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ORGANOSILICON POLYMER DEPOSITION BY TEA CO_2 LASER-INDUCED DECOMPOSITION OF SILANE IN THE PRESENCE OF DIFFERENT OXYGENATED OLEFINS

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ABSTRACT

The infrared multiphoton decomposition of silane in the presence of methyl acrylate, acrolein, allyl methyl ether, allyl acetate, methyl vinyl ether, and vinyl acetate results in the formation of various gaseous compounds and the gas-phase deposition of solid material on cold reactor surfaces. Both multistep molecular reactions between silylene and the oxygenated olefins and radical processes are thought to contribute to the formation of the solid deposit. The latter incorporates all the silicon of reacted silane, the structure of which is inferred from IR and ESCA analysis to consist of different siloxane units.

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INTRODUCTION

Homogeneous polymerization in the gas phase has recently attracted much attention, predominantly due to the use of cloud chambers [1–3], exciplex [4, 5] or infrared [6, 7] laser radiation, particle beam [8], and plasma [9, 10] techniques.

We have reported on the formation of organosilicon polymers from the gas phase by the continuous-wave CO_2 laser-induced decomposition of 1-methyl-1-silacyclobutane [6] or 4-silaspiro(3.4)octane [7]. Pulsed CO_2 laser-induced multiphoton dissociation of silane in the presence of methyl methacrylate [11] has also been reported. The latter reaction was considered to occur by a mechanism of radical steps and a molecular pathway involving the addition of silylene onto the double bond of methyl methacrylate. In addition, it makes use of silane to form mainly solid organosilicon polymer powders.

We were also interested in determining whether a similar material could be produced via pulsed CO_2 laser irradiation of gaseous mixtures of silane with oxygenated olefins, and to investigate the quality of the polymeric materials produced.

This article presents results on the infrared multiphoton dissociation of silane in the presence of methyl acrylate (MA), acrolein (AC), allyl methyl ether (AME), allyl acetate (AA), methyl vinyl ether (MVE), and vinyl acetate (VA). The interaction of pulsed CO_2 laser radiation with mixtures of silane and unsaturated compounds results in the gas-phase deposition of very fine powder particles that are composed of different siloxane units.

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EXPERIMENTAL

Experiments were performed using a grating-tuned TEA CO_2 laser (P. Hilendarski Plovdiv University, 1300 M model) operated on the P(20) line of the 10.6 μm band at 944.19 cm^{-1} with a repetition rate of 1 Hz. The wavelength was confirmed by using a model 16-A spectrum analyzer (Optical Engineering Co.). The laser beam was square (1.5 cm on a side) and was attenuated by polyethylene sheets. Typical temporal profiles of the pulse, as measured with a Rofin photon drag detector, consisted of a 150-ns (FWHM) peak followed by a tail of about 1 μs when the laser was operated with a 4:8:12 CO_2:N_2:He atmospheric gas mixture. The laser beam energy was measured with a laser energy pyroceramic sensor

(Charles University, ml-1JU model). Irradiation of SiH_4-oxygenated olefin mixtures was conducted in a cylindrical (3 cm i.d., 10 cm long) cell constructed of Pyrex and equipped with a NaCl window fixed with a Lukopren seal. The mixtures of SiH_4 and oxygenated olefin were introduced into the cell from a standard vacuum line and the pressures of both components were measured by a manometer and subsequently checked by IR spectrometer (Specord 75 model, Zeiss). The mixtures were irradiated with 50 up to 1000 pulses, and changes in their composition were monitored by IR and GC/MS (Shimadzu QP 1000 quadrupole mass spectrometer) spectrometry (column packed with alumina deactivated with silicone oil, silicone elastomer OV-1, or Porapak P).

Absorptivities of MA (1446, 1397, and 1282 cm^{-1}), AC (1408, 1709, and 1725 cm^{-1}), AME (1128, 1203, and 2836 cm^{-1}), AA (1378, 1441, and 1767 cm^{-1}), MVE (1320, 1457, and 1625 cm^{-1}), VA (1296, 1377, and 1656 cm^{-1}) and silane (2235 cm^{-1}) were used for the determination of the depletion of these compounds. Gaseous reaction products, methane (1300 cm^{-1}), ethene (1440 cm^{-1}), propene (1420 and 1640 cm^{-1}), ethine (730 cm^{-1}), formaldehyde (1743 cm^{-1}), acetaldehyde (1760 and 2736 cm^{-1}), and acetone (1712 and 3005 cm^{-1}), were identified by their infrared spectra and through their mass fragmentation. Ketene (2152 cm^{-1}) and carbon monoxide (2140 cm^{-1}) were detected in the region of the absorption of silane by considering an increase of the P relative to the Q branch of silane.

In order to measure the properties of the deposit by ESCA and SEM analyses, a deposit on a Umafol (poly(vinyl acetate)) sheet was produced in experiments where pieces of the sheet were housed in the cell before irradiation.

The x-ray photoelectron spectra were measured on a VG ESCA 3 MK II spectrometer using AlK_α achromatic radiation ($h\nu$ = 1486.6 eV). The spectrometer was operated in fixed analyzer mode using a 20-eV pass energy. The background pressure during the spectra accumulation was typically 10^{-6} Pa. The samples were fixed to the probe by double-sided adhesive tape. The spectra recorded were Si2p, C1s, and O1s. The C1s binding energy (285.0 eV) was used as the internal standard to compensate for charging effects. Core level binding energies were determined with an accuracy of ± 0.2 eV. To convert integrated intensity data into data on the elemental composition, the linear background was subtracted and the published [12] subshell photoionization cross-sections were used. The deposits were thick enough so that the photoemission lines of the supporting foil were not observed in the spectra.

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TABLE 1. Interaction between Oxygenated Olefin and Silane Induced by Multipulse TEA CO_2 Laser Radiation

Olefin	Energy in pulse, J	Total pressure, torr	SiH_4: olefin ratio	Depletion of SiH_4 and olefin, in torr, after the action of N subsequent laser pulses		
				$N = 50$	$N = 500$	$N = 1000$
MA	2.0	18	1.8	–	1.2/3.9	–
	2.0	19	1.1	–	0.3/0.4	0.9/1.2
AC	1.8	22	1.8	–	2.1/6.0	2.4/6.5
	1.8	23	1.5	–	1.8/7.0	–
	3.0	26	1.1	2.6/6.1	2.6/9.0	2.8/9.5
AME	1.8	26	1.5	–	2.3/7.7	–
	2.0	15	0.8	–	–	0.3/0.3
AA	2.2	14	1.6	–	1.0/1.2	–
	2.0	19	1.3	–	–	0/1.6
MVE	2.0	25	1.8	–	4.8/6.4	5.7/7.1
	2.5	26	1.2	3.0/5.6	3.7/8.0	–
	1.0	25	1.3	–	0.4/2.8	1.0/3.3
VA	2.5	16	1.8	0.1/0.2	0.6/2.2	–
	1.5	16	1.7	–	–	0.3/1
	2.5	17	1.1	–	0.3/1.2	–

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TABLE 1. (continued)

Gaseous products	Gaseous products of laser photosensitized (SF_6) (L) or thermal (T) pyrolysis of oxygenated olefin	Ref.
CH_4, C_2H_2, C_2H_4, CH_2:C:O, CH_2:CHCHO	L: CO, C_2H_4, CH_2:CHCHO, C_2H_2, CH_4, C_3H_6, CH_3CH_2CHO	14
C_2H_4, C_2H_2, CH_2:C:O, C_3H_6	L: C_2H_4, CO, CH_2:CO, CH_4, C_2H_2	This work
CH_4, C_2H_2, CH_2O, C_3H_6, CH_2:C:O	T: C_3H_6, CH_2O	15
CH_4, C_2H_2, CH_2:C:O, C_2H_4, C_3H_6, C_4H_8, CH_3CHO, CH_2:CHCHO, $CH_2=CHCH_2OCH_3$	T: CO_2, CH_4, CO, 1−C_4H_8, C_3H_6, CH_2:CHCHO, C_2H_4, C_2H_6	16
CH_4, C_2H_2, C_2H_4, CH_3CHO, CH_2:C:O	L: C_2H_4, CH_4, CH_2:CO, CH_3CHO	This work
C_2H_2, C_2H_4, CH_2:C:O, CH_3CHO, $CH_3C(O)CH_3$	L: C_2H_4, CH_4, CH_2:CO, CH_3CHO, $CH_3C(O)CH_3$, C_2H_2	This work (see also Ref. 17)

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TEA CO_2 laser photosensitized (SF_6) decomposition of AC, VA, and MVE was carried out with binary mixtures of the reactant (7–10 torr) and sulfur hexafluoride (6–20 torr) in the reported Pyrex cell by using an unfocused laser beam with energy in 2 J pulses.

MA, AC, AA, VA, and sulfur hexafluoride (all Fluka) and silane (99.5% pure, Lachema) were commercial samples distilled prior to use. MVE was obtained by treatment of methanol with ethine after the procedure of Ref. 13, and AME was prepared by the reaction of sodium methoxide with allyl bromide as reported in Ref. 14.

RESULTS AND DISCUSSION

Irradiation of silane-oxygenated olefin mixtures with total pressures of 16–26 torr with a TEA CO_2 laser results in the depletion of both parent compounds (Tables 1 and 2). The formation of various gaseous molecules and gas-phase solid deposition on both windows and the surface of the cell has also been observed. The irradiation is accompanied by a yellowish luminescence which can be observed by using a few initial pulses near the entrance window. The interaction of the laser radiation with binary mixtures of silane with MA, AC, AME, AA, MVE, and VA appears to be affected by the relative content of SiH_4 and by the energy in the pulse. This is similar to the results for the irradiation of mixtures of silane and methyl methacrylate [11]. The depletion of silane and olefin is faster at higher pulse energies or higher SiH_4:olefin ratios. Furthermore, characteristic of all interactions, the olefin is depleted faster than silane.

It is reasonable to assume that the P(20) line of the 10.6-μm band of the CO_2 laser, coinciding with an IR branch transition in the ν_4 mode of silane, induces dissociation of silane into reactive silylene [19–21].

$$SiH_4 \rightarrow SiH_2 + H_2$$

The silylene then reacts with the oxygenated olefins. It is also known that silylene adds to C=C double bonds [22–26] to form three-membered rings which can cleave to form silyl olefins. We can therefore postulate the initial formation of the latter compounds with oxygen not directly bonded to silicon but susceptible to an O→Si coordination bond which can (see Ref. 27) induce cleavage reaction, leading to compounds with formulas as shown in Ref. 28.

H_2Si (alkoxy or acyloxy) alkenyl compounds can undergo numerous

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TABLE 2. Stoichiometry of Organosilicon Polymers

Binary mixture (torr)		Energy in pulse, J	Number of pulses	A_{Si0} [a]	ESCA analysis of deposit	
SiH_4–MA						
(12)	(7)	2.0	1000	0.13	SiC_2O_2	
(11)	(6)	1.8	200		$SiC_{1.3}O_{1.3}$	
SiH_4–AC						
(12)	(13)	3.0	850	0.09	SiC_3O_2	
(14)	(8)	1.8	500		$SiC_{1.5}O_{1.5}$[b]	Si^0 (34%)[b]
(14)	(8)	1.8	500		SiC_2O_2	Si^0 (18%)[c]
(14)	(8)	2.4	1000		SiCO	

(continued)

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TABLE 2. (continued)

Binary mixture (torr)	Energy in pulse, J	Number of pulses	A_{SiO} [a]	ESCA analysis of deposit	
SiH_4–AME					
(16) (11)	1.8	2500	0.05	$SiCO_{1.5}$	
SiH_4–AA					
(10) (7)	2.3	3000	0.06	$SiC_{1.3}O_{1.6}$	
SiH_4–MVE					
(16) (9)	2.3	500	0.01	$SiC_{0.7}O_{1.3}$ [b]	Si^0 (22%) [b]
(16) (9)	2.3	500	0.01	$SiCO_{1.4}$ [c]	Si^0 (28%) [c]
SiH_4–VA					
(11) (6)	2.5	1800	0.05	$SiC_{1.3}O_{1.8}$	

[a] Absorptivity of ν^{as}_{Si-O} band (average value, ±10%) of polymer deposited on cell windows after the 1 torr depletion of SiH_4.
[b] Polymer deposited near the entrance window.
[c] Polymer deposited near the rear window.

scrambling reactions [29] and intermolecular condensations which lead to the final siloxanes. The other pathway can, however, consist of a specific interaction of silylene with the oxygen moiety [30]. An additional channel that cannot be excluded entirely is the SiH_4-photosensitized decomposition of the oxygenated olefin. The observed gaseous products might serve as the basis for differentiation among these alternatives, but they are mostly identical to those originating from thermolysis of the oxygenated olefin (Table 1). It is conceivable that the radical mechanism of the thermal (laser photosensitized) decomposition of the olefin can initiate reactions of radicals with SiH_4 and bring about radical chains. Plots of log k vs $1/T$ for the thermal decomposition of all parent unsaturated compounds, under truly homogeneous conditions, can be helpful to estimate whether the unsaturated compound will decompose easier than silane and thus initiate radical chains at the expense of the silylene reaction. This is definitely not the case with MA [15, 28] and very probably with AME [16], VA, and MVE as well. Therefore, the reaction of silylene can be assumed to be the primary process occurring upon irradiation of the parent mixtures.

The infrared multiphoton decomposition of silane is unlikely at a low partial pressure of silane [21] because SiH_4 can act only as an energy conveying agent. This is also obvious in laser interaction with mixtures of low SiH_4 content, where the laser photosensitized decomposition of only the olefin can occur. This reaction certainly takes place with AA (Table 1), where silane does not decompose but AA does.

The IR spectra of the solid deposit (Fig. 1) corroborates the view that the final product has a siloxane structure. The very low intensity of the absorption band at 2950 cm^{-1} is usually taken as evidence [30] for a large number of dimethylsiloxane units. Besides the absorption bands related to siloxane, the deposit also shows absorptions in the region of C=O and Si—H stretching vibrations; the former band is rather sensitive to exposure of the deposit to air.

The Si2p core level binding energies (102.7 $\pm$ 0.2 eV) of the deposits as well as the values of the Auger parameter, defined as the sum of the Si2p binding energy and the Si KLL kinetic energy (1711.8 eV), fit well into the values reported [32] for methylsilicone resins.

Stoichiometry inferred from ESCA analysis is consistent with different structural units whose occurrence depends not only on the structure of the olefin or laser pulse energy, but also on the place of the deposition of the solid. Thus, the material deposited after irradiation of SiH_4-AC and SiH_4-MVE near and far from the entrance window is found to have

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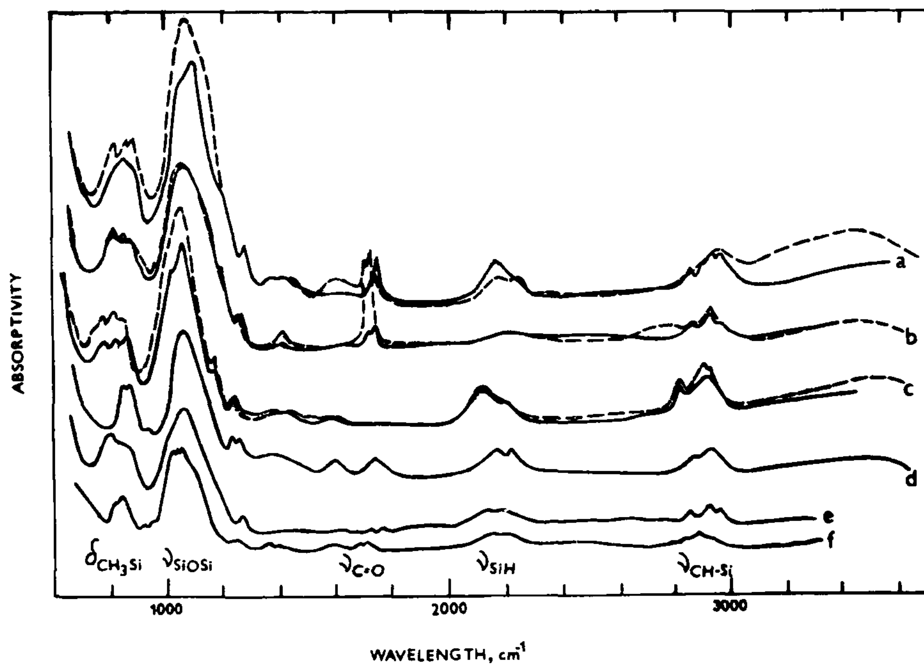

FIG. 1. IR spectra of the deposit from the reaction of silane with MA (a), AC (b), AME (c), AA (d), MVE (e), and VA (f). Spectra measured in an evacuated cell (full curve) or after exposure to air (dashed curve).

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different Si/C/O ratios. In both these cases, elemental silicon was also observed. The latter can be explained by SiH_2 dissociation into Si and H [33].

Silylene is thought [34] to be an important intermediate in the chemical vapor deposition of silicon and hydrogenated amorphous silicon formed through the insertion of SiH_2 into the Si—H bonds. Trapping rate constants [22, 23, 26, 35] of silylene reactions with silane and some unsaturated hydrocarbons show SiH_2 to be a highly reactive and undiscriminating species. The absence of disilane or trisilane, the products of SiH_2 reactions with SiH_4 or Si_2H_6, and the lack of IR absorption of the deposit at 2100 and 880 cm^{-1} after TEA CO_2 irradiation of the SiH_4-methyl methacrylate mixture [11], a characteristic of hydrogenated films [36, 37], has been taken by us as support for the statement that SiH_2 reaction with

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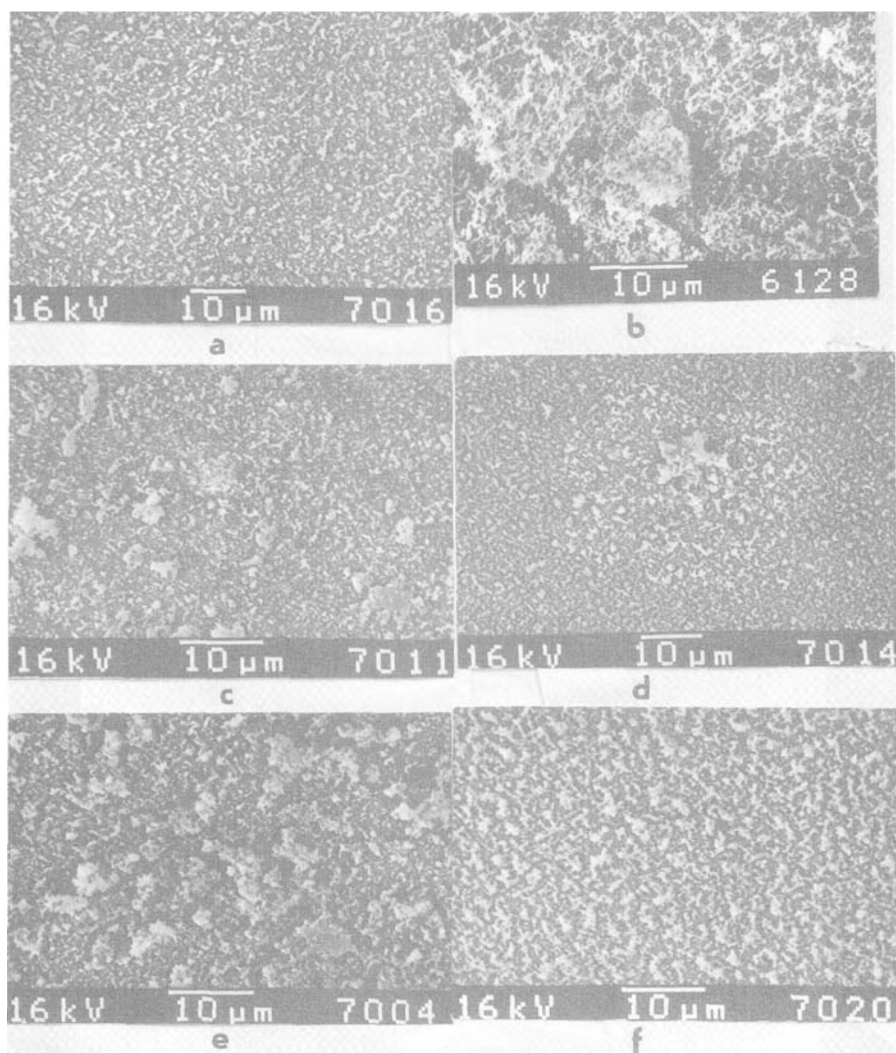
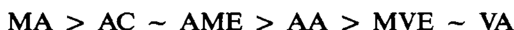


FIG. 2. SEM of the deposit from the reaction of silane with MA (a), AC (b), AME (c), AA (d), MVE (e), and VA (f).

methyl methacrylate is strongly favored over the insertion of SiH_2 into the Si—H bond of silane [11]. Absorption of the deposit in the region of the stretching Si—H vibration (Fig. 1) does not allow us to draw similar conclusions with the mixtures reported here. It is possible that silylene reacts simultaneously with both oxygenated olefin and silane, and that disilane formed by the second reaction undergoes dissociation and is thus removed from the observed gaseous products.

Absorptivity of the ν^{as}_{SiOSi} band of the solid deposits on the cell windows after the 1 torr depletion of silane under comparable conditions (pressure, energy in pulse) has been taken as a criterion of the olefin capability to form siloxane. The following order (Table 2) was revealed:



MA > AC ~ AME > AA > MVE ~ VA

which seems to imply that olefins with oxygen bonded directly to the unsaturated carbon bond (as $CH_2{=}CH{-}OCH_3$) are the least reactive in the formation of siloxane.

In all the silane-oxygenated olefin mixtures, scanning electron microscopy revealed a nonhomogeneous deposition of polymer (Fig. 2) with regions of different morphology, confirming that powder formation occurs in the gas phase.

The technique of the TEA CO_2 laser-induced decomposition of silane in the presence of oxygenated olefins can find application as a method for the preparation of new organosilicon powders and adds to the potential of the infrared multiphoton dissociation of silane to form new silicon-containing materials.

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REFERENCES

[1] H. Reiss, *Science, 238*, 1368 (1987) and references therein.
[2] M. S. El-Shall and H. Reiss, *J. Phys. Chem., 92*, 1021 (1988).
[3] H. Rabeony and H. Reiss, *Macromolecules, 21*, 912 (1988).
[4] M. Buback and H.-P. Vögele, *Macromol. Chem., Rapid Commun., 6*, 481 (1985).

[5] H. Brackemann, M. Buback, and H.-P. Vögele, *Makromol. Chem., 187*, 1977 (1986).
[6] J. Pola, V. Chvalovský, E. A. Volnina, and L. E. Guselnikov, *J. Organometal. Chem., 341*, C13 (1988).
[7] M. Sedláčková, J. Pola, E. A. Volnina, and L. E. Guselnikov, *J. Anal. Appl. Pyrol., 14*, 345 (1989).
[8] C. R. Fritzsche, *J. Electrochem. Soc., 133*, 2131 (1986).
[9] A. M. Wróbel, *J. Macromol. Sci.—Chem., A22*, 1089 (1985).
[10] M. Yasuda, *Plasma Polymerization*, Academic, Orlando, Florida, 1985.
[11] R. Alexandrescu, J. Morjan, C. Grigoriu, I. N. Michailescu, Z. Bastl, J. Tláskal, R. Mayer, and J. Pola, *Appl. Phys. A, 46*, 768 (1988).
[12] J. H. Scofield, *J. Electron Spectrosc. Relat. Phenom., 8*, 129 (1976).
[13] M. F. Shostakovskii and P. V. Tyupaev, *Zh. Obshch. Khim. SSSR, 21*, 1830 (1951).
[14] W. Bailey and N. Nicholas, *J. Org. Chem., 21*, 648 (1956).
[15] J. Pola, *Tetrahedron, 45*, 5065 (1989).
[16] H. Kwart, S. F. Sarner, and J. Slutsky, *J. Am. Chem. Soc., 95*, 5234 (1973).
[17] R. Louw and E. C. Kooyman, *Recl. Trav. Chim. Pays-Bas, 84*, 1511 (1965).
[18] A. Gandini, *Can. J. Chem., 55*, 4045 (1977).
[19] A. N. Oraevski, A. V. Pankratov, A. N. Skachkov, and V. M. Shabarshin, *Khim. Vys. Energ., 12*, 59 (1978).
[20] T. F. Deutsch, *J. Chem. Phys., 70*, 1187 (1979).
[21] P. A. Longeway and F. W. Lampe, *J. Am. Chem. Soc., 103*, 6813 (1981) and references therein.
[22] C. D. Eley, M. C. A. Rowe, and R. Walsh, *Chem. Phys. Lett., 126*, 153 (1986).
[23] G. Inoue and M. Suzuki, *Ibid., 122*, 361 (1985).
[24] D. S. Rogers, H. E. O'Neal, and M. A. Ring, *Organometallics, 5*, 1467 (1986).
[25] D. S. Rogers, K. L. Walker, M. A. Ring, and H. E. O'Neal, *Ibid., 6*, 2313 (1987).
[26] J. M. Jasinski and J. O. Chu, in *Silicon Chemistry* (E. R. Corey, J. Y. Corey, and P. P. Gaspar, eds.), Horwood, Chichester, 1988, Chap. 40.
[27] J. Pola, in *Carbon-Functional Organosilicon Compounds* (V. Chvalovský and J. M. Bellama, eds.), Plenum, New York, 1984, pp. 35–121.

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[28] J. Pola, R. Alexandrescu, J. Morjan, and D. Sorescu, *Chem. Pap., 44*, 21 (1990).
[29] J. C. Lockhart, *Redistribution Reactions*, Academic, New York, 1970.
[30] R. Walsh, Private Communication.
[31] R. G. J. Miller, H. A. Willis, and H. J. Hediger (eds.), *Infrared Structure Correlation Tables and Data Cards*, Heyden, London, 1969, Part 9, K-3.
[32] C. D. Wagner, D. E. Passoja, H. F. Hillery, T. G. Kininski, H. A. Six, W. T. Jansen, and J. A. Taylor, *J. Vac. Sci. Technol., 21*, 933 (1982).
[33] E. Borsela and L. Caneve, *Appl. Phys. B, 46*, 347 (1988).
[34] J. F. Kampas, P. A. Longeway, M. Hirose, and B. A. Scott, in *Semiconductors and Semimetals*, Vol. 21, Part A (Pankove, ed.), Academic, New York, 1984, Chaps. 6–10.
[35] R. Walsh, in *Silicon Chemistry* (E. R. Corey, J. Y. Corey, and P. P. Gaspar, eds.), Horwood, Chichester, 1988, Chap. 41.
[36] B. N. Mukashev, K. H. Nussupov, M. F. Tamendarov, and V. V. Frolov, *Phys. Lett., 87*, 376 (1982).
[37] P. John, I. M. Odeh, M. J. K. Thomas, M. J. Tricker, F. Riddoch, and J. I. B. Wilson, *Philos. Mag. B, 42*, 671 (1980).

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