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Laser irradiation of oligosiloxane copolymer thin films functionalized with side chain bulky carbosilane moieties

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Abstract

Linear oligosiloxanes functionalized with bulky side chain tris(trimethylsilyl)hexyl (TTSH) substituents were transformed into cross-linked materials by UV 193 nm excimer pulsed laser ablation. The process occurred without any catalyst, by reactions of radicals formed in UV laser induced photolysis of side tris(trimethylsilyl)hexyl groups. Chemical changes were monitored by FTIR, LC/UV, GC/MS and solubility tests.

Keywords: UV laser ablation; Siloxane; Tris(trimethylsilyl)methane

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1. Introduction

Tris(trimethylsilyl)methyl ("trisyl", T_{Si})-type ligand is known to provide steric protection in organometallic [1] and polymer systems [2–4]. Once introduced into a macromolecular system, T_{Si} brings about dramatic changes of properties, reflecting a substantial decrease of polymer chain mobility (a considerable increase of the glass transition temperature) [2]. The bulky tris(trimethylsilyl)hexyl (TTSH) group was also shown to improve thermal resistance of polymeric materials [3]. Nevertheless, such materials are brittle and of poor film-forming properties. Thus, the formation of resistant T_{Si}-polymeric systems, preferably of a cross-linked structure, requires often the presence of a reactive moiety. Oxirane rings that can form oligoether cross-links via UV initiated cationic photocuring [3,5] and are often utilized in the synthesis of adhesives, coatings and photoresists [6] can be an example. The synthesis and properties of T_{Si}-modified polymeric systems functionalized by polymerizable glycidoxypropyl moieties were previously reported [3]. In this paper, we present our results on ArF UV laser treatment of TTSH-oligosiloxanes, and formation of cross-linked siloxane-based thin films without any catalyst, by reactions of radicals formed in UV laser induced photolysis of side tris(trimethylsilyl)hexyl groups. The energy delivered by photons at 193 nm corresponding to ~620 kJ/mol is in excess to split all the bonds in the studied material [Si–C (370 kJ/mol), Si–O (530 kJ/mol), C–H (410 kJ/mol)]. Still, the expected primary photolytic process is Si–C bond breaking. Due to the difference in the bond length between inner Si–C and outer $Si–CH_3$ [1,7,8] in T_{Si} ligand, it is expected that dissociation of the former would be more feasible. UV irradiation of T_{Si}-type compounds $T_{Si}SiPh_2I$ and $T_{Si}SiMePhI$ [9], or their thermolysis [10], proceeds with iodine atom abstraction and formation of silyl radicals ($T_{Si}SiPh_2^{\bullet}$, $T_{Si}SiMePh^{\bullet}$). 1,3-Migration of phenyl or methyl group within the radical was observed to cause rearrangement and led to products of intramolecular cyclization. Analogous bulky systems [$(BrMe_2Si)_4C$ and $(BrMe_2Si)_4Si$] were applied as free radical reducing agents for organic bromides [11]. Still, the photolysis of Si–C bond in systems similar to side chain tris(trimethylsilyl)hexyl groups has not been reported so far. The process can be utilized for polymer modification (e.g. nano-lithography) [12]. It is also expected that decomposition products might form new vapor-deposited nano-textured oxycarbosilane materials of valuable properties to be used as ceramic composites or catalyst supports.

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2. Experimental

2.1. Analysis and general methodology

The reactions of oligosiloxane functionalization with TTSH were performed using standard Schlenk technique under an atmosphere of argon. ^{1}H NMR spectra of polymeric precursors were recorded, in $CDCl_3$ as a solvent, using the Bruker AC-200 MHz or the Bruker DRX-500 MHz spectrometer with TMS as a reference. ^{13}C and ^{29}Si NMR spectra were obtained with DRX-500 MHz spectrometer. Size exclusion chromatography (SEC) for linear polymers was performed using a Wyatt Optilab 903 apparatus equipped with two (TSK G4000HLX and G2000HLX) columns using dichloromethane as a solvent. A differential refractive index detector was used and molecular masses were derived from a calibration curve based on polystyrene standards. The UV laser induced molecular weight distribution changes in non-cross-linked part of cured polymers in comparison to the parent materials were studied utilizing liquid chromatography [Hewlet-Packard LC with two columns (tandem arrangement) packed with PL gel (5 μm gel particle size, 0.5 nm or 5 nm pore size), equipped with a diode array UV detector (operating at 220 nm), and tetrahydrofurane as an eluent (1.0 ml/min)]. Identification of low molecular weight compounds, formed during the reaction, was performed by direct-inlet mass analysis (DI-MS) of condensed samples obtained after solubility tests from cross-linked films, using Shimadzu QP5050 mass spectrometer equipped with direct sample inlet device DI-50 with programmable heating (temperature program from 30 °C to 150 °C, heating rate 10 °C/min).

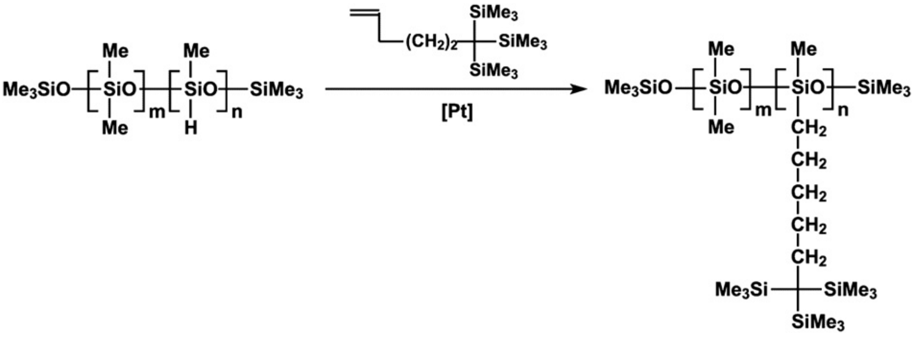
Cross-linking experiments were carried out with an excimer ArF UV laser (ELI model 94, Estland), operating at 193 nm wavelength, at the repetition frequency of 10 Hz. The incident fluence of rectangular (20 × 5 mm) laser beam, measured in front of laser head, was approximately 60–100 mJ/cm^2. The laser beam was reflected to a reaction vessel by a gold mirror (efficiency approximately 15% for 193 nm). The pressure in the vessel was measured using a Barocell MB100 Edwards pressure meter, prior and after vacuum experiments. Experiments were carried out under vacuum or alternatively the reaction cell was filled with Ar (100 kPa) or a mixture of Ar/H_2 (50 kPa each). Changes in the polymer film induced by UV laser irradiation were monitored by FTIR spectrometry [Nicolet Impact 400 FTIR spectrometer (400–4000 cm^{-1})], and UV spectrometry [1601 Shimadzu spectrometer (190–800 nm)]. The solubility tests in control cross-linking experiment were performed also with the use of Nicolet 380 FT-IR spectrometer. IR spectra of cross-linked materials were obtained from a thin film prepared on a KBr pellet. Gaseous products formed during laser irradiation were analyzed with the Shimadzu QP5050 GC-MS spectrometer (positive EI, 70 eV) and the GC 14A Shimadzu gas chromatograph [Porabond Q capillary column, FID detector, programmed (30–210 °C) temperature, He as a carrier gas], and their GC retention times were compared to standards. Quantification of volatile product was performed using areas of GC peaks and FID factors calculated according to literature [13,14]. The insoluble parts of films (prepared on the aluminum plates) were also analyzed by SEM electron microscopy and microanalysis (a Philips XL30 CP scanning electron microscope equipped with EDAX DX-4, an energy dispersive analyzer of X-ray radiation) for their morphology and elemental composition.

2.2. Reagents

6,6,6-Tris(trimethylsilyl)hex-1-ene [3] and tetrakis(trimethylsilyl)methane [15] were prepared according to the literature procedures. Hydrosilylation catalyst – platinum tetramethyldivinyldisiloxane (Karstedt's catalyst, PTDD) complex (3% solution in xylenes) and oligosiloxanes PS-120 ($M_n = 2800$, $M_w = 7000$) and HMS-301 ($M_n = 1600$, $M_w = 3400$), containing respectively 100 and 30% of $-Me(H)SiO-$ monomeric units, were purchased from ABCR. Linear polydimethylsiloxane ($M_n = 116\,000$, $M_w = 65\,000$) and 1,5-hexadiene were purchased from Aldrich. All the reagents were used as received, without purification. All solvents were dried prior to their use according to literature procedures [16].

2.3. General procedure for grafting TTSH on a siloxane backbone

A series of polymers, differing by the number of siloxane segments, functionalized with $(Me_3Si)_3C(CH_2)_3CH{=}CH_2$ as well as dimethylsiloxane monomeric units were obtained (Scheme 1) according to the previously published procedure [3]. 6,6,6-Tris(trimethylsilyl)hex-1-ene was stirred with PTDD ($[Pt]/[CH{=}CH_2] = 1 \times 10^{-4}$) at room temperature for 20 min. A solution of oligosiloxane in toluene was added



Scheme 1. Preparation of oligosiloxanes grafted with tris(trimethylsilyl)hexyl groups.

Table 1
Polymer characteristics (see Scheme 1)

Polymer	x [mmol]	z [g]	Si–H [mmol]	Toluene [ml]	Y [%]	m [%]	n [%]	M_n	PDI
I	7.00	0.397	6.90	6	74	–	100	6700	3.2
II	22.70	4.900	21.10	30	97	70	30	3400	2.2

x – Amount of 6,6,6-tris(trimethylsilyl)hex-1-ene used in the synthesis; z – amount of oligosiloxane used in the synthesis; m – molar amount of Me/Me siloxane units in the main chain; n – molar amount of TTSH/Me siloxane units in the main chain; Y – the polymer yield.

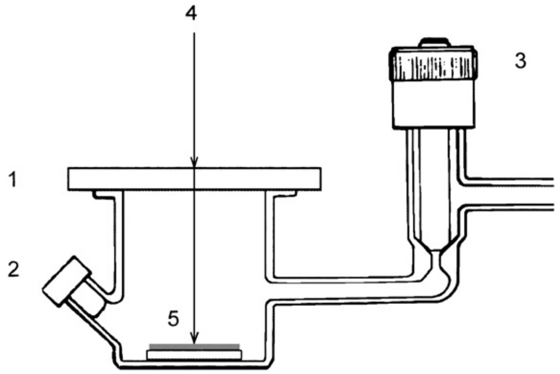
Table 2
FTIR frequencies

Sample	Frequency [cm^{-1}]
$(Me_3Si)_4C$	673.2, 831.8, 853.4, 1260.8, 2904.7, 2958.8, 2984.0
PDMS	662.3, 687.0, 702.0, 799.4, 864.2, 1019.3, 1091.4, 1260.8, 2904.7, 2962.4
TTSH-siloxanes	673.2, 738.1, 770.5, 806.6, 839.1, 849.2, 914.7, 939.5, 961.6, 1022.9, 1095.0, 1174.3, 1253.6, 2857.2, 2879.4, 2901.1, 2915.5, 2951.5, 2973.2

drop-wise and the reaction mixture was stirred for 24 h at room temperature. Progress of the reaction was followed by ^{1}H NMR. In order to achieve total conversion of Si–H bonds, the mixture was stirred at 70 °C for additional 24 h. Volatiles were removed under reduced pressure, and the product was dissolved in a small amount of CH_2Cl_2 and precipitated in methanol, separated and dried for 8 h under vacuum at room temperature. Reaction conditions for polymers' preparation and their characteristics are shown in Table 1, NMR data were published elsewhere [3]. FTIR data are given in Table 2.

2.4. General procedure for laser irradiation of functionalized oligosiloxanes

Samples of polymer films, cast from their solutions (in dichloromethane) on KBr or quartz substrates and dried in air for 1 h, were placed in a Pyrex vessel [furnished with a quartz window, a sleeve with rubber septum and a PTFE valve (Scheme 2)]. The vessel was evacuated prior to laser irradiation to a pressure of 3 Pa and tested for leaks by checking the pressure after 20 min. In the case of experiments carried out in H_2/Ar or Ar atmosphere, the reaction vessel was filled with the gas using Edwards MB1000 pressure meter. After the experiment, the pressure in the vessel was measured again. Gaseous products formed during laser irradiation were sampled through the rubber septum and analyzed by mass spectroscopy and gas chromatography. Cross-linking of cured oligomers was checked by solubility tests. Samples on KBr substrate were immersed in dichloromethane or toluene for given time. Then they were removed from the solvent and dried. The insoluble residue and the soluble part were analyzed by FTIR spectrometry. The solution after solubility test was also analyzed by SEC and the results were compared with the SEC analysis of the parent sample.



Scheme 2. Pyrex vessel used for cross-linking experiments (1 – quartz window; 2 – rubber septum; 3 – PTFE valve; 4 – laser beam; 5 – sample on KBr or quartz substrate).

Laser ablation of model compounds [tetrakis(trimethylsilyl)methane and linear polydimethylsiloxane] was performed in the same way.

2.5. Measurements of UV absorptivity of oligomers and quantification of chemical changes induced by UV laser

The 193 nm absorption coefficients (ε_w, ε_1) were calculated as trend line gradients (Lambert–Beer law, using the least squares method) from UV absorbance measured for weighted thin films of polymers thoroughly cast on rectangle quartz substrates (UV values were corrected for absorption of quartz substrates). The thickness of the polymer film (in mg/cm^2) was calculated, relating its FTIR absorbance measured before experiment to calibration curves obtained from FTIR absorbance of weighted thin films, prepared on KBr substrates. The amount of TTSH group [$n_{D\ (TTSH)}$] cleaved of from the oligomer layers and decomposed to gaseous products (i.e. not contributing to cross-linking) was calculated from the molar amount of Si atoms in the gas phase, which was estimated by quantitative CG and FTIR analysis of carbosilane compounds. It was assumed that on complete decomposition, every TTSH group formed three molecules containing silicon atoms. The calculated amount of decomposed TTSH was related to their content in the irradiated oligomer film (with known thickness and irradiated area).

$$n_{D\ (TTSH)} = \frac{1}{3}\sum[Si]$$

where $n_{D\ (TTSH)}$ = molar amount of TTSH decomposed to gas; $\sum[Si]$ = sum of molar amounts of all Si atom containing volatile products.

The effect of UV laser irradiation on functional groups was estimated from the changes in the relevant IR spectra. The band intensity was measured before and after the experiment, and the relative depletion was determined. The simplest estimation of functional groups' TTSH decomposition (simple method A) can be expressed as:

$$\%\ \text{TTSH decomposed to gas} = 100 \times n_{D\ (TTSH)}/n_{(TTSH)}$$

$$n_{(TTSH)} = c_{(TTSH)} \times s \times w_i/10m_w$$

$n_{(TTSH)}$ = molar amount of TTSH originally present in irradiated part of sample; s = irradiated area of the treated film;

w_i = thickness of the irradiated film in mg/cm^2; m_w = mass of 1 mmol chain units [mg/mmol]; $c_{(TTSH)}$ = relative content of TTSH groups per 10 chain units.

$$\% \text{ TTSH depletion in the film} = 100 \times \left[1 - I_{a(TTSH)}/I_{b(TTSH)}\right]$$

$I_{a(TTSH)}$ = intensity of the FTIR absorbance band corresponding to TTSH, after the experiment; $I_{b(TTSH)}$ = intensity of the FTIR absorbance band corresponding to TTSH, before the experiment.

Because of different film thickness and composition, and thus their different UV absorption it was necessary to recalculate the experimental results to theoretical, idealized values. An ideally homogenous polymer film, containing exactly 10 μmol of chain units per cm^2 and cast uniformly on KBr substrate, that would be irradiated at given experimental conditions was taken as a standard. Thickness w_{10} (in mg/cm^2) and absorptivity α_{10} (absorbed portion of incidental beam in %) were calculated for every type of polymer, for a layer containing 10 μmol of chain units per cm^2 (10 U layer). Then the absorbed portion α of UV light (193 nm) was calculated for every irradiated film using the obtained UV coefficients. In first approximation, neglecting the non-linear effects in the absorption of the laser beam, the absorptivity α of an actually irradiated film and absorptivity α_{10} for 10 U film can be expressed by equations:

$$\alpha[\%] = [1 - \exp(-w_i \times \varepsilon_w)] \times 100\%$$

$$\alpha_{10}[\%] = [1 - \exp(-10 \times \varepsilon_1)] \times 100\%$$

w_i = thickness of the film in mg/cm^2; ε_w = film absorbance (mass) coefficient [mg^{-1} cm^2]; ε_1 = film absorbance (molar) coefficient (for 1 μmol of chain units per cm^2) [μmol^{-1} cm^2].

To estimate the absolute total amount of decomposed TTSH {intensities of the band at 842 cm^{-1} [(Si$-$(CH$_3$)$_3$) group] were used for calculation}, we used the value (%) obtained from the relative changes in FTIR spectra. The absolute value was related to the group content present in 10 U layer before the experiment. The value described decomposition as a percentage of TTSH in theoretical experiment with 10 U layer, under the experimental conditions. The amount of volatilized TTSH for 10 U layer was estimated by multiplying the amount obtained in an experiment by 10 U layer absorptivity α_{10} (in % of incidental beam) and dividing the result by absorptivity α of actual layer (in % of incidental beam). The obtained value was related to the content of TTSH groups in 10 U layer before sample irradiation. It represents the amount of TTSH lost to the gas phase in an idealized theoretical experiment. The amount of decomposed groups' TTSH, if the 10 U layer would be irradiated at the same conditions (method B), can be calculated with equations:

$$\% \text{ TTSH decomposed to gas} = 100 \times n_{D10\,(TTSH)}/n_{(TTSH)}$$

$$n_{D10\,(TTSH)} = n_{D\,(TTSH)} \times \alpha_{10}/\alpha_i$$

$$n_{(TTSH)} = c_{(TTSH)} \times s \times w_i/10m_w$$

α_i = absorptivity of the film (actual layer); α_{10} = absorptivity of the 10 U layer film.

$$\% \text{ TTSH depletion in the film} = 100 \times \left[1 - I_{a(TTSH)}/I_{b(TTSH)}\right] \times (\alpha_{10}/\alpha_i) \times (w_i/w_{10})$$

w_i = actual thickness of the irradiated film [mg/cm^2]; w_{10} = thickness of 10 U film [mg/cm^2].

2.6. Control cross-linking experiments

2.6.1. Method A

Oligosiloxanes (PS-120 or HMS-301) were admixed with 1,5-hexadiene ([SiH]$_0$/[CH=CH$_2$] = 1) and diluted with toluene ([SiH] = 1.76 mol/dm^3 for PS-120 and 0.38 mol/dm^3 for HMS-301). After a short homogenization with magnetic stirring, FTIR spectra of starting mixtures, cast as thin films on KBr pellets, were recorded. Karstedt's catalyst was added ([Pt]/[CH=CH$_2$] = 1×10^{-4}) and mixtures were stirred for 2 min at room temperature. Each solution was cast on a KBr plate and its FTIR spectrum was recorded after solvent evaporation (after 15 min and then 40 min). Each sample was then left in an oven at 50 °C for 2 h (FTIR spectra were recorded again). Each time KBr plates were placed in desiccator and dried under vacuum to remove all residual volatiles. FTIR spectrum of cross-linked and dried film was recorded and then the usual CH$_2$Cl$_2$ solubility tests were performed.

2.6.2. Method B

Oligosiloxane HMS-301 was admixed with a mixture of 1,5-hexadiene ([SiH]$_0$/[CH=CH$_2$] = 0.9) and Karstedt's catalyst ([Pt]/[CH=CH$_2$] = 4×10^{-5}). After a short homogenization with magnetic stirring, the mixture was cast on a KBr plate. The plate was placed in a closed cell filled with N$_2$ and 1,5-hexadiene ([SiH]$_0$/[$\sum$CH=CH$_2$] = 0.5) was added through a septum. The cell was placed in an oven (45 °C) for a given time. Si$-$H disappearance was observed with FTIR. KBr plate was placed in desiccator and dried under vacuum to remove all residual volatiles. FTIR spectrum of cross-linked and dried film was recorded and then the usual CH$_2$Cl$_2$ solubility tests were performed.

3. Results and discussion

We have studied the effect of polymer structure and experimental conditions on the composition of products obtained after irradiation with 193 nm UV laser. Series of experiments were performed in order to estimate the chemical changes, that occurred during the photolysis of tris(trimethylsilyl)hexyl-substituted oligosiloxanes. Oligosiloxanes with variable amount of TTSH-functionalized units were used in order to study the sequence of photolytic reactivity of functional groups, and to relate it to the proportion of decomposition products. The results were compared to those found for model compounds: tris(trimethylsilyl)methane and linear polydimethylsiloxane.

UV (193 nm) absorption of irradiated oligosiloxane films was measured (Table 3). Although the method used for the estimation of absorption coefficients was very simple, it is clear

Table 3
UV (193 nm) absorbance of studied oligosiloxanes (homogeneous films uniformly cast on quartz substrates) and UV parameters for 10 U layers (polymer films with thickness of 10 μmol of chain units per 1 cm^2)

Polymer	c		w_{10} [mg/cm^2]	m [atom m.u.]	m_w [mg/μmol]	ε_w [mg^{-1} cm^2]	ε_1 [μmol^{-1} cm^2]	α_{10} [%]
	TTSH	Me						
PDMS	–	20	0.742	74.2	0.0742	0.0189	0.0014	1.389
II	3	17	1.602	160.2	0.1602	5.388	0.861	99.98

c – Relative content of functional groups per 10 chain units; w_{10} – weight of 1 cm^2 for 10 U film (10 μmol of chain units per cm^2); m – average chain unit mass; m_w – mass of 1 μmol chain units; ε_w – film absorbance coefficient (mass); ε_1 – film absorbance coefficient (molar); α_{10} – absorptivity [part of intensity of incidental beam absorbed in 10 U polymer film (layer containing 10 μmol of chain units per cm^2)].

that oligosiloxanes with TTSH side groups absorb UV light more effectively by one order of magnitude compared to a linear polysiloxane without bulky side groups (PDMS).

3.1. Model compounds – tris(trimethylsilyl)methane and linear polydimethylsiloxane

It is known that carbosilanes exhibit maxima of their UV absorption bands close to 193 nm [17,18], which is the operating wavelength used in this work. Thus, in order to analyze the UV laser initiated decomposition of $Me_3Si–C$ containing oligomers, several experiments with model compound – $(Me_3Si)_4C$ – were made under vacuum (Table 4). The carbosilane was found to be highly UV sensitive. UV laser irradiation at 193 nm of $(Me_3Si)_4C$ film under conditions (irradiation time and dose) analogous to those applied in experiments with oligosiloxanes resulted in almost complete decay of the irradiated material. It was proven by a substantial decrease of intensity of symmetrical CH_3 deformation mode ($Si–CH_3$ band at 1260 cm^{-1} [19]) in FTIR spectra (Fig. 1). After a short experiment (1 min, 6.8 J/cm^2 total UV dose) FTIR spectra showed only ca. 21% of original intensity of $\delta(Si–CH_3)$ band.

The main volatile product formed during the experiment (Table 4) was Me_3SiH (~40 mol%), accompanied by $(Me_3Si)_2CH_2$ and Me_4Si. Methane and ethane were also present in the mixture of gaseous products, the former one in a substantial amount. It suggests that UV photon initiated cleavage of the inner Si–C in $(Me_3Si)_4C$ and generation of $Me_3Si^{\bullet}$ radicals are the major mechanism of decomposition of the model compound. It correlates well with the difference in the bond length between the central C–Si and Si–Me (respectively, 1.886 Å and 1.875 Å in $(Me_3Si)_3CH$ [1]). Si–Me bond splitting occurs more readily at higher energy dose absorbed by the sample (decrease of Me_3Si-containing products in favor of CH_4). At the same time, a disappearance of a short wave band in UV spectrum (190 nm) typical to tris(trimethylsilyl)methane occurred during laser irradiation of the sample.

On longer irradiation (12 min, 10.1 J/cm^2 total UV dose), $Me_3SiOSiMe_3$, Me_3SiOMe, Me_3SiOH and cyclic hexamethyltrisiloxane (D_3) appeared in gas phase. A broad band at ~1030 cm^{-1} with a shape typical for longer or branched polysiloxane chains emerged in FTIR spectra of solid film {peaks in the region of 1100–1000 cm^{-1}, typical for ν(Si–O–Si) band [20]}. After irradiation with a total dose of 161 J/cm^2 this band becomes significant. Formation of oxygen containing products can be explained as a result of reaction of $Me_3Si^{\bullet}$ and $Me_2Si:$ radicals with traces of O_2 in the vessel [the measured increase of the pressure in 39 ml vessel, caused by the leak, was close to 0.5–0.8 Pa/min (1.7–2.8 nmol O_2 per minute)]. The amount of $(Me_3Si)_2O$ and the intensity of Si–O–Si band at 1030 cm^{-1} increased not only on the increase of the UV dose absorbed by the sample but also on the volume of oxygen present in the experimental

Table 4
Relative composition of the mixture of gaseous products obtained in UV laser experiments

Sample	$(Me_3Si)_4C$				PDMS		(I)	(II)	(I)	(II)	(I)	(II)
	Vacuum				Vacuum		Vacuum		H_2/Ar		Ar	
E [J/cm^2]	6.6	161	6.8	236	6.2	219	197	219	259	287	336	365
P_0 [Pa]	<3	<3	124	136	<3	< 3	<3	<3	~1 × 10^5	~1 × 10^5	~1 × 10^5	~1 × 10^5
P_1 [Pa]	12	12	140	247	2	20	101	56	n/a	n/a	n/a	n/a
CH_4 [mol%]	11.71	31.60	21.34	20.55	69.34	42.89	21.88	24.63	30.34	28.38	26.42	41.09
C_2H_4 [mol%]	2.22	5.23	0.49	3.39	2.71	3.69	5.11	4.88	2.17	3.35	2.26	3.59
C_2H_6 [mol%]	5.48	29.59	0.45	10.40	14.02	19.45	13.86	18.03	11.14	12.43	9.48	14.01
C_3H_4 [mol%]	0.24	0.25	–	0.20	0.72	0.24	0.24	0.21	2.71	2.02	2.23	3.23
C_3H_8 [mol%]	0.35	4.71	–	2.39	1.88	2.61	2.61	1.61	0.23	0.10	0.24	0.41
C_6H_{14} [mol%]	–	–	–	–	–	–	5.56	3.11	5.17	4.63	4.26	4.96
Me_2SiH_2 [mol%]	1.80	0.64	0.84	2.57	0.35	0.46	0.10	0.52	0.58	0.39	0.75	0.25
Me_3SiH [mol%]	47.44	15.68	42.07	32.05	10.98	10.77	33.94	35.66	26.17	39.62	33.28	22.95
Me_4Si [mol%]	2.38	2.46	4.00	12.59	–	2.58	3.48	1.12	4.16	0.74	4.08	1.90
$(Me_3Si)_2O$ [mol%]	4.08	8.62	13.45	13.29	–	0.33	8.52	7.16	13.48	4.22	13.59	4.24
$(Me_2SiO)_3$ [mol%]	–	–	3.44	0.59	–	7.12	1.43	0.88	2.37	2.85	2.34	1.37

E – energy absorbed by the sample [J/cm^2]; P_0 – pressure in the cell before start [Pa]; P_1 – decomposition products' pressure [Pa]; n/a – not analyzed.

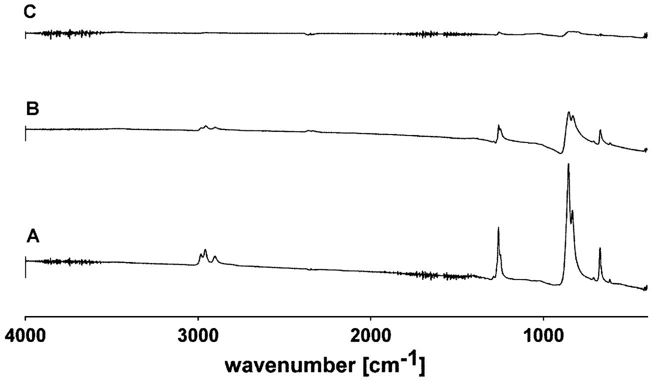


Fig. 1. FTIR spectra of $(Me_3Si)_4C$ film before UV laser irradiation in vacuum (A), after irradiation with 6.6 J/cm^2 dose (B) and 10.1 J/cm^2 dose (C) (all the stacked spectra within each experiment have the same absorbance scale).

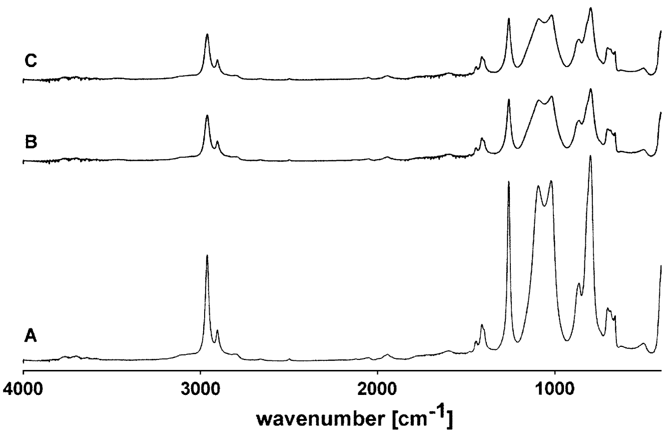


Fig. 2. FTIR spectra of polydimethylsiloxane film before UV laser irradiation in vacuum (A), after irradiation with 6.2 J/cm^2 dose (B) and 219 J/cm^2 dose (C).

cell (Table 5). This observation is in accordance with results obtained for UV (193 nm) laser photolysis of 1,3-disilacyclobutane in oxygen in excess of noble gas [21], which yields solid methylsilicone films [ν(Si—O—Si) band at 1058 cm^{-1}]. The mechanism of reaction involves formation of silylene biradicals MeHSi: their reaction with oxygen and subsequent polymerization. At the same time a secondary process of photolysis, of originally formed oligosiloxanes, seems to occur with the increase of UV dose.

In order to get an insight into the behavior of siloxane backbone of linear polymers under the experimental conditions applied to TTSH-oligosiloxanes, we tested also a commercial, linear polydimethylsiloxane. UV laser irradiation of polydimethylsiloxane film in vacuum did not cause important changes in the polymeric material. It is known that the cleavage of Si—O bond of gaseous permethyldisiloxanes occurs readily under thermolysis conditions, via rearrangement of Si—O bonds as the major degradation mechanism [22]. It does not take place during photolysis [22]. UV laser irradiation of alkylsiloxanes leads mostly to photolysis of Si—C bonds and formation of alkyl radicals [23]. Their recombination and degradation can give methane, ethane, and other hydrocarbons. Photolytic cleavage of Si—O—Si bonds in polymer chain occurs to a much smaller extent, which is usually indicated by the formation of minor quantities of $(Me_3Si)_2O$, $Me_3SiOSiMe_2OSiMe_3$ (OMTS), hexamethylcyclotrisiloxane (D_3) and octamethylcyclotetrasiloxane (D_4). However, megawatt ArF laser irradiation of gaseous disiloxanes, focused to achieve incident fluence of 1 J/cm^2, was reported to give chemical vapor deposition of nano-sized polyoxocarbosilane powders having large surface area [24].

Only some minor changes occurred after irradiation of polydimethylsiloxane (Fig. 2, 6.4 J/cm^2 and 227 J/cm^2). New bands, corresponding to Si—H bond, appear at 2142 cm^{-1} [ν(Si—H)] and at 912 cm^{-1} [δ(Si—H)], in the prolonged experiment (60 min, 318 J/cm^2 total dose). Partial splitting of Si—C bonds (new bands at 844 cm^{-1} and 755 cm^{-1} and a very weak but still recognizable one at 1250 cm^{-1}) as well as the change of the shape of Si—O—Si doublet (1090 cm^{-1}) indicates cleavage of the polymer chain. At the same time the formation of gaseous products was observed [GC/FID analysis (Fig. 3,

Table 5
Formation of volatile $(Me_3Si)_2O$ and deposition of solid siloxane material on KBr substrate (FTIR, the intensity of Si—O—Si band at 1030 cm^{-1}) during the laser irradiation of $(Me_3Si)_4C$

O_2 [nmol]	E [J/cm^2]	Y [nmol]	F [%]
<10	6.6	13.63	0.0
<10	10	18.29	0.0
<10	161	25.24	0.8
339	6.8	8.28	0.6
588	68	85.33	3.8
503	236	357.56	16.8

O_2 — oxygen in the cell before the experiment; E — energy absorbed by the sample [J/cm^2]; Y — the amount of $(Me_3Si)_2O$ in the gas phase; F — relative increase of intensity of siloxane band at 1030 cm^{-1}.

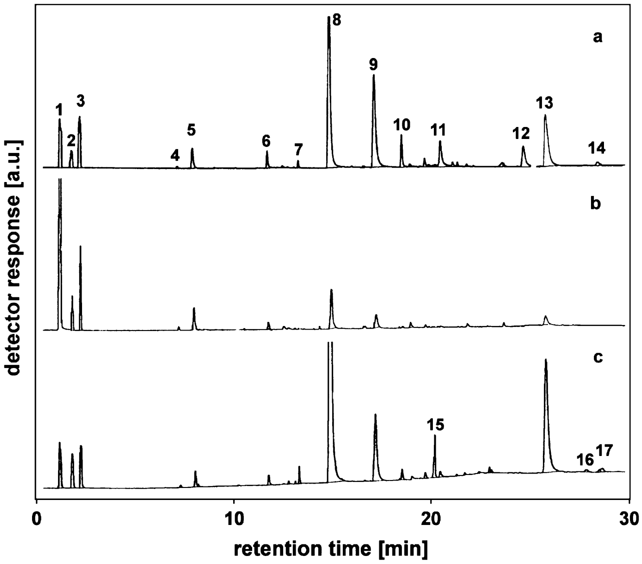


Fig. 3. Typical GC/FID traces of gas and volatile products after UV laser photolysis of $(Me_3Si)_4C$ and functionalized oligosiloxanes. (a) $(Me_3Si)_4C$, (b) poly(dimethyl)siloxane (PDMS), (c) TTSH-oligosiloxanes. Peak labels: 1 — CH_4, 2 — ethylene, 3 — C_2H_6, 4 — C_3H_4, 5 — C_3H_8, 6 — Me_2SiH_2, 7 — n-C_4H_{10}, 8 — Me_3SiH, 9 — Me_4Si, 10 — Me_3SiOH, 11 — Me_3SiOMe, 12 — $(HMe_2Si)_2CH_2$, 13 — $Me_3SiOSiMe_3$, 14 — $Me_3SiOSiMe_2OSiMe_3$, 15 — n-C_6H_{14}, 16 — hexamethylcyclotrisiloxane (D_3), 17 — octamethylcyclotetrasiloxane (D_4).

Table 4)]. It suggests that in the case of PDMS the photolytic process proceeds slowly with partial Si–C and C–H bonds' change. The main gaseous products found were CH_4 and C_2H_6, indicating generation of methyl radicals by cleavage of Si–C bond and their subsequent recombination. The amount of Me_3SiH was remarkably smaller than those observed for $(Me_3Si)_4C$ laser photolysis, but it proved the additional cleavage of terminal siloxane bonds (Me_3Si–O–Si) in the main chain. The effects are quite small and FTIR analysis of δ(Si–CH_3) bands did not give qualitative results, due to the contradictory effects of δ(Si–CH_3) band reduction and broadening of Si–O–Si bands. In the case of Si–H and other new formed Si–C bands, the results are in good accordance with the energy absorbed by the sample.

3.2. *Tris(trimethylsilyl)hexyl-modified oligosiloxanes*

Two types of TTSH-modified oligosiloxanes were studied, *homo*-(TTSH)-oligosiloxane (I) and *co*-(TTSH)methyl-dimethyl-oligosiloxane (II). The samples were irradiated in vacuum, an inert gas (Ar) and a reductive (H_2/Ar) atmosphere (Table 4). Viscosity of the parent polymers was different [white waxy solid (I) and transparent viscous liquid (II)]. After UV laser irradiation the appearance of polymer (I) was not changed, whereas a crust was formed on the top of the liquid film of (II), that may point to a screening effect of the cured surface. Any other visible changes (like ablation, fog, condensate on the walls, etc.) were not observed during the experiments.

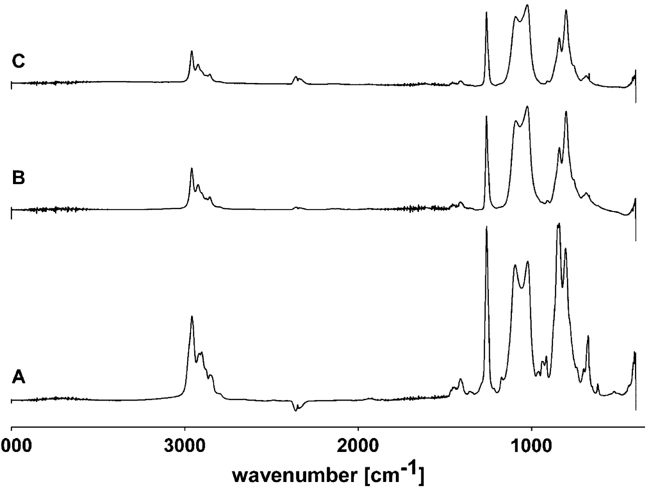


Fig. 5. FTIR spectra of (II) before UV laser irradiation in vacuum (A), after irradiation with 220 J/cm^2 dose (B) and 388 J/cm^2 dose (C).

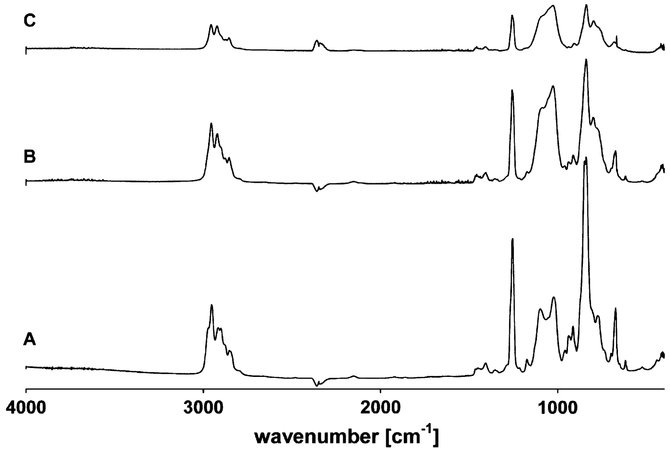


Fig. 4. FTIR spectra of (I) before UV laser irradiation in vacuum (A), after irradiation with 197 J/cm^2 dose (B) and 351 J/cm^2 dose (C).

Significant changes were observed in FTIR spectra of both species cross-linked in vacuum (Figs. 4 and 5). The intensities of ρ(Si–CH_3) (849 cm^{-1}) and δ(Si–CH_3) (1256 cm^{-1}) bands decreased compared to other bands. In the case of (I) the peak intensity of ρ(Si–CH_3) (840 cm^{-1}), related to ν(Si–O–Si) in 950–1200 cm^{-1} region, is smaller by 95% (Table 6). The respective average decrease for (II) is 73%. The cross-linked product remaining after solubility tests showed even more significant differences. The shape of ν(Si–O–Si) band changed remarkably during UV laser irradiation, from a broad band with two maxima (1020 cm^{-1} and 1090 cm^{-1} typical for linear oligosiloxane with chain length >20) to an asymmetric broad peak of more complex structure with a maximum at 1026 cm^{-1} and a shoulder at ~1090 cm^{-1} (typical for branched or longer polysiloxane chains). Characteristic changes were also observed in the shorter wavelength range. A shoulder at 2973 cm^{-1} decreased, whereas peaks at 2924 cm^{-1} and 2855 cm^{-1} increased. Similar effects were observed for oligomer (II). It suggests that TTSH-modified siloxanes decompose on irradiation at 193 nm via photolysis of Si–C bonds. At the same time structural rearrangement, leading to formation of Si–O–Si bonds, occurs. It may indicate the cleavage of the siloxane chain, since 193 nm photon energy should be also sufficient for the cleavage of Si–O bond. However, since only limited Si–O–Si rearrangement was observed during the experiments with PDMS irradiated with similar UV doses, those noted for TTSH-siloxane samples are most probably caused by structural changes in TTSH group (formation of Me_3Si radical and its reaction with traces of oxygen in the reaction vessel). The absorption coefficients measured for PDMS and for oligomer (II) indicate that most of UV energy was absorbed by TTSH groups. The suggestion is supported by the composition of the gaseous products' mixture, formed on irradiation of oligomers (I)

Table 6
Changes in the composition of oligosiloxane films (data derived from FTIR spectra and standardized to band at 1020 cm^{-1})

Atmosphere	Polymer	E [J/cm^2]	A [%]	B [%]	C [%]
Vacuum	PDMS	219	1.9	–	–
	(I)	197	64.98	89.25	81.44
	(II)	219	47.39	94.46	80.70
H_2/Ar	(I)	259	92.91	100.00	99.99
	(II)	287	48.19	99.98	83.32
Ar	(I)	336	68.23	92.36	84.60
	(II)	365	24.54	81.72	61.54

E – energy absorbed by the sample [J/cm^2]; A – relative decrease of 1256 cm^{-1} band; B – relative decrease of 851 cm^{-1} band; C – relative decrease of 843 cm^{-1} band.

and (II). In the case of sample (I) the mixture of gaseous products formed in vacuum contained mostly CH_4 (~22%) and Me_3SiH (~34%), with a significant amount of C_2H_6 and $(Me_3Si)_2O$ (Table 4). Comparative results were obtained for polymer (II). The appearance of hexane (3–5 mol%) for (I) and (II) after their UV laser irradiation proves the cleaving off TTSH groups from the polydimethylsiloxane chain.

No significant variation in FTIR spectrum was observed for copolymer (II) on changing the experimental conditions (experiments carried out in Ar or H_2/Ar atmosphere). Homopolymer (I) showed a considerable sensitivity towards reductive atmosphere. The experiment carried out in a mixture of H_2 and argon resulted in higher degradation of the Si–CH_3 bonds. The atmosphere controls the composition of obtained volatile products (Table 4). An important increase of the relative amount of CH_4 was observed for (I) in the presence of H_2. Surprisingly, the ratio between Me_3SiH and CH_4 is smaller than that found for $(Me_3Si)_4C$. Apparently, hydride radicals are formed more readily than $Me_3Si^•$ ones and their presence may induce the dissociation of Si–CH_3 bonds under the experimental conditions.

The chain branching and cross-linking were confirmed in solubility test. The presence of completely insoluble fraction was proved by FTIR and related to the immersion time (Fig. 6, Table 7). Linear polymers (before cross-linking experiment) dissolved completely in dichloromethane within few seconds. After UV laser treatment the polymer film was much more solvent resistant. Still, it dissolves partly in CH_2Cl_2. The solutions obtained during solubility test evaporated on KBr substrate left films showing FTIR spectra similar to those of not irradiated polymer. The changes in the molecular weight distribution caused in the process of polymer cross-linking were studied by SEC of the soluble fraction (Fig. 7). For both UV laser irradiated polymers, it consists mostly (>70%) of low molecular weight siloxanes ($M_w \approx 400$). The formation of cyclic and linear oligosiloxanes [hexamethylcyclotrisiloxane (D_3), octamethylcyclotetrasiloxane (D_4), octamethyltrisiloxane (MDM) and decamethyltetrasiloxane (MD_2M)] was also confirmed by DI-MS analysis. The presence of oligomeric fraction is in accordance with the formation of oligosiloxanes by the postulated reaction of $Me_3Si^•$ radicals with oxygen.

EDX analysis of oligomers (I) and (II) after the UV irradiation confirmed the loss of TTSH groups during the experiment (Table 8). Even though a semi-quantitative method of analysis for the EDX results was applied, the analysis of uncured oligomer (I) film matches the calculated formula composition. On the contrary, the analysis of the oligomer (I)

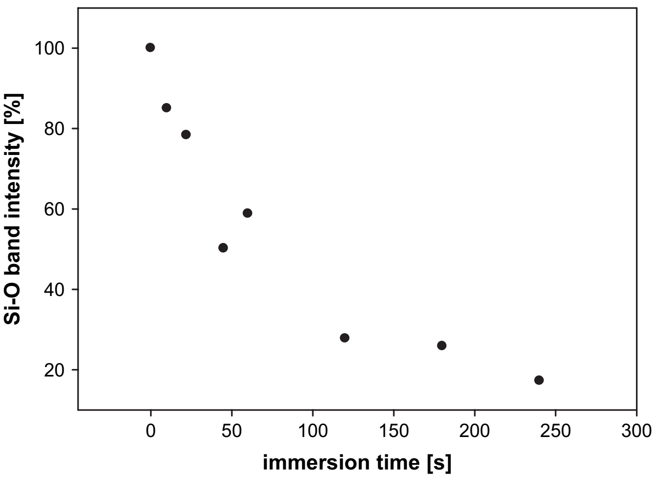


Fig. 6. Solubility of (I) in CH_2Cl_2 after irradiation with UV laser in vacuum (351 J/cm^2 dose) (relative peaks' area in the range 1324–567 cm^{-1} and the intensity of siloxane bond at 1030 cm^{-1} compared to the immersion time of the sample in CH_2Cl_2).

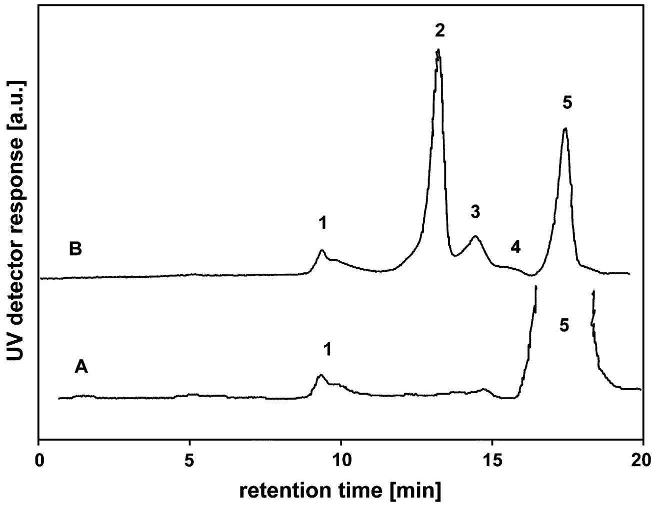


Fig. 7. SEC analysis of TTSH-oligosiloxane (I). Typical LC/UV traces of polymer before (a), and after (b) UV laser photolysis, (1) original polymer, (2), (3), (4) newly formed oligosiloxanes (5) solvent (CH_2Cl_2) used for sample preparations.

Table 7
Solubility of TTSH-oligosiloxane films in CH_2Cl_2

Polymer	Atmosphere	E [J/cm^2]	d [mg/cm^2]	Δ [%]			
				t(20)	t(30)	t(60)	t(120)
(I)	Vacuum	197	0.76	71.32	–	45.31	27.54
(II)		219	0.87	93.36	–	85.73	70.97
(I)	H_2/Ar	259	0.36	–	82.52	81.66	–
(II)		287	0.66	87.40	70.81	70.33	68.26
(I)	Ar	336	0.58	–	95.94	–	56.87
(II)		365	1.45	–	94.05	–	61.88

E – energy absorbed by the sample [J/cm^2]; d – film thickness; Δ – decrease of relative intensity at 1030 cm^{-1} after given immersion time t [s].

Table 8
EDX analysis of films (analyzed area of 50 × 50 μm) after UV photolysis by excimer pulse laser (193 nm) in vacuum

Sample	(I)	(I)	(I)	(II)	(II)	(II)	PDMS
E [J/cm^2]	–	0	336	–	0	219	–
Value	a	b	b	a	b	b	a
x_C [atom%]	76.19	74.29	55.75	68.13	–	59.26	50.00
x_O [atom%]	4.76	10.87	22.21	10.99	–	17.59	25.00
x_{Si} [atom%]	19.05	14.84	21.54	20.88	–	22.92	25.00

E – energy absorbed by the sample [J/cm^2]; x_C – relative concentration of carbon; x_O – relative concentration of oxygen; x_{Si} – relative concentration of silicon; a – theoretical (calculated) value; b – experimental value.

after UV curing experiment differs remarkably from its initial composition (theoretical and measured). It is close to the theoretical composition of PDMS, which could be formed from oligomer (I), in case when each TTSH group would be replaced by methyl group. Similar results were obtained with (II). For both polymers, the EDX analysis confirmed the loss of TTSH groups from the main siloxane chain during the UV experiment.

3.3. Control cross-linking by hydrosilylation

Control cross-linking by hydrosilylation tests was performed in order to compare their results with the observed decrease of film thickness during cross-linking of TTSH-oligosiloxanes. 1,5-Hexadiene was chosen as the cross-linking agent since its structure resembles alkyl chain left after formation of $Me_3Si^{\bullet}$ radicals from TTSH unit. Oligosiloxanes PS-120 and HMS-301 were used for cross-linking by hydrosilylation, since they were utilized, respectively, for preparation of (I) and (II). Solubility probing on immersion in CH_2Cl_2 showed that it is controlled by the degree of cross-linking of the material. The hydrosilylation reaction ($[SiH]_0/[CH{=}CH_2] = 1.0$, $[Pt]/[CH{=}CH_2] = 1 \times 10^{-4}$) was a very fast process. Addition of Pt-divinyltetramethyldisiloxane complex to a mixture of oligosiloxanes and 1,5-hexadiene resulted in uncontrollable and exothermic cross-linking. In order to achieve some control over the process, two different strategies were applied. The goal was to slow down the reaction rate (dilution with an inert solvent or catalyst concentration decrease) and increase of degree of cross-linking (post-cross-linking in vapors of 1,5-hexadiene at elevated temperatures).

Dilution of the reagents with toluene slowed down the cross-linking and polymer films could be cast from the solutions (average film thickness 5.5 mg/cm^2). Solutions of higher relative concentration of Si–H (experiments with PS-120) cured faster and the degree of cross-linking was higher. Thirty-six percent of Si–H in PS-120 was consumed after 10 min at room temperature [the relative amount was calculated in comparison to $\delta(CH_3)$ bending band at 1261 cm^{-1}], whereas only ~20% of Si–H groups in HMS-301 reacted under respective conditions. For both polymers, the conversion of Si–H groups did not increase with time, neither at elevated temperature. When immersed in CH_2Cl_2, both films swell and tend to peel off from KBr plate (after drying the film sets back). After the swelling cycle 17% of cross-linked PS-120 and 13% of HMS-301 were left. The dissolution is fast and the film thickness decreases after 50 s and remains almost the same after 230 s.

Decrease of the amount of catalyst ($[Pt]/[CH{=}CH_2] = 4 \times 10^{-5}$) slowed down the hydrosilylation to the extent that no reaction occurred for 3 days, even at 45 °C. Polymer films (mixtures of HMS-301, 1,5-hexadiene and Karstedt's catalyst) of various thickness were thus subjected to vapors of 1,5-hexadiene at 45 °C for 25 h. HMS-301 was chosen, due to smaller number of Si–H moieties, and therefore lower degree of cross-linking and better penetration of 1,5-hexadiene. Under the applied conditions the Si–H band at 2166 cm^{-1} disappeared completely. The cell was then evacuated, and the dried samples were immersed in CH_2Cl_2. Highly cross-linked HMS-301 was partly soluble (Table 9). It was also found that thinner samples were more solvent resistant than thicker ones.

Table 9

Solubility in CH_2Cl_2 of oligosiloxane films cross-linked by hydrosilylation of 1,5-hexadiene

Run	d [mg/cm^2]	Δ [%]				
		t(10)	t(20)	t(30)	t(60)	t(120)
1	1.38	98.26	96.15	96.85	88.11	83.36
2	1.71	82.94	67.06	56.38	57.03	55.99
3	2.56	88.26	76.39	71.90	65.44	59.89

d – Film thickness; Δ – decrease of relative intensity at 1030 cm^{-1} after given immersion time t [s].

Comparison of the hydrosilylation cross-linked films, with those reported for TTSH-oligosiloxanes cured on UV laser irradiation, did not show any advantage of the former materials. On the contrary, thin film preparation was problematic and high degree of cross-linking required additional post-curing. It seems that, whereas classical hydrosilylation method is very useful for formation of standard cross-linked silicones, it is not suitable for the preparation of uniform and thin polymer layers. The use of TTSH groups for cross-linking is favorable, especially as it brings about the possibility of localized partial destruction of a top layer of a sample.

4. Conclusions

We have described a new process of cross-linking of siloxane polymers by high energy 193 nm UV excimer laser induced photolysis of tris(trimethylsilyl)hexyl group, without any additional catalyst or initiator. The formation of cross-linked films was confirmed by FTIR, GC/MS, SEC, SEM and solubility tests.

Tris(trimethyl)hexyl moiety, due to its sterically hindered structure and thus elongated inner Si–C bonds, was found to be exceptionally photolysis prone, and to decompose with liberation of Me_3Si radicals upon UV laser irradiation. FTIR spectra of the UV laser light treated oligomers as well as the composition of gaseous products formed during the reaction prove such a cross-linking pathway. Similar process was observed in a model UV laser experiment with $(Me_3Si)_4C$ film, which decomposed completely with the formation of Me_3SiH.

The content of Me_3SiH and *n*-hexane found in gaseous products after laser treatment of TTSH-functionalized oligomers was exceptionally high, compared to those obtained in experiment runs with linear PDMS. However, the total amount of other hydrocarbons is substantially higher than that expected from the decomposition of TTSH groups only. Thus, CH_4 present in the gas phase is considered to be a cumulative result of Si–Me bond cleavage in TTSH and the siloxane backbone. UV photon absorption by siloxane bonds leads also to partial cleavage of the main chain. Traces of Me_3SiH and volatile oligosiloxanes present as decomposition products in the gas phase, after UV laser irradiation of PDMS, confirm such a reaction course.

The described effects induce formation of cross-links as a result of recombination of radicals (Si-centered in the main chain and in side TTSH groups), as well as formation of bridges between longer chains by short siloxane linkages. The latter can be formed with the participation of Me_2Si: biradicals. The extent of cross-linking depends on the thickness of polymer film. UV irradiation operates most effectively within uppermost part of the sample. The intensity of laser beam is significantly reduced in deeper layers of polymer film. Easy introduction of various curable groups into TTSH-siloxane systems was previously proven [3,25]. Thus, the properties of cured material can be designed on different levels. Despite of specialty equipment requirement, and thus being cost-inferior to standard methods of polymer cross-linking, the reported process seems to have a significant potential for preparation of high performance materials. For example, local destruction of tris(trimethylsilyl)-methyl groups in top layers of T_{si}-functionalized polymer films can be utilized in nano-lithography.

Acknowledgements

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