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THERMAL DEGRADATION OF POLY[ALKENEBIS(DIMETHYLSILOXANES)]

I. BY PYROLYTIC GAS CHROMATOGRAPHY

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SUMMARY

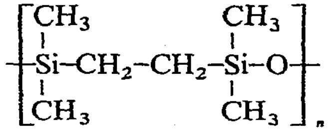
The results of pyrolytic gas chromatographic experiments performed with poly[ethylenebis(dimethylsiloxane)] and poly[propylenebis(dimethylsiloxane] samples have been utilized for the evaluation of the mechanism of the thermal degradation of these polymers.

All the significant peaks on the pyrograms have been identified and the relative amounts of the pyrolysis products have been determined at different pyrolysis temperatures.

According to the experimental results, two types of decomposition reactions occur during pyrolysis, (*a*) a siloxane-type degradation leading to the elimination of cyclic monomers from the polymer chain and (*b*) a radical-type splitting of the C–C or Si–C bond in the hydrocarbon segment followed by an intramolecular radical transfer and subsequent β-scission. These two processes occur simultaneously.

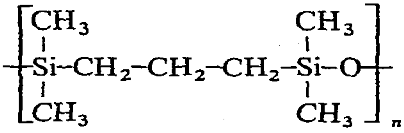
INTRODUCTION

The thermal degradation of poly[propylenebis(dimethylsiloxane)] (PPBDS) has already been investigated at our laboratories by pyrolytic gas chromatography (PGC) in an argon atmosphere[1]. The thermal vacuum degradation of poly[ethylene-



$$\left[-\mathrm{Si}(\mathrm{CH_3})_2-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{Si}(\mathrm{CH_3})_2-\mathrm{O}-\right]_n$$

(PEBDS)



$$\left[-\mathrm{Si}(\mathrm{CH_3})_2-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{Si}(\mathrm{CH_3})_2-\mathrm{O}-\right]_n$$

(PPBDS)

bis(dimethylsiloxane)] (PEBDS) and poly[methylenebis(dimethylsiloxane)] (PMBDS) has been studied by Thomas and Kendrick[2] using thermogravimetric analysis together with gas chromatographic analysis of the product from a single isothermal measurement. It has been shown that the poly[alkylenebis(dimethylsiloxanes)] decompose to small cyclic molecules (monomer and/or dimer) merely on slight heating. This decomposition is similar to that of the poly(dimethylsiloxanes) (PDMS)[3,4] which yield mainly hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane.

In our earlier work[1] we found that an other type of degradation becomes important at about 200° *i.e.* above the temperature at which PPBDS starts to decompose to siloxane rings.

In the present paper a more detailed examination of the thermal decomposition of both PEBDS and PPBDS is given which deals mainly with the second mode of degradation described above and which yields several products of higher volatility than the cyclic monomer.

EXPERIMENTAL

Materials

The polymer samples and standard materials used for the identification of the pyrolysis products were prepared in the Laboratory of Inorganic Chemistry, Institute of Organo-element Compounds, Academy of Sciences of the U.S.S.R. The starting materials for the polymerisation were the cyclic monomers 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane and 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane, respectively.

Pyrolysis

The pyrolyses were carried out in a micropyrolyser constructed in the Research Group for Inorganic Chemistry of the Hungarian Academy of Sciences and described elsewhere[5]. Samples (0.1 mg) were introduced by evaporation of a dilute polymer solution and were formed as a thin film on the inner surface of the pyrolyser boat. The pyrolytic device allowed the elimination of all dissolved volatiles from the polymer samples before pyrolysis, *i.e.* oxygen, solvent or products of a preceding pyrolysis.

In our experiments, the lowest pyrolysis temperature chosen was that just capable of producing a detectable pyrogram. On the other hand, if the pyrolysis temperature was too high it was found that the majority of the products produced were not characteristic for the particular polymer under investigation *i.e.*, cracking of the latter had occurred.

The pyrolyses were carried out in an argon atmosphere in the closed chamber of the reactor. The pyrolysis experiments were usually conducted for various times within the range 30 s–5 min, but it was shown however that the length of time used for the pyrolysis had no unfluence on either the nature or the relative quantities of the volatile degradation products. The total amount of volatiles, however, increases on increasing the length of the pyrolysis time.

Gas chromatographic analysis

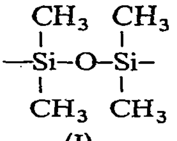
The volatile products from a single pyrolysis experiment were introduced immediately into the injection port of a Perkin–Elmer 900 Gas Chromatograph equipped with a dual flame ionization detector. The separation column, of dimensions 5 m × 2 mm, was filled with a 80–100 mesh Chromosorb G support which had been coated with 5% GE-Versilube F-50 silicon oil. Separation of methane, ethylene and propylene in addition to other volatile products of considerably higher molecular weight was achieved in a single chromatographic run, using a linear temperature program of 8° min^{-1} over the temperature range $-55°$ to $+180°$.

Quantitative evaluation of the pyrograms was based on the peak areas measured by means of a Perkin–Elmer D-24 electronic integrator, the response factors of the flame ionization detector being considered the same for all components of the pyrolysate.

Qualitative analysis of the products was based on a comparison of their respective retention times with those of pure standard materials using three kinds of different stationary phases (F-50, squalane, polyethyleneglycol succinate). In the event of a pure standard not being available, the material corresponding to the unknown peak was collected after gas chromatographic separation and identified by mass spectrometry. In such cases the pyrolysis was performed on a much larger scale than usual and a hot wire detector was employed.

RESULTS

The most important information regarding the various pyrolyses has been obtained from a determination of the chemical nature of the volatile products of the pyrolyses. Methane and ethylene were always found to be present amongst the products of the pyrolysis of PEBDS and PPBDS and, in addition, propylene was present in the latter case. The higher the temperature of the pyrolysis the greater the quantity of these gases present amongst the products. In general, the cyclic monomer was the lowest volatile product produced in any significant quantity. All the other compounds corresponding to peaks on the various pyrograms contained a common single tetramethyldisiloxane segment:



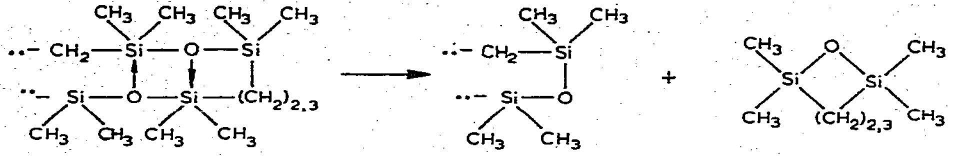
$$-\overset{CH_3}{\underset{CH_3}{\mathrm{Si}}}-O-\overset{CH_3}{\underset{CH_3}{\mathrm{Si}}}-$$

(I)

In the following discussion this segment is depicted as S. Segment S may be terminated either by hydrogen, methyl, vinyl or allyl groups.

Programmed temperature pyrograms taken at different pyrolysis temperatures are schematically illustrated in Figs. 1 and 2 for samples of PEBDS and PPBDS, respectively. The abscissa of the pyrograms represent the retention times. The values of the retention time for several standard materials are given in the last lines of both figures. The heights of the lines for each degradation product indicate the quantity of that product present relative to that of the component present in the largest amount, the latter being taken arbitrarily as equal to 100.

According to Thomas[3], the formation of the cyclic monomer[1,2] is due to a reaction similar to that occurring in the degradation of PDMS and involving the presence of a four-centered complex:



(II) (III)

Figures 1 and 2 show that this reaction predominates at lower pyrolysis temperatures. It is clear, however, that at higher temperatures some other reaction also occurs.

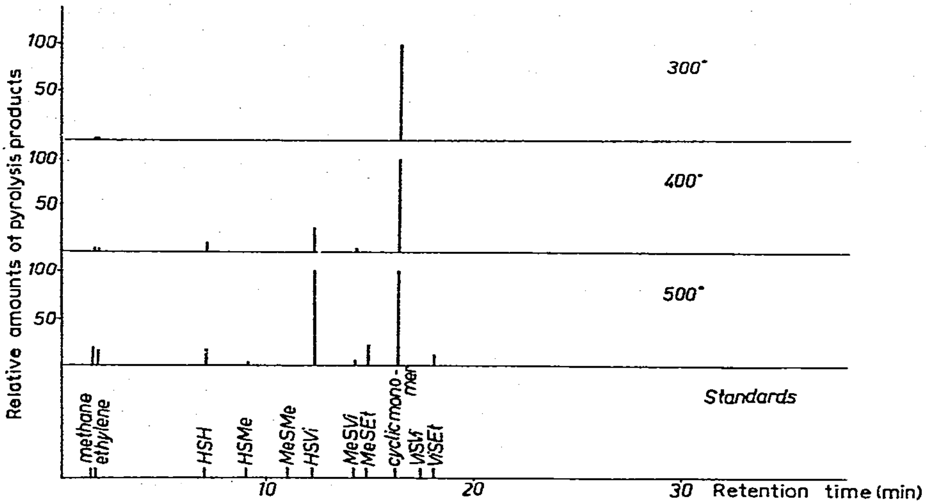


Fig. 1. Bar-graphs of PEBDS pyrograms.

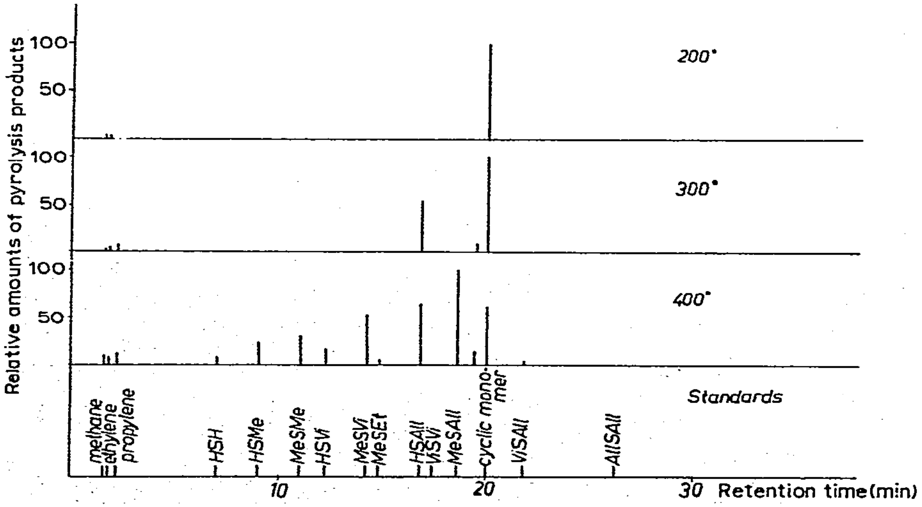


Fig. 2. Bar-graphs of PPBDS pyrograms.

It was initially assumed that the second reaction might consist of a secondary decomposition of the cyclic monomer. Investigation of the products of the pyrolysis of the cyclic monomers of both PEBDS and PPBDS indicated, however, that in both cases the products were different from those obtained from the pyrolysis of the corresponding polymer.

In Table 1 the relative amounts of the pyrolysis products of PPBDS, expressed as an average of the results of seven pyrograms measured at 400°, are recorded. Standard deviations (σ) given in the Table clearly show that, in general, the reproducibility of the pyrograms was extremely poor if a comparison was made between the quantities of product generated in the pyrolysis with that of cyclic monomer, the latter being taken arbitrarily as equal to 100.

TABLE 1

QUANTITATIVE ASSESSMENT OF PPBDS PYROGRAMS ON THE BASIS OF SEVEN REPEATED EXPERIMENTS

Pyrolysis product	*Comparison with MeSAll*			*Comparison with cyclic monomer*		
	Relative quantity (average)	σ_{abs}	σ_{rel} (%)	*Relative quantity (average)*	σ_{abs}	σ_{rel} (%)
Methane	2.8	0.7	23	12	6.5	54
Ethylene	4.5	1.0	22	18.5	9	48
Propylene	3.3	1.0	29	14	7.5	55
HSH	5.3	1.3	25	21	9	43
HSMe	24.5	1.9	8	100	47.5	47
MeSMe	24.2	1.0	4	99.5	48	48
HSVi	9.1	1.1	12	37.5	20	53
MeSVi	37.3	2.4	6	153	78	51
HSAll	38.9	3.8	10	158.5	83	52
MeSAll	100			406	181	44
Cyclic monomer	31.2	16.6	53	100		

However, the deviations become much less if a comparison is made between the product quantities and that of MeSAll (pentamethylallyldisiloxane) obtained from pyrolysis, in this case MeSAll being taken arbitrarily as equal to 100. In the latter case the largest deviation is observed for the cyclic monomer.

On the basis of these observations, it appears that the cyclic monomer is formed as the result of a quite different reaction from those which produce the other volatile products of the pyrolysis and that experimental conditions which we have not been able to reproduce have different effects on these two types of reactions.

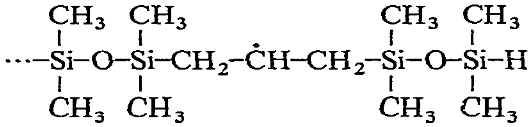
Since, the polymer chain present in the polymers studied consisted of regularly alternating $-Me_2SiOSiMe_2-$ units and short linear hydrocarbon segments, it is not unreasonable to assume that degradation of these polymers might be somewhat similar to that of hydrocarbons and proceed by a free-radical mechanism[6]. According to the free-radical theory of the degradation of polyhydrocarbons[7,8], the initiation step in the thermal decomposition consists of the homolytic scission of the polymer chain to produce primary free radicals. Initiation may then be followed by any of the three reaction steps, (*a*) simultaneous saturation and unsaturation, (*b*) intermolecular transfer, and (*c*) intramolecular transfer of the primary radicals.

The mole ratio of n-alkane, 1-alkene and α,ω-alkadiene produced by reaction step (*a*) above should be 1/2/1, by reaction step (*b*) $(1-\alpha)^2/2(1-\alpha)/1$ and by reaction step (*c*) $(1-\alpha)/1/0$, respectively[9], where α is the fraction of n-alkane radicals consumed by reactions other than hydrogen abstraction.

Similarly, free-radical decomposition of poly[alkenebis(dimethylsiloxanes)] should result in the formation of compounds with an alkyl group and/or a hydrogen at both sides of the sequence S (instead of the formation of n-alkanes), in compounds with an alkyl group or a hydrogen at one side and an alkenyl group at the other side of the sequence S (instead of the formation of 1-alkenes) and in compounds with alkenyl groups at both sides of the sequence S (instead of α,ω-alkadienes). The observed mole ratio of these various types of sequence should indicate which of the three decomposition processes is of principal significance in the degradation of the polymer investigated.

The fact that only small quantities of compounds with alkenyl groups at both sides of the sequence S were produced in those pyrolyses where large quantities of non-cyclic compounds were formed indicates that intramolecular radical transfer is the most important of the three mechanisms mentioned above in the thermal decomposition of both PEBDS and PPBDS.

In the polymers investigated, initiation may proceed either by scission of a Si–C or a C–C bond in the polymer chain. Comparison of the relative bond energies of the Si–C and C–C bond indicates that the former will undergo scission more readily than the latter. If, for instance, in PPBDSSi–C bond scission is followed by intramolecular radical transfer, the hydrogen abstracted during this step comes from one of the carbon atoms of the next alkylene segment, *i.e.* from the fourth, fifth or sixth atom in the primary macro radical. In this way a hydrogen-terminated secondary macro radical is formed,



$$\cdots\text{-}Si(CH_3)_2\text{-}O\text{-}Si(CH_3)_2\text{-}CH_2\text{-}\dot{C}H\text{-}CH_2\text{-}Si(CH_3)_2\text{-}O\text{-}Si(CH_3)_2\text{-}H$$

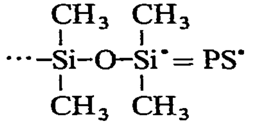
(IV)

Methyl-, ethyl-, and propyl-terminated radicals may be formed in a similar manner from the other possible primary radicals.

It is worth mentioning that in the case of PPBDS, hydrogen abstraction from the fifth atom, *i.e.* from the carbon atom not next to the silicon atom, requires the least energy. Hence, in the resulting secondary radical the unpaired electrons and the hydrogens can be delocalized over three carbon atoms while hydrogen abstraction from a carbon atom next to a silicon atom results in the formation of a radical where delocalization is possible only over two carbon atoms[6].

The secondary radical produced by hydrogen abstraction from the hydrocarbon segment may decompose by β-scission to produce RSVi or RSAll and, in addition, a new macro radical, or alternatively, in the formation of a small radical $RS^{\bullet}$ and a macromolecule terminated by vinyl or allyl group*.

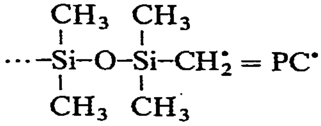
Radical decomposition pathways for the various polymers investigated in this study are schematically depicted in Figs. 3 and 4. It is clear from these figures that two of the primary macro radicals:



$$\cdots-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{Si}}}}-O-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{Si^{\bullet}}}}} = PS^{\bullet}$$

(V)

and



$$\cdots-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{Si}}}}-O-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{Si}}}}-CH_2^{\bullet} = PC^{\bullet}$$

(VI)

are produced during the decomposition of any macro radical formed in the initiation step (unless of course, termination intervenes). Hence, if the kinetic chain length is large, the products of radicals (V) or (VI) will predominate in the system. This has, in fact, been demonstrated experimentally. For PEBDS, the chain reaction involves only radical (V) (Fig. 3).

The volatile end-products of the chain reactions are underlined in Figs. 3 and 4. These are all important constituents of the pyrograms given in Figs. 1 and 2. Comparison of the quantities of these constituents indicates that the amount of HSH, HSMe and MeSMe formed is less than the amount of products containing one unsaturated group. This may be explained by the introduction of an intermolecular hydrogen abstraction step additional to those already discussed above. Thus, the secondary macro radical produced in the above reaction step may decompose by β-scission to give a new primary macro radical (V) or (VI) and a macromolecule terminated by an unsaturated group.

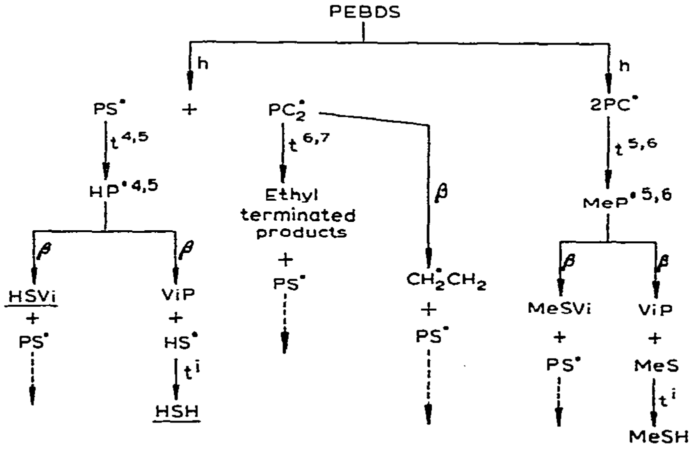


Fig. 3. Radical decomposition scheme for the pyrolysis of PEBDS.

(*For further explanation see under the caption of Fig.* 4)

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* R stands for H, methyl, ethyl or propyl group.

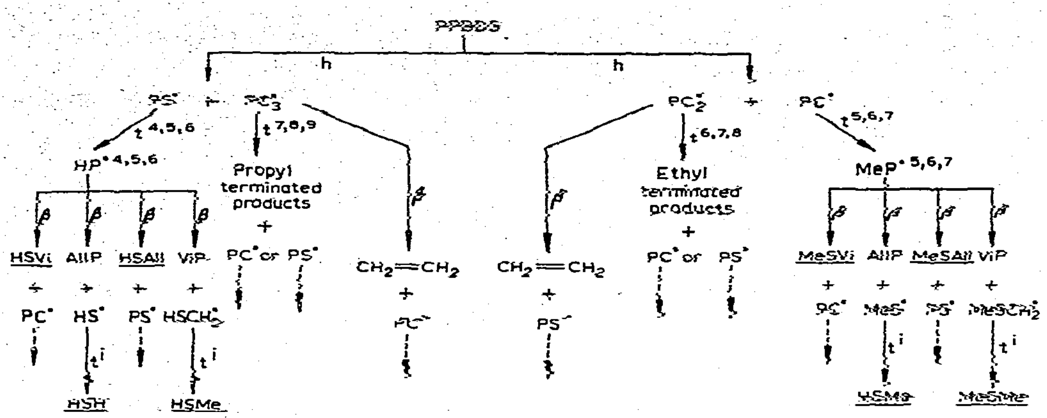
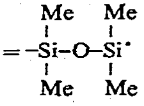
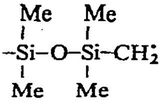
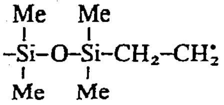


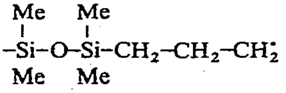
Fig. 4. Radical decomposition scheme for the pyrolysis of PPBDS.

h =homolytic C–C or Si–C bond scission
t^i =intermolecular radical transfer
$t^{n,m}$=intramolecular radical transfer to the *n*th or *m*th atom from the end of a primary macro radical
β =β-scission of a macro radical

PS• =

$$-\overset{Me}{\underset{Me}{Si}}-O-\overset{Me}{\underset{Me}{Si}}{}^{\bullet}$$
macro radical

PC• =

$$-\overset{Me}{\underset{Me}{Si}}-O-\overset{Me}{\underset{Me}{Si}}-CH_2^{\bullet}$$

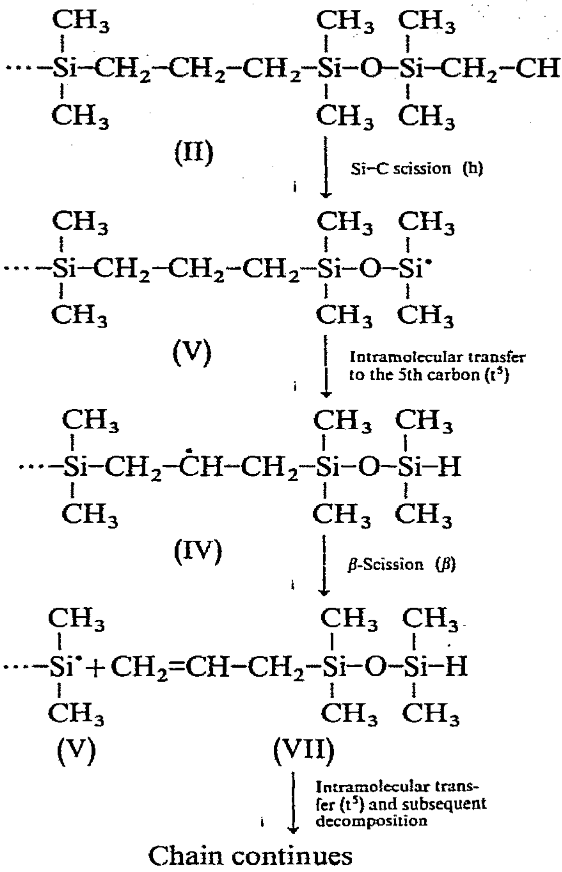
PC₂• =

$$-\overset{Me}{\underset{Me}{Si}}-O-\overset{Me}{\underset{Me}{Si}}-CH_2-CH_2^{\bullet}$$

PC₃• =

$$-\overset{Me}{\underset{Me}{Si}}-O-\overset{Me}{\underset{Me}{Si}}-CH_2-CH_2-CH_2^{\bullet}$$

$RP^{\bullet n,m}$ = R-terminated secondary macro radical, the unpaired electron being located on the *n*th or *m*th atom (R stands for H, methyl, ethyl or propyl)
ZP = Z-terminated macromolecule (Z represents vinyl or allyl)

The pyrolysis temperature has a considerable effect on the extent of free radical participation in the overall degradation of the polymer. From a comparison of the pyrograms obtained at different temperatures (Figs. 1 and 2), it is obvious that free-radical reactions are much more important than siloxane ring formation or cyclic monomer formation at higher temperatures.

The difference between the energies required for Si–C and C–C bond scission together with that between the energies of hydrogen abstraction from different carbon atoms in the polymer chain is clearly revealed in the pyrogram for PPBDS at 300° (Fig. 2). HSAll appears at a lower temperature than the other products of the free-radical decomposition, because it is produced by reactions which require less energy:



All the volatile end-products obtained in the chain reactions are observed in pyrograms measured above 400°. This indicates that a temperature of 400° is sufficient to cause both C–C scission in addition to Si–C scission and intramolecular hydrogen abstraction from any carbon atom in the polymer chain.

Further increases in temperature increase the relative amounts of methane, ethylene, propylene and highly volatile silicon compounds present in the pyrogram, but do not provide any additional information regarding the degradation mechanisms of the polymers investigated.

REFERENCES

1 K. A. Andrianov, G. Garzó, T. Székely, M. Blaszó, L. M. Volkova, N. V. Delezari and J. Tamàs, *Vysokomol. Soedin. B.*, 13 (1971) 593.
2 T. H. Thomas and T. C. Kendrick, *J. Polym. Sci., Part A-2*, 8 (1970) 1823.
3 T. H. Thomas and T. C. Kendrick, *J. Polym. Sci., Part A-2*, 7 (1969) 537.
4 B. Lengyel, T. Székely and G. Garzó, in press.

5 G. Garzó, T. Székely and M. Blazsó, *Chromatographia*, September 1972, special issue.
6 A. Kosiakoff and F. O. Rice, *J. Amer. Chem. Soc.*, 65 (1943) 590.
7 Y. Tsuchiya and K. Sumi, *J. Polym. Sci., Part A*-1, 6 (1968) 357.
8 F. W. Wilmott, *J. Chromatogr. Sci.*, 7 (1969) 101.
9 Y. Tsuchiya and K. Sumi, *Polymer Lett.*, 6 (1968) 357.