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PROTON MAGNETIC RESONANCE SPECTRUM OF POLYSILAZANE OBTAINED BY TRANSAMINATION OF HEXAMETHYLCYCLOTRISILAZANE WITH ETHYLENEDIAMINE

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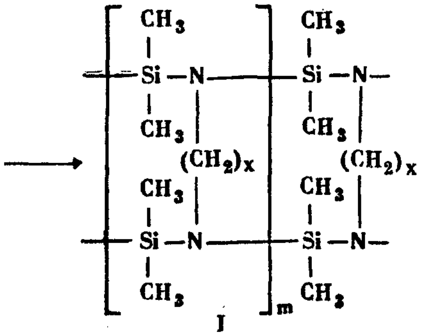
The PMR spectrum of the product of reaction of hexamethylcyclotrisilizane with ethylenediamine is investigated, and shows that both linear-ladder and linear polysilazane can arise from the transamination reaction.

It was previously shown [1] that reaction of polyalkylcyclosilazanes and aliphatic diamines leads to ring scission involving splitting out of ammonia and formation of polyalkylsilazanes containing a tertiary nitrogen atom. A mechanism for reaction of diamine and cyclosilazane was put forward, involving formation of a polymer consisting of silazane chains crosslinked with polymethylene bridges:

$$\cdot n\left[(CH_3)_2SiNH\right]_3 + 1.5nH_2N(CH_2)_xNH_2 \longrightarrow$$



I

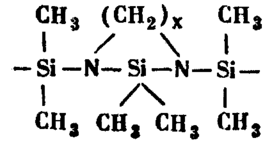
$m=8-10;$

$x=2-6.$

However, the structure put forward for the polymer has remained unproven.

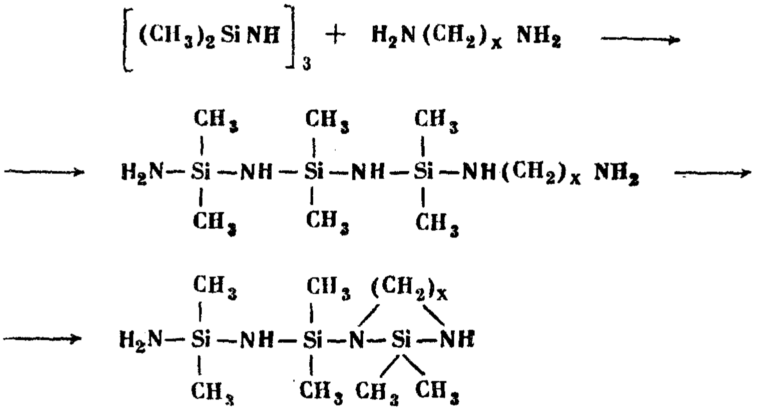
A similar linear-ladder structure is also ascribed to polymers based on dimethyldichlorosilane and diamine, coordinated with cupric chloride [2], whose structure has not been studied either.

At the same time polymers have been prepared with a basic silazane chain where neighboring nitrogen atoms are joined by polymethylene bridges [3, 4]. The structure of such polymers has been investigated by IR spectroscopic methods.



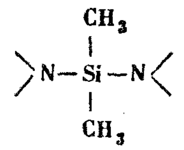
II

Using as the starting point the possibility of formation of a polyalkylsilazane of structure I or II, according to the equations below, when hexamethylcyclotrisilazane reacts with an aliphatic diamine:

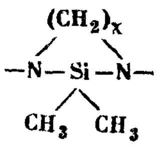


an attempt has been made to determine by proton magnetic resonance the structure of the polymer formed by transamination.

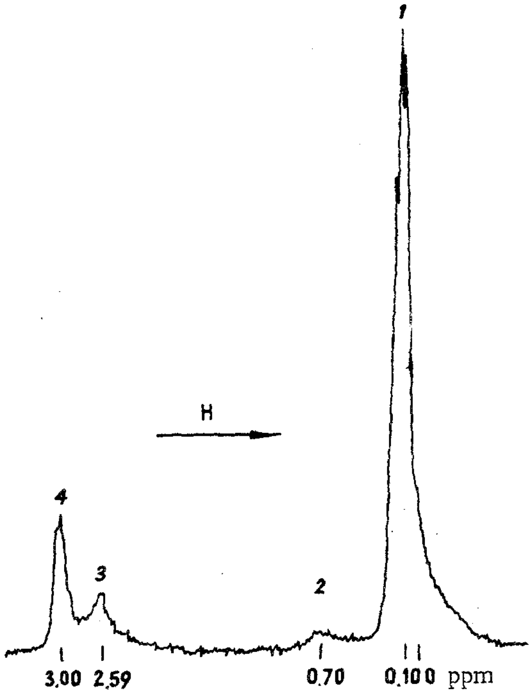
It would be expected that the protons of all the methyl groups in polyalkylsilazanes of linear-stair structure I would be equivalent. So the PMR spectrum of such a structure should consist of a resonance line of the protons of the methyl group, and another line for the protons of the polymethylene bridges. Polyalkylsilazanes with the linear structure II would be expected to have two kinds of methyl group protons:



and



So the PMR spectrum given by such a structure should consist of two resonance lines, of identical intensity of the protons of the methyl groups, and a line of the protons of the polymethylene bridges.



PMR spectrum of polysilazane prepared by transamination of hexamethylcyclosilazane with ethylenediamine.

The specimen of polysilazane was prepared from hexamethylcyclotrisilazane and ethylenediamine by the method described in [1].

The PMR spectrum of the polysilazane dissolved in carbon tetrachloride (volume ratio 1:2), was observed with a J–N–M–3 magnetic spectrometer using a resonance frequency of 40 Mcps (see figure). Chemical shifts were measured in parts per million (ppm) with respect to tetramethylsilane, which served as an internal standard. The accuracy was 0.05 ppm.

The incomplete resolution of the triplet (I) at 0.1 ppm indicates that the polymer contains three types of methyl group protons. Starting from the fact that only structures I and II can exist, the presence of three types of Me groups indicates possible formation of both forms. In view of the diminished mobility of the ethylene bridge in structure II, it is to be expected that the resonance line of the protons of the ethylene bridge in that structure will be wider than the corresponding resonance line of structure I. On the basis of this assumption, the broader line (3) can be ascribed to protons of the ethylene bridge in structure II, and line (4) to the protons of the ethylene bridge in structure I. From a comparison of the intensities of these lines it can be concluded that polymers of structures I and II are present in about equal amounts. Obviously, the broad weak line (2) at 0.7 ppm can be assigned to unsubstituted hydrogen atoms on nitrogen. The ratio of the sum of the intensities of lines (3) and (4) to the total intensity of the triplet (1) is nearly 1/3, corresponding to the ratio of the number of protons in the ethylene bridges of structures I and II, to the number of protons in the methyl groups. This can be regarded as an additional indication in favor of the postulated interpretation of the PMR spectrum of the product of reaction of hexamethylcyclotrisilazane with ethylenediamine.

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