

HIGH TEMPERATURE STABILITY OF POLYSILOXANES

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Pronounced thermal and thermo-oxidative stability are among the most characteristic and at the same time the most technologically important properties of polysiloxanes, $-\text{[Si(R)(R')-O]}_n-$. In general, these polymers can withstand higher temperatures or longer exposures to a given temperature than most comparable organic counterparts.¹ For example, the temperature for the onset of irreversible thermal degradation of polydimethylsiloxane (PDMS), $-\text{[Si(CH}_3)_2\text{O]}_n-$, the parent polymer of the polysiloxane family and still the most commercially important “inorganic” polymer available, may reach to 300-400°C,^{2,3} which is by about 150-250°C higher than the degradation temperatures of most organic -C-C- type polymers, the stability of which can rarely exceed 150-200°C.

Coupled with exceptional elasticity at unusually low temperatures, this high temperature stability provides polysiloxanes with a unique combination of thermal properties that is one of the “trade-marks” of this polymer family. Since the glass temperatures of most alkyl-substituted polysiloxanes are below -70°C and may reach as low as -150°C, depending on the particular substituent groups pendant to the main $-\text{[Si-O]}_x-$ chain backbone,³ this makes these polymers extraordinarily good elastomers with at least 200-250°C wider temperature range of potential applicability than their “purely” organic competitors, the glass temperatures of which generally do not extend below -70°C, characteristic for natural rubber. Hence, polysiloxanes are polymers of choice whenever applications either within an unusually broad range of temperatures, or at unusually high or unusually low temperatures are required. Some of such applications include high temperature fluids or lubricants, sealants, gaskets or coatings for use in automotive, aero-space and naval industry, household appliances and metallurgy, high temperature insulation, chromatographic columns, electronics, etc.

General Features of Polysiloxane Degradation

Pronounced stability of polysiloxanes at elevated temperatures is a direct consequence of a specific interplay of some of their fundamental properties, including: (1) inherent strength of the siloxane (Si-O) bond,⁴⁻⁷ (2) pronounced flexibility of the $-\text{[Si-O]}_x-$ chain segments,^{3,8-11} and (3) entropically higher stability of the low molecular weight cyclic siloxanes than of their high molecular weight open chain counterparts at degradation temperatures.^{3,10}

The siloxane bond is very resistant to homolytic cleavage because of unique synergism of its partially ionic and partially double bond character.* Together, these fundamental properties of this linkage increase its dissociation energy into the range of 100-120 kcal/mol depending on the nature of organic substituents on the silicon.^{4,6} Since this energy is considerably higher than, for example, the corresponding energies of C-C bonds (82.6 kcal/mol), C-O bonds (85.5 kcal/mol), or $\text{C}_{\text{Arom}}-\text{C}$ bonds (98 kcal/mol), as shown in Table 1,¹⁰

*It has been well established that it is a serious oversimplification to consider the Si-O bond as a “simple” $p_\pi-d_\pi$ partially double bond (see for example Reference 6 for further explanation). However, for the purposes of discussing the pronounced high temperature stability of polysiloxanes this is a very convenient first approximation since it intuitively implies stronger bonds than the normal σ linkages and hence higher energies (i.e., temperatures) needed for its homolytic cleavage.

the Si-O bond can withstand exposure to higher temperatures than the bonds normally found in traditional organic polymers. As a consequence, polysiloxanes are as a class more thermally stable than their -C-C- counterparts.

However, inherent thermal stability of the Si-O bonds is countered by the characteristic flexibility of the $-\text{[Si-O]}_x-$ chain segments which enables relatively easy formation of local configurations that facilitate *inter-* and *intramolecular* siloxane redistribution reactions.⁷ These reactions, to which the Si-O bonds are prone due to their relatively high ionic character (usually about 50 %),¹² lead to fragmentation of their linear chains into the smaller cyclic structures that are volatile and thermodynamically more stable at degradation temperatures. As a consequence, this reduces the stability of linear polysiloxanes at elevated temperatures, and causes their actual thermal and/or thermo-oxidative breakdown to occur at temperatures that are lower than what would be expected based on their bond dissociation energies alone.¹⁰ The reasons for this are both thermodynamic (i.e., higher entropic probability of volatile cyclics than of open linear chains at degradation temperatures) and kinetic (i.e., facile formation of transition states that lead to the formation of cyclics), and they directly predetermine the reaction mechanisms by which these polymers undergo high temperature degradation.

In dynamic thermal gravimetric analysis (DTGA) in the absence of oxygen, polysiloxanes generally degrade by a single weight-loss step and without coloration of the residue. The characteristic temperatures of this process (such as the onset of degradation, the maximum rate of degradation, the end of degradation, etc.), depend primarily on the type of the polymer side groups and on the purity of the sample examined. On the other hand, the amount of residue at the end of the degradation process and the relative composition of the volatile degradation products evolved depend on the type of both polymer side-groups and end-groups. In contrast to this, thermo-oxidative degradation of the same polysiloxanes is generally a more complex process, and in DTGA it usually shows two weight-loss steps, leading to pure silica at temperatures above about 600°C. The amount of the resulting residue is usually smaller than what would be expected from the relative content of silicon in the original polymer sample due to the formation of volatile organosilicon degradation products.

Thermal Degradation and Stability of Polysiloxanes

On heating in inert atmospheres, linear polysiloxanes degrade into a mixture of low molecular weight cyclic oligomers that are volatile at degradation temperatures and that have the same chemical composition as the original polymer.^{3,10} In the case of PDMS, for example, this mixture consists of $[(\text{CH}_3)_2\text{SiO}]_n$ cyclics having the degree of polymerization (n) ranging from 3 to as high as 20, as shown in Figure 1.¹³⁻¹⁷ In addition, this degradation process often does not yield infusible residue, which suggests that its mechanism involves redistribution (i.e., splitting and reforming)¹² of the main chain Si-O bonds and not the scission of the Si-C or C-H bonds in the side groups, although the former are homolytically stronger than the latter. In fact, this degradation process represents a depolymerization reaction (shown in Reaction Scheme 1) for which the driving force is the higher thermodynamic stability of small dimethylsiloxane rings relative to that of their long open-chain linear counterparts at the degradation temperatures. It occurs quite readily because of the pronounced polarity of the Si-O bond¹² and flexibility of the $-\text{[Si-O]}_x-$ segments,⁹ either *intramolecularly* within a single polymer molecule, or *intermolecularly* between the two neighboring macromolecules,⁷ as shown in the Reaction Scheme 2.

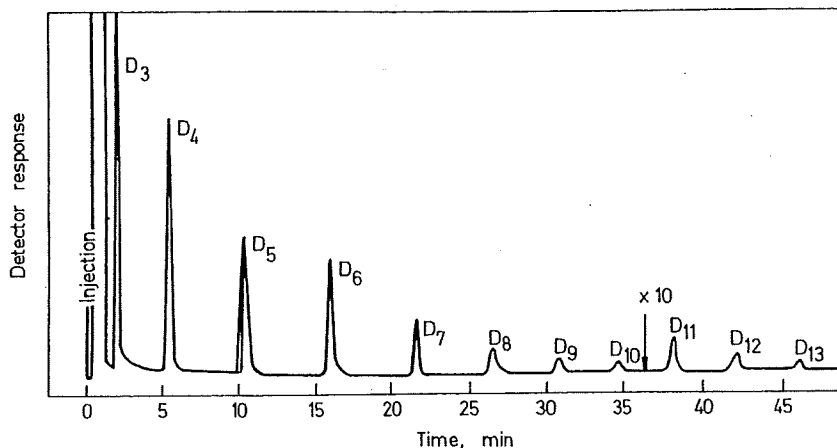
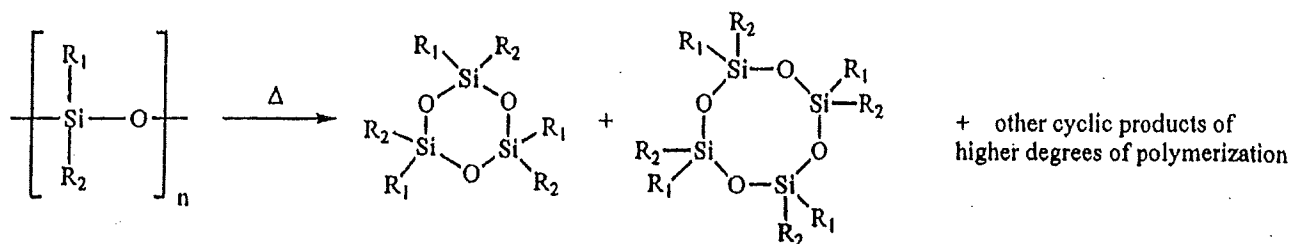
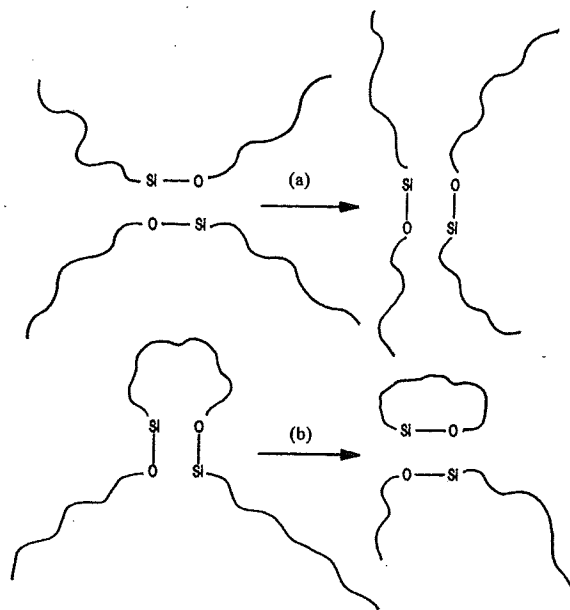


Figure 1:
 Typical GLC chromatogram of a mixture of volatile degradation products obtained from degradation polydimethylsiloxane at 500°C in inert atmosphere. D_x: denotes cyclic polydimethylsiloxanes with the degree of polymerization equal to x. (According to Reference 21.)



Reaction Schemes 1



Reaction Schemes 2

Intermolecular (a) and intramolecular (b) siloxane redistribution

However, although these general features are characteristic for all polysiloxanes, significant differences in degradation behavior may appear between different samples of compositionally identical polymers. These differences may involve the characteristic degradation temperatures (see Figure 2) as well as the type and the relative amounts of degradation products (see Table 2).^{3,10}

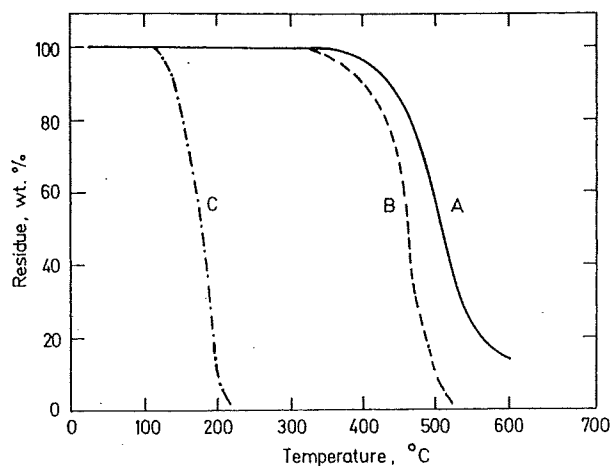


Figure. 2
 Typical DTGA traces of polydimethylsiloxane in nitrogen. Polymer with trimethylsilyl end-groups (A); with silanol end-groups (B) and with 5 % KOH added to sample B (C). (According to Reference 21.)

Figure 2

Table 2: Products of Thermal Degradation of Polydimethylsiloxane Under Different Heating Conditions

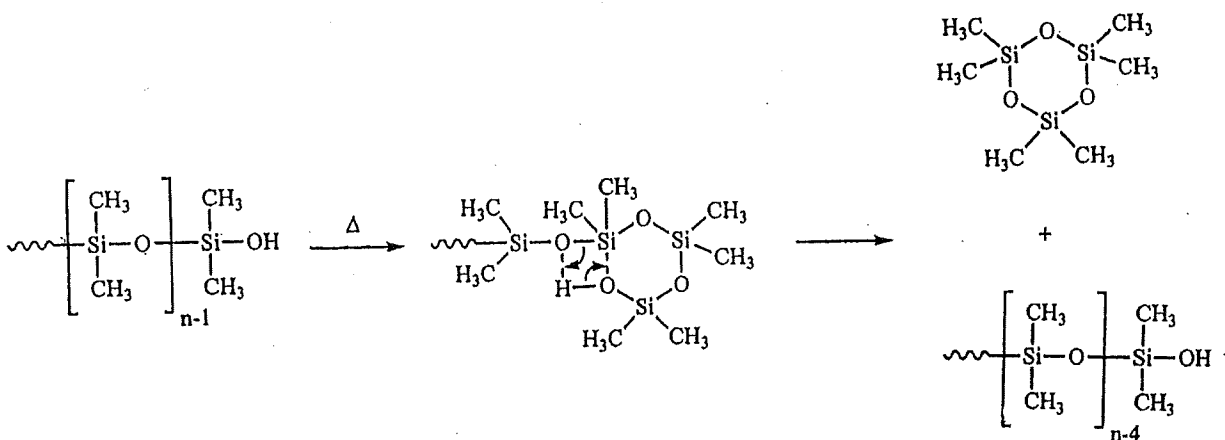
Product, DP	A	B	C	D	E
<i>Cyclic Siloxanes</i>					
3	73	61	56	51	44
4	13	22	23	20	23
5	4	10	8	7	10
6	6	11	9	9	11
7	1	7	3	6	7
8 and higher	1	5	0.3	6	5
<i>Linear Siloxanes</i>					
2				1	0.3
3					1

A: Grassie and MacFarlane: average values for temperature range 275-405°C in nitrogen (Reference 21).
 B: Kleinert and Weschler: from flash pyrolysis (Reference 31).
 C: Ballistreri et al.: from pyrolysis directly into the mass spectrometer (Reference 32).
 D: Zeldin et al.: trimethylsilyl-terminated polymer heated under reduced pressure (Reference 33).
 E: Thomas and Kendrick: trimethylsilylated polymer heated for 5 hours at 420°C under reduced pressure (Reference 20).

It has been established that the differences in degradation behavior of such samples result from two main factors: (1) the type and the relative concentration of polymer end-groups,² and (2) the purity of the examined sample (i.e., the presence or absence of even catalytic amounts of ionic impurities, including additives and/or residual polymerization catalyst).¹⁰ In fact, these factors are so important that they can completely change the mechanism (and hence the characteristic features) of the depolymerization process. As a consequence, polysiloxanes may degrade by three different reaction mechanisms, including: (1) the “unzipping” mechanism (proposed by Alexandrova¹⁸ and Rode¹⁹ in 1968-69); (2) the “random scission” mechanism (proposed by Thomas and Kendrick²⁰ in 1969); and (3) the “externally catalyzed” mechanism (proposed by Grassie and Macfarlane²¹ in 1978).

Mechanisms of Polysiloxane Thermal Degradation

Polysiloxanes containing either silanol (Si-OH) or hydroxyalkyl (Si-R-OH) end-groups depolymerize by “unzipping” degradation mechanism.¹⁸ Because of pronounced inherent flexibility of the $-\text{[Si-O]}_x-$ chain segment, these end-groups can “back-bite” their own polymer molecules to initiate an *intramolecular* exchange or rearrangement that results in the formation of low molecular weight cyclic species, as shown in the Reaction Scheme 3.



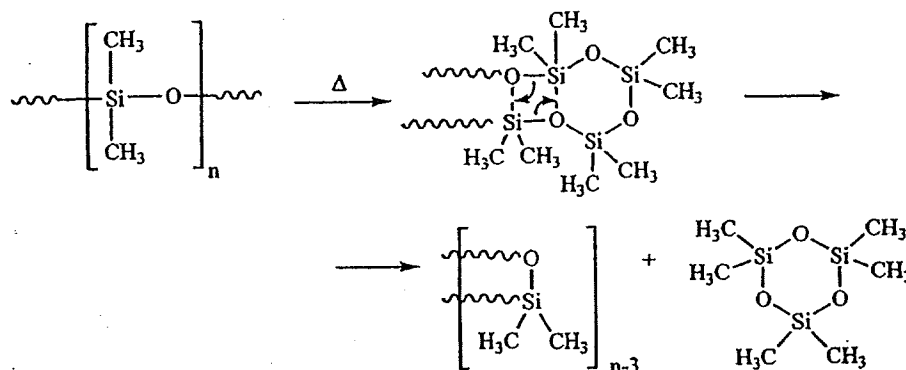
Reaction Scheme 3: The unzipping mechanism

The trimeric and tetrameric cyclosiloxanes (i.e., $x = 3$ and 4 , respectively) are the most prominent products of this fragmentation because they are the most thermodynamically stable species at the degradation temperatures and their evaporation adds an additional driving force for the completion of the degradation process. In addition to this, depolymerization from the chain-ends leads to complete annihilation of the original polymer macromolecules (i.e., there is no non-volatile residue left at the end of the process, see Table 2),¹⁰ and it does not involve any change in chemical composition of the resulting products relative to that of the starting polymer. As the polymer is heated, its molecular weight first sharply increases with activation energy of about 8.5 kcal/mol, which is typical for the silanol condensation reactions and hence indicative of an *intermolecular* reaction between the polymer chain ends. This reaction reaches its maximum intensity at about 250-260°C, above which the depolymerization takes over, as manifested by the subsequent decrease in the polymer

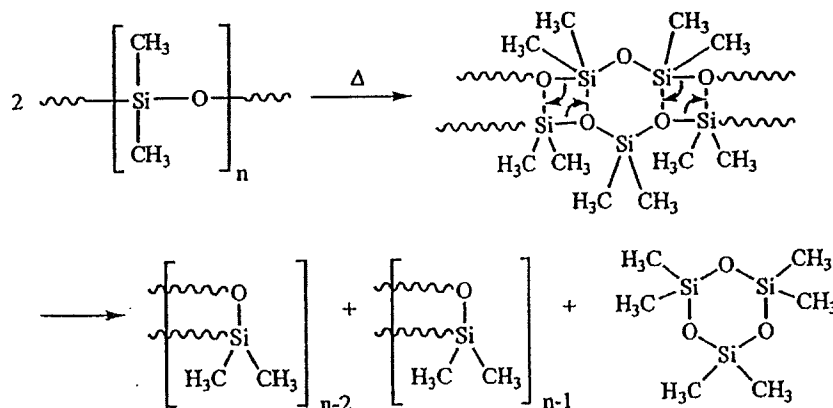
molecular weight and formation of the volatile cyclics.²¹ This decrease of polymer molecular weight is linear with the extent of volatilization, consistent with a stepwise nature of the process of volatiles formation and generally characteristic for the unzipping reaction mechanism.

Since the necessary requirement for *intramolecular* depolymerization of polysiloxanes by unzipping is the presence of either silanol or Si- R-OH end-groups, the end-capped derivatives cannot undergo degradation in this manner. Instead, they degrade by either *inter-* or *intramolecular* siloxane redistribution reactions that occur randomly between the siloxane bonds located inside the polymer chains and proceed through the formation of intermediate four-center transition states yielding volatile cyclic siloxanes as shown in the Reaction Scheme 4.^{20,22}

(a) *Intramolecular depolymerization:*



(b) *Intermolecular depolymerization:*



Reaction Scheme 4: The random scission mechanism

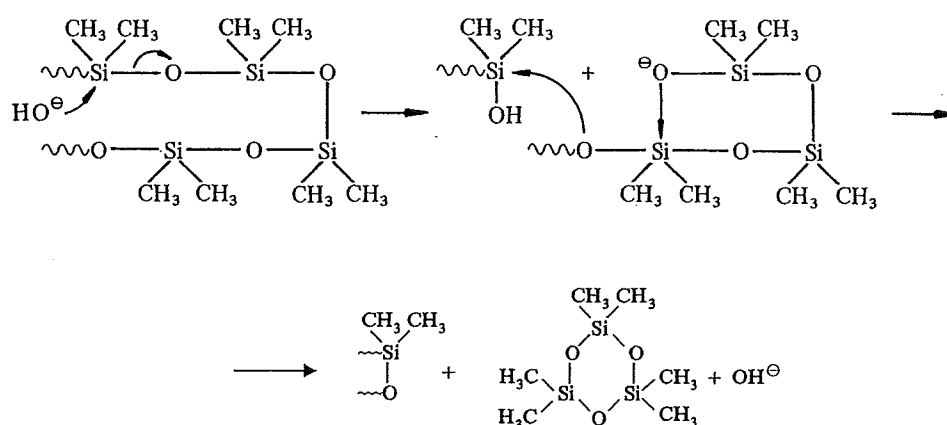
Because this process is controlled by polymer chain flexibility and kinetic factors, it has surprisingly small activation energy, which, depending on particular degradation conditions, usually ranges between 35 and 45 kcal/mol,^{23,24} that is not even a half of energy required for the homolytic cleavage of the siloxane bond (see Table 1).¹⁰ In addition, this type of redistribution reactions may occur at any point within the polymer chain where a temporary kink or loop may be formed (see Reaction Scheme 2), and it does not require the presence

of reactive end-groups (as is the case with the unzipping mechanism), nor of ionic impurities (as is the case with the externally catalyzed one). Instead, these reactions only require: (a) sufficient flexibility of the polymer chain segments; (b) high polarity of the siloxane bonds; and (c) higher thermodynamic stability of the degradation products (i.e., small molecular weight cyclosiloxanes) than that of the reagents (i.e., open-chain macromolecules) at degradation temperatures. Since all these requirements perfectly match all fundamental characteristics of polysiloxanes, the random scission mechanism is always possible when these polymers are exposed to high enough heat, and it is, therefore, their most general degradation mechanism regardless of the fine structure (i.e., capped or non-capped chain ends, specific side groups, etc.) and actual degree of sample purity.

In a clear contrast to unzipping, the random scission mechanism results in a dramatic decrease of polymer molecular weight from the very onset of the degradation process and in simultaneous broadening of molecular weight distribution. Both effects are typical for a random process and are caused by the fact that the most probable location for the occurrence of random scission is towards the middle of polymer chains. As a consequence, a several million molecular weight PDMS may break down into an only several hundreds of thousands molecular weight sample after losing less than one third of its original weight.²⁰ In addition to this, in the later stages of degradation, measurable quantities of *bistrimethylsilyl* terminated low molecular weight linear compounds (such as siloxane dimers or trimers; see Table 2), may also form from the capped chain ends of the original polymer which cannot participate in the ring-closure reactions.

Yet another mechanism was proposed²¹ for thermal degradation of polysiloxanes that contain ionic or polar impurities or additives, even in very small amounts.^{16,17,23,24} In contrast to the previous two, this mechanism involves heterolytic cleavage of the Si-O backbone bonds by foreign species, which initiate the degradation process as shown in Reaction Scheme 5.²¹

(a) activation by anionic species

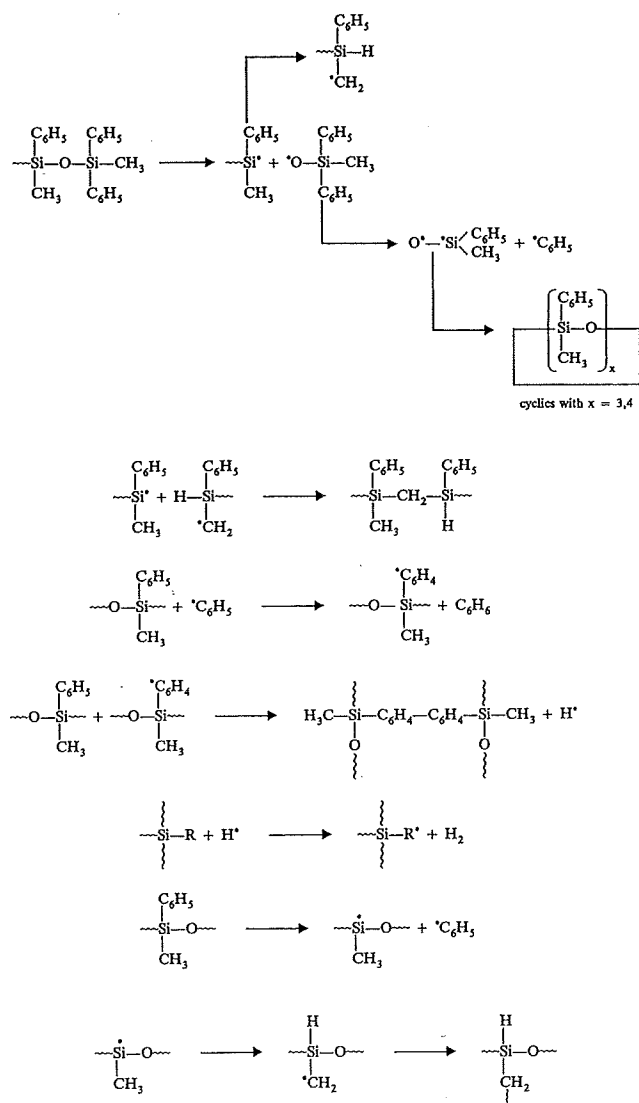


(b) activation by cationic species

Reaction Scheme 5: The externally catalyzed mechanism

Expectedly, the activation energy for such degradation process is very low (i.e., ranging between 5-15 kcal/mol),^{25,26} and the onset of the polymer weight loss may start already at 100-120°C, if, for example, only 5 wt. % of a base, such as KOH, is present in the sample.²¹ Like random scission, this mechanism is also not limited by the nature of the polymer end-groups, but it frequently yields unusual by-products (such as methane),^{18,27} which result from reactions that form linked cyclosiloxanes.¹⁰ In fact, the presence of ionic impurities in polysiloxanes may completely ruin one of the most characteristic and desirable properties of these polymers: their high temperature stability, and that is why only well purified samples (without even trace amounts of acidic or basic impurities, including the left-over polymerization initiators) should be considered for high temperature applications.

In contrast to polyalkylsiloxanes, phenyl substituted polysiloxanes yield above about 450°C relatively large amounts of insoluble and gaseous degradation products.²⁸ It is believed that these polymers degrade in two stages: (1) at lower degradation temperatures (i.e., below about 450°C) they undergo the same type of siloxane redistribution reactions as those occurring in PDMS, while (2) above this temperature, the scission of the phenyl groups from the main chains begins to predominate. The latter results in the formation of free radical species that subsequently onset a variety of different cross-linking reactions that produce the observed degradation products as illustrated in the Reaction Scheme 6.^{10,28}



Reaction Scheme 6

Thermo-oxidative Degradation and Stability of Polysiloxanes

When subjected to heat in the presence of air or oxygen, polysiloxanes oxidize through natural tendency of silicon to bond with oxygen and form pure silica at the end of the oxidation process. In a typical DTGA experiment, this is usually manifested as a two-step weight loss process, in which the first step generally starts at temperatures that are very similar to those encountered in the purely thermal degradation in inert atmospheres, while the second onsets at about 350°C, and is characterized by an activation energy of about 20-30 kcal/mol^{21,29} (see Figure 3).

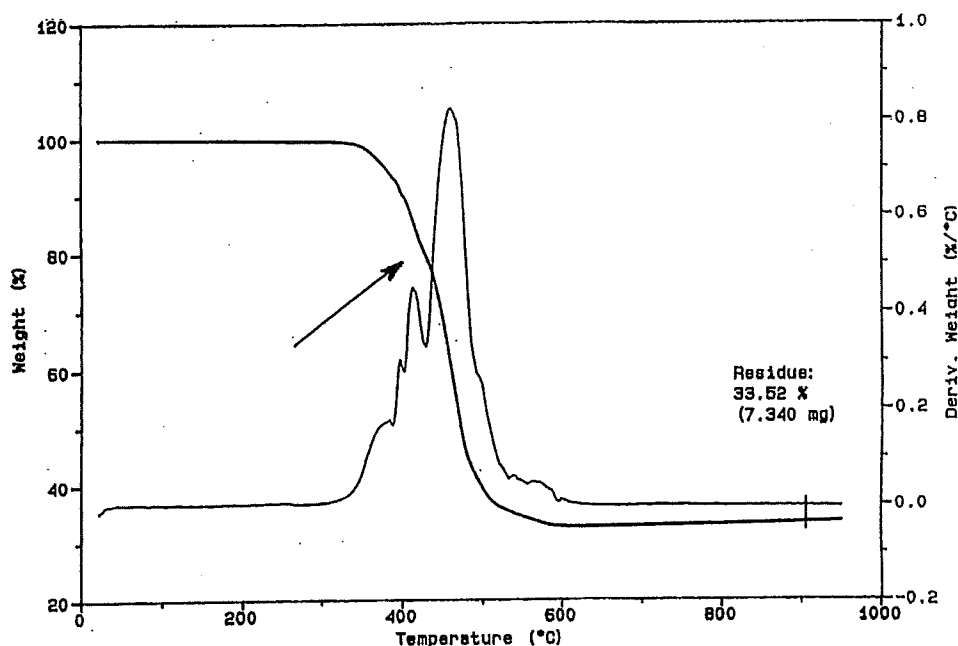
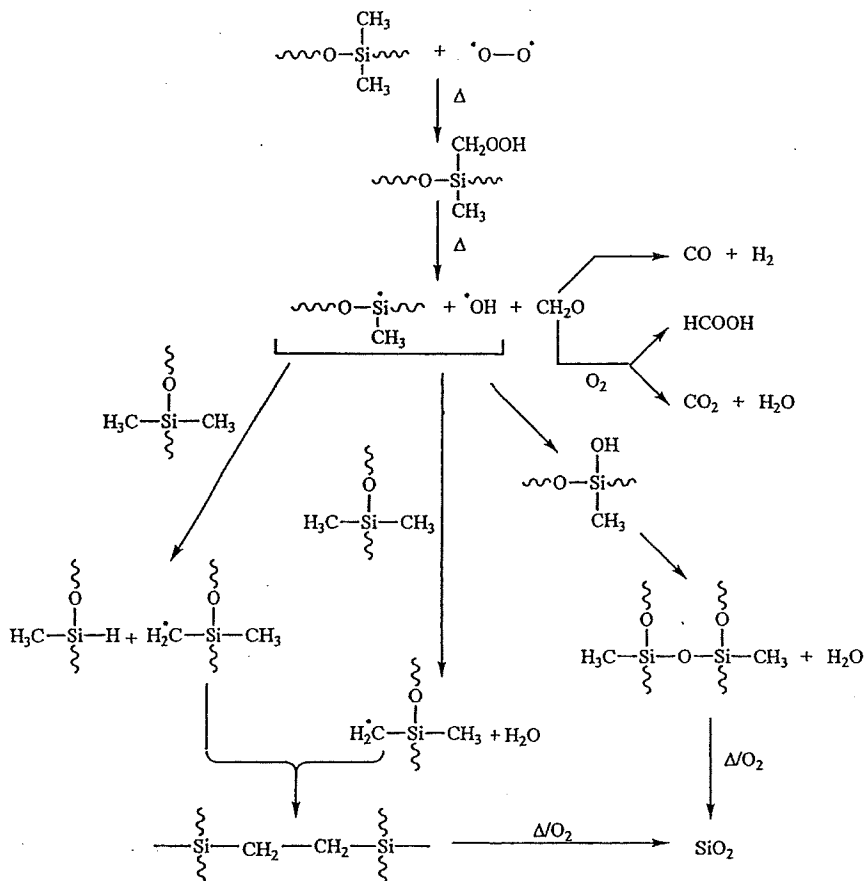


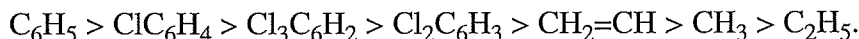
Figure 3:
Typical DTGA trace of trimethylsilyl-terminated polydimethylsiloxane in air. Heating rate was 15°C/min. Arrow points to the knee in the curve where the first degradation step ends and the second step begins.

In the early stages, this degradation is believed to occur through the formation of side-chain peroxides, followed by the splitting of the polymer side groups, so that, in the case of PDMS in air, for example, about 12% of the -CH₃ groups are lost after about five hours at 300°C (as judged by the decrease of the carbon to silicon ratio from 2:1 in the original sample to 1.74:1 in the degraded product).³⁰ With further increase in temperature, this process accelerates, and only about 15% of the original -CH₃ groups are still retained at about 350°C. In sharp contrast to purely thermal degradation, the volatile products of this thermo-oxidative process do not contain cyclosiloxanes at all, but instead they typically consist of: CO (about 25%), H₂O (about 17%), CH₂O (about 4%), CO₂ (about 2%), methanol and traces of formic acid. As the degradation progresses, the structure and composition of the residue change, resulting in pure SiO₂ above about 600°C. To account for all these observations, a free radical mechanism (shown in Reaction Scheme 7), was proposed by Andrianov to occur below about 350-400°C,³⁰ followed by the siloxane redistribution reactions at higher temperatures.



Reaction Scheme 7

In agreement with this mechanism, the thermo-oxidative stability of polysiloxanes is predominantly determined by the nature of their side groups, and the following order of stability has been established:²⁸

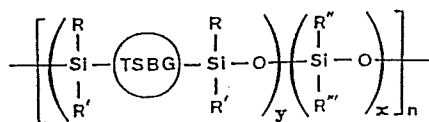


When used in air, polysiloxanes normally retain their flexibility for thousands of hours at temperatures of up to about 200°C, or for several hours at 220°C. The loss of flexibility marks the onset of cross-linking reactions, which prevent or greatly reduce the loss in polymer molecular weight and formation of volatile degradation products at these temperatures.³⁰ Hence, in contrast to many organic counterparts, polysiloxanes do not abruptly deteriorate at elevated temperatures in air, but instead they undergo a gradual reduction of mechanical properties over a period of time.

High Temperature Siloxane Polymers

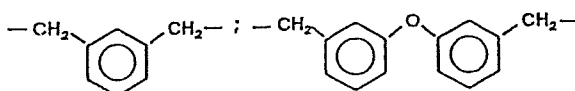
In attempts to further improve thermal stability of polysiloxanes while still retaining their highly desirable low temperature flexibility, many investigations have been directed at various siloxane-containing derivative polymers.¹⁰ The most successful efforts resulted from polymers with thermally stable bulky groups (see Figure 4) incorporated into the polysiloxane backbone chains, wherein such groups were expected to prevent or at least greatly reduce the formation of cyclic degradation products (see Reaction Scheme 1) by imposing severe steric hindrance to the ring closure by any of the above described depolymerization mechanisms.

Generalized Polymer Structure:

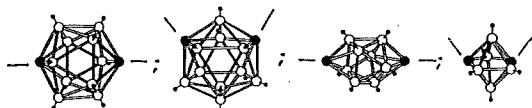


TSBG Thermally Stable Bulky Group: Ar; R-Ar-R; C_{B_q}H_qC

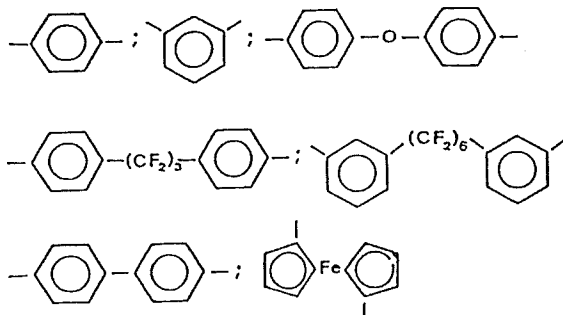
I, Silalkarylene-Siloxane Polymers, R-Ar-R:



II, Carboranylene-Siloxane Polymers, C_{B_q}H_qC:



III, Silarylene-Siloxane Polymers, Ar:



Side Groups, R, R', R'':

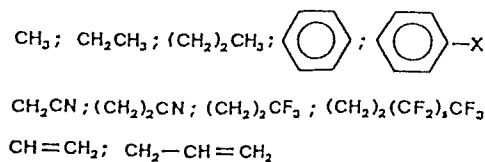


Figure 4:
High temperature siloxane polymers with thermally stable bulky groups in the main chain.

Among the investigated polymers, the best results were obtained from silalkarylene-siloxane, I, carborane-siloxane, II, and silarylene-siloxane, III derivatives of Figure 4, of which the last mentioned ones showed the best combination of properties, availability and relative ease of preparation.¹⁰ Among them, the optimal combination of low and high temperature properties have been obtained from the polymers with alternating silarylene and siloxane building blocks in the main chain backbone, that is from those with aromatic units in place of every third oxygen atom of the parent polysiloxane chain.³⁴⁻³⁶ Several such polymers (especially those containing *m*-phenylene,³⁷ *p*-phenylene³⁸⁻⁴⁰ or *p,p'*-diphenyl ether³⁸⁻⁴⁰ aromatic groups) were found not to exhibit substantial weight loss in DTGA until about 450°C regardless of the nature of degradation atmosphere (see Figures 5 and 6), and not to lose more than 5 % of the original weight on isothermal heating for 5 hours

at 400°C in nitrogen or at 255°C in air. This is clearly a significant improvement over PDMS which under comparable heating conditions loses almost 90 % of its original weight in nitrogen and over 20 % in air.⁴¹ In addition to this, some of the silarylene-siloxane polymers (especially the *p*- and *m*- phenylene derivatives), retain their glass temperatures below -60°C,³⁹ thus extending the range of possible application temperatures by well above 100-150°C relative to that of PDMS.

A variety of different mechanisms has been proposed for degradation of silarylene-siloxane polymers, from a rather simple one that is analogous to the depolymerization of PDMS and involves siloxane segments that connect the neighboring aromatic groups,⁴² to quite complex thermo-chemical schemes that involve more than one, temperature-dependent degradative process.^{10, 43-50} The latter were generalized in a three-stage degradation mechanism¹⁰ which onsets with the reactions in the polymer side groups that result in the formation of observed gaseous products (such as H₂, CH₄, CH₃CH₃, CH₂=CH₂, CO),^{43,44} continues through *intra*- and/or *intermolecular* siloxane exchange reactions that lead to the formation of cyclic dimethylsiloxanes and polymer backbone rearrangement (at temperatures up to about 350-400°C)⁴⁵ and finally ends with the silarylene bond cleavage¹⁰ which starts a complex network of free radical reactions that yields to chain branching and eventual cross-linking into insoluble, infusible degradation residue. Although such complex, high energy, thermo-chemical processes are quite difficult to study and often open to subjective interpretation, the silarylene-siloxane polymers (particularly those with alternating arrangement of the constitutive building units) clearly represent the most promising precursors for high temperature elastomers. The main obstacle to their larger scale production, however, still remains the need for metal-involving reactions in the synthesis of necessary monomers.¹⁰

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