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THE POLYSILANE HIGH POLYMERS

ROBERT WEST

Department of Chemistry, University of Wisconsin, Madison, WI 53706 (U.S.A.)

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I. Introduction

Most industrial polymers are, of course, carbon-based, with main chains consisting entirely of carbon atoms (as in vinyl and diene polymers) or mainly so (as for polyesters, polyamides, etc.). Two classes of synthetic polymers based on inorganic main chains are, however, commercially important: the well-known silicones, with polymer chains made up of alternating silicon and oxygen atoms, and the newer polyphosphazenes, with alternating phosphorus and nitrogen atoms in the backbone. The polysilanes represent a new class of polymers, which may now be approaching commercialization, in which the polymer chain is made up entirely of silicon atoms. The unique feature of the polysilane structure is their uninterrupted runs of silicon atoms, which allow significant delocalization of electrons along the polymer chain. This gives these polymers highly unusual properties, quite unlike those of most other classes of polymers.

The modern era of research on polysilanes began only within the last decade. This paper is an informal account of some of the beginnings of this field, along with a brief description of the properties of polysilanes and of their potential technological applications. Polysilanes are treated in an earlier review [1], but an up-to-date, definitive survey of the field is still lacking.

Historical. Polysilanes were probably made by F.S. Kipping and his coworkers as early as the 1920's, from the reaction of diphenyldichlorosilane with sodium, but these materials were not well characterized [2]. The first clear description of a polysilane was in a classic paper by Burkhard in 1949, in which the synthesis of both poly(dimethylsilylene), Me_2Si and the six-membered ring oligomer $(Me_2Si)_6$ were reported [3]. In this 1949 paper, $(Me_2Si)_n$ was characterized as a white powder, extremely insoluble in organic solvents, which decomposed without melting when heated above 250°C; in other words, as a completely intractable solid. Burkhard's description, though quite accurate, was discouraging and may have contributed to the neglect which these polymers suffered for nearly thirty years.

However the stage was being set in other ways: Kumada and his group prepared linear permethylpolysilanes up to $Me(SiMe)_{12}Me$ [4], and this series was later extended by Allred to $Me(SiMe_2)_{24}Me$ [5]. At Wisconsin we had initiated research

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on the cyclic polysilanes, especially the permethyl compounds, and described their intriguing electronic properties resulting from delocalization of electrons in the Si–Si σ bonds [6,7]. One outgrowth of our work was the discovery that very large rings, up to $(Me_2Si)_{35}$ or higher, could be prepared [8,9]. Peralkylcyclosilanes were also attracting the attention of other research groups, especially those of Hengge in Austria [10] and Nagai in Japan [11]. Finally, an important use had been found for the classic poly(dimethylsilylene) of Burkhard: Yajima and Hayashi had discovered that $(Me_2Si)_n$ could be transformed into silicon carbide by heating to high temperatures [12,13].

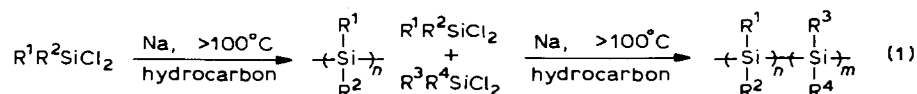
The discovery of soluble polysilanes in our laboratories was quite accidental, arising in an attempt to synthesize phenylundecamethylcyclohexasilane from a mixture of dimethyldichlorosilane and phenylmethyldichlorosilane [13a]. The six-membered ring can be made by condensing these chlorosilanes with lithium. However in this experiment we chose to use sodium instead, and obtained a polymer. What surprised us was that unlike Burkhard's $(Me_2Si)_n$, the polymer appeared to melt when heated, and was somewhat soluble in organic solvents. Introduction of phenyl groups at intervals along the polymer chain in $(Me_2Si)_n$ evidently breaks up the high crystallinity, so that the polymer became thermoplastic and soluble. Additional experiments with various mixtures of Me_2SiCl_2 and PhMe-$SiCl_2$ showed that minimum crystallinity is obtained at a Me_2Si/PhMeSi ratio of about 1.

These copolymers were mentioned in our 1978 paper with Dr. K. Mazdyasni of the Air Force Materials Laboratory [14], and described more fully in 1981 [15]. At about the same time, soluble polysilane polymers were discovered independently by Wesson and Williams at Union Carbide Corporation [16] and Trujillo at Sandia Laboratories [17]. In very recent years the center of gravity of polysilane research has shifted westward as activity has increased at Sandia and especially at IBM-San José Research Laboratories.

Interest in the polysilanes derives partly from their unusual constitution and behavior, and partly from their potential technological utility. Polysilanes may be useful in at least three applications: (1) as precursors to silicon carbide ceramics; (2) as resist materials in photolithography and (3) as photoinitiators for polymerization of vinyl monomers. The first of these possibilities was evident from the work of Yajima and Hayashi [12], but the other two were not so obvious, and arose only in the course of research.

II. Synthesis of polysilane polymers

In the usual synthesis of polysilanes, diorganodichlorosilanes are treated with sodium metal, in a hydrocarbon diluent, at temperatures above 100°C [18–22]. Either homopolymers or copolymers can be made (eq. 1). Because the groups R^1–R^4



can include a wide variety of aryl and alkyl groups, the number of possible kinds of polysilane polymers is very large. A listing of representative polymers and some of their properties appears in Table 1.

TABLE 1

PROPERTIES OF SOME POLYSILANE POLYMERS

R^1	R^2	Yield (%)	$\overline{M}_w$ [a]	λ_{max}
A. Homopolymers, $(R^1R^2Si)_n$				
Me	n-Pr	32	640,000	306
Me	n-Bu	34	110,000	304
Me	n-Hex	11	520,000	306
Me	n-$C_{12}H_{25}$	9	480,000	309
Me	PhC_2H_4	35	290,000	303
Me	Cy-Hex	25	800,000	326
Me	Ph	55	190,000	335
Me	*p*-Tol	25	75,000	337
Me	*p*-Biphen	40	80,000	352
n-Bu	n-Bu	12	1,800,000	314
n-Hex	n-Hex	9	2,500,000	316

R^1	R^2	R^3	R^4	n/m	$\overline{M}_w$ [a]	λ_{max}
B. Copolymers, $(R^1R^2Si)_n(R^3R^4Si)_m$						
Me	Me	Me	n-Hex	1.52	170,000	303
Me	Me	Me	Ph	1.51	900,000	330
Me	Me	Ph	Ph	1.13	350,000	351
Me	Cy-Hex	Me	PhC_2H_4	1.49	150,000	310
Me	Cy-Hex	Me	*p*-Tol	1.78	92,000	338
Me	PhC_2H_4	Me	Ph	1.77	400,000	326

[a] High mol.wt. peak from GPC, usually bimodal. $\overline{M}_w$'s given are relative to polystyrene standards; actual $\overline{M}_w$ values are higher by 2–3×.

The reactions leading to the formation of polysilane polymers appears to be complex. The likely first step is electron transfer from sodium to form a chlorosilane anion radical, but the course of the reaction from that point is not at all clear. Condensation may take place partly on or near the sodium surface, and partly in solution. Possible intermediates include, inter alia, $R_2SiCl^{\cdot}$, R_2SiCl^-, R_2Si, $R_2Si^{\cdot-}$,

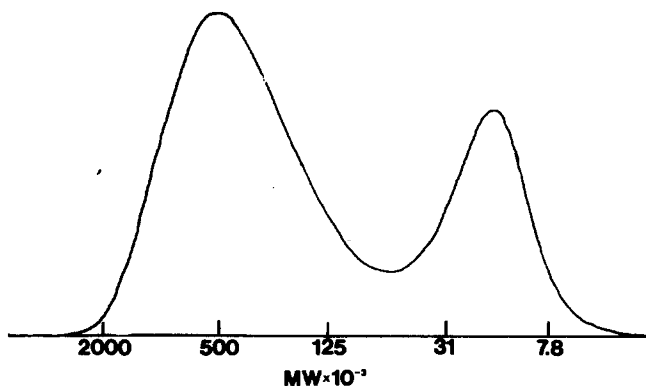


Fig. 1. Gel permeation chromatograph of (n-HexSiMe)$_n$ in THF. Molecular weights are relative to polystyrene standards; actual molecular weights are larger by a factor of ~ 3.

$R_2Si{=}SiR_2$ and cyclic $(R_2Si)_n$ ($n = 3$ or 4), as well as the growing polymeric species. In the presence of excess sodium, all of the Si–Cl bonds can eventually be destroyed, and at this point most of the product appears to be anionically-terminated living polymer. Cyclic and other oligomers are always obtained along with high polymer; in many syntheses oligomers are the dominant products.

The complexity of the condensation is indicated also by the fact that bimodal molecular weight distributions are frequently observed, as shown in the gel permeation chromatograms. An example is given in Fig. 1. If an ether (diglyme) is present along with the hydrocarbon diluent, the yield of poly(dialkylsilylene)s is often increased.

Sorting out the steps in the condensation of dichlorosilanes to polysilanes is a major problem, which will likely be solved only after a great deal of work in coming years.

Physical properties. The properties of polysilanes vary greatly, depending upon the nature of the organic groups attached to silicon. The dimethyl homopolymer, and other polysilanes with very small alkyl substituents, are highly crystalline and insoluble. Lengthening an alkyl chain changes the properties rapidly; $[Me(n\text{-}Pr)Si]_n$ is a soluble solid, and $[Me(n\text{-}Hex)Si]_n$ is an elastomeric, rubbery material. Aryl groups raise the softening point of the polymer; $(PhMeSi)_n$ is a glassy solid which flows only at temperatures > 200°C. The glass transition temperatures vary correspondingly from > −50°C for elastomeric polysilanes to > 120°C for the aryl compounds.

Preliminary studies of a few polysilanes in solution have been carried out by light-scattering methods [23]. The results, outlined in Table 2, show extremely high molecular weights, in the millions for two of the three samples investigated. The radii of gyration for the polymers are also shown. Polysilane polymers form random coils in solution, but initial indications are that they show greater persistence lengths and hence reduced flexibility compared with, for example, polyolefins. The polysilanes may be "semiflexible" polymers, with properties intermediate between those of rigid rods and highly flexible coils. Further light-scattering studies on carefully purified samples would be most valuable.

III. Electronic properties

Delocalization of σ-electrons in polysilanes is apparent from their ultraviolet absorption spectra. The polymers show characteristic strong electronic absorption

TABLE 2

MOLECULAR WEIGHTS, RADII OF GYRATION AND SECOND VIRIAL COEFFICIENTS FROM LIGHT SCATTERING STUDIES

Polymer	Solvent	$\overline{M}_w$	R_G (nm)	A_2 [a]
$(cycloHexSiMe)_n$	cyclohexane	2.5×10^6	76	1.24
$(n\text{-}Hex_2Si)_n$	hexane	6.2×10^6	108	0.76
$(n\text{-}Hex_2Si)_n$	cyclohexane	7.4×10^6	102	0.47
$(n\text{-}PrSiMe)_n$	THF	2.1×10^5	31	2.2

[a] $cm^3\ mol/g^2 \times 10^4$.

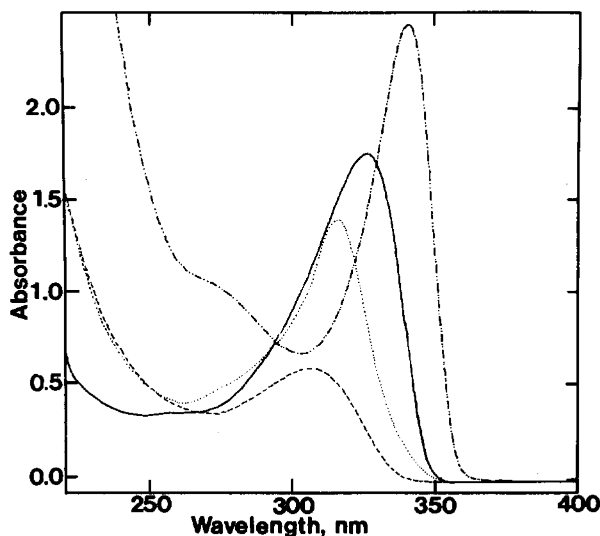


Fig. 2. Ultraviolet spectra of representative polysilanes, 1 cm path length, concentration in mol l^{-1} of Si–Si bonds in THF, - - -, $(n\text{-}C_{12}H_{25}SiMe)_n$, 1.1×10^{-4}; · · ·, $(n\text{-HexSiMe})_n$, 1.3×10^{-4}; ———, $(\text{cycloHexSiMe})_n$, 2.3×10^{-4} in cyclohexane; – · · – · · –, $(\text{PhSiMe})_n$, 2.6×10^{-4}.

bands usually falling in the region from 300–350 nm. Some examples are shown in Fig. 2, and typical λ_{max} values appear in Table 1. The electronic transition is ascribed to excitations involving electrons in the Si–Si σ bonds *. Earlier workers have shown that very simple orbital overlap calculations using the LCBO ** or Sandorfy C models, account well for the UV spectra of short-chain organosilanes [25]. With increasing chain length, the absorption maxima move to lower energy, as shown in Fig. 3, eventually reaching a constant value as the number of silicon atoms becomes larger than ~ 25 (Fig. 3).

The UV absorption bands of polysilanes (room temperature, solution) depend on the substituent groups. As the size of alkyl substituents is increased, λ_{max} moves to longer wavelength, from about 305 nm for small alkyl substituents to 326 nm in $(\text{cyclo-}C_6H_{11}SiMe)_n$. This difference may be due to differences in the chain conformation with larger alkyl groups favoring a greater proportion of *trans* conformations, as discussed further below. Aryl groups interact electronically with the polysilane chain and cause a marked lowering of the transition energy, to λ_{max} of 345 nm for $(PhMeSi)_n$ and still longer wavelength when electron-donating substituents are present ***.

* For a discussion of the electronic spectra of polysilanes, see ref. 1. The electronic excited state in the polysilanes is not well understood; it may contain Si–Si σ^*, Si–C σ^*, and perhaps Si-3*d* character. The related problem of the nature of the singly occupied molecular orbital (SOMO) in cyclosilane anion-radicals is treated in ref. 24.

** LCBO = linear combination of bond orbitals.

*** The bathochromic shift is probably due mainly to $\pi-\sigma$ mixing of the aryl π with the Si–Si σ orbitals. This mixing can account also for the profound effect of aryl groups in lowering the oxidation potential in polysilanes [26]. The UV excitation energy may also be reduced by mixing of the σ^*-like, excited state orbitals with aryl π^*. For a discussion of the effects of aromatic substitution on electronic spectra of polysilanes see refs. 1 and 27.

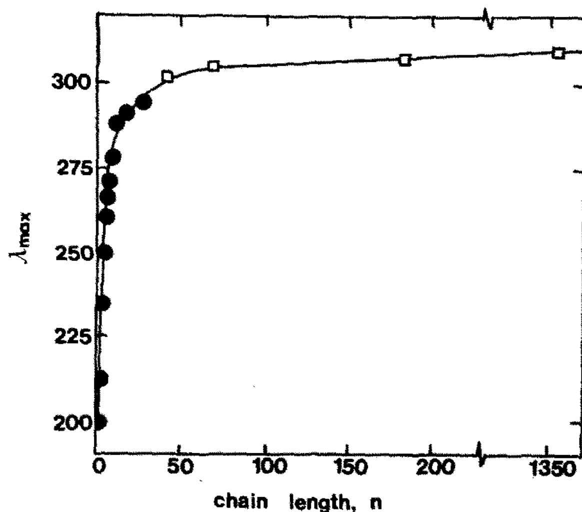


Fig. 3. Wavelength of absorption band (λ_{max}) as a function of chain length for poly(dialkylsilylene)s. Circles are data for $Me(SiMe_2)_nMe$ oligomers; squares are data for $(n\text{-}C_{12}H_{25}SiMe)_n$.

The electronic spectra of polysilanes exhibit several surprising effects. For instance, the extinction coefficients per silicon (atom) increase with increasing chain length. This effect is especially marked for the arylpolysilane $(PhMeSi)_n$ (Fig. 4). Also, many polysilanes show strong thermochromic behavior [28,29]. For some, such as $(n\text{-}BuSiMe)_n$, λ_{max} shifts gradually and reversibly to longer wavelength as the

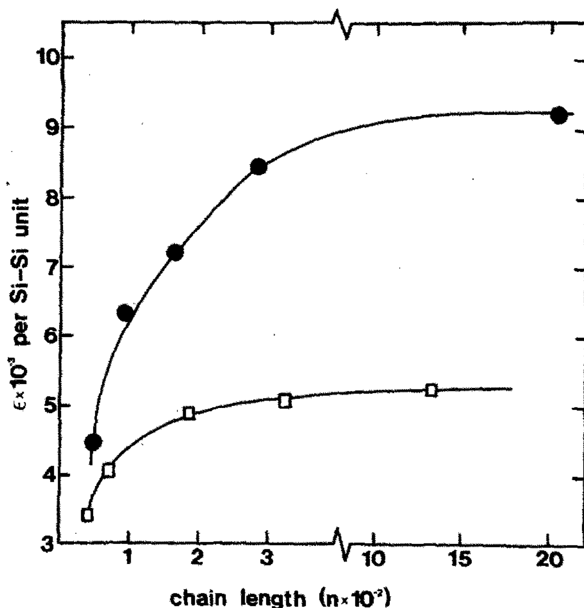


Fig. 4. Increase of extinction coefficient (ϵ) per silicon atom with molecular weight of polysilanes; circles, $(PhMeSi)_n$; squares, $(n\text{-}C_{12}H_{25}SiMe)_n$. Data were taken at λ_{max} for each polymer.

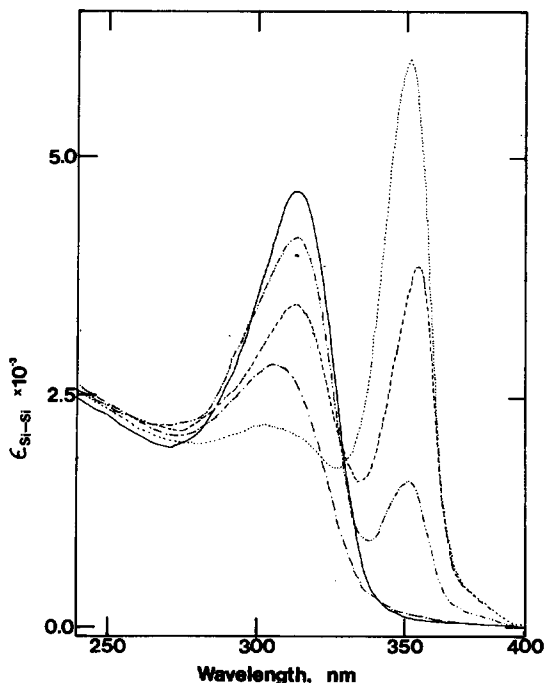


Fig. 5. Ultraviolet spectrum vs. temperature for poly(di-n-butylsilylene), 0.0055% in hexane, showing discontinuous thermochromic change. ·—·—·, 72°C; ———, 18.5°C; —··—, −18.5°C; ---, −38°C; ···, −61°C.

temperature is lowered. It is probable that this thermochromism reflects changes in conformation along the polymer chains, with the proportion of *trans* conformations increasing as the temperature is decreased. This model, which also accounts for the increase in λ_{max} with size of alkyl substituents requires the reasonable assumption that *trans* polysilanes have lower excitation energy than *cis*.

Polysilanes with two moderately long-chain alkyl groups, such as $(n\text{-}Bu_2Si)_n$ and $(n\text{-}Hex_2Si)_n$, show discontinuous thermochromic changes, in which one absorption band disappears and a new band grows in at longer wavelength, as temperature decreases (Fig. 5). In such cases, if the solution is kept for some time below the transition temperature precipitation occurs and the change in the UV spectrum is no longer reversible. This change has been ascribed to a coil-to-rod transition; but light-scattering studies on $(n\text{-}Hex_2Si)_n$ as a function of temperature suggest that a phase change (microcrystallization) takes place at the transition temperature [23]. Further work is needed.

Equally surprising thermochromic effects are found for solid films of polysilanes such as $(n\text{-}Hex_2Si)_n$ [30]. The latter undergoes a reversible change in λ_{max} from 313 to 374 nm with a transition temperature near 40°C. Detailed studies indicate that crystallization of the side chains takes place below the transition temperature, presumably enforcing the *trans* conformation on long segments of the polymer.

Firm experimental evidence for conformations in polysilane polymers is still lacking, but molecular modeling calculations using the MM2 method have been

TABLE 3

RELATIVE ENERGIES OF CONFORMERS OF PENTAMERIC FRAGMENTS FROM POLYMERS ($kcal\ mol^{-1}$)

Conformation	$Me(SiMe_2)_5Me$	$Me(n\text{-}hexyl_2Si)_5Me$
G^+G^+	0.0	3.0
GT	0.8	1.5
TT	0.9	0.0
G^+G^-	38.4	–

carried out on pentasilane fragments [31]. According to the results, for $(Me_2Si)_n$ the all *gauche* conformation (G^+G^+) is slightly preferred over all *trans*; if this is true $(Me_2Si)_n$ may have a helical structure (Table 3). However as the size of the groups on silicon is increased, the all-*trans* conformation becomes favored [32]. These calculations indicate that there is great conformational flexibility in polysilane chains; the results are quite consistent with equilibrium between *gauche* and *trans* conformations, as proposed above to account for the thermochromism of polysilanes.

The polysilanes are insulators, but become semiconducting upon treatment with oxidizing agents such as SbF_5 or AsF_5 [20]. Typical conductivity data are shown in Table 4. The mechanism of conductivity is somewhat different from that for other conducting polymers, since it depends on delocalization of σ electrons rather than π electrons. We envision that oxidation produces a cation-radical, analogous to a "hole" in elemental silicon, and that the positive charge is mobile along the polysilane chain. While the doped polysilanes are very interesting scientifically, they are unlikely to be useful in a practical sense because they react rapidly with air and moisture.

The oxidation of a few polysilanes have recently been studied by cyclic voltammetry. Dialkylpolysilanes undergo oxidation at potentials from 1.4 to 1.6 V (vs. SCE), but this potential drops to 1.0 V for $(PhMeSi)_n$ and to 0.69 V for $(p\text{-}CH_3OC_6H_4SiMe)_n$ in which an electron-donating substituent is present [26]. These results provide further evidence for electron-donation from aryl substituents to the polysilane chain.

TABLE 4

CONDUCTIVITY OF POLYSILANES DOPED WITH OXIDANTS

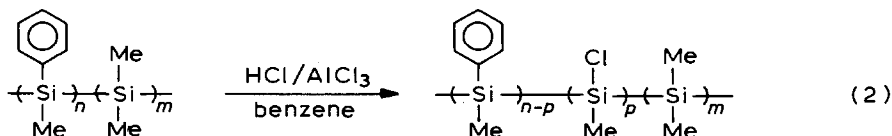
Polymer	Dopant	P(Torr)	$\sigma(ohm\ cm^{-1})$
$[(Me_2Si)_{1.0}(PhMeSi)_{1.0}]_n$	none		$<1 \times 10^{-12}$
$[(Me_2Si)_{1.0}(PhMeSi)_{1.0}]_n$	AsF_5	15	1.5×10^{-6}
$[(Me_2Si)_{0.5}(PhMeSi)_{1.0}]_n$	AsF_5	100	5×10^{-5}
$[(Me_2Si)_{0.5}(PhMeSi)_{1.0}]_n$ [a]	SbF_5	5	5×10^{-7}
$[(Me_2Si)_{0.5}(PhMeSi)_{1.0}]_n$ [a]	AsF_5	10	2×10^{-1}
$(Me_2Si)_n$	AsF_5	700	7×10^{-3}

[a] Photocrosslinked polymer.

IV. Reactions of polysilane polymers

In this section the few chemical reactions of polysilanes known at this time will be discussed. Photochemistry will be treated in Section V and reactions leading to crosslinking will be considered in Section VI.

A. Aryl replacement. Phenyl or other aryl groups on silicon can be selectively replaced by halogens, by treatment with a hydrogen halide and a Lewis acid. This reaction has been employed with phenyl-containing polysilanes to replace phenyl groups by chlorine (eq. 2) [33].

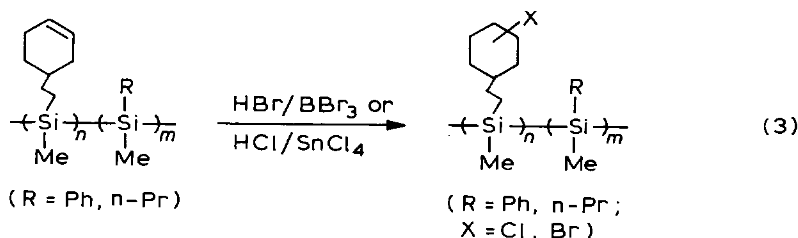


(2)

The fraction of phenyl groups replaced, p/n in eq. 2, can be varied depending upon the amount of HCl used and the reaction conditions. Silicon–chlorine linkages in the resulting polymer are quite reactive toward nucleophilic displacement as expected. Thus treatment of the polymer with excess n-butyllithium replaces most of the chlorine with n-butyl groups. However it is quite difficult to replace all of the chlorine, and if Si–Cl bonds remain the polymer undergoes hydrolysis and subsequent crosslinking upon exposure to air.

Better results might be obtained with nucleophilic substitution on polymers containing Si–H groups, which are not so sensitive to moisture, but the required experiments have not been carried out.

B. HX addition to alkenylpolysilanes. Introduction of functional organic groups into polysilanes is limited by the vigorous conditions usually employed in the condensation reaction. Vinylsilicon moieties are destroyed under the usual conditions, although they might survive if condensation were carried out at lower temperatures. Good results are obtained with 3-cyclohexenylethyl groups, in which the C=C bonds are well-insulated from the silicon chain [34]. The polymers shown in eq. 3 have been made by sodium condensation in reasonable yield, and shown to add HBr or HCl under mild Lewis acid catalysis to produce polysilanes containing C–Br or C–Cl bonds. Little degradation of the polymer takes place during the addition reaction.



(3)

C. Oxidation. Oxidation of silicon–silicon bonds by peroxides to form siloxanes is a well-known reaction for disilanes, and also takes place in cyclic polysilanes. Peroxide oxidation of the polysilane, poly(methylcyclohexylsilylene), has been investigated using *m*-chloroperbenzoic acid (MCPBA) as the oxidant [35]. A surprising finding was that the UV absorption band shifts relatively little upon oxidation, from

TABLE 5

QUANTUM YIELDS FOR SCISSION AND CROSSLINKING FOR POLYSILANES

Polymer	Concentration *c* [a]	(Φ(S)	Φ(X)	Φ(S)/Φ(X)
$(n\text{-}C_{12}H_{25}SiMe)_n$	0.005%	0.20	0.00	∞
$(PhMeSi)_n$	0.005%	0.97	0.12	7.9
$(PhMeSi)_n$	thin film	0.17	0.0036	4.7

[a] In Spectrograde THF.

326 nm only to 320 and 312 nm after reaction of the polymer with 0.5 and 1.0 equivalents of MCPBA, respectively. If the oxygen were being inserted into the polymer chain at random, a much greater shift in λ_{max} would be expected. The results suggest that MCPBA reacts preferentially with a Si–Si bond adjacent to a siloxane link, so as to produce blocklike regions of siloxane in the polysilane.

V. Photochemistry and scission

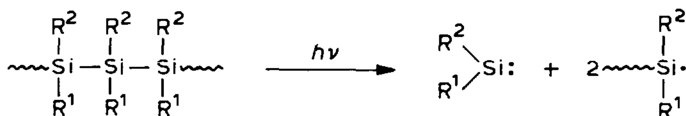
The photochemical processes of polysilanes are quite unusual, and are vital to the potential uses of these polymers. Photoscission is usually the main process, especially upon irradiation in air or in solution, but aryl polysilanes show a sizeable photocrosslinking component also.

Quantum yields for scission, Φ(S), and for crosslinking, Φ(X), are shown in Table 5 for $(n\text{-}C_{12}H_{25}SiMe)_n$ and $(PhMeSi)_n$ [36]. The solution quantum efficiency for scission is especially high for $(PhMeSi)_n$, which has $\Phi(S) \sim 1$. Apparently phenyl substitution makes the polymer more photolabile, but the reason for the difference is not understood. Crosslinking is unimportant for $(n\text{-}C_{12}H_{25}SiMe)_n$ but is significant for $(PhMeSi)_n$. Similar radiation-induced crosslinking is found for aryl-substituted polyethylenes [37]. The effective quantum efficiency of $(PhMeSi)_n$ as a thin film is much lower than in solution, presumably because of cage effects in the solid which impede motion and promote recombination of polymer ends. Similarly the ratio Φ(S)/Φ(X) decreases in the solid state.

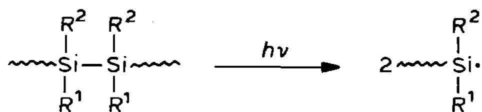
Because scission predominates over crosslinking when Φ(S)/Φ(X) is greater than 4, scission was dominant under all the conditions used. However the proportion of crosslinking increases when solid films are irradiated in the absence of oxygen and with longer wavelength (350 nm) radiation, so that it is possible to crosslink some aryl polysilanes photochemically [19].

The mechanisms involved in photodegradation in solution have been studied, at least in a preliminary way [38]. Initially, the photoreactions A, B and C of Scheme 1 were considered as possible contributors to scission. Reaction C would produce only products derived from silylenes, R^1R^2Si:; reaction B would yield products from silyl radicals, and reaction A would lead to both types of products. Since silylenes are known to insert rapidly into Si–H bonds, exhaustive photolysis of several polysilane polymers was carried out using 254 nm radiation in the presence of triethylsilane to intercept any silylenes formed. The results (Table 6) show that the silylene-trapped compound, $Et_3Si\text{–}R^1R^2Si\text{–}H$, is the principal product for all of the polymers studied. Thus a reaction producing silylenes, C, must be important in each case. The

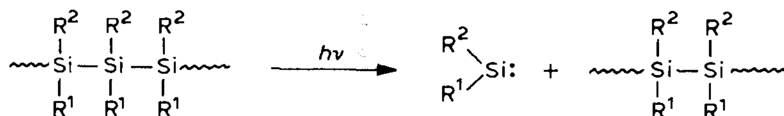
Reaction A



Reaction B



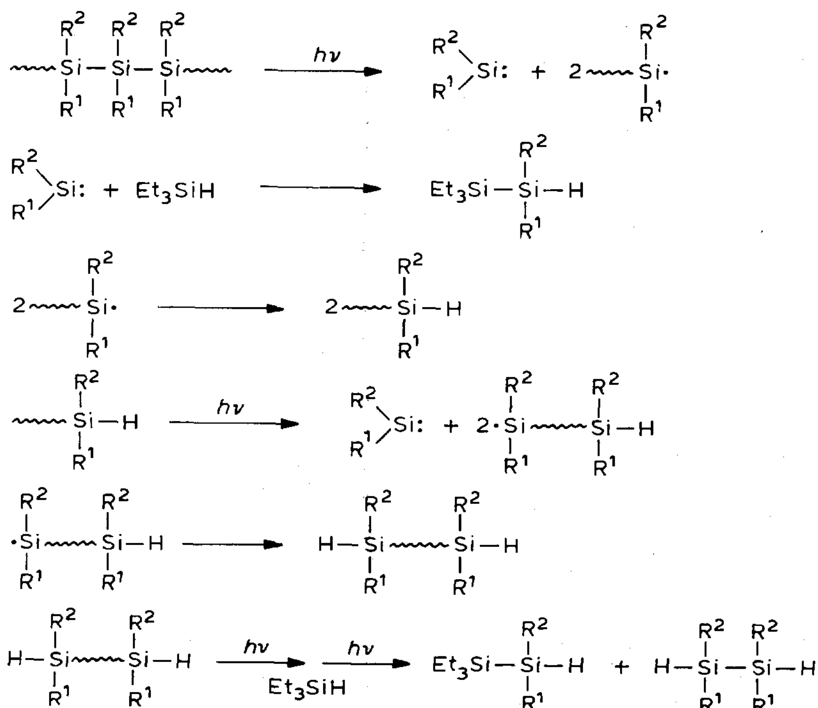
Reaction C



SCHEME 1. Possible reactions for the photodegradation of polysilane polymers.

other main product, disilane $H(SiR^1R^2)_2H$, can be produced in radical processes, by hydrogen abstraction.

A mechanism accounting reasonably for the products can be constructed using reaction A, with the proviso that chain recombination occurs in many instances to



SCHEME 2. Mechanistic hypothesis for the photodegradation of polysilane polymers.

TABLE 6

PRODUCTS FROM PHOTODEGRADATION OF POLYSILANES WITH Et_3SiH (%)

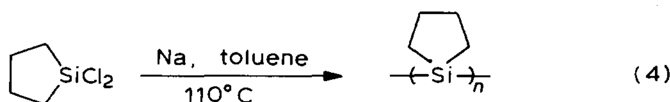
Polymer	$Et_3Si-SiRR'-H$	$H(SiRR')_2H$
$(n-Bu_2Si)_n$	59	11
$(n-HexSiMe)_n$	70	11
$(cycloHexSiMe)_n$	71	14

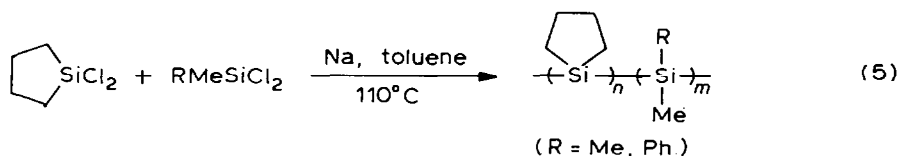
give effectively C. We have proposed the photochemical cascade shown in Scheme 2. Silylene fragments insert into triethylsilane to form Et_3SiSiR_2H; the silyl radicals at the ends of the polymer chains abstract hydrogen from solvent to give Si–H terminated polymer. Repeated absorption of photons and scission ultimately degrades the polymer down to the disilane fragments, $HSiR_2SiR_2H$, which no longer absorb light at 254 nm. Photodegradation experiments using alcohols as traps also give results consistent with the mechanism indicated in Scheme 2.

VI. Crosslinking of polysilanes

Crosslinking of polysilane polymers is important in the use of these materials as precursors to ceramics; if the polymers are not crosslinked, most of the silicon is volatilized during thermolysis rather than remaining as silicon carbide. Crosslinking is also a necessary part of the use of polysilanes as negative-acting photoresists. Accordingly several methods have been developed for improved chemical and lightinduced crosslinking of polysilanes [39].

A. Oxidative crosslinking: poly(cyclotetramethylenesilylene)s. Silacyclopentane rings are somewhat strained, and undergo ring-opening reactions at a silicon–carbon bond rather easily. As shown in eq. 4 and 5, polysilane polymers incorporating this group can be made using cyclotetramethylenedichlorosilane as one of the monomers.

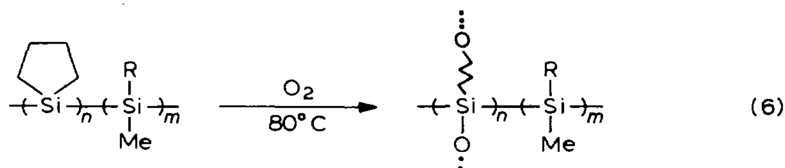




These polymers resemble other polysilane homo- and co-polymers, except that the ultraviolet absorption spectra are unusual. The cyclotetramethylene polysilanes absorb at unusually short wavelengths, near 285 nm for the homopolymer and dimethyl copolymer, whereas normal poly(dialkylsilylenes) absorb at 300–315 nm. The abnormal λ_{max} may result from conformational effects due to the strained heterocyclic rings in these polymers.

Ring strain in these polymers is also manifested in their abnormally high reactivity toward oxygen. When they are heated in air to about 80°C, rapid oxygenation takes place to give crosslinked, insoluble products. Oxidative crosslinking even takes place at room temperature, although very slowly. The infrared spectra

of the crosslinked polymers indicate that they contain Si–O–Si and Si–O–C bonds. We believe that crosslinking takes place by ring-opening as shown in eq. 6. Linkages to other polysilane chains are indicated by dotted lines.



Air curing of polymers such as these is very simple to carry out, but the crosslinked polymers of course contain oxygen, which may be undesirable for some uses.

B. Chemical crosslinking ("room temperature vulcanizing") of hydrosilylene polymers [40]. Several polymers have been made containing phenylhydrosilylene units, –PhSiH–, as shown in Table 7. These are made by the usual sodium condensation route from $PhSiHCl_2$ and other dichlorosilanes, but both the polymerization and the workup must be carried out quite carefully so that the Si–H groups are not hydrolyzed. In the initial condensation, care was taken to insure that the silicon–chloride bonds were completely consumed, so that the polymer was in the silyl anion terminated form. This "living" polymer was end-capped with diphenylmethylchlorosilane (eq. 7). The polymers, now end-blocked with Ph_2MeSi groups, were then isolated under strictly neutral conditions to avoid solvolysis of the Si–H

$$^{-}SiR_2(SiR_2)_nSiR_2^{-} + 2\ Ph_2MeSiCl \rightarrow Ph_2MeSi(SiR_2)_{n+2}SiMePh_2 \quad (7)$$

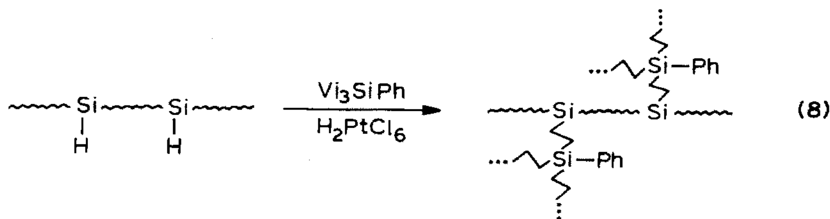
linkages. The resulting polymers had relatively low molecular weights (Table 7) and were meltable solids or even flowable liquids. Crosslinking was effected by hydrosilylation, with trivinylphenylsilane as the crosslinking agent and a trace of chloroplatinic acid as catalyst, according to eq. 8. In practice any compound containing several C=C double bonds could presumably be used. The mixture of reactants is a viscous liquid or paste which gradually sets to a firm crosslinked polymer. These are therefore room-temperature vulcanizing polysilanes, analogous to the well-known RTV silicone elastomers.

TABLE 7

POLYSILANE POLYMERS CONTAINING Si–H GROUPS, $Ph_2MeSi[PhSiH(R^1R^2Si)_m]_nSiMePh_2$

R^1	R^2	m	$\overline{M}_w$ [a]	Appearance
-	-	0	1000	white powder
Me	Me	0.63	1200	white powder
Me	Ph	0.69	1000	white powder
Me	Ph	4.5	1100	white powder
Me	PhC_2H_4	1.15	1000	resinous solid
Me	PhC_2H_4	5.4	1200	resinous solid
Me	Cy-Hex [b]	0.7	1100	white powder
Me	Cy-Hex [b]	5.3	1300	white powder
Me	n-Hex	0.91	1000	grease
Me	n-Hex	4.8	1500	fluid

[a] From GPC elution volume, relative to polystyrene. [b] Cyclohexyl.

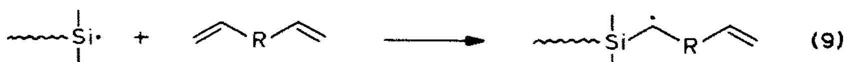


Other crosslinking reactions could be carried out with polymers containing Si–H bonds, such as solvolysis, reaction with diols, etc.

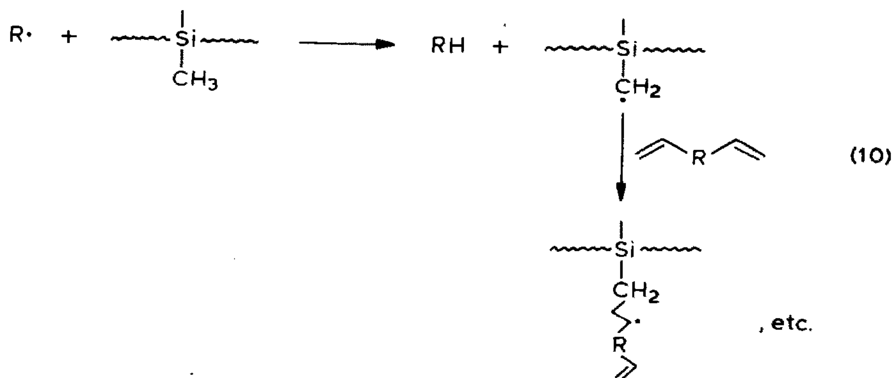
C. Photocrosslinking of alkenylpolysilanes. As mentioned in Section IV, aryl groups as substituents on polysilanes promote photocrosslinking. This effect is much more pronounced for olefinic groups. Thus the (cyclohexenylethyl)methylsilylene polymers, whose chemistry was discussed in Section IVB, undergo crosslinking as thin films when exposed to ultraviolet light, preferably with $\lambda > 300$ nm [34]. In the photocrosslinking process, the silyl radicals formed in the irradiation probably add to C=C double bonds, either on the same or on neighboring chains, producing carbon radicals. The latter can continue the chain by adding to another C=C bond; if this is on a neighboring chain a crosslink results.

D. A general method for thermal or photochemical crosslinking. A very simple way to bring about crosslinking of any polysilane polymer is to mix it with a compound containing multiple unsaturation, and then initiate free-radical formation either thermally or by photolysis [41]. Crosslinking agents which have proved effective include tetravinylsilane, 1,2-bis(trivinylsilyl)ethane, 1,6-bis(trivinylsilyl)hexane, methylvinylcyclotetrasiloxane, 1,4-cyclooctadiene, 1,9-decadiene, and triallyl benzene-1,3,5-tricarboxylate. Both alkyl- and aryl-silane polymers are crosslinked under these conditions; typical polymers studied were poly(phenylmethylsilylene) and poly(cyclohexylmethylsilylene-co-n-hexylmethylsilylene).

Photochemical crosslinking probably takes place through initial cleavage of the polysilane chain to form radicals, which add to the C=C double bonds of the crosslinking agents. The addition produces crosslinks, and in addition generates new carbon radicals which may cause further crosslinking reactions (eq. 9).



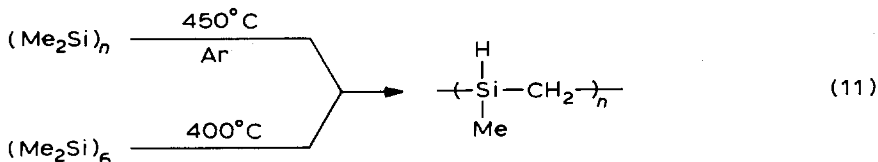
Using thermal radical initiators, the first steps may be either addition of initiator radicals to the double bonds of the polyunsaturated compound, or abstraction of hydrogen from organic groups on the polysilane. For instance, loss of hydrogens from methyl groups on the polysilane would lead to formation of crosslinks (eq. 10).



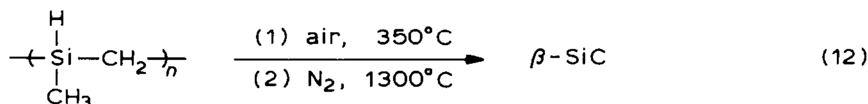
VII. Technological applications of poly(diorganosilylenes)

In this section the possible industrial uses of polysilanes will be briefly considered. Three potential applications have arisen for these polymers: 1. as precursors to ceramics; 2. as photolithographic materials and 3. as photoinitiators for polymerization.

A. Polysilanes as silicon carbide precursors. The original process for thermal generation of silicon carbide ceramic from polymeric precursors was pioneered by Yajima and Hayashi [12,13]. The starting materials are either poly(dimethylsilylene), $(Me_2Si)_n$, or the ring compound $(Me_2Si)_6$. Thermolysis of these materials at 400–450°C leads to a complex series of changes in which insertion of CH_2 groups takes place into many of the Si–Si bonds, leaving hydrogen bound to silicon (eq. 11).



The product is a polymeric material with idealized structure shown, termed a polycarbosilane. The hexane-soluble, non-volatile portion of the polycarbosilane is fractionated by precipitation to give a material with a molecular weight of about 8000. This polymer fraction is then melt-spun into fibers, which are oxidized on the surface by heating in air. Surface oxidation makes the fibers rigid enough so they maintain their shape upon further heating. Finally, these fibers are pyrolyzed at higher temperatures, whereupon loss of methane and hydrogen takes place, producing silicon carbide (eq. 12):



Amorphous silicon carbide is apparently formed near 800°C; as the temperature is raised to 1300°C, crystals of β-silicon carbide form in the fibers, which are actually a mixture of β-SiC with amorphous silicon carbide, carbon and silicon dioxide. With tensile strengths of ~ 350 kg/mm^2, the fibers are among the strongest substances known. Silicon carbide fibers made in this way are now available in kilogram quantities from Nippon Carbon Company and are distributed in the United States by Dow Corning Corporation.

The Yajima group also found that the carbosilane polymer produced from polysilane starting materials could be used to produce β-SiC in the form of sintered moldings and composites, which are not readily obtainable in other ways. However, this technology has the disadvantages that the thermolysis must be carried out in two steps, the intermediate polycarbosilane must be solution-fractionated to separate the useful part, and that air oxidation is necessary to strengthen the polycarbosilane fibers before final pyrolysis, introducing some oxygen into the final ceramic material.

Soluble polysilane polymers can also be used as precursors to silicon carbide. The first such application, using dimethylsilylene-phenylmethylsilylene copolymers, was to strengthen silicon nitride ceramics. The Si_3N_4 ceramic body was soaked in

polysilane and refired, leading to the formation of silicon carbide whiskers in the pore spaces and a consequent increase in strength [13].

As these experiments indicate, polysilanes can in some cases be converted to silicon carbide directly, without the necessity for formation of polycarbosilane, fractionation, or oxidation. For example, $(PhMeSi)_n(Me_2Si)_m$ copolymers can be formed into films or fibers and then crosslinked by irradiation with UV light. The crosslinked polysilane forms silicon carbide when heated to 1100°C in vacuum [18]. Crosslinked fibers retain their shape during conversion; an example of a tubular fiber made by this process is shown in Fig. 6. This method can be used in a "printing" mode, if a film of polysilane is cast onto a ceramic or metal substrate, then exposed to UV light through a mask, and finally heated. The unexposed polysilane is volatilized, leaving a silicon carbide coating only where the polysilane was exposed, and thus forming a pattern [42].

For a 1/1 $PhMeSi$-Me_2Si copolymer, a theoretical yield of silicon carbide of 50% is possible. Early experiments gave lower ceramic yields, 15–30%, but in recent trials by Sinclair and coworkers at 3M Company the theoretical limit has been approached. The ceramic product has an infrared spectrum and other properties similar to material produced by the Yajima process.

Other more complex polymers containing silicon–silicon bonds can also be used as precursors to silicon carbide or silicon nitride ceramics. These polymers however have properties quite different from these of the linear polysilanes, and will not be considered here.

B. Polysilanes as photoresists. In the winter of 1981 the author visited the University of Utah, for collaborative research with Professor Josef Michl as well as for the skiing. Dr. Robert Miller of IBM-San José Research Laboratories was there for the same two reasons, and the idea of trying polysilanes as photoresists arose in a conversation. We promptly sent some samples to IBM, and when they proved highly promising, established a continuing collaboration, later extended to include Professor Gary Fickes of the University of Nevada.

As photoresists the polysilanes are unusually versatile, in that they can be made to operate in the negative mode (by photocrosslinking) or in the positive mode (by photoscission). The greatest interest at present in microelectronics is in positive acting photoresists, and most of the work done with polysilanes has been in this mode [43]. A polysilane layer is exposed to UV radiation, leading to scission into small fragments. These are removed selectively by washing with solvent, leaving the unexposed polysilane still in place. With the higher exposure possible using an excimer laser, the polysilanes can even be volatilized during exposure, so that no solvent treatment is necessary; such a process is called "self-developing" [22].

The polysilanes are valuable as photoresists because upon exposure to UV light their absorption bands in the ultraviolet disappear or bleach. This phenomenon results from the peculiar absorption properties of polysilanes described in more detail in Section III. Photobleaching is rapid and complete because as UV light is absorbed and the polymer molecular weight declines, the absorption band both becomes less intense and moves to shorter wavelengths, as shown in Fig. 7. Photoscission of some polysilanes can also be sensitized by the addition of halogen compounds such as *p*-bis-trichloromethylbenzene, which speed scission by transferring halogen to the silyl radicals and inhibiting recombination [43]. Photobleaching of a polysilane film is illustrated in Fig. 7.

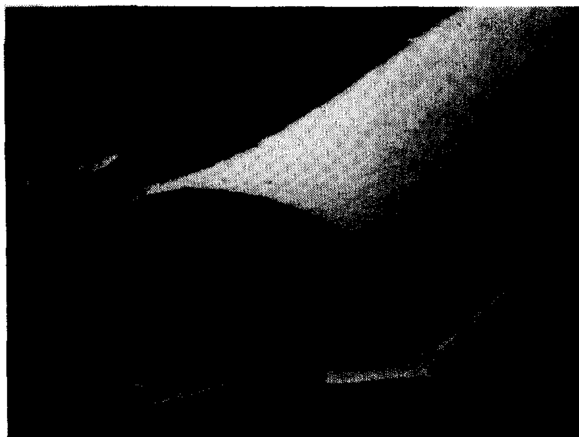


Fig. 6. Fiberlike "tube" of silicon carbide made by pyrolysis of photocrosslinked PhMeSi–Me_2Si copolymer. Length of bar is 50 μm.

A second advantage of the polysilanes is that they undergo oxidation forming a resistant layer of SiO_2 when treated with oxygen ions. Advantage is taken of this property in a bilayer construction, in which a silicon wafer is first coated with a thick phenolic planarizing layer and then with a polysilane imaging layer. After exposure and development by washing with solvent, the wafer is exposed to oxygen plasma which etches the phenolic but only superficially oxidizes the polysilane. The eventual result is an image with a steepsided, deep profile (Fig. 8) [44]. This polysilane system will easily produce lines with a separation (resolution) of 0.75 μm, finer than the present production standard of 1.0 μm. Another application of these polymers in microlithography, as a contrast-enhancing layer, also takes advantage of the bleaching properties of the polysilanes [45].

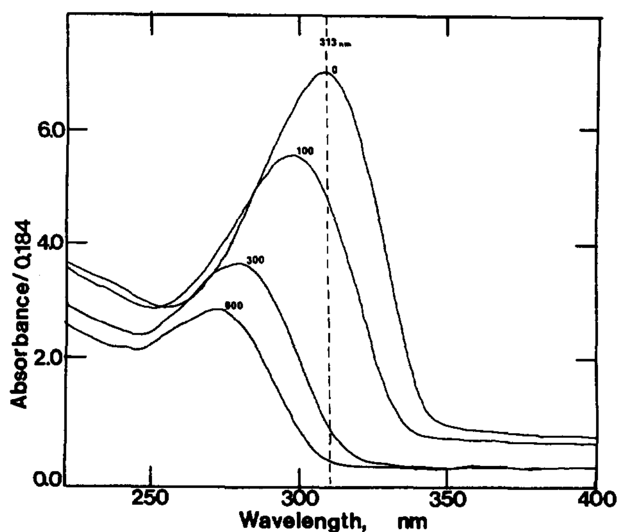


Fig. 7. Bleaching of $(n\text{-HexSiMe})_n$ film upon irradiation at 313 nm. Doses are in mJ/cm^2.

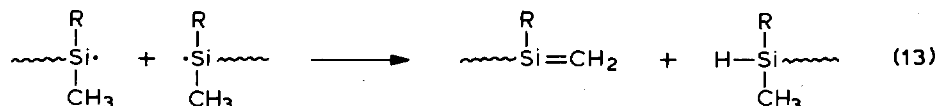
Fig. 8. Bilayer photoresist, polysilane over phenolic resin, after imaging, development and oxygen reactive ion etching. The top layer of polysilane has been oxidized from a resistant coating of SiO_2. Resolution is 0.8 μm. Photo courtesy of IBM San José Research Laboratories.

C. Polysilanes as photoinitiators. Research on the photochemistry of polysilanes, discussed in Section V, indicates that they undergo photoscission with high quantum yields to produce silyl radicals as well as silylenes. Independently it has been shown that silyl radicals will add to the C=C double bond in 1,1-di-t-butylethene to give carbon radicals detectable by ESR spectroscopy [46].

It therefore seemed possible that polysilanes might be useful as sources of radicals for chain reactions, for example the polymerization of olefins. This possibility was realized by Andrew Wolff in our laboratories, one Saturday afternoon in the fall of 1982. He simply filled a number of test tubes with styrene or methylmethacrylate, added to each a small amount of a polysilane polymer, and left the tubes on a window ledge exposed to sunlight while he attended the University of Wisconsin football game. Upon this return he found that the monomer in all of the tubes containing polysilane had undergone polymerization, while control tubes containing monomer but no polysilane were unchanged.

A surprising aspect of these results is that polymerization occurred although no attempt was made to remove atmospheric oxygen. In fact the polysilanes appear to be relatively insensitive to the effects of oxygen, and become even less so in the presence of amines as protective catalysts [47].

Since these initial experiments, we have found that photoinitiation of radical-induced vinyl polymerization is quite general for polysilane polymers [42]. Their initiation efficiency is rather low, about 10^{-3} for $(PhMeSi)_n$ and styrene, but this is in part compensated by the very high extinction coefficients of the polysilane in the 300–350 nm region. Low photoefficiency means that, although most of the photons lead to chain scission, the radicals produced do not initiate vinyl polymer chains [48]. The initially-formed silyl radicals must be lost in other ways; one possibility is hydrogen transfer to give a silane and a silene (eq. 13).



This sort of disproportionation has been shown to occur for disilanes. If a silene is indeed formed, this might account for the relative insensitivity of the polysilanes to oxygen inhibition, because the silicon–carbon double bond should be a very effective scavenger of oxygen.

Acknowledgement

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