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"Radiation Sensitivity of Soluble Polysilane Derivatives: Science and Applications"

by
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ABSTRACT: Polysilane derivatives have very unusual electronic properties associated with extensive sigma delocalization along the polymer backbone. Strong electronic transitions which depend on the nature of the substituents, the polymer molecular weight and the conformation of the backbone appear in the UV. These materials are radiation sensitive and are degraded to lower molecular weight fragments upon exposure to light and ionizing radiation. This review attempts to overview the nature of these radiation induced processes and describes some potential applications primarily in the field of microlithography.

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The first diaryl substituted polysilane derivative was probably prepared over sixty years ago by Kipping (1). The simplest dialkyl substituted material, poly(dimethylsilane), was described in 1949 by Burkhard (2). These materials were, however, highly insoluble and intractable and attracted little scientific interest until recently. The modern era in polysilane chemistry began about 10 years ago with the synthesis of a number of soluble homo and copolymers (3-5). The current interest in substituted silane polymers has resulted in a rapidly expanding list of new potential applications. In this regard, polysilane derivatives have been described as [1] thermal precursors to β -silicon carbide (6-8); [2] oxygen insensitive photoinitiators for vinyl polymerizations (9); [3] a new class of polymeric charge conductors (10,11); [4] radiation sensitive materials for microlithographic applications (12,13) and [5] a new class of polymeric materials with interesting nonlinear optical properties (14-15).

High molecular weight substituted polysilanes are usually prepared by modified Wurtz coupling of the respective dichlorosilanes using sodium metal (16). Other procedures have recently been described (17-21) but these generally result in the production of lower molecular weight polymers or oligomers. Using the modified Wurtz coupling, a large number of high molecular weight soluble polysilane derivatives have been prepared (16,22). The mechanism of this heterogeneous polymerization is quite complex and significant solvent effects have been reported (12,16,23).

One of the most interesting characteristics of the polysilanes is their unusual electronic spectra (16). Even though the backbone is fully sigma bonded, all substituted silane polymers absorb strongly in the UV-visible region. Their absorption spectra depend to some extent on the nature of the substituents. In this regard alkyl substituted, atactic, amorphous materials absorb from 300-325 nm with sterically bulky groups producing a shift to longer wavelengths (13,24), while aryl substituents which are directly bonded to the silicon backbone result in significant red shifts of 25-30 nm (24). Recently it has been reported that the absorption spectra of polysilane derivatives also depends on the conformation of the silicon backbone (25-31). This results in a curious

thermochromic behavior for many polysilane derivatives both in the solid state and also in solution (32,33). It is now generally agreed that the planar zig zag conformation results in large spectral red shifts and that the position of the absorption maximum is quite sensitive to changes in the backbone conformation (31). Soluble substituted diaryl polysilane derivatives are the most red shifted of all and it has been suggested that this effect is also mainly conformational in origin (31,34). Recent light scattering studies have provided some additional support for the hypothesis that the diaryl polysilanes are significantly extended even in solution (35).

The absorption spectra of polysilane derivatives also depend somewhat on the molecular weight (24). In this regard, the λ_{max} moves progressively to longer wavelengths with increasing catenation for short oligomeric chains but rapidly approaches a limiting value for high molecular weight polymers at a degree of polymerization of around 40-50 as shown in Fig. 1. A similar limiting effect is observed for the molar extinction coefficients as a function of molecular weight.

The polysilanes constitute a new class of radiation sensitive materials which are sensitive to uv light as well as to various types of ionizing radiation (vide infra). The observed dependence of both the position of the absorption maximum and the molar extinction coefficients on the polymer molecular weight suggests that any process which significantly reduces the molecular weight should result in spectral bleaching. This effect would have major lithographic consequences (vide infra). The response of a typical polysilane derivative to irradiation is shown in Fig. 2. The strong bleaching suggests that there is a significant reduction in the molecular weight of the polymer upon exposure. The bleaching phenomenon is characteristic of both alkyl and aryl substituted polysilanes upon exposure to uv light and is quite general. Subsequent studies have confirmed that there is a significant reduction in the polymer molecular weight upon exposure. This effect is demonstrated in Fig. 3 which shows the decrease in the molecular weight of a typical polysilane poly(dodecylmethylsilane) in solution upon exposure to uv light. Similar effects are observed upon irradiation of solid polysilane

films. Although spectral bleaching with attending molecular weight reduction occurs both in air and under high vacuum, there appears to be little doubt that some oxidation of the silicon backbone occurs in the presence of air. This was first demonstrated by Zeigler and coworkers (13) who reported the appearance of a strong band at 1020 cm^{-1} in the infrared characteristic of SiOSi functionality upon exposure of a film of poly(cyclohexylmethyl-co-dimethylsilane) at 254 nm in the presence of air. We have also observed that similar changes occur in films of poly(di-n-pentylsilane) upon irradiation in the presence of air (Fig. 4). In addition to the appearance of the characteristic band at 1021 cm^{-1} , weaker bands at 2080 and 3382 cm^{-1} which are ascribed to SiH and SiOH vibrations are also apparent.

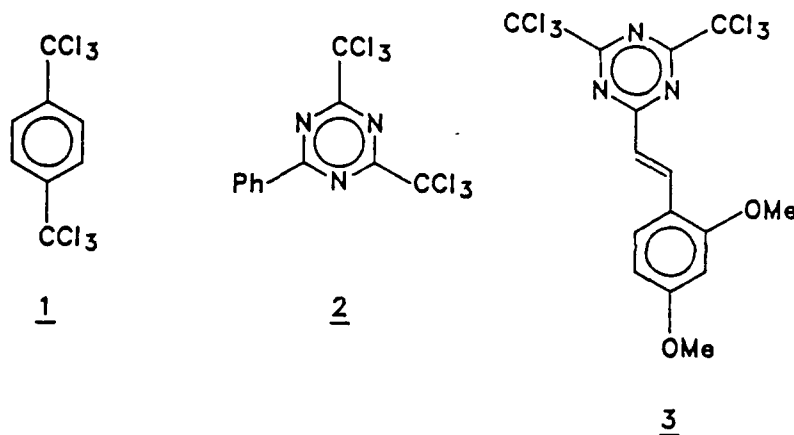
Since most imaging processes utilizing polysilanes employ the materials in thin film form and are most often conducted in air, the effect of air on the photochemical degradation assumes some importance. In a study of the spectral bleaching rates for a number of polysilanes in air relative to those observed in vacuum, we have noticed that the effect in air depends strongly on the structure of the polymer, although some acceleration is observed for almost all of the samples when irradiated in air (36). At this point, it is not clear whether the differences in the bleaching rates are only a function of the nature of the substituents and/or the physical characteristics of the polymer (Mw, Tg, etc.) since the latter could influence reactivity by changing the mobility of reactive sites, the rate of diffusion of oxygen, etc. A detailed study of the effect of air has recently been reported by Ban and Sukegawa (37). These authors analyzed the siloxane content of irradiated films of poly(methyl phenylsilane) (PMPS) and poly(n-propylmethylsilane) (PMPrS) by infrared in comparison with authentic polysiloxane samples. On the basis of these experiments, the authors conclude that at 254 nm PMPS and PMPrS are almost completely oxygenated at saturation. The extent of oxygenation of both samples was considerably less at 330 nm presumably due to spectral bleaching of the initial absorption band resulting in inefficient light absorption. In each case, there was also an attending reduction in the molecular weight of the oxygenated polymer. Subsequent

imaging studies on these materials irradiated comparatively in air and under vacuum suggested that photooxidation plays an important role in subsequent pattern development.

We have also observed that the rate of bleaching of solid polysilane films upon irradiation is considerably slower than that observed for solutions at comparable optical densities (36). While this is consistent with the observed decrease in the quantum yields for scission (Φ_s) in going from solution to the solid state (24) (*vide infra*), the decreased sensitivity is inconvenient for imaging processes. For this reason, we began to search for compatible additives which might influence the bleaching rate of polysilane derivatives in the solid state. In this regard, we have found that a number of polyhalogen substituted aromatic derivatives such as 1 – 3 greatly accelerate the rate of bleaching of a number of polysilane derivatives in the solid state (38). This effect is dramatically demonstrated in Fig. 5 for a poly(methylphenylsilane) film doped with ~20% by weight of 1,4-bis trichloromethylbenzene 1. Similar results were obtained using substituted triazine sensitizers such as 2. In these cases, the polysilane is the primary absorber of the incident radiation. Interestingly, when 3, which absorbs at ~400 nm, was incorporated into a film of poly(methylphenylsilane) and the sample irradiated at 404 nm where only the sensitizer absorbs, both the polysilane and the sensitizer absorptions at 343 and 400 nm, respectively, were efficiently bleached. This accelerated bleaching in the solid state appears, however, not to be a general phenomenon and depends on the structure of the polysilane. For example, the incorporation of sensitizer 2 into a film of a typical dialkyl polysilane such as poly(cyclohexylmethylsilane) did not accelerate the bleaching of the polymer film. In fact, the presence of 2 seems to actually inhibit the photochemical bleaching process somewhat.

The mechanism by which the halogenated additives promote the bleaching of poly(methylphenylsilane) while inhibiting the same process in poly(cyclohexylmethylsilane) is a source of some speculation and is currently under investigation. Although it is conceivable that halogenated sensitizers such as 1 – 3,

could serve simply as halogen atom transfer reagents to inhibit the recombination of incipient reactive silicon chain fragments (e.g., silyl radicals), it seems unlikely that they would do so selectively only for the fragments derived from poly(methylphenylsilane). It has also been suggested that the photochemistry of polysilane derivatives occurs via the triplet state (13,30) on the basis of the observation of a weak structured phosphorescence characteristic of a localized excited state for a number of polysilane derivatives. In principle, the halogenated additives could be promoting intersystem crossing via an intermolecular heavy atom effect (39). Again, however, it is hard to see why the two structurally similar polysilanes should respond so differently to the presence of the additive.



One possible explanation for the selective accelerated decomposition of poly(phenylmethylsilane) in the presence of the chlorinated additives is that the photochemical bleaching occurs by electron transfer. In this regard, the two polysilane derivatives may well behave differently since the oxidation potential of a thin film of PMPS is lower by almost 0.5 eV than typical dialkyl substituted polysilane derivatives (40). In addition, the electrochemical oxidation of PMPS is highly irreversible and the polymer film is removed from the electrode presumably as smaller silicon containing fragments. Such a photochemical mediated electron transfer reaction would also be facilitated by the high electron affinities of polyhalogenated aromatics which subsequently decompose by dissociative electron attachment (41). The instability of

both the polysilane radical cations and the polyhalogenated radical anions should improve the overall efficiency of the process by inhibiting back electron transfer.

Photochemistry

It is curious that in spite of the considerable interest in the radiation sensitivity of polysilane high polymers, there have been relatively few detailed studies on the nature of the products and intermediates produced upon irradiation. This is certainly not true for oligomeric polysilanes derivatives which have been extensively studied (42). Since the results of these pioneering investigations form the basis for the interpretation of many of the subsequent photochemical studies on the polysilane high polymers, this background will be described here.

The simplest radiation sensitive polysilane is one containing disilane structural units. Although simple alkyl substituted disilanes absorb in the far and vacuum ultraviolet, aromatic substituents cause a red shift to the accessible uv region. It is generally agreed that the photochemical decomposition of disilanes leads predominately to silicon-silicon bond homolysis and the production of substituted silyl radicals. Silyl radicals once generated may abstract hydrogen or halogen atoms from suitable donors, add to vinyl and aromatic groups, react with alcohols by abstracting either hydrogen atoms or alkoxy radicals and many other characteristic reactions (43). Due to the relatively low bond energy of the SiH bond ($81-88 \text{ kcal mol}^{-1}$) (44), the abstraction of hydrogen atoms from typical alkanes is normally endothermic except for the most highly activated carbon-hydrogen bonds. Encounters between silyl radicals in solution or in the gas phase usually result in recombination and disproportionation (45). The latter results in the production of silanes and highly reactive silenes. The disproportionation reaction is thermodynamically favorable because of the formation of a silicon-carbon double bond which, while subsequently chemically reactive, is worth $\sim 39 \text{ kcal mol}^{-1}$ (44). In this regard, it has recently been demonstrated that in the case of pentamethyldisilanyl radicals, disproportionation is kinetically competitive with radical dimerization (46). In a earlier study by Sommer and coworkers shown below (Scheme I), the authors

conclusively demonstrated by isotopic substitution and trapping that the silyl radicals generated by photolysis undergo disproportion as well as presumably dimerization (47). In deuterated methanol the silanes produced were predominately undeuterated while the methoxy diphenylmethyl silane was extensively deuterated in the α position. The results of these experiments strongly implicated the substituted silene produced by disproportionation.

Scheme I

In another model study by Ishikawa and coworkers (42,48) on phenylpentamethyldisilane it was shown that phenyl substituted silyl radicals can undergo ortho radical addition to produce unstable silenes which can be subsequently trapped and identified (Scheme I). Subsequent spectral studies have identified the silene as a reactive intermediate in this process (49).

Ishikawa and coworkers have also studied the photolysis of a number of polymeric disilane derivatives. In this regard, they have examined both derivatives with pendant silicon substituents (50) and also those materials where the disilane moiety is incorporated into the polymeric backbone (51). In the former case shown below in Scheme II, irradiation destroys the characteristic phenyl disilane absorption at 235 nm and the polymer is insolubilized through crosslinking. Infrared examination of the photodegraded polymer showed a weak -SiH absorption in the infrared at 2150 cm^{-1} . Model studies on 1,1-bis-trimethylsiloxy-1-phenyltrimethyldisilane showed that SiSi bond homolysis occurs and products characteristic of silyl radical abstraction and substitution were isolated. On the basis of these model studies, the mechanism shown below which involves SiSi bond homolysis followed by characteristic silyl radical reactions was postulated. Furthermore, oxidation studies on the photodegraded polymer suggested that, unlike phenylpentamethyl disilane, the siloxy disilane polymer shows

little inclination toward trimethylsilyl radical addition in the ortho position of the incipient phenyl silyl chain radical.

Scheme II

Ishikawa and coworkers have also reported the photodegradation of backbone disilane polymers and the results are shown in Scheme III. In this case, as in the previous example with pendant silyl substituents, silicon-silicon bond homolysis to produce silyl radicals seems to be the predominate process. When irradiated in toluene, the photodegraded polymer shows a substantial - SiH band at 2150 cm^{-1} in the infrared. Similarly, NMR examination of the irradiated polymer shows evidence of silyl radical substitution into the solvent toluene. Irradiation of the polymeric disilane in methanol-d produced no SiD in the IR and resulted in the incorporation of the elements of methanol into the chain ends (NMR). For the phenyl substituted polymer, NMR evidence indicates < 5% of any rearranged cyclohexadiene derivatives were formed. On the basis of these experiments coupled with molecular weight studies on the photodegraded samples which confirmed that a considerable reduction in molecular weight had occurred, the authors have postulated a mechanism involving silicon-silicon bond homolysis followed by radical disproportionation. Irradiation of solid films resulted in increased solubility in the exposed areas and the formation of very little SiH in the photodegraded sample (this depends somewhat on the nature of the silicon substituents). Instead the IR spectra of the products show strong absorption bands attributed to - SiOH and SiOSi groups which suggests that in the solid films the incipient silyl radicals are efficiently scavenged by oxygen to produce predominately silanols and siloxanes.

Scheme III

Although it seems clear that polymeric disilane derivatives photodecompose by bond homolysis to produce silyl radicals, model studies on larger silicon catenates indicate that their photochemistry may be more complex and this work is summarized below in Scheme IV. Cyclosilanes derivatives appear to extrude monomeric silylenes upon irradiation producing smaller cyclosilanes (52). The proposed silylene intermediates have been spectroscopically identified (49,53) and trapping adducts have been isolated in solution. Exhaustive irradiation ultimately results in acyclic silanes which have been suggested to result via hydrogen abstraction by silyl radicals. The extrusion of substituted silylenes from the larger cyclosilanes is interesting and in at least in one reported case the stereochemistry of the starting material is preserved suggesting that the extrusion and rebonding may be a synchronous process (56). Similar extrusion reactions also occur for acyclic polysilanes (57). In the latter examples, the isolation of hydrogen terminated silanes containing fewer silicon atoms than the starting materials was taken as evidence for the intermediacy of silyl radicals and the importance of chain scission seemed to increase with increasing catenation.

Scheme IV

High Molecular Weight Polysilane Photolysis

Similar trapping experiments have been performed using high molecular weight soluble polysilanes in the presence of suitable trapping reagents (58). Since silyl radicals readily abstract a chlorine atom from chlorinated alkanes (43), a sample of high molecular weight poly(cyclohexyl methyilsilane) was irradiated at 300 nm in carbon tetrachloride. The formation of hexachloroethane was taken as indicative of the presence of trichloromethyl radicals possibly formed by chlorine atom abstraction by silyl radicals. In this regard, the yield of hexachloroethane was 33% based on the number of monomer units which would suggest that ~66 trichloromethyl radicals were formed for every 100 silicon atoms in the backbone. While instructive, this experiment

doesn't rule out the possibility that the trichloromethyl radicals could be produced by electron transfer rather than by halogen atom abstraction.

A number of polysilane homo and copolymers were also irradiated in the presence of trapping reagents such as triethylsilane, methanol and n-propanol. The results from the exhaustive irradiation of a number of polysilane derivatives at 254 nm in the presence of triethylsilane (TES) are shown below (Table I). In each case, the adduct of the diakyl substituted silylene and TES was the predominate product. Also produced concurrently in significant yields were the corresponding disilanes. Similar products were produced from copolymers such as poly(cyclohexylmethyl-co-dimethylsilane) and materials characteristic of the copolymer composition were obtained. In this regard it is significant that three disilanes (i.e., 1,2-dicyclohexyl-1,2-dimethyl; 1,1,2,2-tetramethyl; and 1-cyclohexyl-1,2,2-trimethyl) as well as the two substituted silylene adducts were produced from the predominately random copolymer. It is assumed that the disilanes, which are taken to be diagnostic of silyl radical abstraction, accumulate in the mixture because they no longer absorb light significantly at 254 nm. The photoinstability of a model trisilane 2-n-butyl-(1,1,1 2,3,3,3-heptamethyl trisilane) was demonstrated under the reaction conditions even though its absorption maximum occurs around 215 nm.

Table I

Similar results were obtained for the photolysis of poly(n-hexylmethylsilane) using either methanol or n-propanol as the trapping reagent and these results are shown in Table II. The additional complexity of the disilane products is anticipated since silyl radicals can alternatively abstract either a hydrogen atom or an alkoxy radical. Although the alkoxy disilanes could conceivably be produced by other mechanisms (e.g., alcoholysis of SiH bonds or addition to an intermediate disilene) these routes were considered unlikely on the basis of appropriate control experiments or the lack of literature precedent.

Table II

The results of exhaustive irradiation of substituted silane high polymers in solution suggest that two intermediates (i.e., silylenes and silyl radicals) are produced. On the basis of this information a tentative reaction scheme (Scheme V) is shown below. It should be emphasized that this proposal is based only on the trapping of the reactive intermediates. It does not preclude the existence of independent photochemical channels which might produce exclusively silylenes or silyl radicals or that these pathways may be occurring concurrently as would seem likely from the thermodynamic considerations. It also does not preclude the possibility that silylenes are produced from silyl radicals by a cascade process, although there appears no compelling reason either based on thermodynamics or literature precedent (46) to so conclude or that the photochemical intermediates are even necessarily the same when they are produced from high polymer or smaller oligomeric fragments. Obviously the elucidation of a photochemical mechanism for the photodegradation of a high polymer is a complex task and in the case of the polysilanes there is certainly room for additional mechanistic studies

Scheme V

While the production of substituted silylenes in the exhaustive photolysis of substituted silane high polymers in solution seems secure from the diagnostic trapping products, the suggested intermediacy of silyl radicals rests only on the isolation of fragments which contain SiH bonds which are presumably formed by hydrogen abstraction. Recently, however, Michl and coworkers have reported the ESR detection of persistent radicals produced upon irradiation of a number of dialkyl polysilanes in 3-methylpentane at room temperature (59). The ESR signals are overlapping and complex are probably derived from at least two radical species. The radicals have been

tenatively and identified as silicon centered based their G values, the observation of a ^{29}Si hyperfine interaction, as well as their reactivity with oxygen and chlorocarbons. In no case, however, was a persistent radical observed which is split by four equivalent α -hydrogens as would be expected for a radical produced by simple chain scission. In the case of poly(di-n-hexylsilane) PDHS an early radical with a G value of 2.0046 was observed with a ^{29}Si hyperfine splitting of $\sim 75\text{G}$. This G value is consistent with those previously reported for persistent silicon centered radicals (43). The low value for the ^{29}Si hyperfine splitting is most consistent with a polysilylated silyl radical. Continued irradiation produces another persistent silicon centered radical which shows no proton splitting and whose ^{29}Si hyperfine splitting is $\sim 56\text{G}$. Irradiation of PDHS in deuterated pentane produces no photodegraded materials which show an SiD stretch in the infrared. On the other hand, irradiation of PDHS which had been fully deuterated in the α -carbon positions at 248 nm results in both SiH and SiD bands. Faced with the task of generating a series of sterically hindered polysilyl substituted radicals upon irradiation, the authors have proposed a tentative reaction scheme involving silyl radical formation, disproportionation to silanes and silenes followed by readdition of silyl radicals to the silenes. The disproportionation of silyl radicals is a well established process which is kinetically competitive with recombination. Repetition of this process would eventually lead to a highly sterically encumbered and undoubtedly persistent silicon based radicals carrying only silicons in the α -positions. While such a scheme would explain much of the data in this obviously very complex process, the postulate is very tentative and other possible sources of persistent silyl radicals have not been ruled out.

The suggestion that silyl radical disproportionation may play a significant role in hindering chain repair by silyl radical recombination suggests that polysilane derivatives which have no α -hydrogens might be more resistant to photochemical degradation as determined by spectral bleaching. Unfortunately, fully alkyl substituted polysilanes with no α -hydrogens are very sterically hindered and synthetically inaccessible. Diaryl substitution relieves some steric congestion, but the simplest derivative

poly(diphenylsilane) is extremely insoluble and intractable. Recently we have described the preparation of a number of poly(bis-p-alkylphenylsilanes) (PBHPS) which are soluble and can be spin cast into films (34). These materials have no α -hydrogens, although they do contain reactive benzylic hydrogens in the remote para positions. Figure 6 shows that in solution poly(bis-p-n-hexylphenylsilane) is extremely photolabile and bleaches readily upon exposure similarly to the alkyl substituted polysilane derivatives. This is not surprising since the chain end mobility in solution is such that the benzylic hydrogens might be available to allow disproportionation to be kinetically competitive with silyl radical recombination. In the solid state, however, where this mobility is greatly restricted, the remote benzylic hydrogens should be much less accessible to a silyl radical produced by chain scission. Consistent with this proposal is the observation that (PBHPS) bleaches extremely slowly in the solid state (Fig. 6).

These photochemical studies on polysilane high polymers suggest that they constitute a new class of photosensitive materials. The bleaching studies indicate that significant molecular weight reduction occurs upon irradiation either in air or in vacuo which in turn implies that the polymers are predominately of the scissioning type.

For polymers which undergo simultaneous scissioning and crosslinking, an estimation of the relative efficiencies of each process can be obtained by monitoring the change in the number and weight average molecular weight as a function of the absorbed dose (60). The relationship between the molecular weights and the respective quantum yields is described by the equations shown below.

$$\frac{1}{M_n} = \frac{1}{M_n^0} + (\Phi(s) - \Phi(x)) \frac{D}{N_A}$$

$$\frac{1}{M_w} = \frac{1}{M_w^0} + \left(\frac{\Phi(s) - 4\Phi(x)}{2} \right) \frac{D}{N_A}$$

In these equations D represents absorbed dose and N_A is Avogadro's number. The slopes of the respective plots of $1/M_n$ and $1/M_w$ versus dose produce two simultaneous

equations the solution of which yields values for $\Phi(s)$ and $\Phi(x)$. We have analyzed the data obtained for a number of polysilane derivatives using GPC to evaluate the respective molecular weights and distributions and the results are reported in Table III (61). Polystyrene standards were used for molecular weight calibration.

Table III

Although the numbers in Table III are approximate (uncertainties of up to 20% would not be unreasonable) due to variations in the molecular weight distributions of the individual samples, uncertainties in actinometry, the use of polystyrene calibration samples for the molecular weight determinations, etc., certain interesting features are apparent. The quantum yields for scission in solution are, in general, high ranging from ~ 0.5 -1.0. In each case, the polymers are predominately scissioning as predicted from the spectral bleaching studies. Crosslinking is more important for those derivatives where aromatic substituents are directly bonded to the silicon backbone. One particularly striking feature is the significant decrease in the quantum yields for both processes in going from solution to the solid state. This would be expected if species such as silyl radicals are involved in the polymer degradation due to decreased chain mobility and solid state cage effects.

Polysilane Lithography

The polysilanes possess a number of unique characteristics which make them ideally suitable for many lithographic applications. They are: soluble and castable into high optical quality films, thermally stable, imagable over a broad spectral range, strongly absorbing yet readily bleached upon exposure and resistant to oxygen etching in plasma environments. The last property is particularly important for multilayer resist schemes employing oxygen reactive ion etching (O_2 -RIE) for image transfer. This technique has been proposed for the production of high aspect ratio, high resolution images over chip topography (62). This image transfer technique requires an imagable

polymer which is considerably more stable in oxygen plasma environments than normal carbon based polymers so as to serve as an effective etch barrier for the protection of the unexposed regions during the transfer step (63). In this regard, the polysilanes by virtue of their high silicon content which leads to the formation of a thin, highly resistant, silicon oxide etch barrier in an oxygen plasma (64), are ideally suited. An example of a typical bilayer process for the production of high resolution images is shown in Fig. 7. The thin top layer plays a dual role serving both as the imaging layer and also as a barrier layer in the subsequent image transfer process.

Because of their desirable properties and radiation sensitivity, the polysilanes have been employed in a variety of microlithographic applications. In this regard, they have been exercised as: [1] mid UV contrast enhancing materials [2] imaging layers in a variety of bilayer lithographic processes and [3] new resist materials for ionizing radiation.

Contrast Enhanced Lithography

Contrast enhanced lithography is a clever technique which utilizes a thin layer of a bleachable contrast enhancing layer coated over a conventional photoresist to sharpen the mask image of which has been distorted somewhat due to optical diffraction effects (65,66). The actual process is beyond the scope of this discussion and interested readers are encouraged to consult the literature cited for further details. An effective contrast enhancing layer must possess certain essential characteristics. It must be thermally stable, soluble in solvents which permit casting on photoresist layers with no mixing at the interface, strongly absorbing in the desired spectral region and bleachable upon exposure. In addition, this layer should be easily removed from the exposed photoresist prior to image development. Certain polysilane derivatives possess all of these characteristics and have been utilized in the mid UV (300-340 nm) spectral region. In this regard, it is significant that the polysilanes are readily bleached at shorter wavelengths since this potentially provides the improved resolution intrinsic to shorter wavelength exposure sources.

Bilayer Applications

Polysilane derivatives have been utilized as a combined imaging and O₂-RIE barrier layer in a number of bilayer processes such as described in Fig. 7 (12). In this regard, the images have been developed both by classical wet development processes and in an "all dry" technique involving photoablative imaging. In the first case, the polysilane is imaged in a conventional fashion and the images developed to the planarizing polymer layer using an organic developer. These images can be subsequently transferred to the substrate by O₂-RIE. Figure 8 shows some high resolution submicron images generated by such a process. The images in Fig. 8 were initially generated by exposure using a 1:1 commercial projection printer and a mid uv exposure source. Because the etching process can be highly anisotropic, near vertical wall profiles can be produced for high aspect ratio features.

Polysilane Self Development

A second technique which involves photoablative imaging has attracted considerable interest recently because the procedure represents an alternative which does not require the use of organic solvents for development. For this reason, the photoablation of polysilane derivatives has been studied extensively (12,13,64,67-69) and will be discussed in some detail below.

It was first reported in 1982 that organic polymers could be self developed in an imagewise fashion by using high energy density light sources such as UV excimer lasers. Since these initial reports the field has rapidly expanded (70,71).

The first report of self development in the polysilanes appeared in 1984 (67). This was an exciting prospect since the polysilanes had been shown to resist oxygen plasma etching due to the rapid formation of a protective coating of (SiO_x). Since images created in the polysilane can be transferred through a planarizing organic polymer by O₂ reactive ion etching (see above), laser image self development should lead to an all dry (solventless), multilayer lithographic imaging process. Zeigler *et al.* have also

reported the self development imaging of thick polysilane films upon excimer laser exposure (13).

We have investigated the self developing characteristics of a typical aromatic polysilane, poly(p-t-butylphenyl methylsilane) (PTBPMS) using a quartz crystal microbalance to monitor the rate of polymer removal in real time (64,68). This technique is particularly useful for measuring thickness changes in materials which are soft and where stylus penetration from mechanical profilometers is a problem. Changes in the weight of the polymer cause an attending alteration in the crystal oscillation frequency which can be translated into changes in the polymer thickness. This technique is sensitive on a nanogram scale. Figure 9 shows the change in the crystal oscillation frequency for a sample of PTBPMS upon exposure to 248 nm radiation from a KrF excimer laser at various fluences in air. A number of features are obvious from examination of Fig. 9. There appears to be a threshold fluence above which significant weight loss occurs. Above this threshold the loss of material/pulse is roughly constant and the weight loss/pulse increases with laser fluence. Near the threshold significant weight loss does not occur even though photochemistry is occurring as evidenced by spectral bleaching. Interestingly, below the threshold there actually appears to be a small weight gain. This would be consistent with the photooxidation of the polymer via reaction of oxygen with intermediates such as silyl radicals and/or silylenes. Although the rate of photoablation above the threshold is not particularly sensitive to the nature of the bath gas, it does depend on the pressure. In this regard, at a fluence of 76 mj/cm^2 -pulse the rate of weight loss of PTBPMS is approximately 4-6 greater in vacuum (10^{-6} Torr) than at atmosphere pressure. In vacuum, the energy utilization efficiency for PTBPMS at 248 nm is estimated around ~ 1 -1.2 Joules/ cm^2 - μm . Interestingly, a sample of poly(di-n-pentyisilane) which absorbs only weakly at 248 nm was ablated very slowly at a fluence of 75 mj/cm^2 -pulse. However, ablation increased markedly using a XeCl source (308 nm) whose spectral output is near the absorption maximum of the sample (313 nm). For this sample at 308 nm an ablation threshold was also observed

around 50 mJ/cm^2 -pulse. This experiment suggests that the energy deposited per unit volume is an important feature of the ablation process.

We have also demonstrated that poly(p-t-butylphenylsilane methylsilane) can be utilized in a bilayer configuration in an "all dry" lithographic process. Figure 10 shows submicron images produced initially in the bilayer upon exposure at 248 nm and subsequently transferred by O_2 -reactive ion etching.

Other workers have also investigated the phenomenon of polysilane self development. In this regard, Zeigler and coworkers (13) have studied the self development of a number of polysilane homo and copolymers and these workers have found that the self development efficiencies increase with the size of the substituents. They have also suggested that the material removal process for alkyl polysilanes at low fluences ($< 50 \text{ mJ/cm}^2$ -pulse) appears to be photochemical rather than photothermal. Using a 1:1 copolymer poly(methyl-n-propyl-co-isopropyl methylsilane) images were generated by excimer laser exposure at 248 nm.

The same copolymer has been recently investigated in some detail by Hansen and Robitalle (69) using He-Ne interferometry for real time monitoring of the film thickness changes upon exposure at both 248 and 193 nm. At 248 nm and fluences between 60 and 200 mJ/cm^2 -pulse the energy utilization efficiencies varied from $0.3\text{-}2 \text{ J/cm}^2\text{-}\mu\text{m}$ which are similar to those observed in the earlier studies. These values are also similar to results obtained for other organic polymers such as polymethylmethacrylate, poly(ethylene terephthalate) etc. These authors, however, suggest that high peak power values are necessary to cleanly remove material and that the presence of oxygen is detrimental for the production of clean images.

The mechanism of the photovolatilization of polysilanes derivatives has been investigated by several groups who have probed the nature of the gaseous products by mass spectrometry. Zeigler and coworkers (13) studied the fragments ejected from the copolymer poly(cyclohexylmethyl-co-dimethylsilane) in vacuo upon irradiation in the

deep uv and concluded that the major fragments were primarily single monomer units (silylenes) with small amounts of chain fragments up to pentamers. The irradiation source and/or fluence regime was not specifically mentioned in this case. In the presence of oxygen a number of peaks ascribed to the presence of various cyclic siloxanes were identified.

We have investigated the gaseous products ejected from a wide variety of polysilane homo and copolymers using a triple-quadrupole mass spectrometer for the mass analysis (72). The excitation source was a XeCl excimer laser (308 nm) operated at 10 Hz. Ionization of the fragments was induced either by electron impact (50 ev) or by multiphoton ionization (MPI). The experiments were conducted mainly in the high fluence regime (90-250 mj/cm²-pulse) considerably above the ablation threshold. Seven homopolymers including samples of poly(di-n-hexylsilane) which had been specifically labeled with deuterium in either the α or β -positions or carbon-13 on the α sites as well as a number of copolymers were investigated. A typical laser desorption impact mass spectrum of a typical polysilane poly(dimethylsilane) is shown in Fig. 11 (72).

As a result of these studies a number of conclusions may be drawn relative to the laser induced volatilization of polysilanes derivatives at 308 nm. The organosilanes are volatilized in a range of sizes ranging from one to at least five monomer units. The mass spectra obtained argue against the generation of significant quantities of isocyclic cyclosilane derivatives, since these materials usually show strong parent ion peaks. The observation of considerable intensities for ions of structure $(R_1R_2Si)_nH^+$ is interesting since electron impact studies on model organosilanes indicate that the formation of these ions is relatively rare. This suggests that SiH compounds are probably formed prior to ionization. Isotopic labeling studies indicate that the hydrogens come from positions other than just the α and β -side chain positions and also that silicon atoms become attached to carbon atoms other than those originally bonded in the α positions.

There also seems to be no compelling evidence for the presence of monomeric silylenes ($RR'Si$) as the bulk of the ejected neutrals. This conclusion is based on a number of observations. First, in all but one case studied, the monomeric parent ion intensity is quite low and considerable quantities of higher mass silicon fragments are evident. Multiphoton ionization studies (345-505 nm) of the gaseous products from poly(dimethylsilane) failed to produce any significant enhancement in the mass spectra for dimethylsilylene and higher mass fragments were always present. Finally cryotrapping of the gaseous products in an argon matrix did not produce any evidence of dimethylsilylene in absorption.

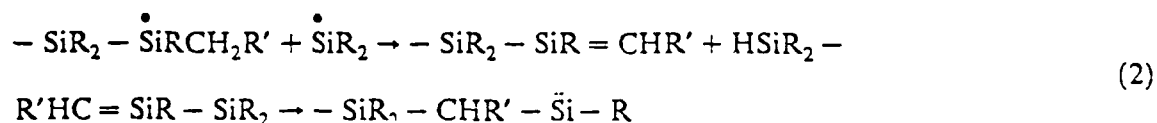
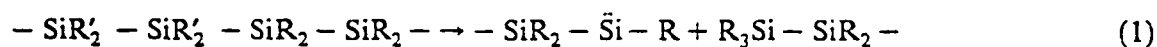
Another interesting observation is that significant silicon-carbon bond cleavage occurs in the high fluence regime. This is manifested by the appearance of the characteristic mass spectra for the olefin derived from the aliphatic side chain. In the case of poly(cyclohexylmethyl silane) and poly(phenyl methyl silane) cyclohexene and benzene are produced. Simple silicon-carbon bond homolysis to generate the corresponding alkyl radicals is considered unlikely based on the absence of any alkane being produced concurrently. The corresponding olefins are produced *prior* to ionization as demonstrated by trapping and analysis of the gaseous products from ablation. Furthermore, isotopic labeling experiments indicate that the olefin is formed by the loss of one β -hydrogen. Although the ratio of olefin to silicon containing fragments decreases with decreasing fluence, the presence of olefinic products (derived from the longer alkyl substituents) persists even at low fluences.

The olefins represent the first stable products isolated from the photoablation of substituted silane polymers and as such require discussion regarding any mechanistic hypothesis. The absence of literature precedent for photochemical silicon-carbon bond cleavage suggests the possibility of a thermal route. This suggestion is further strengthened by the observation that exposure of a number of polysilanes to infrared radiation from a cw CO_2 laser results in gaseous mixture whose composition by mass spectral analysis closely resembles that produced by irradiation at 308 nm.

The origin of the olefin product requires some interesting speculation. To our knowledge the only silicon containing intermediates which are known to lose an alkene fragment thermally with the specific transfer of a β -hydrogen are the alkyl silylenes. ($E_a \sim 30$ kcal-mole) (73-76). Since no clear cut evidence of dimethylsilylene



was obtained upon irradiation of poly(dimethylsilane) it seems unlikely that longer chain dialkylsilanes are thus produced. A attractive, albeit tentative, alternative would be an alkyl silyl silylene formed from the polymer chain. Two thermodynamically reasonable routes to such intermediates are shown below. The first is a 1,1-elimination to produce the silyl silylene directly which has precedent in organosilane thermal processes (77,78). The second hypothesis involves a rearrangement from a silene produced by the disproportionation (79-81) of two silyl radicals caused by bond homolysis. This type of rearrangement has also been described in the literature (82). The postulated silylsilylenes are also attractive intermediates to explain the rebonding of silicon to carbon atoms other than those in the original α positions (CH insertion) which is obvious from analysis of the mass spectrum of the gaseous products from the laser ablation of isotopically labeled poly(di-n-hexylsilane).



Radiation Chemistry of Polysilanes

While it is clear that the presence of oxygen can play a role when polysilanes are photodegraded in air, it has also been demonstrated that photobleaching with attendant molecular weight reduction takes place when polysilane derivatives are photodegraded under an inert atmosphere or under vacuum. This prompted us to investigate the potential of substituted polysilane derivatives as e-beam resists. In this regard, Fig. 12

shows images created in a bilayer composed of thin layer of a typical polysilane coated over a thick hard baked layer of a typical AZ type photoresist. After solvent development of the imaged layer, the pattern was transferred by O_2 -RIE. The process described is unoptimized, but demonstrates that the polysilanes can be imaged in a positive mode even when the imaging is conducted in vacuum using ionizing radiation sources.

In order to learn something of the structural sensitivity of the polysilanes to ionizing radiation, a number of samples were irradiated using a calibrated ^{60}Co source and the degraded materials analyzed by GPC in a manner similar to that described for the determination of the photochemical quantum yields (60). In these cases, the slopes of the respective molecular weight *versus* absorbed dose plots yield the G values for scissioning and crosslinking rather than the respective quantum yields. These values, which represent the number of chain breaks or crosslinks/100 ev of absorbed dose, are indicative of the relative radiation sensitivity of the materials. The data for a number of polysilanes are tabulated in Table IV. Also included in the table for comparison is the value for a commercial sample of poly(methyl methacrylate) run under the same conditions. In this case, the G(s) value compares favorably with number reported in the literature for this material (83).

The data in Table IV shows that the polysilanes undergo predominately scission during γ -radiolysis. In all cases the G(s)/G(x) ratios were greater than 10. When aromatic substituents are directly attached to the aromatic ring the G(s) decreases significantly. This is consistent with the previous observation that the G values for polystyrene derivatives are considerably lower than those observed for comparable saturated carbon backbone polymers suggesting that aromatic substituents impart some radiation stability (83). The data in Table IV suggests that for the polysilanes this effect is limited to aromatic substituents which are directly attached to the polymer backbone, since the G(s) value for poly(phenethyl methylsilane) is among the highest that we have measured. This raises the interesting question of whether remote aromatic substitution

in carbon based polymers will still impart the radiation stability characteristics of substituted polystyrene derivatives. This data while preliminary and somewhat incomplete, suggests that structural variations in polysilane high polymers can result in significant differences in their sensitivity to ionizing radiation. These preliminary trends provide some insight for the development of new silane polymers for resist studies.

In summary, polysilane derivatives constitute a new class of radiation sensitive materials for which a number of new applications have appeared. Much of the interest has centered around their unusual electronic properties and their sensitivity to various types of radiation. The nature of these radiation induced processes is very complex and although some progress has been made recently it remains a fertile field for future study.

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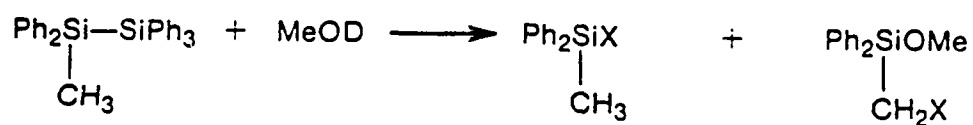
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Scheme I



X=H; >95%

X=H 10%

X=D; <5%

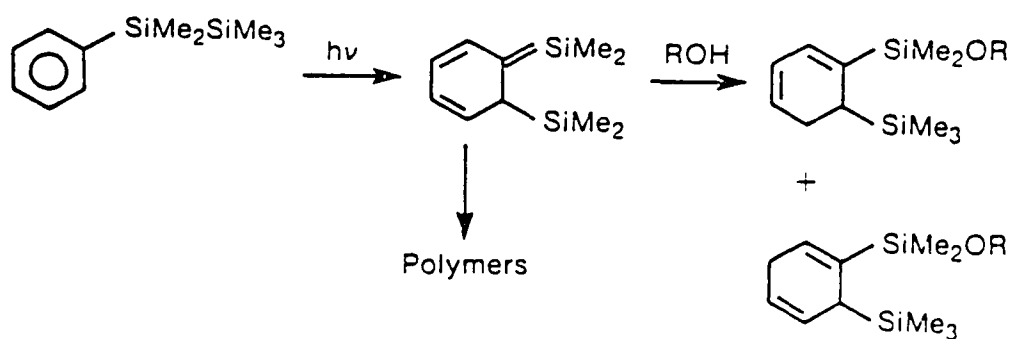
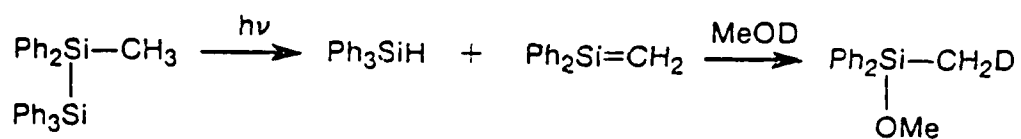
X=D 90%

+ Ph₃SiX

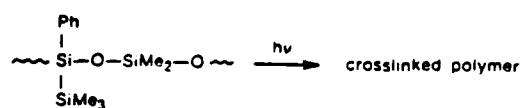
+ Ph₃SiOMe

X=H 90%

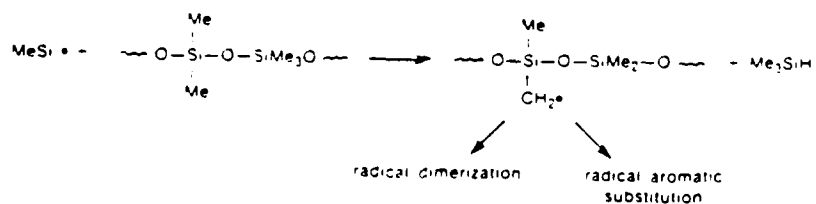
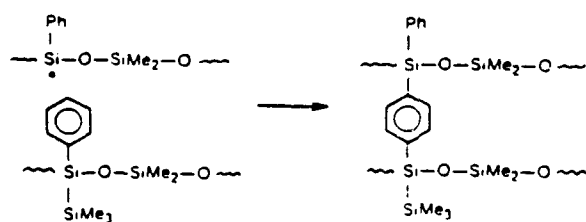
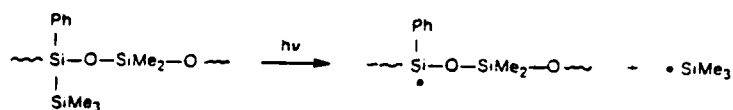
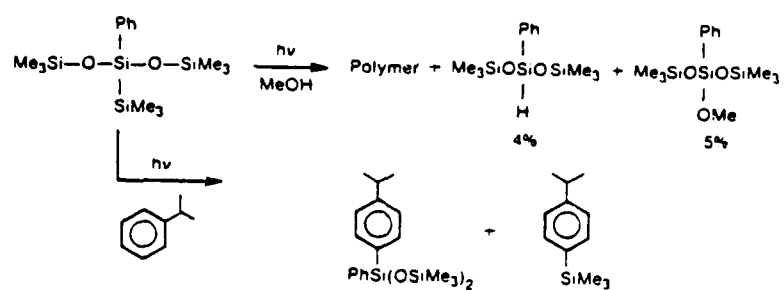
X=D 10%



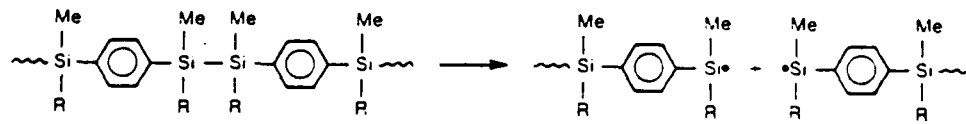
Scheme II



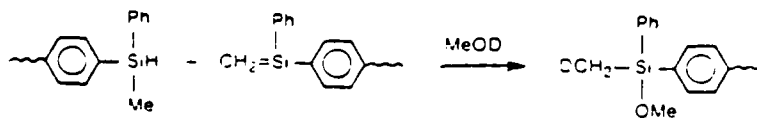
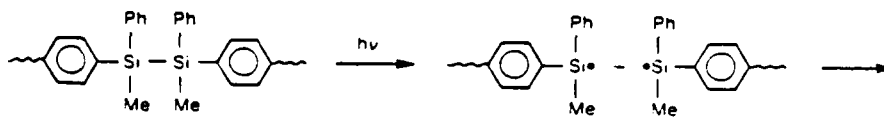
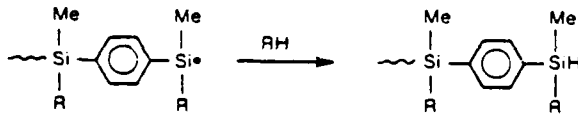
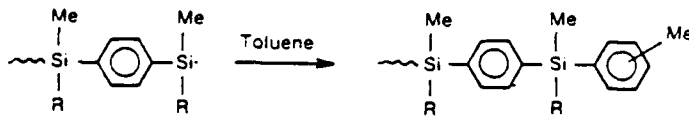
Model Studies



Scheme III

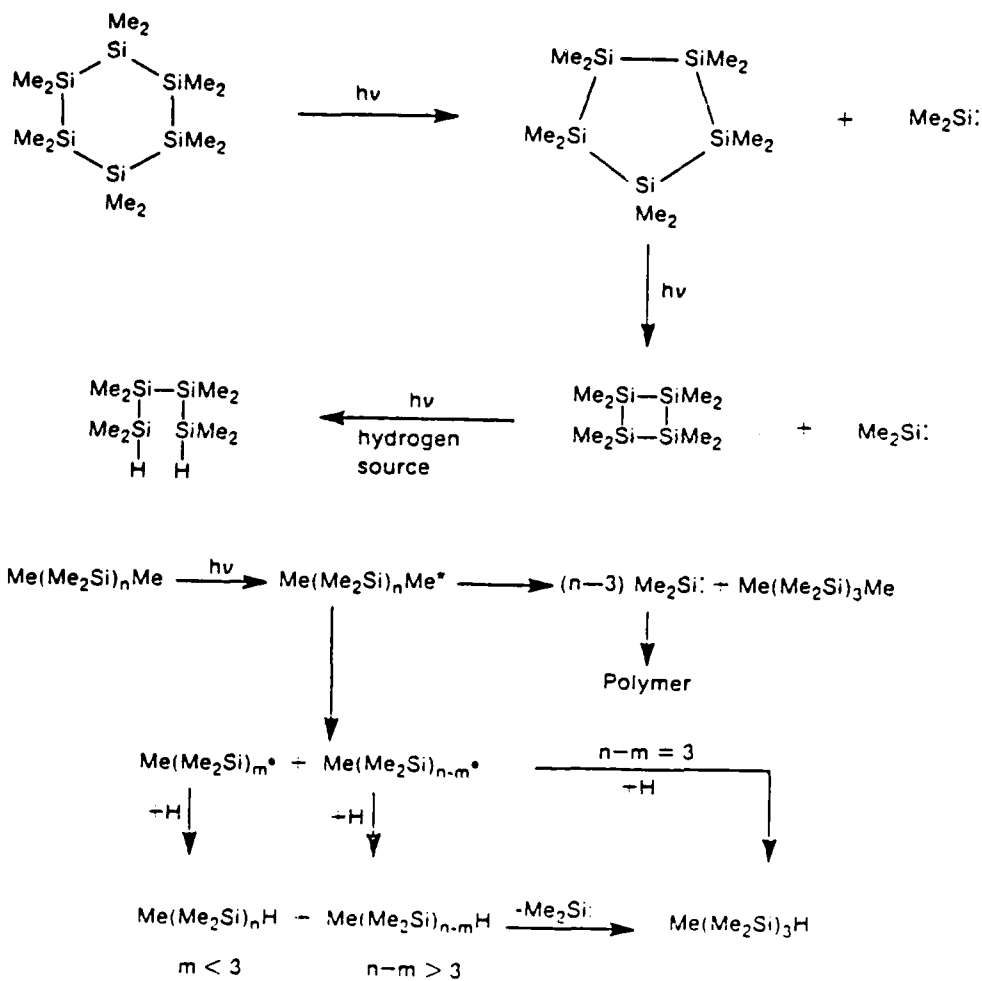


R = Ph, Et

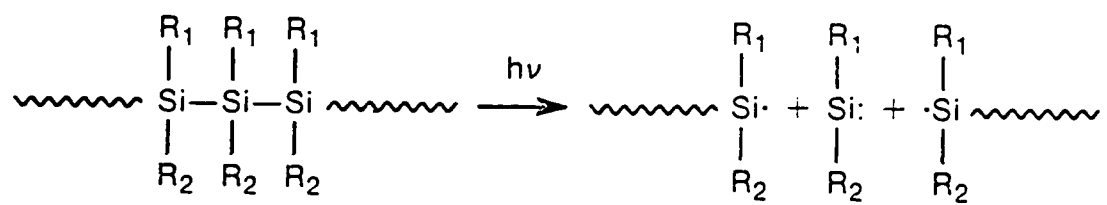


- no SiD in MeOD
- < 5% rearranged cyclonexadene

Scheme IV



Scheme V



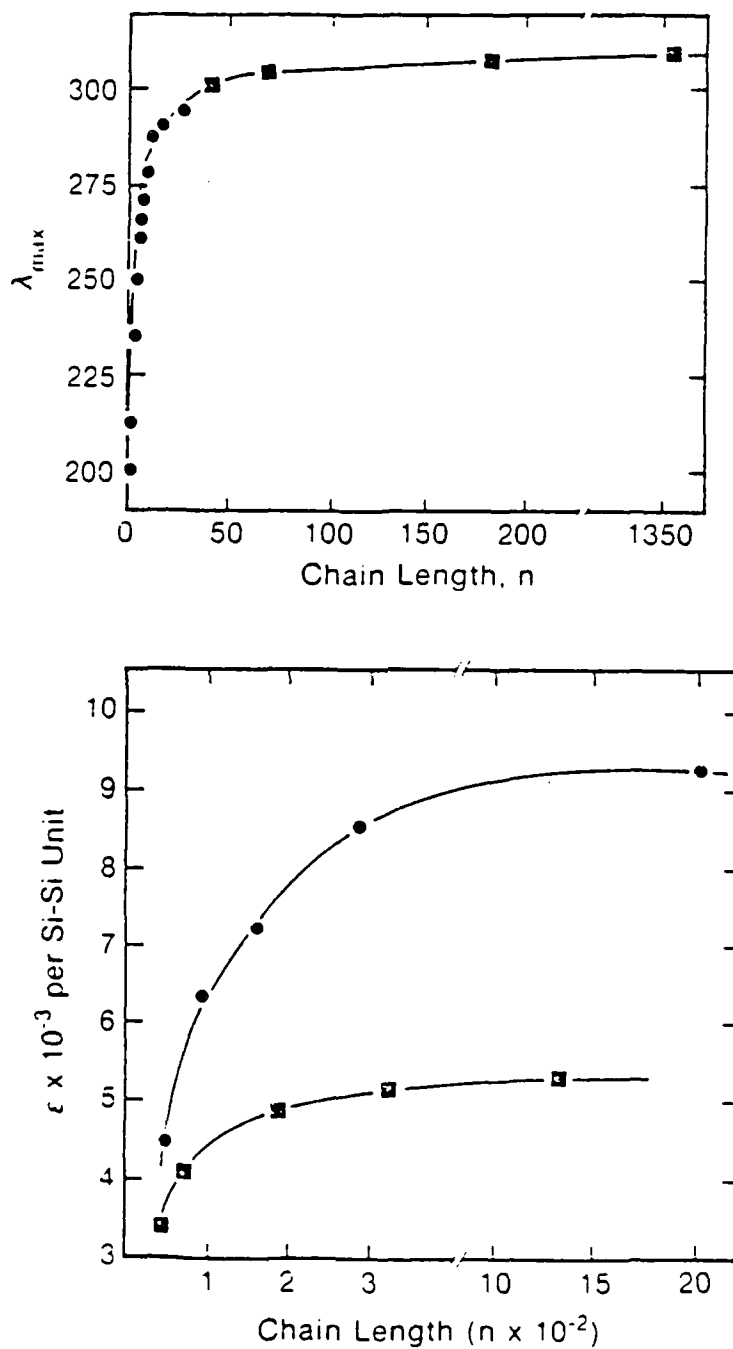


Figure 1. (Top) Plot of uv absorption maxima versus chain length (n) for poly(alkylsilanes). The (●) represent $\text{Me}(\text{Me}_2\text{Si})_n$ and the (■) represent $[(n - \text{dodecyl})(\text{Me})\text{Si}]_n$; (bottom) plot of absorptivity per Si-Si bond at λ_{max} versus chain length n . The (●) represent $[\text{PhMeSi}]_n$ and (■) represent $[(n - \text{dodecyl})(\text{Me})\text{Si}]_n$.

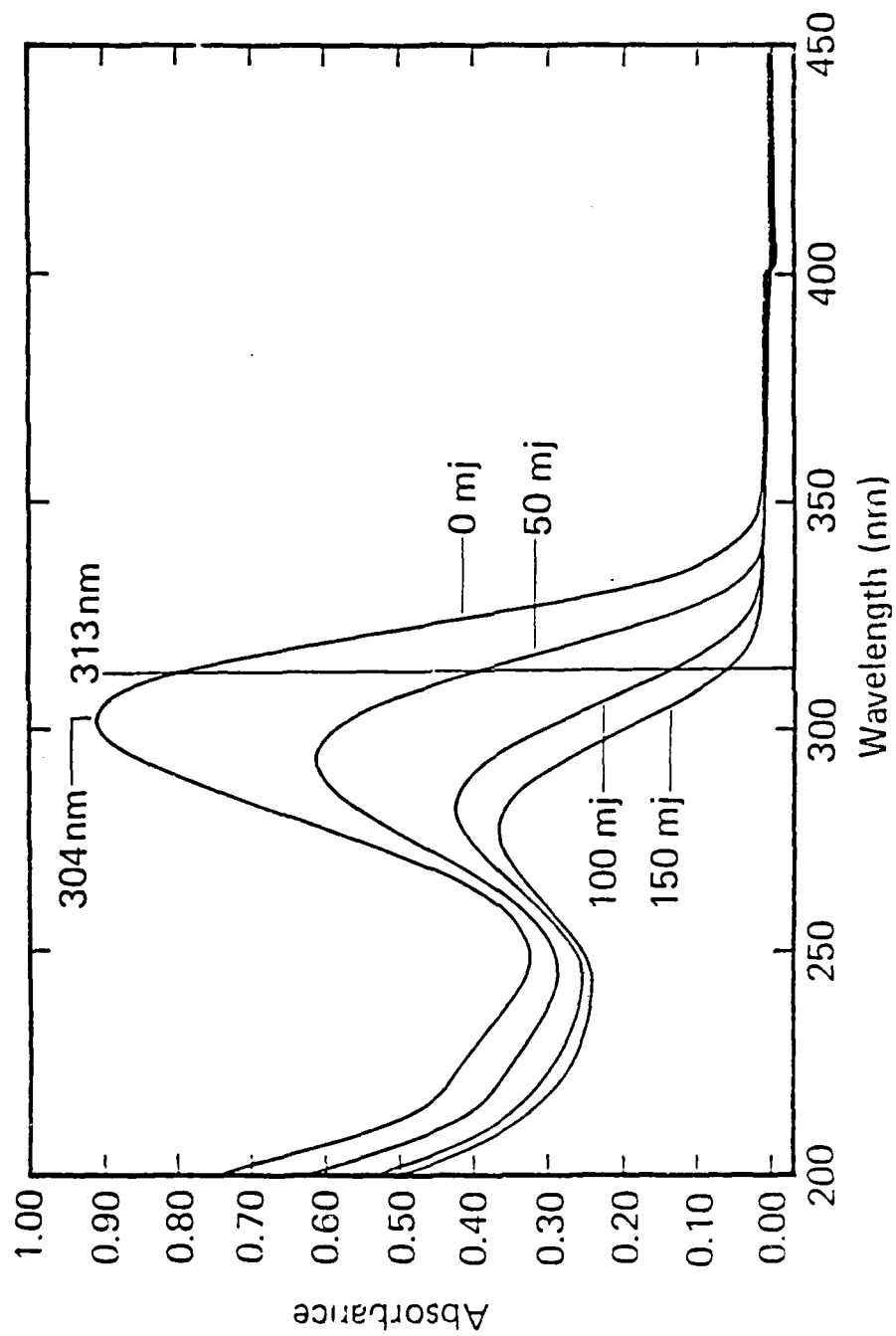


Figure 2. Spectral bleaching of a film of poly(n-hexyl methylsilane) upon irradiation at 313 nm.

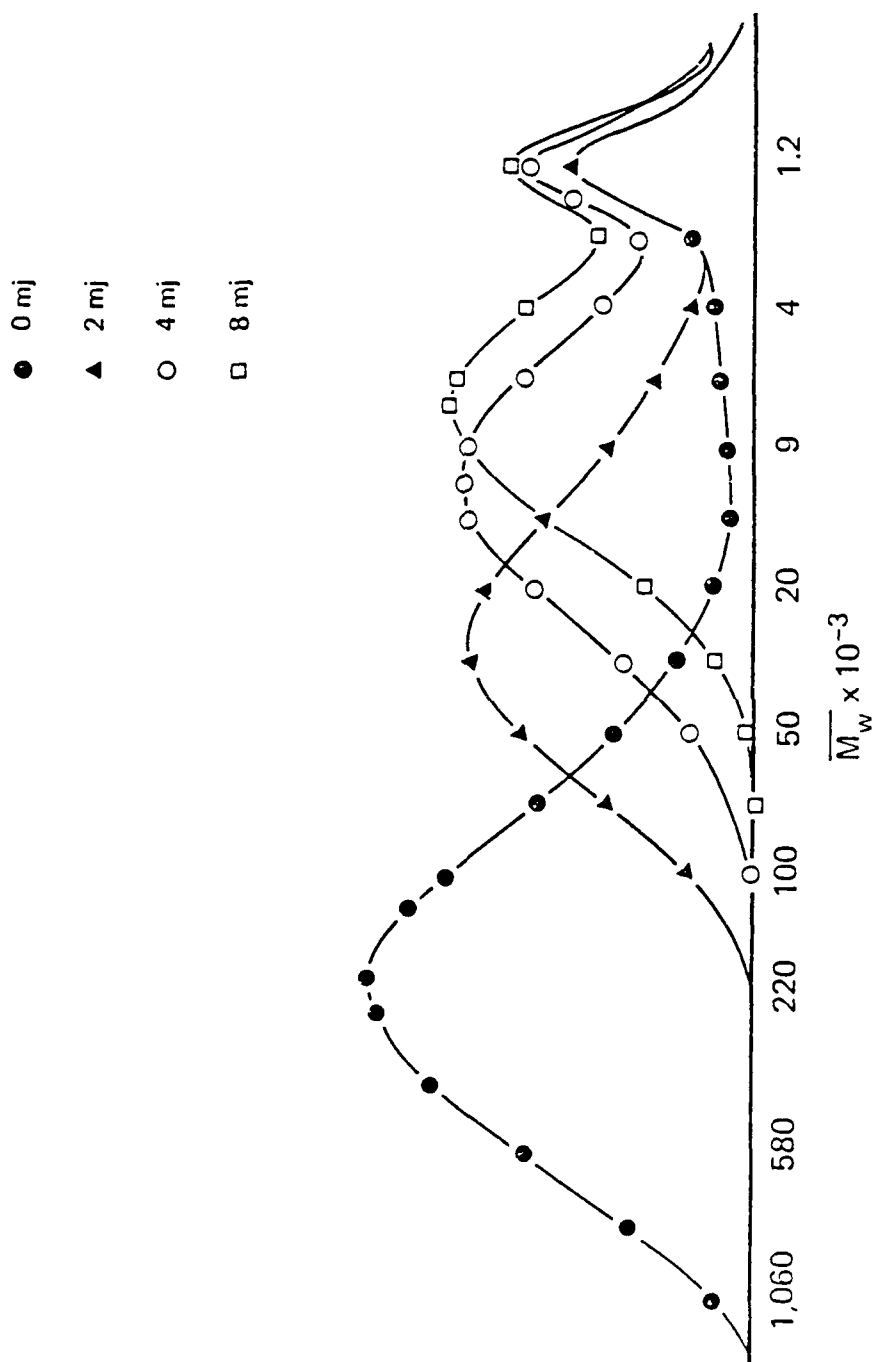


Figure 3. The change in molecular weight of a 0.006% solution of poly(dodecyl methylsilane) upon irradiation at 313 nm: (○) 0 mj/cm², (▲) 2 mj/cm², (○) 4 mj/cm², (□) 8 mj/cm².

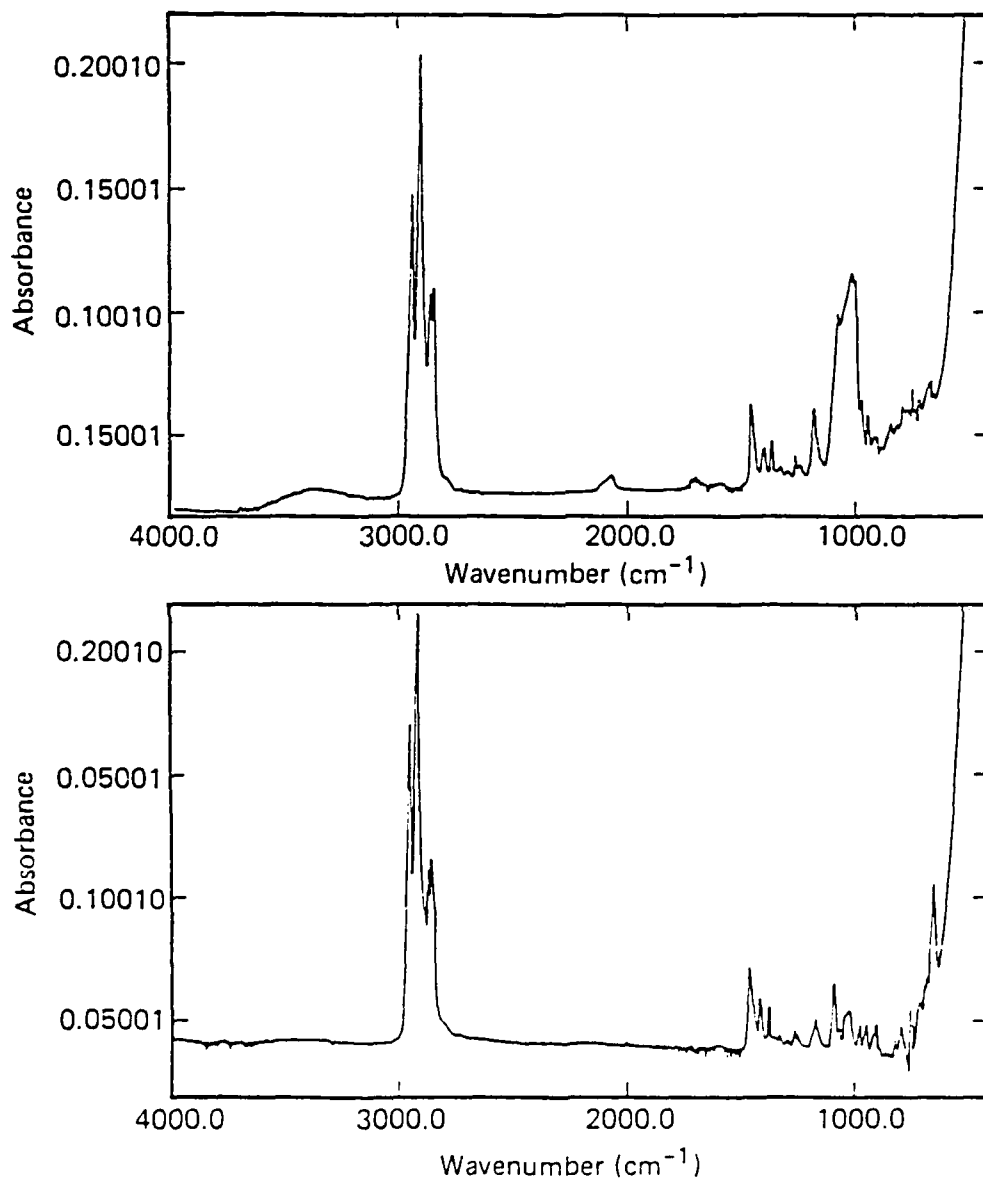


Figure 4. Irradiation of a film (815 nm) of poly(di-n-pentylsilane) at 254 nm in air; (bottom) prior to exposure; (top) after exposure (400 mJ/cm²).

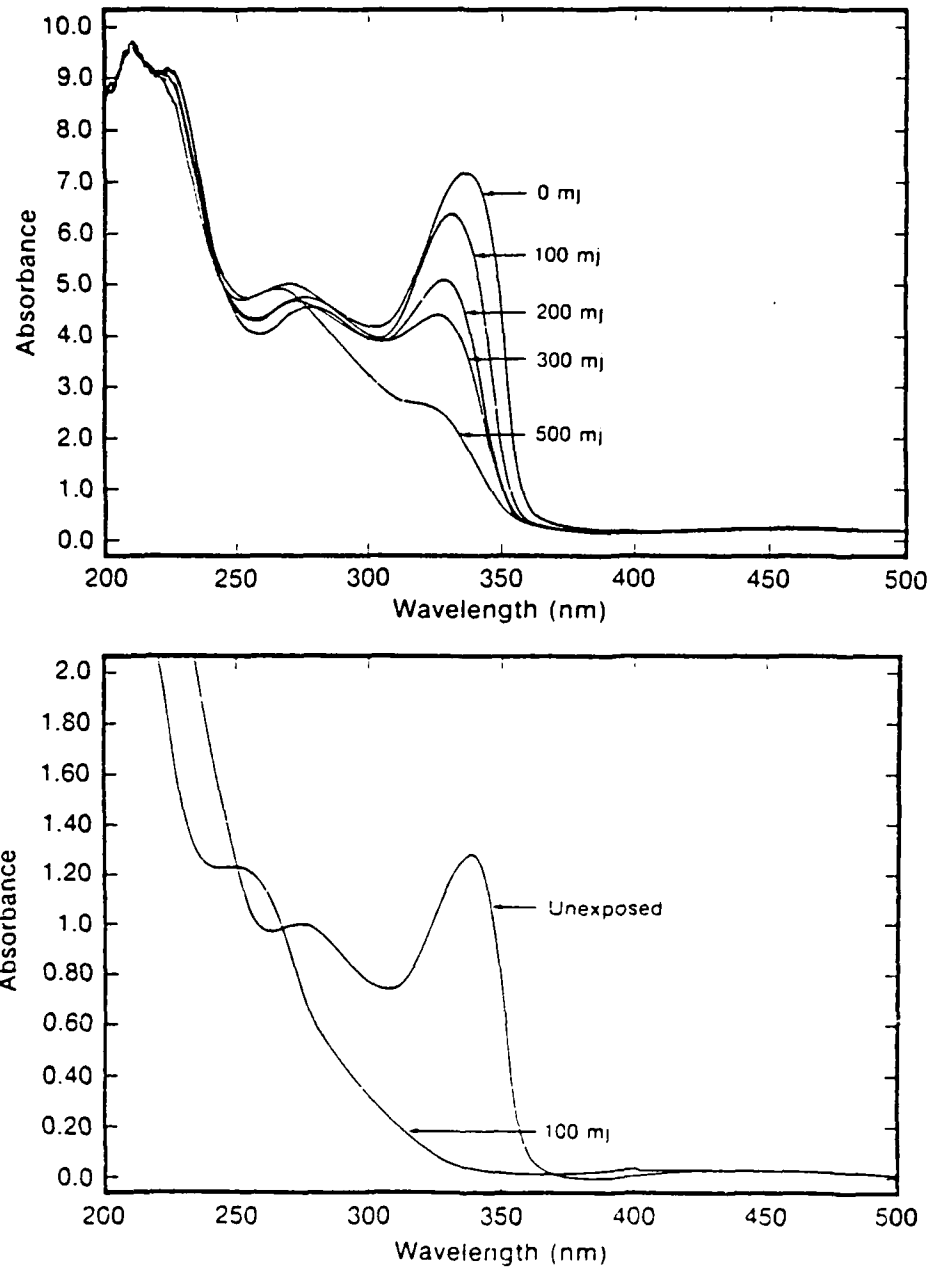


Figure 5. Irradiation of poly(phenyl methylsilane) at 313 nm, in the presence and absence of poly hydrogenated additives; (top) film containing no additive, (bottom) film containing approximately 20% by weight of 1,4-bis-trichloromethyl benzene.

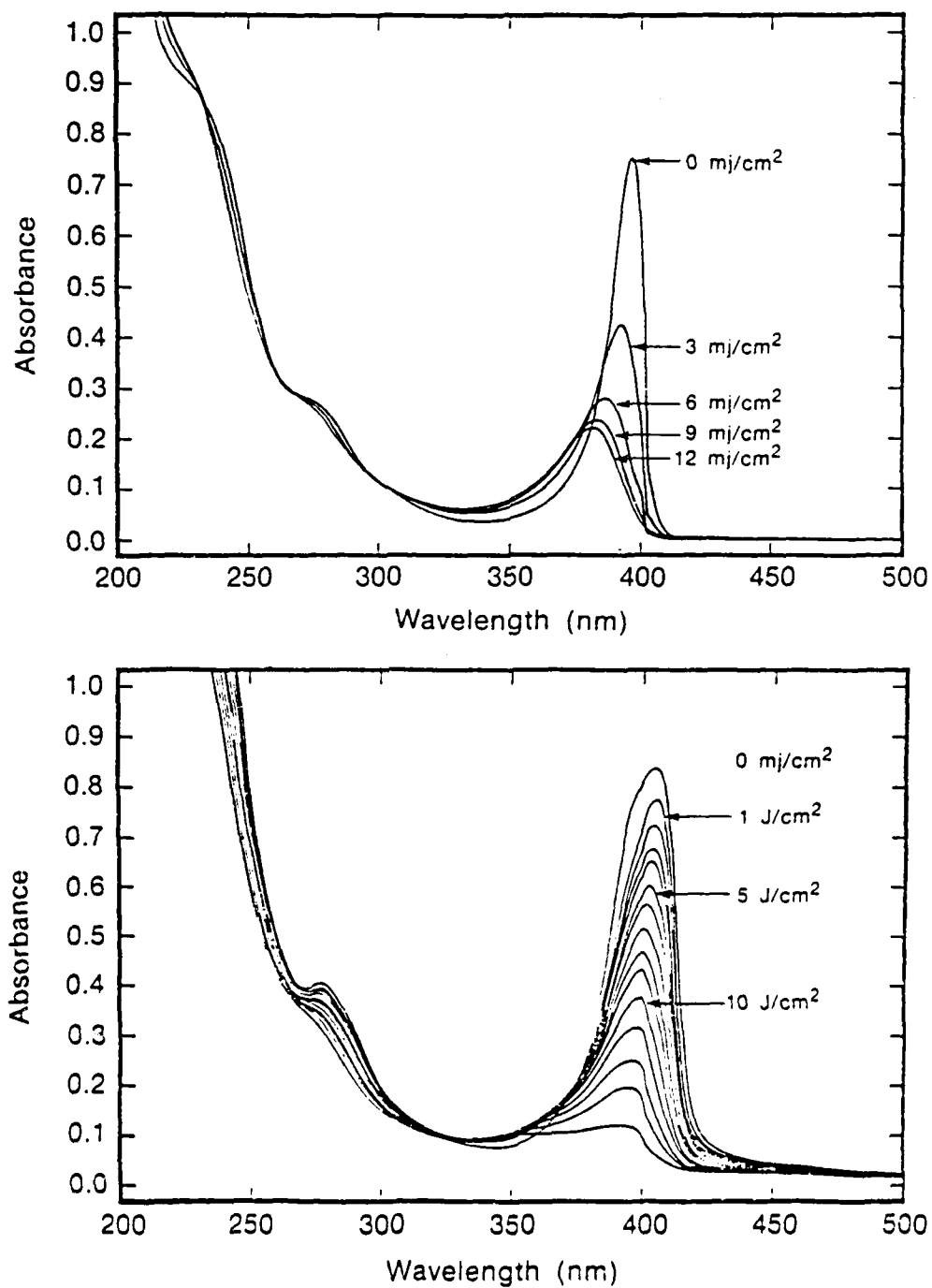


Figure 6. Irradiation of poly(bis-p-n-hexylphenylsilane) at 404 nm; (top) solution in cyclohexane (bottom) film.

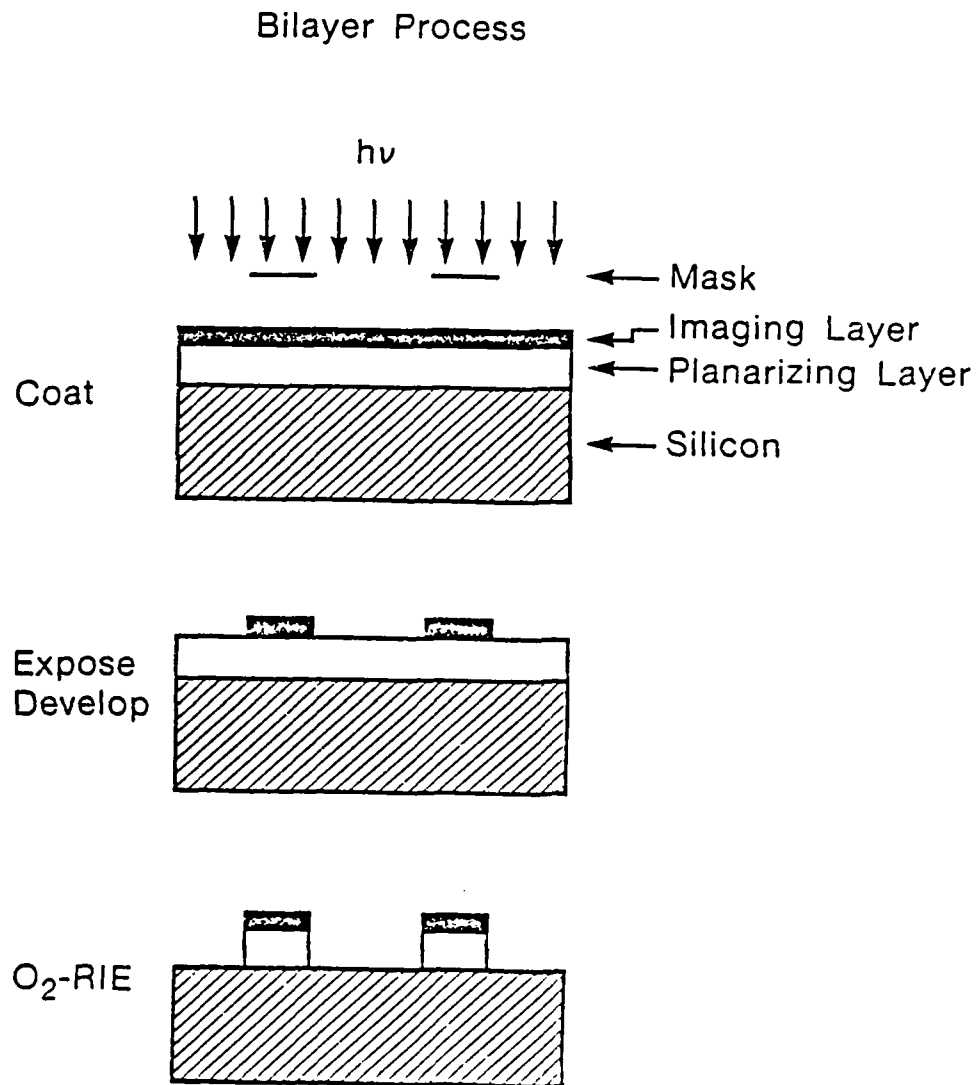


Figure 7. A bilayer process for the production of high resolution images using O₂-RIE techniques for image transfer.

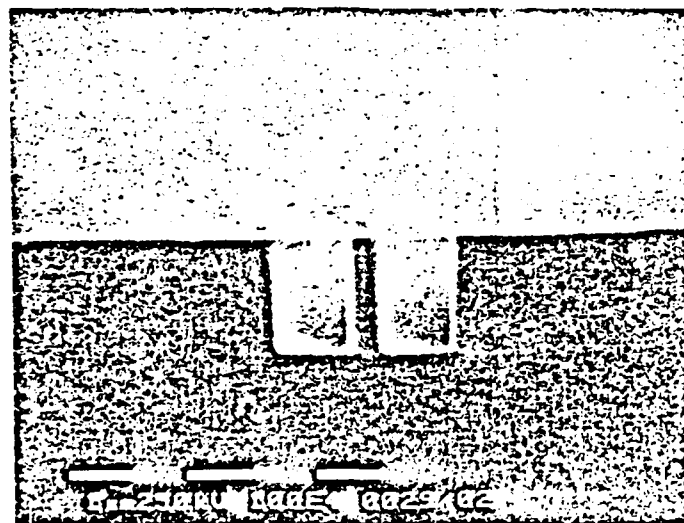
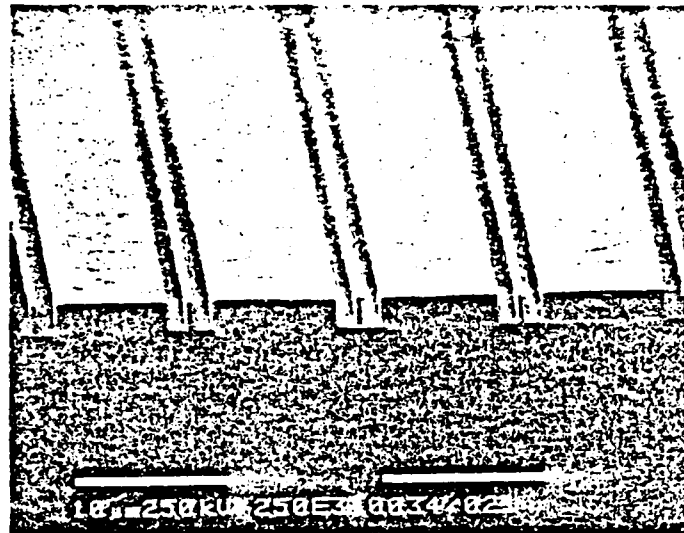


Figure 8. $0.75 \mu\text{m}$ features generated in a bilayer of $0.2 \mu\text{m}$ of poly(cyclohexyl methylsilane) coated over $2.0 \mu\text{m}$ of a hardbaked AZ photoresist using mid uv projection lithography, $100 \text{ mJ}/\text{cm}^2$. Image transfer was accomplished using O_2 -RIE.

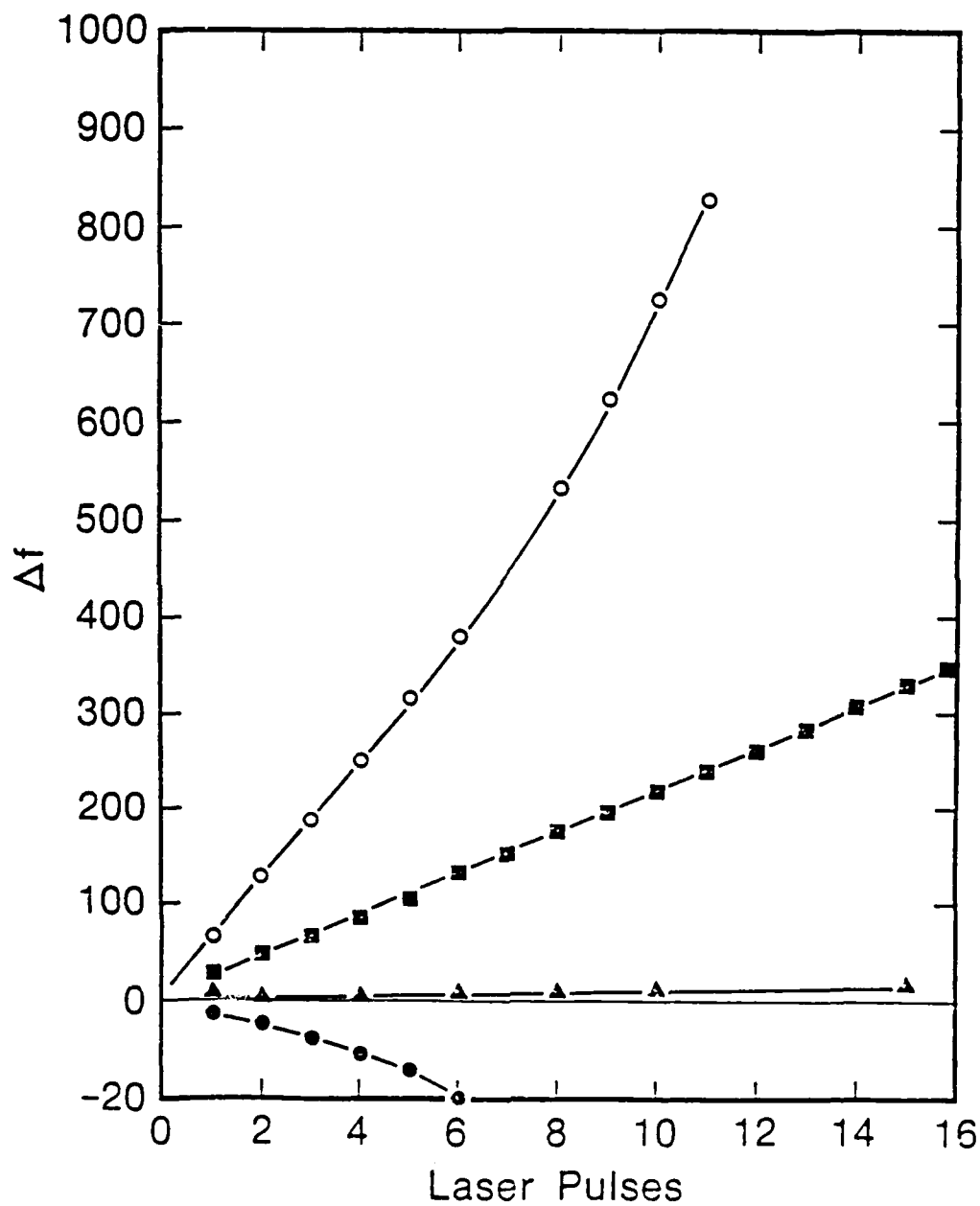


Figure 9. The self development of a thin film ($\sim 0.2 \mu\text{m}$) of poly (p-t-butylphenyl methyl silane) upon irradiation at 248 nm (KrF excimer laser) in air. Mass loss is proportional to the frequency change (Δf) of the quartz crystal microbalance.

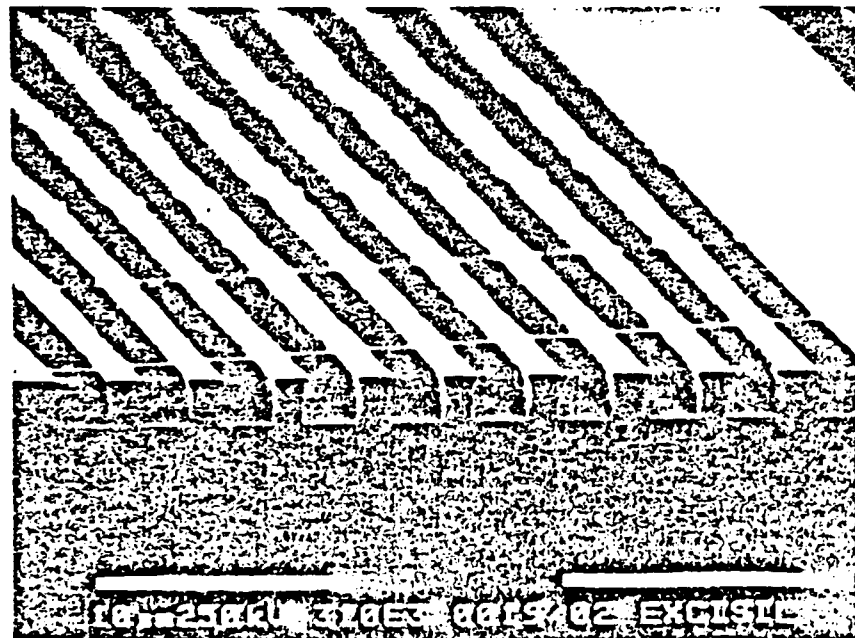
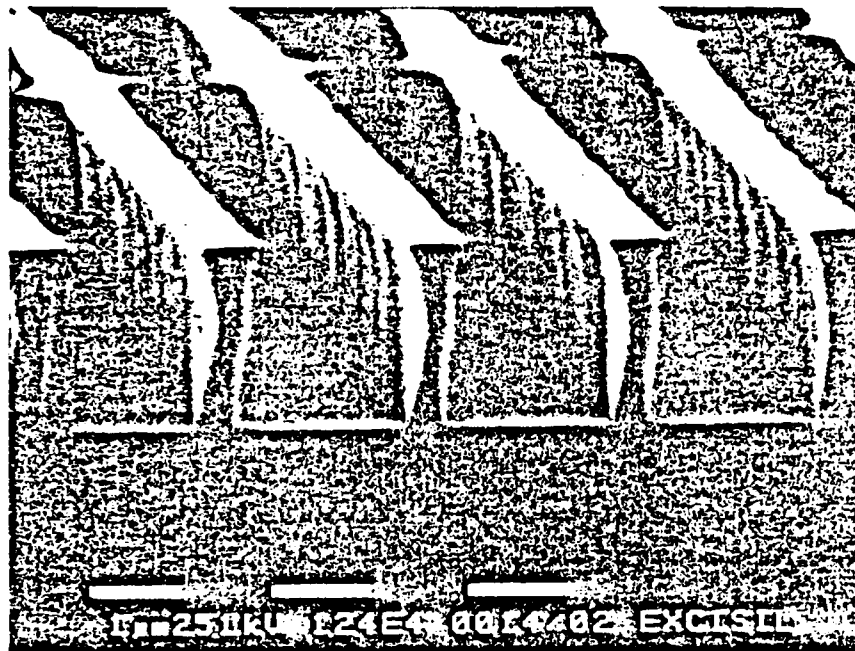


Figure 10. Self developed submicron images produced in a thin film ($0.2 \mu\text{m}$) of poly(p-t-butylphenyl methylsilane) by irradiation at 248 nm ($55 \text{ mJ}/\text{cm}^2$ -pulse), 550 mJ total dose. The images were transferred into $2.0 \mu\text{m}$ of a hardbaked AZ photoresist by O_2 -RIE.

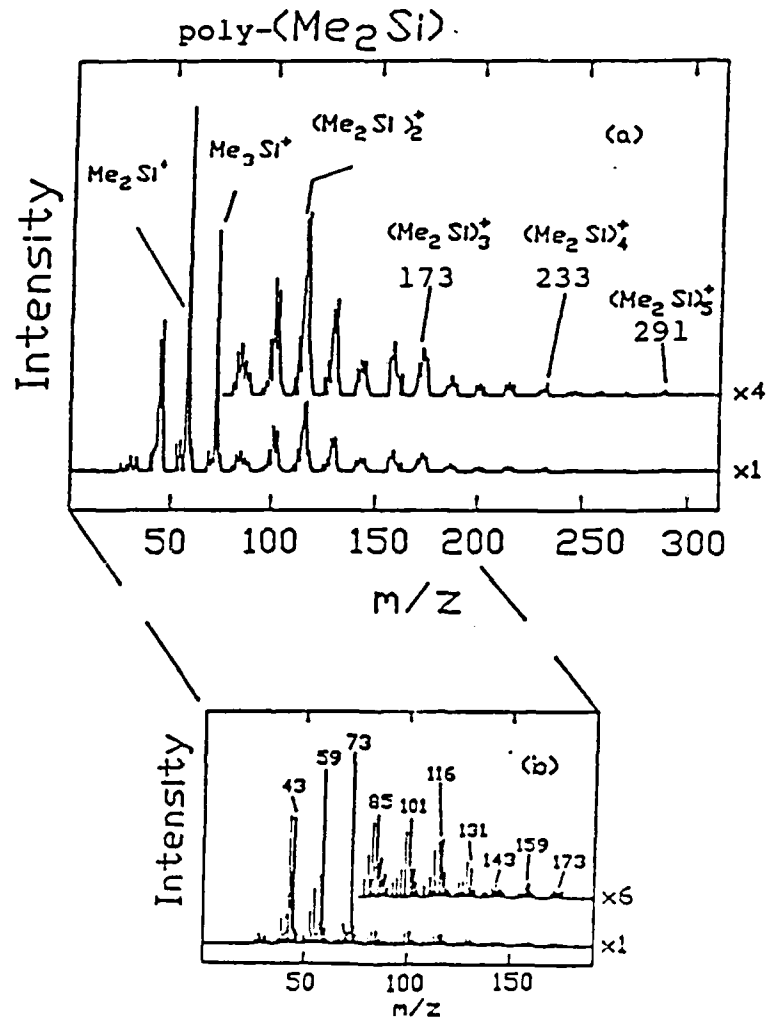


Figure 11. Laser desorption impact mass spectrum of poly-(Me₂Si) under low (top) and high (bottom) resolution.

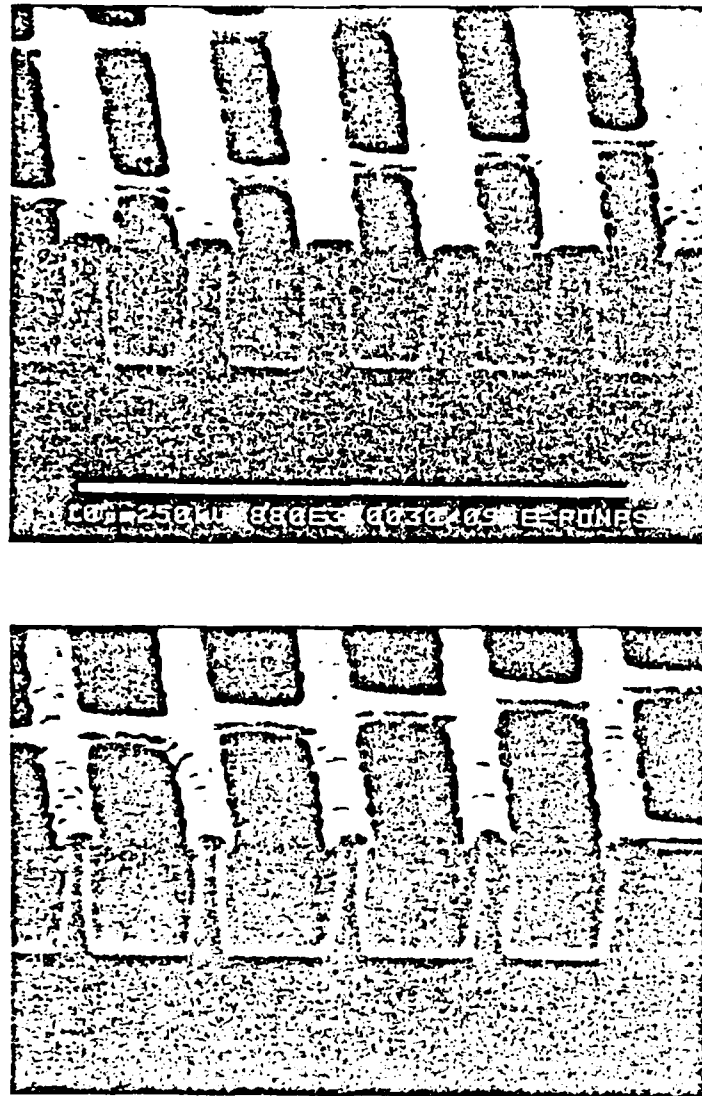


Figure 12. e-Beam imaging of poly(di-n-pentylsilane) ($0.14 \mu\text{m}$) coated over $2.0 \mu\text{m}$ of a hardbaked AZ photoresist, $20 \mu\text{C}$, O_2 -RIE image transfer.

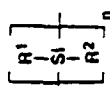
Product	R ¹ = n-C ₄ H ₁₁ R ² = n-C ₄ H ₁₁	R ¹ = n-C ₆ H ₁₃ R ² = Me	R ¹ = c-C ₆ H ₁₁ R ² = Me
Et ₃ SiR ¹ R ² SiH	59%	70%	71%
HSiR ¹ R ² —SiR ¹ R ² H	11%	11%	14%
Et ₃ Si—R ¹ R ² SiSiEt ₃	a	3%	a
HSiR ¹ R ² —O—SiR ¹ R ² H	a	a	2
Et ₃ Si—O—SiR ¹ R ² SiR ¹ R ²	a	a	3

Table I. Product distribution and yields from 254 nm photolysis of high molecular weight (R¹R²Si)_n with trichylsilane present as a chemical trapping reagent (58). (a) No attempt was made to identify these and other products whose yields were less than 2%.

Photolysis of poly(*n*-hexyl methylsilane) in alcohols (ROH, 254 nm)

Products	Yields (%)	
	R = Me	R = <i>n</i> -Pr
$\begin{array}{c} n\text{-C}_6\text{H}_{13} \\ \\ \text{Me-Si-OR} \\ \\ \text{H} \end{array}$	65	39
$\begin{array}{c} n\text{-C}_6\text{H}_{13} \\ \\ \text{Me-Si-OR} \\ \\ \text{OR} \end{array}$	0	5
$\begin{array}{cc} n\text{-C}_6\text{H}_{13} & n\text{-C}_6\text{H}_{13} \\ & \\ \text{H-Si} & \text{---} & \text{Si-H} \\ & & \\ \text{Me} & & \text{Me} \end{array}$	7	7
$\begin{array}{cc} n\text{-C}_6\text{H}_{13} & n\text{-C}_6\text{H}_{13} \\ & \\ \text{H-Si} & \text{---} & \text{Si-OR} \\ & & \\ \text{Me} & & \text{Me} \end{array}$	15	20
$\begin{array}{cc} n\text{-C}_6\text{H}_{13} & n\text{-C}_6\text{H}_{13} \\ & \\ \text{RO-Si} & \text{---} & \text{Si-OR} \\ & & \\ \text{Me} & & \text{Me} \end{array}$	7	12

Table II. Product distribution and yields from 254 nm photolysis of high molecular weight poly(*n*-hexyl methylsilane) in toluene with excess methanol and *n*-propanol, respectively (58).



Photolysis of Substituted Polysilanes of Structure

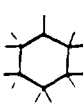
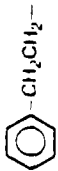

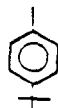
R ¹	R ²	Solvent	M _w ⁰ x 10 ⁻³	λ _{ox}	Solution		Solid Film	
					φ _s	φ _x	φ _s	φ _x
	-CH ₃	Toluene	41.4	355	1.2	0.06	0.022	0
2 C ₆ H ₁₃	C ₆ H ₁₃	Toluene	44.6	353	0.6	0	-	-
3 	-CH ₃	Toluene	208.9	347	0.97	0.08	-	-
4 C ₁₂ H ₂₅ -	-CH ₃	Toluene	185.1	347	0.54	0	-	-
5 C ₃ H ₇ -	-CH ₃	-	3900	-	-	-	0.011	0.0013
			190				0.015	0.0013
6 	-CH ₃	THF	245	313	0.97	0.12	0.015	0.002
7 	-CH ₃	Toluene	633.6	367	1.00	0.18	-	-

Table III. Quantum yields for the photodecomposition of a number of substituted polysilane derivatives; (a) molecular weights were determined by GPC analyses and are relative to polystyrene calibration standards; (b) Ban, H.; Sukegawa, K.; J. Polym. Sci.: Polym. Chem., 1988, 26, 521.

Polymer	$\bar{M}_n^0 \times 10^{-3}$	G(s)	G(x)	G(s)/G(x)
$[(C_4H_9)_2Si]_n$	304.9	0.42	0.023	18
$[(C_5H_{11})_2Si]_n$	807.6	0.40	—	—
$[(C_6H_{13})_2Si]_n$	971.9	0.42	0.041	10.5
$[(C_{14}H_{29})_2Si]_n$	1472.9	0.86	0.035	24.6
$(PhMeSi)_n$	738.2	0.26	0.014	18.6
$(\text{---} \text{C}_6\text{H}_4 \text{---} \text{MeSi})_n$	153.9	0.14	0.004	35
$(\text{---} \text{C}_6\text{H}_4 \text{---} \text{CH}_2\text{CH}_2\text{MeSi})_n$	167.3	0.90	0.03	30
PMMA	428.7	1.40	—	—

Table IV. ^{60}Co γ -radiolysis of a number of substituted polysilane derivatives.

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