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SOME ASPECTS OF THERMAL DEGRADATION AND STABILIZATION OF POLYDIMETHYLSILOXANE

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INVESTIGATION of degradation of polydimethylsiloxane (PS) and improvement of its thermal stability have been the subjects of a number of papers.(1–6) Heating of polydimethylsiloxane in an inert medium or *in vacuo*(1) depolymerizes it into cyclic low-molecular weight products. It was also stated(2, 3) that thermal degradation of polydimethylsiloxane essentially depends upon the presence of impurities and traces of polymerization catalysts which cause formation of active centres and substantially decrease the stability. The Czech authors have shown that addition of benzoic or carbonic acids, ammonium or iron hydroxides, beryllium, aluminium or iron oxides into polydimethylsiloxane deactivates the active centres and improves its thermal stability.(4–6)

The influence of impurities and catalyst traces on thermal destruction of polydimethylsiloxane, on the other hand, depends both upon the method of purification of starting materials and its thoroughness and upon purification of the polymer itself. Meanwhile, besides the catalyst impurities, there are other factors influencing thermal degradation of polydimethylsiloxane; their function still remains far from clear.

The present communication describes the dependence upon polymer molecular weight of the structural changes in thermal decomposition of polydimethylsiloxane under oxygen free atmosphere; effects of the nature of terminal groups and the addition of some stabilizing metal compounds to the polymer are also considered.

EXPERIMENTAL

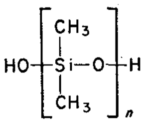
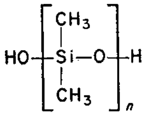
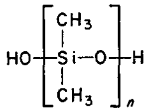
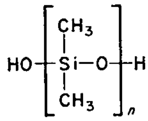
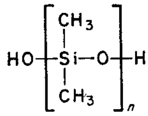
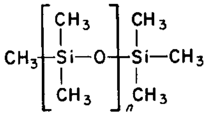
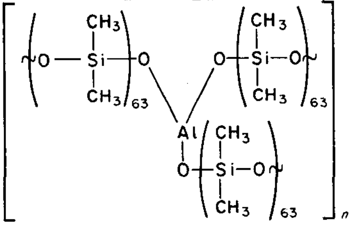
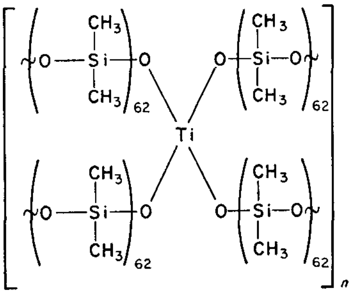
Polydimethylsiloxanes with terminal hydroxy and methyl groups and different molecular weights have been the subjects of the present study. Thermal destruction of polyaluminium- and polytitaniumdimethylsiloxanes has been also investigated (Table 1). The polymers with terminal hydroxy groups (PS-1, PS-2, PS-3, PS-4) have been prepared by fractional sedimentation with methanol of dimethylsiloxane SKT type rubber (PS) from its 1 per cent benzene solution. Polydimethylsiloxane with terminal methyl groups (PS-M) has been synthesized by polymerization of octamethylcyclotetrasiloxane in the presence of hexamethyldisiloxane (0·1 wt. per cent) and concentrated H_2SO_4 (2 wt. per cent)(7, 8) with subsequent washing (negative reaction for SO_4^{2-} ion).

Polyaluminium (PSA) and polytitaniumdimethylsiloxanes (PST) have been obtained according to procedures described.(9, 10) By the reaction with excess of copper, iron and zirconium acetyl acetonates carried out in solution in *m*-xylene at 120°–130° for 4 hr, polydimethylsiloxanes containing metals in the terminal groups have been prepared from the PS-4 by substituting its hydroxy groups.

Prior to the experiments, the polymers were purified by repeated precipitation with methanol from benzene solutions and dried *in vacuo* at 80° to constant weight.

Molecular weights of polydimethylsiloxanes have been determined using the formula $[\eta] = 1{\cdot}2 \times 10^{-4} \times M^{0{\cdot}68}$(11) by measuring intrinsic viscosities of benzene solutions, as well as by the method of light scattering.(12)

TABLE 1. CHARACTERISTICS OF INITIAL DIMETHYLSILOXANE POLYMERS

Structure	Definition	[η] dl/g	Mol.wt. (M.10^{-5})
 $HO-[Si(CH_3)_2-O]_n-H$	PS	0·62	5·93
 $HO-[Si(CH_3)_2-O]_n-H$	PS-1	0·85	11·17
 $HO-[Si(CH_3)_2-O]_n-H$	PS-2	0·70	7·57
 $HO-[Si(CH_3)_2-O]_n-H$	PS-3	0·58	5·18
 $HO-[Si(CH_3)_2-O]_n-H$	PS-4	0·43	2·84
 $CH_3-[Si(CH_3)_2-O]_n-Si(CH_3)_3$	PS-M	0·37	2·10
	PSA	0·29	0·72
	PST	0·26	0·86

Solvents (benzene, methanol, acetone) were used for addition of a variety of metallic derivatives as stabilizers to the polymer; a ratio of metal equivalent to the number of dimethylsiloxane units was always kept at 1:62.

Such proportion was convenient when a comparison of the present data was made with the data obtained in thermal degradation of polyaluminium and polytitaniumdimethylsiloxanes.(22) 0·01 wt. per cent of polymerization catalyst (NaOH or H_2SO_4) was added to the starting polymer.(4)

The thermal degradation was studied in a special apparatus(13) providing a vacuum down to 10^{-3} – 10^{-5} mmHg and supplied with gas chromatographic analyzer. The volatile products were collected in a dry-ice trap for subsequent quantitative analysis. When the experiments were carried out in saturated water vapour atmosphere, the installation was a small quantity of water was frozen in a trap, the system was evacuated and then the trap was warmed.

RESULTS AND DISCUSSION

Investigation of thermal degradation of PS with terminal hydroxy groups indicates that, even at low conversion, some change in molecular weight of the polymer occurs even before there is a loss of weight. Destruction of PS, on the other hand, predominates at high temperatures giving volatile low molecular weight cyclic products.

Heating the polymer *in vacuo* from 170° up to 300° was shown to increase considerably its molecular weight (Fig. 1); this was probably due to a polycondensation involving terminal hydroxy groups. Subsequent increase in temperature decomposed the polymer and hence decreased its molecular weight (Fig. 1), but the polymer remained soluble at all stages of thermal ageing. Examination in an ultracentrifuge indicates that the molecular weight distribution of PS during its thermal ageing varies little.

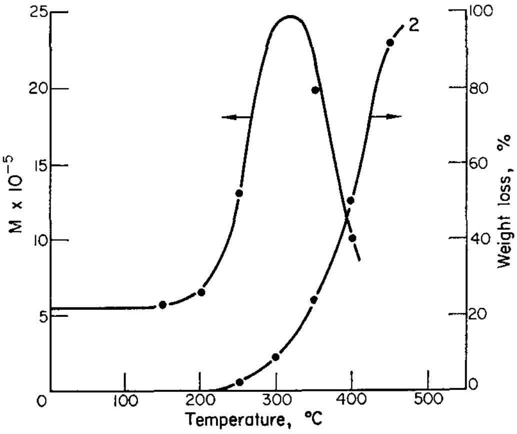
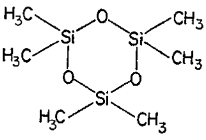


FIG. 1. Molecular weight (1) of PS and its weight loss (2) in thermal degradation during 4 hr.

The curve of weight losses (Fig. 1) shows that thermal decay of PS proceeds only above 220°. Its weight losses are governed by the rate of evolution of the volatile organosilicon degradation products increasing with temperature. As shown by analysis, these products consisted of cyclic dimethylsiloxanes with three, four and more silicon atoms in the ring and resulted from depolymerization. The analysis indicated no gaseous products in the mixture.

Thermal destruction of PS *in vacuo* leads to volatile products consisting mostly of cyclic trimer-hexamethylcyclotrisiloxane (HMCS, 99 wt. per cent).



Detailed investigation of thermal degradation has shown that terminal hydroxy groups in the polymer facilitate a depolymerization process from the ends of siloxane chain. It was in particular supported by the fact that the rate of the PS depolymerization depends upon the value of its initial polymerization coefficient. The rate of evolution of HMCS may be described by equation:

$$\frac{dA}{d\tau} = K \cdot g_\tau$$

where A is the amount of evolving HMCS, g_τ is the amount of polymer at the time τ, K is the depolymerization constant depending upon the temperature, nature of the polymer and the mean polymerization coefficient (N_0), i.e.

$$K = f(N_0^m).$$

When depolymerization involves the ends of the chain ($m \leqslant 0$), K decreases with increasing N_0, when depolymerization is random ($m \geqslant 0$), K increases with N_0.(14)

Thermal degradation of dimethylsiloxane polymers with terminal hydroxy groups and various N_0 (Table 1) shows that the depolymerization rate constant (K) decreases with increase in N_0 (Fig. 2), i.e. $m < 0$. Such dependency indicates depolymerization involving the ends of polydimethylsiloxane macromolecules.

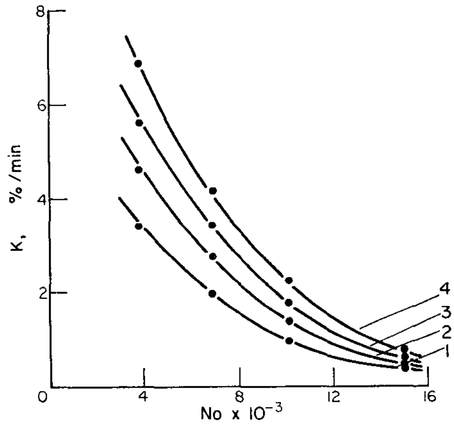


FIG. 2. Depolymerization rate constant of PS vs. its mean polymerization coefficient at various temperatures (1) 300°, (2) 350°, (3) 375°, (4) 400°.

The decrease in molecular weight of the polymer is proportional to the amount of evolved monomer when depolymerization involves the ends of the chain.(15) But, as mentioned above, treatment of PS *in vacuo* also causes its polycondensation, deactivating its terminal hydroxy groups, increasing the molecular weight of the polymer and changing the course of the whole process. Thus the only possibility of observing a change in the molecular weight is to slow down or to suppress completely the polycondensation process.

For such a purpose, the treatment of PS was carried out in an atmosphere saturated with water vapour. The siloxane bond is known to be stable to hydrolytic action of water at high temperature in the absence of catalysts and oxygen.(16) The hydrolytic stability of the siloxane bond under the conditions of thermal destruction in the present study was supported for such specimens as polydimethylsiloxane with terminal methyl groups (PS–M) and HMCS with strain in the siloxane ring much exceeding that in the linear structure. These results lead to the conclusion that siloxane bonds in a ring are unaffected by the presence of water up to 350°. On the other hand, if polydimethylsiloxane with terminal hydroxy groups is subjected to destruction in the presence of saturated water vapour at 250°–350°, its molecular weight does not increase but instead gradually decreases; a cyclic trimer is a depolymerization product. This indicates that thermal treatment of the polymer in an atmosphere of saturated water vapour does not notably effect depolymerization but suppresses the polycondensation. This effect is probably associated with solvation complexes of terminal hydroxy groups with water molecules preventing the bimolecular reaction of polycondensation and decreasing the reactivity of these groups. On the other hand, this solvation should not much influence deploymerization of the polymer, this being a monomolecular reaction. Moreover, depolymerization of polydimethylsiloxane is also facilitated by spiral-like structure of siloxane chains(18, 19) favouring the closure of rings and formation of cyclic decomposition products.

The dependency shown in Fig. 3 confirms the decrease in the molecular weights of polydimethylsiloxanes with terminal hydroxy groups proportionally to the amount of

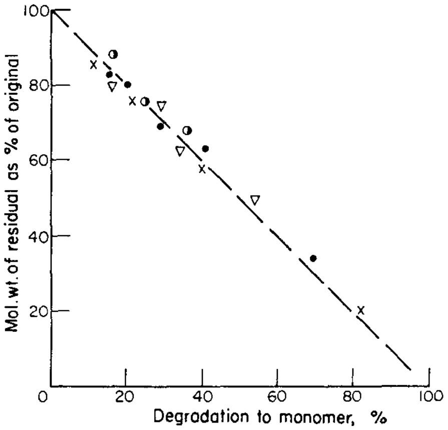


FIG. 3. Molecular weight of PS vs. amount of HMCS generating in thermal degradation under atmosphere of saturated water vapour.

PS-1 at 300° (◑); 350° (●)
PS-3 at 300° (▽); 350° (×)

the cyclic trimer evolved during thermal degradation of the polymer. Such dependency undoubtedly indicates depolymerization involving terminal hydroxy groups.

This idea was also supported by the analysis of thermal destruction data for polydimethylsiloxane containing microquantities of polymerization catalysts. As seen from Table 2, the molecular weight of such a polymer sharply decreases at the beginning of destruction without significant evolution of cyclic trimer.

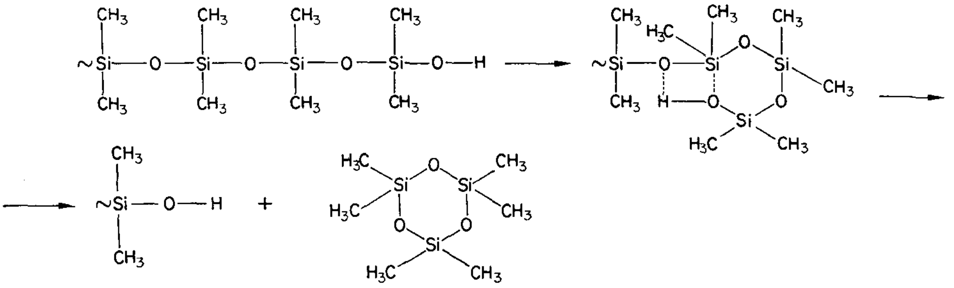
TABLE 2. CHANGE OF PS POLYMERIZATION COEFFICIENT IN DEGRADATION IN THE PRESENCE OF CATALYSTS

Polymer	Degradation temperature (°C)	Degradation time (min)	0·01% NaOH Amount of monomer (wt. %)	N_0	0·01% H_2SO_4 Amount of monomer (wt. %)	N_0
PS-1	Initial	—	0·0	15100	0·0	15100
PS-1	300	10	0·0	214	0·0	4200
PS-1	300	20	5·3	470	2·4	2100
PS-4	Initial	—	0·0	3800	0·0	3800
PS-4	300	10	0·0	600	0·0	920
PS-4	300	20	2·2	350	1·6	460

Such dependency arises from the fact that the main polymer chain splits according to the scheme previously suggested.(15) Hence the mechanism of thermal degradation, when there are traces of catalyst in the polymer, is essentially different. This in its turn again indicates deploymerization involving terminal hydroxy groups in thermal degradation when the polydimethylsiloxane contains no catalytic impurities.

The results presented show that thermal degradation of the polymer with terminal hydroxy groups is a complex process proceeding through the polycondensation which leads to increasing of molecular weight of the polymer, as well as through depolymerization from terminal hydroxy groups causing a decrease in molecular weight proportionally to evolution of cyclic products.

Generation of cyclic products at the ends of dimethylsiloxane chain in depolymerization is likely to occur through an intermediate activated complex, as in most chemical reactions. We may now suggest a mechanism of depolymerization through hydroxy groups. Owing to high mobility and the spiral-like structure of siloxane chains with three silicon atoms in a turn, there occur the closure of rings and the generation of a transition complex with excited Si . . . O and O . . . H bonds; redistribution of energy results in decomposition of the complex

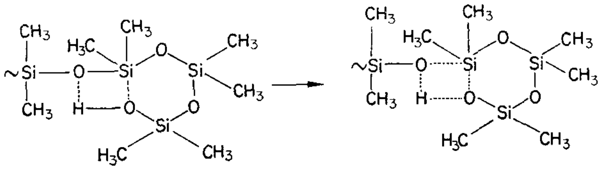


splitting off the cyclic product but leaving a hydroxy group at the end of the siloxane chain. Repetition of such elementary acts is a step-wise process.

For generation of activated Si . . . O and O . . . H bonds in the transition complex some energy barrier, i.e. the activation energy of depolymerization process, should be overcome. We have calculated this energy using the known additivity principle for bond energies.[20] According to this principle, the activation energy is made up from a contribution from energies of splitting bonds $(Q)_{\text{cleav.}}$ minus that from exciting bonds (Q^x)

$$E = \sum_{\text{cleav.}} Q - \sum Q^x.$$

In the case of the cyclic trimer, cleavage from the end of siloxane chain corresponds to a cleavage of a Si–O bond (bond energy 89 Kcal/mol[17]) and one O–H bond (bond energy 103 Kcal/mol[21]) activated complex.



In the activated complex, four excited bonds are generated: two O . . . H bonds each of 52·5 Kcal/mol bond energy[21] and two Si . . . O bonds each with the energy of 36·5 Kcal/ mol. The bond energy of the activated Si . . . O bond was interpolated from the diagram (Fig. 4) taken from reference.[20] The activation energy will be

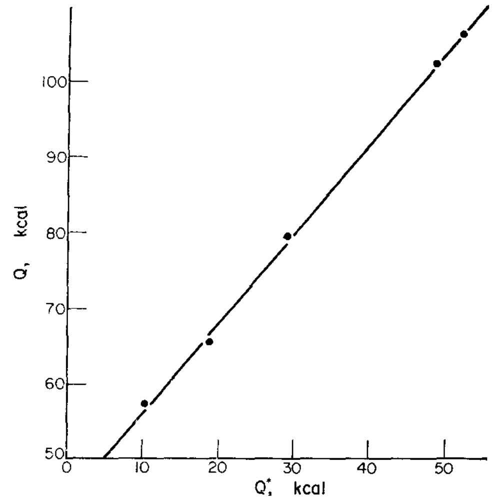


FIG. 4. Bond energies between atoms in a molecule (Q) vs. bond energies in a complex (Q^*).

$$E = (89 + 103) - (36{\cdot}5 \times 2 + 52{\cdot}5 \times 2) = 14 \text{ Kcal/mol}.$$

Experimental activation energies found from plots of log K vs. $1/T$ (Fig. 5) for thermal destruction of polydimethylsiloxanes, having different molecular weights, are in good agreement with the value predicted by the theory.

With decreasing molecular weight of polydimethylsiloxane, i.e. with increasing concentration of terminal hydroxy groups, the values of activation energy satisfactorily approach the theoretical value (Fig. 6).

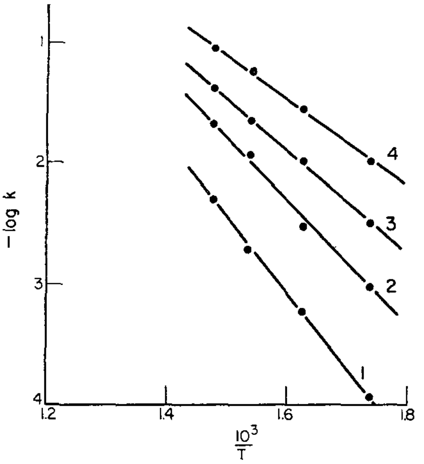


FIG. 5. Thermal destruction rate constant of PS vs. reciprocal temperature (*in vacuo*) (1) PS-1, (2) PS-2, (3) PS-3, (4) PS-4.

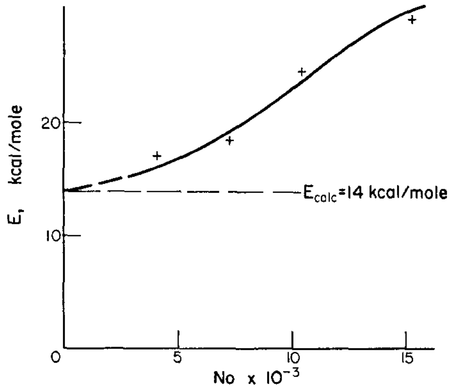


FIG. 6. Effective activation energy of degradation of PS vs. its polymerization coefficient.

Hence the cleavage of cyclic products from polydimethylsiloxane in the thermal degradation is a step-wise depolymerization reaction, proceeding through an activated transition complex. The presence of terminal hydroxy groups in the polymer permits propagation of the depolymerization from the ends of polymer chain.

This implies that the presence of terminal groups of lower reactivity in polydimethylsiloxane should result in some different structure for the transition complex and, hence, change its stability.

This idea was supported by the data on thermal destruction of a dimethylsiloxane polymer in which terminal hydroxy groups were replaced by methyl groups (PS–M). Comparison of rate constants for destruction of polymers with equivalent molecular weights shows (Table 3) that replacement of hydroxy groups by methyls considerably descreases the decomposition rate and increases the thermal stability of the polymer.

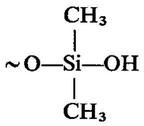
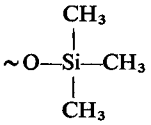
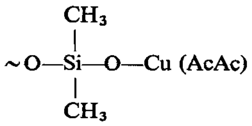
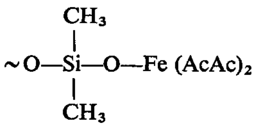
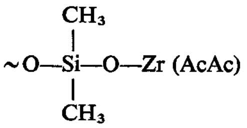
This led us to the idea of other possibilities for blocking the terminal hydroxy groups, in particular to employ some metallic derivatives. Thus, acetylacetonates of

TABLE 3. RATE CONSTANT OF THERMAL DEGRADATION OF PS-4 AND PS–M VS. CONVERSION AT 400°

Conversion (%)	Rate constant, k.10^3 PS–4	PS–M
5	108	2·6
10	106	2·3
15	98	2·0
20	87	1·6

copper, iron and zirconium are much more effective than the presence of terminal methyl groups in the polymer (Table 4). As seen from these data, the nature of metal in the compound plays an important function in thermal stabilization of polydimethylsiloxane which cannot be explained only by a blocking of hydroxy groups. Moreover, thermal stability of the polymer in this case was observed to approach that of polyelementdimethylsiloxane(22) with corresponding heteroatoms in siloxane chain.

TABLE 4. EFFECT OF TERMINAL GROUPS ON THERMOSTABILITY OF POLYDIMETHYLSILOXANE AT 400° FOR 4 hr

Terminal groups	Weight loss (%)
 $\sim O-\overset{CH_3}{\underset{CH_3}{Si}}-OH$	84·8
 $\sim O-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$	32·3
 $\sim O-\overset{CH_3}{\underset{CH_3}{Si}}-O-Cu\ (AcAc)$	11·7
 $\sim O-\overset{CH_3}{\underset{CH_3}{Si}}-O-Fe\ (AcAc)_2$	14·8
 $\sim O-\overset{CH_3}{\underset{CH_3}{Si}}-O-Zr\ (AcAc)$	8·2

AcAc = acetylacetonate fragment.

For elucidation of these interesting phenomena, we have studied destruction of PS stabilized by various organometallic additives.

This investigation was carried out on the basis that addition of metallic compounds to PS should result not only in blocking of terminal hydroxy groups but also in subsequent interaction of the added compound with the PS macromolecules during destruction, and in the development of some new thermostable high molecular weight compounds containing heteroatoms in the siloxane chain. Good support for this suggestion was found from comparison of data on thermal destruction of stabilized PS with those on destruction of some polymetaldimethylsiloxanes of regular structure when both polymers had the same number of corresponding metal heteroatoms.(22, 23)

The mechanism of thermal destruction of PS stabilized by organometallic additives considerably differs from that of non-stabilized polymer. Thus, the polymer stabilized by transition metal compounds has a higher thermal stability than non-stabilized polymer. On the other hand, pronounced crosslinking was observed in the former even at moderate temperature. The crosslinking first shows up in increasing intrinsic viscosity of the soluble part (Fig. 7) then, at a certain stage, in precipitation of the insoluble part in the form of gel-fraction. The last stage was not observed for non-stabilized polymer. Intrinsic viscosity decreases with increasing concentration of gel-fraction. Maximum viscosity in all cases indicates the beginning of gelation (Fig. 7).

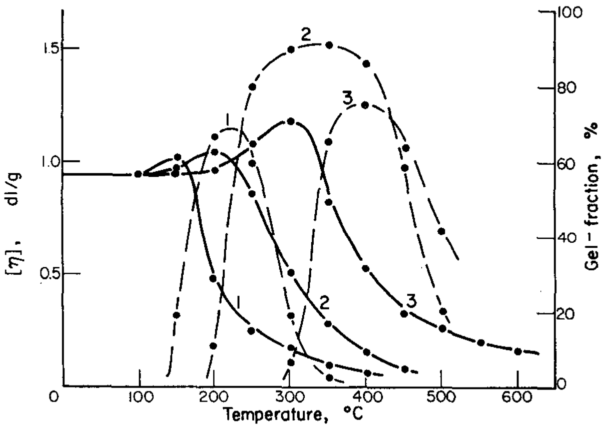


FIG. 7. Intrinsic viscosity (in benzene, full lines) and amount of precipitated gelf-raction (dotted lines) vs. the temperature for 4 hr destruction of PS containing additives of tributoxy aluminium (1), trihexoxyiron (2), and tetrabutoxytitanium (3).

An interesting point should be noted that structural changes in the polymer stabilized by organometallic additives are in many cases associated with the nature of the metal in the additive fixing the temperature at which gel formation begins and at which intrinsic viscosity has its maximum value. For aluminium derivatives, this temperature is lower than for titanium and iron compounds (Fig. 8).

A comparison of experimental results shows that, for both PS stabilized by metallic compounds and for polymetaldimethylsiloxanes of regular structure, there is the same character of thermal degradation.

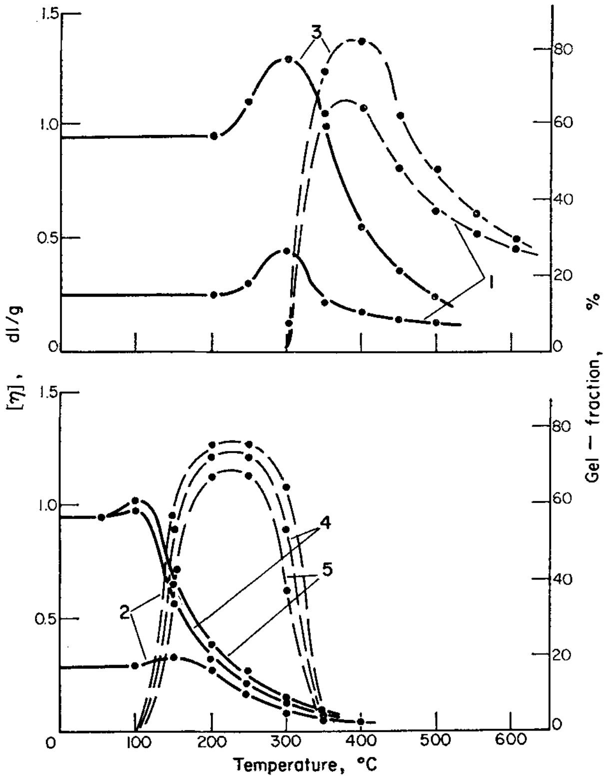


FIG. 8. Intrinsic viscosity (in benzene, full lines) and amount of precipitated gel-fraction (dotted lines) vs. the temperature for 4 hr destruction of PST (1), PSA (2) and PS containing additives of tetrabutoxytitanium (3), tributoxyaluminium (4) and aluminium acetylacetonate (5).

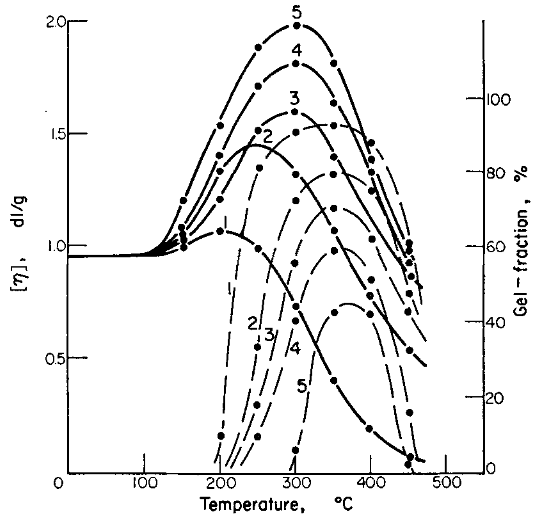


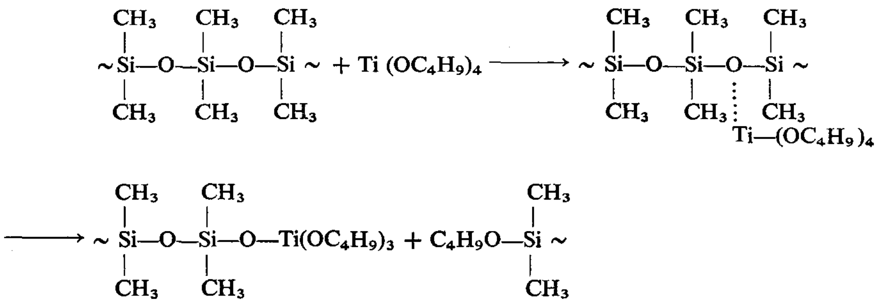
FIG. 9. Intrinsic viscosity (in benzene, full lines) and amount of gel-fraction (dotted lines) vs. the temperature for 4 hr degradation of PS containing additives of trihexoxyiron (1), iron acetylacetonate (2), iron acetate (3), iron carbonate (4) and iron oxide (5).

It was most clearly illustrated when structural changes in polyaluminium or polytitanium dimethylsiloxane were compared with those in PS stabilized by aluminium and titanium additives (Fig. 8). One may see that the same metals provide the same temperature of maximum intrinsic viscosities and they also give matching gelation curves. Such identity of two processes of crosslinking confirms our suggestion and testifies that new high molecular weight compounds, with structures and properties identical to those of corresponding polymetaldimethylsiloxanes, are produced by the interaction of PS macromolecules and metallic additives.

The chemical compositions of additives also influence to some extent the changes in structure of PS. As seen from curves of gel-formation and thermal degradation of PS with iron-containing additives (Fig. 9), the latter may be arranged according to decreasing ability to effect degree of crosslinking in the following order: alkoxy-derivatives > acetylacetonates > acetates > carbonates > oxides.

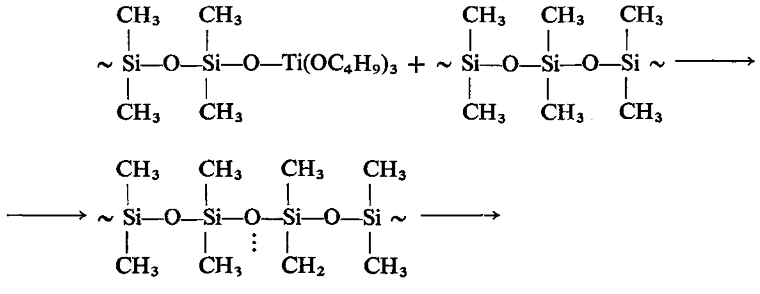
This may probably be explained by different reactivities of above derivatives.

The interaction of additives with the PS macromolecules during thermal ageing may be associated with reactions leading to cleavage of the siloxane chain and insertion of metal heteroatoms into the latter. The last fact was unequivocally supported by investigating some model process, for example the reactions of octamethylcyclotetrasiloxane or polydimethylsiloxane with tetrabutoxytitanium. Carrying out these reactions and maintaining the time–temperature conditions of thermal degradation experiments, we have prepared titaniumdimethylsiloxane polymer with the Ti–O–Si bond confirmed by the absorption band at 916 cm ^{1} in the i.r. spectrum and by elemental analysis of the polymer. Results obtained and those in the literature(24, 25) provide a basis for concluding that reaction of tetrabutoxytitanium with PS at elevated temperatures involves several stages, i.e. insertion of a titanium atom into the siloxane chain and formation of titaniumdimethylsiloxane polymer.



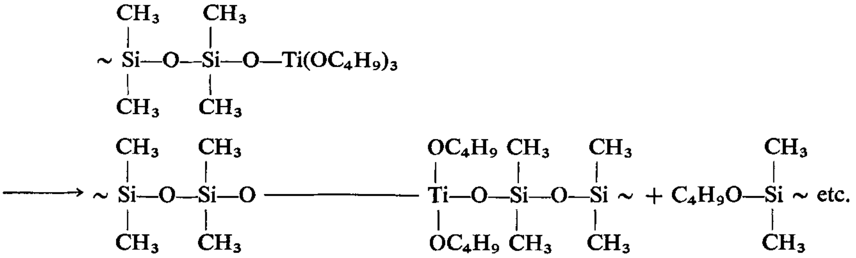
$$\sim\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}\sim + Ti(OC_4H_9)_4 \longrightarrow \sim\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3\,\vdots}{\overset{CH_3}{Si}}-O-\underset{\substack{CH_3\\ Ti-(OC_4H_9)_4}}{\overset{CH_3}{Si}}\sim \qquad (1)$$

$$\longrightarrow \sim\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-Ti(OC_4H_9)_3 + C_4H_9O-\underset{CH_3}{\overset{CH_3}{Si}}\sim$$



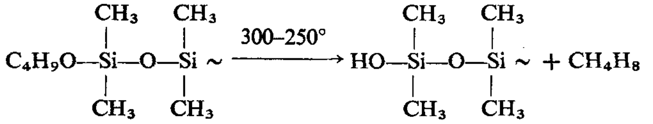
$$\sim\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-Ti(OC_4H_9)_3 + \sim\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}\sim \longrightarrow \qquad (2)$$

$$\longrightarrow \sim\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3\,\vdots}{\overset{CH_3}{Si}}-O-\underset{CH_2}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}\sim \longrightarrow$$

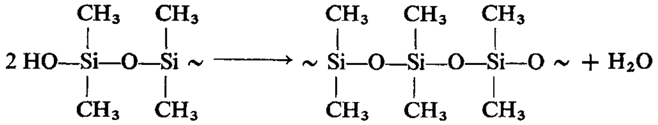


$$\sim\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-Ti(OC_4H_9)_3$$

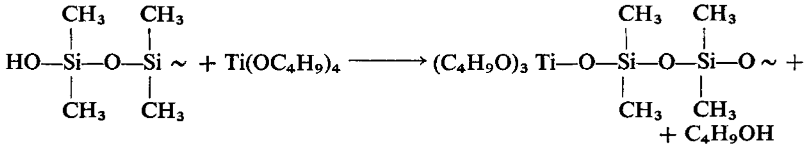
$$\longrightarrow \sim\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{OC_4H_9}{\overset{OC_4H_9}{Ti}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}\sim + C_4H_9O-\underset{CH_3}{\overset{CH_3}{Si}}\sim \text{ etc.}$$



$$C_4H_9O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}\sim \xrightarrow{300\text{–}250^\circ} HO-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}\sim + CH_4H_8 \qquad (3)$$



$$2\,HO-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}\sim \longrightarrow \sim\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O\sim + H_2O \qquad (4)$$



$$HO-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}\sim + Ti(OC_4H_9)_4 \longrightarrow (C_4H_9O)_3\,Ti-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O\sim + C_4H_9OH \qquad (5)$$

High temperature degradation of PS stabilized by metallic additives shows that the main volatile product responsible for weight loss was, as in case of non-stabilized polymer, a cyclic trimer (hexamethylcyclotrisiloxane) formed during cleavage of siloxane bonds in the main polymer chain. Moreover, detailed investigation of the volatile products evolved during destruction of stabilized polymer indicates the homolytic cleavage of Si–C and C–H bonds above 350° which was not the case for unstabilized polymer. This cleavage was indicated by the negligible evolution (down to 0·3 wt. per

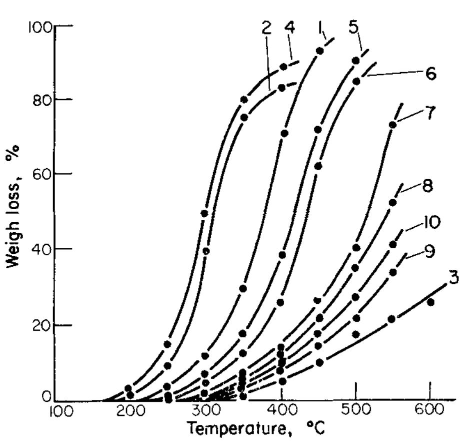


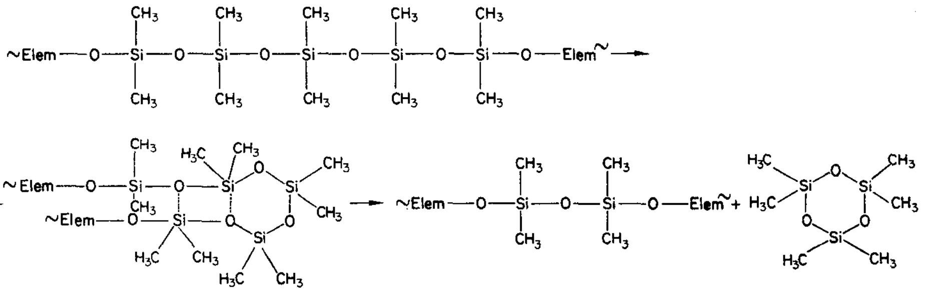
Fig. 10. Weight loss in 4 hr thermal degradation of PS (1), PSA (2), PST (3) and PS containing additives of acetylacetonates of aluminium (4), zinc (5), cobalt (6), copper (7), iron (8), zirconium (9) and tetrabutoxytitanium (10).

cent) of gaseous products, hydrogen, methane and ethane. The above homolytic cleavage should also occur during destruction of unstabilized PS. But owing to low thermostability, the latter depolymerizes before the accumulation of sufficient gaseous products for analysis.

The curves of weight loss (Fig. 10) of PS stabilized by organometallic additives, as well as those for some polymetaldimethylsiloxanes, indicate that, although Al and Zn organic derivatives do not notably increase the stability of PS, the compounds of transition metals markedly improve its stability. This implies the following order for heteroatoms able to increase the thermal stability of the polymer: Al < Zn < Co < Cu < Fe < Ti < Zr.

Thus, specific features of the destruction of PS stabilized by organometallic additives and polymetaldimethylsiloxanes, as well as their increased thermostability, testify that the changes in composition and structure of the polymer after introduction of heteroatoms into siloxane chain lead to changes in its depolymerization mechanism. This depolymerization may involve remaining unblocked terminal hydroxy groups; it may terminate on the nearest heteroatom and so not play a decisive role in the whole process. Hence, the cleavage of the cyclic trimer in this case proceeds through an activated complex having a structure different from that than in depolymerization involving terminal hydroxy groups.

Here we probably have a transition complex with activated Si–O bonds randomly occurring in any part of the chain. This results in cleavage of the chain between heteroatoms:



Employing the additivity principle, one may estimate an activation energy for generating the transition complex in certain cases. At an elementary act of cleavage of the cyclic trimer, there occurs the cleavage of two Si–O bonds (bond energy 89 Kcal/mol). Four activated Si–O bonds occur in the activated complex (bond energy 36 Kcal/mol). The activation energy will be $E = (89 \times 2) - (36{\cdot}5 \times 4) = 32$ Kcal/mol.

Experimental activation energies, from kinetic curves of weight loss in depolymerization of stabilized PS and polymetaldimethylsiloxane containing some metal heteroatoms (Table 5), are in good agreement with the calculated energy. This fact undoubtedly supports the mechanism suggested for depolymerization of dimethylsiloxane polymers containing metal heteroatoms in siloxane chain.

It should be noted that increase in activation energy of depolymerization with increasing molecular weight of non-stabilized PS (Fig. 6), i.e. with decreasing concentration of terminal hydroxy groups, may be explained by a smaller contribution from

TABLE 5. EFFECTIVE ACTIVATION ENERGIES OF DEGRADATION OF POLYTITANIUM DIMETHYLSILOXANE AND STABILIZED PS

Polymer	Additive	E.kcal/mol
PST	—	32·8
PS	Trihexoxyiron	30·5
PS	Tetrabutoxytitanium	32·4
PS	Zirconium acetylacetonate	33·0

depolymerization involving terminal groups in the total process and by a greater contribution from the random process.

The data on degradation of stabilized PS permit an estimate of the effect of some factors associated with the nature of metal heteroatoms introduced into the polymer on its thermal stability. A comparison of results obtained and chemical properties of heteroatoms shows that increasing functional and co-ordination abilities of the heteroatom decrease lability of siloxane chains and thus increase the thermal stability of

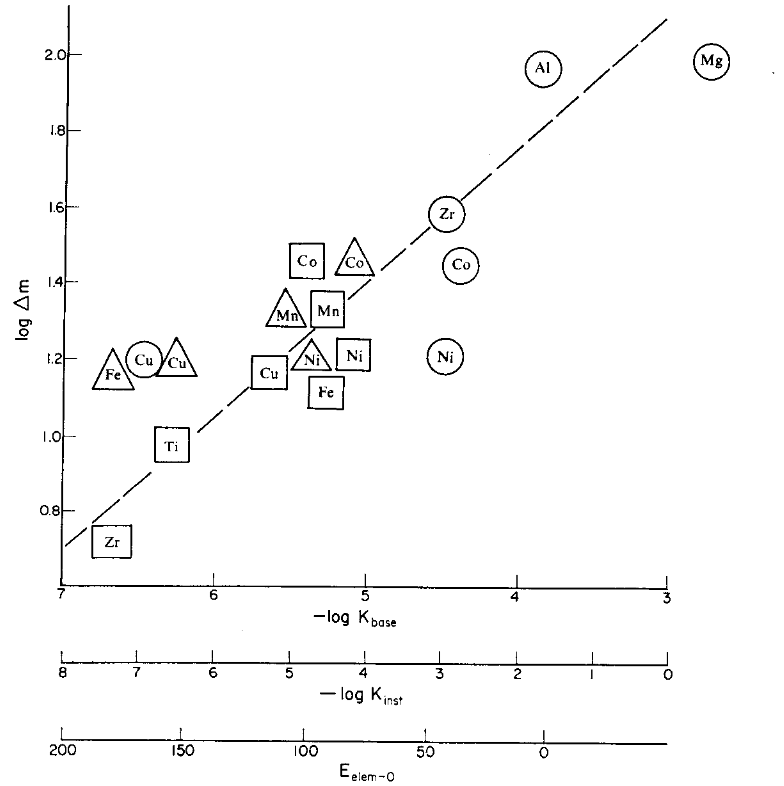


FIG. 11. Nature of heteroatom vs. thermal stability of polyelementdimethylsiloxanes. Δ*m*—weight loss of the polymers during 4 hr at 400° (wt. per cent).

$K_{bas.}$—dissociation constants of metal hydroxides (○)
$K_{instab.}$—instability constants of metal acetylacetonates (△)
$E_{elem.}$—heteroatom–oxygen bond energy (□)

polydimethylsiloxane. Increasing basic properties of heteroatoms on the other hand and lower bond energies between heteroatom and oxygen, decrease thermal stability of the polymer. This dependency is shown in a diagram (Fig. 11) where some tendency is apparent for the above criteria, characterizing the nature of metal heteroatoms introduced into the chain, to affect the thermal stability of PS.

REFERENCES

(1) W. Patnode and D. Wilcock, *J. Am. chem. Soc.* **68**, 258 (1946).
(2) C. W. Lewis, *J. Polym. Sci.* **33**, 153 (1958).
(3) C. W. Lewis, *J. Polym. Sci.* **37**, 425 (1959).
(4) M. Kučera, J. Lanicova and M. Jelinek, *J. Polym. Sci.* **53**, 301 (1961).
(5) M. Kučera, M. Jelinek, J. Lanicova and K. Vesely, *J. Polym. Sci.* **53**, 311 (1961).
(6) M. Kučera and J. Lanicova, *J. Polym. Sci.* **54**, 375 (1961).
(7) M. I. Hunter, E. L. Warrick, I. F. Hyde and C. C. Currie, *J. Am. chem. Soc.* **68**, 2284 (1946).
(8) I. K. Stavitski, B. E. Neymark, Z. M. Kryukovskaya, V. A. Kirichenko and V. N. Chumarova, Chemistry and Chemical Application of Organo-Silicon Compounds, U.S.S.R., **2**, 65 (1958).
(9) K. A. Andrianov, G. E. Golubkov, V. I. Yelinek, N. A. Kurasheva, M. F. Manucharova, L. F. Litvinova and B. K. Artemiev, *Vysokomolek. Soedin.* **7**, 680 (1965).
(10) K. A. Andrianov and A. V. Zhdanov, *Izv. Akad. Nauk SSSR*, Otd. Khim. Nauk 837 (1962).
(11) V. Crescensi and P. I. Flori, *J. Am. chem. Soc.* **86**, 141 (1964).
(12) S. A. Pavlova and S. R. Rafikov, *Vysokomolek. Soedin.* **1**, 387 (1959).
(13) I. V. Zhuravleva, V. V. Rodé and S. R. Rafikov, *Izv. Akad. Nauk SSSR*, Ser. Khim. 269 (1965).
(14) L. A. Dudina and N. S. Enikolopyan, *Vysokomolek. Soedin.* **4**, 869 (1962).
(15) N. Grassie, *Chemistry of High Polymer Degradation Processes*, Butterworths (1956).
(16) D. T. Hurd, *J. Am. chem. Soc.* **77**, 2998 (1955).
(17) K. A. Andrianov, *Organo-Silicon Compounds*, Goskhimizdat, Moscow (1955).
(18) H. W. Fox, P. W. Taylor and W. A. Zisman, *Ind. Engng Chem.* **39**, 1401 (1947).
(19) S. M. Ohlberg, L. E. Alexander and E L. Warrick, *J. Polym. Sci.* **27**, 1 (1958).
(20) F. B. Moin, *Dokl. Akad. Nauk SSSR*, **161**, 392 (1965).
(21) F. B. Moin, *Dokl. Akad. Nauk SSSR*, **152**, 1169 (1963).
(22) S. R. Rafikov, M. A. Verkhotin, V. V. Rodé and K. A. Andrianov, *Dokl. Akad. Nauk SSSR*, **175**, 1352 (1966).
(23) M. A. Verkhotin, K. A. Andrianov, A. A. Zhdanov, N. A. Kurasheva, S. R. Rafikov and V. V. Rodé, *Vysokomolek. Soedin.* **8**, 1226 (1966).
(24) K. A. Andrianov, Sh. V. Pichkhadze, V. V. Komarova and Ts. N. Vardosanidze. *Izv. Akad. Nauk SSSR*, Otd. Khim. Nauk, 833 (1962).
(25) B. N. Dolgov and Yu. N. Volnov, *Zh. obsch. Khim.* **1**, 330 (1931).