Thermally Stable Polyoxocarbosilane Thin Films by Pulsed IR Laser Ablation of Poly[oxy(tetramethyldisilane-1,2-diyl)]

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Received September 4, 2001. Revised Manuscript Received December 10, 2001

Pulsed IR laser-induced ablation of bulk poly[oxy(tetramethyldisilane-1,2-diyl)], $[(CH_3)_2Si(CH_3)_2SiO]_n$,yields thin polyoxocarbosilane films whose polymeric structure consists of a backbone composed of $-(CH_3)_2Si(CH_3)_2SiO-$ and $-O(CH_3)_2SiO-$ units, which is cross-linked via $SiSiC_2O$, C_3SiO, C_2SiHO, $CSiHO_2$, and $CSiO_3$ moieties. These laser-fabricated hybrides of siloxanes and polysilylenes are insoluble in organic solvents and thermally superior to siloxanes and polysilylenes, which makes them intriguing for applications in thermally exposed devices.

1. Introduction

The potential of pulsed laser ablation[1] for deposition (PLAD) of thin adherent polymeric films using *ultraviolet* radiation has been recently demonstrated by a number of cases.[2] This process consists of depolymerization followed by repolymerization. It involves both photochemical and thermal features[1c,3] and its importance stems from high yields of fragments which can recombine into the original polymer.

Laser evaporation/deposition of polymers by using *infrared* laser radiation has been, however, little studied.[4] This process is achieved through multiphoton resonant absorption of energy-poor infrared photons leading to high vibrational excitation density in the solid.[5] The energy accumulation in the solid must be sufficient to break the weakest bond and is achieved through multiphoton absorption of infrared photons in a suitable vibrational mode coinciding with the wavenumber of the tuned laser radiation. Conversion of the initially vibrational excitation energy into random thermal energy is a complex process in which the vibrational energy is transferred into rotation and translational modes.

This IR laser-induced ablation can be suitable for fabrication of thin films from materials that are poor UV absorbers. Although the primary event of the IR laser pulse is thermal, the high heating rates ($\approx 10^{6-11}$ $K \cdot s^{-1}$) and high cooling rates ($\approx 10^{3-6}$ $K \cdot s^{-1}$) can provide rather kinetic than thermodynamic control of polymer degradation and lead to ablative deposition of materials which cannot be produced by slow conventional heating.

Successful IR laser ablation/deposition of polymeric films was demonstrated with poly(chlorotrifluoroethylene), poly(tetrafluoroethylene), polysulfone, polycarbonate, and polyimide (all ref 4a), with poly(fluoroethylene) (ref 4b), and with polysilanes and polycarbosilanes composed of $-(CH_3)_2Si-$, $-(CH_3)_2Si(CH_3)_2SiCH_2-$, $-R(CH_3)Si-$, and $-R(CH_3)Si(CH_3)_2SiCH_2CH_2-$ units where R = methyl, adamanthyl, phenyl, and H (ref 4c).

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10.1021/cm0112338 CCC: $22.00

The important class of organosilicon polymers are peralkylsiloxanes whose thin intractable films produced by pulsed UV or IR laser ablation/deposition would find many applications in materials science and microelectronics. However, UV photolysis of these polymers occurs only very reluctantly at the Si−C bonds,[6] conventional pyrolysis of peralkylsiloxanes results in extrusion of stable low-molecular cyclic oligomers,[7] and pulsed IR laser irradiation of peralkylsiloxanes leads to the formation of gaseous hydrocarbons through extensive cleavage of the Si−C bonds.[8] These facts indicate that fabrication of thin intractable peralkylsilicone films accomplished through reorganization of the Si−O−Si backbone by the PLAD method is an impossible task.

Some siloxane films have been recently prepared by frozen matrix assisted pulsed UV laser evaporation (MAPLE) of fluoroalcoholpolysiloxane.[9] This technique is claimed as unique for deposition of highly functionalized polymeric materials whose structure is the same as that of the initial, laser-exposed polymer.

There is also an important need for processes that do not yield the native, but modified polymers with improved properties. Fabrication of novel-type, intractable, and highly thermally stable silicones by a controllable way from a synthetically available precursor is therefore a subject of continuing research (e.g., ref 10).

Considering that the thermal and photolytic vulnerability of siloxanes exposed to IR and UV laser radiation stems from[6,8,11] primary cleavage of the Si−C and not Si−O bonds lead us to examine IR laser interaction with a member of poly(oxybismultimethylsilylenes)−$[(SiR_2)_mO]_n$−containing not only strong Si−O−Si units but also weak Si−Si bonds.

We show that poly[oxy(tetramethyldisilane-1,2-diyl)], $-[(CH_3)_2Si(CH_3)_2SiO]_n-$, is cleaved with pulsed IR laser radiation at the weak Si−Si bonds, producing macromolecular biradicals which spontaneously rearrange and repolymerize during their ejection onto a cold nearby substrate. This process makes possible fabrication of intractable and thermally superior cross-linked polymeric films whose backbone is composed of $(CH_3)_2Si(CH_3)_2SiO$ and $O(CH_3)_2SiO$ units.

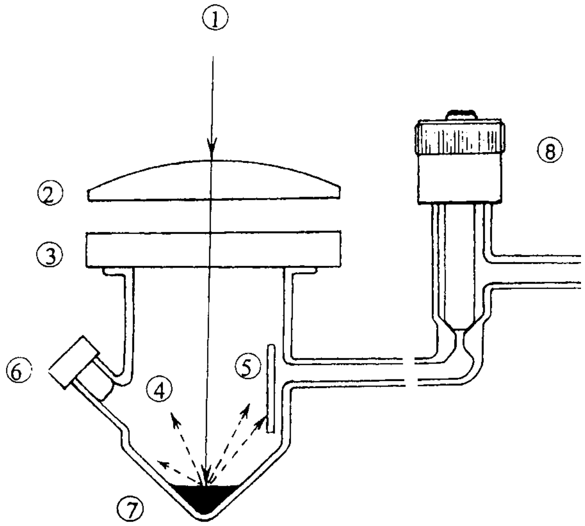

Figure 1. Experimental setup for IR laser ablation of poly[oxy(tetramethyldisilane-1,2-diyl)]. 1, laser beam; 2, NaCl lens; 3, NaCl window; 4, material ablation; 5, KBr substrate; 6, rubber septum; 7, bulk parent polymer; 8, P.T.F.E. valve.

2. Experimental Section

The irradiation experiments were performed in a Pyrex vessel (of 42 mL in volume) equipped with a sidearm with rubber septum, a P.T.F.E. valve and an NaCl window (Figure 1). The bulk poly[oxy(tetramethyldisilane-1,2-diyl)] (0.1 g) was irradiated in a vacuum (initial pressure <10 Pa) at a repetition frequency of 1 Hz by pulses from a tunable TEA CO_2 laser (Plovdiv University) which was operated on the *P*(20) line of the $00^01 \rightarrow 10^00$ transition (944 cm^{-1}) with incident fluence 1.6 $J\cdot cm^{-2}$.

The deposit was produced on the substrates (KBr, metal, and quartz) and the inner walls of the vessel and was analyzed as thin films by FTIR spectroscopy and by the SEM technique. The ablation with ≈100 pulses yielded films about 1 μm thick, and the ablation repeated with many samples yielded much thicker layers which were scraped down and accumulated for analysis by NMR and mass spectroscopy and thermal analysis. The gases formed in the vessel were transferred under vacuum to an IR spectroscopic cell for FTIR spectroscopic analysis and were also analyzed by GC and GC/MS methods.

The analyses of gases were performed on an FTIR Nicolet Impact spectrometer, a Shimadzu QP 1000 quadrupole mass spectrometer (Porapak P), an MS 80 Kratos GC/MS spectrometer (CBP 10-S50−050 capillary column), and a GC 14A Shimadzu gas chromatograph (Porapak P and OV 17 column, programmed temperature 30−150 °C).

The analyses of the solid deposit were conducted on the FTIR Nicolet Impact spectrometer and a Tesla BS 350 ultrahigh-vacuum instrument. FTIR absorption spectra of thin films of the original and deposited polymers on KBr were taken. Mass spectra analysis (direct inlet sampling) of products of thermal decomposition of the initial and deposited polymers were conducted on an MS 80 Kratos GC/MS spectrometer with programmed heating of the direct inlet from 30 to 350° C.

Solid-state MAS and CP MAS NMR experiments were conducted on a Bruker DSX200 NMR spectrometer in a 4-mm broadband probe. ^{13}C and ^{29}Si NMR spectra were externally referenced to the carbonyl line of glycine ($\delta = 176.03$) and to the M unit line of M8Q8 ($\delta = 11.5$), respectively. The samples were spun with a spinning speed of 1300 and 1700 Hz for ^{29}Si experiments of the deposited and parent poly[oxy(tetramethyldisilane-1,2-diyl)] polymer, respectively. A relaxation delay of 60 s and 1000 and 2800 scans were used for the ^{29}Si MAS spectrum of the parent and the deposited polymer. Similarly, a 60-s relaxation delay, 1000 scans, and a spinning speed of 5200 Hz was used for the acquisition of ^{13}C MAS spectra of the deposited polymer. A relaxation delay of 6 s, a CP delay of 5 ms, and 340 and 12 000 scans were applied for the acquisi-

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tion of ^{29}Si CP MAS spectra of the parent and deposited polymer, respectively. A ^{13}C CP MAS spectrum of the deposited polymer was acquired with a relaxation delay of 6 s, spinning speed of 3500 Hz, and 27 000 scans.

SEM photographs were obtained using a Philips XL30 CP scanning electron microscope.

Thermal analysis of the initial poly[oxy(tetramethyldisilane-1,2-diyl)] (sample weight 38 mg) and of the laser deposited polymer (sample weight 3 mg) was carried out by heating the samples up to 860 °C at the rate of 3.6 °C/min, using Cahn D-200 recording microbalances in a stream of argon (82 mL/min). The temperature was controlled by a T48 temperature controller (Red Lion Controls). The downward stream of argon chosen prevented measurement irregularities observed with the upward stream of argon. These were brought about by condensation of thermolysis products on the extension wire of the balances. The sample residue remaining on the balance weighing pan was analyzed in a KBr pellet by FTIR spectroscopy. Along with the decrease of the sample weight, the composition of the outgoing gases was analyzed every 10 min by an automatic sampling gas chromatograph, Hewlett-Packard GC5890, equipped with FID and TCD detectors and Porapak P packed column (i.d. 2 mm, length 2 m). The quantification of the chromatographic data was made using streams of argon mixed with measured amounts of methane and ethyne as controlled by mass flow AFC 2600 controllers (Aalborg Instruments, Inc.) The residues and some volatilized solid products were measured for their FTIR spectra (a Nicolet Impact 400 spectrometer) using the KBr pellet technique. The residues were also analyzed by electron microscopy.

Poly[oxy(tetramethyldisilane-1,2-diyl)] has been prepared as reported.[12] The polymerization was carried out in a glass reactor, having a stopcock for withdrawing samples. Octamethyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane (50% in methylene chloride) was placed in the reactor purged with dry nitrogen. Then, the reactor was accommodated in a thermostat at 25 ± 0.1 °C, and an appropriate amount of CF_3SO_3H stock solution in CH_2Cl_2 was introduced by a Hamilton syringe to obtain the initiator concentration 5×10^{-3} mol dm^{-3}. When 85% of the monomer conversion was achieved (after 8 h), the reaction was quenched by introduction of triethylamine in CH_2Cl_2. The polymer was precipitated in methanol and thoroughly rinsed with methanol. Then, the solvent was evaporated and the polymer heated at 90 °C under vacuum (10^{-2} Torr) for 20 h.

3. Results and Discussion

The TEA CO_2 laser irradiation of bulk poly[oxy(tetramethyldisilane-1,2-diyl)] with as many as 1000−2000 pulses resulted in the formation of gaseous products and solid particles that were propelled from the irradiated bulk material and deposited on a nearby cold surface of the vessel. With as many as 2000 pulses, the ablation of ≈0.07 g of the polymer resulted in an increase in pressure to 10−12 Torr. Considering the formed gaseous products (see later), this reveals that the preponderance (≈95%) of the ejected sample yields solid particles.

Gaseous Products. The very minor volatile products (in mol %) include methane (57), ethane (8), ethene (15), ethyne (12), propene, propyne, propadiene, and 1-butene (all ≈1), methylsilane (0.5), dimethylsilane (<2), trimethylsilane (1.5), and tetramethylsilane (0.3) (Figure 2) and also tetramethyldisiloxane (1), hexamethylcyclotrisiloxane (0.3), and pentamethyldisiloxane and hexamethyldisiloxane (both <0.2). A number of higher linear (e.g., hexamethyltrisiloxane) and cyclic (e.g., octamethylcyclotetrasiloxane) siloxanes and of trace compounds assigned to cyclic siloxanes with a Si−Si bond (all <1) were also observed.

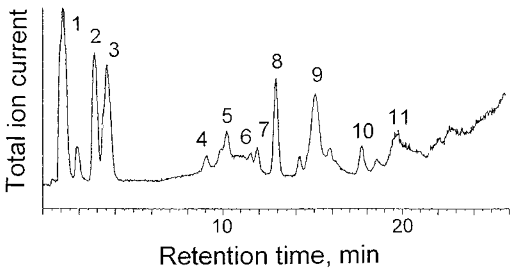
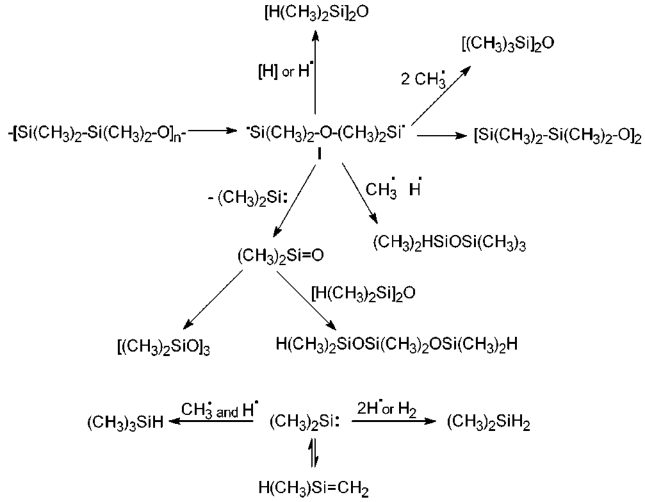


Figure 2. GC/MS trace of gaseous products (Porapak P, 30−150 °C). Peak identification: 1, air and CH_4; 2, C_2H_4; 3, C_2H_6 and C_2H_2; 4, CH_3SiH_3; 5, C_3H_6; 6, $CH_3C{\equiv}CH$; 7, $H_2C{=}C{=}CH_2$; 8, $(CH_3)_2SiH_2$; 9, $(CH_3)_3SiH$; 10, $(CH_3)_4Si$; 11, $(CH_3)_4H_2Si_2O$.

Scheme 1. Reactions Leading to Volatile Products



The volatile products can be explained to be formed by a cleavage of the weaker Si−C (360−370 kJ/mol) and Si−Si (340−360 kJ/mol)[13] bonds, but not of the strong Si−O (ca. 550 kJ/mol)[13] bond. Methane, ethane, ethene, and ethyne originate from the methyl radical and are produced by reactions $2CH_3^{\bullet} \rightarrow C_2H_6$, $CH_3^{\bullet} \rightarrow [:CH_2 + H] \rightarrow C_2H_4 + H_2$, etc. The presence of the unsaturated C_2 hydrocarbons indicates that the irradiated system contains molecular hydrogen. The Si-containing products can be explained as formed via step by step and/or 2-fold cleavage of the Si−Si bonds of the polymer into the diradical (**I**) and by the reactions of this species analogous to those reported in the literature[14] (Scheme 1).

Deposited Films. The solid films deposited on the nearby substrates possess very good adhesion to KBr and glass and they survive the tape test. The films are insoluble in common organic solvents (hexane, trichloroethene, dichloromethane, and acetone), which is in keeping with a very high molecular weight and/or cross-linked structure.

Infrared Spectra. Their typical IR absorption pattern {[ν/cm^{-1} (relative absorptivity)]: 801 (0.79), 1026 (1.0),

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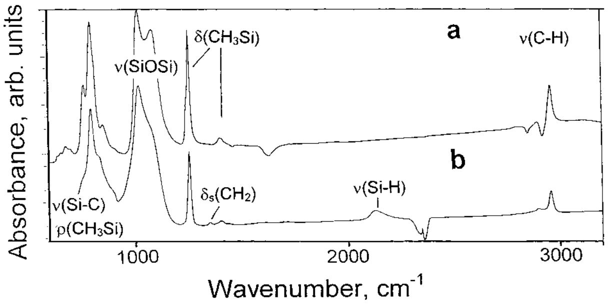

Figure 3. Comparison of FTIR spectra of the initial poly[oxy-(tetramethyldisilane-1,2-diyl)] (a) and the laser-deposited solid film (b).

Table 1. Mass Spectra[a] of Polymers

initial polymer	deposited polymer	assignment[b]
281 (8)	281 (29)	$Me_7Si_4O_4$
265 (12)	265 (31)	$Me_7Si_4O_3$
249 (9)		$Me_7Si_4O_2$
207 (47)	207 (27)	$Me_5Si_3O_3$
205 (20)	205 (40)	$Me_7Si_3O_1$
191 (87)	191 (33)	$Me_5Si_3O_2$
175 (5)		Me_5Si_3O
147 (14)	147 (31)	Me_5Si_2O
133 (12)		$Me_3Si_2O_2$
131 (9)	131 (23)	Me_5Si_2
117 (10)		Me_3Si_2O
116 (13)		Me_4Si_2
88 (11)		
	75 (31)	$MeSiO_2$
73 (100)	73 (100)	Me_3Si

[a] In [*m*/*z* (relative intensity)]. [b] Reference 16.

1092 (sh), 1259 (0.54), 1357 (0.01), 1406 (0.03), 2129 (0.07), 2902 (0.02), 2960 (0.17)} is very similar to that of the original polymer {[ν/cm^{-1} (relative absorptivity)]: 681 (0.06), 801 (0.93), 1024 (1.0), 1090 (0.82), 1261 (0.79), 1402 (0.06), 2895 (0.09), 2961 (0.23)} and reveals that neither positions of absorption bands nor their relative intensity is substantially altered (Figure 3). However, some new features in the IR spectra of the ablated films are weak absorptions at 1357 and 2129 cm^{-1} which assign to δ_s(CH$_2$) in Si−CH$_2$−Si and to ν(Si−H), respectively. These new bands along with some decrease in the δ(CH$_3$Si) absorbance as well as the change of the shape of the absorption bands due to ν(SiOSi) and ν(Si−C) + ρ(CH$_3$)Si vibrations (Figure 3) are in keeping with modification of the polymer structure.

Mass Spectra. Mass spectral analysis (direct inlet sampling) of the initial and deposited polymer reveals that both polymers show the total ion current signal at the same scan range. The intensity of the signal of the deposited polymer being by an order of magnitude lower compared to that of the initial polymer indicates that the deposited polymer possesses higher thermal stability. The fragmentation pattern of both polymers somewhat differs (Table 1); that of the initial polymer (see also ref 15) being more complex indicates that the deposited polymer cannot split via so many routes as the initial one. The signals at *m*/*z* 281, 207, 147, and 73 observed in both spectra correspond to common ions observed[16] in mass spectra of permethylated silicones. The signal at *m*/*z* 75 is observed with the deposited but not the initial polymer and reveals contribution of the MeSiO$_2$ fragment.

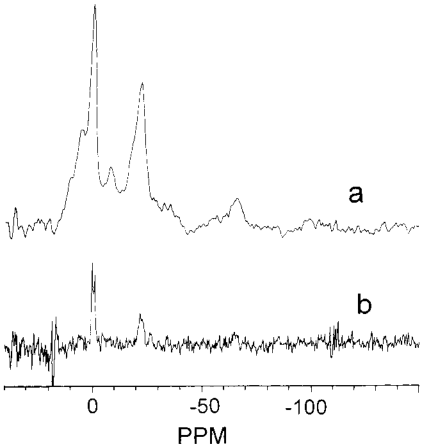

Figure 4. ^{29}Si CP MAS (a) and MAS (b) spectrum of the deposited polymer. The r.f. noise in the MAS spectrum at ≈25−40 ppm and around 110 ppm.

^{29}Si NMR Spectra. The ^{29}Si NMR spectra of the initial and deposited polymer have different features. The ^{29}Si MAS NMR spectrum of the initial polymer is dominated by a peak of the basic oxy(tetramethyldisilane) unit at 0.7 ppm possessing a very narrow (≈0.1 ppm) line width, indicating a high uniformity or a high mobility of the parent polymer backbone. The high mobility of the initial polymer backbone, which is in agreement with its very low (148 K) glass temperature,[17] is evidenced by the failure to obtain the ^{29}Si CP MAS NMR spectrum. The ^{29}Si MAS NMR spectrum of the deposited polymer (Figure 4) shows narrow signals of the OMe$_2$SiMe$_2$SiO and C$_2$SiO$_2$ units and we suggest that these signals come from relatively mobile parts of the polymer network. The accessible ^{29}Si CP MAS NMR spectrum of the deposited polymer indicates that the structure of the deposited polymer is more rigid. This spectrum consists of four main broad peaks and of a shoulder (Figure 4). The first region between 15 and −5 ppm mainly involves[18] a contribution of the −OMe$_2$SiMe$_2$-SiO− unit; the smaller signal at 5.4 ppm can originate from C$_3$SiO or other Si$_n$SiC$_2$O units. The second region between −5 and −13 ppm is characteristic of signals of C$_2$SiHO fragments. The strong peak of the third region between −13 and −25 ppm is assignable to C$_2$SiO$_2$ units and the peak in the fourth region between −60 and −70 ppm corresponds to CSiO$_3$ fragments. The shoulder between −25 and −40 ppm covers the region of CSiHO$_2$ units. ^{13}C MAS NMR and ^{13}C CP MAS NMR spectra of the deposited polymer show only one line at 1.9 ppm belonging to the (CH$_3$)$_n$Si fragment, which can include other signals, for example, a signal of (Si)CH$_2$(Si) units

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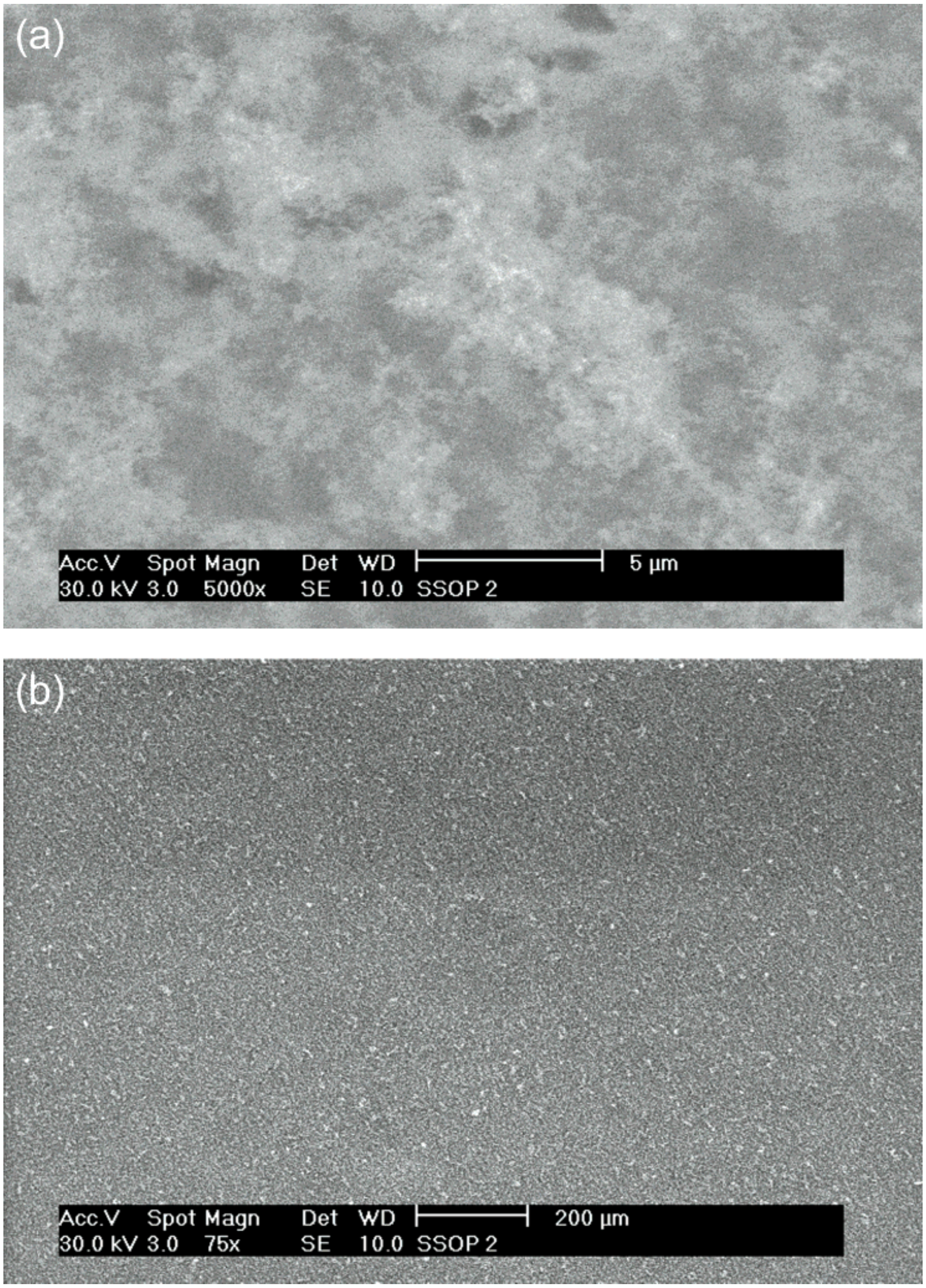


Figure 5. SEM of the laser-deposited film. The bar equals 5 μm (a) and 200 μm (b).

expected[18] in the region 1.6−3 ppm. ^{1}H NMR MAS spectrum of the deposited polymer consists of only one sharp line assignable to a mobile CH_3(Si) group.

The broadness of the signals points to a higher disorder or a lower flexibility. The NMR spectral data thus show that the deposited polymer is composed of mobile and rigid structures; the former contain mostly the initial $-Me_2SiMe_2SiO-$ unit and also the C_2SiO_2 units, whereas the latter are contributed by other $SiSiC_2O$ units, the C_3SiO, C_2SiHO, $CSiHO_2$, and $CSiO_3$ units, which represent the cross-linking sites.

Scanning Electron Microscopy. Scanning electron microscopic (Figure 5) analysis shows that the deposited films possess a textured surface consisting of agglomerates which are bonded together. This continuous structure is in line with polymerization of the once-deposited particles through their reactive centers.

Structure and Formation of the Deposited Polymer. The low amounts and the nature of the gaseous products together with the data on the deposited polymer are in line with the ablation occurring via two important routes. This is the cleavage at the Si−Si bonds yielding high molecular-weight diradicals,

$$^{\bullet}Si(CH_3)_2{-}O{-}[(CH_3)_2Si(CH_3)_2SiO]_n{-}(CH_3)_2Si^{\bullet}$$

and radical steps introducing cross-linking sites into the polymer network.

We assume that the Si-centered macromolecular biradicals possessing sufficient vibrational energy are ejected into the gas phase, undergo rearrangements and sequences of cleavages and recombinations within their bodies, and recombine spontaneously after deposition onto the nearby cold surface. Alternative cleavage into

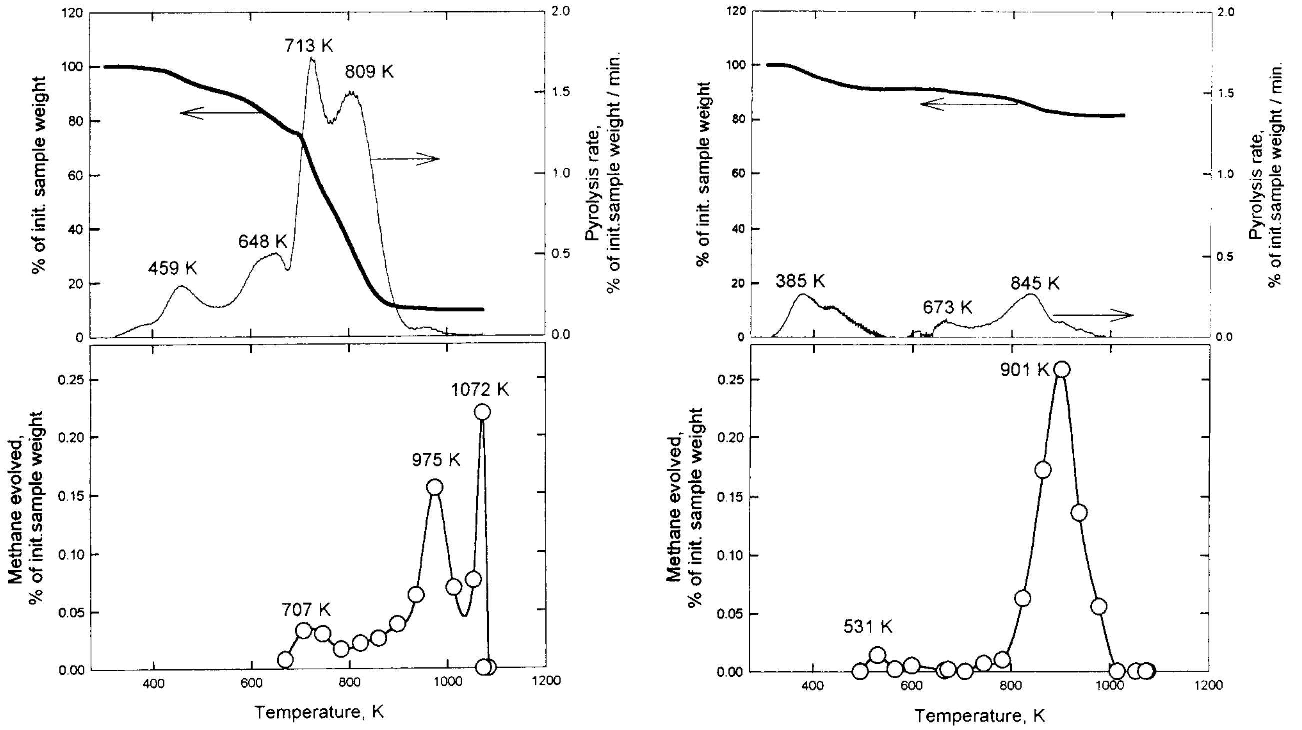
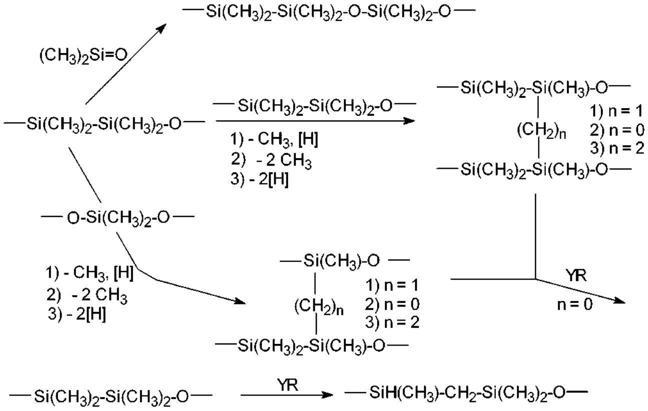


Figure 6. Thermal decomposition of the poly[oxy(tetramethyldisilane-1,2-diyl)] (a) and the laser-deposited polymer (b).

Scheme 2. Reactions Involved in the Formation of the Laser-Deposited Polymer



and subsequent polymerization of volatile cyclic $-[(CH_3)_2Si(CH_3)_2SiO]_n-$ compounds with $n = 1, 2$ seems less probable because the compound with $n = 2$ has been detected among the degradation products only in trace amounts.

The $-OSiC_2O-$ moieties assessed on the basis of the ^{29}Si MAS NMR data as a part of the mobile structure can be formed[14] via extrusion of dimethylsilanone and its insertion into the Si−O bond of the $-[(CH_3)_2Si(CH_3)_2SiO]_n-$ backbone (Scheme 2).

The cross-linking steps can be envisaged as coupling of the Si-centered and $\equiv SiCH_2^{\bullet}$ radicals to form Si−Si and $Si-(CH_2)_nSi$ ($n = 0-2$) linkages, the radical centers being produced via homolysis of the $Si-CH_3$ bond and H-abstraction from the $CH_3(Si)$ group. The $Si-CH_2-Si$ bridges can be also formed by the Yajima rearrangement[19] (YR) of the $-(CH_3)_2Si-Si(CH_3)_2-$ mobile and/or cross-linking units. The feasible cross-linking steps are illustrated in Scheme 2. They result in the formation of the $SiSiC_2O$, $SiSi_2CO$, and SiC_2O_2 structures which fall in the first and the third region of the observed ^{29}Si NMR spectrum. The assigned C_3SiO and C_2HSiO cross-linking units can be introduced through coupling between the C-centered radical and the Si-centered radical (**II**)

Table 2. Mass Balance of the Thermal Decomposition of Poly[oxy(tetramethyldisilane-1,2-diyl)] and the Laser-Deposited Polymer

decomposition product, wt %	poly[oxy(tetramethyl-disilane-1,2-diyl)]	laser-deposited polymer
CH_4	2.8	5.8
solid residue	9.5	83.4
liberated[a]	87.7	10.8

[a] Calculated to 100%.

$$\underset{\textbf{II}}{-CH_2-\dot{S}i(R)-O-} \qquad R = CH_3$$

generated after the Yajima rearrangement, whereas the $CSiO_3$ cross-linking units can result from the dimethylsilanone insertion between the Si−H bond of the $O-Si(CH_3)H-O-$ fragments which can arise from H-abstraction by the $CO_2Si^{\bullet}$ unit.

Thermal Analysis. The comparison of thermal behavior of the initial poly[oxy(tetramethyldisilane-1,2-diyl)] and the deposited polymer is given in Figure 6. Both materials decrease their weight, evolve methane and a high molecular weight material, and leave a residue (Table 2).

The thermogram of poly[oxy(tetramethyldisilane-1,2-diyl)] is described by the degradation rate reaching four

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maxima (at 459, 648, 713, and 809 K) and by the evolution of methane attaining three maxima (at 707, 975, and 1072 K). The black residue (<10 wt % of the initial sample) and the measured amount of methane (≈3 wt % of the initial sample) indicate that the major portion of the sample was evaporated, condensed below the hot zone, and not passed to the gas chromatograph. This behavior is similar to that found for the static system.[15]

The decomposition of the deposited polymer is very different. The decomposition rate attains three maxima (at 385, 673, and 845 K) and the evolution of methane reaches two maxima (at 531 and 901 K), indicating that the rate maximum at 385 K is very likely due to desorption of traces of ubiquitous water. The measured amount of methane (≈6 wt % of the initial sample) and that of the whitish residue (83 wt % of the initial sample) reveal that the evolution of the high molecular weight portion is insignificant.

The deposited polymer is thus disclosed as not changing its color and withstanding temperatures up to 800 K. Its high thermal stability is obviously caused by the cross-linked structure, the feature absent in the initial poly[oxy(tetramethyldisilane-1,2-diyl)].

4. Inferences

The fast laser heating of solid poly[oxy(tetramethyldisilane-1,2-diyl)] results in the ablative deposition of thin films of cross-linked polyoxocarbosilane with both siloxane and Si−Si substructures.

The formation of this laser-deposited material is interpreted as taking place via expulsion of Si-centered macromolecular biradicals that undergo cross-linking reactions during their transfer in a vacuum and repolymerize after having been deposited on the nearby cold surface.

The structure of the deposited polymer consists of the backbone composed of $-(CH_3)_2Si(CH_3)_2SiO-$ and $-O(CH_3)_2SiO-$ units and of the cross-linking $SiSiC_2O$, C_3SiO, C_2SiHO, $CSiHO_2$, and $CSiO_3$ moieties.

The laser-deposited polyoxocarbosilane exerts very high thermal stability (up to 800 K) that is attributed to the fact that thermal extrusion of sizable polymer portions (observed with siloxanes[7]) is inhibited in the cross-linked structures. We point out that thermal stability of the laser-deposited polyoxocarbosilane is higher than that of poly(dimethylsilylene) (670−720 K, ref 19) or polydialkylsiloxanes (620−670 K, refs 7 and 20). We also emphasize that the temperature of its maximum decomposition rate being 901 K exceeds that of highly cross-linked polysiloxanes (793 K, ref 10c). These findings reveal that the laser-fabricated films of the hybride of siloxanes and polysilylenes are thermally superior to those of siloxanes and polysilylenes. The IR laser ablation of poly[oxy(tetramethyldisilane1,2-diyl)] can thus find important applications in fabrication of insulating and protecting films in thermally exposed devices.

Acknowledgment. The authors thank the Grant Agency of the Czech Republic (Grant A 203/00/1288) for support.

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