Autoxidation of Poly(hydrosilane)s

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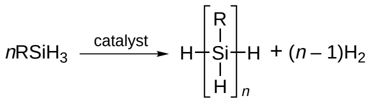
Poly(hydrosilane)s obtained by dehydrocoupling of the corresponding $RSiH_3$ were found to be air sensitive. Analyses based on GPC, IR, and heterocorrelated $^{1}H-^{29}Si$ NMR indicate the formation of some siloxane-type structures on the polymer backbone. Kinetic studies carried out by EPR spectroscopy using fusinite as a paramagnetic probe of the oxygen concentration allowed the oxidizability of some polysilanes to be obtained. Oxidizability values of 1.2×10^{-2} and 1.8×10^{-2} $M^{-1/2}$ $s^{-1/2}$ were found for poly(*n*-hexylsilane) and poly(phenylsilane), respectively. Model studies on the oxidation of $(Me_3Si)_2Si(H)Me$ with a mixture of $^{16}O_2$ and $^{18}O_2$ suggest that the main reaction path proceeds via a free-radical chain mechanism and involves either two or three consecutive, unimolecular steps. Poly(hydrosilane)s react with nitroxides (TEMPO) under free-radical conditions and in the absence of molecular oxygen to give the corresponding amine in good yields.

Introduction

Polysilanes, whose backbones consist entirely of silicon atoms, have been shown to possess a number of interesting chemical and physical properties which have enormous potential for technological use.[1] For example, polysilanes may exhibit chromotropic behavior such as thermochromism,[2] electrochromism,[3] piezochromism,[4] or solvatochromism[5] as well as photoreactivity[6] and liquid crystalline properties.[7] Nonlinear optical and semiconductive properties, such as high hole mobility,[8] photoconductivity,[9] and electrical conductivity,[10] have been investigated in some detail. These properties have been attributed to the extensive delocalization of σ-electrons along the silicon backbone.[1]

Among the most common synthetic procedures for polysilanes is the Harrod-type dehydrogenative coupling of $RSiH_3$ in the presence of group 4 metallocenes (eq 1).[11] Most of the work to date has been limited to



$$n\text{RSiH}_3 \xrightarrow{\text{catalyst}} \text{H}{-}\left[\overset{\text{R}}{\underset{\text{H}}{\text{Si}}}\right]_n{-}\text{H} + (n-1)\text{H}_2 \qquad (1)$$

phenylsilane and has been carried out in the laboratories of Harrod,[12,13] Tilley,[14] and Corey.[15,16] With the exception of methylsilane,[17] which is particularly active

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in dehydropolymerization, alkylsilanes are much less reactive than phenylsilane.[18]

One of the characteristics of the product obtained by reaction 1 is the presence of Si−H moieties, hence the name poly(hydrosilane)s. The bond dissociation energy of the Si−H bond is relatively weak when silyl groups are attached at the silicon atom.[19] Therefore, poly(hydrosilane)s are expected to exhibit rich radical-based chemistry.[20] Waymouth and co-workers[21,22] reported the reaction of CCl_4, CBr_4, cyclohexanone, valeraldehyde, and a number of alkenes with poly(phenylsilane) under free-radical conditions.[23] We have shown that poly(hydrosilane)s are effective hydrogen donors toward alkyl radicals, qualifying them as good radical-based reducing agents.[24] Silyl radicals obtained from these polysilanes add to a variety of substrates containing double bonds to give the corresponding adducts for which EPR spectra have been recorded.[24]

The importance of poly(hydrosilane)s in radical chemistry is manifested in their applications as processing stabilizers for organic polymeric materials subject to oxidative degradation.[25] The degradation of polyolefins during processing takes place by a widely accepted free-radical mechanism. The ability of poly(hydrosilane)s to stabilize polypropylene during multiple extrusion is a relevant observation.[25] The effectiveness of hydrogen donation of these polysilanes is not expected to be the only reason for this phenomenon. Poly(hydrosilane)s obtained by dehydrocoupling of the corresponding $RSiH_3$ were found to be air sensitive in our laboratories.[26−29] In this paper, we report our investigation of the reactions of poly(hydrosilane)s and model compounds with molecular oxygen. We believe that this radical chain reaction has a great importance in the use of poly(hydrosilane)s as processing stabilizers of polyolefins.

Results and Discussion

Reaction of Poly(phenylsilane) with Air. Poly(phenylsilane) was prepared by a partial modification of the procedure of Harrod and co-workers.[13] To an anhydrous toluene solution of Cp_2ZrMe_2, prepared in situ at −65 °C, the silane was added over a period of ca. 30 min at 0−5 °C, and then the mixture was stirred at room temperature for ca. 2 days. The crude mixture was dissolved in toluene, and the solution was stirred for 1 h with Tonsil.[30,31] Filtration followed by removal of the solvent gave the desired pure material. GPC analysis of the poly(phenylsilane) showed a typical bimodal distribution with 17% of low molecular weight and 83% of high molecular weight peaks ($M_w = 2340$, $M_w/M_n = 1.72$ against a polystyrene standard). Broad featureless signals in the range from 3.9 to 5.0 ppm are shown in the ^1H NMR spectrum of this material.[11e] The ^{29}Si INEPT spectrum displays a set of overlapping bands in the range from −52 to −68 ppm.[32] The heterocorrelated $^1H-^{29}Si$ HMQC spectrum is given in Figure 1a.[33] The typical Si−H stretching vibration at 2104 cm^{-1} and the SiH_2 bending vibration at 915 cm^{-1} are revealed in the IR spectrum.[11]

A solution containing 2 g of poly(phenylsilane) in 10 mL of xylene was refluxed for 12 h in a system exposed to the air. After removal of the solvent, the remaining material was analyzed. GPC analysis indicated a bimodal distribution with 47% of low molecular weight and 53% of medium molecular weight peaks ($M_w = 1850$, $M_w/M_n = 1.97$ against a polystyrene standard). Therefore, only minor changes can be observed by GPC. On the other hand, the intense absorption band around 1050 cm^{-1} and two absorptions at 2170 and 2111 cm^{-1} (Si−H stretching) found in the IR spectrum of the product are characteristic of siloxanes containing a Si−H bond.

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(27) It is worth poiting out that the autoxidation of oligo- and polysilanes is almost unexplored. Strained cyclic oligosilanes, when not self-protected by steric hindrance, react spontaneously with atmospheric oxygen to give siloxane products. The reaction of molecular oxygen with oligosilanes having larger ring sizes and with linear polysilanes, both having two organo substituents on the silicon atoms, seems to be unimportant. For a review, see: Hengge, E.; Janoschek, R. *Chem. Rev.* **1995**, *95*, 1495−1526.

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(30) Celite diatomite (Tonsil) is a light, siliceous, friable deposit derived from the remains of diatoms. It can be used as a filter aid and an absorbent and was purchased from B. H. Schilling S.p.A.

(31) Radical-based degradation of poly(hydrosilane)s coupled with purification methodologies have been carried out in our laboratories (Chatgilialoglu, C.; Siskos, M.; Barbieri, A. Manuscript in preparation).

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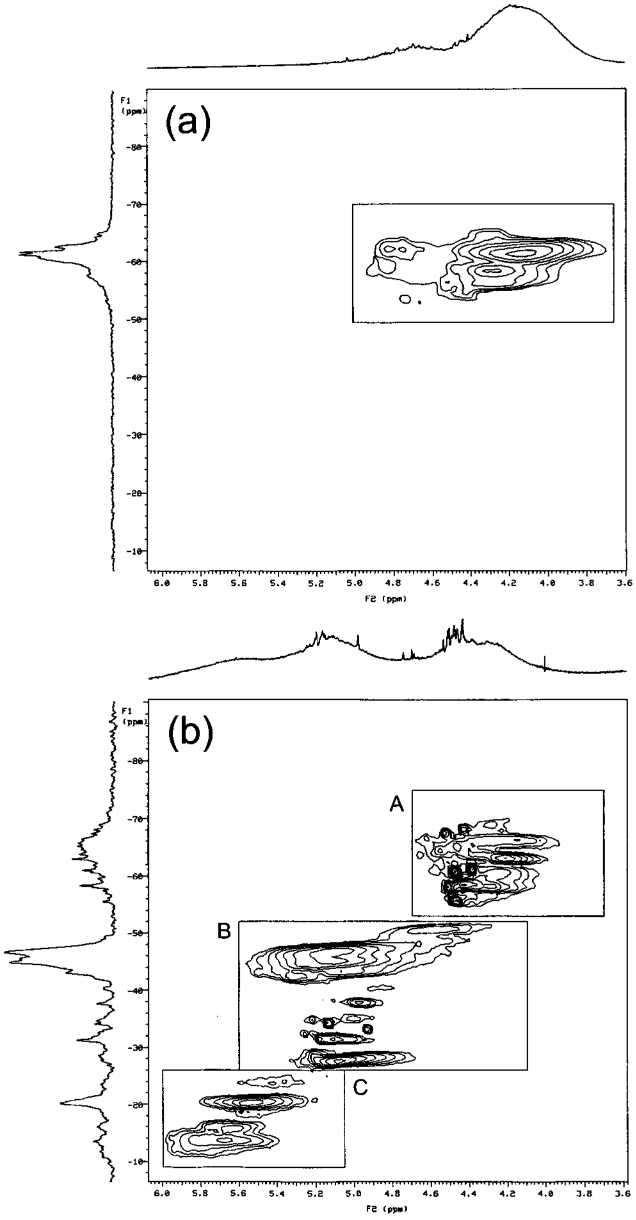


Figure 1. Expanded region of the ^{1}H-^{29}Si HMQC spectra (a) poly(phenylsilane) and (b) oxidized material.

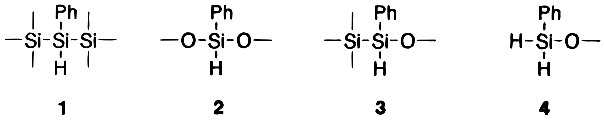
Further indications regarding a siloxane structure derive from detailed NMR analysis. In particular, the product was examined by means of ^{1}H NMR, ^{29}Si INEPT, and ^{1}H-detected ^{1}H−^{29}Si HMQC spectroscopies. In both the ^{1}H and ^{29}Si INEPT spectra, the resonance regions are wider than those of the starting poly(phenylsilane). The ^{1}H spectrum shows broad featureless signals in the range from 3.5 to 6.0 ppm, whereas the ^{29}Si INEPT spectrum displays broad signals around −66 ppm and in the range from −16 to −52 ppm. The ^{1}H and ^{29}Si resonances may be delineated in clearly separated regions by means of heterocorrelated ^{1}H−^{29}Si HMQC spectroscopy.[33] The results are shown in Figure 1b and tabulated in Table 1, and the structural units are labeled in Scheme 1. The region A is present in both the starting material and the oxidized product (cf. Figure 1a and b) and, therefore, can be assigned to the units **1**. On the basis of literature data,[34] the regions B and C can be assigned to units **2** and (**3** + **4**), respectively. The relative integrated volumes of these regions are reported in Table 1. On the basis of this analysis, the integral ratio between cumulated regions B and C and region A may give an estimate of the degrees of oxidation. In our experiment, we found this ratio to be 1:2.7, which suggests that the environment around ca. 70% of the catenated silicons was altered.

Table 1. Resonance Reprints and Integrated Volumes in Heterocorrelated ^{1}H−^{29}Si HMQC Spectra of Starting Material (SM) and Oxidized Material (OM)

				integrated volumes	
reprints	units[a]	$\Delta\nu(^1H)$, ppm	$\Delta\nu(^{29}Si)$, ppm	SM	OM
A	**1**	3.7−5.0	−75 to −53	1.0	1.0
B	**2**	4.1−5.6	−52 to −26	0.0	2.0
C	**3**, **4**	5.0−6.0	−26 to −9	0.0	0.7
(B + C)/A					2.7

[a] For the structural definition of units, see Scheme 1.

Scheme 1



Reaction Mechanism Based on a Model Compound. The simplest model compound that represents the skeleton of poly(hydrosilane) has been identified as silane **5** (eq 2). That is, the Si−H moiety is bonded to

$$\underset{\mathbf{5}}{(Me_3Si)_2Si(H)Me} + O_2 \rightarrow (Me_3SiO)_2Si(H)Me \quad (2)$$

two silicon atoms and to a methyl group. This silane does not react spontaneously with air or molecular oxygen at room temperature. However, a reaction takes place at 80 °C when air or molecular oxygen is bubbled into the pure material or its solutions to form a major product (eq 2), which was identified by comparison with an authentic sample together with other minor ones.[35] In general, yields of $(Me_3SiO)_2Si(H)Me$ are about 50%, although the percentages of conversion and yield depend on the experimental conditions. The fact that the reaction is retarded by common inhibitors, e.g. 2,6-di-*tert*-butyl-4-methylphenol, suggests a free-radical chain reaction. Tetrakis(trimethylsiyl)silane cannot be oxidized under the same conditions. This also suggests that reaction 2 occurs by a free-radical mechanism rather than by direct insertion of an oxygen molecule on the Si−Si bond followed by a molecular rearrangement.

The mechanisms that we conceive for reaction 2, following the fundamental concepts of free-radical chemistry, are outlined in Schemes 2 and 3 and are termed *intermolecular* and *intramolecular*, respectively.[20,36] By *intermolecular* mechanism, we imply that the two

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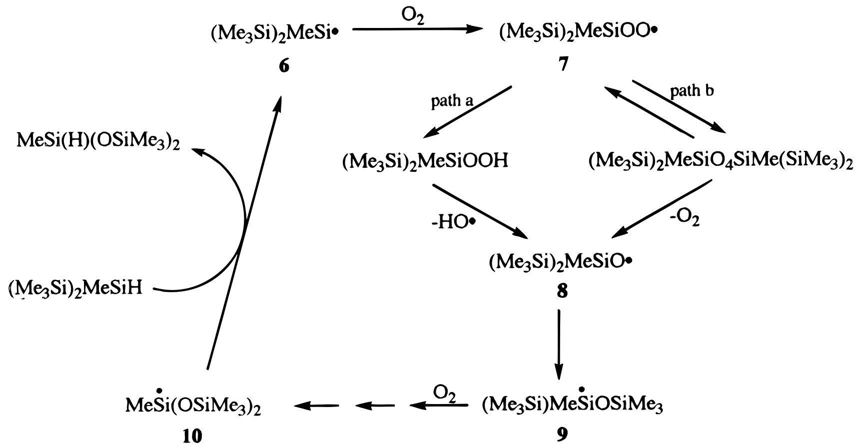
(34) Williams, E. A. *Annu. Rep. NMR Spectroscopy* **1983**, *15*, 235−289.

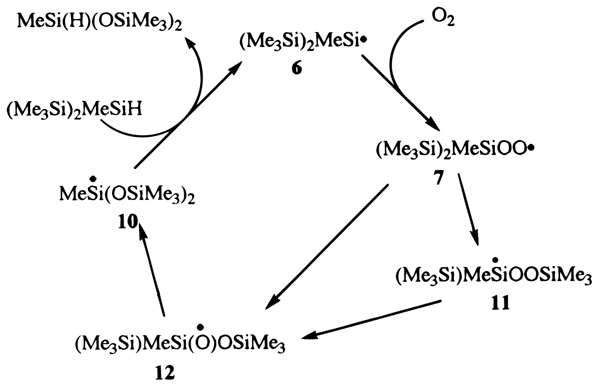
(35) Although an unambiguous identification of other compounds was not obtained, the product with the second highest yield was identified as $Me_3Si(Me_3SiO)Si(OH)Me$. This assignment is based on the GC/MS analysis of the reaction mixture before and after silylation with Me_3SiCl/Pyridine.

(36) The autoxidation of $(Me_3Si)_3SiH$ has been studied at room temperature, and an intramolecular mechanism was found to be exclusively operative, see: Chatgilialoglu, C.; Guarini, A.; Guerrini, A.; Seconi, G. *J. Org. Chem.* **1992**, *57*, 2207−2208.

Scheme 2. *Intermolecular* Mechanism



Scheme 3. *Intramolecular* Mechanism



oxygen atoms in the final product arise from two different oxygen molecules, whereas in the *intramolecular* mechanism, the two oxygen atoms arise from the same oxygen molecule. Thus, in Scheme 2, silyl radical **6** adds to molecular oxygen to form the peroxyl **7**, which may be transformed into the silyloxyl **8** following either path a or path b, in accordance with the autoxidation of hydrocarbons.[37] A 1,2-shift of the Me_3Si group[38,39] will give the silyl radical **9**, which may repeat the above reaction sequence to finally give radical **10**. In Scheme 3, the peroxyl radical **7** rearranges to **11** by means of an unusual 1,3-shift of the Me_3Si group, which then undergoes a homolytic internal substitution to form the silyloxyl radical **12**. Another possibility would be the direct rearrangement of **7** to **12**. The latter could rearrange to **10** by a 1,2-shift of the Me_3Si group.[38,39] In both schemes, hydrogen abstraction from the silane by radical **10** gives the desired product and the $(Me_3Si)_2MeSi^{\bullet}$ radical, thus completing the cycle of this chain reaction.[40]

Oxygen-labeling experiments were carried out to distinguish between the *intramolecular* and the *intermolecular* mechanism. Silane **5** was treated with a mixture of $^{16}O_2$ and $^{18}O_2$ (eq 3). The crude products

$$(Me_3Si)_2MeSiH + (55.4\%\ ^{16}O{-}^{16}O/0.8\%\ ^{16}O{-}^{18}O/43.8\%\ ^{18}O{-}^{18}O) \rightarrow (Me_3Si^{16}O)_2Si(H)SiMe_3\ (52.9\%) + (Me_3Si^{16}O)(Me_3Si^{18}O)Si(H)SiMe_3\ (4.8\%) + (Me_3Si^{18}O)_2Si(H)SiMe_3\ (42.3\%) \quad (3)$$

were analyzed by mass spectrometry to determine the isotopic distribution. From the EI mass spectrum recorded by GC/MS analysis of the reaction mixture, the relative amounts of the coeluting isotopomers $(Me_3Si^{16}O)_2Si(H)Me$, $(Me_3Si^{16}O)(Me_3Si^{18}O)Si(H)Me$, and $(Me_3Si^{18}O)_2Si(H)Me$ could be determined by analysis of the isotopic cluster of $[M - 1]^+$. A completely *intramolecular* mechanism would result in the same label distribution in the products as in the reactants, whereas an *intermolecular* mechanism would lead to a statistical distribution of the labels in the products. The mass spectrometric results are reported in eq 3. Analysis of the data reveals that the product of interest is formed in 92% of the cases following the intramolecular path (Scheme 3) and in 8% of the cases following the intermolecular path (Scheme 2).

We have also studied the autoxidation of the model compound by measuring the oxygen consumption using EPR spectroscopy. The rate of oxygen consumption was determined experimentally in a closed system using the paramagnetic probe fusinite, a derivative of coal totally insoluble in organic solvents.[41] The decrease of oxygen with time inside the reaction vessel was revealed by a decrease of the EPR line width. The use of the above technique to perform autoxidation studies has been described in previous papers.[42] The fusinite probe did not interfere with the autoxidation reaction, since it is

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(37) For the thermal decomposition of silyl hydroperoxides, see: Dannley, R. L.; Jalics, G. *J. Org. Chem.* **1965**, *30*, 3848−3851. Shubber, A. K.; Dannley, R. L. *J. Org. Chem.* **1971**, *36*, 3784−3787.

(38) For 1,2-migration of the trimethylsilyl group in free radicals, see: Harris, J. M.; MacInnes, I.; Walton, J. C.; Maillard, B. *J. Organomet. Chem.* **1991**, *403*, C25−C28 and references therein.

(39) A similar 1,2-migration of the Me_3Si group from Si to O has been observed, see: Ballestri, M.; Chatgilialoglu, C.; Lucarini, M.; Pedulli, G. F. *J. Org. Chem.* **1992**, *57*, 948−952.

(40) The initiation step remains in doubt.

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(42) (a) Cipollone, M.; Di Palma, C.; Pedulli, G. F. *Appl. Magn. Reson.* **1992**, *3*, 99−106. (b) Pedulli, G. F. In *Free Radicals and Antioxidants in Nutrition*; Corongiu, F., Banni, S., Dessi, M. A., Rice-Evans, C., Eds.; Richelieu Press: London, 1993; pp 169−185. (c) Pedulli, G. F.; Lucarini, M.; Pedrielli, P.; Sagrini, M.; Cipollone, M. *Res. Chem. Intermed.* **1996**, *22*, 1−14.

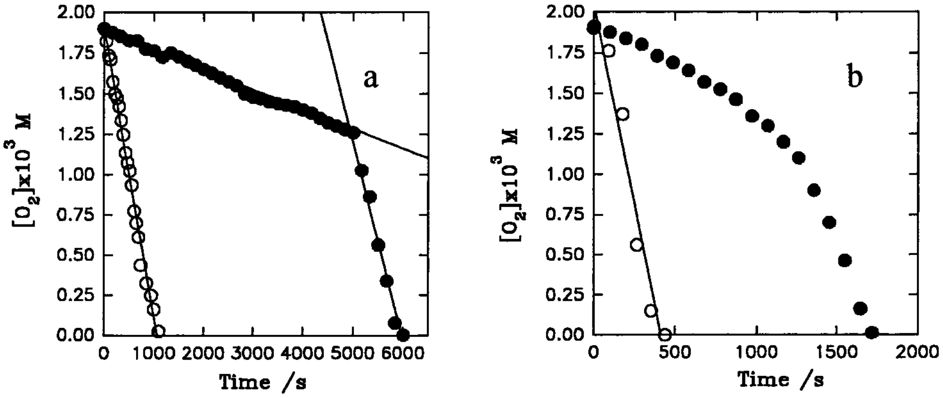

Figure 2. (a) Oxygen consumption during the AIBN-initiated (0.026 M) autoxidation at 50 °C of $(Me_3Si)_2Si(H)Me$ (0.3 M) in benzene in the absence (○) and in the presence (●) of α-tocopherol (2 × 10^{-4} M). (b) Oxygen consumption during the di-*tert*-butyl peroxide-initiated (0.017 M) autoxidation at 50 °C of $(Me_3Si)_2Si(H)Me$ (0.26 M) in benzene in the absence (○) and in the presence (●) of α-tocopherol (1.4 × 10^{-4} M).

insoluble in the reaction mixture. The conversion of the width of the fusinite EPR line and the oxygen concentration was performed by means of calibration curves, as already described.[42]

A benzene solution of $(Me_3Si)_2Si(H)Me$, containing a small amount of α-tocopherol, was either thermolyzed at 50 °C in the presence of α,α′-azoisobutyronitrile (AIBN) or photolyzed with di-*tert*-butyl peroxide at the same temperature. When the reaction is initiated thermally with AIBN, the rate of oxygen consumption is strongly retarded for a period whose length depends on the initial concentration of α-tocopherol (eq 4).

$$\tau = \frac{2[\alpha - \text{tocopherol}]}{R_i} \qquad (4)$$

Solving eq 4 by taking[43] R_i as 8.5 × 10^{-8} M s^{-1} we obtain an induction period of 4705 s, which is in good agreement with the experimental value of 4800 s (Figure 2a). This indicates that peroxyl radicals, formed by combination of oxygen with the alkyl radicals deriving from the decomposition of AIBN, are trapped efficiently by α-tocopherol so that they cannot initiate the autoxidation reaction of the substrate. When using the photoinitiator di-*tert*-butyl peroxide, the resulting alkoxyl radicals react directly with the silane[44] to afford the corresponding silyl radical and, after combination with molecular oxygen, the peroxyl radical, **7**. This radical can then start the autoxidation process by following either the *intermolecular* or the *intramolecular* reaction path. A completely *intermolecular* mechanism would lead to a behavior similar to that observed when the reaction is initiated with AIBN, since the reaction of the peroxyl radical **7** with α-tocopherol can compete with the hydrogen transfer to the same radical from the starting silane. In particular, by taking[47] R_i as 4.7 × 10^{-7} M s^{-1}, from eq 4 we expect an induction period of 595 s and the concomitant oxygen consumption equal to twice the α-tocopherol concentration, i.e., 2.8 × 10^{-4} M, if all peroxyl radicals were trapped by α-tocopherol. From Figure 2b it can be seen that both the induction period (ca. 1250 s) and the oxygen consumption during the inhibition (ca. 9 × 10^{-4} M) are larger than expected. This diverse behavior can be explained by admitting that the *intramolecular* mechanism is also operative. In this case, the reaction of α-tocopherol with the peroxyl radical **7** competes with the unimolecular rearrangement to give the reactive species **12**, which can propagate the autoxidative chain with a consequently less pronounced induction period.

The agreement between the oxygen-labeling experiments and EPR studies is gratifying, and both suggest that the autoxidation follows the mechanism conceived in Scheme 3 mainly.

Oxidizability of Poly(hydrosilane)s. With the aim of quantifying the ease by which poly(hydrosilane)s undergo oxidation, we carried out a series of experiments in which a benzene solution of poly(phenylsilane) or poly(*n*-hexylsilane) was oxidized under air at 50 °C using AIBN as the radical initiator, i.e., under identical conditions of the above-mentioned model compound.

On the basis of the previous section, the radical chain reactions mainly responsible for the autoxidation can be described by the reaction sequence shown in Scheme 4. Using the usual steady-state approximation, the overall rate of oxidation is given by eq 5, from which the oxidizability, $k_p/(2k_t)^{1/2}$, a convenient parameter characterizing the ease by which a substrate is oxidized, can be obtained.

$$-\frac{d[O_2]}{dt} = R_i + \frac{k_p}{\sqrt{2k_t}}[R_3SiH]\sqrt{R_i} \qquad (5)$$

Since the formation of oxidized polymers could result in different reactivities, the oxidative experiments were carried out with a large excess of silane (0.2−0.5 M in

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(43) The value of R_i has been determined by performing the autoxidation of styrene in the presence of a known amount of α-tocopherol by employing the same experimental conditions used in the autoxidation of the silane.

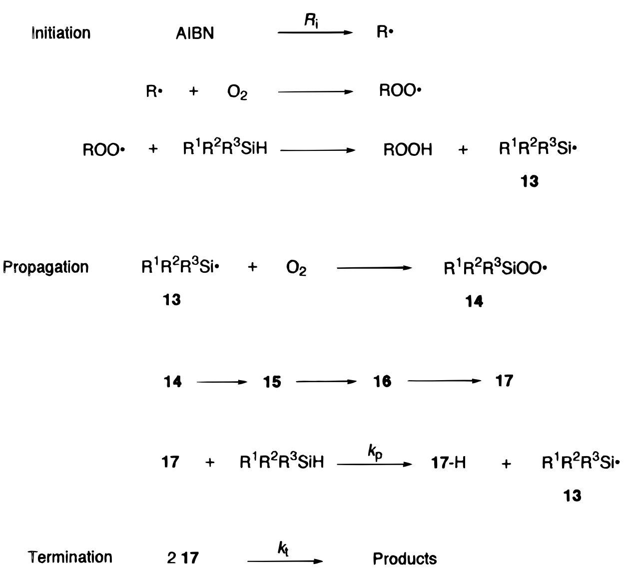
(44) *tert*-Butoxyl radicals abstract the hydrogen atom from $(Me_3Si)_2Si(H)Me$ and α-tocopherol with a rate constant of 6 × 10^7 and 3.1 × 10^9 M^{-1} s^{-1}, respectively.[45,46] Under our experimental conditions ($(Me_3Si)_2Si(H)Me$ (0.5 M) and α-tocopherol ((1−2) × 10^{-4} M)], the reaction of butoxyl radicals with α-tocopherol can be safely neglected.

(45) Chatgilialoglu, C.; Guerrini, A.; Lucarini, M. *J. Org. Chem.* **1992**, *57*, 3405−3409.

(46) Valgimigli, L.; Banks, J. T.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1995**, *117*, 9966−9971.

(47) The value of R_i has been determined by following, by EPR spectroscopy, the growth of the phenoxyl radicals generated b[y photolyzing di-*tert*-butyl peroxide in the presence of tri-*tert*-butylphenol, in the same experimental conditions employed in the autoxidation of the silane.

Scheme 4 [a]



[a] **14**, **15**, **16**, and **17** correspond to **7**, **11**, **12**, and **10** in Scheme 3.

Table 2. Oxidizability of Polysilanes and of Some Representative Compounds

substrate	$k_p/(2k_t)^{1/2}$, $M^{-1/2}$ $s^{-1/2}$	ref
poly(phenylsilane)[a]	1.8×10^{-2}	this work
poly(*n*-hexylsilane)[a]	1.2×10^{-2}	this work
$(Me_3Si)_2Si(H)Me$	1.8×10^{-2}	this work
cumene	1.2×10^{-3}	49
styrene	7.9×10^{-3}	49
methyl linoleate	1.9×10^{-2}	49

[a] Value for each Si−H groups (see text).

active sites) with respect to oxygen (1.91×10^{-3} M). The values of the oxidizability at 50 °C for the two polysilanes examined, reported in Table 2 together with that of the model compound, were calculated by using the molar concentration of −(RSiH)− groups in eq 5.[48] For comparison, the analogous values of the two hydrocarbons, styrene and cumene, and of methyl linoleate, which all represent examples of easily oxidizable substrates, are also reported. It can be seen that poly(hydrosilane)s are oxidized with similar rates.

Reaction of Poly(hydrosilane)s with TEMPO. In a second series of experiments, we also checked whether the stable nitroxide 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) could be used as the oxygen probe. This radical is very convenient for these kinds of studies provided that the chain-propagating radical reacts with oxygen faster by 1 or 2 orders of magnitude than with the nitroxide probe. In this case, oxygen consumption can be followed by measuring the square root of the reciprocal of the peak intensity, $I^{-1/2}$, of one of the three lines of TEMPO, which should vary linearly with the oxygen concentration[42] as shown in eq 6, where W_{int} is the intrinsic line width in the absence of oxygen, R is the interaction radius between oxygen and the nitroxide radical, and D_{ox} is the diffusion coefficient of molecular oxygen in the medium.

$$I^{-1/2} \propto W_{int} + 4\pi R D_{ox}[O_2] \qquad (6)$$

In the case of the autoxidation reaction of the polysilanes, however, we obtained nonlinear plots of $I^{-1/2}$. To explain this unexpected behavior, we investigated the reactivity of polysilanes with nitroxides under free-radical conditions in the absence of oxygen.

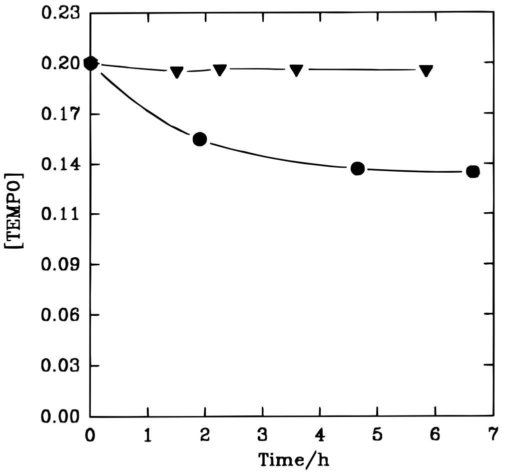


Figure 3. Nitroxide concentration measured at different times in the absence (▼) and in the presence (●) of poly(phenylsilane) (0.25 M) at 85 °C. [AIBN] = 0.02 M.

In the first experiment, TEMPO (0.2 M) was reacted in a sealed EPR tube under nitrogen at 85 °C with the radical initiator AIBN (0.02 M) and poly(phenylsilane) (0.25 M in active Si−H groups) in a cyclohexane solution. The nitroxide concentration was measured at different times, and the result is reported in Figure 3. After an initial decrease, the radical concentration reached a plateau corresponding to ca. 70% of the starting TEMPO within ca. 5 h. The various samples collected at different times were then reacted with *m*-chloroperbenzoic acid, and in every case this resulted in an increase of the EPR signals of TEMPO. Double integration of the EPR spectra indicated that, after chemical oxidation, the TEMPO concentration was practically identical (within experimental error) to the initial value. Repeating this experiment in the absence of polysilane, no appreciable decay of the nitroxide signals was observed (see Figure 3).

These results can be explained as follows. In the absence of polysilane, the alkyl radical formed in the decomposition of AIBN reacts reversibly with the nitroxide[50] and eventually combines or disproportionates leaving the total concentration of TEMPO unchanged (Scheme 5). When polysilane is present, the reaction affords a product which can be easily oxidized to give back the starting nitroxide. This could be either the hydroxylamine **18** or the amine **19**, both of which are precursors of TEMPO under oxidative conditions. We have, therefore, analyzed the reaction mixture by GC using authentic samples as references and found that the amine **19** is formed in 85% yield with respect to the nitroxide consumed during the experiment, while the hydroxylamine **18** is absent.

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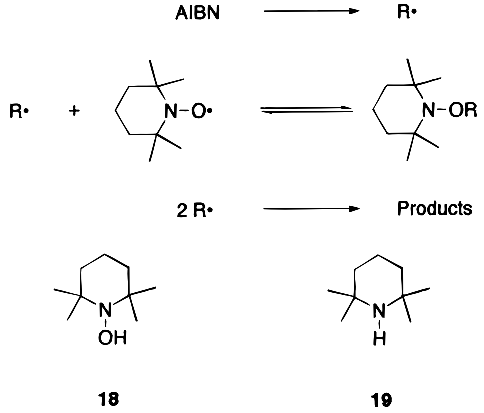
(48) The rate of initiation, R_i, was measured by following the oxygen consumption during the thermal decomposition of AIBN, in the presence of α-tocopherol. Under these conditions, oxygen is removed from the solution at the constant rate R_i by the alkyl radicals generated from the azo initiator and the resulting peroxyl radicals, in turn, are trapped by α-tocopherol.

(49) Howard, J. A. In *Free Radicals*; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol II, Chapter 12, pp 3−62.

(50) (a) Howard, J. A.; Tait, J. C. *J. Org. Chem.* **1978**, *43*, 4279−4283. (b) Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Org. Chem.* **1988**, *53*, 1629−1632.

Scheme 5



The reaction between TEMPO (0.1 M) and a polysilane in the presence of a radical initiator was repeated with both poly(phenylsilane) and poly(*n*-hexylsilane) (0.5 M) using *tert*-butyl perbenzoate (10% v/v) as the initiator in *tert*-butylbenzene at 120 °C for 2 h. GC analysis of the reaction mixture indicated that the nitroxide was completely consumed, and the resulting tetramethylpiperidine was formed in a 85% yield with poly(*n*-hexylsilane) and 88% yield with poly(phenylsilane). When repeating the reaction in the absence of polysilane, no amine was formed and the nitroxide was almost totally recovered.

These results indicate that nitroxides are easily reduced to amines by polysilanes under free-radical conditions in the absence of oxygen. The propagation steps that we conceived for this radical chain process are outlined in Scheme 6. The silyl radicals, initially generated by small amounts of initiator, combine with nitroxide radical to form an adduct that undergoes N−O bond cleavage to give an aminyl radical.[51,52] Hydrogen abstraction from the polysilane gives the amine and regenerates silyl radicals, thus completing the cycle of this chain reaction.[53]

Conclusions

Poly(hydrosilane)s obtained by dehydrocoupling of the corresponding $RSiH_3$ were found to be air sensitive. The GPC data for the initial and oxidized material are similar, and therefore, this technique is unable to properly evaluate the oxidative degradation of poly(hydrosilane)s. On the other hand, spectroscopic techniques such as IR and/or NMR are more appropriate for following the course of the reaction. During our studies we found that IR can be used routinely to achieve this goal. On the basis of heterocorrelated $^1H-^{29}Si$ HMQC spectra, the oxidized material contains the units **1**−**4** shown in Scheme 1. From the spectra, it could be inferred that units **2**−**4** are present in ca. 70% after exposure of poly(phenylsilane) to air for 12 h at 140 °C. Moreover, we have also shown by means of EPR spectroscopy that poly(hydrosilane)s are oxidized with rates comparable to those of styrene and methyl linoleate, two easily oxidizable substrates.

Model studies on the oxidation of $(Me_3Si)_2Si(H)Me$, either as product studies of oxygen-labeling experiments or as measurements of the rate of oxygen consumption by EPR techniques, allow us to forward a free-radical chain mechanism as the major pathway, in which the final siloxane contains two oxygen atoms arising from the same oxygen molecule. To rationalize this observation, we suggest that the strength of the silicon−oxygen bond is a potent driving force in these reactions. Although we believe that Scheme 3 also represents an important path in the autoxidation of poly(hydrosilane)s, we are conscious that the overall mechanism could be much more complex.

Finally, our results could also have an impact on the field of processing stabilizers. The effectiveness of poly(hydrosilane)s in stabilizing polypropylene during multiple extrusion[25] is believed to be due to the synergism of hydrogen donation to carbon-centered radicals and its capability to scavenge the traces of oxygen present during the extrusion process.

Experimental Section

Materials. The crude poly(phenylsilane) and poly(*n*-hexylsilane) were prepared by following the procedure of Harrod and Dioumaev.[13] Purification was obtained by dissolving the crude mixture in toluene, and the solution was stirred for 1 h with Tonsil.[16] $(Me_3Si)_2Si(H)Me$ was prepared following the literature procedure.[54] All other materials were commercially available and used as received.

NMR Studies. The NMR spectra of poly(phenylsilane) and oxidized material dissolved in $CDCl_3$ were recorded on a Varian Unity model 400 FT spectrometer. The INEPT experiments[32] were recorded with a refocusing delay of $1/(3J)$, based on a J_{Si-H} of 250 Hz. The ^1H-detected HMQC spectra[33] were obtained with the States−Haberkorn hypercomplex method and BIRD cancellation with a time delay of $1/(2J)$, based on a J_{Si-H} of 250 Hz. Within a t_1 spectral width of 12 800 Hz, 64 increments of 16 scans of 1K data points were acquired under ^{29}Si WALTZ-16 decoupling. After zero filling, the 1K × 1K matrix was transformed with unshifted Gaussian filtering in both dimensions.

Oxygen-Labeling Studies. GC/MS was performed by using a Varian 3600 GC linked to a Finnigan MAT 8400 double-focusing instrument. The mass spectrometer was operated in EI ionization (70 eV) at a resolution of 1000, while the magnet was scanned from m/z 33 to 500 in 0.8 s. The molar ratio of the $^{16}O_2/^{18}O_2$ gas mixture was determined from the intensities of the $^{16}O_2^{+\bullet}$ and $^{18}O_2^{+\bullet}$ molecular ion peaks, recorded by electron impact ionization of the gas mixture.

Autoxidation of Polysilanes. A solution of the polysilane (0.2−0.5 M in active Si−H groups) and 2,2′-azobis(2-methylpropionitrile) (0.008−0.04 M) in benzene was air saturated at room temperature and introduced (ca. 200 μL) into a capillary tube with an internal diameter of ca. 1.85 mm. A small amount of fusinite was introduced in the bottom of the tube, in contact with the solution. A second capillary tube (external diameter of 1.60 mm), sealed at one end, was introduced into the sample tube so as to leave very little dead volume space. The oxygen uptake at 50 °C was followed by an EPR method previously described.[42]

Reactivity of Polysilanes with Nitroxides. A solution containing the nitroxide (0.1−0.2 M), a polysilane (0.25−0.5 M in active Si−H groups), and a radical initiator in cyclohex-

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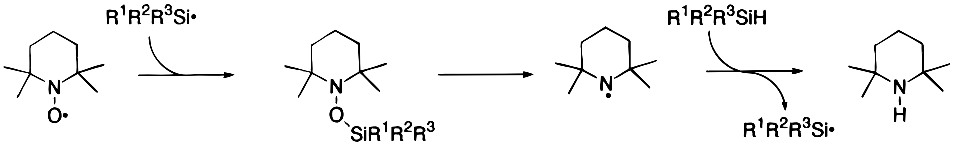
[51] Jensen, R. K.; Korcek, S.; Zimbo, M.; Gerlock, J. L. *J. Org. Chem.* **1995**, *60*, 5396−5400.

[52] Deoxygenation of TEMPO with thiophenols has recently been reported, see: Carloni, P.; Damiani, E.; Iacussi, M.; Greci, L.; Stipa, P.; Cauzi, D.; Rizzoli, C.; Sgarabotto, P. *Tetrahedron* **1995**, *51*, 12445−12452.

[53] Lucarini, M.; Marchesi, E.; Pedulli, G. F.; Chatgilialoglu, C. *J. Org. Chem.* **1998**, *63*, 1687−1693.

[54] Kumada, M.; Ishikawa, M.; Maeda, S. *J. Organomet. Chem.* **1964**, *2*, 478−484.

Scheme 6



ane or *tert*-butylbenzene was heated and then analyzed by GC using a 30 m × 0.53 mm HP-5 column with temperature programming from 50 to 250 °C using an HP Series II chromatograph. Yield and consumption were quantified using dodecane as the internal standard and authentic samples to calibrate the response of the detector. The disappearance of TEMPO was followed by using a Bruker ESP300 EPR spectrometer. Radical concentrations were measured by comparing the double integral of the EPR spectrum of the nitroxide with that given by a DPPH solution of known concentration and by using an artificial ruby crystal as the internal standard.

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Supporting Information Available: ^{29}Si INEPT and IR spectra of poly(phenylsilane) and of oxidized material; details of the oxygen-labeling experiment and oxygen consumption by EPR (10 pages). Ordering information is given on any current masthead page.

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