Laser-induced formation of polymers from unsaturated (organyl)trimethylsilanes in the gas phase

J. Pola[a,*], M. Urbanová[a], Z. Bastl[b], J. Šubrt[c], M. Sakuragi[d], A. Ouchi[d], H. Morita[e]

[a]*Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 165 02 Prague 6, Czech Republic*
[b]*J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, 182 23 Prague 8, Czech Republic*
[c]*Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 250 86 Rez near Prague, Czech Republic*
[d]*National Institute of Materials and Chemical Research, AIST, MITI, Tsukuba 305, Japan*
[e]*Graduate School of Science and Technology, Chiba University, Chiba 263, Japan*

Abstract

ArF laser irradiation into gaseous trimethyl(propynyloxy)silane, trimethyl(ethenoxy)silane and trimethyl(ethynyl)silane results in chemical vapour deposition of thin films of solid organosilicon polymers. UV excitation of the two former compounds leads to polymerization at the triple bond as a major process to yield, respectively, saturated poly(trimethylsilyloxyhydrocarbon) and poly(trimethylsilylhydrocarbon), whereas that of the latter compound is controlled by cleavage reactions to afford poly(methylsiloxane). The processes represent a unique photopolymerization in the absence of photoinitiators. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Trimethyl(propynyloxy)silane; Trimethyl(ethenoxy)silane; Trimethyl(ethynyl)silane

1. Introduction

Lasers are increasingly used in inducing polymerization in the liquid phase [1], but studies on laser-induced polymerization in the gas phase are relatively few. Thus, the laser-induced formation of polymers in the gas phase has been achieved via: (a) polymerization of short lived species (silenes [2], silanone [3], methanimine [4], and pyridinyl radical [5]) generated by IR and UV laser radiations; or via (b) UV laser excitation of molecules (methyl acrylate [6], acrolein [7,8] and carbon disulphide [9]) producing reactive species prone to take part in inter-molecular reactions.

Conventional (lamp) photolysis of some unsaturated organic compounds carried out in the gas phase have been known for long as accompanied by unwanted polymerization steps which were regarded more as a nuisance rather than a useful facet (e.g. Refs. [10,11]).

We have earlier demonstrated [12–14] that the interaction of gaseous unsaturated organosilicon compounds $RSiH_3$ (R = H_2C=CH, HC≡C, ClHC=CH, H_2C=CHCH$_2$) with UV or IR laser radiation results in cleavage of these compounds and formation of transient unsaturated species which polymerize in and deposit from the gas phase as solid low H-content polycarbosilanes. In these processes, dehydrogenation at silicon was an important step.

Now we report that organosilicon polymers can be formed in the gas phase by UV laser irradiation into gaseous organyltrimethylsilanes $(CH_3)_3SiR$ (R = HC≡CHCH$_2$O, H_2C=CHO and HC≡C). This irradiation results in efficient chemical vapour deposition of solid films of mostly saturated organosilicon polymers and is controlled by reactions which differ depending on the R substituent.

2. Experimental

The laser irradiation experiments were carried out in a reactor which consisted of two orthogonally positioned Pyrex tubes, one fitted with two quartz windows and the other furnished with two NaCl windows. Trimethyl(propynyloxy)silane (TMPOS) (18 Torr), trimethyl(ethenoxy)-silane (TMEOS) (30 Torr) and trimethyl(ethynyl)silane (TMES) (5 and 50 Torr) were irradiated at a repetition frequency of 10 Hz by pulses from an ArF laser (an ELI 94 or an Lambda Physik LPX 200 model) using, in the given order, incident fluence of 20, 35 and 20 mJ cm^{-2}. The laser pulse energy in was measured with a pyroelectric joulmeter (Gentec ED-500).

* Corresponding author.

Table 1
Yields of volatile products

Parent compound	Product (yield[a])
TMPOS	C_2H_2 (<0.06), $[(CH_3)_3Si]_2O$ (<0.06), $Si_2C_5H_{14}O$ (<0.06),
TMES	$CH_3C\equiv CH$ (0.08), CH_4 (0.07), C_2H_2 (0.04), C_2H_6 (0.05), C3 hydrocarbons, $H_2C=CHCH=CH_2$, $(CH_3)_3SiH$ (all 0.005–0.001), $(CH_3)_2SiH_2$, $(CH_3)_2C=CH_2$ (both traces)
TMEOS	CH_4 (0.26), C_2H_4 (0.20), C_2H_6 (0.13–0.17), $CH_3CH=CH_2$ (0.08), $H_2C=CHCH=CH_2$ (0.02), C_3H_8 (<0.01), $(CH_3)_3SiH$ (<0.005), $(CH_3)_4Si$ (<0.005)

[a] In mole/mole of depleted parent compound.

The progress of the photolysis was monitored by FTIR spectroscopy (a Nicolet Impact FTIR spectrometer and a Shimadzu FTIR 4000 spectrometer) using absorption bands at 1112 cm^{-1} (TMPOS), 1330 cm^{-1} (TMEOS) and 2043 cm^{-1} (TMES), and by gas chromatography on a Shimadzu GC 14A chromatograph (a 1.5 m long column packed with Porapak P, programmed temperature 20–180°C, connected with a Shimadzu CR 5A Chromatopac data processor) or on a Gasukuro Kogyo 370 chromatograph (60 m long capillary Neutra Bond-1 and 2 m long SUS Unipak S columns, programmed temperature 30–150°C, connected with a Shimadzu CR 5A Chromatopac data processor). Identification of gaseous photolytic products was accomplished by means of FTIR spectroscopy and by a GC/MS technique (a Shimadzu QP 1000 mass spectrometer, 70 eV, Porapak P, programmed temperature 20–180°C).

The photolysis course with each of the parent compounds was slowed down by the deposition of the polymeric material onto the window of the reactor, since the white solid films are opaque to the 193 nm radiation. Thus, the 80% depletion of TMPS (10 min irradiation), ca. 50% depletion of TMES (20 min irradiation) and only 5 or 9% depletion of TMEOS (500 pulses and 4000 pulses, respectively) was achieved with successive positioning the laser beam onto clean parts of the entrance reactor window.

Properties of the solid materials deposited from the gas phase onto the surface of the reactor or onto substrates (NaCl, Al, Cu) accommodated in the reactor prior to irradiation were examined by FTIR spectroscopy, scanning electron microscopy (a Tesla BS 350 ultra high vacuum instrument), transmission electron microscopy (a Philips 201 microscope), as well as by X-ray photoelectron spectroscopy (XPS) and X-ray excited Auger electron spectroscopy (XAES) (a VG ESCA 3 Mk II electron spectrometer). The deposits were measured as received and after sputtering with argon ions ($E = 5$ keV, $I = 30$ μA, $t = 3$ min).

TMPOS was prepared by reaction of hexamethyldisilazane with propargyl alcohol, while TMEOS (Shin Etsu Silicon chemicals) and TMES (Aldrich) were commercial samples. Purity of all the compounds was better than 98% as checked by gas chromatography.

3. Results and discussion

All the TMPOS, TMEOS and TMES are good absorbers of 193 nm radiation, their absorptivity at this wavelength being 1.06×10^{-2} Torr^{-1} cm^{-1}, 4.0×10^{-3} Torr^{-1} cm^{-1} and 9.7×10^{-3} Torr^{-1} cm^{-1}, respectively. They deplete when irradiated with ArF laser in the gas phase as confirmed by FTIR spectra taken before and after irradiation with measured numbers of pulses. The depletion of the organyltrimethylsilanes is accompanied by the formation of some volatile compounds and concomitant deposition of thin films on the inside of the entire reactor.

3.1. Photolysis features and volatile products

The ArF laser irradiation of TMPOS results in the depletion of TMPOS and formation of small amounts of volatile ethyne, hexamethyldisiloxane and a $Si_2C_5H_{14}O$ compound {mass fragmentation pattern [m/z(relative intensity): 146 (100), 103 (71), 75 (44), 73 (26), 59 (14)]} assignable to a tetramethyldisilaoxacyclobutane. Concomitantly, production in all the reactor volume and deposition upon the entire reactor surface but mostly on its lowest parts of a white smog is clearly observed. The volatile being produced in very low yields (Table 1) indicates that more than 90% of the photolysed TMPS is consumed for the formation of the solid deposit that must originate from TMPS polymerization.

The ArF laser irradiation of TMES induces the depletion of TMES and formation of methane, ethyne, trimethylsilane, ethane, propyne, buta-1,3-diene, dimethylsilane, isobutene and C3 hydrocarbons. The yields of these volatile products (Table 1) were almost constant during the photolysis progress 10–70% and can account for only ca. 10–20% of the depleted TMES, which indicates that ca. 80–90% of TMES is consumed for the formation of a solid material deposited onto reactor walls.

The ArF laser irradiation of TMEOS results in the TMEOS decrease and formation of relatively large amounts of volatile hydrocarbons and small amounts of methylsilanes (Table 1). Thin transparent films were simultaneously deposited on the inside of the entire reactor.

3.2. Properties of deposited materials

FTIR spectra of the deposited films (Table 2) show some different features. Thus, the material deposited from TMPOS is a partly unsaturated polyhydrocarbon with Si–O bonds; no absorption due to the ν(H–Csp^2) stretch above 3000 cm^{-1} but a significant absorption due to the
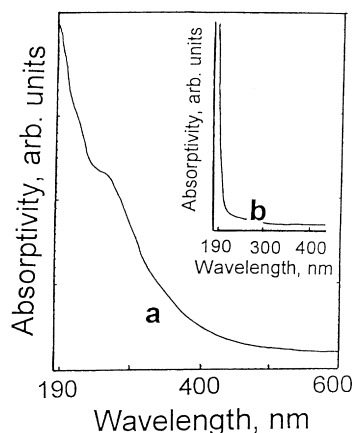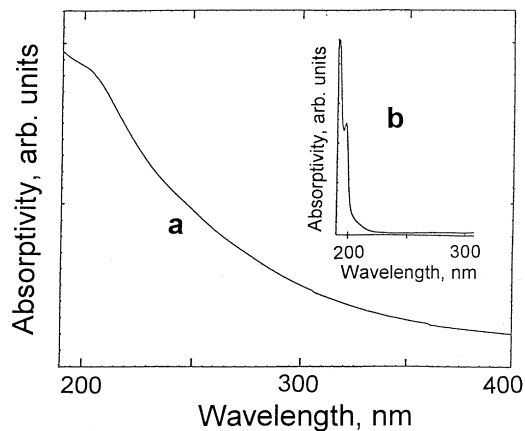
Fig. 1. UV/VIS absorption spectrum of the deposit from TMPOS (a) and of TMPOS (b).

Table 2
FTIR spectra of solid deposits

Vibration	Relative absorptivity/wavelength in cm^{-1}		
	Deposit from TMPOS	Deposit from TMEOS	Deposit from TMES
$\nu(Si{-}C)$	0.43/800	0.35/806	0.14/680
$\rho(CH_3Si)$	0.53/837	0.42/845	1.0/836
$\nu(Si{-}O)$	1.0/1060	1.0/1040	0.09/1043
	0.10/1178		
$\delta(CH_3Si)$	0.34/1257	0.41/1260	0.54/1247
	0.15/1381		
$\nu(C{=}C)$	0.61/1620		
$\nu(C{\equiv}CH)$			0.07/2033
$\nu(Si{-}H)$			0.04/2119
$\nu(C{=}O)$	0.30/1730		
$\nu({-}CH)$	0.12/2838	0.10/2853	0.11/2893
	0.20/2916	0.23/2926	0.24/2951
	0.17/2956	0.14/2962	
$\nu({\equiv}CH)$			0.06/3290

$\nu(H{-}Csp^3)$ stretch below 3000 cm^{-1} reveals that it contain some $-C{=}C-$ units, but that H atoms are very mostly bonded to saturated fractions of the polymer framework. The FTIR spectra of the solid deposited from TMES indicate that it contain carbon atoms in sp^3 and sp but not in sp^2 states. The deposit obtained from TMEOS does not possess absorption bands belonging to $H(Csp^x,\ x=1,2)$ bonds (above 3000 cm^{-1}) and can be described as a completely saturated polysiloxane.

These FTIR spectroscopic features are in keeping with the UV/VIS spectra of these materials. Thus, the UV spectrum of the deposit from TMPSO shows absorption peaking at 190 nm, a shoulder at ~260 nm and a tailing to 500 nm (Fig. 1), and that of the deposit from TMES shows maximum absorption at 190 nm, a shoulder at 205 nm and a tail to ca. 350 nm (Fig. 2). Conversely to that, the UV/VIS spectrum of the deposit from TMEOS (Fig. 3) possesses only a maximum at ca. 204 nm, while TMEOS itself shows, due to a blend of contributions of both chromophore $H_2C{=}CH$ and Si–O–C groups, a bathochromic shift (a maximum at 212 nm).

XPS analysis of the deposit from TMES shows that its stoichiometry is $Si_{1.0}C_{3.7}$ and that it possess by ca. 25% less carbon than TMES. The Si (2p) core level binding energies and Auger parameters for the as received deposit (101.7 eV, 1712.0, resp.) and sputtered sample (101.6 eV and 1714.3, respectively) fall in the range of values known for organo-silicon compounds. XPS analysis of the deposit based on the C KLL derivative spectra and comparison to that of diamond and graphite reveals that the topmost (ca. 5 nm) layers of the deposit are dominated by Csp^3 atoms. The energy separation between the most positive maximum and most negative minimum can be used [15–17] to estimate the carbon sp^3/sp^2 hybridization ratio. Our results obtained for graphite (22.4 eV) and diamond (13.6 eV) agree well with the literature data [16] and allowed us to apply the linear relationship between this separation and the sp^3/sp^2 ratio to our samples to estimate that sp^3 carbon atoms predominate on the surface of the as received deposits. This situation is very different after Ar ion sputtering of

Fig. 2. UV/VIS absorption spectrum of the polymer deposited from TMES (a) and of TMES (b).
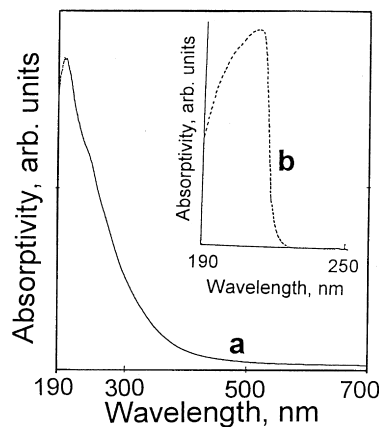

Fig. 3. UV/VIS absorption spectrum of the deposit from TMEOS (a) and of TMEOS (b).
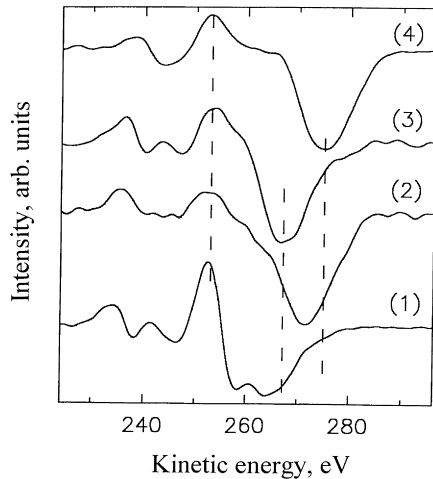
Fig. 4. C KLL X-ray excited derivative Auger spectra of: (1) as received deposit from TMES; (2) deposit from TMES after Ar ion sputtering; (3) diamond; and (4) graphite.

the surface after which about 75% of C atoms on the sputtered surface are sp^2 hybridized. The behaviour of the spectral feature located at $\sim$245 eV (Fig. 4) is also in agreement with this finding [18]. It thus follows that Ar ion sputtering of the deposited films can significantly change carbon hybridization of their topmost layers.

XPS analysis of the films from TMEOS shows different composition depending on where the films are deposited. The films obtained at the reactor bottom which is outside the laser beam possess stoichiometry $Si^{\alpha}_{0.1}Si^{\beta}_{1.0}C_{4.5}O_{1.0}$, while those deposited onto the substrates affixed several mm behind the entrance quartz window and facing the laser beam show stoichiometry $Si^{\beta}_{1.0}C_{3.3}O_{1.0}$. The Si^{α} relates to elemental silicon and Si^{β} to silicon in organosiloxane

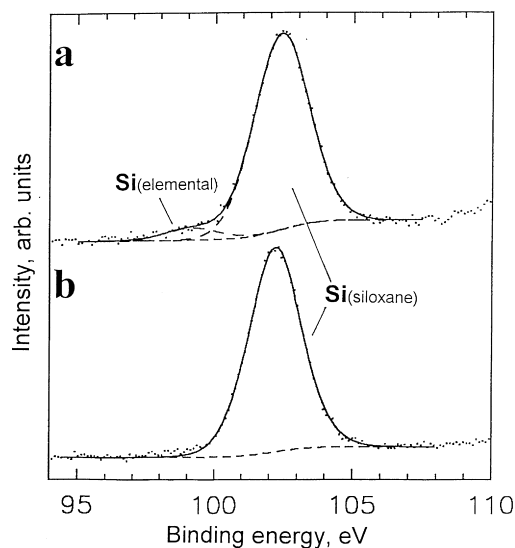Fig. 6. SEM (a) and TEM (b, magnification 150,000×) image of the deposit from TMPOS.

Fig. 5. The Si (2p) core level spectra of films deposited from TMEOS on substrate positioned: (a) outside the laser beam; and (b) facing the laser beam.
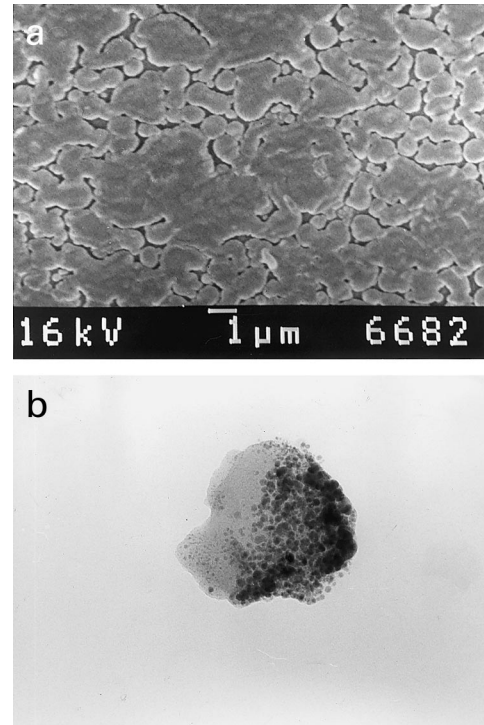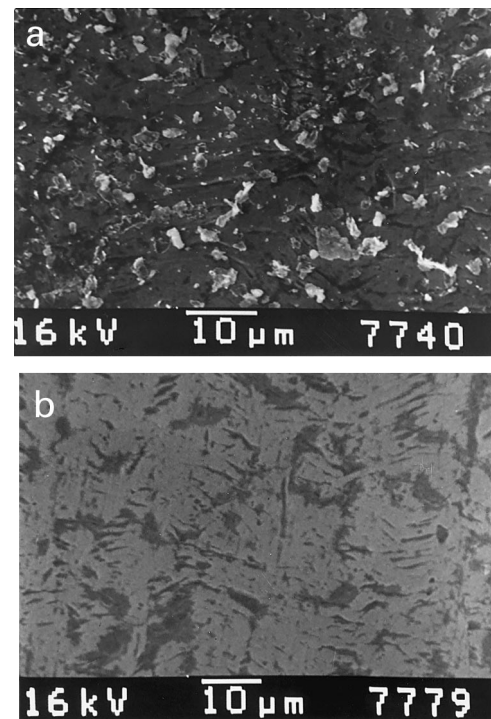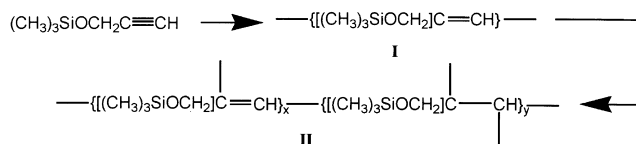

Fig. 7. SEM of films deposited from TMEOS on substrate placed on reactor bottom outside the laser beam (a), and exposed to the laser beam behind the quartz window (b).

$$(CH_3)_3SiOCH_2C\equiv CH \longrightarrow \quad -\{[(CH_3)_3SiOCH_2]C=CH\}- \quad -$$

I

$$-\{[(CH_3)_3SiOCH_2]C=CH\}_x \quad -\{[(CH_3)_3SiOCH_2]C-CH\}_y- \quad \longleftarrow$$
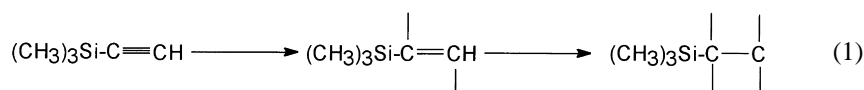
II

Scheme 1.

polymer, respectively. The organosiloxane silicon highly prevails in the former and is the only form of silicon in the latter (Fig. 5). This assignment is in line with the spectrum of Si(2p) electrons of both films, which is dominated by the peak located at 102 ± 0.2 eV. It also gets support from the obtained values of the modified Auger parameter 1711.9 ± 0.2 eV and from the separation

$$(CH_3)_3Si-C\equiv CH \longrightarrow (CH_3)_3Si-C=CH \longrightarrow (CH_3)_3Si-C-C \qquad (1)$$

between O (1s) and Si (2p) photoemission lines 430.4 ± 0.2 both of which are characteristic of organosiloxane-polymer [19,20].

The materials are insoluble in common organic solvents (tetrahydrofuran, dichloromethane, acetone, toluene), which is compatible with a highly cross-linked structure.
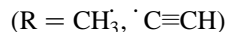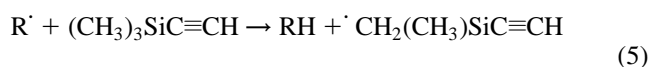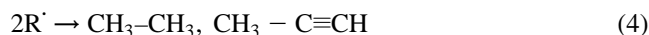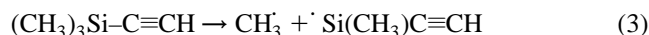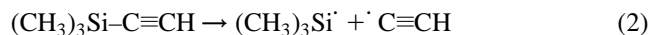
SEM and TEM patterns of the deposited materials are different. The morphology of the deposit produced from the white smog from TMPOS (Fig. 6) reveals agglomerates bonded together and consisting of units of ca. 10 nm size. This indicates that the once deposited particles retain some degree of polymerization reactivity and combine with others when in close proximity to them during the deposition process. SEM images of the films deposited onto the reactor bottom from TMEOS (Fig. 7) show particulate structure and consist of well separated agglomerates size of which ranges below 10 μm, whereas those of the films deposited onto substrates facing the laser beam behind the entrance window reveal a discrete continuous structure. The latter morphology can be taken as an evidence of laser-formation of reactive centres in the deposit; the once deposited particles apparently increase their size through reactions of their reactive centres with gaseous unsaturated fragments which are not rich in carbon. This is in line with the observation of their lower content of carbon. Similar reactivity of the once deposited solid particles was observed in laser evaporation of several solid organosilicon polymers [21]. Scanning electron microscopy of TMES (Fig. 8) shows that the deposit can be described as a rather homogeneous film formed by μm-sized agglomerates.

3.3. Gas-phase chemistry leading to polymers

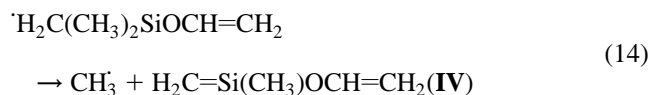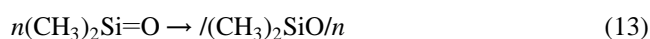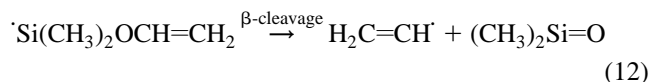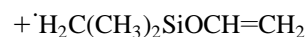The data on the volatile products and solid deposited films allow to assess chemical reactions taking place in the gas phase and leading to the formation of polymers.

The major route during the ArF laser-induced photolysis of TMPOS is polymerization at the triple and subsequently at the double bond leading first to a conjugated polymer (**I**) and finally to a partly saturated and cross-linked polymer (**II**) (Scheme 1).
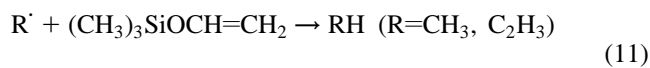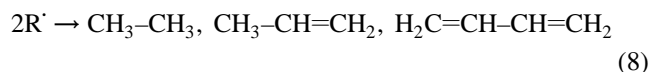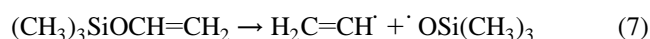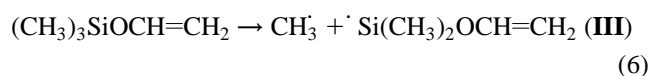
Cleavage reactions of TMPOS are insignificant.

The ArF laser irradiation of TMES is dominated by polymerization at the triple bond Eq. (1) which is accompanied by relatively minor cleavage of the Si–C bonds. The formation of the minor gaseous products can be interpreted by cleavage of TMES Eqs. (2) and (3), recombination Eq. (4) and H-abstraction Eq. (5) of ethynyl and methyl radicals

$$(CH_3)_3Si-C\equiv CH \rightarrow (CH_3)_3Si^{\cdot} + {}^{\cdot}C\equiv CH \qquad (2)$$

$$(CH_3)_3Si-C\equiv CH \rightarrow CH_3^{\cdot} + {}^{\cdot}Si(CH_3)C\equiv CH \qquad (3)$$

$$2R^{\cdot} \rightarrow CH_3-CH_3, \ CH_3 - C\equiv CH \qquad (4)$$

$$R^{\cdot} + (CH_3)_3SiC\equiv CH \rightarrow RH + {}^{\cdot}CH_2(CH_3)SiC\equiv CH$$

$$(R = CH_3^{\cdot}, {}^{\cdot}C\equiv CH) \qquad (5)$$

The ArF laser irradiation into TMEOS can be characterized as a process yielding a number of reactive products which undergo a multitude of reactions as further cleavages and polymerization [22]. It is common view that the Si–C, but not the much stronger Si–O bonds can be photolytically cleaved and our results confirm that volatile hydrocarbons produced via the Si–C fission are the major cleavage products. However, the formation of trimethylsilane and tetramethylsilane from TMEOS indicates that minor cleavage of the Si–O bond by 193 nm photons is feasible. Complex reaction scheme and radical-chain reactions are supported by the estimated number of TMEOS molecules depleted with one 193 nm photon. Within less than 5% photolysis progress, this value ranges between 4 and 5. The relative amounts of gaseous products being virtually independent on the photolysis progress are in line with combination Eq. (8), disproportionation Eq. (9),

cross-disproportionation Eq. (10) and H-abstraction reactions Eq. (11) of $H_2C=CH^.$ and $CH_3^.$ radicals produced upon cleavages of the CH_3–Si Eq. (6) and O–CH Eq. (7) bond of TMEOS. Another plausible route is subsequent decay (β-cleavage, Eq. (12) of the radical (**III**) yielding very reactive dimethylsilanone which is known [23] to polymerize Eq. (13). Trimethylsilane and tetramethylsilane are obviously produced via cleavage of the strong Si–O bond and by consecutive H-abstraction by $(CH_3)_3Si^.$ radical [24], and by recombination of $CH_3^.$ and $(CH_3)_3Si^.$ radicals, respectively. The detected final products indicate that TMEOS depletes by a blend of monomolecular decomposition and consecutive H-abstraction reactions of TMEOS with radicals Eq. (11) producing the unstable unsaturate which can split into methyl radical and yield silene **IV** Eq. (14)

$$(CH_3)_3SiOCH=CH_2 \rightarrow CH_3^. + {}^.Si(CH_3)_2OCH=CH_2 \text{ (III)}$$
$$(6)$$

$$(CH_3)_3SiOCH=CH_2 \rightarrow H_2C=CH^. + {}^.OSi(CH_3)_3 \qquad (7)$$

$$2R^. \rightarrow CH_3–CH_3, \ CH_3–CH=CH_2, \ H_2C=CH–CH=CH_2$$
$$(8)$$

$$2H_2C=CH^. \rightarrow H_2C=CH_2 + HC\equiv CH \qquad (9)$$

$$CH_3^. + H_2C=CH^. \rightarrow CH_4 + HC\equiv CH \qquad (10)$$

$$R^. + (CH_3)_3SiOCH=CH_2 \rightarrow RH \ (R=CH_3, \ C_2H_3)$$
$$(11)$$
$$+ {}^.H_2C(CH_3)_2SiOCH=CH_2$$

$${}^.Si(CH_3)_2OCH=CH_2 \xrightarrow{\beta\text{-cleavage}} H_2C=CH^. + (CH_3)_2Si=O$$
$$(12)$$

$$n(CH_3)_2Si=O \rightarrow /(CH_3)_2SiO/n \qquad (13)$$

$${}^.H_2C(CH_3)_2SiOCH=CH_2$$
$$(14)$$
$$\rightarrow CH_3^. + H_2C=Si(CH_3)OCH=CH_2 \textbf{(IV)}$$

4. Inferences

The results on the ArF laser-induced photolysis of the selected trimethyl(organyl)silanes $(CH_3)_3SiR$ demonstrate that UV excitation of $(CH_3)_3SiR$ molecules results in polymerization and cleavage reactions. The extent of the cleavage reactions is very dependent on the structure of $(CH_3)_3SiR$: the cleavage is unimportant with R = HC≡CCH$_2$O, small with R = HC≡C and a major process with R = H$_2$C=CHO.

The polymerization of $(CH_3)_3SiR$ (R = HC≡CCH$_2$O, HC≡C) affords partly unsaturated cross-linked materials both of which show some extent of unsaturation and conjugation. In the polymers from $(CH_3)_3SiOCH_2C\equiv CH$ the
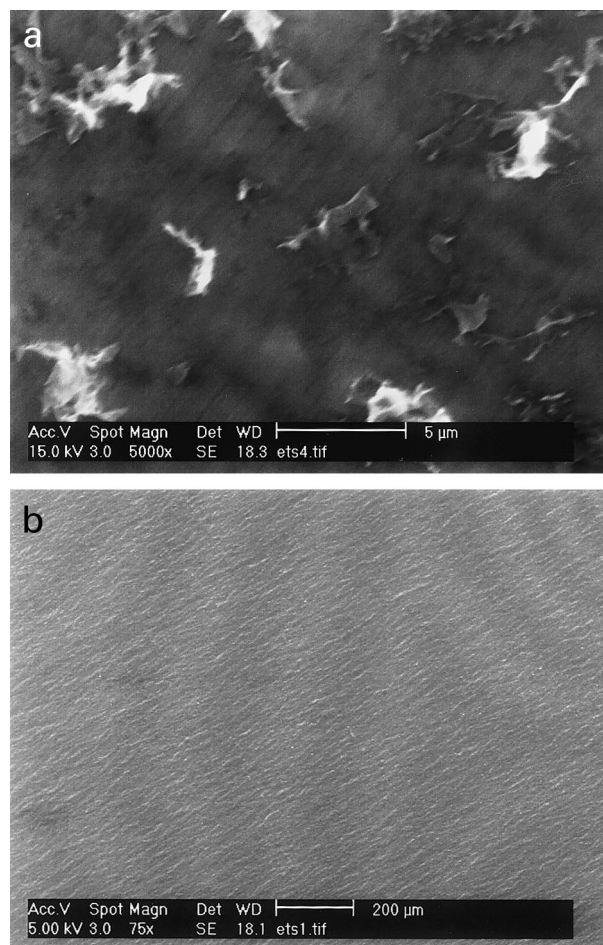

Fig. 8. SEM images of the deposit from TMES.

conjugation is effective with the C=C bonds, whereas in the polymers from $(CH_3)_3SiC\equiv CH$ the conjugation is due to the presence of the C≡C bonds.

The UV laser excitation of TMPOS yields –$\{[(CH_3)_3SiOCH_2]C=CH\}_x$–$\{[(CH_3)_3SiOCH_2]C–CH\}_y$ agglomerates. The known reactivity of $(CH_3)_3Si$–O moiety towards hydrolysis [25] makes these macromolecules promising precursors to polymers possessing OH bonds. The latter can find use as permeation barrier coatings [26], pH responsive films [27] and sensing materials [28].

We emphasize that the photolysis of TMES resulting in the formation of polymers with a high content of sp^3-hybridized carbons differs from the traditional polymerization routes of alkynes involving metal carbenes- [29–32], metal halides- [33,34] and transition metals- [35] based catalysts. We note that other non-catalyst polymerization of alkynes are carried out at very different conditions and involve high-temperature (460°C) polymerization of allenes and alkynes to carbonaceous black films with up to 10% of sp^3-hybridized carbon [36], and the glow-discharge polymerization of TMES involving radical and ionic species and cleavage of the Si–C bond [37].

The photolysis of TMEOS leading to the formation of a

multitude of gaseous hydrocarbons provides an efficient way for deposition of polysiloxane films. These films can be used as insulants in microelectronics and as precursors for silicon oxycarbides. This class of materials is of increasing interest in various fields of applied research (e.g. Refs. [38–41]) and is important in ceramic sensors for oxygen detection in high temperature corrosive conditions and in photodetectors and solar cells [42,43]. The reported chemical vapour deposition of siloxanes thus adds to other technique by means of which different kinds of the Si/C/O and Si/C/H/O materials (black glasses by pyrolysis of polysiloxane gels [44–46], nanosized particles by pyrolytic laser–aerosol interaction [47–49] and solid films by plasma-[50–52] or IR laser-induced pyrolysis of gaseous organosilicon monomers [53–57]) can be produced.

Our results show that volatile compounds with a triple C≡C bond attached directly to the silicon, or those with the silicon and a triple bond interlinked by the OCH_2 moiety, can be UV laser-photopolymerized in the gas phase in the absence of photoinitiators. Polymers produced by catalyst- or (photo)initiator-free polymerization are now of importance for medical applications and optical data storage and processing. A continuing effort for finding routes leading to polymers without such additives (e.g. Refs. [58,59]) is worthy and the laser-induced formation of polymers in the gas phase affording deposition of thin polymer films on cold substrates is promising because of these reasons.

Acknowledgements

References

[1] Davis TP. J Photochem Photobiol, A 1994;77:1.

[2] Pola J. Radiat Phys Chem 1997;49:151 (and references therein).

[3] Pola J, Urbanová M, Dřínek V, Šubrt J, Beckers H. Appl Organometal Chem 1999;13:655.

[4] Pola J, Lycka A, Gusel'nikov LE, Volkova VV. J Chem Soc, Chem Commun 1992:20.

[5] Urbanová M, Vítek J, Bastl Z, Ubik K, Pola J. J Mater Chem 1995;5:849.

[6] Morita H, Sadakiyo T. J Photochem Photobiol, A Chem 1995;87:163.

[7] Morita H, Shimizu M. J Phys Chem 1995;99:7621.

[8] Morita H, Semba K, Bastl Z, Pola J. J Photochem Photobiol, A Chem 1998;91:116.

[9] Matsuzaki A, Hamada Y, Morita H, Matsuzaki T. Chem Phys Lett 1992;190:337.

[10] Bamford CH, Tipper CFH, editors. Comprehensive chemical kinetics, vol. 5. Amsterdam: Elsevier, 1972.

[11] Calvert JG, Pitts JN. Photochemistry. New York: Wiley, 1966.

[12] Pola J, Bastl Z, Subrt J, Abeysinghe JR, Taylor R. J Mater Chem 1996;6:155.

[13] Pola J, Vitek J, Bastl Z, Urbanova M, Šubrt J, Taylor R. J Mater Chem 1997;7:1415.

[14] Pola J. Res Chem Intermed 1999;25:351.

[15] Galuska AA, Maden HH, Allred RE. Appl Surf Sci 1988;32:253.

[16] Lascovich JM, Giorgi R, Scaglione S. Appl Surf Sci 1991;47:17.

[17] Jackson ST, Nuzzo RG. Appl Surf Sci 1995;90:195.

[18] Pola J, Urbanova M, Bastl Z, Plzak Z, Šubrt J, Vorlicek J, Gregora I, Crowley C, Taylor R. Carbon 1997;35:605.

[19] NIST X-ray Photoelectron Spectroscopy Database. US Dept. of Commerce, NIST, Gaithersburg 1997.

[20] Urbanová M, Morita H, Dřínek V, Bastl Z, Šubrt J, Pola J. J Anal Appl Pyrolysis 1998;44:219.

[21] Pola J, Vitek J, Polyakov YP, Gusel'nikov LE, Matveychev PM, Bashkirova SA, Tlaskal J, Mayer R. Appl Organomet Chem 1991;5:57.

[22] Khachatryan L, Volnina EA, Fajgar R, Pola J. J Organomet Chem 1998;566:263.

[23] Raabe G, Michl J. In: Patai S, Rappoport Z, editors. The chemistry of organic silicon compounds, New York: Wiley, 1989.

[24] Tokach SK, Koob RD. J Phys Chem 1979;83:774.

[25] Bažant V, Chvalovský V, Rathouský J. Organosilicon compounds. Prague: Publishing House of the Czechoslovak Academy of Sciences, 1965.

[26] Crowley RL, Evans JL. J Vac Sci Technol, A 1991;9:824.

[27] Kitade T, Tanizaki Y, Harumi Y, Kitamura K, Hozumi K. Bunseki Kagaku 1990;39:637 (Chem Abstr 109/112138b).

[28] Hozomi K. Pure Appl Chem 1988;60:697.

[29] Zeigler JM. Polym Prepr (Am Chem Soc, Div Polym Chem) 1984;25:223.

[30] Kunzler J, Percec V. Polym Prepr (Am Chem Soc, Div Polym Chem) 1988;29:219.

[31] Katz TJ, Lee SL. J Am Chem Soc 1980;102:422.

[32] Liaw JD, Soum A, Fontanille M, Parlier A, Rudler H. Makromol Chem Rapid Commun 1985;6:309.

[33] Voronkov MG, Pukhnarevich VB, Sushchinskaya SP, Annenkova VZ, Annenkova VM, Andreeva NJ. J Polym Sci, Polym Chem Ed 1980;18:53.

[34] Okano Y, Masuda T, Higashimura T. J Polym Sci, Polym Chem Ed 1984;22:1603.

[35] Heeres HJ, Teuben JH. Organometallics 1991;10:1980.

[36] Kretschmer O, Hopf H, Naarmann N. Synth Met 1991;41–43:1567.

[37] Inagaki N, Yamazaki H. J Appl Polym Sci 1984;29:1369.

[38] Hurwitz FI, Heimann P, Farmer SC, Hembree DM. J Mater Sci 1993;28:6622 (and references therein).

[39] Shimoo T, Chen H, Okamura K. J Mater Sci 1994;29:456.

[40] Breval E, Hammond H, Pantano CG. J Am Ceram Soc 1994;77:3012.

[41] Bois L, Maquet J, Babonneau F, Mutin H, Bahloul D. Chem Mater 1994;6:796.

[42] Quick NR. Proc Int Conf Lasers 1992, p. 881, Publ. 1993.

[43] Fortunato E, Martins R, Ferreira I, Santos M, Macarico A, Guimaraes L. J Non-Cryst Solids 1989;115:120.

[44] Chi FK. Ceram Engng Sci Proc 1983;4:704.

[45] Babonneau F. Polyhedron 1994;13:1123.

[46] Kamiyama K, Yoko T, Sano T, Tanaka K. J Non-Cryst Solids 1992;119:14.

[47] Fusil S, Armand X, Herlin N, Cauchetier M. Key Engng Mater 1997;132:141.

[48] Kortobi YE, Espinose de la Caillerie J-B, Legrand A-P, Armand X, Herlin N, Cauchetier M. Chem Mater 1997;9:632.

[49] Herlin N, Armand X, Musset E, Martinengo H, Luce M, Cauchetier M. J Eur Ceram Soc 1996;16:1063.

[50] Buccellato GM. Diss Abstr Int B 1993;54:3211.

[51] Geissler M, Kieser J, Rauchle E, Wilhelm J. Vac Sci Technol A 1990;8:908.

[52] Bartella J, Herwig U, Fresenius J. Anal Chem 1993;346:351.

[53] Alexandrescu R, Morjan J, Grigoriu C, Michailescu IN, Bastl Z, Tláskal J, Mayer R, Pola J. Appl Phys A 1988;46:768.

[54] Papoušková Z, Pola J, Bastl Z, Tláskal J. J Macromol Sci, Chem A 1990;27:1015.

[55] Manders WF, Bellama JM. J Polym Sci, Polym Chem Ed 1985;23:351.

[56] Pola J, Alexandrescu R, Morjan J, Sorescu D. J Anal Appl Pyrolysis 1990;18:71.

[57] Pola J, Pokorná D, Bastl Z, Šubrt J. J Anal Appl Pyrol 1996;38:153.

[58] Roth W, Henkel H-J, Hoffmann KW, Market H. Adv Mater 1990;2:497.

[59] Roth W, Hoffmann KW, Kurz W. J Polym Sci, Part A: Polym Chem 1994;32:1893.