

Solution photochemistry of poly(dialkylsilanes): a new class of photoresists

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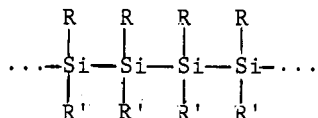
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ABSTRACT

Polysilanes represent a new class of polymeric materials of considerable theoretical and practical interest. Although formally saturated, they have an intense absorption band in the near UV and undergo rapid photodegradation. After a review of the present understanding of the electronic structure of poly(dialkylsilanes) as a function of backbone conformation, we summarize their photophysics and describe recent advances in the understanding of their solution photochemistry.

INTRODUCTION

Polysilanes (1) are high-molecular weight polymers with a silicon backbone and remarkable properties. (ref 1) Although the structure is formally saturated, they have an intense absorption band in the near UV region, between 300 and 400 nm depending on substitution, and suffer rapid photochemical degradation when irradiated at these wavelengths. Their utility as photoresists has already been demonstrated (ref 2, 3) and continues to be of great interest in the electronics industry, as is the promise of these materials as electron beam and X-ray resists. Free radicals are formed in the UV-radiation induced process, and polysilanes have been proposed for use as polymerization initiators (ref 4). They are also currently under investigation as non-linear optical materials,(ref 5) positive charge conductors,(ref 6,7) and as ceramic precursors.(ref 8) The recent wave of industrial interest in these materials is due to the advances in the synthesis of soluble polysilanes (ref 9) which can be cast as thin films and otherwise processed. This progress was due to the use of suitable substituents as side-chains; materials containing only methyl or only phenyl substituents are quite insoluble and intractable. (ref 10) A recent review of polysilanes is available, and the interested reader is referred there for further detail. (ref 1)



Although diaryl and arylalkyl substituted polysilanes are known and exhibit interesting interactions between the conjugated substituent and the silicon backbone, the present survey of recent results from our laboratory will be restricted to dialkyl substituted polysilanes, which have the simplest electronic structure. It shall also be largely restricted to the photochemical behavior of these polysilanes solutions at room temperature. Many of the polysilanes are thermochromic, both in the solid state and in solution, presumably as a result of temperature-induced conformational changes in the polymer backbone. (ref 2,11-14) The relation between conformational changes in solution and the process of aggregation and microcrystallite formation has not yet been fully elucidated, and we shall avoid the issue by concentrating on the behavior of the room temperature conformers in solution. The materials we have investigated have high molecular weight, mostly in excess of a million, and have been synthesized by standard procedures.

Although photochemistry of the neat polysilane solids is of intense interest for the process of dry etching and direct laser writing, (ref 3, 16-19) processes occurring in laser ablation appear to be thermal rather than photochemical in nature, at least when performed with an excimer laser at 308 nm, (ref 18) and will not be discussed in the present context.

Most of the attention devoted to polysilanes so far has concentrated on their fundamental properties such as molecular conformation, electronic structure, nature of the excited states, and photophysics, and very little is known about the mechanism of the photochemical degradation which is our primary focus presently. The only mechanistic solution study of polysilanes that we are aware of to date (ref 20) concluded that irradiation at 254 nm causes both homolytic cleavage with the formation of polysilyl radicals and the extrusion of monomeric silylenes $RR'Si$. The evidence was the formation of short oligosilane chains terminated by Si-H bonds and the trapping of $RR'Si$ with triethylsilane. Both of these processes are well known from the photochemistry of short-chain oligosilanes. (ref 21) Although our work has fully confirmed these initial observations on poly(dialkylsilanes), we shall see below that the picture is considerably more complicated than might appear at first sight.

Before proceeding with the discussion of photochemistry it will be useful to review briefly the fundamentals of poly(dialkylsilanes) conformation, electronic structure, and photophysics.

BACKBONE CONFORMATION

According to light-scattering studies, poly(di-n-alkylsilanes) form a random coil in solution. (ref 22) The detailed conformation of the chain in solution is not known with certainty but much can be deduced from the known conformations in solids, from model calculations, and from electronic spectroscopy. Many of the solid poly(di-n-alkylsilanes) exhibit a highly ordered low-temperature phase and disordered high-temperature phase. (ref 2, 11, 12, 14) In the ordered phase of poly(di-n-hexylsilane), and presumably also of polysilanes with slightly longer alkyl chains, the backbone is arranged in a planar all-trans "zig-zag" conformation. (ref 12). In poly(di-n-pentylsilane), and presumably also in polysilanes with shorter alkyl chains, the structure is helical; that of poly(di-n-pentylsilane) is derived from the planar all-trans arrangement by a 30° twist at each Si-Si bond (7/3 helix). (ref 23). A similar structure has been found for the ordered phase of poly(di-n-butylsilane). (ref 24) Polysilanes with two very long n-alkyl chains and those with two chains of different lengths such as methylhexyl-polysilane are believed to have more complicated helical structures. There seems to be a correlation between the degree of twist by which the conformation deviates from the all-trans planar form and the position of the absorption maximum in the ordered solid phase. Thus, the planar backbone of the poly(di-n-hexylsilane) is characterized by an absorption peak at or near 375 nm and that of the 30° twisted poly(di-n-hexylsilane) by an absorption peak near 313 nm. Of course, since the transition to the ordered form in a solid is associated with crystallization of the alkyl side chains, it is possible that this crystallization enforces a change in the Si-Si-Si valence angle in the backbone and that this is responsible for the very different transition energy as well.

The disordered solid phase exhibits absorption maxima at shorter wavelengths, similar to those observed in room temperature solutions. It is quite likely that the structures are similar and consist of a statistical distribution of lengths of either fully planar (all-trans) or only moderately helical segments separated by one or more strongly twisted turns in the backbone such as gauche links, presumably in a rapid dynamic equilibrium.

The structural calculations that have been performed so far by molecular mechanics and semiempirical methods on short model oligosilanes have concentrated on chains carrying hydrogen or methyl substituents and need not be fully representative of the situation in the soluble polysilanes containing longer chains. The conclusions obtained from these models (ref 25) are that the trans and the gauche arrangements are of comparable energies and are separated by only a small barrier. Moreover the trans minimum is extremely flat and the optimal geometry may indeed involve a non-zero twist away from planarity. Some calculations with longer substituents have also been performed and the conclusions were similar. (ref 26)

Considerable insight into the solution conformation of poly(di-n-hexylsilanes) has been provided by photophysical studies. (ref 24, 27, 28) Although the fluorescence and fluorescence excitation spectra of poly(dialkylsilanes) in solution are largely independent of the wavelength of excitation and wavelength of monitoring respectively, closer inspection shows a systematic shift of the high-energy edge of the fluorescence to the red as the wavelength of excitation increases and an even more pronounced shift of the lower energy edge of the excitation spectrum to the blue as the monitoring wavelength decreases. (ref 28) Coupled with the observation that the fluorescence decay is exponential only upon excitation into the red edge of the absorption band (ref 27, 28) and with the observation that the quantum yield for all of the polydialkylsilanes) investigated drops considerably as the wavelength of excitation is decreased, (ref 14, 28) this suggests strongly that the long-chain polysilane backbone in solution is best viewed as a collection of only loosely coupled chromophores with a statistical distribution of lengths and of the corresponding excitation energies, among which energy transfer occurs very rapidly (about 10^{-11} s). The drop in the fluorescence quantum yield with increasing excitation energy will then be understood as a result of competition between photochemical processes, intersystem crossing, energy transfer, and fluorescence, all of which would have different rate constants for chromophores of different lengths. A specific structure for these chromophores was suggested by results of INDO/S calculations (ref 27) which offered a simple MO explanation for the conformational dependence of excitation energy of the polysilane chain using chains up to 40 silicon atoms in length. The lower excitation energy of the planar zig-zag arrangement of the backbone can be understood as a result of 1,4 interactions between the approximately sp^3 -hybridized orbitals used by the silicone atoms for Si-Si bonding. The sign of the 1,4 resonance integral changes as twisting from the trans through the gauche to the cis form occurs and this readily accounts for the observations. The picture proposed there was one of approximately all-trans segments terminated by a strong twisted "gauche" turn to represent the individual chromophores.

It is quite likely that the exact geometry of the chromophoric segment is a function of the nature of the side groups. For certain side groups such as possibly n-hexyl, the preferred geometry may be completely planar whereas for others, such as n-pentyl, it may be helical, and this will affect the exact excitation energy for each chromophore. Of course, in a room temperature solution many geometries in the vicinity of the potential minimum will be populated. There will then be altogether three reasons to expect the absorption line to be inhomogeneously broadened. First of all, a distribution of lengths of the chromophores; second, for any given chromophore length, a distribution of geometries around the optimal one; and third, for any given chain segment geometry a distribution of side chain and solvent molecule arrangements in the vicinity. INDO/S calculations suggest that the decrease of the excitation energy of a backbone chromophore with its increasing length, which is steep at first, levels off somewhere in the vicinity of 10 silicon atoms in the chain. The statistical distribution of chain lengths that corresponds to an infinite chain is not approached until the polymer backbone reaches about 50 or 100 silicon atoms, since only then the absorption maximum stabilizes as a function of increasing molecular weight. (ref 29)

Although the above picture of the polysilane conformation in room temperature solutions has not been proven definitively, it represents a reasonable starting point for the discussion of the photophysics and photochemistry of these materials.

ELECTRONIC STRUCTURE

Sigma conjugation

The delocalized electronic structure of the polysilane backbone can be perhaps most simply understood by reference to a simple Hückel-type description in terms of a basis set containing two approximately sp^3 -hybridized orbitals on each silicon atom, used to form the Si-Si bonds. This type of description has become known as the Sandorfy C model. (ref 30) It has seen considerable use for alkanes, (ref 31) and has recently been popularized further. (ref 32) It produces both a bonding and an antibonding set of delocalized molecular orbitals, both needed in the discussion of electronic excited states. For some purposes, such as discussion of photoelectron spectra, only the occupied bonding orbitals are needed and a description using the localized Si-Si σ bonding orbitals as

the basis set is adequate. (ref 33) For an extensive discussion of the use of the Sandorfy C model for the understanding of electronic spectra of short-chain linear oligosilanes, see ref 34.

In this model, the description of the electronic structure of linear polysilanes is topologically equivalent to the description of the π system of polyenes with alternating single and double bonds. The alternation of resonance integrals along the polyene carbon chain is due to the alternation of bond length. The less pronounced it is, the more "delocalized" the system becomes. In this sense, π systems such as those in the cyanine dyes are more perfectly delocalized than those in uncharged polyenes. The alternation of resonance integrals in the linear polysilane chain is provided by the difference in the values of the vicinal resonance integral between the two sp^3 hybrids on adjacent atoms pointed at each other and the geminal resonance integral between the two sp^3 hybrids on the same silicon atom.

Notice that in the simple picture the electronic structure is unaffected by rotations around the cylindrically symmetrical σ bonds between silicon atoms and thus is independent of the conformation of the backbone. Nevertheless, this picture can still be viewed as a useful first approximation, and is essentially confirmed by higher level semiempirical (ref 27, 35, 3) as well as *ab initio* (ref 37, 38) calculations. Because of their more complicated nature, most of the latter calculations have been restricted to rather short polysilane model chains.

Conformational effects on the σ_{SiSi} and σ^*_{SiSi} MO's

The complication introduced by the effect of the polymer backbone conformation on the electronic structure can be described in very simple terms. (ref 27) While the vicinal and geminal nearest neighbor resonance integrals between members of the sp^3 -hybridized basis set are invariant with respect to rigid rotation around the Si-Si bonds, as are even the 1,3 next-nearest neighbor interactions, this is no longer true for the 1,4 interactions. These are due to an overlap of a mixed σ and π type. In the planar all-trans ("zig-zag") geometry, the 1,4 interactions are of the anti-periplanar type (ref 39) and the resonance integral is positive. As the rotation around the Si-Si bond gradually changes the interaction into the syn-periplanar type, the resonance integral clearly becomes negative and somewhere along the way it passes through zero. This occurs relatively close to the gauche geometry. As a result, the effect of the 1,4 interaction is very much more pronounced at the planar all-trans geometry than at the all-gauche geometry.

It is relatively easy to envisage the structure of the delocalized MO's that result from the simple model as well as the further perturbations in their energies introduced by the 1,4 interactions as a function of the twist angle. (ref 27) To derive the form of the bonding MO's we note that they are bonding between every pair of silicons and therefore have no nodal planes across the Si-Si bond lines, but differ from each other by the relative phase of the individual regions between the silicon atom pairs. Those which are the least stable will have a relatively large number of sign changes upon moving across silicon atoms. For each such sign change the geminal resonance interaction is destabilizing. The highest of the bonding orbitals, the HOMO, will have such a destabilizing geminal interaction at each silicon atom. The sign sequence of the coefficients of the HOMO as one proceeds along the chain will therefore be ...Si + + Si - - Si + + Si - - Si ...

It is readily seen that all 1,4 interactions in this array of signs will be destabilizing in the planar all-trans form in which the 1,4 resonance integral is positive, since they will always involve two coefficients of equal signs. The HOMO energy is therefore highest for the planar zig-zag conformation and decreases as the chain is twisted.

In a similar fashion, the antibonding Si-Si σ^* orbitals will have a node across each silicon atom. The most stable among these, the LUMO, will have no sign change across any of the silicon atoms in which case all geminal resonance integrals will make stabilizing contributions. The coefficient sign sequence will therefore be ...Si + - Si - + Si + - Si - +... In this case the contribution of the 1,4 interactions will be stabilizing in the all-trans conformation for which the 1,4 resonance integral is positive since the two coefficients located in the 1,4 relation will always have opposite signs.

So far it would appear that the effects of adding the 1,4 interactions will be equal in magnitude and opposite in sign when HOMO and LUMO are considered. This is not quite correct since an important element has been left out of the consideration so far. When we combine the sp^3 orbitals of the basis set into the bond orbitals of the σ and σ^* type in a first step and then added a consideration of the effect of the geminal resonance integrals in a second step, we only considered the mutual mixing of the bonding orbitals and the mutual mixing of the antibonding orbitals. However, this interaction will also cause some mixing of the orbitals of the bonding manifold with those of the antibonding manifold. The effect of this will be a change in the relative importance of the p and s contributions to the bonding orbital sets as well as the antibonding orbital set. Within each set the more stable orbitals will have a larger s orbital contribution and the less stable ones a larger p orbital contribution. As a result the HOMO and the orbitals close to it are relatively strongly of p character whereas the LUMO and the orbitals close to it are relatively strong in s character. Since that part of the 1,4 interaction integral which is responsible for its angular variation is due to the p contribution to the hybrid orbitals alone, it is clear that the change with twist angle in the energy of the HOMO and orbitals close to it will be more pronounced than that in the LUMO and its neighboring orbitals. These expectations are fully confirmed by numerical calculations by the semiempirical INDO/S method.

It is of course possible to describe the electronic structure of the polysilane chain without reference to hybridization, using only the 3s and 3p basis set orbitals. This is the approach normally used by solid state physicists when they describe the electronic structure of an infinite chain in terms of the band structure model.(ref 40) This description makes it particularly obvious why HOMO is largely composed of p orbital contributions whereas LUMO has much more s character.

Other orbitals present

Another complication that needs to be introduced is the presence of silicon orbitals which are used for bonding to the alkyl side chains and the presence of the corresponding orbitals used by the substituents to bond to the silicon atoms. In the planar zig-zag chain, both the former and the latter will form a symmetric (σ) and anti-symmetric (π) pair of orbitals. Numerical calculations suggest that the bonding orbital of π symmetry has a relatively large contribution on the more electronegative carbon or hydrogen atom and is energetically well below HOMO. The antibonding orbitals of π symmetry have a large contribution from 3p orbitals on the silicon atoms and the most stable among them are close in energy to the σ^* type LUMO discussed above. Although the significance of virtual orbitals obtained in a restricted Hartree-Fock procedure should not be overestimated, in such calculations the lowest among the π^* symmetry orbitals actually represent the LUMO. Experimentally, there are some indications that the radical anions of linear polysilanes may indeed contain most of the spin density in orbitals of π^* symmetry, as discussed in ref 38.

The orbitals of the σ symmetry pair which results from the interaction of orbitals used to form bonds between the silicons and their substituents mix with the orbitals that we discussed above as resulting from the Si-Si bond hybrid orbitals. Numerical results demonstrate that the mixing into the HOMO and LUMO orbitals and those close to them energetically is quite negligible. This result was obtained both in semiempirical (ref 27) and ab initio (ref 38) calculations.

Finally, the description of all orbitals would be improved by an increase in the basis set size. Specifically, it has been suggested at times that silicon 3d orbitals are important for a proper description of the bonding and particularly the antibonding orbitals. Numerical results (ref 38) suggest that this is not the case and that the admixture of d character into the orbitals that we have discussed so far represents at best a minor perturbation.

Localization and delocalization of HOMO and LUMO in the polymer backbone

In a perfectly symmetrical infinite chain the MO's will be totally delocalized; this is the situation described by the band theory model (ref 40). In a real polymer backbone deviations from symmetry will always occur due to defects, thermal motion at finite temperatures, or lack of symmetry

in the molecular environment. These perturbations will tend to localize the MO's as can be seen from the very simple following argument for the HOMO and LUMO as an example. As the length of the polysilane backbone increases, the energy of the HOMO increases and that of the LUMO decreases. The rate of change is large at first but when a chain with about a dozen or so silicon atoms is reached, the energies become nearly constant and hardly change with the increasing chain length any more. This is due to the alternation of the resonance integrals along the chain, as is well known from the theory of conjugated polyenes, and leads to a finite HOMO-LUMO gap even for the infinite chain. Only with a completely uniform set of resonance integrals without alternation would a vanishing HOMO-LUMO gap be expected.

Consider now an example of a localizing perturbation on an Si-Si bond which joins two perfectly symmetrical backbone segments of unequal lengths. If both are long enough, the energies of their respective HOMOs will be very nearly the same and will also be nearly equal to the energy of their in-phase and out-of-phase combination, which would be totally delocalized. The driving force for the localization will therefore be miniscule. Already small imperfections such as a different twist angle will lead to a localization. It has been proposed some time ago, (ref 27) and we still believe it to be correct, that in the case of linear polysilanes the primary imperfections which lead to orbital localization are not due to vibrations or the solvent environment, but rather to conformational differences in the backbone. The HOMO, in particular, is clearly strongly affected by a twist away from the planar zig-zag geometry. Calculations at the INDO/S level indicate that in a long chain the HOMO tends to be localized in a planar or nearly planar zig-zag chain terminated on each side by a more strongly twisted link, such as a gauche twist. Localization is less pronounced for the LUMO because of its predominantly s character as discussed above.

Each relatively planar segment will have its own HOMO as well as LUMO and their energies will depend on segment length. This picture is quite compatible, using Koopmans' theorem, with the experimental results on the mobility of positive holes in solid polysilanes, which is presumably limited by the need for hopping from the HOMO of one approximately planar segment to that of the next.

Electronically excited states

The early days of oligosilane spectroscopy were dominated by the uncertainty as to the assignment of the observed near UV transition bands. There was little doubt that excitation occurs from a Si-Si σ orbital which is relatively high in energy, but it was not clear what the terminating orbital is, one choice being $\sigma \rightarrow \sigma^*$ excitation, the other $\sigma \rightarrow \pi^*$ excitation. Since the two excited states differ in symmetry, at least for a planar zig-zag conformation of the backbone, it was possible to reach an unequivocal decision by measurements of transition polarization. This was performed on a stretched sheet of poly(di-n-hexylsilane) (ref 27) which demonstrated unequivocally that the $\sigma \rightarrow \sigma^*$ assignment is correct. This is also the result reached from INDO/S (ref 27) and CNDO/S (ref 35) calculations. The polarization measurements on stretched poly(di-n-hexylsilane) were subsequently confirmed and extended to other polymers. (ref 14) Additional support was obtained from measurements of flow dichroism. (ref 28)

This conclusion is still perfectly compatible with the above mentioned possibility that the LUMO is of π^* rather than σ^* character, and the arguments to the opposite in ref. 38 are spurious. The reason is that orbital energy differences are not a reliable measure of excitation energies. Indeed, they are frequently larger by as much as a factor of two, and even in the simplest single-determinant approximation without configuration interaction it is necessary to subtract certain large electron repulsion integrals from the orbital energy difference in order to arrive at the excitation energy (for a pedagogical treatment see ref 41). The magnitude of these integrals can vary significantly depending on the nature of the orbitals involved in the transition, and the term which needs to be subtracted could very well be much larger for $\sigma \rightarrow \sigma^*$ excitation than for a $\sigma \rightarrow \pi^*$ excitation, since the latter orbitals avoid each other better in space. Thus the radical anion could have the unpaired electron in a π symmetry orbital and yet the lowest excitation could be of $\sigma \rightarrow \sigma^*$ type. Indeed, the experimental results described above leave no doubt that the latter is the case.

Already the very high intensity of the near UV absorption band of polysilanes and its regular increase with increasing chain length (ref 29) in themselves provide convincing evidence that the transition is of the $\sigma \rightarrow \sigma^*$ type. While $\sigma \rightarrow \pi^*$ type transitions are undoubtedly also present at high energies, their expected low intensity will make detection difficult. After all, their transition densities are analogous to those of $n \rightarrow \pi^*$ transitions in organic compounds. More likely to be detected at higher energies are additional transitions of the $\sigma \rightarrow \sigma^*$ type involving σ orbitals other than the HOMO and orbitals other than the LUMO.

The intensities, polarizations, and energies of these transitions can be estimated very simply from exciton theory (ref 42) in which every Si-Si bond is taken to contribute a transition dipole directed along the Si-Si axis. A simple consideration of the mutual electrostatic interaction of these dipoles provides information about the transition energy and vectorial addition of the dipoles provides information about the transition dipole moment. The length of the vector sum dictates the intensity of the transition and its direction gives the polarization direction. An application of the simple form of exciton theory yields results in full agreement with the INDO/S calculations of ref 27 in that the lowest energy transition is strongly allowed and is polarized along the chain axis in an all-trans backbone and in chains which are only slightly twisted. In the MO language this transition corresponds to the HOMO-LUMO excitation with little admixture of other configurations, and its transition density is exactly that obtained from the simple exciton model, in that it corresponds to in-phase addition of the local transition dipoles. A different arrangement of these dipoles with a single plane of anti-symmetry perpendicular to the chain yields a higher energy transition of much lower intensity polarized in the zig-zag plane but perpendicular to the backbone axis. It is possible that transitions of this type contribute detectably to the tail of the absorption band at higher energies but they have not been unequivocally detected so far.

An illustration of the lowest excitation energies computed by the INDO/S method as a function of the silicon chain length in a permethylated polysilane up to Si_7 is provided in Figure 1 for the case of a completely planar zig-zag silicon backbone and for several degrees of regular twist along each bond. The calculated effect of small twist angles is negligible, but the hypsochromic shift becomes pronounced once the eclipsed geometry is reached. If this result corresponds to reality, much of the difference between the planar zig-zag and the slightly helical forms of the polysilane chain discussed above must be due to other factors such as differences in the Si-Si-Si valence angles. The calculations indeed suggest that for a chain with a constant number of silicon atoms the excitation energy increases fairly rapidly with the increasing valence angle in the region of experimental interest, about $115-120^\circ$, for all of the low-lying $\sigma \rightarrow \sigma^*$ excitations. As noted above, experimentally, only the lowest one is observed. It also is the one with the largest calculated oscillator strength by far. At much larger values of the valence angle the behavior changes, and this is currently being analyzed.

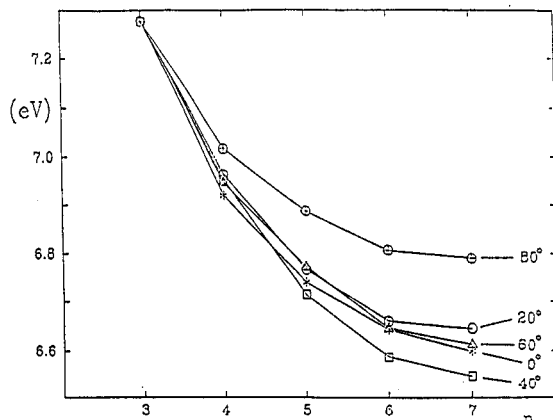


Fig 1. The lowest singlet excitation energy (INDO/S) of permethylated oligosilanes $\text{Si}_n\text{Me}_{2n+2}$ as a function of number of Si atoms in the chain. All Si-Si bonds were twisted equally from the all-trans planar arrangement by the amounts given. The geometries were optimized by the MNDO method for the all-trans planar backbone; the Si-Si bond lengths and Si-Si-Si valence angles were then frozen, a twist imposed, and other geometrical parameters reoptimized.

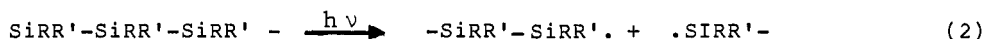
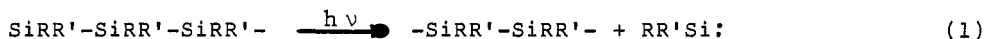
Localization of electronic excitation

The arguments presented above for the localization of the HOMO, and to a lesser degree the LUMO orbital, by strong twists in the otherwise planar or mildly helical polymer backbone apply also for the localization of electronic excitation. As shown by INDO/S calculations (ref 27) the transition density for the HOMO-LUMO excitation is concentrated on planar or approximately planar zig-zag segments of the polymer terminated by strongly twisted links, for example, gauche, and this is a simple consequence of the lower excitation energy for the all-trans arrangement due to 1,4 orbital interactions as explained above. Of course, the residual weak delocalization will ensure a relatively significant degree of interaction between neighboring chromophores which should lead to a fairly rapid energy transfer in the downhill sense. This agrees with the experimental finding that energy transfer must be competitive on the 10 ps time scale. Fluorescence polarization data (ref 27) are also in good agreement with this picture.

The INDO/S calculations published so far (ref 27) were performed for polymer backbones with strictly all-trans segments separated by strictly gauche links. It is now clear that for many choices of alkyls the real geometries of the localized chromophores may be somewhat helical and the separating twists need not be exactly gauche; however, the same principals apply.

PHOTOPHYSICS OF POLY(DIALKYLSILANE) PHOTODEGRADATION

Although the electronic structure and photochemistry of polysilanes have clearly received a great deal of attention, curiously little is known about the actual process that makes them interesting as photoresists, namely, their photochemical degradation. The first study of the subject (ref 20) provided evidence that the rapid photodegradation of molecular weight is due to homolytic cleavage to yield polysilyl radicals which then abstract hydrogen atoms and yield SiH-terminated disilane and trisilane fragments when the irradiation is done at 254 nm, where all longer polysilanes absorbed. The formation of radicals was subsequently supported by the observation that radical photopolymerization of simple olefins is induced by the presence of polysilanes. (ref 4) Trapping experiments with triethylsilane (ref 20) demonstrated that homolytic cleavage is not the only important photochemical process since large amounts of the dialkylsilylene monomer $RR'Si$ were trapped. Since the energy of the photon at 254 nm (112.5 kcal/mol) and the energy of the relaxed lowest excited singlet state (85-90 kcal/mol) are too small for a simultaneous rupture of two Si-Si bonds with the formation of both a silylene $RR'Si$ and a radical pair $2SiRR'$ upon absorption of a single photon, it is most likely that two concurrent and competing reactions were being observed. One of these is silylene extrusion which only shortens the polymer chain by one unit and does not affect the molecular weight significantly (1); the other is homolytic cleavage which cuts the average molecular weight approximately in half (2):



Both processes are well established in low molecular weight oligosilanes. (ref 21) In addition to this chemical evidence some photophysical observations pertinent to the photochemical mechanism have been published. (ref 14,28) In particular, the observed fluorescence quantum yield is quite large, of the order of 0.5, at the longest wavelength of excitation, but drops to about half of this value as the wavelength of excitation decreases. This behavior has not been analyzed in detail but suggests that channels competing with fluorescence open up when excitation is into the shorter chromophore segments, and at least one of these channels could well be photochemical. The relatively narrow spectral width of the fluorescent emission suggests a high degree of delocalization and this in turn suggests that the relaxed lowest excited singlet may not be the photochemical reactive state since it might have difficulty concentrating the excitation energy in any single bond. It has been suggested (ref 14) that the photochemical process occurs by intersystem crossing and reaction in the triplet manifold. In some cases very weak phosphorescence was observed at low temperature and its fine structure, albeit poorly developed, was taken to suggest the triplet is localized and photochemically active.

Photophysical observations have also been used to obtain information on the length of the emitting chromophores. (ref 27) The values of the observed fluorescence quantum yield and observed fluorescence lifetime lead to an oscillator strength of 1.8 for the emitting chromophore in poly(di-n-hexylsilane). From the observed absorption intensities one derives an increment of roughly 0.09 per Si-Si bond for the oscillator strength. This suggests a maximum of about 20 silicon atoms in the lowest energy chromophores that emit at 335 nm. The number could be smaller, perhaps only 10 or so, because the emitting chains have extended all-trans geometries and are likely to have a disproportionately large increment per Si-Si bond for the absorption strength.

We have made four new photophysical observations that may be relevant to the understanding of the photochemical mechanism. First, we have confirmed the previously reported (ref 14) very weak phosphorescence from several poly(dialkylsilanes) in organic glasses at 77 K.

In addition, we have been able to measure the excitation spectrum of the phosphorescence from polymethylpropylsilane and found that it agrees quite closely with the absorption spectrum (Fig. 2), proving that it is intrinsic and not due to an impurity. Our spectrum confirms the much broader nature of phosphorescence relative to fluorescence but it does not contain the fine structure observed by the previous authors. (ref 14) This may be related to our use of a lamp/monochromator combination rather than laser for the excitation.

An extrapolation of the energy of the relaxed triplet state from the phosphorescence curve is not easy because of overlap with the fluorescence but its energy appears to be comparable with that of an Si-Si bond (of the order of 75-80 kcal/mol). This indeed makes the triplet state a potential candidate for the photochemical precursor to homolytic bond cleavage. Also, simple potential energy diagrams suggest the triplet as opposed to singlet as the likely precursor state, since the dissociation limit for the ground state and the triplet state is a pair of radicals, whereas the dissociation limit of the excited singlet is an ion pair, much higher in energy.

Second, our attempts to directly prove the involvement of the triplet state in the photodegradation process have given somewhat ambiguous results. For some polymers, such as poly(di-n-hexylsilane), we have observed no quenching of fluorescence nor of the initial rate of disappearance of the polymer absorption peak in the well-known triplet quencher, piperylene, as solvent. For other polysilanes, such as polymethylpropylsilane, significant quenching of the degradation rate but not of fluorescence was observed. At least in some polysilanes then, direct proof exists of the involvement of the triplet state in the photodegradation processes responsible for rapid decrease of the molecular weight. It is quite possible that for the remaining poly(dialkylpolysilanes) the triplet is too short lived to be quenched even by a neat solvent. More detailed and quantitative analysis of the quenching process remains to be performed.

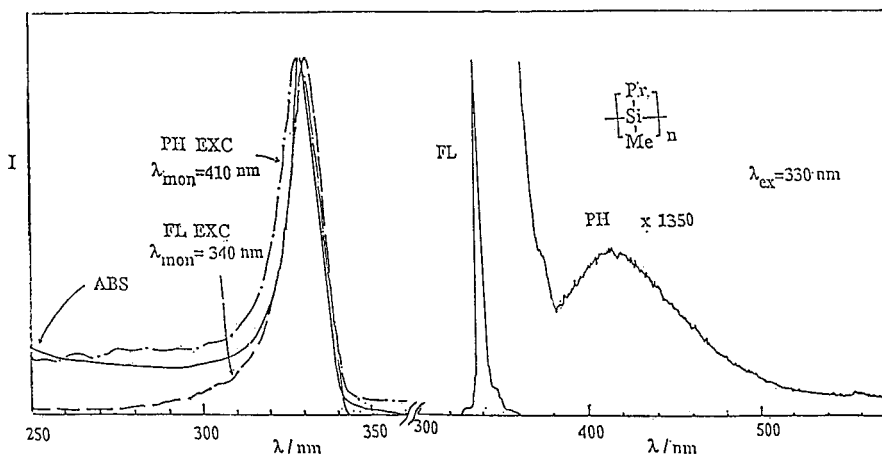


Fig. 2. The fluorescence (FL), phosphorescence (PH), fluorescence excitation (FL EXC), phosphorescence excitation (PH EXC) and absorption (ABS) spectra of poly(methylpropylsilane) in 3-methylpentane at 77 K. The wavelengths at which emission was excited (λ_{ex}) and monitored (λ_{mon}) are given.

Third, we have measured the fluorescence quantum yields as a function of the excitation wavelength for a fair number of poly(dialkylsilanes) and found the same general behavior already noted earlier: (ref 14,28) the quantum yield drops in the range of 340 to about 310 nm and then remains approximately constant at shorter excitation wavelengths. Isotopic substitution on poly(di-n-hexylsilane) had an unexpected effect. While the limiting short wavelength quantum yield for the unlabeled material and for material fully deuterated in the β positions of the hexyl chains is about 0.3, that of the material fully deuterated in the n-hexyl side chains and of the material carrying (ref 13) C in all positions of the n-hexyls is only about 0.2. The difference is well reproducible. There is much less difference at the longer wavelength of excitation where all the quantum yields are higher and reach values close to 0.5, although possibly even here the α labeled material has somewhat lower quantum yields. This results suggest some involvement of the silicon carbon bond in the photochemical processing competing with fluorescence, and we shall return to this subject below.

Fourth, we have measured the relative photodegradation rate as defined by the initial decrease of the intensity of the polymer absorption peak as a function of irradiation wavelength, and for poly(di-n-hexylsilane) find that a maximum is reached near 325 nm. At longer wavelengths the rate decreases and this is presumably complementary to the increase of fluorescence. However, even at shorter wavelengths, where fluorescence quantum yield remains constant, the relative initial photodegradation rate decreases somewhat. This effect needs to be investigated in additional detail but a tentative attribution to the opening of a new photochemical channel (1) at short wavelengths will become obvious in the following.

It is clear that additional photophysical studies are called for but before engaging in these, we have attempted a more thorough analysis of the reaction products in order to establish the chemical reaction paths followed. To our surprise this led to the discovery of a new reaction path for polymer chain degradation. (ref 43)

PHOTOCHEMISTRY OF POLY (DIALKYL SILANE) PHOTODEGRADATION IN ROOM-TEMPERATURE SOLUTION

We have recently confirmed the previous report on the chemistry produced by irradiation of polysilane solutions at room temperature (ref 20) and obtained four new results. (ref 43)

First, the formation of dialkylsilylenes $RR'Si$ only occurs at relatively short excitation wavelengths, whereas the photodegradation of molecular weight occurs at all wavelengths that are absorbed. The generality of this surprising observation is still being examined. Second, we have obtained information on the fate of the primary products. Third, we have determined the structure of the persistent radicals formed in the photolysis experiments, and fourth, we have discovered a novel photochemical degradation path (3). Most of the experiments were performed on poly(di-n-hexylsilane) but poly(di-n-butylsilane) appears to behave very similarly in most respects.

Wavelength dependence of silylene extrusion

In a cyclohexane - triethylsilane mixture (1:1) exhaustive irradiation at either 248 or 254 nm produces the expected silylene adduct as described in ref 20. The use of deuterated triethylsilane yields the expected Si-D insertion product and Si-H terminated disilane and trisilane. The silylene trapping product appears without an induction period so that the monomeric $RR'Si$ is clearly being generated from the polymer itself. As the wavelength of irradiation is increased, the quantum yield of the silylene trapping product gradually decreases and reaches zero above 300 nm. Under these conditions the polymer absorption band at 316 nm still disappears rapidly during the irradiation process and ESR signals appear, as they did at shorter wavelengths. Relative to the quantum yield at 250 nm, those at 270 nm, and 308 nm are only 70%, 17% and 0% respectively. This result has several important consequences. First, the uncoupling of the formation of the monomeric silylene and of the polysilyl radicals clearly demonstrates that they do not need to originate simultaneously, but rather in two distinct and competing processes as noted above. Second, the fact that the radicals are still produced under conditions that yield no silylene demonstrates that they do not undergo a thermal fragmentation with a sequential loss of single silylene units at room temperature as proposed

previously. (ref 3) This also agrees with recent observations (ref 44) on the pentamethyldisilyl radical. Third, if we accept the above description of the polysilane chain as consisting of a series of chromophoric absorbing units of different lengths and excitation energies, and if we assume that the photochemistry of each individual chromophore is wavelength independent, as is often the case in organic photochemistry, we are led to the suggestion that excitation of short chromophores of relatively high excitation energy, say up to Si₇, is necessary for the silylene extrusion reaction (1) while the longer chromophoric segments do not undergo this process. Thus, the spectroscopic heterogeneity of the polysilane chain is paralleled by its photochemical heterogeneity. It is even possible that the short chromophoric segments do not undergo any homolytic cleavage. Rather, they could transfer the singlet excitation energy to the longer chromophores, or undergo intersystem crossing and then transfer triplet excitation energy to the longer chromophores, which would then undergo the homolytic cleavage reaction (2).

Fate of the primary products

We find that 308 nm irradiation of poly(di-n-hexylsilane), either unlabeled or fully β deuterated in the n-hexyl chains, produces only Si-H and no Si-D bonds in pentane, pentane-d₁₂, cyclohexane, cyclohexane-d₁₂, or Et₃SiD as solvents, as judged by FT-IR spectroscopy. On the other hand, poly(di-n-hexylsilane) fully deuterated in the α positions of the n-hexyl chains yields only Si-D and no Si-H bonds at this irradiation wavelength. This result is compatible with standard radical disproportionation (ref 1,4,28) but not with more or less random hydrogen abstraction from the solvent (ref 1) or from the side chains (ref 3) by polysilyl radicals with formation of carbon-based radicals which have also been proposed. Additional evidence for the formation of polysilyl radicals and their recombination is provided by the presence of cross-products such as HSiH_xSiBu₂H among the photoproducts from the 248 nm irradiation of a mixture of poly(di-n-hexylsilane) and poly(di-n-butylsilane) in a mixture of cyclohexane and triethylsilane. The yield of the cross products increases very strongly in the absence of the triethylsilane since then the monomeric silanes formed are not scavenged and are free to insert into Si-H chain termini, providing another route to the cross products. Thus, we feel that there now is good evidence supporting the often postulated homolytic cleavage of the polysilane chain (2) as one of the important mechanisms for chain length degradation.

The formation of Si-H in addition to Si-D bonds in the 248nm irradiation of poly(di-n-hexylsilane) fully deuterated in the α position is not due to β hydrogen abstraction from the silene formed by disproportionation as proposed originally. (ref 28) since the formation of Si-H bonds is suppressed in the presence of Et₃SiD, it is clear now that they must originate from di-n-hexylsilylene by intramolecular C-H insertion. This could be photochemical as observed recently in di-t-butyl-silylene, (ref 45) or more likely, thermal. Similar cyclization forms an important part of the mechanism proposed to account for laser desorption mass spectra of neat poly(dialkylsilanes) obtained with 308 nm line of the excimer laser and believed to be a predominantly thermal process. (ref 13, 14) In room temperature solutions, di-n-hexyl-silylene does not insert into C-H bonds in an intermolecular fashion since no SiD bond formation is observed upon irradiation of poly(di-n-hexylsilane) in cyclohexane-d₁₂ at 248 nm. An isomer of poly(di-n-hexyl-silylene) was detected among the products obtained after exhaustive irradiation of di-n-hexylpolysilane in cyclohexane at 248 nm and its structure is currently under investigation. In addition to recombining and disproportionating, the polysilyl radicals formed in the primary photochemical step can also add to double bonds. This has already been demonstrated for C-C double bonds and olefins (ref 4) but a similar addition to the Si-C double bond may be responsible for the removal of the other product of polysilyl radical disproportionation, a silene, from the reaction mixture. We do not observe the volatile products that ought to result from exhaustive irradiation of the 1,3-disilacyclobutane dimers that would normally be expected from dimerization of silenes and it appears probable that polysilyl radicals present in large concentrations attack the silene on the carbon of the double bond, producing a new silyl radical which can again participate in a disproportionation reaction until either all α hydrogens have been removed or steric hindrance has increased enough to make the silene unreactive. The resulting β -silylated silene would then have a high enough molecular weight to escape detection by our GC-MS technique after exhaustive photolysis. The fate of the silenes, however, still clearly remains to be investigated further.

The structure of the persistent radicals

We have observed the formation of quite strong ESR signals in the irradiated room temperature solutions of polysilanes and noted that more than one persistent radical appears to be present. (ref 28) We have now succeeded in elucidating the structure of the initially formed persistent radical. It corresponds formally to a loss of one or the other alkyl radical from one of the silicon atoms of the chain, with similar probabilities. Spin counting established that the yield of the radicals is relatively small: only a few percent of the total number of silicon atoms become radical centers. Any wavelength absorbed by the polymer can be used to produce the radicals. They are not formed by a simple homolytic C-Si bond cleavage since the resulting alkyl radical should give rise to an alkane and alkene. While the alkene would be consumed under the conditions of the experiment as tested independently, the alkane would survive, but it has not been observed by GC-MS.

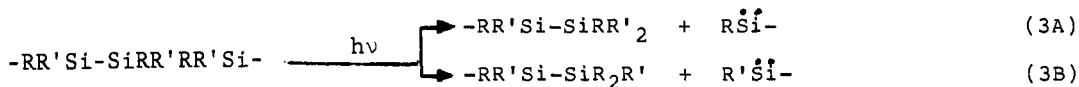
The analysis of the spectra of the radicals was complicated by their temperature dependence, presumably due to hindered rotation of the alkyl attached to the radical center around the Si-C bond. We believe that the tricoordinate silicon, is nearly planar and that the two preferred conformations have either one or the other C-H bond lined up close to normal to the plane. The rate of the hindered rotation decreases with temperature and also with the increasing size of the alkyl substituent.

In spite of this complication, the ESR and ENDOR evidence for the structure assignment is firm. The results are quite similar for the different alkyls used and the numbers for poly(di-n-hexylsilane) will be quoted as representative. The g value, $g = 2.00472$, is compatible only with disilylsilyl or trisilylsilyl radicals. Si satellites produce coupling constants of $a_{\alpha} = 5.8$ G (2Si) and $a_{\beta} = 75$ G (this signal is weak, presumably due to incomplete motional averaging of this highly isotropic interaction). The two coupling constants are assigned to the $-\text{Si}^{\alpha}-\text{Si}^{\beta}-\text{Si}^{\alpha}-$ moiety. The proton coupling constants correspond to large coupling to two equivalent protons near the high temperature limit, $a_{\alpha} = 6.99$ G (2H). Near the low temperature limit this changes into two unequal coupling constants, $a_{\alpha} = 121$ G (1H) and $a_{\alpha}' = 3$ G (1H). In addition, ENDOR spectroscopy has demonstrated the presence of smaller coupling to more distant hydrogens, $a_{\beta} = 0.34$ G and $a_{\gamma} = 0.13$ G. The assignment of the proton coupling constants to the alkyl chain on the tricoordinate silicon, $-\text{CH}_2^{\gamma}-\text{CH}_2^{\beta}-\text{CH}^{\alpha}-\text{H}^{\alpha}-\text{Si}^{\alpha}$, is based on the effects of α and deuteration on the ESR and ENDOR spectra. Two of the polymers gave radicals with distinctly different proton coupling patterns. These were, first, the case with a methyl on the tri-coordinate silicon, which yields a temperature-independent coupling constant $a_{\alpha} = 9.4$ G (3H) and second, the case in which the substituent on the tricoordinate silicon is cyclohexyl, which yields a temperature-independent spectrum attributed to a mixture of two conformers. These are not interconverting on the time scale of the experiment and have $a_{\alpha}' = 15.5$ (1H) and $a_{\alpha}'' = 2.6$ G (1H), where primes distinguish the two conformers. Finally, the ^{13}C coupling constants from the di-n-hexyl substituted polymer labeled by ^{13}C in all α -positions are $a_{\alpha} = 4$ G (1C) and $a_{\beta} = 4.12$ G (4C). These are assigned to $-\text{C}_2^{\beta}\text{Si}^{\alpha}-\text{Si}^{\alpha}-\text{Si}^{\alpha}-\text{C}_2^{\beta}-$

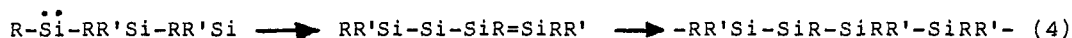
Upon irradiation or extended standing the signals of the initially formed persistent radicals are transformed into signals of another radical whose structure has not yet been elucidated.

Chain cleavage by reductive elimination

It is interesting to speculate about the mechanism of formation of the observed persistent radicals. Since the alkyl lost from one of the silicons does not appear to be lost as a free alkyl radical, it is apparently being transferred in a photochemical step to another silicon atom or, less likely, to another carbon atom. In the former case, trialkylsilyl terminal groups would be produced and we have therefore searched for oligosilanes with such terminal groups in mixtures of products obtained upon exhaustive photolysis of polysilanes in the absence of trapping agents. We found that these materials are indeed formed and represented over 10 percent of the volatile constituents. This leaves little doubt that reductive elimination analogous to the thermal decomposition of disilanes (ref 47) must indeed be a primary photochemical process. (3)



While direct evidence for the trialkylsilyl terminated chains is thus available, an attempt to trap the other reaction product, an alkylsilylene-terminated polysilane, with Et_3SiD , was not successful and no Si-D bonds were observed in the FT-IR spectrum. This is perhaps not a surprise since the rearrangement of disilylsilylenes to silyldisilenes is known to be extremely facile. (ref 48) If the expected disilene is indeed formed, its Si-Si double bond could be expected to suffer a fate similar to that of an intentionally added C=C double bond in the same reaction mixture, namely addition of one of the polysilyl radicals. Such an addition should occur at the less hindered end (4) and would produce the persistent radical observed



We feel that the combination of equations 2, 3, and 4 provides a fairly convincing mechanism for the formation of the observed persistent radicals.

CONCLUSIONS

Although many aspects of the photodegradation of polysilanes in solution remain to be elucidated, we believe that some of the gross features are beginning to become clear. It now appears very likely that it is correct to view the polysilane chain as a collection of weakly interacting chromophores with a statistical distribution of lengths, each acting as an independent absorber and also as an independent photochemical substrate. Although the detailed nature of the electronic states involved in each of the three primary photochemical processes that have been established is not known with any certainty, the chemical processes involved in the three reactions are now clear. They are (1) silylene extrusion, (2) homolytic chain cleavage, and (3) chain cleavage by reductive elimination. Even the successive fate of the primary products from each of these steps has now been in part elucidated and the stage is set for a more quantitative investigation of these photochemical processes.

Acknowledgement This project was supported by the U. S. National Science Foundation (CHE 8796257) and by IBM Corporation (7097312). R. D. Miller gratefully acknowledges partial support from the Office of Naval Research.

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