Applied Organometallic Chemistry (1987) 1 7–14

Photoinitiation of vinyl polymerization by polysilanes

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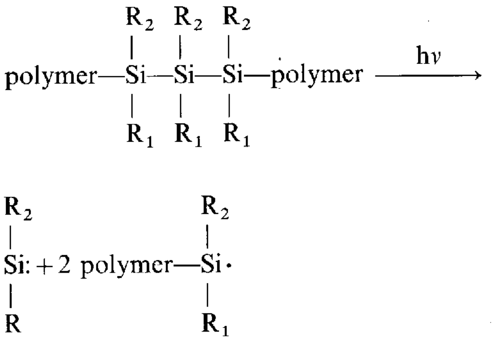
Received 6 January 1986 Accepted 6 May 1986

Polysilanes were found to photoinitiate the polymerization of a variety of vinyl monomers including methyl methacrylate, styrene, ethyl acrylate and acrylic acid. Polymerization initiated by polysilane photolysis is rather insensitive to oxygen inhibition, which may make it especially suitable for polymerization of thin films. The initiation efficiency of poly(phenylmethylsilylene) in styrene was determined from dilatometry data to be 1×10^{-3}. This rather low efficiency is counterbalanced by the very high extinction coefficient of polysilane polymers, ca. $4–8 \times 10^3$ per silicon atom. Possible reasons for the low initiation efficiency and reduced oxygen inhibition of polysilane photoinitiators are discussed.

Keywords: Polysilanes, photoinitiation, polymerisation, vinyl monomers, thin films, photolysis

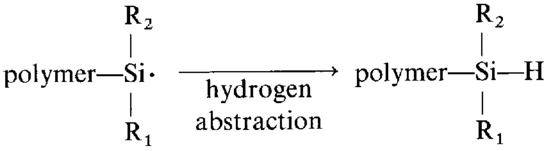
INTRODUCTION

The polysilane (diorganosilylene) polymers have strong ultraviolet absorption bands in the region 300–350 nm, depending on the nature of the organic substituents.[1,2] Irradiation of this band leads to photoscission, sometimes accompanied by crosslinking.[3] A recent study of polysilane photodegradation indicated that the scission produces both silyl radicals and silylenes (Eqns 1–3).[4,5]

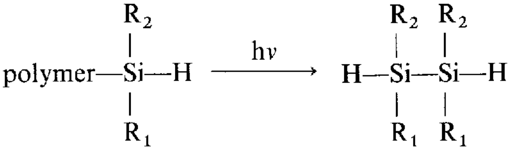


$$\text{polymer}-\underset{R_1}{\overset{R_2}{Si}}-\underset{R_1}{\overset{R_2}{Si}}-\underset{R_1}{\overset{R_2}{Si}}-\text{polymer}\xrightarrow{h\nu}$$

$$\underset{R}{\overset{R_2}{Si}}: + 2\,\text{polymer}-\underset{R_1}{\overset{R_2}{Si}}\cdot \qquad [1]$$



$$\text{polymer}-\underset{R_1}{\overset{R_2}{Si}}\cdot \xrightarrow[\text{abstraction}]{\text{hydrogen}} \text{polymer}-\underset{R_1}{\overset{R_2}{Si}}-H \qquad [2]$$



$$\text{polymer}-\underset{R_1}{\overset{R_2}{Si}}-H \xrightarrow{h\nu} H-\underset{R_1}{\overset{R_2}{Si}}-\underset{R_1}{\overset{R_2}{Si}}-H \qquad [3]$$

In another study, silyl radicals produced by the photolysis of phenyldisilanes at 254 nm have been shown to add to 1,1-di-*tert*-butylethylene to give radical species detectable by electron spin resonance spectroscopy.[6] Thus, the silyl radicals from photoscission of polysilanes should add to other olefinic substrates and might thereby initiate radical chain polymerization. In this paper we report studies on the initiation of vinyl polymerization using polysilane polymers as initiators (see Table 1).

EXPERIMENTAL

Monomers

Acrylate and methacrylate monomers were passed through an activated alumina column to remove inhibitor, then argon or dry nitrogen was bubbled through the liquids to remove oxygen. For kinetic studies styrene was purified by shaking twice with 1 mol dm^{-3} KOH followed by washing three times with water. The styrene was then filtered through a cone of anhydrous $MgSO_4$ and stirred over CaH_2 for 24 h. The flask containing the styrene was then vacuum degassed and backfilled with dry argon four times prior to a final vacuum distillation at 20°–30°C from CaH_2 directly into the dilatometer.

Initiators

Polysilanes were prepared as previously reported.[1,8] Benzoin methyl ether (BME) was obtained from Aldrich Chemical Co. and recrystallized from hexane prior to use.

Polymerization

Polymerization was carried out under three similar sets of conditions. In the first, monomer ($10\,cm^3$) was added to initiator in a clean dry 13 cm Pyrex test tube in air and the solution was agitated with ultrasound to speed dissolution of the initiator. The solution was then exposed to sunlight and observations were taken during the polymerization. In the second method, a clean dry 13 cm Pyrex or quartz test tube containing initiator was sealed with a septum and $10\,cm^3$ of monomer were introduced by syringe. A long needle was introduced and either dry nitrogen or argon was vigorously bubbled through the solution for 30 seconds. The solutions were then irradiated at 254, 300 or 350 nm for 10,000 sec and the polymers were collected for GPC study. The third method was used to study the rate of polymerization. Initiator was added to a clean dry Pyrex dilatometer (see below) and the dilatometer was evacuated and backfilled with inert gas several times. Monomer was then vacuum distilled into the dilatometer, and the dilatometer was examined for the presence of gas bubbles. If any were found the entire solution was discarded and the dilatometer was cleaned and thoroughly dried before refilling. Irradiation was carried out at 350 nm and all polymer samples were promptly precipitated in dry methanol when irradiation was complete.

In general, vinyl polymers produced by photoinitiation with polysilanes were quenced by pouring the polymer solution in monomer directly into excess methanol, precipitating the polymer. However, polyethyl acrylate, a polymer soluble in methanol, was first dissolved in THF and then precipitated by addition of at least a six-fold excess of water. The polymers were all isolated by filtration and drying in vacuo for 6–24 h. In the experiments involving ethyl acrylate, polymerization reported in Table 2, $10\,cm^3$ of ethyl acrylate was used with an amount of polysilane sufficient to provide 0.22 mmol *of* R_2Si *units.*

Equipment

Irradiations were carried out in a Rayonet model RPR-100 photoreactor fitted with sixteen 250, 300 or 350 nm lamps. Irradiations at or below 300 nm were performed in quartz equipment.

Gel Permeation Chromatography (GPC) was carried out on both the polysilane initiators and the polyalkene products. Freshly distilled THF was employed as solvent using a Waters single pump HPLC system fitted with UV absorbance and refractive index detectors, and four Microstyragel columns (10^3, 10^3, 10^5 and 10^6 Å). All data is reported in polystyrene equivalents. Polydispersivities were calculated by hand for polyethylacrylate irradiated at 254, 300 and 350 nm as well as for polystyrene from the dilatometry runs.

Silicon-29 NMR data were taken on a JEOL Model FX-200 multinuclear spectrometer using C_6D_6 and a 10 mm sample tube at room temperature. Data acquisition was enhanced by using Morris and Freeman's INEPT pulse sequence.[9]

Dilatometry

Dilatometry was carried out in a Pyrex glass dilatometer (Kontes Glass Co.) with a volume of $11.00\,cm^3$ and an additional stem of precision bore tubing graduated from 0 to $1.400\,cm^3$ in $5\,\mu L$ increments. Readings were taken to the nearest $0.5\,\mu L$ along with temperature to the nearest 0.1°C at intervals of 10–60 sec. All data was recorded by manually and corrected by hand to 19.0°C[10] before being entered into a Harris computer for plotting and linear regression. The dilatometer was backfilled with argon and capped before each irradiation, then thermally equilibrated in a glass water bath. Irradiation was carried out using 350 nm lamps, with the radiation further filtered through three layers of Pyrex glass, two from the water bath and one from the dilatometer itself.

In order to obtain rate data for the reference initiator (BME) at the same optical density, UV absorbance spectra of both the poly(phenylmethylsilylene) and BME were taken in styrene and digitized by hand at 1 nm intervals. The emission spectrum of the Rayonet 350 nm lamp was also taken at 1 nm intervals over the entire output range, 310–460 nm, and likewise digitized by hand. The product of the emission intensity and the absorbance, summed for all wavelengths, was taken as the optical density for each sample. Poly(phenylmethylsilylene) was found to have an optical density 25.97 times as large as that for BME.

It has previously been shown that for benzoin ethers, rate is proportional to the square root of concentration[11] so rate data were taken at one concentration and scaled appropriately. Following Lissi and Encina[12]

$$R_i = I_a f;\ (R_p)_i = \frac{(R_i)^{\frac{1}{2}} k_p [M]}{(k_t)^{\frac{1}{2}}}$$

where R_i is the rate of initiation, I_a = intensity absorbed, f = photoinitiation efficiency, $(R_p)_i$ is the rate of polymerization in the presence of photoinitiator, and k_p and k_t are the rate constants for polymerization and termination, respectively (properties of the monomer), and $[M]$ is the monomer concentration. If the rate of autopolymerization $(R_p)_0$ is not zero, the rate of polymerization R_p is composed of two terms:

$$(R_p)^2 = (R_p)_0^2 + (R_p)_i^2.$$

Substituting the previous equations for R_p and R_i:

$$(R_p)^2 = (R_p)_0^2 + \frac{I_a f k_p^2 [M]^2}{k_t}$$

where f is the initiation efficiency. Solving for f:

$$f = [(R_p)^2 - (R_p)_0^2] \frac{k_t}{I_a k_p^2 [M]^2}.$$

For two photoinitiators whose concentration has been adjusted to the same optical density ($I_{a_1} = I_{a_2}$), the ratio of the initiator efficiencies is:

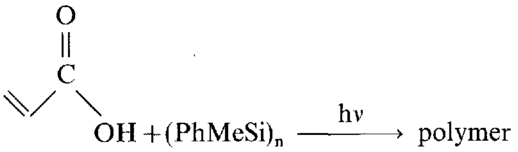
$$\frac{f_1}{f_2} = \frac{[(R_p)_1^2 - (R_p)_0^2]}{[(R_p)_2^2 - (R_p)_0^2]}$$

providing the initiator concentration does not significantly affect the monomer concentration.

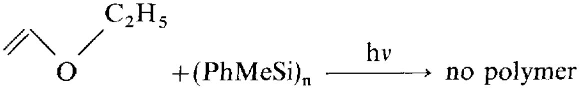
After adjusting styrene solutions of benzoin methyl ether (BME) and poly(phenylmethylsilylene) to the same optical density versus the output of the 350 nm Rayonet lamp, rates of polymerization were obtained by dilatometry for the polysilane or BME and styrene. Under the conditions employed $(R_p)_0$ was an order of magnitude less than the polysilane-catalyzed rate and consequently had little effect on the calculated efficiency.

RESULTS AND DISCUSSION

The mechanism of polymerization was shown to be radical in nature by attempting to polymerize acrylic acid and vinyl ethyl ether (Eqns 4 and 5).



[4]



[5]

Since acrylic acid does not polymerize via an anionic mechanism and vinyl ethyl ether requires a cationic mechanism,[13] the observation of polymer in the first case and not in the second eliminates both anionic and cationic mechanisms leaving only a radical mechanism. The radical mechanism is also demonstrated by characterization of the polyvinyl products: polydispersitivities for polyethyl acrylate and polystyrene (Mw/Mn) are 1.5 ± 0.2 and 1.9 ± 0.2 respectively, compared with values of 1.5 and 2.0 from known free-radical polymerization.[14]

In order to confirm that photoinitiation of vinyl monomers was a property of polysilanes in general, a variety of polysilanes were added to Pyrex test tubes containing methyl methacrylate. (MMA) or styrene (St) and exposed to sunlight. The sample tubes containing polysilanes all showed volume contraction, increased viscosity and gelling (in the case of methyl methacrylate), although control tubes containing monomer with no polysilane were unchanged throughout. In these experiments no attempt was made to exclude oxygen. The surprising lack of oxygen inhibition of polysilane photoinitiation will be discussed below.

In Table 1, the polysilanes are listed from most to least efficient as judged by the yield of polymethylmethacrylate (PMMA) observed after 48 h. Several interesting effects can be seen from Table 1. For example, while poly(phenylmethylsilylene) is the most efficient initiator at a molecular weight of 10 000, at $\bar{M}_n = 3500$ it is the least efficient, indicating a dependence of initiator efficiency on molecular weight. Table 1 also shows that relative initiation efficiency is dependent both on λ_{max} and solubility. Polysilanes with both a high λ_{max} and a good solubility such as $[(PhC_2H_4SiMe)(PhMeSi)_{0.56}]_n$ and $(PhMeSi)_n$

Table 1 Summary of polysilanes used to photoinitiate methylmethacrylate (MMA) and Styrene (St). Polymers are ranked from best to worst as photoinitiators of MMA

Polysilane	λ_{max}(nm)	$\varepsilon \times 10^{-3}$/Si	Polysilane $\bar{M}_n$	Concentration $\times 10^{-2}$ (moles silylene/dm^3)	Solubility[b]
(PhMeSi)	337	7.0	1×10^4	2.5 (MMA) 2.4 (St)	2
$(PhC_2H_4SiMe)_1$ $(PhMeSi)_{0.56}$	327	5.8	4×10^5, 8.4×10^4 (bimodal)	2.0 (MMA) 2.0 (St)	3 3
(cyclo-He × SiMe)$_{0.63}$ $(PhMeSi)_1$	334	7.8	8×10^4	2.6 (MMA) 2.5 (St)	2 3
(PhC_2H_4SiMe)	306	6.8	1.8×10^5	2.1 (MMA)	3
(p-$CH_3C_6H_6SiMe)_{0.91}$ $(Me_2Si)_1$	332	5.0	1.7×10^5	3.2 (MMA) 3.3 (St)	2 2
$(PhC_2H_4SiMe)_{0.67}$ (cyclo-He × SiMe)$_1$	310	6.7	1.5×10^5	2.2 (MMA) 2.2 (St)	1 3
$(PhC_2H_4SiMe)_{0.79}$ $(Me_2Si)_1$	305	5.0	3.3×10^5, 1.1×10^4 (bimodal)	2.8 (MMA) 3.1 (St)	2 3
(cyclo-He × SiMe)$_{0.66}$ $(Me_2Si)_1$	309	4.3	9.10^5, 7×10^4 (bimodal)	3.5 (MMA) 3.6 (St)	0 1
(cyclo-He × SiMe)	326	7.6	1.7×10^5	2.5 (MMA) 2.3 (St)	0 1
(PhMeSi)	254, (310t)$^{+}$	1.5	3.5×10^3	7.2 (MMA) 7.2 (St)	3 3

[a] +A UV absorption tail is observed to extend past 310 nm

[b] Solubilities range from 0, insoluble, to 3, completely soluble

are superior to polysilanes that have a high λ_{max} and poor solubility (cycloHe × SiMe) and polysilanes with good solubility but a low λ_{max}, $[(PhC_2H_4SiMe)_{0.79}\text{-}(Me_2Si)]_n$. These observations explain the apparent molecular weight dependence of initiation efficiency: lower molecular weight polysilanes have an enhanced solubility but a reduced λ_{max}.

A more detailed experiment was carried out at three different wavelengths to investigate the dependence of relative initiation efficiency on molecular weight and as a function of irradiation wavelength (see Table 2). The three polymers used all had good solubility in ethyl acrylate, forming homogeneous solutions with minimal turbidity (which quickly gave clear solutions on irradiation).

At 350 nm in the presence of equivalent molar amounts of polysilanes (based on the total number of silylene units present), the high molecular weight polysilanes were better photoinitiators than the corresponding low molecular weight species. That is, the polyethylacrylate initiated by polysilane oligomers had a higher molecular weight, indicating fewer polymer chains formed (thus fewer radicals generated) than polyethylacrylate photoinitiated by higher molecular weight polysilanes. While the principal UV absorbance for these polysilane oligomers was at or below 254 nm, a long UV absorbance tail was noted in all cases extending past 310 nm. It is probable that photoinitiation for these species involves absorbance into this tail and subsequent chain scission to produce silyl radicals.

When irradiated at 350 nm the high molecular weight polysilanes showed an inverse correlation between the polysilane λ_{max} and polyethyl acrylate chain length: the longer the λ_{max} of the polysilane, the shorter the polyethyl acrylate chain length. This is what would be predicted at 350 nm; polysilanes which absorb nearest the emission maximum would be expected to undergo more chain scissions than those that absorb further away, and would be expected to initiate more polymer chains producing a lower molecular weight vinyl polymer.

Table 2 Photoinitiation of polyethylacrylate by various polysilanes

			$\bar{M}_n$ polyethylacrylate produced		
Initiator	$\bar{M}_n$ (initiator)	λ_{max}(nm)	At 350 nm	300 nm	254 nm
$(PhMeSi)_n$	1.05×10^4	337	5.6×10^5	8.5×10^5	8.5×10^5
$\begin{array}{cc}\text{Ph} & \text{Me}\\ \vert & \vert \\ (\text{Si—} & \text{Si})_n\\ \vert & \vert \\ \text{Me} & \text{Me}\end{array}$	1.7×10^5	325	6.4×10^5	8.5×10^5	8.5×10^5
$(PhC_2H_4SiMe)_n$	8.5×10^5	303	9.5×10^5	8.5×10^5	7.1×10^5
$(PhMeSi)_n$	3.5×10^3	253	9.0×10^5	9.0×10^5	7.1×10^5
$\begin{array}{cc}\text{Ph} & \text{Me}\\ \vert & \vert \\ (\text{Si—} & \text{Si})_n\\ \vert & \vert \\ \text{Me} & \text{Me}\end{array}$	3.5×10^3	245	9.0×10^5	8.5×10^5	7.1×10^5
$(PhC_2H_4SiMe)_n$	4×10^3	<220	9.0×10^5	8.5×10^5	7.1×10^5

When polymerization is initiated at shorter wavelengths the initiation activity of the oligomers increases relative to the higher molecular weight polysilanes. This can be understood on the basis of the UV λ_{max} of the oligomers. Irradiation at shorter wavelengths allows the oligomers to absorb more efficiently while the high polymers actually absorb less efficiently; ε decreases at wavelengths shorter than λ_{max} for high molecular weight polysilanes, in some cases by more than a factor of 2.[8] Thus, if solubility is controlled, relative initiation efficiency depends almost entirely on the UV absorbance characteristics of the polymer.

As shown in Table 1, high molecular weight polysilanes have large UV extinction coefficients: $4\text{–}8 \times 10^3$ per silylene unit, depending on polymer molecular weight and substituents. This is one or two orders of magnitude larger than for benzoin ethers, another class of photoinitiators with strong UV absorbance. At moderately high concentrations of polysilane in the monomer, this may lead to product molecular weights which increase with time of irradiation, as shown in Fig. 1. For an 0.7 wt. % solution of $(PhSiMe)_n$, (5.8×10^{-2} moles/L), with $\varepsilon = 4000$, according to Beer's law 99% of the incident UV will be absorbed in the first 1.3×10^{-2} cm. Thus all the initiating radicals are formed in a very small volume of the total solution. Since chain termination by radical recombination will be dependent on the square of the concentration of radicals, the molecular weight of the product polymer will be lower than if the same number of radicals were distributed uniformly throughout the solution. As irradiation proceeds and the polysilane degrades, both ε and λ_{max} decrease, so that the path length for the incident UV through the solution becomes longer. The distance between radicals then becomes greater, leading to a higher molecular weight product.

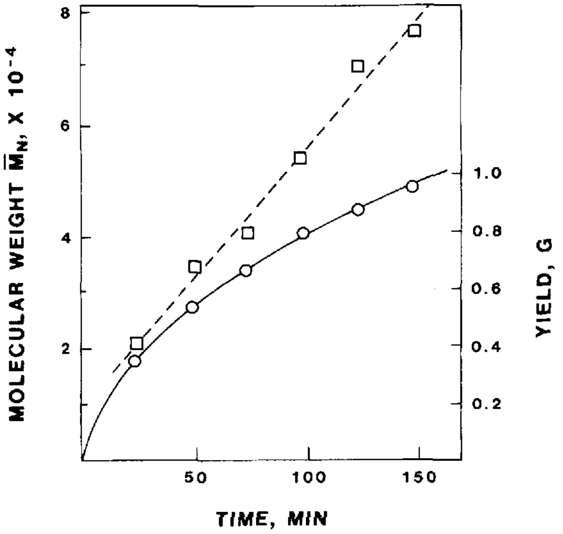


Figure 1 Molecular weight (----) and yield in grams (——) of polystyrene photoinitiated with poly(phenylmethylsilylene) as a function of time of irradiation.

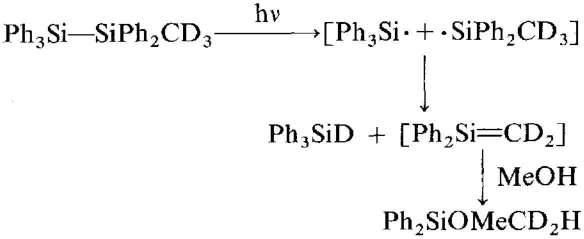
To study the rate and efficiency of initiation, carefully purified styrene monomer was used, with either poly(phenylmethylsilylene) or BME as initiator. The rate of initiation, R_i, is related to the absorbed intensity, I_a, by $R_i = I_a f$, where the initiation efficiency, f, is the fraction of polymer chains produced per photon absorbed. Values of f range from 1.0 for di-*tert*-butylperoxide to 1×10^{-4} for acetone.[12]

Typical results are shown in Fig. 2 and summarized in Table 3. As can be seen from the table, the initiation efficiency for poly(phenylmethylsilylene) is quite low, $\sim 1 \times 10^{-3}$. This is surprising in light of its high quantum efficiency for chain scission. A possible explanation for this low initiation efficiency is that the radical pairs formed upon photolysis react with themselves by hydrogen transfer more rapidly than they react with styrene. Such reactions are known for simple silyl radicals, as illustrated in Eqn 6.[16] The silyl radicals formed from

Table 3 Summary of photoinitiation kinetics data and calculated photoinitiation efficiencies (f)

Initiator	Concentration (wt %)	Rate (moles styrene/sec)	f
None	—	3.10×10^{-9}	—
BME	0.60	1.57×10^{-6}	0.275[a]
$(PhMeSi)_n$	0.20	7.7×10^{-8}	7.06×10^{-4}
$(PhMeSi)_n$	0.048	1.48×10^{-7}	1.17×10^{-3}

[a]Reference 15.



$$\begin{tikzcd} Ph_3Si{-}SiPh_2CD_3 \arrow[r, "h\nu"] & {[Ph_3Si\cdot + \cdot SiPh_2CD_3]} \arrow[d] \\ & Ph_3SiD + [Ph_2Si{=}CD_2] \arrow[d, "MeOH"] \\ & Ph_2SiOMeCD_2H \end{tikzcd}$$

[6]

polymer chain scission are bulkier than the monosilane radicals and would be slower to diffuse apart; this could enhance the probability of hydrogen abstraction.

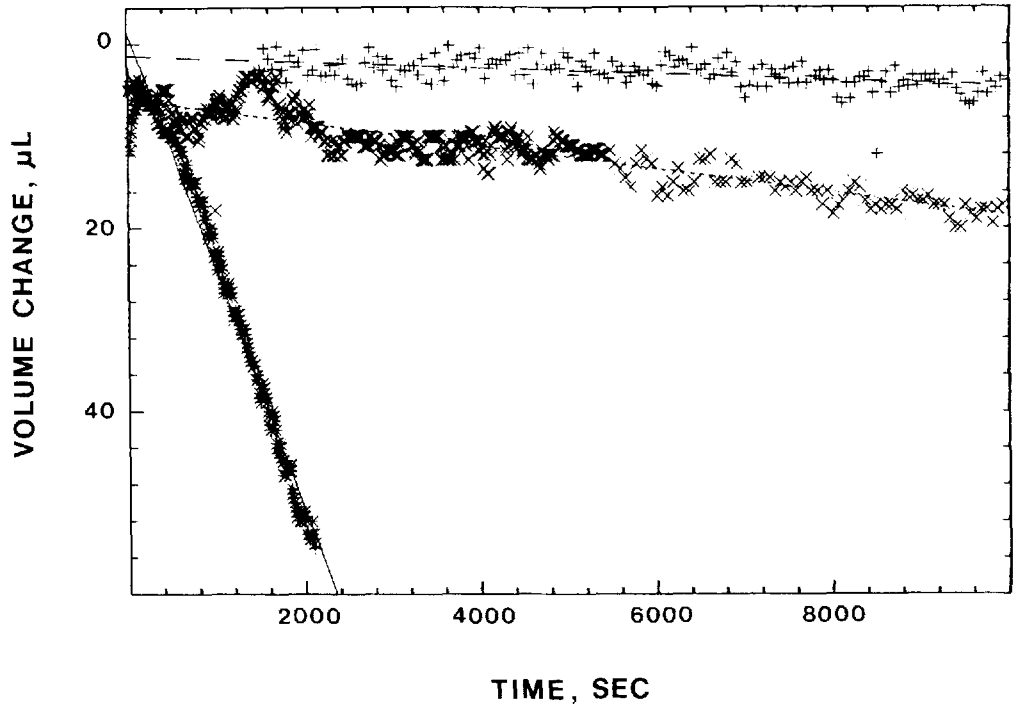


Figure 2 Representative polymerization rate data for styrenes from dilatometry experiments. ---, no initiator; ----, 0.020 wt.%$(PhMESi)_n$; ——, 0.60 wt.%BME. Fluctuations in volume with time early in the photolysis reflect residual minor variations in sample temperature.

However, since the dilatometry measurements involved photolysis in neat styrene, which presumably forms a solvent cage about the polyphenylmethylsilyl radical pair, the fact that the radical pair should prefer hydrogen abstraction to addition to an alkene is surprising. It is possible however that the addition of polysilyl radicals to styrene is strongly hindered sterically.[6] If steric hindrance greatly slows the addition leading to chain initiation, this may allow the hydrogen transfer to compete effectively, accounting for the low initiation efficiency.

Besides not reacting with styrene, if the rearrangement product silene is formed, it can also act as an oxygen scavenger according to Eqn 7.[17] This reaction may explain the insensitivity of polysilane-photoinitiated polymerizations toward oxygen.

$$3RR'Si{-}CH_2 + 3O_2 \rightarrow (RR'SiO)_3 + CH_2{=}O \qquad [7]$$

The fact that oxygen inhibition is reduced for polysilanes, compared to other polymerization photoinitiators, makes the polysilanes especially attractive for polymerization of thin films, for example in industrial or commercial tape manufacture or in photoresist applications.

Novel polystyrene characteristics

Since the initiators used are themselves polymeric, fragments of the polysilane chain might become incorporated into the polystyrene to give a black copolymeric structure. Some indication that this takes place is given by the ultraviolet spectrum in Fig. 3, displaying the difference in UV absorption between polystyrene initiated with poly(phenylmethylsilylene) and with azo(bisisobutyronitrile). The polysilane-initiated polymer shows excess UV absorbance from 200 to beyond 300 nm; as photolysis proceeds the absorbance beyond 300 nm is bleached while the peak near 245 nm becomes stronger. Absorption near 245 corresponds to a polysilane fragment containing about three silicon atoms. Examples of phenyl-containing trisilanes and their λ_{max} values[18] are shown in Table 4. The shoulders at longer wave-

Table 4 UV λ_{max} data for some phenylmethylsilylene-containing trisilanes

Trisilane	λ_{max}(nm)[a]
$Me_3SiSiPhMeSiMe_3$	243.0
$PhMe_2SiSiMe_2SiPhMe_2$	243.0
$PhMe_2SiSiMe_2SiMe_3$	240.0

[a]Data from reference 18.

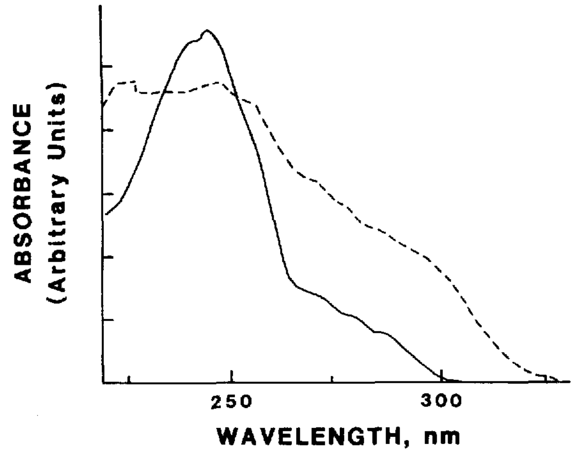


Figure 3 The UV difference spectrum of polystyrene after photoinitiation with poly(phenylmethylsilylene), run against similar molecular weight polystyrene photoinitiated by AIBN. ----, 1500 sec photolysis; ——, 9000 sec photolysis.

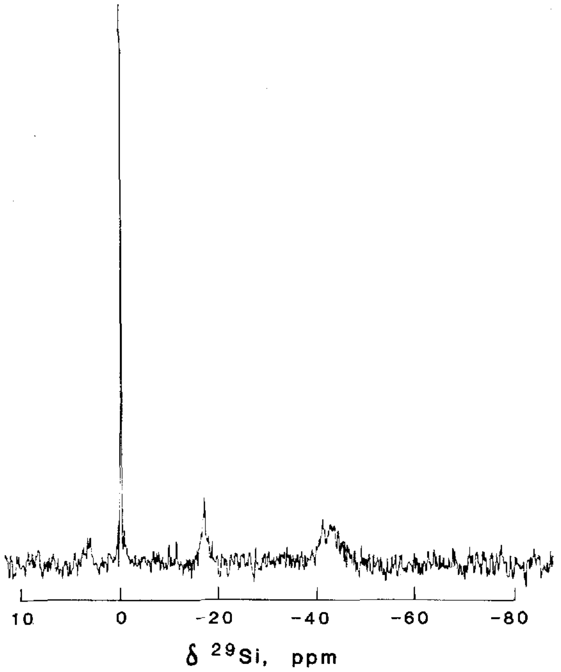


Figure 4 Silicon-29 NMR of polystyrene photoinitiated by $(PhMeSi)_n$. The peak at −16.8 ppm probably represents silylenes alpha to the polystyrene chain. The resonance at 0.0 is the reference, Me_4Si.

lengths probably represent polysilane fragments with ~4–6 silicon atoms.

A further indication of the incorporation of polysilane fragments is given by the ^{29}Si NMR spectrum of polystyrene photoinitiated by $(PhMeSi)_n$, shown in Fig. 4. The two resonance peaks observed can be assigned based on literature data for permethylpolysilanes;[19] the peak at −17 ppm is probably due to silicon atoms directly attached to the polystyrene chain, while the absorption between −40 and −45 ppm represents interior silicon atoms in polysilane chains.

The evidence thus indicates that polysilane fragments probably become incorporated as blocks or caps on the polystyrene chain,* and that these polysilane moieties become shorter with continued photolysis. The effects of the incorporation of polysilane on the properties of vinyl polymers remains to be investigated.

Acknowledgement This work was performed under grants from the 3M Corporation, whose support is gratefully acknowledged, and by the US Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Contract No. F49620-83-C-0044. The United States Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notaion thereon. The authors thank Professor Hyuk Yu for many helpful discussions and also Mark D. Janette and Carl J. Schwabe for valuable assistance in data collection.

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*The UV and ^{29}Si NMR data do not conclusively distinguish between a covalently-bound copolymer and a physical mixture. However, because the polymer was precipitated in a 20-fold excess of methanol and oven-dried for a minimum of 6 h, it is unlikely that polysilane oligomers remained physically mixed with the polystyrene.