

# Highly Thermally Resistant UV-Curable Poly(siloxane)s Bearing Bulky Substituents

A. Kowalewska\* and W. A. Stańczyk

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences,  
Sienkiewicza 112, 90-363 Łódź, Poland

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Novel thermally stable polysiloxanes with bulky side chain tris(trimethylsilyl)hexyl and reactive glycidopropyl substituents were synthesized via hydrosilylation route and were further cross-linked in the presence of diaryliodonium salt upon exposure to UV light. The cross-linking was necessary to stabilize the shape of the linear tris(trimethylsilyl)hexyl group modified siloxanes which potentially can be used as membranes for fluid separation at high temperatures. Formation of oligoether cross-linking chains was proved by solid state  $^{13}\text{C}$  NMR analyses. Six copolymers of diverse molecular architecture were made based on methylsiloxane and methylsiloxane-*co*-dimethylsiloxane backbones. The ratio between [tris(trimethylsilyl)hexyl](methyl)-siloxane and (glycidopropyl)(methyl)siloxane monomeric units in polymer chain, ranging from 0.5 to 5.4, was found to be an important factor affecting the thermal properties of cross-linked films, as shown by TGA.

## Introduction

In recent years, functionalized polysiloxanes with a variety of substituents at the silicon atom, other than a methyl group, have attracted increasing academic and industrial attention.<sup>1</sup> Such polymers with inorganic backbones are challenging because of their physical and chemical differences from their organic counterparts. They allow for a unique combination of traditionally well recognized features such as high flexibility and ability to preserve physical properties over a wide range of temperatures with a variety of novel factors brought in by architecturally diverse side substituents. Often, by means of a relatively simple modification process, features such as solubility,<sup>2</sup> ionic conductivity,<sup>3</sup> or liquid crystallinity<sup>4</sup> are created and materials with enhanced free volume<sup>5</sup> and increased thermal and hydrolytic stability (see below) can be synthesized. Industrial demand for such specialty products is still growing because, apart from the recently dominant hydrosilylation-based modification processes, novel catalytic routes have become available. They allow now for effective attachment of side chain moieties bearing various functional groups, using, e.g., organometallic complexes of platinum, palladium, ruthenium, and molybdenum as catalysts.<sup>6</sup>

As part of our continuing research on application of the tris(trimethylsilyl)methyl ("trisyl",  $\text{TSi}$ ) moiety in polymer chemistry, we have been especially interested in the synthesis of siloxane polymers with high thermal stability as potential membrane materials in separation processes. "Trisyl" type substituents, due to their steric bulk and thus a stabilizing effect comparable to that of  $-\text{C}_6\text{H}_2(t\text{-Bu})_3$ ,<sup>7</sup> allowed for a deeper knowledge of new processes and new stable structures in the field of organometallic chemistry. The much greater steric protection exerted by "trisyl" and related substituents, compared to that of other groups, sufficiently limits reactivity of organometallic and organosilicon systems. Much chemistry previously unobservable, because of the great ease of nucleophilic attack at functional centers in "normal" organosilicon systems, can be revealed by using the very bulky ligand to hinder that attack.<sup>8</sup> In our previous paper we have described for the first time the synthesis of "trisyl"-modified macromolecular systems: polysiloxanes and polystyrene-*co*-chloromethylenestyrene.<sup>9</sup> Dramatic changes of properties were observed, especially in the case of modification of polysiloxane backbones. The value of glass transition temperature increases from  $-139^\circ\text{C}$  for poly(methylhydrosiloxane) to  $\sim 70^\circ\text{C}$  for its "trisyl"-modified analogue, reflecting the substantial increase in the macromolecular chain rigidity of the novel polysiloxanes bearing very bulky side chain substituents.

\* To whom correspondence should be addressed. Phone: +48 42 681 4041. Fax: +48 42 684 7126. E-mail anko@cbmm.lodz.pl.

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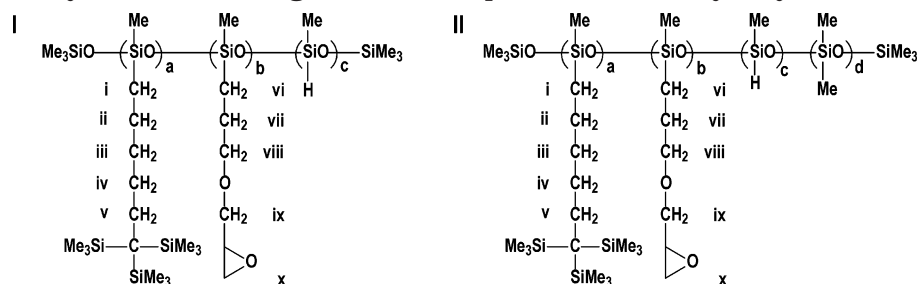
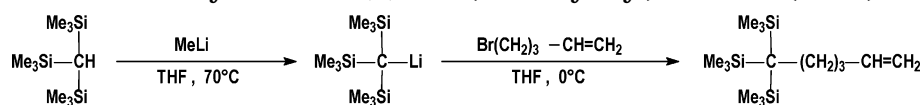
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**Scheme 1. Linear Polysiloxanes Bearing Tsi Side Groups and Cationically Polymerizable Oxirane Moieties****Scheme 2. Synthesis of 6,6,6-Tris(trimethylsilyl)Hex-1-ene (TTSH)**

Closer approach to applied side (membranes) of novel "trisilated" systems requires, however, not only an increase in thermal and hydrolytic resistance but also formation of a stable network. In this paper we report on a synthetic route for preparation of such cross-linked materials. UV-initiated cationic photocuring<sup>10</sup> often utilizes oxirane rings<sup>11</sup> (e.g., for preparation of adhesives, coatings, and photoresists).<sup>12</sup> Following this approach, structurally diverse linear polysiloxanes, bearing sterically overloaded T<sub>Si</sub> side groups in parallel with cationically polymerizable oxirane moieties (Scheme 1) were made and described below, both with preliminary evaluation of the properties of the novel polysiloxane elastomers.

**Experimental Section**

**Analysis, Reagents, and General Methodology.** All hydrosilylation reactions were performed using standard Schlenk or syringe techniques under an atmosphere of argon. <sup>1</sup>H NMR spectra were recorded, in CDCl<sub>3</sub> as a solvent, on Bruker AC-200 MHz or DRX-500 MHz spectrometers with TMS as a reference. <sup>29</sup>Si NMR spectra were obtained using a paramagnetic relaxation agent: chromium acetylacetonate [Cr(acac)<sub>3</sub>]. Solid-state NMR spectra were recorded on a Bruker MSL-300 MHz spectrometer. GC-MS EI analyses were run on a Finnigan MAT 95 spectrometer equipped with a BD-1 (30-m) capillary column in the temperature range (GC) 60–240 °C, programmed at the rate of 20 °C/min. Size-exclusion chromatography (SEC) was performed using a Wyatt Optilab 903 apparatus equipped with two (TSK G4000HLX and G2000HLX) columns and working with dichloromethane as a solvent. A differential refractive index detector was used and molecular masses were derived from a calibration curve based on polystyrene standards. Differential scanning calorimetry traces were recorded with a 2920 Modulated DSC apparatus (TA Instruments) calibrated to indium and copper in nitrogen atmosphere in the following temperature range: first heating (–50 to 200 °C) and second heating (–50 to 240 °C). Samples of about 10 mg were placed in hermetic aluminum pans and heated/cooled with 20 °C/min speed. Thermogravimetric analyses were performed using a Hi-Res TGA 2950 thermogravimetric analyzer (TA Instruments) in nitrogen atmosphere (maximal speed 50 °C/min, resolution 3, sensitivity 3). The UV lamp used was a Blak-Ray UVP model B 100 AP/R with a 100-watt spot bulb providing UV light of high-intensity and 7° beam width to give an incident light intensity of 21 mW/cm<sup>2</sup> for samples placed at a distance of 5 cm from the lamp, and 8.9 mW/cm<sup>2</sup> at a distance of 25 cm. No specific filter, cutting off precise wavelength, was applied.

5-Bromo-1-pentene, allyl glycidyl ether (AGE) (97 and 99% respectively), and methyllithium (1.6 M solution in diethyl ether) were purchased from Aldrich and used as received. The

hydrosilylation catalyst platinum tetramethyldivinylsiloxane (PTDD) complex (3% solution in xylenes) and polysiloxanes (PS-120, HMS-501), containing 100 and 50% of –Me(H)SiO– monomeric units, respectively, were purchased from ABCR. Diphenyliodonium tetrafluoroborate (DPFT)<sup>13</sup> and tris(trimethylsilyl)methane (T<sub>Si</sub>)<sup>14</sup> were obtained according to published procedures. All solvents were dried prior to their use as described in the literature.<sup>15</sup>

Synthesis of 6,6,6-Tris(trimethylsilyl)hex-1-ene (TTSH) (Scheme 2). A solution of tris(trimethylsilyl)lithium in THF (50 mL), prepared from tris(trimethylsilyl)methane (T<sub>Si</sub>H) (10.6 g, 46 mmol) and MeLi (50 mmol, 31 mL of 1.6 M solution in Et<sub>2</sub>O)<sup>12</sup> was stirred at 70 °C. 5-Bromo-1-pentene (10.7 g, 72 mmol) was added dropwise to the cool solution of T<sub>Si</sub>Li and the reaction mixture was stirred at 0 °C for 1 h and then allowed to reach room temperature overnight. THF was evaporated at room temperature under reduced pressure. Solid residue was extracted in pentane (100 mL) and LiBr was filtered off. Crude product, after pentane was stripped off, was vacuum distilled. The fraction boiling at 110 °C/2 mmHg was collected and proved (see below) to be pure (Me<sub>3</sub>Si)<sub>3</sub>C(CH<sub>2</sub>)<sub>3</sub>CH=CH<sub>2</sub> (9.0 g, 65% yield). <sup>1</sup>H NMR(CDCl<sub>3</sub>): δ/ppm = 0.12 (s, 27H, C[Si(CH<sub>3</sub>)<sub>3</sub>]), 1.6 (m, 4H, ≡Si–CH<sub>2</sub>–CH<sub>2</sub>–CH=CH<sub>2</sub>), 2.0 (m, 2H ≡Si–CH<sub>2</sub>–CH<sub>2</sub>–CH=CH<sub>2</sub>), 5.0 (m, 2H ≡Si–CH<sub>2</sub>–CH<sub>2</sub>–CH=CH<sub>2</sub>), 5.8 (m, 1H, ≡Si–CH<sub>2</sub>–CH<sub>2</sub>–CH=CH<sub>2</sub>), 13.54 (≡Si–CH<sub>2</sub>–CH<sub>2</sub>–CH=CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ/ppm = 2.78 [Si(CH<sub>3</sub>)<sub>3</sub>], 29.42 (≡Si–CH<sub>2</sub>–CH<sub>2</sub>–CH=CH<sub>2</sub>), 30.63 (≡Si–CH<sub>2</sub>–CH<sub>2</sub>–CH=CH<sub>2</sub>), 35.28 (≡Si–CH<sub>2</sub>–CH<sub>2</sub>–CH=CH<sub>2</sub>), 114.56 (≡Si–CH<sub>2</sub>–CH<sub>2</sub>–CH=CH<sub>2</sub>), 138.54 (≡Si–CH<sub>2</sub>–CH<sub>2</sub>–CH=CH<sub>2</sub>). <sup>29</sup>Si NMR (CDCl<sub>3</sub>): δ/ppm = 2.2 [Si(CH<sub>3</sub>)<sub>3</sub>]. GC-MS (EI, 70 eV): *m/z* = 285 (M<sup>+</sup> – CH<sub>3</sub>, 4%), 226 [M<sup>+</sup> – Si(CH<sub>3</sub>)<sub>3</sub>H, 3%], 211[M<sup>+</sup> – Si(CH<sub>3</sub>)<sub>3</sub>H – CH<sub>3</sub>, 4%], 197 [M<sup>+</sup> – Si(CH<sub>3</sub>)<sub>4</sub> – CH<sub>3</sub>, 7%], 138 [M<sup>+</sup> – Si(CH<sub>3</sub>)<sub>3</sub>H – Si(CH<sub>3</sub>)<sub>4</sub>, 28%], 73 [Si(CH<sub>3</sub>)<sub>3</sub><sup>+</sup>, 100%]. Anal. Calcd for C<sub>15</sub>H<sub>36</sub>Si<sub>3</sub>: C, 59.91%; H, 12.07%; Si, 28.02%. Found: C, 59.2%; H, 12.4%; Si 28.4%.

**General Procedure for Grafting TTSH and AGE on Siloxane Backbones.** Two series of polymers were made: (Ia–d) based on methylsiloxane homopolymer (PS-120), and (IIa–d) based on dimethylsiloxane-*co*-methylsiloxane copolymer (HMS-501). Ia was made as follows: A mixture of (Me<sub>3</sub>Si)<sub>3</sub>C(CH<sub>2</sub>)<sub>3</sub>CH=CH<sub>2</sub> (TTSH) (1.8 g, 6 mmol) and allyl glycidyl ether (AGE) (0.29 g, 2.5 mmol) was stirred with PTDD, ([Pt]/[–CH=CH<sub>2</sub>] = 1.8 × 10<sup>–4</sup>, at room temperature for 20 min. Then a solution of siloxane (PS-120) (0.5 g, [SiH] = 1.1 mol/dm<sup>3</sup>) in toluene (7.0 mL) was added dropwise and the

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**Table 1. Reaction Conditions for Preparation of Series I and II of Tris(trimethylsilyl)Hexyl- and (Glycidoxypropyl)-modified Siloxane Polymers**

polymer	TTSH		AGE		starting polymer	<i>m</i> [g]	toluene [mL]	[SiH] mol/dm <sup>3</sup>	[Pt]/[−CH=CH <sub>2</sub> ]
	<i>m</i> [g]	<i>n</i> [mmol]	<i>m</i> [g]	<i>n</i> [mmol]					
Ia	1.8	6	0.29	2.5	PS-120	0.5	7.0	1.1	$1.8 \times 10^{-4}$
Ib	0.9	3	0.342	3	PS-120	0.35	5.0	1.1	$1.8 \times 10^{-4}$
Ic	0.81	2.7	0.72	6.3	PS-120	0.524	8.0	1.1	$1.9 \times 10^{-4}$
Id			1.93	17.0	PS-120	0.704	10.0	1.3	$0.5 \times 10^{-4}$
IIa	0.49	1.63	0.05	0.41	HMS-501	0.255	4.0	0.5	$4.5 \times 10^{-4}$
IIb	0.51	1.7	0.13	1.13	HMS-501	0.335	5.0	0.5	$4.3 \times 10^{-4}$
IIc	0.5	1.67	0.285	2.5	HMS-501	0.536	8.0	0.5	$4.4 \times 10^{-4}$
IId			1.77	15.5	HMS-501	1.924	10.0	1.0	$0.4 \times 10^{-4}$

**Table 2. <sup>1</sup>H NMR (CDCl<sub>3</sub>) Resonances (δ/ppm) of Polymers Ia and IIa**

polymer	chemical shift [ppm]	
	Ia	IIa
−Si(CH <sub>3</sub> )O−	0.05 (s)	0.05 (s)
−Si(CH <sub>3</sub> ) <sub>2</sub> O−		0.07 (s)
−OSi(CH <sub>3</sub> ) <sub>3</sub>	0.09 (s)	0.09 (s)
−Si(CH <sub>3</sub> ) <sub>3</sub>	0.12 (s)	0.11 (s)
SiH	4.7 (m)	4.7 (m)
CH	3.11 (m)	3.13 (m)
CH <sub>2</sub> [i + vi]	0.5 (m)	0.5 (m)
CH <sub>2</sub> [ii]	1.33 (m)	1.33 (m)
CH <sub>2</sub> [iii]	1.26 (m)	1.26 (m)
CH <sub>2</sub> [iv]	1.48 (m)	1.48 (m)
CH <sub>2</sub> [v]	1.60 (m)	1.60 (m)
CH <sub>2</sub> [vii]	1.51 (m)	1.56 (m)
CH <sub>2</sub> [viii]	3.39 (m)	3.40 (m)
CH <sub>2</sub> [ix]	3.44 and 3.65 (m)	3.45 and 3.66 (m)
CH <sub>2</sub> [x]	2.57 and 2.76 (m)	2.59 and 2.78 (m)

**Table 3. <sup>13</sup>C NMR (CDCl<sub>3</sub>) Resonances (δ/ppm) of Polymers Ia and IIa**

polymer	chemical shift [ppm]	
	Ia	IIa
−Si(CH <sub>3</sub> )O−	−0.25	−0.31
−Si(CH <sub>3</sub> ) <sub>2</sub> O−		1.22
−OSi(CH <sub>3</sub> ) <sub>3</sub>	1.97	1.91
Si(CH <sub>3</sub> ) <sub>3</sub>	2.67	2.85
C <sub>q</sub>	6.07	6.06
CH	50.78	50.83
CH <sub>2</sub> [i]	17.79	17.69
CH <sub>2</sub> [ii]	22.99	22.94
CH <sub>2</sub> [iii]	35.15	35.07
CH <sub>2</sub> [iv]	30.06	30.0
CH <sub>2</sub> [v]	31.13	31.10
CH <sub>2</sub> [vi]	13.54	13.48
CH <sub>2</sub> [vii]	23.22	23.22
CH <sub>2</sub> [viii]	74.13	74.21
CH <sub>2</sub> [ix]	71.43	71.4
CH <sub>2</sub> [x]	44.24	44.29

reaction mixture was stirred for 24 h at room temperature. Progress of the reaction was followed by <sup>1</sup>H NMR. To increase conversion of Si−H bonds, the mixture was stirred at 70 °C for an additional 24 h. The product was precipitated in methanol, separated, and dried under vacuum at room temperature. Purified product (1.53 g) was obtained with 63% yield. Reaction conditions for preparation of polymers Ib−d and IIa−d are shown in Table 1 together with typical NMR data for representative materials in both series of side chain products (Ia, IIa; Tables 2–4). Figure 1 presents an exemplary <sup>1</sup>H NMR spectrum of a typical polysiloxane with Tsi and oxirane groups grafted as side substituents.

**UV-Initiated Cross-Linking of Linear Copolysiloxanes.** A solution of copolysiloxane (Ia−d, IIa−d) (~0.15 g) in dichloromethane (1.5 mL) was mixed with a solution of DPTF in acetone (0.15 mL) (the molar ratio of epoxy moieties/DPTF = 7). The mixture was cast on a glass plate (2 cm<sup>2</sup>), the plate was placed in a dark cabinet, and the solvents were allowed to evaporate slowly at room temperature overnight. The polymer film was exposed to UV irradiation for 30 min (not

optimized time) giving a relevant cross-linked material. The thickness of prepared film measured after irradiation was of 60–80 μm.

## Results and Discussion

In this study, modification of polysiloxanes by grafting the tris(trimethylsilyl)methyl and oxirane moieties was achieved via hydrosilylation of the respective alkenes with poly(methylhydrosiloxane) (PS-120) and poly(methylhydrosiloxane)-*co*-poly-(dimethylsiloxane) (HMS-501) in the presence of Karstedt catalyst (Scheme 3). As a result three different copolymers based on poly(methylsiloxane) chain, containing from 31 to 70% of side substituents, bearing “trisyl” moieties were made (Ia−c). In all the cases residual amounts of Si−H bonds remained in unsubstituted monomeric units along the chain (5–6 M %), reflecting the steric bulk of the overloaded pendants. It can be limited to 1–4 M % (IIa−c), once dimethylsiloxane monomeric units are also present in the starting polysiloxane copolymer, decreasing the “density” of side substituents in final materials. Yield of the modified products varies from 60 to 73%, and despite the difference in steric requirements of the alkenes used, the composition of the monomeric units in resulting polymers, closely reflects the molar ratio of alkenes used in hydrosilylation (Table 5). Also, two polymers (Id and IId, Table 5) with solely oxirane moieties grafted on siloxane backbone were prepared for the purpose of comparing their thermal properties with those brought in by “trisyl” moieties into polysiloxane chain.

Note that some Markovnikov addition occurs also during hydrosilylation under these conditions (~2%) (Scheme 3) and it is attributed to the hydrosilylation of allyl glycidyl ether (AGE). The ratio of Markovnikov/anti-Markovnikov addition increases linearly with the concentration of AGE used as a substrate. No other side reactions were observed during the hydrosilylation process, i.e., oxirane ring-opening polymerization in the presence of transition metal complex<sup>16</sup> or oxirane − Si−H coupling.<sup>17</sup>

It is well-known that elution volume and molecular weight measured by SEC depend on the molecular architecture of a polymer. The introduction of Tsi groups is believed to strongly alter the shape of the polymer chain and to cause less entanglements of the polymer backbone due to steric hindrance. Hydrodynamic volume of statistical oligomers of the same initial structure of polymer chain may vary also, probably due to their different ratio of tris(trimethylsilyl)hexyl and (glycidox-

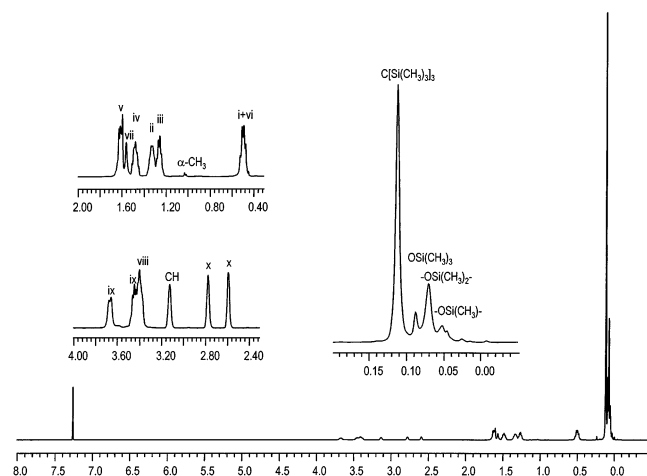
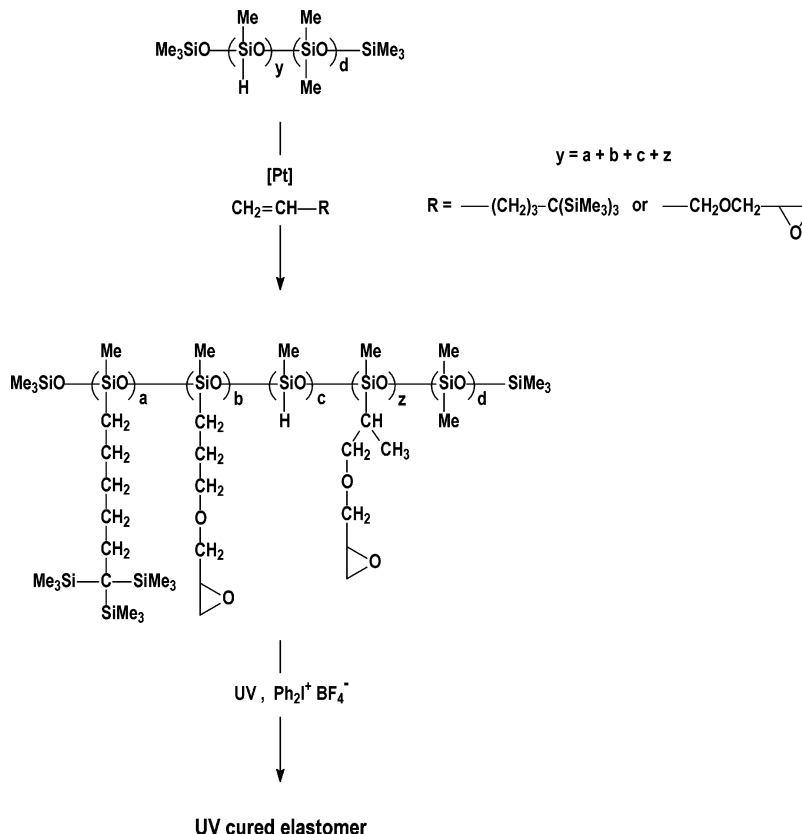
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**Table 4.**  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ) Resonances ( $\delta/\text{ppm}$ ) of Polymers Ia and IIa

polymer	chemical shift [ppm]	
	Ia	IIa
siloxane monomeric units	set of peaks from $-22.1$ to $-23.3$	$-21.9$ , $-22.2$ , $-22.5$ , and $-22.7$
$-\text{C}(\text{SiMe}_3)_3$	2.13	2.15
$-\text{OSi}(\text{CH}_3)_3$	7.1	7.2

**Scheme 3. Synthesis and Photo Cross-Linking of Linear Polysiloxanes Bearing Tsi and Oxirane Moieties as Side Groups****Figure 1.**  $^1\text{H}$  NMR spectrum of polymer IIB.

propyl) groups for individual macromolecules (with the overall polymer ratio being close to the molar ratio of alkenes used in reaction). The molecular weight of such oligomers has to be different, and therefore the overall PDI increases. This presumption is supported by the fact that the increase of PDI on increasing the amount of Tsi-siloxane units, found for polymers Ia–c, can be seen also to a much smaller extent for series IIa–c (Table 5). Series of polymers I and II differ by the

amount of dimethylsiloxane units. That certainly makes their hydrodynamic volumes different, and may cause a more distinct increase of polydispersity in the case of polymers with higher amounts of siloxane units modified by Tsi groups and lower amounts of dimethylsiloxane units. Moreover, polymers without Tsi groups, which were prepared in an analogous way, have  $M_n$  almost equal to  $M_{\text{theoret}}$  (Id) or even lower (IId), with PDI decreased in both cases. This observation seems to support the structural and statistical background of the apparent inconsistency of the results obtained for Tsi-modified polymers.

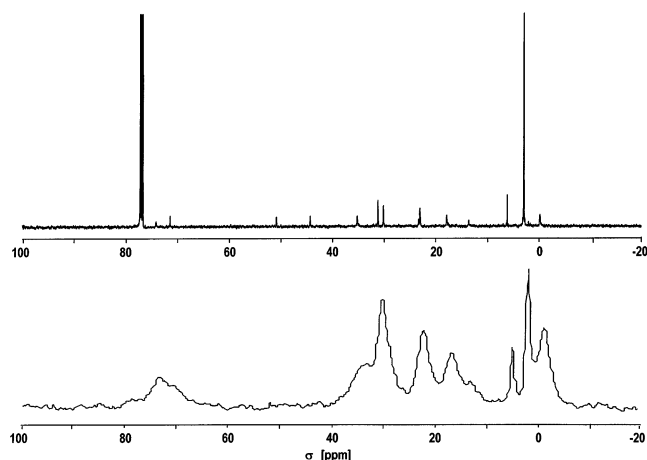
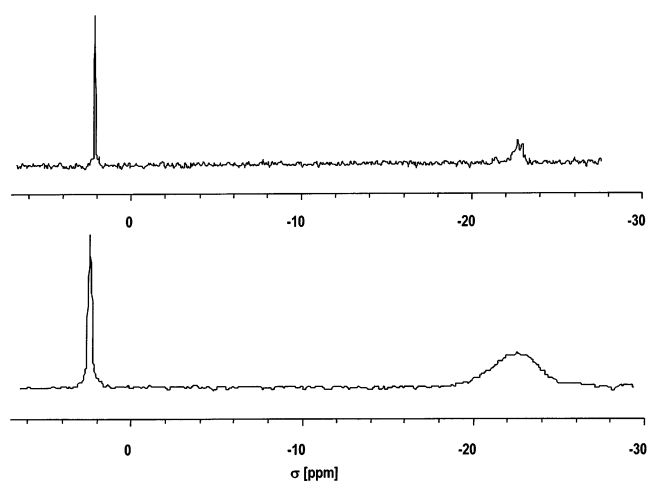
Ring-opening polymerization of epoxy groups in the presence of diaryl iodonium tetrafluoroborate was found to be an efficient way of formation of cross-linked TSi-containing silicone materials. Comparison of the  $^{13}\text{C}$  NMR spectra of copolymers (in  $\text{CDCl}_3$ ) before and after curing (solid-state NMR) showed disappearance of the resonances assigned to the epoxy ring at 44.2 and 50.8 ppm<sup>18</sup> and appearance of a new broad ones at  $\sim 70$  ppm characteristic of ether moieties<sup>19</sup> (Figure 2), proving thus the formation of oligoether cross-links. Additionally,  $^{29}\text{Si}$  NMR spectra also indicate that no novel silicon

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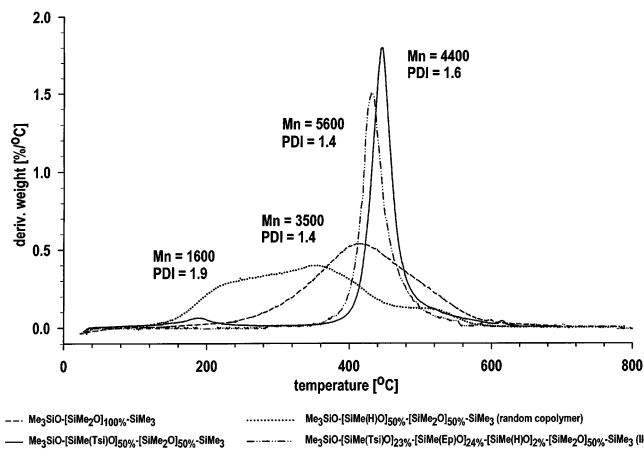
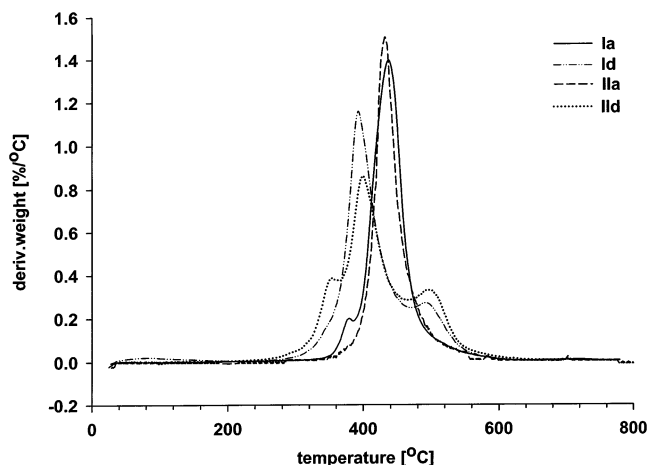
**Table 5.**  $^1\text{H}$  NMR and SEC Data for Tris(trimethylsilyl)Hexyl- and (Glycidoxypopyl)-Modified Siloxane Polymers<sup>a</sup>

polymer	substrate			product										
	$M_n$	PDI	$y$	$a_0$	$b_0$	$a$	$b$	$c$	$d$	$z$	$M_{\text{theor}}$	$M_n$	PDI	% yield
Ia	2800	2.5	100	76	32	70	24	6		<1	13600	11800	6.2	63
Ib	2800	2.5	100	54	54	55	38	5		2	11900	15400	5.4	71
Ic	2800	2.5	100	32	75	31	60	6		3	10000	18000	3.3	73
Id	2800	2.5	100		106		90	5		5	7200	7100	1.9	83
IIa	1600	1.9	50	43	11	41	8	1	50	<1	4600	4700	1.6	72
IIb	1600	1.9	50	34	22	31	18	<1	50	1	4200	4700	1.5	60
IIc	1600	1.9	50	21	32	23	24	2	50	1	3700	5600	1.4	65
IId	1600	1.9	50		108		38	8	50	4	2600	3600	1.6	85

<sup>a</sup> Abbreviations:  $M_n$ , molecular mass (SEC in  $\text{CH}_2\text{Cl}_2$ ); PDI, polydispersity index (SEC in  $\text{CH}_2\text{Cl}_2$ );  $y$ , molar amount of Si-H groups in the polymer chain of the substrate;  $a_0$ , initial molar ratio  $[\text{TTSH}]/[\text{SiH}] \times 10^2$  in the reaction mixture;  $b_0$ , initial molar ratio  $[\text{AGE}]/[\text{SiH}] \times 10^2$  in the reaction mixture;  $a$ , molar amount ( $\times 10^2$ ) of Tsi-functionalized monomeric units ( $^1\text{H}$  NMR);  $b$ , molar amount ( $\times 10^2$ ) of oxirane-functionalized monomeric units;  $c$ , molar amount ( $\times 10^2$ ) of Si-H containing monomeric units;  $d$ , molar amount ( $\times 10^2$ ) of dimethylsiloxane monomeric units;  $z$ , molar amount ( $\times 10^2$ ) of monomeric units with anti-Markovnikov addition;  $M_{\text{theor}}$ , expected molecular mass.

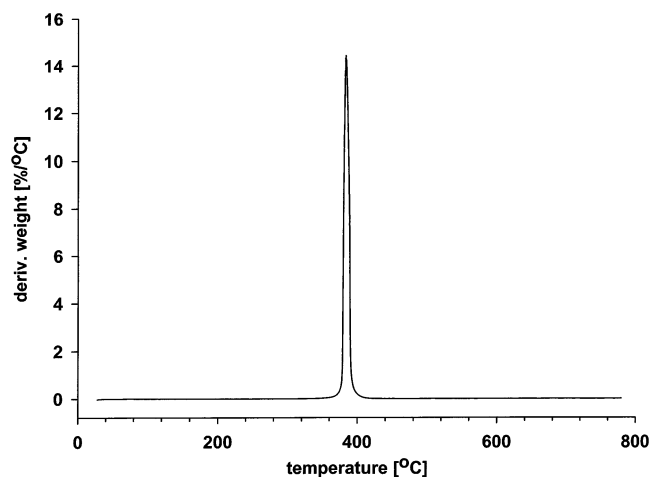
**Figure 2.**  $^{13}\text{C}$  NMR spectra of polymer Ia before and after curing with  $\text{Ph}_2\text{I}^+ \text{BF}_4^-$ .**Figure 3.**  $^{29}\text{Si}$  NMR spectra of polymer Ia before and after curing with  $\text{Ph}_2\text{I}^+ \text{BF}_4^-$ .

environment was created on exposure to UV light in the presence of epoxy groups (Figure 3). TGA analyses show a large increase in thermal stability (over  $220^\circ\text{C}$ ) of TSi-modified silicones compared to that of their parent materials (PS-120 and HMS-501) as well as poly(dimethylsiloxane)s of similar molecular weight and polydispersity (Figure 4). Because of the protective function provided by the TSi groups and their shielding of siloxane backbone, decomposition processes that occur on thermal treatment of standard dimethylsilicones are to a large extent restricted.<sup>20</sup> The presence of epoxy-terminated side groups in linear macromolecules only

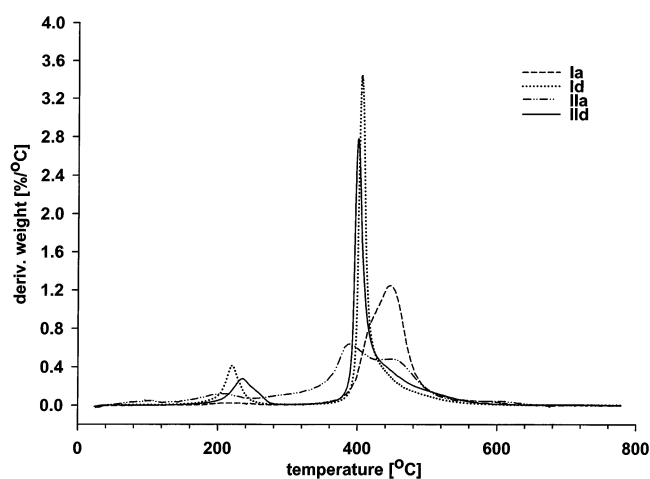
**Figure 4.** Thermal resistance of Tsi-modified siloxanes.**Figure 5.** Comparative TGA of Tsi/oxirane grafted polymers (Ia, IIa) and oxirane-only grafted materials (Id, IId) before curing.

slightly reduces the thermal resistance found for solely TSi-modified polymers. Direct comparison of "trisylated" polymers Ia and IIa with their oxirane analogues Id and IId gives clear evidence of the role played by sterically hindered groups in the studied system (Figure 5). Materials functionalized only with the use of AGE start to decompose at lower temperatures ( $260^\circ\text{C}$  compared to  $340^\circ\text{C}$  for TTSH/AGE modified siloxanes) and separate decomposition processes evidently occur subsequently

(20) Kendrick, T. C.; Parbhoo, B.; White, J. W. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappaport, Z., Eds.; Wiley: Chichester, U.K., 1989; pp 1319–1341.

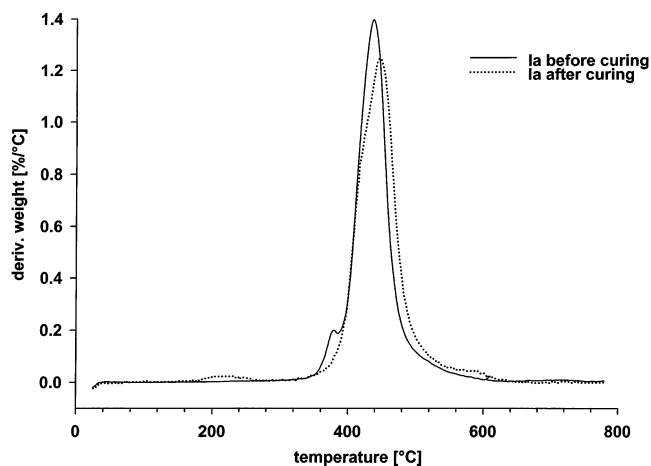


**Figure 6.** TGA of standard poly(ethylene oxide) of  $M_n = 200\,000$  (Aldrich; 18,199-4).

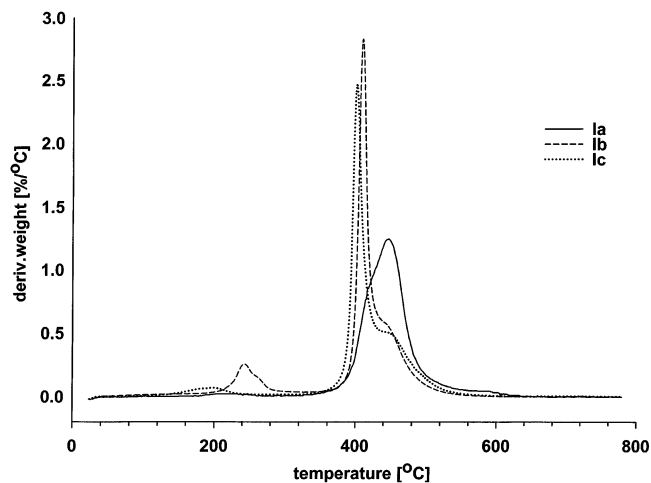
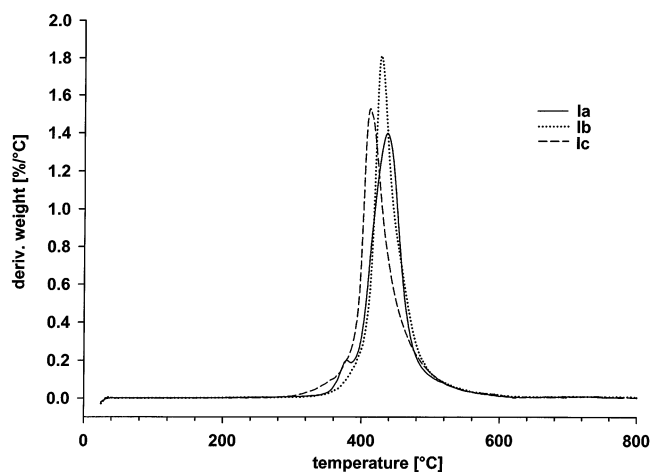


**Figure 7.** Comparative post-curing TGA of Tsi/oxirane grafted (Ia, IIa) and oxirane-grafted polymers (Id, IId).

on heating of the samples. It seems that the presence of ether linkages strongly affects the process of degradation: the characteristic peak representing a substantial sample weight loss at about 390 °C can be attributed to decomposition of C–O bonds [confirmed by TGA diagram of commercial poly(ethylene oxide) (Figure 6) in which the polymer degrades sharply at 383 °C]. Likewise, the polymers Ia, Id, IIa, and IId were examined for their thermal resistance after curing in the presence of iodonium salt. Once arranged in a network, glycidyl-modified polysiloxanes undergo sharp thermal decomposition, similarly to PEO, with a peak tail at higher temperatures due to the decomposition of siloxane (Figure 7). The presence of the Tsi group substantially inhibits degradation. The thermal decomposition occurs more slowly especially for materials having a high content of Tsi groups. An evident difference was found between cross-linked poly(methylsiloxane)s and poly(methylsiloxane)-*co*-poly-(dimethylsiloxane)s, grafted with tris(trimethylsilyl)-methyl and oxirane moieties. The cured polymers of group I do not differ much from their precursors (Figure 8), yet the increase of the ratio between epoxide and trisyl-modified siloxane segments results in a slight decrease of thermal stability (Figure 9a and b). The temperature range of decomposition of the cross-linked materials containing dimethylsiloxane units (group II) is wider than that of the starting linear



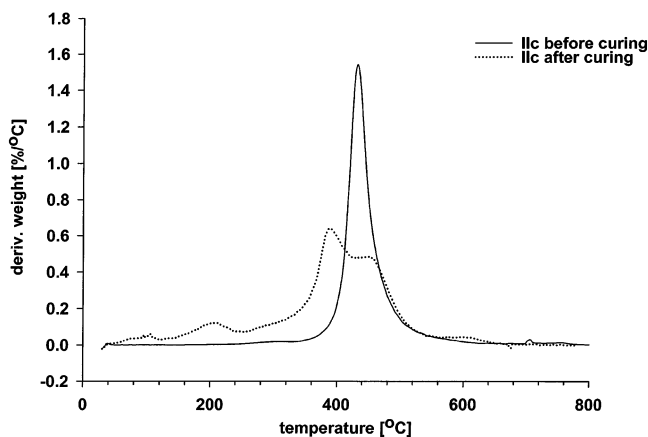
**Figure 8.** TGA of polysiloxane Ia before and after curing with  $\text{Ph}_2\text{I}^+ \text{BF}_4^-$ .



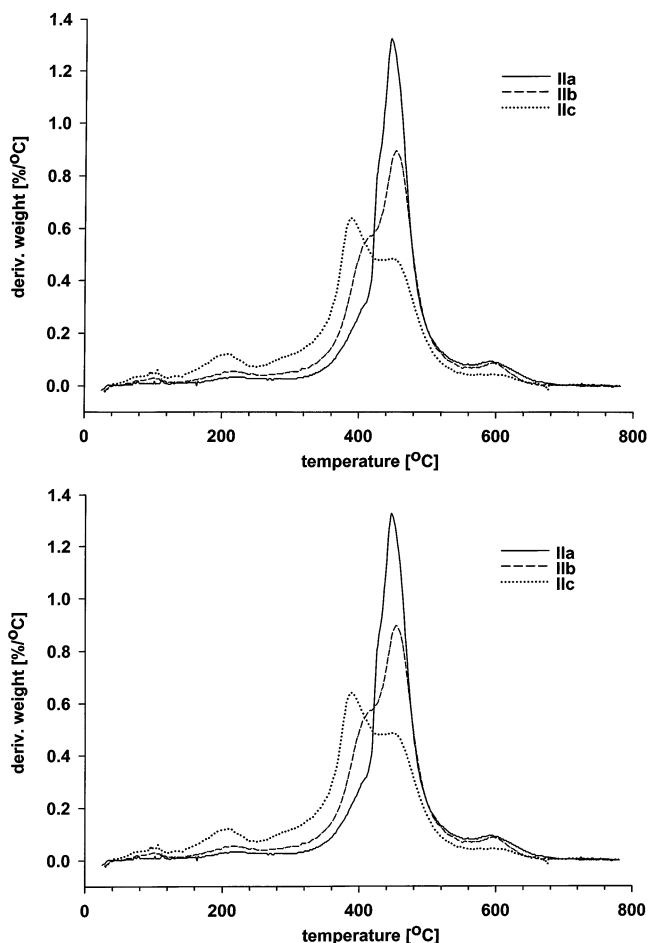
**Figure 9.** Comparative TGA of Tsi/oxirane modified siloxane polymers (a) before and (b) after curing with  $\text{Ph}_2\text{I}^+ \text{BF}_4^-$  (series I).

siloxanes with  $\text{T}_{\text{Si}}$  and epoxy-containing side substituents (Figure 10) [the decrease of thermal resistance also being highest for structures having the largest amount of oxirane-containing pendants (Figure 11a and b)].

Apart from lower thermal resistance, the polymers with larger amounts of glycidoxypentyl groups exhibit higher shrinkage on UV-initiated curing. This contraction is obviously due to the formation of a much more compact network via cross-links generated during the

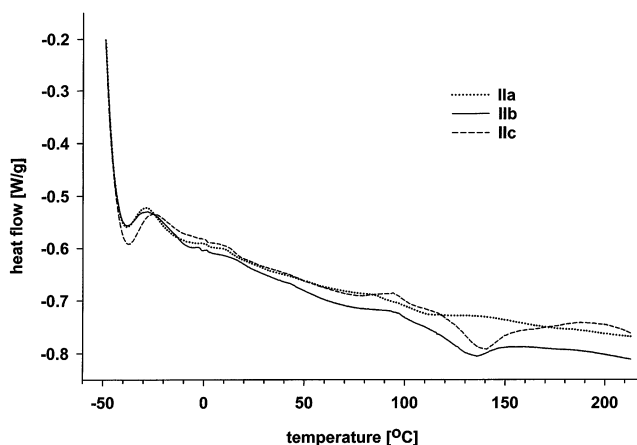


**Figure 10.** TGA of polysiloxane IIc before and after curing with  $\text{Ph}_2\text{I}^+ \text{BF}_4^-$ .



**Figure 11.** Comparative TGA of Tsi/oxirane modified siloxane-co-dimethylsiloxane-polymers (a) before and (b) after curing with  $\text{Ph}_2\text{I}^+ \text{BF}_4^-$  (series II).

polymerization of reactive oxirane groups. DSC measurements of studied materials did not show any distinct first or second order changes which could be ascribed to the known phase transitions observed for polymers. On first heating run the cross-linked polymers yielded a substantial endothermic peak with minimum at 140 °C (Figure 12) presumably due to thermal post-curing in the cross-linked material. Samples with higher



**Figure 12.** DSC of Tsi/oxirane modified siloxanes cured with  $\text{Ph}_2\text{I}^+ \text{BF}_4^-$  (series II).

amounts of epoxy units are characterized by more distinct transitions in this range. Second heating of cured samples as well as both heating runs performed for starting materials did not exhibit such minimum effects.

## Conclusion

We have detailed the preparation and characterization of novel siloxane copolymers bearing two types of side chain substituents. Among those, the bulky tris(trimethylsilyl)hexyl group provides high thermal resistance of the materials, and the reactive glycidoxypopyl moiety can be further exploited in preparation of relevant elastomers via oligoether cross-links. The potential use of such materials as fluid-separating membranes and thus the necessity of retaining their precise shape was the major purpose of their cross-linking. Linear systems are made in a one-pot modification of commercial methylsiloxane and methylsiloxane-co-dimethylsiloxane polymers by hydrosilylation, using mixtures of functionalized alkenes. The hydrosilylation proceeds with overwhelming anti-Markovnikov addition of Si-H bonds across the double bond of the alkenes. Oxirane function in linear thermally stable materials (maximum decomposition rate at 410–440 °C before curing) can be utilized for UV-initiated cross-linking in the presence of diphenyliodonium tetrafluoroborate. Once cross-linked, this maximum shifts toward a higher temperature range by ~10 °C for copolymers with high TTSH/AGE ratio, while the series containing also dimethylsiloxane monomeric units starts to decompose at temperatures lower by 100 °C. Properties of these novel materials can be tuned by varying the “density” of tris(trimethylsilyl)hexyl moieties along the siloxane backbone.

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