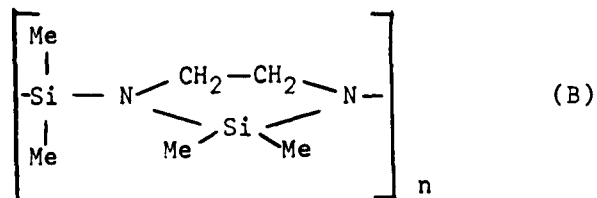
The assignment of the SiCH_3 resonances renders no difficulties. Three chemically unequivalent $-\text{SiMe}_2-$ groups (in dashed lines e, f, g with a proton ratio of 2:2:1) can be recognized in (A). This corresponds to the observation of the three SiCH_3 proton signals which are listed in Table 2. By comparison with the SiCH_3 chemical shifts of the two monomeric compounds of Table 2 the signal at 9.97 τ was assigned to group (e), the signal at 9.91 τ to group (g), and the signal at 9.87 τ to group (f), respectively. The calculated and observed relative intensities are in substantial agreement with this assignment. The assignment of the signal at 9.97 τ to (e) was verified by chemical reactions (see next paragraph).

A similar detailed analysis of the proton resonance spectrum of Polymer I gave the same results. The ratio of chain/ring units in this case was 1.00:1.87. The respective analytical data are given in Tables 1, 2 and 3.

This result indicates that the choice of the solvent and temperature of the reaction has no specific influence on the structure of the polymers formed. This was first expected to explain the different products reported by Minné and Rochow⁽²⁾ and Henglein and Lienhard⁽⁴⁾. Three repetitions of these reactions supported the initial conclusions (Polymers III, IV, V). The NMR spectra of all polymers show the same structure that was discussed for Polymer II, proving a very similar chemical structure. The only variable is the ratio of chain to ring-units, which changes for the different polymers from about 1:1.5 to 1:3 and affects, of course, the intensity distribution of the SiCH_3 proton signals. In no case could a polymer corresponding to a pure linear or a pure cyclic structure be isolated. The NMR data of these polymers are given in Tables 2 and 3, and preparative details in the experimental part.

It is, however, possible to convert the described polymers into pure

cyclic polymers by heating them for several hours to 300-350°C in vacuo. Ethylene diamine is cleaved out of the starting material and isolated in a cooled trap. The polymers change during this process from viscous oils to tacky gums. The internal changes are revealed by the NMR spectrum. The chain CH_2 proton signal of the original polymer disappears as well as the SiCH_3 proton signal at 9.97 τ , leaving the ring CH_2 signal at 7.03 τ , which is slightly broadened, and the two SiCH_3 signals at 9.87 and 9.91 τ . No new signals appear. The relative intensities of the CH_2 signal and the combined SiCH_3 signals are about 1:3, which is the ratio calculated for the pure ring polymer (B) (Table 2, 3)



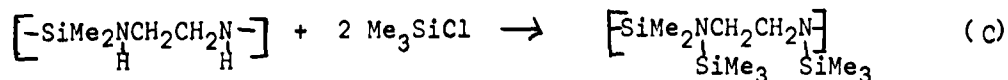
The microanalytical data of this polymer (VI) (Table 1) and the IR spectrum (characteristic ring peak at 1340 cm^{-1} ; no NH peak ^{at} 3400 cm^{-1}) are in full agreement with this formula.

As (B) contains no $\text{—SiMe}_2\text{—}$ groups connecting a ring and a chain unit, the disappearance of the SiCH_3 signal at 9.97 τ is a direct proof that this signal belongs to a $\text{—SiMe}_2\text{—}$ group connected to a chain. Moreover, (B) shows an equal amount of ring $\text{—SiMe}_2\text{—}$ and ring connecting $\text{—SiMe}_2\text{—}$ groups. In accordance with this the two remaining SiCH_3 signals of Polymer VI have almost equal intensity.

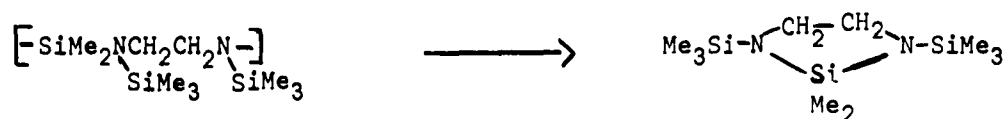
If the polymer is heated to still higher temperatures ($> 400^\circ\text{C}$), decomposition occurs with formation of lower boiling liquids and a dark porous residue. This is true also for the other polymers.

as

A polymer of the same composition^{as} Polymer VII was obtained when Polymer III was reacted with Me_3SiCl in an attempt to replace the hydrogen of the NH groups of this polymer by Me_3Si -groups according to

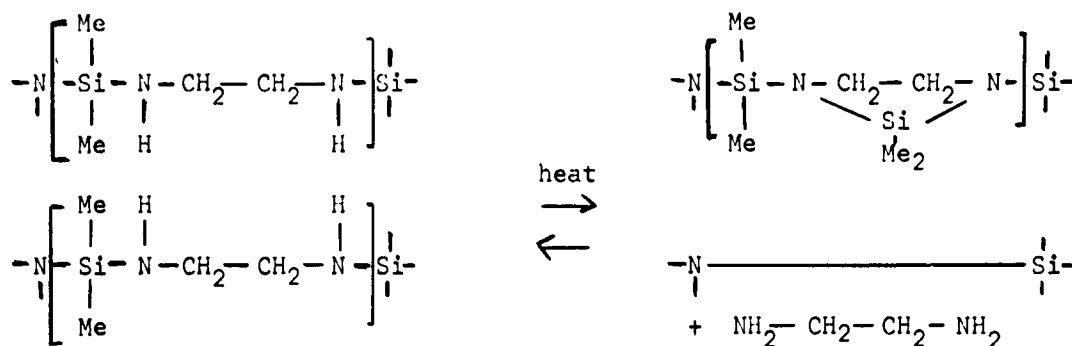


Apparently this reaction occurred in the first step (amine hydrochloride was formed), but in a second step cleavage and cyclisation of (C) took place according to



thus removing all chain units of the original polymer and leaving a pure ring polymer of the composition (B). (When the polymeric reaction product was heated in vacuo to remove low boiling components, a liquid could be isolated which consisted to a large part of 1,3-bis(trimethylsilyl)-2-dimethyl-1,3-diaza 2-silacyclopentane). The NMR spectrum of this polymer (VII), a horny resin, is identical with that of Polymer VI (Analytical data Tables 1,2,3). This result indicates that the monomeric structure of (C) is favored to the polymeric, a fact which is in agreement with the investigation of the reaction of $\text{Me}_3\text{SiNHCH}_2\text{CH}_2\text{NHSiMe}_3$ and Me_2SiCl_2 ^(1a,4,5).

The heat cleavage reaction of ethylene diamine which can be described according to



is reversible. When Polymer III was heated in the presence of ethylene diamine the reaction proceeded in the direction of the lower arrow. When the excess of ethylene diamine was removed at 30-40° in vacuo, products with a maximal ratio of 1 chain to ca. 0.6 ring-units could be obtained (identified by their NMR spectra). These materials are extremely unstable at higher temperatures. Although they contain free ethylene diamine only in small amounts (~5%) at 30-40°C (which can easily be identified in the NMR spectrum) they cleave off ethylene diamine in considerable quantities when one tries to remove the residual free ethylene diamine at temperatures above 40°C. A polymer of this kind which could be obtained completely free of ethylene diamine by heating it for 4 hours to 70° in vacuo, had a chain/ring ratio of 1:1.32 (Polymer VIII, analytical data appear in Tables 2, 3). It was impossible even with a great excess of ethylene diamine to obtain or even identify in the ethylene diamine solution a substance of a pure chain structure. This configuration apparently is very instable and rearranges partially to the cyclic structure, until finally a sufficient amount of the latter species stabilizes the residual linear groups. This evidently is the case when a ratio of about 1:1 is reached and every linear unit is separated of the next linear group by a ring unit. Solvents or ethylenediamine dihydrochloride have no visible effect on the reaction.

TABLE 1

Analytical Data for Organosilylethylenediamine Polymers

	%	C	H	N	MW
Silylamine Polymer					
$[-\text{SiMe}_2\text{NHCH}_2\text{CH}_2\text{NH}-]_n$	Calc.	41.33	10.41	24.10	----
Silazane Polymer					
$[-\text{SiMe}_2\text{NCH}_2\text{CH}_2\text{NSiMe}_2-]_n$	Calc.	41.80	9.36	16.25	----
Polymer I	Found	41.54	9.63	19.03	ca. 1500
	Calc. ^x	41.70	9.71	18.88	
Polymer II	Found	41.51	9.76	18.66	ca. 2400
	Calc. ^x	41.65	9.69	18.77	
Polymer VI	Found	41.22	9.23	16.03	
	Calc.	41.80	9.36	16.25	
Polymer VII	Found	41.19	9.31	15.68	
	Calc.	41.80	9.36	16.25	

x These values are calculated on the basis of the integration ratios of the ring and chain units in the respective polymers (as given by the relative intensities of the CH₂ proton signals in their NMR spectra (Table 3) for mixtures of the pure silylamine and silazane polymers.

TABLE 2

Proton Chemical Shifts of Organosilylethylenediamine Compounds

Compound	Chemical Shifts, ^x τ units $\pm$ 0.02					
	CH ₂ (ring)	CH ₂ (chain)	NH	-SiMe ₂ -	-SiMe ₃	
$\begin{array}{c} \text{Me}_3\text{Si} \quad \text{SiMe}_3 \\ \diagdown \quad \diagup \\ \text{H} \quad \text{NCH}_2\text{CH}_2\text{N} \quad \text{H} \end{array} \quad 1b)$	---	7.38	9.42	---	9.99	
$\begin{array}{c} \text{Me}_3\text{Si}-\text{N}-\text{CH}_2-\text{CH}_2-\text{N}-\text{SiMe}_3 \quad 1b) \\ \quad \quad \quad \diagup \quad \diagdown \\ \quad \quad \quad \text{Si} \\ \quad \quad \quad \diagdown \quad \diagup \\ \quad \quad \quad \text{Me} \quad \text{Me} \end{array}$	7.04	---	---	9.89	9.94	
				g ^{xx}	f ^{xx}	e ^{xx}
Polymer I	7.03	7.37	9.24	9.87	9.91	9.97
Polymer II	7.03	7.37	9.24	9.87	9.91	9.97
Polymer III	7.03	7.37	9.24	9.87	9.91	9.97
Polymer IV	7.03	7.37	9.24	9.87	9.91	9.97
Polymer V	7.03	7.37	?	9.87	9.91	9.97
Polymer VI	7.03	--	--	9.87	9.91	--
Polymer VII	7.03	--	--	9.87	9.91	--
Polymer VIII	7.03	7.37	9.24	9.87	9.91	9.97

x Measured in dilute CCl₄ solution with SiMe₄ as internal standard

xx For explanation see formula (A)

TABLE 3

*
Relative Proton Resonance Intensities of Organosilylethylenediamine Polymers

Polymer	Relative Intensities Signal				
		cyclic CH_2	linear CH_2	NH	SiCH_3
I	Found	1.96	[1.00]	0.54	7.54
	Calc.			0.50	7.39
II	Found	2.13	[1.00]	0.5	7.97
	Calc.			0.50	7.89
III	Found	3.03	[1.00]	0.53	10.23
	Calc.			0.50	10.59
IV	Found	1.79	[1.00]	0.5	7.00
	Calc.			0.50	6.86
V	Found	3.03	[1.00]	?	10.76
	Calc.				10.59
VI	Found	[1.00]	--	--	2.94
	Calc.				3.00
VII	Found	[1.00]	--	--	3.12
	Calc.				3.00
VIII	Found	1.32	[1.00]	0.52	5.49
	Calc.			0.50	5.46

The calculated values were obtained on the assumption that the numbers of protons in the linear group (formula (A)), $\text{CH}_2\text{:NH:SiCH}_3$ stood in the ratio of 2:1:3, and the numbers in the cyclic group stood in the ratio 1:0:3.

* The term "relative intensities" as used throughout this work, and quite generally elsewhere, actually refers to the relative areas of the different signals as obtained by the integrating circuit of the NMR spectrometer.

EXPERIMENTAL

The Preparation of the Polymers. All experiments were carried out in an atmosphere of dry nitrogen.

Polymer I : 17.4 g (0.15 mole) Me_2SiCl_2 were added, with stirring, to 18 g (0.3 mole) of anhydrous ethylene diamine which was diluted with 80 ml xylene, over a 30 minute period. The temperature of the reaction mixture was kept below 30° by means of an ice-bath. After all the chlorosilane had been added, stirring was continued for 10 minutes at room temperature and then the reaction flask was warmed gradually to the reflux temperature of xylene. At about 80° the fine white suspension of amine hydrochloride congealed to a yellowish mass, leaving a pale yellow supernatant liquid. After 50 minutes of reflux the mixture was allowed to cool. The solid material was separated by suction filtration through a medium glass frit, was washed three times with petrol ether, and then was dried. It weighed 23 g. Calcd. for ethylene diamine dihydrochloride 20 g. Anal. Calcd. for $\text{C}_2\text{H}_6\text{N}_2\text{Cl}_2$ N = 21.0; Cl = 53.4 Found: N = 20.73; Cl = 51.74.

The solution was freed from xylene at reduced pressure (1 mm) at room temperature. To remove the last traces of xylene the residue was then heated to $70-100^\circ$ for 2 hours at 1 mm. The xylene which was distilled from the residue during this time contained no ethylene diamine. Yield: 12 g. of a very viscous oil.

Polymers III and IV were prepared in the same way as Polymer I with one exception: The dimethyl dichlorosilane was diluted in both cases with xylene in the ratio of 1:1. The polymers obtained were very viscous oils.

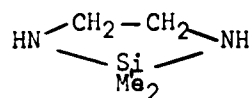
Polymer II: 19.4 g (0.15 mole) Me_2SiCl_2 were added dropwise, with stirring, to 18 g (0.3 mole) of anhydrous ethylene diamine which was diluted with 30 ml of benzene over a 30 minute period. The temperature of the reaction mixture was kept below 30° by means of an ice-bath. After all chlorosilane had been added, stirring was continued for three hours at room temperature. The solid material was separated by suction filtration and was washed six times with petrolether. Twenty-two g of slightly impure ethylene diamine dihydrochloride were obtained. (Calcd. 20 g)

Anal. Calcd. for $\text{C}_2\text{H}_6\text{N}_2\text{Cl}_2$: N = 21.0; C = 53.4
Found N = 20.68; Cl = 51.63

The bulk of the benzene was distilled from the colorless solution at normal pressure, the last traces were removed by heating the residue at 1 mm to ca. 180°C for 4 hours. No ethylene diamine was found in the volatile substance (benzene). Eleven g of a very viscous oil were obtained.

Polymer V: 6 g. (0.1 mole) of anhydrous ethylene diamine, 19.4 g (0.1 mole) of $\text{Me}_2\text{Si}(\text{NEt}_2)_2$ and mesitylene (60 ml) were refluxed for two hours. Then the mixture was distilled to remove the lower-boiling reaction products (Et_2NH and unreacted ethylene diamine) and the solvent. The soft waxy polymeric residue (10 g) was freed of the last traces of mesitylene by heating for two hours to 100° in vacuo.

The difference between the composition of this polymer and ^{that of} the polymer which was obtained by Henglein and Lienhard^(4,5) by essentially the same reaction must be due to the fact that contrary to the original description^(4,5) a solvent was used in this case. The higher reaction temperature which is finally reached without solvent favors the formation of the pure ring polymer as it is also shown by our experiment (see Polymer VI). The solvent had been added in this experiment to see whether the monomeric compound



could be obtained by this method (dilution principle). However, not even traces of this compound could be detected in the distillate (as indicated by the NMR spectrum).

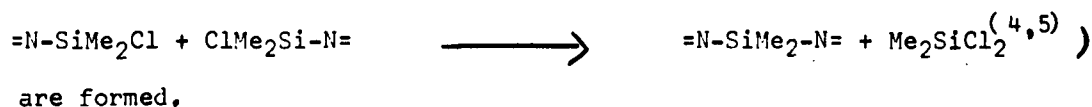
Polymer VI: 14 g of Polymer III were heated to 370°C for 5 hours at 1 mm.; 0.6 g. of ethylene diamine (identified by its NMR spectrum) with minor unidentified impurities was isolated in a trap cooled with liquid nitrogen. Two g of oligomers were distilled over at 300-320° C/1 mm. The residue (10.4 g) was a brown viscous resin (Polymer VI), insoluble in benzene as such, but the heat softened or melted resin was soluble in benzene.

Polymer VII: 39 g. of Polymer III were dissolved in 300 ml of diethyl ether. An excess of Me₃SiCl (50 g) was added. The solution was warmed to the reflux temperature of ether. A fine white suspension appeared.

After twelve hours the reaction mixture was allowed to cool. The white precipitate (ca. 3 g) was removed by suction filtration. The yellow solution was freed of ether and excess Me_3SiCl at reduced pressure at 30°C and was distilled. Four g of a liquid (b.p. $146-148^\circ/65\text{ mm}$) were isolated, consisting mainly of 1,3-bis(trimethylsilyl)-2,2'-dimethyl-1,3-diaza-2-silacyclopentane (b.p. $470/1\text{mm}^{(1a)}$) (identified by its NMR spectrum). The residue was then heated in vacuo (1 mm) to ca. 320°C for 6 hours. During this period 2 g. of methylchlorosilanes (isolated in a trap cooled with liquid nitrogen) and 2 g of a soft waxy material, which condensed on the cooler parts of the reaction flask, were removed from the residue. The formation of the methylchlorosilanes is explained by the presence of terminal =SiCl groups in the original reaction product. The groups are formed by a cleavage reaction of Me_3SiCl with Polymer III according to



At higher temperatures this reaction is reversed and Me_3SiCl and Me_2SiCl_2 (according to



The residue (28 g) was a brown horny resin which was insoluble in benzene as such, but the heat-softened or melted resin was soluble in benzene.

The Reactions of Polymer III and Ethylene Diamine: Polymer III has a ring/chain unit ratio of ca. 3:1 (Table 3). A molecular unit of three rings and one linear ethylene diamine group has a molecular weight of 632. To convert this unit into a pure linear configuration, three ethylene diamine units are needed for each such polymeric unit. According to this calculation 14.5 g of Polymer III were allowed to react with 4 g of ethylene

diamine. The reaction mixture was heated under reflux for two hours. An NMR spectrum showed a large amount of unreacted ethylene diamine. The mixture was refluxed for another period of four hours. There were still large amounts of free ethylene diamine present, which were finally condensed from the reaction mixture into a trap cooled with liquid nitrogen (at 1 mm, 25°C). The last traces of ethylene diamine could only be removed by heating the reaction flask to 70° for 4 hours. The chain/ring ratio of the polymer changed from 1.00:0.70 to 1.00:1.32 during this process (checked by NMR spectra before and after the heating). The polymer was then free of ethylene diamine; a total of 3.4 g of ethylene diamine had been recovered from the reaction mixture. (VIII) was a clear yellow viscous liquid. After it had stood for several weeks, a white precipitate was formed which was not investigated.

The reaction of Polymer III and ethylene diamine was repeated with the following variations: a) Use of a great excess of ethylene diamine (compared with the quantity used in the first experiment), b) Different reaction times, ranging from 2-24 hours, c) Use of xylene as a solvent, d) Reflux of the reaction mixture in the presence of ethylene diamine dihydrochloride.

The products of these reactions were identified by their NMR spectra. The spectra were analysed for the ratio of ring and linear polymer units and the presence of free ethylene diamine (which is easily recognized by the sharp resonance signal of the CH₂ protons at 7.45 τ .) The results are discussed in the general part.

The NMR spectra were obtained with a Varian A-60 high resolution NMR spectrometer, the IR spectra with a Perkin-Elmer IR spectrophotometer 21. The analytical determinations were done by Schwarzkopf

Microanalytical Laboratories, Woodside, New York. Molecular weights were determined cryoscopically in benzene.

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Fig. 1 CH_2 proton resonance of Polymer I at 60 Mc in dilute CCl_4 solution. The sharp resonance signal of the ring CH_2 protons is incompletely shown because the instrument was adjusted for maximum clarity of the chain CH_2 proton response.

