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THERMAL DECOMPOSITION OF CYCLO-LINEAR METHYLSILOXANE POLYMERS

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Summary

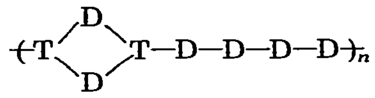
The pyrolysis products from two cyclo-linear methylsiloxane polymers have been analysed, and formation of the important products interpreted in terms of a simple decomposition mechanism. This mechanism is very similar to that of the polydimethylsiloxane degradation; thus cyclic oligomers are formed from the linear segments, and polycyclic compounds from the cyclic segments of the cyclolinear methylsiloxane polymers.

Introduction

Thermal decompositions of branched chain methylsiloxane polymers have been studied previously [1,2]. Methylsiloxane cycles and polycycles have been found as volatile products of the methylsiloxane resin pyrolysis [1—5]. The results indicate that the decomposition of the methylsiloxane resins under pyrolysis is similar to that observed with methylsiloxane chain polymers [6]. A relation between the polymer structure and the thermal degradation products can be interpreted in terms of this decomposition mechanism, but a resin of irregular stucture does not provide a proper system for studying this relation.

We describe below our examination of the thermal decomposition products of two methylsiloxane polymers of strictly regular and known structure, carried out in order to clarify the relations mentioned. The polymers investigated include di- and tri-functional structural units (i.e. $(CH_3)_2SiO_{2/2}$ denoted by —D— and $CH_3SiO_{3/2}$ denoted by $-T\!<$) and involve cyclo-linear chain structures, as follows:

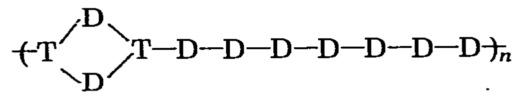
$(T_2D_6)_n$:



$$-\!\!\left(T\!\begin{smallmatrix}D\\ \\ D\end{smallmatrix}\!T-D-D-D-D\right)\!\!-_n$$

and

$(T_2D_9)_n$:



$$-\!\!\left(T\!\begin{smallmatrix}D\\ \\ D\end{smallmatrix}\!T-D-D-D-D-D-D-D\right)\!\!-_n$$

These structures are ensured by the method of synthesis used (see Experimental).

Results

The thermal decomposition of the investigated cyclo-linear methylsiloxane polymers at 350° C leads to cyclic methylsiloxane oligomers. The polymer $(T_2D_6)_n$ decomposes mainly to D_3, and polymer $(T_2D_9)_n$ to D_3, D_4, D_5 etc., like poly(dimethylsiloxane) does, but degree of the conversion is very low at this temperature. At higher temperatures several polycyclic compounds are also produced from both polymers. The relative amounts of products from pyrolysis at 550°C as given by GLC, are shown in Fig. 1. The gas chromatographic peak areas are related to the peak area of the most abundant product. Between 450—600° C the product distribution does not change significantly with the pyrolysis time nor with the pyrolysis temperature. We have identified ten of the fifteen main products by comparison of the gas chromatographic retention times with those of pure standard substances on three different GC stationary phases. The polycyclic siloxane standards were obtained from methylsiloxane resin by pyrolysis followed by preparative gas chromatography.

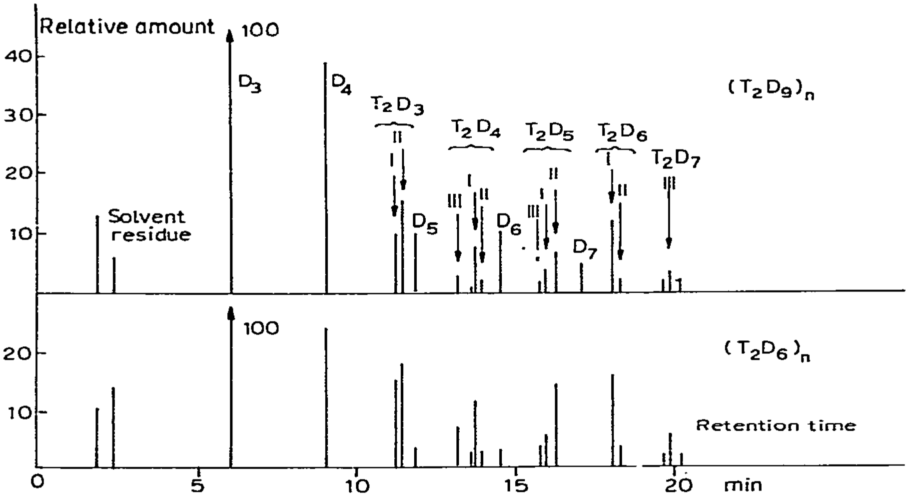


Fig. 1. Pyrolysis products from cyclo-linear methylsiloxane polymers separated on OV-1 gas chromatographic phase.

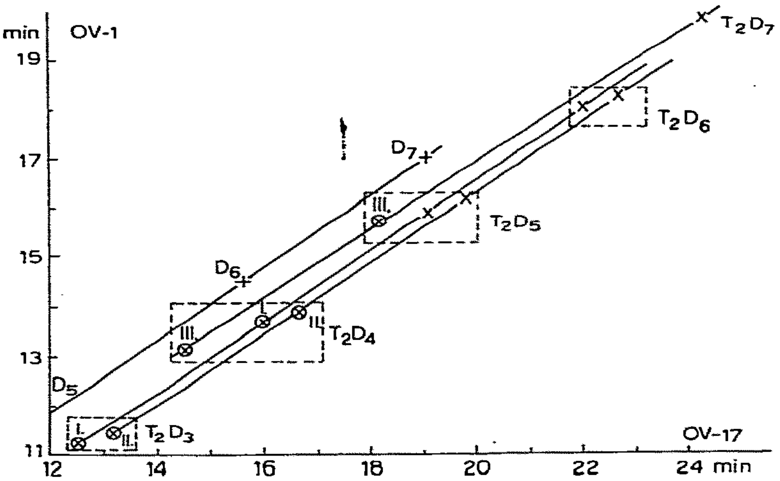


Fig. 2. A plot of retention time against retention time for the pyrolysis products on temperature programmed columns coated with OV-1 and OV-17 phase, respectively.

Their identities were confirmed by MS, ^{29}Si NMR spectroscopy and X-ray diffraction [2—5]. Standards are not available for some important products, but these seem to be homologous with the products identified. This is indicated by the straight lines which join the points given by the retention time values of the products measured on two different stationary phases with a linear temperature program (Fig. 2 and 3). The identified products are represented by circled points in the figures.

On examining the structures and amounts of the pyrolysis products we can see some correlation between the polymer structure and the pyrolysis products.

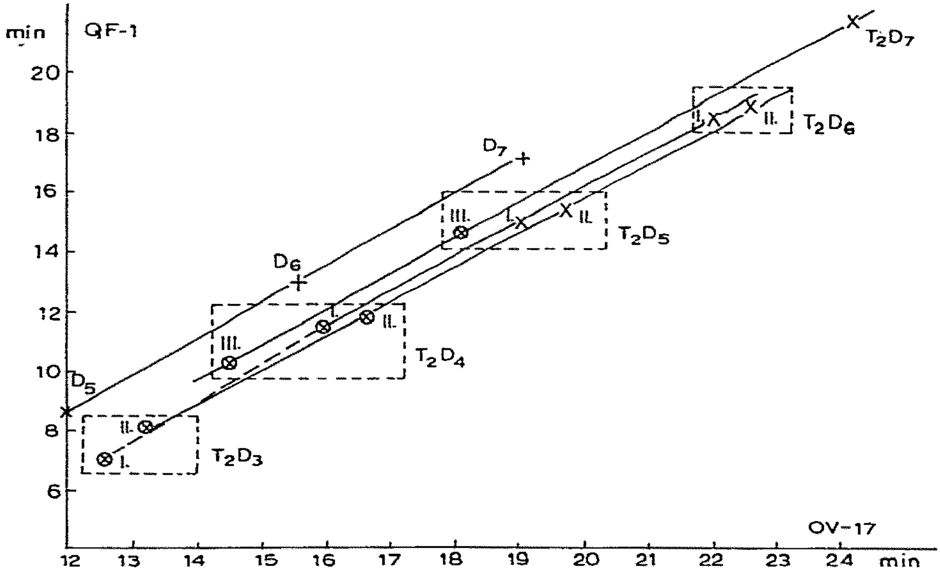
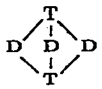
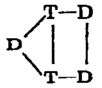
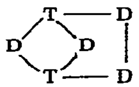
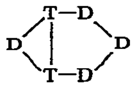
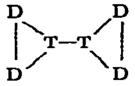
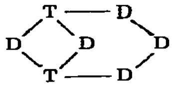
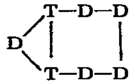
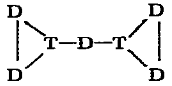
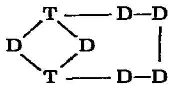
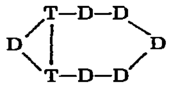
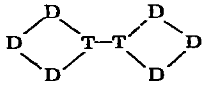
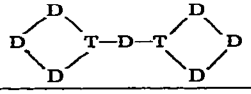


Fig. 3. A plot of retention time against retention time for the pyrolysis products on temperature programmed columns coated with QF-1 and OV-17 phase, respectively.

TABLE 1

HOMOLOGOUS SERIES OF PYROLYSIS PRODUCTS OF CYCLO-LINEAR METHYLSILOXANE POLYMERS

Composition	Series I	Series II	Series III
T_2D_3			
T_2D_4			
T_2D_5			
T_2D_6			
T_2D_7			

The pyrolysis products are either cyclic or bicyclic methylsiloxanes ranging from 3 to 9 siloxane units. In the pyrolysate of polymer $(T_2D_9)_n$ there is a larger amount of cyclic products than in that of $(T_2D_6)_n$. The relative amounts of the cyclic products D_3, D_4 and D_5 in the pyrogram of $(T_2D_9)_n$ are similar to that found in the pyrogram of poly(dimethylsiloxane), but a smaller amount of D_4 and D_5 was found from $(T_2D_6)_n$.

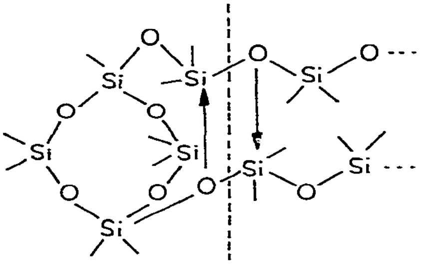
All the important pyrolysis products belong to a homologous series of siloxane units (see Fig. 2 and 3). Three such series have been found for the bicycles shown in Table 1. None of the products include more than two T units.

Quantitative evaluation of the total amounts of T and D units found in the pyrolysate gives a T/D ratio corresponding with that in the original polymer. For the conversion of peak area values into weights we used published [7] response factors for the Flame Ionization Detector.

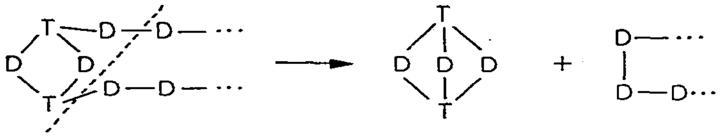
Discussion

The structures of the volatile degradation products show that all of these molecules were split off from the cyclo-linear polymer by the mechanism first suggested by Thomas [6] for poly(dimethylsiloxane). In this mechanism, degradation starts with the formation of an intermediate four centered complex, then the two siloxane bonds involved rearrange. The resulting volatile product is an oligomer cycle in the case of the poly(dimethylsiloxane) chain. Similarly D_3, D_4, D_5 cyclic oligomers are split off from the linear part of the investigated cyclo-linear methylsiloxanes.

When siloxane bond rearrangement takes place between two linear segments bonded to the same cycle of the polymer, a bicycle of the Series I can split off as follows:

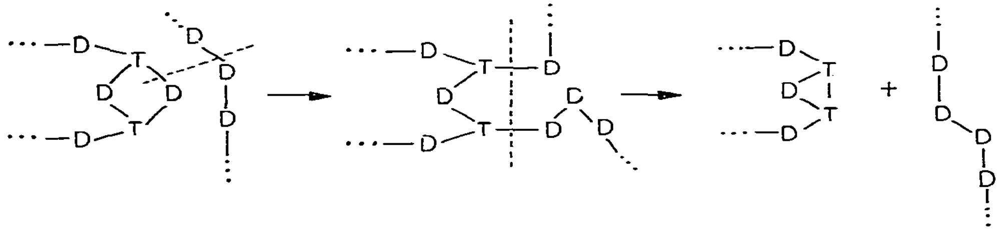


With T and D symbols:



(1)

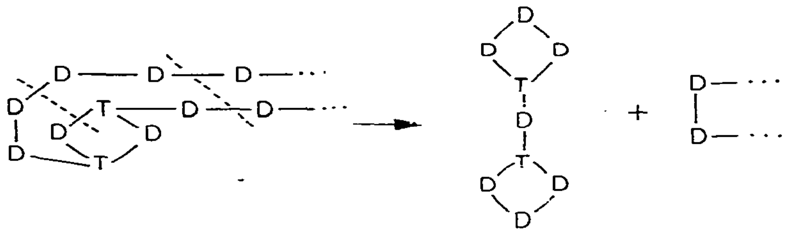
Bicycles of Series II may form similarly, but the macromolecular segment in which the siloxane bond rearrangement is taking place has to include a three membered siloxane cycle ($\cdots\!-\!\mathrm{T}\underset{\mathrm{D}}{\diagdown\;-\;\diagup}\mathrm{T}\!-\!\cdots$). This modified molecular segment may result from such an inter- or intramolecular rearrangement, as follows:



(2)

Consequently Series II products are assumed to be the products of three consecutive rearrangement steps.

Distinct bicycles were also found among the pyrolysis products. Their formation can be described in terms of bond rearrangement between the linear part and the adjacent cycle of the polymer, as follows:



(3)

In reaction 3 the two cleavages have to occur simultaneously. The absence of products with more than two T units indicates, that no secondary reactions of the primary products takes place.

Under the pyrolysis conditions we used the stoichiometric composition of the total pyrolyzate is similar to that of the polymer. In addition, no change in functionality of siloxane units takes place, confirming our earlier result [2].

Accordingly, the structure of the degradation products is closely connected with the macromolecular structure. The original linear segments of the macromolecule appear in the pyrolyzate as cyclic oligomers, and the branching points come away with the adjacent fragments as polycycles. The ratio of the amounts of monocyclic and bicyclic products characterizes the average frequency of the branching points in the polymer network. The exact description of the structures of the bicyclic products may help to get to know the distribution of the branching points, and thus the microstructure of methylsiloxanes.

Experimental

Synthesis of $(T_2D_6)_n$ polymer. 1.64 g (0.5 mmol) 1,5-dichlorohexamethylcyclo-tetrasiloxane in 0.7 ml of benzene was introduced into the reaction vessel. 1.57 g (0.5 mmol) 1,7-dioxyoctamethyltetrasiloxane and 0.79 g (1 mmol) pyridine in 1.2 ml of benzene was added gradually, at 20—22° C, dropwise by stirring. After lengthy stirring, 10 ml benzene was poured into the vessel. The precipitated pyridine hydrochloride was filtered off and the solution was repeatedly washed with water, then dried over Na_2SO_4. Benzene was removed under vacuum. 1.84 g polymer was obtained, $[\eta] = 0.15$. Anal. Found: C, 29.16; H, 7.39; Si, 39.21. $C_{14}H_{42}Si_8O_9$ calcd.: C, 29.04; H, 7.28; Si, 38.81%.

$(T_2D_9)_n$ polymer was synthesized analogously.

Synthesis of 1,5-dichlorohexamethyl-cyclo-tetrasiloxane. 100 ml of anhydrous diethyl ether was introduced into the reaction vessel. A solution of 21.6 g (0.068 mol) 1,1,5.5-tetrachloro-1,3,3,5-tetramethylsiloxane (prepared according to ref. [8]) in 200 ml of diethyl ether as well as the solution of 6.26 g (0.068 mol) dimethylsilanediol (prepared from $(CH_3)_2SiCl_2$ as in ref. [9]) and 12.64 g (0.136 mol) pyridine in 200 ml of diethyl ether was slowly added dropwise, the mixture being kept at room temperature. The precipitated pyridine hydrochloride was filtered off and the solvent was removed by distillation. The residue was distilled to give 6.1 g (26.7%) of 1,5-dichlorohexamethylcyclo-tetrasiloxane (b.p. 201—203° C/760 mmHg). Anal. Found. C, 22.42; H, 5.69; Cl, 20.09; Si, 33.70. $C_6H_{18}Cl_2O_4Si_4$ calcd.: C, 21.34; H, 5.33; Cl, 21.02; Si, 33.31%.

Pyrolysis. Thermal degradation of the polymers was carried out at 300—600° C in argon in a ribbon type pyrolyser constructed in our laboratory, and described previously [10]. The sample weights were about 0.1 mg, and the pyrolysis times ranged from 30 s to 3 min.

For the GC analysis the pyrolyser was coupled with a Perkin—Elmer 900 gas chromatograph equipped with a flame ionization detector. The peak areas of the separated pyrolysis products were measured on a Perkin—Elmer D-26 electronic integrator. Three packed gas chromatographic colums were used: 3.5 m, 2 mm ID column; support: 80—100 mesh Chromosorb G, phase: 5% OV-1; temperature program: from 40° C to 280° C at 10° C/min.

3 m, 2 mm ID column; support: 80—100 mesh Chromosorb G, phase: 3% QF-1; temperature program from 40° C to 220° C at 5° C/min.

2.5 m, 2 mm ID column; support 80—100 mesh Chromosorb G; phase: 5% OV-17; temperature program from 40° C to 280° C at 6.5° C/min.

Identification of pyrolysis products was based on the identities of the retention times for the unknown and pure authentic materials on the three columns coated with different stationary phases.

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