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PYROLYSIS GAS CHROMATOGRAPHY OF BRANCHED-CHAIN METHYLSILOXANE POLYMERS

GABRIELLA GARZO AND KJELL PEHRSSON

Research Group for Inorganic Chemistry of the Hungarian Academy of Sciences, Budapest (Hungary)

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SUMMARY

The catalyzed and non-catalyzed thermal degradation of a branched-chain methyl siloxane polymer system has been investigated by pyrolysis gas chromatography measurements using the pyrolysis unit described in a previous paper.

The effects of the catalysts KOH, DMSO and KOH+DMSO, in addition to that of the pyrolysis time, upon the nature and distribution of the products has been examined.

The pyrolysis products have been identified and it has been shown that during the course of thermal treatment slow processes occur in the presence of DMSO. For this reason, the mechanism of thermal degradation in the presence of DMSO is different from that of the non-catalyzed and KOH-catalyzed pyrolysis. The slow processes mentioned above are most probably related to the migration of the CH_3 groups along the Si–O–Si skeleton.

INTRODUCTION

In the assessment of the thermal properties of polymers, and in the investigation of their molecular structure, the study of the pyrolysis of polymers has been of major importance. An essential part of most pyrolysis experiments is the analysis of the reaction products, an analysis which may now be performed most rapidly and conveniently by gas chromatography. Combination of pyrolysis and gas chromatography (PGC) has proved to be a valuable tool in the study of various kinds of pyrolyses, and many types of polymers have been characterized and identified on the basis of their PGC curves. Studies of the degradation kinetics and mechanisms of polymer pyrolysis utilizing PGC have been reported with increasing frequency recently[1-4].

Few such studies have been undertaken with organic siloxanes, more specifically with methylsiloxane polymers[5-9], although the thermal degradation of these polymer systems appears to possess certain favourable features in comparison with organic polymers. For this reason the use of PGC studies should be particularly well suited for drawing conclusions regarding the degradation mechanisms of these polymers and about the structure of the original polymer. The degradation of methylsiloxanes is generally slower—and therefore more easily studied—than that of most organic polymers, and in addition the silicon–carbon bond is not usually cleaved during the thermal process. Furthermore the pyrograms arising from PGC studies of these polymers are characterized by their fine detail. This is due to the high thermal stability of the different methylsiloxane molecules containing 3–8 silicon atoms, and this results in a great number of characteristic features being exhibited by the pyrograms which may be directly related to the fine structure of the polymer.

Methylpolysiloxane systems have been the subject of investigations for quite some time in this laboratory. In an earlier paper[9] we have dealt with the identification of the major components in the pyrogram of a branched-chain methylpolysiloxane system, a polymer similar to that discussed in the present paper. Peak identification was achieved by the technique of peak coincidence with the aid of standard samples. These standard samples were isolated from the macro-pyrolysate of the polymer in question and identified by mass-spectrometry. The results of peak identification for a characteristic pyrogram are shown in Fig. 1 and in Table 1. The serial numbers of the pyrogram peaks and of the listed compounds are identical. In addition to the cyclic compounds*, D_5, D_6 and D_7, about 15 further volatile methylsiloxane compounds appear in various proportions on the pyrograms. The results show that there are a number of compounds with isomeric structures among the pyrolysis products. Direct evidence concerning the structures of the isomers is not as yet available, although indirect structural evidence is being collected from gas-chromatographic data. On the basis of electron diffraction data calculations for certain structures are also in progress in order to elucidate the molecular structure of the degra-

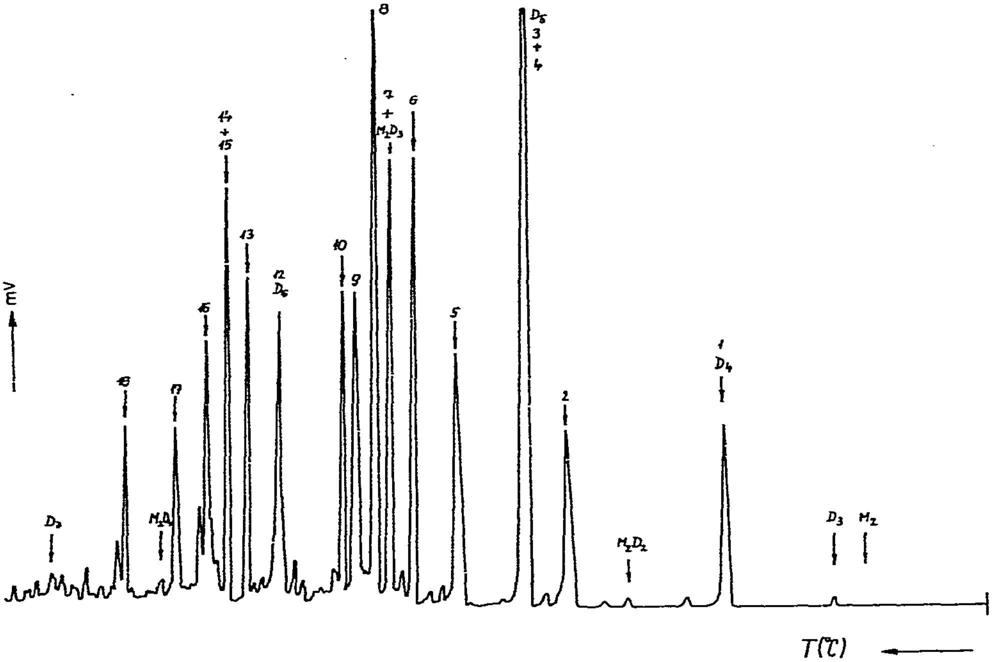

Fig. 1. Pyrogram of the branched-chain methylpolysiloxane investigated using an APL coated capillary column, 50 m; temperature program from 60 to 250° at a rate of 3.5°/min.

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* $D=(CH_3)_2SiO$.

dation products. (For the meaning of the numbers appearing in the last two columns of Table 1 the reader is referred to the paper quoted[9].)

The present paper presents a summary of our observations during PGC investigations of the non-catalyzed and catalyzed thermal degradation of a branched-chain methylsiloxane polymer composed exclusively of T and D structural units. The following abbreviations for structural units are used throughout this paper: $M=(CH_3)_3SiO_{0.5}$, $D=(CH_3)_2SiO$, $T=CH_3SiO_{1.5}$, $Q=SiO_2$. Thus, $M_2=[(CH_3)_3Si]_2O$ = hexamethyldisiloxane.

TABLE 1

MOLECULAR FORMULAE AND CHARACTERISTICS OF THE PYROLYSIS PRODUCTS

No. of peak	Mol. wt.	Molecular formula	Retention index SE-30; 125°	Symbol of compound[a]	Number of isomeric T-D molecules[b]	Number of isomers[c]
2	356	$Si_5O_6C_8H_{24}$	1124	T_2D_3	2	6
4	356	$Si_5O_6C_8H_{24}$	1138	T_2D_3	2	6
3		$Si_5O_5C_{10}H_{30}$	1160	D_5		
5	416	$Si_6O_8C_8H_{24}$	1212.5	T_4D_2	4(5)	8
7	416	$Si_6O_8C_8H_{24}$	1246.5	T_4D_2	4(5)	8
6	430	$Si_6O_7C_{10}H_{30}$	1254	T_2D_4	4	8
8	430	$Si_6O_7C_{10}H_{30}$	1285	T_2D_4	4	8
10	430	$Si_6O_7C_{10}H_{30}$	1293	T_2D_4		
12		$Si_6O_6C_{12}H_{36}$	1350	D_6		
13	476	$Si_7O_{10}C_8H_{24}$	1359	T_6D	2	9
11	490	$Si_7O_9C_{10}H_{30}$	1363	T_4D_3		
14	490	$Si_7O_9C_{10}H_{30}$	1393	T_4D_3	10	10
15	490	$Si_7O_9C_{10}H_{30}$	1395.5	T_4D_3		
16	504	$Si_7O_8C_{12}H_{36}$	1416	T_2D_5		
17	504	$Si_7O_8C_{12}H_{36}$	1437	T_2D_5		
		$Si_6O_5C_{14}H_{42}$	1442.5	M_2D_4		
18	504	$Si_7O_8C_{12}H_{36}$	1464.5	T_2D_5	6	10
	550	$Si_8O_{11}C_{10}H_{30}$		T_6D_2	9	12
		$Si_7O_7C_{14}H_{42}$	1510	D_7		

[a] Assuming T and D structural units only. [b] With different ring combination. [c] With different combinations of Q, M, T and D units.

The processes occurring during non-catalyzed thermal degradation are compared to those occurring under identical conditions, but in the presence of KOH, dimethyl sulphoxide (DMSO), and KOH+DMSO as catalysts.

EXPERIMENTAL

A branched-chain polymer system prepared by the cohydrolysis of CH_3SiCl_3 and $(CH_3)_2SiCl_2$[10] was used. The polymeric product so obtained still contained considerable amounts of reactive OH groups and was soluble in various organic solvents. The elementary composition of the polymer was found to be: C, 18.9; H, 5.6; Si, 41.8%; C/Si ratio R, 1.1. In addition to the original polymer the following catalyst-containing samples were investigated: Polymer containing 0.2 w/v % KOH;

Polymer containing 5 w/v% DMSO; Polymer containing 0.2 w/v% KOH + 1 w/v% DMSO. KOH was added to the tert-butanol solution of the polymer while DMSO was added to a toluene solution. The solvents were subsequently removed by evaporation in vacuum below 100°.

Micro-pyrolysis was performed in the pyrolysis unit described in our previous paper[9]. All micro-pyrolyses were carried out by prolonged heating of the polymer sample (0.5–1 mg) in the closed chamber of the pyrolysis unit in an inert atmosphere, followed by flushing of the gaseous pyrolysis products into the column inlet by means of a stream of carrier gas. The separation column was an APL coated capillary 50 m in length, whose temperature was raised by a linear temperature program from 60 to 250° at the rate of 3.5°/min.

Nitrogen was used as the carrier gas with an inlet pressure of 1.8 kg/cm^2, flow rate 2 ml/min. A splitting ratio 150/1 was used before the column inlet. The gas chromotagraph was a Carlo Erba Fractovap Model C type CID/ff dual FID instrument.

In preliminary experiments a 3.5 m × 2 mm column was used packed with 10% SE-30 coated 80–100 mesh DMCS treated Chromosorb W. The temperature of the column was increased by means of the program at the rate of 5°/min.

For samples containing catalyst the identification of the peaks was based on a micro-pyrogram and was performed with the aid of standards using the peak coincidence technique. To show the presence of M_2 and tetramethylsilane a macro-pyrolysate, made from the polymer, was used. Mass-spectrometric identification of the corresponding peak in the preparative GC fraction of the macro-pyrolysate was employed to prove the formation of M_2. The presence of tetramethylsilane was also shown in the macro-pyrolysate by means of standard samples.

RESULTS AND DISCUSSION

Figures 2, 3 and 4 show pyrograms taken on packed columns containing SE-30 as the liquid phase. The results indicate that differences exist between the chemical processes involved in the pyrolyses of the catalyzed and the simple non-catalyzed polymer. It is immediately obvious that the bulk of compounds obtained during non-catalyzed pyrolysis have retention values between those of D_5 and D_7. The use of the catalyst mixture KOH + DMSO results in the appearance of degradation products more volatile than D_4. The chromatogram characterizing the KOH-catalyzed pyrolysis belongs to a transitional type.

As is demonstrated in Fig. 3, the entities M_2 and M_2D can be positively identified as present among the volatile products of the KOH + DMSO catalyzed pyrolysis. On the other hand, these compounds were not found among the degradation products obtained without catalysts (see Fig. 2). It is very probable that the peaks characterized by T_R values 68 and 94°, respectively, on the pyrogram shown in Fig. 4, correspond to M_2 and M_2D, although this assumption has not as yet been proved experimentally. It is, however, obvious that these two components are not characteristic for the chemical processes occurring during alkaline pyrolysis, due to their relatively small proportions in the final products.

The appearance of volatile pyrolysis products containing the unit M was rather unexpected. Their presence indicates that in contrast to the processes occurring

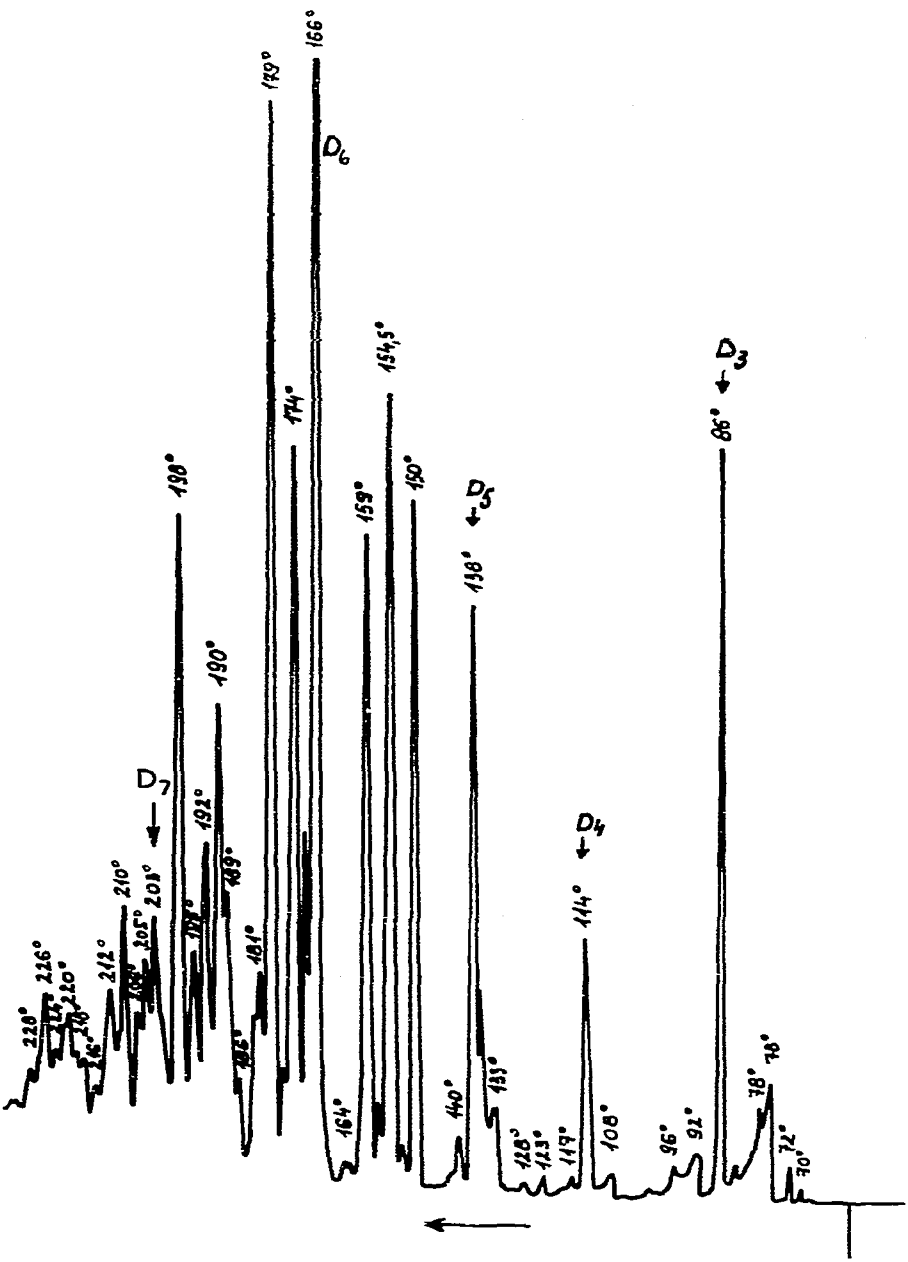


Fig. 2. Pyrogram of the branched-chain methylpolysiloxane investigated using a 3.5 m × 2 mm column packed with 10% SE-30 coated on 80–100 mesh DMCS treated Chromosorb W. Temperature programmed.

in the thermal degradation of non-catalyzed polymers, the degradation of samples in the (KOH+DMSO)-catalyzed pyrolysis is accompanied by chemical rearrangement of the structural units. In other words, changes in the functionality of the Si atoms in the polymer skeleton occur. The appearance of molecules containing M

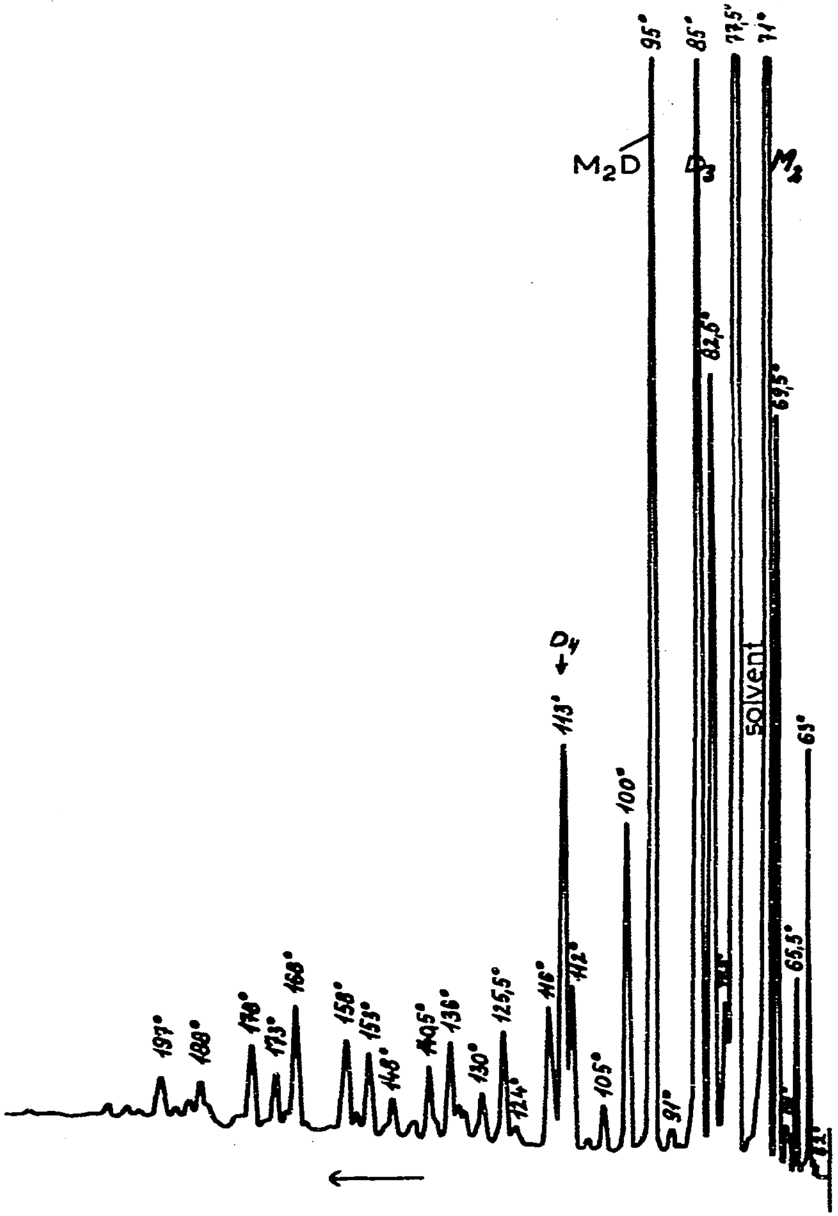


Fig. 3. Pyrogram of the branched-chain methylpolysiloxane investigated, in the presence of 0.2% KOH+1.0% DMSO. Separating conditions as in Fig. 2.

units also means that the volatile pyrolysis products formed during (KOH+DMSO)-catalyzed pyrolysis are richer in carbon atoms in comparison to those present in the mixture arising from the pyrolysis of non-catalyzed polymer.

Some additional experiments support this suggestion. Results of the analysis

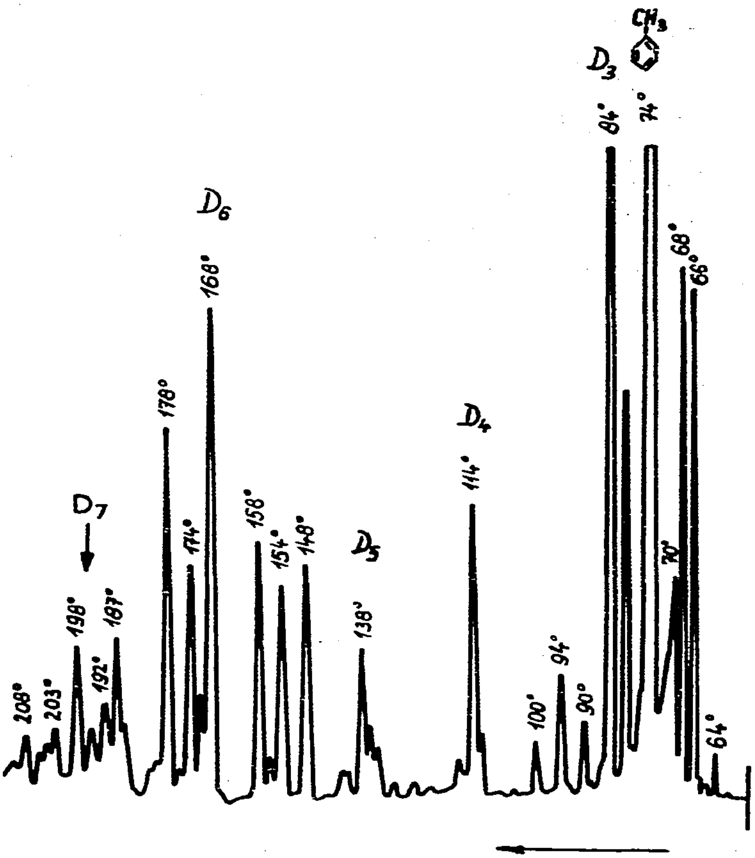


Fig. 4. Pyrogram of the branched-chain methylpolysiloxane investigated, in the presence of 0.2% KOH. Separating conditions as in Fig. 2.

TABLE 2

COMPOSITION OF SOLID MATERIAL REMAINING AFTER PYROLYSIS

Material	Weight (%)			C/Si
	C	H	Si	
Original polymer	18.9	5.6	41.8	1.1
At 650°; non-catalyzed	12.4	3.5	40.9	0.7
At 900°; catalyzed with 1% DMSO+0.2% KOH	0.9	1.8	49.1	0.04
At 650°; catalyzed with 1% DMSO+0.2% KOH	8.1	3.1	45.9	0.4
At 650°; catalyzed with 0.2% KOH	12.4	4.87	41.3	0.7

of the solid material remaining after pyrolysis are shown in Table 2, from wich it is evident that the highest carbon proportion is lost during the course of (KOH+DMSO)-catalyzed pyrolysis. In this case the polymer is converted almost completely to SiO_2 when pyrolysis is continued up to 900°.

The weight losses summarized in Table 3 were determined following the heating of the polymer samples in a nitrogen flow until a steady weight was achieved at 900°.

The data in Table 3, show that at the same time as the pyrolysis of (KOH+DMSO)-catalyzed polymers leads to a high carbon loss, material loss in the form of volatile compounds is only slightly higher than in non-catalyzed pyrolysis. This leads to the conclusion that a greater proportion of the Si–O–Si skeleton is left intact in the solid involatile phase remaining after pyrolysis of the catalyzed material.

The functionality change which occurs following the catalytic effect of KOH+DMSO is further substantiated by the observation that a small amount of tetramethylsilane is present in the pyrolysate arising from polymers treated with this catalyst. This product is very volatile and normally present only in trace amounts,

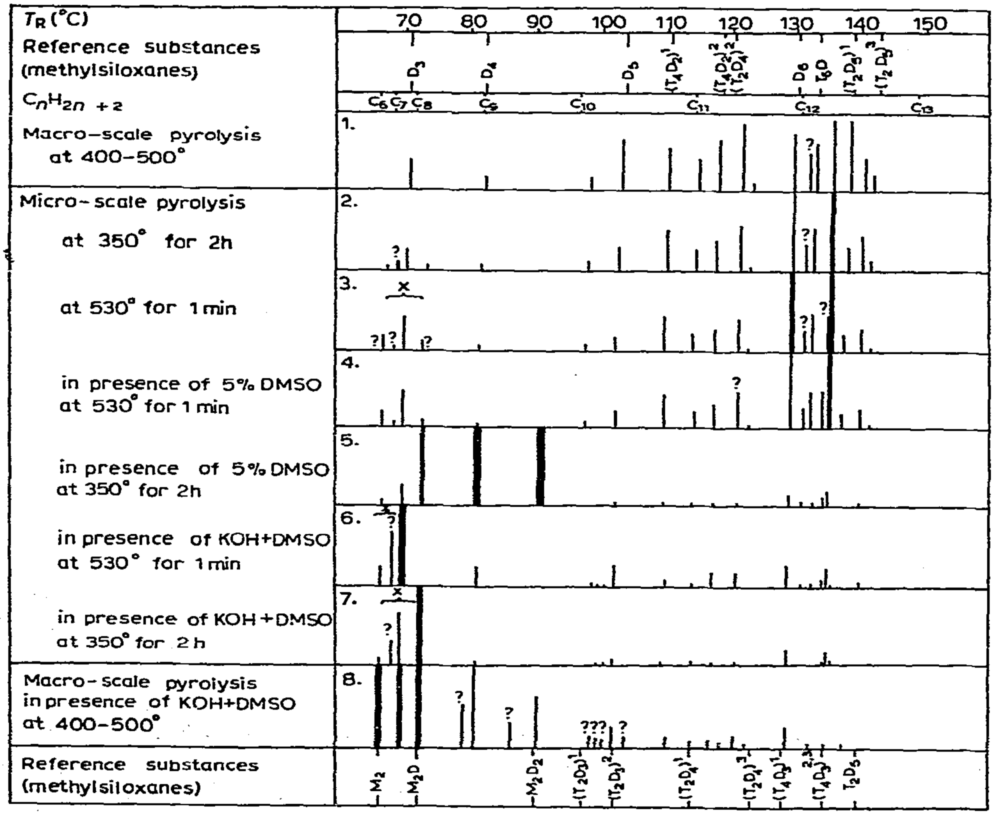
TABLE 3

WEIGHT LOSS OF POLYMER DURING PYROLYSIS

Sample	Original weight (mg)	Weight loss at 900°	
		(mg)	(%)
Polymer with 1% DMSO+0.2% KOH	15.18	3.6	23.7
Catalyst-free polymer	29.40	5.5	18.7

TABLE 4

Pyrograms obtained in the various pyrolysis procedures



the analysis of volatile pyrolysis products arising from approximately 100 g polymer being necessary to prove its presence. All further information obtained during the course of this study is tabulated in Table 4.

Eight pyrograms, based on programmed temperature APL capillary chromatograms, are schematically illustrated in this table, the retention temperature, T_R being marked along the common abscissa of the line-pyrograms. In the second and last rows of the table the retention temperatures of a few standard materials used in peak-identification are given while in the third row the retention temperatures of a few normal paraffins are illustrated on the same T_R scale for comparative purposes. The height of the lines representing the various degradation products at various retention temperatures approximately indicates the relative amounts of these materials in the eight pyrograms. The first column of the table indicates the experimental conditions employed during the pyrolyses, *viz.*, the system investigated, the pyrolysis temperature and the duration of thermal treatment.

The pyrograms in Table 4 lead to the conclusion that M terminated oligomeric methylsiloxane chains are found in the pyrolysate only when the pyrolysis is carried out with DMSO. Dimethylsiloxane cycles *i.e.* D_n molecules are formed without exception in all pyrolytic experiments illustrated in this table. In the pyrolysis of non-catalyzed material, however, the bulk of the pyrolysis products are apparently methylsiloxane polycycles, characterized by the general formula $T_{2n}D_m$, as illustrated in Table 1.

It is necessary to stress this latter point regarding general formulae since even with the standard samples only the stoichiometric formulae and molecular weights are available for the chemical characterization and identification of the peaks found in the pyrograms. A given stoichiometric formula, *e.g.* $Si_6O_8C_8H_{24}$, may be symbolized by seven further isomeric formulae, in addition to T_2D_4, *i.e.* by T_5M, QT_2D_3, QT_3DM, Q_2D_4, Q_2TD_2M, $Q_2T_2M_2$ and Q_3DM_2. These latter formulae can, however, only be encountered if it is assumed that the silicon atoms in the skeleton of the branched siloxane chain undergo a functionality change during simple pyrolysis. Such an assumption is supported neither by references in literature, nor by our experimental findings.

Comparing pyrograms serial No. 1, 2 and 3 in Table 4, it can be seen that the volatile products in all these pyrolyses are identical and consist mainly of polycyclic compounds containing 5–8 silicon atoms. The relative quantity of these polycycles does, however, depend on the duration of thermal treatment. For micro-pyrolyses over two hours and for even shorter (one minute) time—in comparison the macro-pyrolysis illustrated by pyrogram No. 1 took 6 hours—the relative quantities of the three T_4D_3 isomers increase virtually in a linear manner. Presumably these volatile molecules are present as preformed structural units in the polymer structure. It is, however, also possible that such structures are formed in the initial stages of the degradation processes as preferred chemical structures. The lesser quantities of these isomers in the macro-pyrolysate suggests that in slow gas-phase reactions they are transformed into other $T_{2n}D_m$ molecules possibly due to the greater thermodynamic stability of the latter.

It is interesting that the pyrogram corresponding to one-minute thermal treatment carried out in the presence of DMSO (serial No. 4) is very similar to pyrogram No. 3 which illustrates the results of the one-minute catalyst-free pyrolysis. On the other hand, the two-hours micro-pyrogram of the DMSO-containing polymer (serial No. 5) presents an entirely different pattern. This suggests that the functionality change brought about in the siloxane skeleton by the presence of DMSO is a slow process.

There is a striking difference between pyrograms serial No. 4 and 6 which occurs despite the use of identical pyrolysis temperatures and duration, the appearance of the dominating D_3 peak in pyrogram serial No. 6 being very important. This illustrates the influence of the presence of KOH on the generation of D_3 in these pyrolyses. Previous studies of the pyrolysis of the dimethylpolysiloxanes, on the other hand, have shown that the presence of KOH causes a significant decrease in the amount of D_3 present among the pyrolysis products, a decrease of from 70% to 43–62% being common. These results illustrate that the well-known equilibrating effect of KOH appears to function differently for straight- and branched-chain polymers.

Pyrograms serial No. 7 and 8, together with that of serial No. 5, illustrate that an increase in the length of the pyrolysis time leads to the formation of more M-containing decomposition products at a given pyrolysis temperature in the presence of DMSO. At the same time an increase in the length of pyrolysis favours the production of M_2.

CONCLUSION

The introduction of DMSO during thermal degradation leads to a new mechanism for the decomposition of the siloxane skeleton of branched-chain methylsiloxane polymers.

Several authors have dealt with the mechanism for the thermal degradation of dimethylpolysiloxanes[8,12], and have suggested that the degradation processes for these systems may be formulated as follows:

$$[(CH_3)_2SiO]_x \rightleftharpoons x/n\,[(CH_3)_2SiO]_n \tag{1}$$

The reversible process suggested in this equation means that both polymerization and depolymerization of the dimethylpolysiloxanes can be described, although probably only formally, by the same overall equation. The same materials, acids or bases, serve both as polymerization and depolymerization catalysts, and their presence in the reaction system allow the possible heterolytic cleavage of the silicon–oxygen bond even at the reflux temperatures used for the preparation of these polymers. Cleavage could follow by, for example, the reaction scheme given below:

$$-\underset{|}{\overset{|}{Si^1}}-O-\underset{|}{\overset{|}{Si^2}}- + KOH \rightarrow -\underset{|}{\overset{|}{Si^1}}-OK + -\underset{|}{\overset{|}{Si^2}}-OH \tag{2}$$

$$-\underset{|}{\overset{|}{Si^1}}-OK \rightleftharpoons -\underset{|}{\overset{|}{Si^1}}-O^- + K^+ \tag{3}$$

$$K^+ + -\underset{|}{\overset{|}{Si^1}}-O^- + -\underset{|}{\overset{|}{Si^3}}-O-\underset{|}{\overset{|}{Si^4}}- \rightarrow -\underset{|}{\overset{|}{Si^1}}-O-\underset{|}{\overset{|}{Si^3}}- + -\underset{|}{\overset{|}{Si^4}}-OK \tag{4}$$

This type of decompostion of the SiO skeleton is not accompanied by any functionality change and it leads to the formation of rings from chains, or *vice versa*. It takes place spontaneously at temperatures higher then 300° ; process (3) in the above scheme

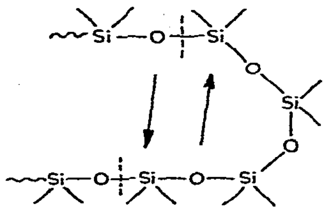


Fig. 5. Four-centered transition state in a dimethylpolysiloxane chain (after Thomas).

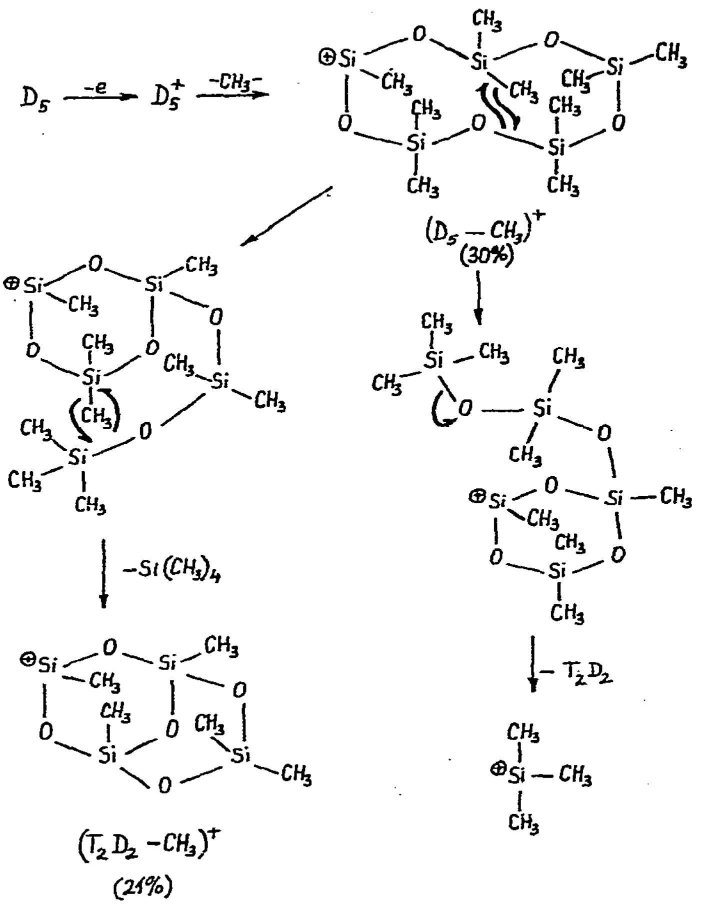


Fig. 6. Methyl group migration followed by rearrangement of the SiOSi skeleton (mechanism of degradation upon electron impact in the mass spectrometer).

yielding the silanolate anion, is initiated, according to Thomas[8], by a four-centered transition state, arising from chain-spiralization (see Fig. 5). This transitional configuration can arise stochastically at any location in the chain and it initiates degradation as long as the chain is not so small as to inhibit spiralization.

The results of our previous communication[9] suggest that the mechanism of thermal degradation for branched-chain methylsiloxane polymers is essentially similar to the above mechanism. This means that the originally cyclic or even polycyclic structures (containing 3–5 Si atoms per cycle), present in the polymer system, remain essentially unchanged during pyrolysis and degradation takes place mainly in the chain fragments connecting these polycyclic "cages". This process would lead to the formation of the polycyclic materials found as the main components of the pyrolysate. It cannot, however, be overlooked that ring closure, as suggested in Fig. 5, can also lead to the formation of "giant rings" containing more than six silicon atoms.

From the available data in the literature[13], it was expected that DMSO, due to its strong dipole character, would accelerate the KOH-catalyzed ionic degradation still further, by promoting process (3) described above. This hypothesis has not, however, been substantiated as the introduction of DMSO apparently leads to a functionality change.

On the basis of mass-spectrometric degradation schemes proposed for different methylsiloxane molecules[9], it is possible to make some suggestions regarding the mechanism of degradation entailing functionality change as observed in the present study. With linear, cyclic and polycyclic methylsiloxanes it has been observed that methyl group migration followed by rearrangement of the Si–O–Si skeleton, *i.e.* intramolecular scrambling reaction accompanied by the formation of a new cycle in the molecule, occurs as a consequence of electron bombardment. This phenomenon is demonstrated in Fig. 6, compound D_5 serving as an example.

Similar suggestions have been put forward to explain the non-catalyzed and catalyzed thermal reactions of other silicon compounds, *e.g.* the behaviour of methylchlorosilanes and $[Si(CH_3)_2]_n$ polymers[14,15]. These have been described in the literature as examples of random substituent exchange reactions.

The DMSO-catalyzed processes described in the present paper apparently form a "logical link" between rearrangement reactions induced by high energy bombardment (scrambling) and the well-known catalytic random substituent exchange reactions.

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