J. Am. Chem. Soc. **1991**, *113*, 2003–2010

Solution Photochemistry of Poly(di-*n*-alkylsilane)s. An EPR–ENDOR Study of the Structure of the Persistent Radicals

Allan J. McKinley,[1a] Takashi Karatsu,[1a] Gregory M. Wallraff,[1b] Dennis P. Thompson,[1b] Robert D. Miller,[1b] and Josef Michl*[,1a]

Contribution from the Center for Structure and Reactivity, Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712-1167, and IBM Research Laboratories, Almaden Research Center, San Jose, California 95120-6099.

Received August 31, 1990

Abstract: The structure of the initial persistent radicals formed by UV irradiation of poly(di-*n*-alkylsilane)s has been determined by EPR–ENDOR spectroscopy to be $-RR'Si-RSi^{\bullet}-RR'Si-$. A mechanism of formation is proposed. A study of the temperature dependence of the EPR spectra shows that the rotation of the methylene group attached to the radical center is not free and that the average conformation of the alkyl substituent is dependent both on its structure and on temperature. Various isotopically labeled derivatives of poly(di-*n*-hexylsilane) have been studied and this has allowed the determination of the hyperfine splitting constants of nine inequivalent nuclei around the radical center on the polymer chain.

Introduction

Polysilanes[2] P-(RR'Si), light-sensitive high molecular weight polymers with a purely silicon containing backbone, have attracted considerable interest as novel photoresists.[3,4] Although considerable attention has been paid to the mechanism of the rapid photodegradation of their molecular weight in neat films[4,5] and in solution,[6–8] it is still only poorly understood. Homolytic scission of Si–Si bonds is generally believed to play a critical role. Indirect evidence for photochemical generation of radicals has been obtained from analysis of the stable low molecular weight products of exhaustive photodegradation[7] and from the induction of alkene polymerization,[9] but direct observations have been limited. We now elaborate our preliminary report[10] on the subject and provide a full description of an EPR–ENDOR–TRIPLE study of the persistent radicals formed by the irradiation of poly(dialkylsilane)s in solution.

The polysilanes investigated were poly(di-*n*-alkylsilane)s P-(R_2Si), where R = butyl (Bu), pentyl (Pn), 4-methylpentyl (4MePn), hexyl (Hx), octyl (Oc), decyl (De), and tetradecyl (Td), as well as poly(dialkylsilane)s P-(RR'Si) where R,R' = methyl and propyl (MePr), cyclohexyl and methyl (c-HxMe), methyl and hexyl (MeHx), ethyl and hexyl (EtHx), and propyl and hexyl (PrHx). Various isotopically labeled polymers P-(Hx_2Si) were also studied: P-(Hx_2Si)-*α-D*, fully deuterated on the α-carbons of the side chains, P-(Hx_2Si)-*β-D*, fully deuterated on the side-chain β-carbons, P-(Hx_2Si)-α-^{13}C, with 98% labeled α-carbons, and P-(Hx_2Si)-α-0.1^{13}C, with 10% labeled α-carbons.

Experimental Section

The preparation of the poly(dialkylsilane) samples followed the lines described elsewhere.[11] The molecular weights were determined by GPC with polystyrene standards and were in excess of 1 million. EPR samples were prepared by dissolving approximately 1 mg of the polymer in 0.5 mL of dry solvent and then degassed by several freeze–pump–thaw cycles. The solvents were spectroscopic grade pentane, hexane, cyclohexane, octane, and hexadecane and high-purity propane, butane, and perdeuterated pentane. Light sources were a Lambda Physik EMG 102 excimer laser operating at 308 nm (XeCl) or EMG 50 excimer laser operating at 248 nm (KrF), a medium-pressure mercury lamp (254 nm), and a high-pressure xenon/mercury lamp combined with a monochromator (330 nm). Irradiation was continued until a pale brown color could be discerned in the sample.

EPR–ENDOR measurements were performed on a Bruker ESP 300 EPR spectrometer equipped with an EN810 ENDOR accessory. The ENDOR power amplifier was an ENI Model A-500. The *g* values were determined by using a Bruker ER035M NMR gaussmeter and in-cavity probe to measure the magnetic field at the sample and a Hewlett-Packard 5350A frequency counter to measure the spectrometer frequency. Absolute spin concentrations were determined against standard DPPH solutions prepared in the same solvent and sample tube with identical cavity placement as the unknown sample. UV–visible spectra were recorded on a Varian 2300 instrument. GC–MS results were obtained on a Hewlett-Packard 5995 instrument. Spectral simulations were performed on an Alliant FX/8 computer using a modified version of the computer program YKEXCH.[12] The ^{29}Si satellites and ^{13}C splittings for the 98% ^{13}C-labeled polymer were added subsequently by Fourier transform techniques.[13]

Results

Radical Formation. Ultraviolet irradiation of high molecular weight poly(dialkylsilane)s dissolved in any of a variety of aliphatic hydrocarbon solvents was monitored by EPR and resulted in the formation of a persistent radical (I), in most cases stable at room temperature in the absence of air for several days. Further irradiation produced a second persistent radical (II), which was even

---

(1) (a) The University of Texas. (b) IBM Research Laboratories. This project was initiated at the University of Utah, Salt Lake City, UT 84112.

(2) West, R. *J. Organomet. Chem.* **1986**, *300*, 327. Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359.

(3) Miller, R. D.; Rabolt, J. F.; Sooriyakumaran, R.; Fleming, W.; Fickes, G. N.; Farmer, B. L.; Kuzmany, H. In *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K., Allock, J., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988; Chapter 4. Miller, R. D.; Hofer, D.; McKean, D. R.; Willson, C. G.; West, R.; Trefonas, P. T., III In *Materials for Microlithography*; Thompson, L. F., Willson, C. G., Frěchet, J. M. J., Eds.; ACS Symposium Series 266; American Chemical Society: Washington, DC, 1984; Chapter 14.

(4) Zeigler, J. M.; Harrah, L. A.; Johnson, A. W. *Proc. SPIE, Adv. Resist Technol. Process.* II **1985**, *539*, 166.

(5) Magnera, T. F.; Balaji, V.; Michl, J.; Miller, R. D. In *Silicon Chemistry*; Corey, J. Y., Corey, E. R., Gaspar, P. P., Eds.; Ellis Horwood, Ltd.: Chichester, U.K., 1988; Chapter 45.

(6) Karatsu, T.; Miller, R. D.; Sooriyakumaran, R.; Michl, J. *J. Am. Chem. Soc.* **1989**, *111*, 1140.

(7) Trefonas, P., III; West, R.; Miller, R. D. *J. Am. Chem. Soc.* **1985**, *107*, 2737.

(8) Michl, J.; Downing, J. W.; Karatsu, T.; Klingensmith, K. A.; Wallraff, G. M.; Miller, R. D. In *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K., Allcock, J., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988; Chapter 5, p 61.

(9) West, R.; Wolff, A. R.; Peterson, D. J. *J. Radiat. Curing* **1986**, *13*, 35.

(10) McKinley, A. J.; Karatsu, T.; Wallraff, G. M.; Miller, R. D.; Sooriyakumaran, R.; Michl, J. *Organometallics* **1988**, *7*, 2567.

(11) Magnera, T. F.; Balaji, V.; Michl, J.; Miller, R. D.; Sooriyakumaran, R. *Macromolecules* **1989**, *22*, 1624. Sun, Y.-P.; Miller, R. D.; Sooriyakumaran, R.; Michl, J. *J. Inorg. Organomet. Polym.*, in press. Trefonas, P. T., III; Djurovich, P. E.; Zhang, X.-H.; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 819. Miller, R. D.; Thompson, D.; Sooriyakumaran, R.; Fickes, G. N. *J. Polym. Sci., Part A, Polym. Chem.*, in press.

(12) Program obtained from Dr. R. F. C. Claridge, University of Canterbury, Christchurch, New Zealand.

(13) Evans, J. C.; Morgan, P. H.; Renaud, R. H. *Anal. Chim. Acta* **1978**, *103*, 175.

0002-7863/91/1513-2003\$02.50/0

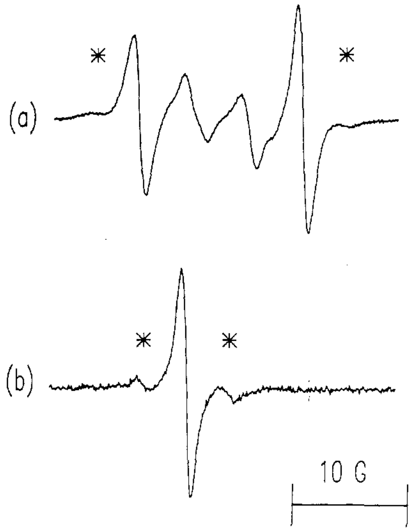


Figure 1. EPR spectra of radicals I and II formed by UV irradiation of P-(Td_2Si), recorded at 300 K: (a) radical I, (b) radical II. The lines marked with an asterisk are ^{29}Si satellites.

more stable (Figure 1). However, it is not clear whether radical II is formed from radical I or from the virgin polymer. The stability of radical I was enhanced by longer chain substituents on the polymer. In one case, P-(MePrSi), radical I was not detected at all and only radical II was observed. In all other polymers, including the mixed-alkyl polymer P-(MeHxSi), both radicals I and II were observed. Above room temperature the rate of decay increased. For instance, radical I formed from P-(Hx_2Si) decayed in a few minutes at 340 K. The same radicals were produced with either pulsed or continuous irradiation between 248 and 330 nm. However, the shorter irradiation wavelength apparently produced shorter chain fragments, which were more soluble at lower temperatures. The solubility of radical I increased during irradiation, presumably again due to chain fragmentation. P-(4MePnSi) was found to be soluble in liquid propane at −78 °C. Irradiation at this temperature with 308-nm light was ineffective, but 248-nm light produced the same initial persistent radical as irradiation at room temperature.

When the EPR signal of radical I formed from P-(Hx_2Si) with 308-nm light was monitored concurrently with the change in UV absorption of the polymer, it became clear that radical I was formed from the beginning of the irradiation. Integration of the EPR intensity, standardized against DPPH solutions, and the assumption that the decrease in UV absorbance was directly proportional to the number of Si–Si bonds broken, led to an estimate of the radical yield as being less than 5% of the total number of Si–Si bonds broken. The yield of radical II was much lower than that of radical I. For polymers with substituents longer than propyl, it was negligible at short irradiation times.

Room-temperature sonication of a solution of P-(Hx_2Si) in hexane in an ultrasonic bath did not produce persistent radicals. Addition of a spin trap (2,4,6-tri-*tert*-butylnitrosobenzene)[14] to the solution before the sonication demonstrated that transient radicals were indeed being produced from the polymer, but provided little evidence for their structure. The persistent EPR signal of the trapped radicals consisted of a triplet of triplets (10 G, assigned to the nitrogen, and 1.9 G, assigned to the meta hydrogen atoms). Sonication of a solution of the spin trap in hexane alone did not produce EPR signals.

Attempts to use this spin trap to intercept the primary radicals formed during the irradiation experiments were thwarted as the spin trap itself absorbed light, even in the absence of a polysilane, and produced radicals that had an EPR spectrum very similar to that described above.

Photoproduct Stability and UV–Visible Spectra. Prior to irradiation there is little absorption above 360 nm. As the irradiation progresses and the solution turns brown, new bands appear, centered around 360 and 440 nm. After longer irradiation these bands diminish, and radical II becomes dominant in the EPR spectrum. Irradiation into the 440-nm band did not bleach it. Upon standing, the color and the EPR signal of radical I gradually disappeared; however, a strong EPR signal for radical II could still be observed from the resulting colorless solution. The color and both radical signals were destroyed immediately if air was admitted to the sample tube. Addition of carefully deoxygenated pyridine, trimethylmethoxysilane, methanol, triethylsilane, nitrous oxide, or hexene by distillation under vacuum also destroyed the color and the EPR signals of both radicals. Addition of hexane under the same conditions caused only a small decrease in the EPR signal, presumably due to the introduction of small amounts of oxygen. Irradiation of the solutions after the addition of the above reagents did not regenerate radical I or II.

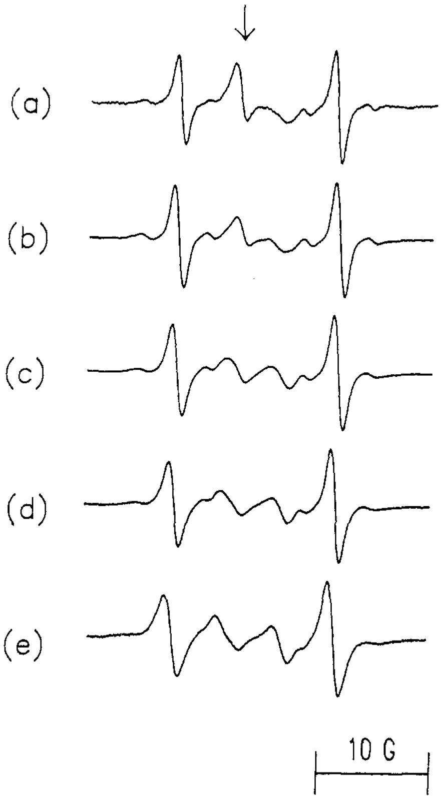


Figure 2. EPR spectra of radicals I and II formed by UV irradiation of P-(RR′Si), recorded at 300 K: (a) R = Hx, R′ = Et; (b) R = R′ = Bu; (c) R = R′ = Hx; (d) R = R′ = Oc; (e) R = R′ = Td. The arrow indicates the position of the signal due to radical II.

The UV–visible spectra of the irradiated solutions were not sufficiently specific to be of value in structural assignments and are noted here only for completeness. The observed bands may, but need not be due to radical I. Simple silyl radicals absorb strongly near 300 nm and weakly near 400 nm,[15] but nothing seems to be known about the absorption spectra of silyl-substituted derivatives.

After irradiation at 248 nm of P-(Hx_2Si) dissolved in pentane, GC–MS analysis did not show the presence of hexane. Hexene, even when added intentionally before irradiation, was not detected after the irradiation, presumably because it reacts with silyl radicals (cf. ref 9).

EPR Spectra. The EPR spectrum at 300 K of radical I from those polysilanes P-(R_2Si) whose R was longer than methyl, and not branched at the α position of the side chain, displayed a four-line pattern, with the central pair broader than the outside pair (Figure 1). As the length of the substituent was decreased from tetradecyl to butyl the members of the central pair became

---

[14] Obtained from Professor M. Tabata, Hokkaido University.

[15] Chatgilialoglu, C.; Ingold, K. U.; Lusztyk, J.; Nazran, A. S.; Scaiano, J. C. *Organometallics* **1983**, *2*, 1332.

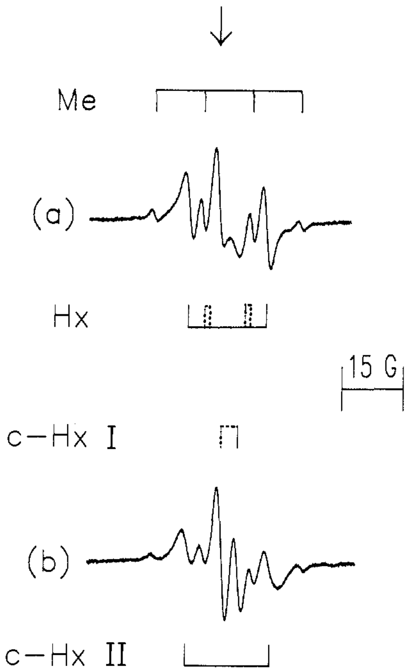


Figure 3. EPR spectra of radicals I and II formed by UV irradiation of (a) P-(MeHxSi) and (b) P-(c-HxMeSi), recorded at 300 K. The arrow denotes the position of the signal due to radical II.

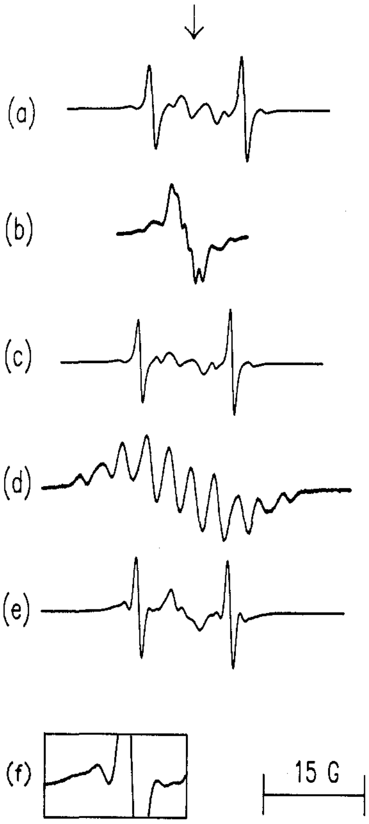


Figure 4. EPR spectra of radicals I and II formed by UV irradiation of various isotopically labeled P-(Hx$_2$Si): (a) P-(Hx$_2$Si); (b) P-(Hx$_2$Si)-α-*D*; (c) P-(Hx$_2$Si)-β-*D*; (d) P-(Hx$_2$Si)-α-^{13}C; (e) P-(Hx$_2$Si)-α-0.1^{13}C; (f) ^{13}C satellites of (e) expanded 2.4 times. 300 K (a–c); 330 K (d–f). The arrow denotes the position of the signal of radical II.

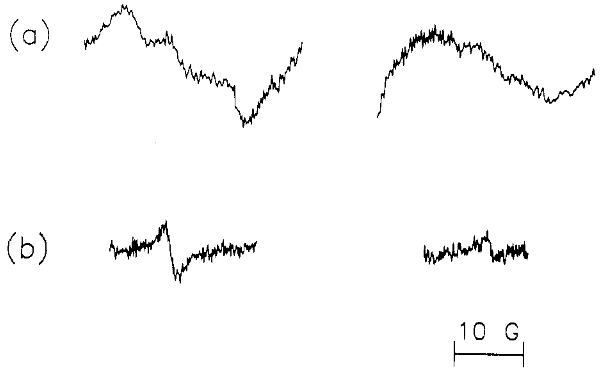


Figure 5. ^{29}Si satellites of radical I and II formed from P-(Hx$_2$Si), recorded at 300 K: (a) radical I, (b) radical II.

broader and their separation decreased (Figure 2). This change is very similar to that observed upon increasing the temperature for any one of these radicals. In all cases, the spectrum of radical II was an unstructured singlet.

In the case of polymers P-(RR′Si) where R $\neq$ R′, the simultaneous presence of more than one radical of type I was observed. P-(MeHxSi) gave EPR spectra that were a superposition of two distinct radicals of type I. The first was identical with that obtained from P-(Hx$_2$Si), and the second was a 1:3:3:1 quartet. On standing, the latter decayed more rapidly than the former. P-(c-HxMeSi) gave three types of radical I, The first was the same quartet as obtained from P-(MeHxSi) and two others were 1:1 doublets of different spacing. Again, the quartet was the least stable. These spectra are shown in Figure 3.

The EPR spectra of the radical I produced from isotopically labeled derivatives of P-(Hx$_2$Si) are shown in Figure 4. Radical I from P-(Hx$_2$Si)-α-*D* had an EPR spectrum that was a complicated structured singlet, the large splittings seen with P-(Hx$_2$Si) having been removed (Figure 4b). The EPR spectrum of radical II from this polymer was essentially identical with that obtained from the unlabeled polymer. For P-(Hx$_2$Si)-β-*D*, the EPR spectra of both radicals I (Figure 4c) and II were identical with those obtained from the unlabeled polymer. P-(Hx$_2$Si)-α-^{13}C gave a less well resolved many-line spectrum for radicals I and II. This spectrum sharpened as the temperature was increased. The spectrum shown in Figure 4d was recorded at 330 K. P-(Hx$_2$Si)-α-0,1^{13}C gave a spectrum very similar to that of the unlabeled polymer P-(Hx$_2$Si), except for the presence of larger shoulders on the outside doublet (Figure 4e,f). Irradiation of a 1:1 mixture of P-(Hx$_2$Si)-α-*D* and P-(Hx$_2$Si)-α-^{13}C resulted in an EPR spectrum that was the sum of the spectra observed when the polymers were irradiated individually, and no features attributable to new mixed products were observed. Irradiation of unlabeled P-(Hx$_2$Si) in perdeuterated pentane resulted in the same EPR spectra as obtained in undeuterated solvents.

For both radicals I and II formed from P-(Hx$_2$Si), satellite lines were observed. These have been attributed to coupling with ^{29}Si nuclei in natural abundance (4.7%). For radical I, two sets of satellites were found, one with a splitting constant of 75 G (Figure 5a) and the other with a splitting constant of 5.8 G (Figure 1a). The intensity of the lines with the 5.8-G splitting constant was consistent with two silicon atoms. However, the lines with the 75-G splitting constant were weaker than would be expected for coupling to one silicon atom, The value of the large splitting constant for radical I from P-(Bu$_2$Si) was found to be invariant between 280 and 340 K. The intensity of the 75-G satellites increased slightly with temperature, as did the resolution of the hyperfine structure within each satellite, The low-field satellite was better resolved than the high-field one. The hyperfine structure within each of the 75-G satellites mirrored the temperature changes of the central group. For radical II, two sets of satellites were also observed, one with a splitting constant of 56 G (Figure 5b) and the other with a splitting constant of 7,4 G (Figure 1a), The intensity of the lines with the smaller splitting constant of 7.4 G was consistent with the presence of three silicon atoms in this radical, However, the lines with the 56-G splitting constant were weaker than would be expected for coupling to one silicon atom,

The EPR spectrum of the radical I from P-(R$_2$Si)$_n$, where R is longer than methyl and not branched at the α position of the side chain, was relatively sensitive to the applied microwave power,

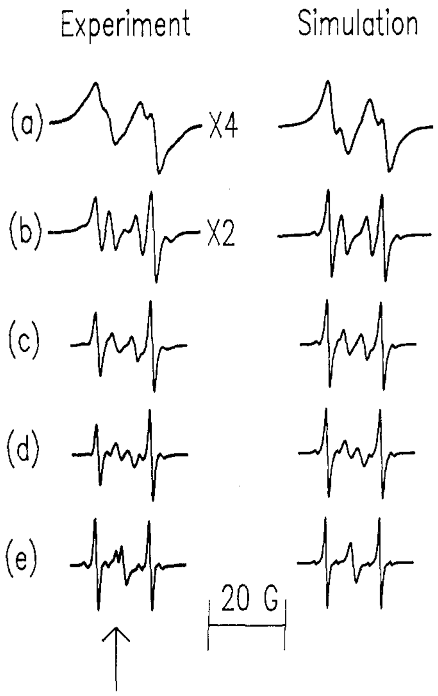


Figure 6. Temperature dependence of the EPR spectrum of radical I formed by UV irradiation of P-(4MePn$_2$Si). Experimental spectra on the left and computer simulation on the right, using parameters in Table II. (a) 200 K, (b) 240 K, (c) 280 K, (d) 320 K, (e) 360 K. The arrow indicates a signal due to radical II.

The resulting saturation showed as a broadening of the central doublet and an increase of the intensity of this doublet compared with the outside doublet. However, the position of the zero crossings of the lines was not affected. The saturation was easier for the less soluble polymer fragments.

As the temperature was lowered, the onset of precipitation of the polymer, as observed by turbidity in the solution, caused a quite characteristic sudden broadening of the radical signal. Aside from this effect, a temperature dependence was observed for the EPR spectrum of radical I formed from the polymers P-(R$_2$Si) whenever R was longer than methyl and not branched at the α position of the side chain. In the case of radical I formed from P-(4MePn$_2$Si), whose solubility remains high even at low temperatures, the situation is particularly clear. The EPR spectrum, shown on the left in Figure 6, changes from a pair of overlapping doublets at 200 K to a triplet at 390 K.

In contrast, the EPR spectra of all three kinds of radical I derived from P-(c-HxMeSi) and the quartet spectra from P-(MeHxSi) were found to be independent of temperature.

ENDOR Spectra. The ENDOR spectra for radicals I generated from P-(Hx$_2$Si), P-(Hx$_2$Si)-*α-D*, P-(Hx$_2$Si)-*β-D*, and P-(Hx$_2$Si)-*α*-^{13}*C* are shown in Figure 7. ENDOR signals were only observable from very concentrated solutions over a small temperature range near room temperature. EPR signals that were sufficiently intense to observe ENDOR were only obtained from the polymers of type P-(R$_2$Si). The ENDOR signal was enhanced with higher molecular weight polymers. RF power levels exceeding 250 W and microwave power of 10 mW were required for a good signal-to-noise ratio. Unfortunately, this led to heating problems in the cavity and often very poor base lines, especially at low frequency.

With P-(Hx$_2$Si) only two very small hyperfine couplings are observed. Both are due to ^{1}H nuclei and correspond to 0.15 and 0,35 G, respectively (Figure 7a). The ENDOR-induced EPR (EIE) spectra obtained by pumping these ENDOR lines were in good accord with the EPR spectrum. At least one large coupling must be absent in the ENDOR spectrum as the two small couplings observed are both smaller than the EPR line width. Since the EIE spectrum corresponds to the observed EPR, however, EPR and ENDOR are clearly monitoring the same radical,

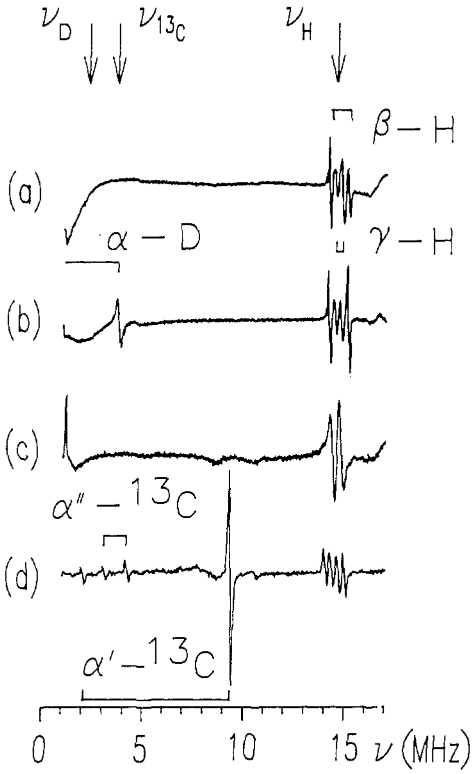


Figure 7. ENDOR spectra of radical I formed by UV irradiation of (a) P-(Hx$_2$Si), 300 K; (b) P-(Hx$_2$Si)-*α-D*, 305 K; (c) P-(Hx$_2$Si)-*β-D*, 270 K; (d) P-(Hx$_2$Si)-*α*-^{13}*C*, 330 K.

In the case of P-(Hx$_2$Si)-*α-D*, the same two couplings were observed, showing that neither is due to hydrogens in the α position of the side chain, plus a new absorption at 3.74 MHz, presumably due to the ^{2}H nucleus in the α position of the side chain (Figure 7b). Changing the magnetic field at which the ENDOR was observed had only the expected effect on the position of this line, i.e., just the shift expected from the change of the deuteron Larmor frequency. The width of this line was considerably broader than that of the hydrogen lines and was not temperature dependent over the 20 °C temperature range in which ENDOR signals could be observed for this radical. The expected partner for this line would be either at 0.75 MHz or at 8.23 MHz. As our ENDOR apparatus only allows scans from 1 MHz up and no absorption was detected around 8 MHz, this line is assigned to the high-frequency member of the pair. This assignment corresponds to a deuterium splitting constant of 1.07 G. When this value is converted to a hydrogen splitting constant (6.94 G), the extent of the EPR spectrum observed for P-(Hx$_2$Si) can be simulated by assuming two equivalent hydrogens in the α position of the side chain.

The ENDOR spectrum from P-(Hx$_2$Si)-*β-D* (Figure 7c) showed only the smaller of the two couplings observed for P-(Hx$_2$Si), and we conclude that the hydrogens responsible for the larger coupling had been replaced by deuterium. Confirmation of this substitution by the appearance of a new coupling centered about the free deuteron frequency was not obtained, probably due to the base-line irregularities below ~3 MHz, and to the predicted lower intensity compared with the hydrogen signals due to the smaller hyperfine enhancement factor.[16]

For P-(Hx$_2$Si)-*α*-^{13}*C*, four new lines were observed in addition to the four due to the small hydrogen couplings (Figure 7d). They converted to two splitting constants due to ^{13}C nuclei, one large (4.06 G) and one small (0.39 G),

The ENDOR of radical II shows one hydrogen coupling, which converts to 0.4 G. This splitting appears unaffected by α or β

---

(16) Kurreck, H.; Kirste, B.; Lubitz, W. *Electron Double Resonance Spectroscopy in Solution*; VCH: New York, 1988.

Table I. Magnetic Parameters for Silyl Radicals[a]

	radical I from P-$(R_2Si)_n$ 300 K			radical II from P-$(R_2Si)_n$				
	R = Me[b]	R = Hx[b]	R = c-Hx[b]	R = Hx[b]	$Me_3Si^•$[c]	$Me_2Si^•SiMe_3$[c]	$MeSi^•(SiMe_3)_2$[c]	$Si^•(SiMe_3)_3$[c]
g	2.0047 (1)	2.00472 (3)	2.0044 (1)	2.0056 (1)	2.0029	2.0037	2.0045	2.0050
$a_{H_1}{}^{\alpha}$	9.4 (2)	+9.1 (1)	15.5 (2) 2.6 (2)		6.3	8.21	9.36	
$a_{H_2}{}^{\alpha}$		+4.9 (1)						
$a_H{}^{\beta}$		−0.34 (1)	0.4			0.47	0.47	0.44
$a_H{}^{\gamma}$		+0.13 (1)						
$a_{^{13}C}{}^{\alpha}$		4.06 (5)						
$a_{^{13}C}{}^{\alpha'}$		3.4 (1)						
$a_{^{13}C}{}^{\alpha''}$		0.4 (1)						
$a_{^{29}Si}{}^{i}$		75 (1)		56 (1)	183	137	71	65
$a_{^{29}Si}{}^{\alpha}$		5.8 (2)		7.4 (2)				6.2

[a] Splitting constants in gauss. [b] This work. [c] Reference 17.

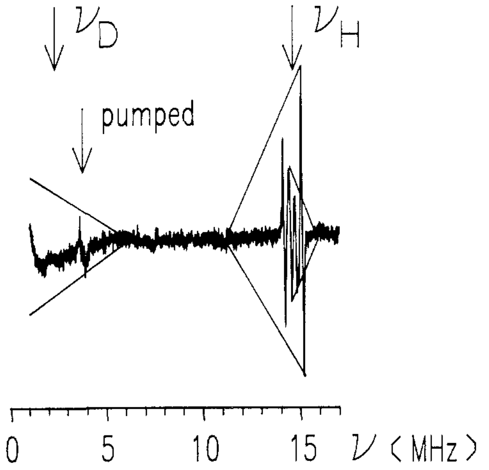


Figure 8. General TRIPLE spectrum of radical I formed by UV irradiation of P-(Hx_2Si)-α-*D* at 305 K.

deuteration. The signal level was too weak to obtain ^{13}C ENDOR signals from radical II.

General TRIPLE Spectra. These were obtained from both P-(Hx_2Si)-α-*D* (Figure 8) and P-(Hx_2Si)-β-*D*. In all cases the relative changes in intensity were consistent for all lines when pumped. This experiment confirmed that all the ENDOR lines arise from the same radical as they all changed when one line was pumped. It also showed the relative signs of the three hydrogen couplings: the signs of the 6.94- and 0.15-G couplings are the same and opposite to that of the 0.35-G coupling.

Discussion

Radical Structure. The magnetic parameters at 300 K for the polymer-based radicals I and II formed from P-(Hx_2Si), considered representative of all the alkyl substituents longer than methyl and not branched at the α position of the side chain, and from P-(c-HxMeSi) and P-(HxMeSi), are listed in Table I together with comparative values for some simple silyl radicals. The mixed polymers P-(c-HxMeSi) and P-(HxMeSi) each give more than one type of radical I. In both cases one is a quartet with an 1:3:3:1 intensity ratio indicative of a methyl group at the radical center. The other radical has an EPR spectrum compatible with the other alkyl remaining attached to the radical center; in the case of P-(HxMeSi) this is identical with the spectrum of the radical from P-(Hx_2Si). In itself, this suggests that the radical structure is related to the polymer structure by removal of a single alkyl chain, $-RR'Si-RSi^•-RR'Si-$. The spectral evidence discussed below leaves no doubt that this indeed is the case,

Since precipitation of the polymer at lower temperatures has a dramatic effect upon the EPR spectra of radicals I and II, presumably due to incomplete motional averaging of the hyperfine interactions, and since the ease of saturation clearly depends on the polymer solubility as well, the radical centers appear to be carried by large polymer fragments.

In the following, we continue to use the chain atom labeling common in polysilane chemistry, even though it disagrees with the notation usual in EPR spectroscopy. Thus, the carbon atom attached to the Si radical center is labeled α, as are its associated hydrogens. The carbon atom once removed, and its associated hydrogens, are labeled β. The next carbon atom, with its hydrogens, is labeled γ, etc. Further, the radical-carrying Si atom is called ipso, its silicon neighbors, α, next nearest neighbors, β, etc. The methylene groups in the alkyl chains attached to the α-Si atoms are primed (α', β', ...); those in chains attached to the β-Si atoms are doubly primed (a″, β'', ...); etc.

Radical I. The observed g values are only consistent with a silicon-centered radical center carrying two or more silyl groups.[17] Given that the radical is part of a long silicon chain, the g value would be slightly higher than those of the small molecules cited for comparison, and we conclude that radical I has two silyl groups attached to the silicon center. This is supported by the intensities of ^{29}Si satellites observed at natural abundance. The 75-G ^{29}Si satellites are very weak, presumably due to incomplete motional averaging of a large anisotropy, and are assigned to the ipso silicon at the radical center. Comparison with other known radicals (Table I) also shows that this size of a ^{29}Si splitting is consistent with the presence of two silyl groups attached to a planar or nearly planar ipso silicon radical center. The 5.8-G ^{29}Si satellites with intensities corresponding to two ^{29}Si atoms are then assigned to the two α-silicons adjacent to the radical center. These are expected to be much less anisotropic and much less sensitive to intensity distortion by incomplete motional averaging. The size of this coupling constant again agrees perfectly with expectations (Table I).

The large hydrogen couplings are assigned to the hydrogens on the α-CH_2 groups of the chain attached to the radical center, as these couplings are removed upon α deuteration. These α-hydrogens are not equivalent, since four rather than three lines are seen in the EPR spectrum in the low-temperature limit. This must be due to restricted rotational mobility around the $C-Si^•$ bond as discussed further below, which also makes it understandable why two distinct species are observed for radical I when the alkyl group is c-Hx. These couplings were not observed in the ENDOR spectrum of radical I from P-(Hx_2Si). However, a single line corresponding to their average was seen for P-(Hx_2Si)-α-*D*. We attribute this behavior to motional effects, the magnitude of which will depend on the relative rate of interchange of the two nuclei and the difference in their coupling constants. If the interchange rate is similar for the unlabeled and the deuterated radical, the two would be expected to be in quite different spectral regimes as the individual coupling constants for the deuterated radical would be 6.7 times smaller than for the unlabeled radical.

The two smaller couplings seen only by ENDOR are assigned to hydrogens of the β- and γ-CH_2 groups on the alkyl chain attached to the radical center respectively, as only the larger of the two disappears with β deuteration.

Absolute signs for the hydrogen splitting constants are obtained from the relative signs determined by the general TRIPLE ex-

---

(17) Cooper, J.; Hudson, A,; Jackson, R. A. *Mol. Phys.* **1972**, *23*, 209.

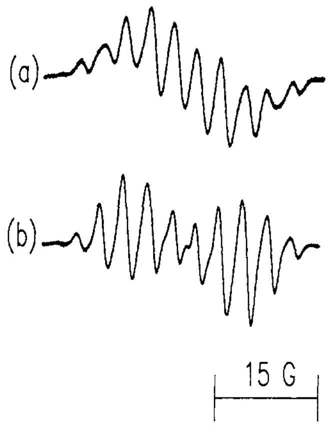


Figure 9. Comparison of observed and simulated EPR spectra of radical I from UV irradiation of P-(Hx_2Si)-α-^{13}C at 330 K.

periment, assuming that the hyperfine coupling to the hydrogen of the α-CH_2 group would be positive as usual, since the predominant hyperfine coupling mechanism would be hyperconjugation. Hyperconjugation and spin polarization would both be expected to contribute to the hyperfine coupling to the hydrogens of the β- and the γ-CH_2 groups. The sign alternation observed shows that spin polarization dominates.

The ^{13}C ENDOR spectra showed the presence of two types of carbon, with splitting constants of 4.06 and 0.39 G. However, analysis of the EPR spectra of radical I from P-(Hx_2Si)-α-0.1 ^{13}C showed shoulders corresponding to a ^{13}C splitting constant of 3.4 G and a relative intensity consistent with 3.6 carbons. Apparently, the carbons responsible for this hyperfine interaction do not yield ENDOR signals under conditions of observation accessible to us. The EPR spectrum of radical I from P-(Hx_2Si)-α-^{13}C was simulated by taking the EPR spectrum of the unlabeled radical and adding four splittings of 3.4 G and one splitting of 4.06 G. The 0.39-G splitting by four equivalent carbons was assumed to still lie within the line width. The result of this simulation is shown in Figure 9 and it can be seen that there is good agreement with the experimental spectrum, also shown in Figure 9. The agreement is not perfect, but motional effects upon the carbon splitting constants were not included and can be invoked to account for the small deviations. These splittings are then assigned as follows: 4.06 G to the carbon of the α-$^{13}CH_2$ group attached to the radical center, 3.4 G to the α-$^{13}CH_2$ groups of the four carbons on the silicons adjacent to the radical center (α'), and 0.39 G to the four carbons of α-$^{13}CH_2$ groups attached to the silicons separated by one SiR_2 group from the radical center (α''). The absence of the 3.4-G splitting in the ENDOR spectrum is attributed to unfavorable relaxation rates for these carbons.

Figure 10 shows a summary of all the splitting constants determined for radical I.

Radical II. The g value of radical II implies a silicon center with three silyl groups attached. This is confirmed by the splitting constants of the two kinds of ^{29}Si satellites. The 0.4-G hydrogen splitting observed in ENDOR is quite reasonable for α-hydrogens on the alkyl chains attached to the vicinal silicons of these silyl groups. The lack of expected changes upon deuteration in the α position can be understood if scrambling occurs during the formation of this radical. Clearly, the structure of radical II is not as firmly secured as that of radical I, but it most likely is ($-SiRR'$)$_3Si^\bullet$.

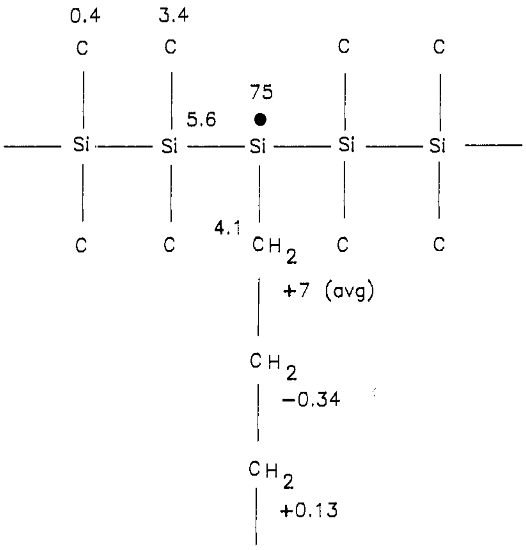


Figure 10. Summary of the splitting constants (G) determined for radical I formed by UV irradiation of P-(Hx_2Si).

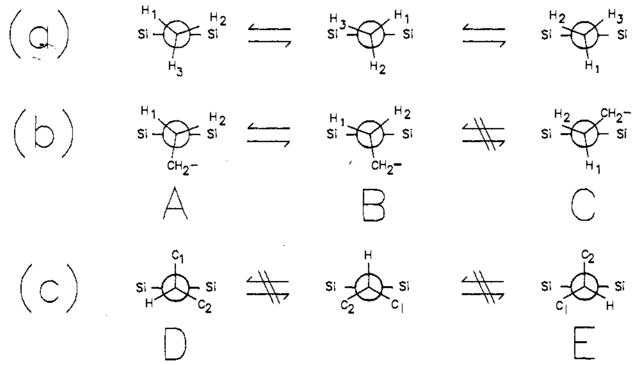


Figure 11. Conformations of radical I: (a) R = Me, (b) R = Et − Td, (c) R = c-Hx.

Radical Conformation. The temperature effect observed for radical I appears to be an alternating line-width effect caused by the out-of-phase motional modulation of the two hydrogens of the α-CH_2 group attached to the radical center. This type of effect is observed when the difference in frequency between the coupling constants is comparable to the frequency of interconversion.[18] A likely candidate for the modulation is restricted rotational motion about the C–$Si^\bullet$ bond between the radical center and the alkyl substituent, caused by the difficulty of eclipsing the C_α–C_β bond with one of the two Si–$Si^\bullet$ bonds (Figures 10 and 11). In the case of R = Me or R = c-Hx no temperature dependence is observed. For R = Me the rotation about the C–$Si^\bullet$ bond would be expected to be fast, making the three hydrogens equivalent (Figure 11a). For a secondary alkyl such as R = c-Hx such rotation is expected to be quite slow, and if eclipsing of the C_α–C_β with the Si–$Si^\bullet$ bond is indeed difficult, it makes sense that two distinct noninterconverting radicals are observed in EPR, given that conformations labeled D and E in Figure 11c would give the same EPR spectra. In the case of the primary alkyl substituents, ranging from ethyl to tetradecyl, the motional behavior ought to be intermediate between methyl and a secondary alkyl, giving three possible conformers labeled A–C in Figure 11b, At the lowest temperature reached, limited by the solubility of the radical, the spectrum tends toward a doublet of overlapping doublets, giving the values of 11.2 and 2.8 G, respectively, for the two hydrogen splitting constants, As the radical center is planar or nearly planar judging by the 75-G ipso ^{29}Si splitting constant,[17] the hydrogen with the small splitting constant must be quite close to the nodal plane of the singly occupied silicon p orbital. Conformer C cannot be responsible for the spectrum observed in the low-temperature limit since a very large splitting constant would be expected for the hydrogen of the C–H bond that nearly eclipses the singly occupied p orbital. A rotation by more than 180° around the C–$Si^\bullet$ bond would amount to an interconversion of conformers B and C and would require the eclipsing of the C_α–C_β bond with the Si–$Si^\bullet$ bond. This rotation therefore appears highly unlikely to be the hydrogen equalizing motion. It is much more likely that

---

[18] Sullivan, P. D.; Bolton, J. R. In *Advances in Magnetic Resonance*; Waugh, J. S., Ed.; Academic Press: New York, 1970; Vol. 4, p 39.

the motion involved is a rocking interchange of the two α-hydrogens between the conformations A and B. This would result in an out-of-phase variation of the α-hydrogen splitting constants.

As the temperature is increased, the rate of interchange between the two conformers increases and the average environments of the hydrogens gradually become more equivalent. The radical is not quite stable enough at elevated temperatures to permit the observation of complete equivalence; however, the spectrum does become a 1:0.4:1 triplet at 350 K. Increasing the temperature to 390 K has little additional effect.

The splitting constant for the hydrogens of the α-CH_2 group of the chain, which are located in positions of type β relative to the radical center, is expected to follow the Heller–McConnell relationship[19]

$$B_2 \cos^2 \langle\phi\rangle + B_0 = a_H$$

Here, $\langle\phi\rangle$ is the average value of the angle ϕ between the axis of the p orbital containing the unpaired electron and the β- hydrogen, defined by $\cos^2 \langle\phi\rangle = \langle\cos^2 \phi\rangle$, where the pointed bracket indicates ensemble averaging. We define Θ as the dihedral angle between the axis of the p orbital and the C_α–C_β bond (Figure 12) and have solved the quadratic equation for the unknowns, B_2, B_0, and $\langle\Theta\rangle$, by assuming trigonal symmetry around the carbon of the C_α–Si$^\bullet$ bond. We have used the α-CH_2 splitting constants of 11.2 and 2.8 G for the –(4MePn$_2$Si)–(4MePnSi$^\bullet$)–(4MePn$_2$Si)– radical at the low-temperature limit and assumed unrestricted rotation of the methyl substituent in the –(HxMeSi)–(MeSi$^\bullet$)–(HxMeSi)– radical, with a splitting constant of 9.4 G. The unknowns B_2, B_0, and $\langle\Theta\rangle$ were determined to be either 21.1 G, 1.1 G, and 13.7°, or 13.9 G, –2.4 G, and 52.1°, respectively. The second solution was rejected as (i) the 15.5-G hydrogen splitting constant observed for –(c-HxMeSi)–(c-HxSi$^\bullet$)–(c-HxMeSi)– cannot be accounted for, and (ii) the angle predicted placed the carbon uncomfortably close to the Si–Si bond.

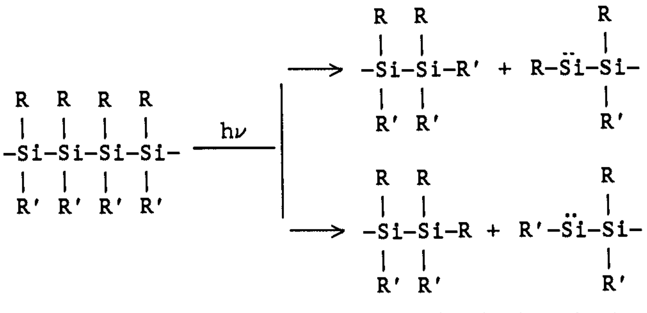
In order to analyze the temperature dependence of the spectra, the simplest possible model was chosen. This is the two jump model.[18] It was found that good agreement could not be obtained by taking two values for the α-hydrogen splitting constants at the low-temperature limit and then increasing the interconversion rate. On the other hand, when both the interconversion rate and the α-hydrogen splitting constants were varied, given a constant sum for the splitting constants, good agreement was obtained. A comparison of the simulation with experiment for radical I from P-(4MePn$_2$Si) is shown in Figure 6. A collection of the interconversion rates and splitting constants derived from the simulation of the EPR spectra of radical I formed from P-(R$_2$Si), where R = butyl, 4-methylpentyl, hexyl, and octyl, is given in Table II.

The variation in the splitting constants as a function of temperature probably corresponds to a change in $\cos^2 \langle\phi\rangle$, which is attributed to an anisotropy in the well in the rotational potential, as an increase in the amplitude of the rocking motion would change $\langle\Theta\rangle$ within each conformer. A change in the degree of delocalization of the unpaired electron with temperature can be rejected as the cause of this variation since the splitting constant of the central silicon did not vary between 280 and 340 K within the experimental error. $\cos^2 \langle\phi\rangle$ also varies between substituents: $\langle\Theta\rangle$, calculated from the larger splitting constant at 300 K, increased from 7.6° to 8.8° as the length of the substituent increased, from butyl to octyl, probably due to steric effects. It is a little odd that a constant value of the sum of the splitting constants is observed. Given that $\langle\Theta\rangle$ changes with temperature, the sum of the splitting constants should also be a function of temperature if the Heller–McConnell relationship were followed exactly. However, we note that the values of $\langle\Theta\rangle$ that follow from the parameters derived above are such that the sum of the splitting constants goes through a minimum and is nearly constant within a wide region marked by arrows in Figure 12.

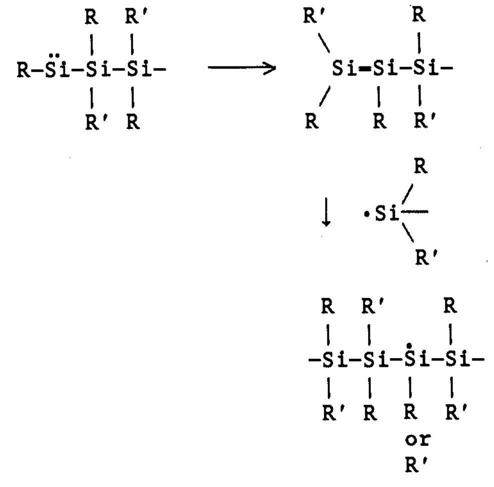
Alternatively, it is conceivable that the overall conformations of the polymer side chains could have a small effect on the value of Θ. Therefore, as in solution a distribution of conformations for the side chains would be expected, there would be a distribution of the values of Θ. This distribution would be expected to be temperature and substituent dependent and hence the splitting constants would vary with temperature and substituent.

Further analysis of the data obtained from the simulations to derive the activation parameters of the interconversion process was not attempted as the parameters derived showed too little variation with temperature for significant results to be obtained.

Radical Formation Mechanism. The structure of radical I from P-(RR′Si) is formally related to that of the parent polymer by a loss of an alkyl group by homolytic cleavage of a Si–C bond. If this were the actual photochemical reaction mechanism, alkanes RH or R′H would be expected to be among the products, but GC–MS showed no detectable quantities of these hydrocarbons. However, GC–MS analysis of the volatile products after exhaustive 248-nm irradiation of P-(c-HxMeSi) solutions showed the presence of 10–15% of trialkylsilyl-terminated fragments.[10] Their appearance suggests that the lost alkyl group is not released as a free radical, but rather, that it is transferred to a neighboring silicon atom in a process of chain breaking by reductive elimination, analogous to the thermal degradation of disilanes:[20]



More recently, we have observed this type of fission by reductive elimination in peralkylated tetrasilanes and trisilanes as well.[21] An attempt to trap an alkylsilylene-terminated polysilane with Et$_3$SiD was unsuccessful, and no Si–D bonds were observed in the IR of the irradiated polymer after the trapping agent was removed by evaporation. This is presumably due to a disilylsilylene to silyldisilene rearrangement, known to be very facile.[22] It is proposed that this disilene then adds a polysilyl radical at the less hindered chain end in a well-precedented[9] process. This automatically leads to the actually observed radical structure:



The disilene may well be at least partly responsible for the observed color of the irradiated solutions,

The proposed mechanism is consistent with the observation that the EPR spectrum of an irradiated mixture of P-(Hx$_2$Si)-α-*D* and

---

[19] Heller, C.; McConnell, H. M. *J. Chem. Phys.* **1960**, *32*, 1535.

[20] Walsh, R. *Organometallics* **1988**, *7*, 75, and references therein.

[21] Davidson, I. M. T.; Michl, J.; Simpson, T., submitted for publication.

[22] Sakurai, H.; Nakadaira, Y.; Sakaba, H. *Organometallics* **1983**, *2*, 1484; Nagase, S.; Kudo, T. *Organometallics* **1984**, *3*, 1320.

Table II. Temperature Dependence of EPR Results for Radical I

polysilane	T^a	line width[b]	splitting const[c] a_1	a_2	interchange rate[d]
P-(Oc_2Si)	250	1.1	10.4	3.6	0.7
	260	1.1	10.3	3.7	1.0
	270	1.1	10.1	3.9	1.1
	280	0.9	9.9	4.2	1.2
	290	0.7	9.6	4.4	1.3
	300	0.7	9.4	4.6	1.3
	310	0.65	9.2	4.8	1.3
	320	0.65	9.0	5.0	1.3
	330	0.65	8.9	5.1	1.4
	340	0.6	8.8	5.2	1.5
	350	0.6	8.7	5.3	1.7
P-(Hx_2Si)	270	1.1	9.7	4.3	1.2
	280	0.9	9.5	4.6	1.2
	290	0.8	9.2	4.8	1.2
	300	0.7	9.1	4.9	1.2
	330	0.6	8.9	5.1	1.5
P-(Bu_2Si)	260	0.9	9.65	4.35	1.5
	270	0.65	9.65	4.35	1.5
	280	0.65	9.35	4.65	1.5
	290	0.65	9.15	4.85	1.8
	300	0.65	8.95	5.05	1.9
P-($4MeP_2Si$)	200	2.5	11.2	2.8	0.7
	210	1.9	11.0	3.0	0.7
	220	1.4	10.8	3.2	0.8
	230	1.2	10.6	3.4	0.8
	240	1.0	10.4	3.6	0.8
	250	0.9	10.2	3.8	0.9
	260	0.9	10.1	3.9	0.9
	270	0.9	9.9	4.1	1.0
	280	0.8	9.5	4.5	1.0
	290	0.7	9.5	4.5	1.2
	300	0.7	9.3	4.7	1.3
	310	0.7	9.2	4.8	1.3
	320	0.7	9.0	5.0	1.4
	330	0.6	8.8	5.2	1.5
	340	0.5	8.6	5.4	1.7
	350	0.5	8.3	5.7	2.0
	360	0.5	8.1	5.9	2.1
	370	0.5	7.9	6.1	2.3

[a] Temperature (±1 K). [b] In gauss, ±0.05 G. [c] In G, ±0.1 G. [d] In $10^7\ s^{-1}$, ±0.1.

P-(Hx_2Si)-α-^{13}C equals the sum of the spectra of each polymer irradiated separately.

The proposed mechanism also is consistent with the fact that the radicals I and II are not formed in the sonication experiment, in which homolytic Si–Si bond rupture presumably also occurs, but disilene is absent. Simple rupture of the Si–Si bond by sonication is consistent with the EPR spectrum of the radical observed after spin trapping with tri-*tert*-butylnitrosobenzene, which shows no evidence of splitting by H atoms originating in the trapped radical. In the absence of an added trap, the primary radicals of the –RR′Si• type would be expected to decay by recombination or disproportionation, and the resulting silene should also trap them. Apparently, the resulting adduct radicals are not sufficiently sterically hindered to produce persistent EPR signals under the conditions of our experiments. This also accounts in a natural fashion for the low yield of the observed persistent radicals, since only a small fraction of the primary photoproduct radicals –RR′Si• would be expected to add to disilene. Our attempts to trap the postulated primary silylene or disilene were not fruitful, as all trapping reagents reacted with the radicals I and II as well.

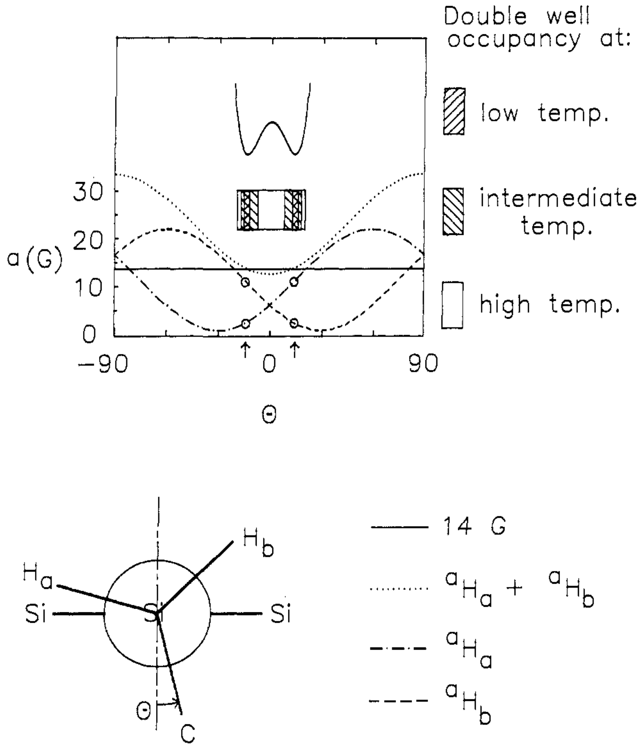


Figure 12. Plot of the angular dependence of the splitting constants a_1 and a_2 of the α-hydrogens H_a and H_b and their sum. The angle Θ is zero when the methylene carbon and the axis of the silicon p orbital with the unpaired electron are eclipsed. The arrows on the Θ axis denote the value of ⟨Θ⟩ observed at the low-temperature limit. The proposed potential for the rotational motion is shown schematically.

The observation that 308-nm irradiation of P-($4MePe_2Si$) at −78 °C in liquid propane did not lead to the formation of the persistent radical I, whereas 248-nm irradiation did, may have mechanistic implications and remains to be investigated further.

Conclusions. The structure of the polymer-centered persistent radical I resulting from the irradiation of poly(dialkylsilane)s in solution has been established beyond doubt and information on its conformation has been obtained. The structure is unexpected, but a plausible mechanism for its formation has been formulated.

Acknowledgment. This work was supported by the U.S. Air Force (Grant AFOSR 87-0001) and the IBM Corp. (Grant 707312). We thank Dr. P. H. Kasai (IBM Research Laboratory, Almaden Research Center, San Jose, CA) and Dr. J. W. Downing (Center for Structure and Reactivity, Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, TX) for helpful discussions.

Registry No. P-(Bu_2Si) (homopolymer), 97036-65-2; P-(Bu_2Si) (SRU), 95999-72-7; P-(Pn_2Si) (homopolymer), 97036-66-3; P-(Pn_2Si) (SRU), 96228-24-9; P-(($4MePn)_2Si$) (homopolymer), 117652-54-7; P-[($4MePn)_2Si$] (SRU), 117652-58-1; P-(Hx_2Si) (homopolymer), 97036-67-4; P-(Hx_2Si) (SRU), 94904-85-5; P-(Oc_2Si) (homopolymer), 97036-68-5; P-(Oc_2Si) (SRU), 98865-30-6; P-(De_2Si) (homopolymer), 117652-57-0; P-(De_2Si) (SRU), 107999-69-9; P-(Td_2Si) (homopolymer), 117652-56-9; P-(Td_2Si) (SRU), 107999-70-2; P-(MePrSi) (homopolymer), 88002-81-7; P-(MePrSi) (SRU), 88003-13-8; P-(c-HxMeSi) (homopolymer), 88002-85-1; P-(c-HxMeSi) (SRU), 88003-16-1; P-(MeHxSi) (homopolymer), 88002-83-9; P-(MeHxSi) (SRU), 88003-15-0; P-(EtHxSi) (homopolymer), 125121-01-9; P-(EtHxSi) (SRU), 125121-30-4; P-(PrHx) (homopolymer), 125121-02-0; P-(PrHx) (SRU), 125121-31-5.