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Laser evaporation of some solid organosilicon polymers

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Continuous wave (cw) CO_2 laser irradiation of some organosilicon polymers composed of $-Me_2Si-$, $-Me_2SiMe_2SiCH_2-$, $RMeSi-$ and $RMeSiMe_2SiCH_2CH_2-$ units (where R = methyl, adamantyl, phenyl and hydrogen) leads to the evaporation of the polymer and is dominated by the formation of a solid deposit that has a continuous structure. It is assumed that chemical changes occur prior to the transfer of ejected material to the gas phase and that these consist mainly of the formation of high molecular biradicals or 1,2-disilacyclobutane monomer that both re-polymerize spontaneously upon their deposition onto a nearby cold surface. The mechanism of these specific decompositions of the polymers is assessed on the basis of the IR spectra of the deposits and, for the minor gaseous products, identification by GC MS techniques.

Keywords: Laser evaporation, deposition, polysilane, poly(sila-alkene)

INTRODUCTION

The interaction of laser radiation with solid organic polymers attracts current attention due to its relationship with various applied aspects of polymer processing. Research devoted to ablative decomposition with UV laser radiation[1] is linked with the application of this technique for the precise etching of polymer surfaces for microelectronics. The irradiation of polymer films with IR lasers has been used to obtain more complete polymerization[2,3] and to degrade polymer into monomer, decomposition products and parent polymer low-molecular fragments that are ejected in a stream of gaseous products.[4,5] In a vacuum, this laser vaporation is followed by deposition of thin films, but the amounts of gaseous decomposition products are always either much higher than, or comparable with, those of solid particles.[5] Furthermore, in none of the reported papers did the ejected particles undergo reactive changes upon their deposition.

UV laser ablative decomposition of organosilicon polymers has already been studied,[6-8] but thermal IR laser processing of these materials has not been examined so far. We report that irradiation by a CO_2 laser in a vacuum of *Si*-methyl or *Si*-phenyl substituted poly(1,2-disilabutanes), poly(dimethylsilanes), poly(1,1,2,2-tetramethyl-1,2-disilapropanes) and copolymers of 1,1,2,2-tetramethyl-1,2-disilaethene with adamantyl(methyl)-, phenyl(methyl)-, dimethyl- and methylsilylenes induces a process during which the major portion of the polymers is decomposed into lower-molecular polymer units which are transferred through space onto a cold surface nearby, where they repolymerize. This laser evaporation of the organosilicon polymers seems quite unique and promising in the preparation of thin polymer surfaces that can be used as precursors for β-SiC fibres, as impregnating agents for strengthening ceramics and as dopable semiconductors.

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EXPERIMENTAL

Experiments were carried out with a glass optical cell which was 10 cm long with an internal diameter of 3.5 cm, and two NaCl windows. The cell was equipped with one valve and a port with a rubber septum. A mercury manometer and small glass tube (i.d. 0.7 cm, length 1.5 cm) sealed to the cell body was positioned in the middle of the cell along its symmetry axis. A tunable continuous-wave (cw) CO_2 laser[9] operated at the P(20) line of the $00^01 \rightarrow 10^00$ transition was used for the irradiation of a compact polymer sample melt beforehand and housed in the tube. The laser beam (10 W output) was mildly focused by a germanium (Ge) lens (focal length 10 cm) to obtain an incident energy density of $\sim 30 \text{ W cm}^{-2}$. The evacuated cell, containing the polymer samples (typically 0.10–0.15 g), was irradiated for tens of seconds until some transfer of material from the irradiated spot and an increase in pressure (3–8 torr) were observed. The arrangements allowed us to check the IR spectra of both the mixture of gaseous products and the material that was deposited on the entrance window and surface of the cell. After helim expansion into the cell, gaseous samples withdrawn through the septum by a syringe were analysed by GC MS techniques. The design of the cell allowed us to measure the IR spectra of the solid deposit after its re-evacuation. Properties of the deposit by scanning electron microscopy (SEM) analysis were measured on thin pieces of glass or on sheets of Umafol [poly(vinyl acetate)] accommodated inside the cell before irradiation.

The analyses were performed on a Perkin–Elmer model 621 infrared spectrometer, on a Shimadzu GC MS model QP 1000 gas chromatograph–mass spectrometer (using columns packed with Porapak P or silicon elastomer OV17), and on a Tesla BS 350 microscope equipped with an energy-dispersive analyser of X-ray radiation Edax 9100/65.

The identification of gaseous products was performed by means of mass-spectral fragmentation, consulting mass spectra details on organosilicon compounds from the literature and also by using authentic samples of 1-methyl-l-silacyclobutane and trimethyl(vinyl)silane.

Infrared spectra of the solid polymers **I**–**VIII** were measured in KBr pellets (before irradiation) and as deposits on the NaCl windows of the cell in which the irradiations were performed after the irradiation).

All the organosilicon polymers studied in this work were obtained by procedures reported previously.[10–12]

RESULTS AND DISCUSSION

CO_2 laser irradiation of poly(1,1,2,2-tetramethyl-1,2-disilabutane) (**I**), poly(1-phenyl-1,2,2-trimethyl-1,2-disilabutane) (**II**), poly(1,1,2,2-tetramethyl-1,2-disilapropane) (**III**), poly(dimethylsilane) (**IV**), and the copolymers poly(1, 1, 2, 2 - tetramethyl - 1, 2 - disilabutane - co - dimethylsilane) (**V**), poly(1,1,2,2-tetramethyl-1,2-disilabutane-co-methylsilane) (**VI**), poly(1, 1, 2, 2 - tetramethyl - 1, 2 - disilabutane - co - methylphenylsilane) (**VII**) and poly (1,1,2,2-tetramethyl - 1, 2 - disilabutane - co - adamantylmethylsilane) (**VIII**) results in the formation of gaseous products and solid particles that are propelled from the irradiated surface in a visible aerosol form. All the samples can be laser-evaporated practically completely except for polymer **II**, which retained more than 5–10% by weight of carbonized material. In all the experiments, the deposition of solid white films all over the surface of the cell and a small increase in pressure (3–8 torr) were observed, which indicated that the solid films contained not less than 85% of the vaporized material. Typically, only about 5% or less of the polymers remained on the irradiated spot as solid sintered material. The most intriguing feature of these laser heating processes is the pattern of the solid deposits (Fig. 1). We assume that both the discrete continuous structures of very thin films observed with polymers **I**, **IV**–**VI** and **VIII** (Fig. 1a, d–f and h) and the smooth surface of thicker films (with outstanding nodules) observed with polymers **II**, **III** and **VII** (Fig. 1b, c and g) can be taken as sufficient evidence that repolymerization takes place during the deposition process. The deposit being the major product thus indicates that (a) the dominant mechanism of the laser degradation is a pathway through which the parent polymer is regenerated either in the original or modified structure and that (b) the gaseous products, shown in Fig. 2, are produced by only very minor reactions that add to the total reaction scheme.

The temperature in our experiments can be estimated as being higher than 600°C, the value at

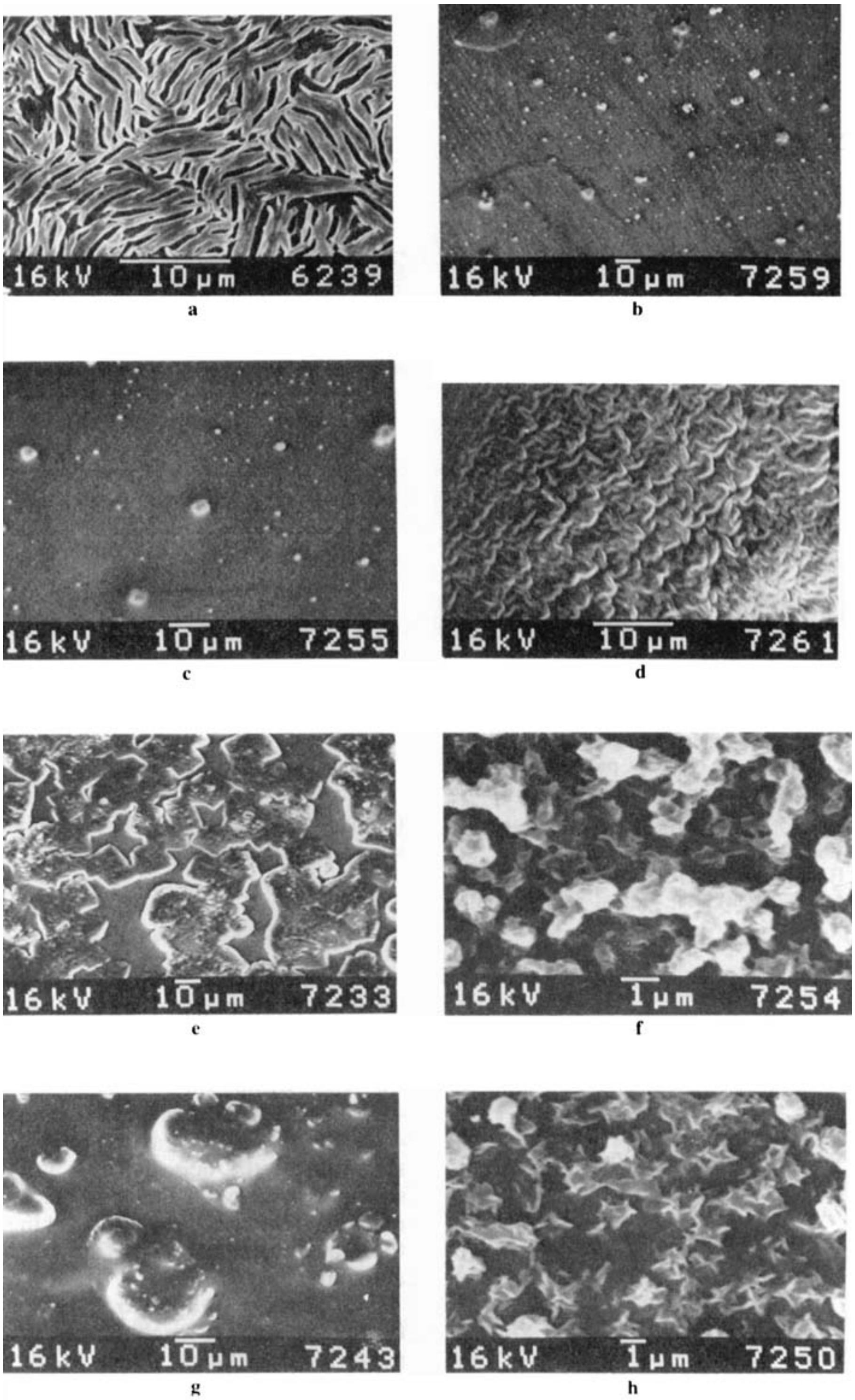


Figure 1 SEM of deposit obtained by laser heating of polymer **I–VIII** (a–h, respectively).

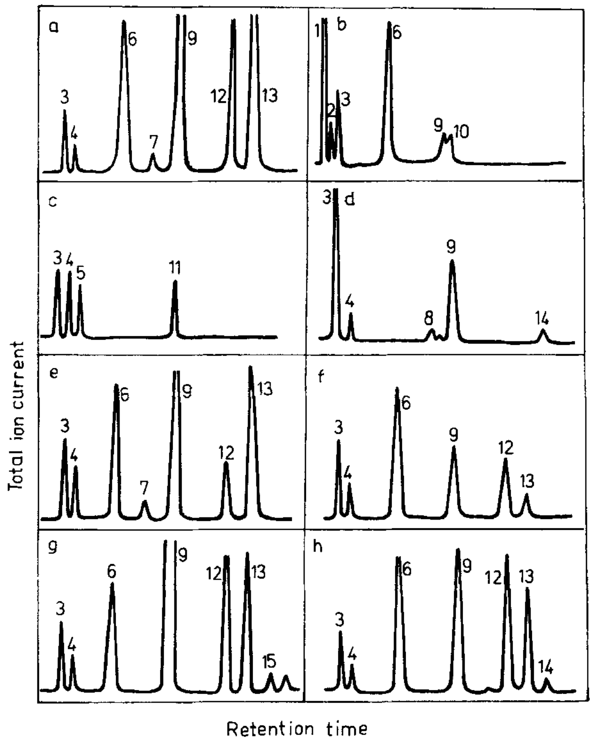


Figure 2 GC MS traces of gaseous mixtures obtained by CO_2 laser irradiative degradation of polymers **I–VIII** (in the given order a–h). Conditions: Column, 3 m, packed with OV-17 silicon elastomer, temperature 10–150°C programmed within 20 min. Peak identification: 1, SiH_4; 2, $MeSiH_3$; 3, Me_2SiH_2; 4, Me_3SiH; 5, Me_4Si, 6, $\mathrm{MeH\overline{Si(CH_2)_2C}H_2}$; 7, $Me_3SiCH{=}CH_2$; 8, $Me_2HSi{-}SiMeH_2$; 9, $Me_2SiH{-}Me_2SiH$; 10, C_6H_6; 11, $HSiMe_2{-}CH_2SiMe_2H$; 12, $(CH_2{=}CH)Me_2Si{-}SiMe_2H$; 13, $Me_3Si{-}SiMeH{-}SiMeH_2$; 14, $Me_3Si{-}SiMeH{-}SiMe_3$; 15, $PhMe_2SiH$.

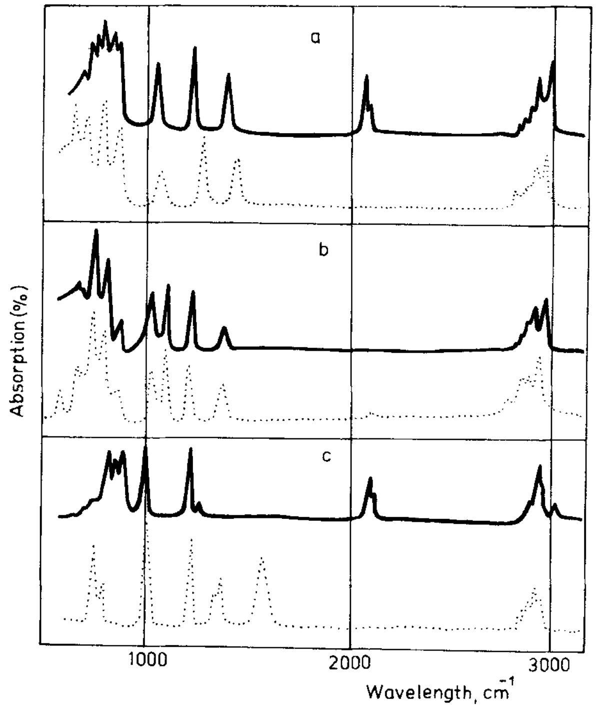


Figure 3 Infrared spectra of polymers **IV** (a), **I** (b) and **III** (c) (dotted line) and of the deposits (full line) obtained by their irradiation.

which thermogravimetric analysis of poly(silastyrene) and poly(dimethylsilane) reveals that portions of these samples are driven off as volatile silicon compounds.[13]

Laser evaporation of poly(dimethylsilane) (**IV**) can take place either via extrusion of Me_2Si units (synchronous or sequential scission of two Si–Si bonds), or via 1,1-elimination on silicon (Eqn [1]), the mechanism favoured for the pyrolysis of di- and tri-silanes.[6, 14–16]

$$-\mathrm{SiMe_2{-}SiMe_2{-}SiMe_2{-}SiMe_2}- \longrightarrow -\mathrm{SiMe_2{-}}\ddot{\mathrm{Si}}\mathrm{{-}Me} + \mathrm{Me_3Si{-}SiMe_2}- \quad [1]$$

The other alternatives can be (a) cleavages of two remote Si–Si bonds to yield biradicals ($^{\bullet}\mathrm{SiMe_2}\!\sim\!\mathrm{Me_2Si}^{\bullet}$) or (b) reorganization of polysilane to polycarbosilane skeleton (Eqn [2]) and

$$-(\mathrm{Me_2Si})n- \longrightarrow \xrightarrow{\Delta} \longrightarrow -(\mathrm{HSiMeCH_2})_n- \quad [2]$$

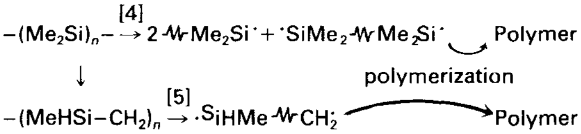
subsequent cleavage of Si–C bonds to form radical centres at silicon and carbon atoms. The second process has been previously postulated[17, 18] for the formation of polycarbosilanes with $-SiMeHCH_2-$ units arising as intermediates in a 400°C pyrolysis of **IV** and is supported by the IR spectrum of the deposit (Fig. 3a), which shows strong absorption at 2100 cm^{-1} ($\nu_{\mathrm{Si-H}}$) and closely resembles the spectrum obtained in studies of the thermal treatment of poly(dimethylsilane) in an autoclave.[18]

The cleavage of the two Si–Si bonds belonging to the one or two neighbouring silicon atoms in poly(dimethylsilane) yields Me_2Si: or $Me_2Si{=}SiMe_2$ species which are known to cycloadd or to undergo Diels–Alder addition to dienes.[20, 21] Dimethylsilylene is also capable of insertion into the Si–H bond.[22,23] Neither of these reactions were, however, confirmed during trapping experiments when poly(dimethylsilane) was irradiated in the presence of 100 torr of 1,3-butadiene or trimethylsilane, and transient formation of dimethylsilylene and tetramethyldisilylene thus seems unlikely. Tetramethyldisilylene is also known[21,24–26] to experience rearrangement into 1,3-disilacyclobutanes, but these compounds, being absent, seem to disprove tetramethyldisilylene formation also. Cleavage of the two neighbouring Si–C bonds in polycarbosilane results in the formation of methylsilene, $MeHSi{=}CH_2$. Depending upon reaction conditions this compound undergoes cyclodimerization[27] or polymerization.[28] The fact that no cyclodimer was detected during the laser evaporation supports the assumption that transient methylsilene is either not formed or it repolymerizes immediately in the close proximity of the irradiated spot (Eqn [3]).

$$-(HSiMeCH_2)_n- \rightleftarrows n\,HSiMe{=}CH_2 \qquad [3]$$

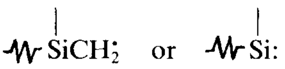
The depolymerization of the polycarbosilane according to Eqn [3], a transfer of methylsilylene from the irradiated spot onto a cold nearby surface and its polymerization on the surface, can also be rejected, since trapping experiments with 1,3-butadiene should lead[29] to the formation of 1,1-dimethyl-1-silacyclopentenes and 1-methyl-1-silacyclohexene (the products of cycloadditon of methylsilene or its rearranged product[30] dimethylsilylene to 1,3-butadiene), but none of these adducts was detected.

We propose that the continuous structure of the deposit (Fig. 1d) originates from gradual recombination reactions between two higher-molecular biradical moieties that are ejected onto the cold surface as 'living' particles. A sequence of intramolecular recombinations (cyclization) of these biradicals during their transfer to the cold surface and their subsequent surface reaction (presumably hydrogen abstraction) with a living particle can only yield another radical species and cannot thus be used as an explanation of polymer growth during deposition. We assume that the production of the continuous polymer deposit is associated with the combination of reactions [4] and [5] (Scheme 1).



Scheme 1

We are aware of other possibilities for structural change induced by cleavage of the CH_3–Si bond, e.g. generation of



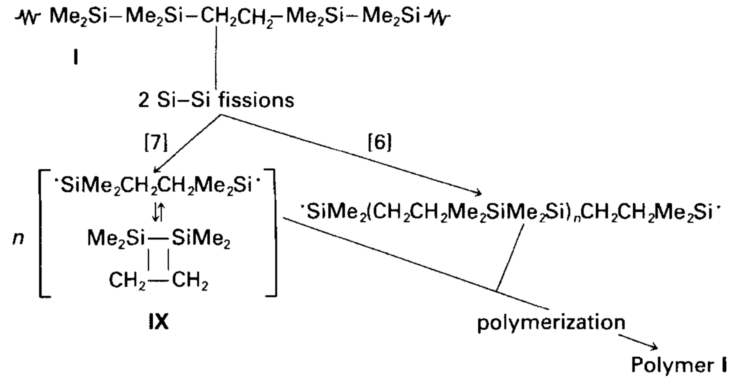
$$\sim\!\overset{|}{\mathrm{Si}}\mathrm{CH_2^{\cdot}} \quad \text{or} \quad \sim\!\overset{|}{\mathrm{Si}}\mathrm{:}$$

species,[14,25,27,31–33] but cannot see how other opportunities for rearrangement provide a better explanation.

To comment on the formation of the minor gaseous products Me_2SiH_2, Me_3SiH, $Me_2SiH{-}SiMeH_2$, $(HSiMe_2)_2$ and $Me_3SiSiHMeSiMe_3$, we presume that they are formed via hydrogen abstraction reactions of Me_2Si: or $Me_3Si^{\cdot}$ species. The latter can arise by the Si–Si bond cleavage of the $Me_3Si{-}SiMe_2-$ moiety formed in a process of 1,1-elimination (Eqn [1]). Me_3SiH can be also produced by the elimination of Me_3SiH from polycarbosilanes. This reaction takes place when Me_3Si and H units are attached exclusively to silicon and it is accompanied by the formation of stable cyclic products.[34]

Laser irradiation of $(Me_2SiMe_2SiCH_2CH_2)_n$ (**I**) yields a white solid deposit with an interesting fibrous structure (Fig. 1a) whose IR spectrum is practically identical with the parent polymer (Fig. 3b). Minor gaseous products were confirmed to be Me_2SiH_2, Me_3SiH, $Me_3SiCH{=}CH_2$, $HMe\overline{Si(CH_2)_2C}H_2$, $(HSiMe_2)_2$, $CH_2{=}CHMe_2SiSiMe_2H$ and $Me_3SiSiMeHSiMeH_2$ (Fig. 2a). Assuming that (a) the major decomposition process leads to the parent polymer and that (b) the dissociation energy of the Si–Si bond is lower than that of the Si–C or C–H bond,[14] we propose that the dominant decomposition pathway for polymer **I** can be depicted as shown in Scheme 2 (reaction steps [6] and [7]) and involves cleavage of two Si–Si bonds.

Such a reaction scheme is supported by the occurrence of 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane among the gaseous products when experiments were carried out in the presence of small amounts (~1%) of oxygen. This compound is known[35] to be formed by the reaction of 1,1,2,2-tetramethyl-1,2-disilacyclobutane (**IX**) with molecular oxygen. The presumed inter-



Scheme 2

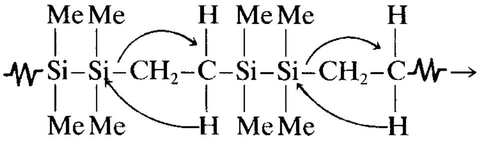
mediacy of **XI** is also strongly suggested by its ability to polymerize and yield exactly the polymer **I**.

The less energetically favourable cleavage of Si–Si and Si–C bonds of the polymer backbone should produce $^{\bullet}SiMe_2CH_2CH_2^{\bullet}$ biradicals from which the observed Me_2SiH_2 can be formed by the following steps (Eqn [8]).

$$\rightarrow {}^{\bullet}SiMe_2\text{–}CH_2CH_2^{\bullet} \xrightarrow[-C_2H_4]{} Me_2Si: \xrightarrow{2[H]} Me_2SiH_2 \quad [8]$$

Cleavage of the polymer backbone at two Si–C bonds leading obviously to 1,3-disilacyclobutenes, or cleavage at two C–C bonds or Si–Si and C–C bonds, both resulting in the formation of methylsilene cyclodimer, do not apparently take place, because neither of these four-membered cyclic compounds was observed.

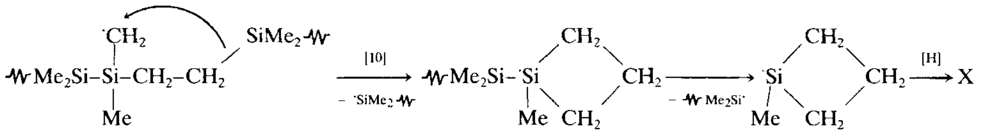
We suggest that the minor products with Si–H and Me–Si bonds are produced via reactions similar to those assumed for the evaporation of the polymer **IV**. 1,1,2,2-Tetramethyl-1-vinyldisilane might be generated by a cleavage of the $Si\text{–}CH_2$ bonds and a 1,4-shift of hydrogen from the methyl group to silicon as illustrated in Eqn [9].



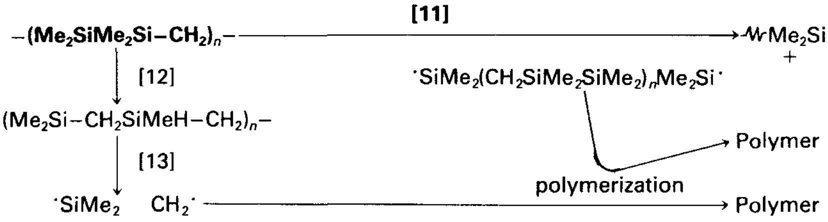
$$\sim Me_2Si\text{–}SiMe_2H + CH_2{=}CHSiMe_2SiMe_2H + CH_2{=}CH\sim \quad [9]$$

The formation of 1-methyl-1-silacyclobutane (**X**) is quite interesting and we can speculate that **X** arises in Scheme 3 initiated by the abstraction of hydrogen from the Me(Si) group. Step [10] is similar to the earlier assumed[33] intramolecular closure of the diradical $^{\bullet}CH_2CH_2SiMeRCH_2^{\bullet}$ to silacyclobutane, which is the reverse reaction of the silacyclobutane cleavage into silene and ethene.

Laser evaporation of poly(1,1,2,2-tetramethyl-1,2-disilapropane) (**III**) results in the formation of gaseous Me_2SiH_2, Me_3SiH, Me_4Si and $HSiMe_2CH_2SiMe_2H$ compounds (Fig. 2c). The deposit (Fig. 1c) shows an IR spectrum different from that of the initial polymer (Fig. 3c), which exhibits absorption at 2100 cm^{-1} ($\nu_{Si\text{–}H}$). We suggest that the deposit can be formed by a mechanism similar to that assumed for the decomposition of poly(dimethylsilane) (reaction steps [11]–[13] in Scheme 4).



Scheme 3



Scheme 4

The $\sim Me_2SiMe_2SiCH_2^{\bullet}$ radical, which can be also formed, can undergo rearrangement into the $\sim Me_2Si{-}CH_2{-}Me_2Si^{\bullet}$ radical, or experience[36] cleavage of a methyl group to give $\sim Me_2Si{-}MeSi{=}CH_2$. These intermediary products can be expected to cleave and yield silene species, but cyclodimers of these compounds were not detected. This implies that the above reactions do not occur. As for the gaseous products with Si–H bonds, they can be formed by reactions assumed in the degradation of **IV**. Bis(dimethylsilyl)methane can be generated via Si–Si cleavage and hydrogen abstraction by the $\sim CH_2Me_2Si^{\bullet}$ radical formed.

Laser evaporation of polymer **II** proceeds apparently similarly to that of polymer **I**, and that of the co-polymers **V–VIII**, consisting of both $-RMeSi-$ and $-RMeSiMe_2Si.CH_2CH_2-$ units, seems to possess the features of the evaporation of polymers **I** and **IV**. The continuous structure of all the deposits (Fig. 1) and their absorption at $2100\,cm^{-1}$ are in line with the assumption of the repolymerization of 'living' particles according to the process in Eqn [2]. We note that higher-molecular biradical species travelling from the laser-irradiated spot to the nearby cold surface can possess an increased stability due to their bulkiness and an easier stabilization of both radical centres inside long (coiled) entities.

Our results do not permit an unequivocal assignment of the processes involved, but show that laser-induced evaporation of organosilicon polymers with $-MeRSi-$, $-Me_2SiMe_2SiCH_2-$ and $-MeRSiMe_2SiCH_2CH_2-$ units in their backbone is an easy and efficient method for the preparation of thin organosilicon layers and that it adds to the potential of other laser-induced techniques[28,37–41] for the preparation of thin solid organosilicon materials.

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