

**From spirosiloxane precursors via intramolecular hydrosilylation to photoinduced polysiloxane architectures**

Christian A. Anger,<sup>a</sup> Konrad Hindelang,<sup>a</sup> Tobias Helbich,<sup>a</sup> Tobias Halbach,<sup>b</sup> Jürgen Stohrer<sup>b</sup> and  
Bernhard Rieger <sup>\*a</sup>

<sup>a</sup> - WACKER-Lehrstuhl für Makromolekulare Chemie, Technische Universität München,  
Fakultät für Chemie, Lichtenbergstraße 4, Garching 85748, Germany

Email: [rieger@tum.de](mailto:rieger@tum.de)

<sup>b</sup> - Consortium für elektrochemische Industrie der Wacker Chemie AG,  
Zielstattstraße 20, München 81379, Germany

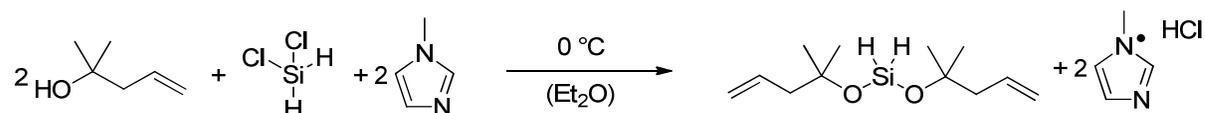
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- 1 General
- 2 Experimental procedures and characterization data
- 3 Spectra

### 1. General

All chemicals were purchased from commercial sources and were used as received. Diethyl ether and dichloromethane were dried and purified directly before their usage by a solvent purification system (MBRAUN SPS-800). 1-Methylimidazole was dried by distillation over sodium and stored over molecular sieve (4 Å). Infrared spectra were recorded on a ReactIR™ 45m of Mettler-Toledo and the irradiation was executed with a MAX-302 of ASAHI SPECTRA. Nuclear magnetic resonance spectra were recorded on a Bruker Avance 500 UltraShield (500 MHz) and an Avance 300 (300 MHz). They were recorded in ppm and the solvent was used as an internal standard (CDCl<sub>3</sub> at 7.26 ppm for <sup>1</sup>H and at 77.0 ppm for <sup>13</sup>C{<sup>1</sup>H}). The coupling constants *J* are given in Hertz (Hz) and the multiplicities were abbreviated as follows: s = singlet, d = duplet, m = multiplett. Mass spectras were recorded on a Thermo Scientific DFS (electron impact, EI, 70 eV). 2-Methylpent-4-en-2-ol and tris(pentafluorophenyl)borane were prepared according to literature methods.<sup>[1,2]</sup>

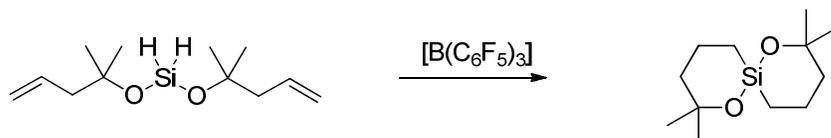
### 2. Experimental procedures and characterization data



**SI Scheme 1.** Synthesis of bis(2-methylpent-4-en-2-yl)oxy)silane

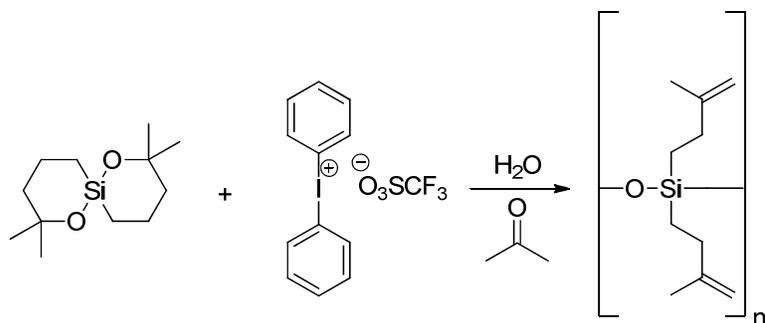
**Bis(2-methylpent-4-en-2-yl)oxy)silane** In a baked out Schlenk three-necked flask fitted a dropping funnel, reflux condenser and an Ar inlet about one quarter of the previously prepared mixture of 31.9 g (389 mmol, 2 eq) 1-methylimidazole and 38.9 g (389 mmol, 2 eq) 2-methylpent-4-en-2-ol in 50 mL diethyl ether were added from the dropping funnel to 250 mL diethyl ether. The 19.6 g (194 mmol, 1 eq) dichlorosilane which precondensed into a Schlenk tube at -78 °C was allowed to slowly diffuse into the stirred reaction mixture at -78 °C. Meanwhile the residual mixture from the

dropping funnel was slowly added to the reaction mixture which is then stirred for a further 10 h at room temperature. The resulting methylimidazole hydrochloride was then filtrated through a Schlenk frit and the solvent removed under reduced pressure (200 mbar). After fractionated condensation in vacuo (0.3 mbar, 60 °C) 35.7 g (156 mmol, 81 %) bis((2-methylpent-4-en-2-yl)oxy)silane were obtained as a colorless liquid. **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>, 300 K): δ [ppm] = 5.97 – 5.76 (m, 2H), 5.14 – 5.00 (H, 4H), 4.67 (s, 2H), 2.29 (d, <sup>3</sup>J = 7.3 Hz, 2H), 1.3 (s, 12). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, 300 K): δ [ppm] = 134.8 (s), 117.7 (s), 75.5 (s), 49.0 (s), 29.1 (s). **MS** (EI), m/z (%): 213.16 (13) [(M-CH<sub>3</sub>)<sup>+</sup>], 187.13 (100), 129.08 (87). [(M-C<sub>6</sub>H<sub>11</sub>O)<sup>+</sup>]. **HRMS** (C<sub>11</sub>H<sub>21</sub>O<sub>2</sub><sup>28</sup>Si = [(M - CH<sub>3</sub>)<sup>+</sup>]): calcd:213.1311, found: 213.1305.



**SI Scheme 2.** Synthesis of compound **1**.

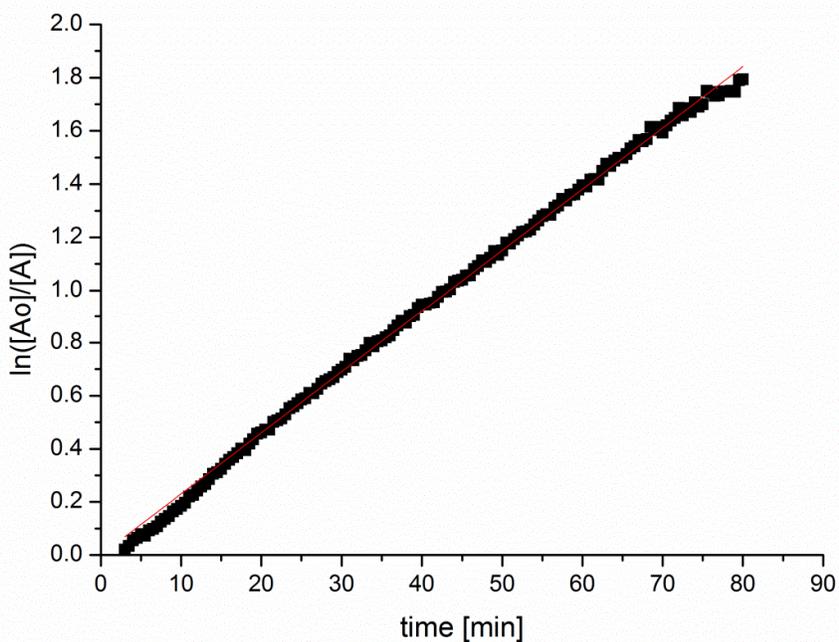
**2,2,8,8-Tetramethyl-1,7-dioxa-6-silaspiro[5.5]undecane (1).** To 23.8 g (104 mmol, 1 eq) of the bis((2-methylpent-4-en-2-yl)oxy)silane in 400 mL dry dichloromethane, 1.06 g (2.07 mmol, 2 mol%) B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was added with constant stirring at room temperature. The reaction mixture was then stirred for a further 12 h. The solvent was then removed under reduced pressure (200 mbar). Purification of the liquid residue by fractionized condensation (0.3 mbar, 60 °C) yielded 15.45 g (67.6 mmol, 65 %) of the spiro compound as a colorless liquid. **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>, 300 K): 1.91 – 1.64 (m, 4H), 1.60 – 1.38 (m, 4H), 1.29 (s, 6H), 1.20 (s, 6H), 0.68 – 0.42 (m, 4H). **<sup>13</sup>C-NMR** (126 MHz, CDCl<sub>3</sub>, 300 K): 74.4 (s, 2C), 40.9 (s, 2C), 31.7 (s, 2C), 30.2 (s, 2C), 17.8 (s, 2C), 12.1 (s, 2C). **<sup>29</sup>Si-NMR** (99 MHz, CDCl<sub>3</sub>, 300 K): 14.41 (s). **MS** (EI), m/z (%): 228 (7) [M<sup>+</sup>], 213 (100), [(M-CH<sub>3</sub>)<sup>+</sup>], 185 (21), 129 (26), 131 (27), 129 (39), 127 (34), 103 (33), 99 (50). **HRMS** (C<sub>12</sub>H<sub>24</sub>O<sub>2</sub>Si): calcd: 228.1546, found: 228.1542.



**SI Scheme 3.** Photoacid activated polymerization

In a two necked quartz Schlenk tube a solution of 75.3 mg (0.18 mmol, 2 mol%) of the photoacid generator **PAG 2**, and 0.79 mL (0.044 mmol, 0.5 mol%) water in 5 mL dry acetone was prepared and used for the background measurement of the IR spectrometer. The recording was then started and after 1 min 2.00 g (8.75 mmol, 1 eq) of 2,2,8,8-tetramethyl-1,7-dioxa-6-silaspiro[5.5]undecane were added to the solution. The light source was activated and the reaction mixture was irradiated for 2 hours.

**SI Figure 1.** Monomer first order in the polymerization reaction (plot of  $\ln \frac{[A_0]}{[A]}$  vs. time)



## Copolymerisation experiments

All polymerizations are done in the same way. To OH-terminated poly(dimethylsiloxane), **1** were added in a two necked quartz Schlenk tube. During stirring a solution of triphenylsulfonium triflate and diphenyliodonium triflate in acetone were added via a syringe. After that the irradiation with 200 – 300nm was started for two hours. Immediately after the reaction finished gpc measurements in THF are done. By all reactions the parameters were varied (table 1 and 2).

**SI Table 1.** Copolymerization parameters / PAG = Diphenyliodonium triflate

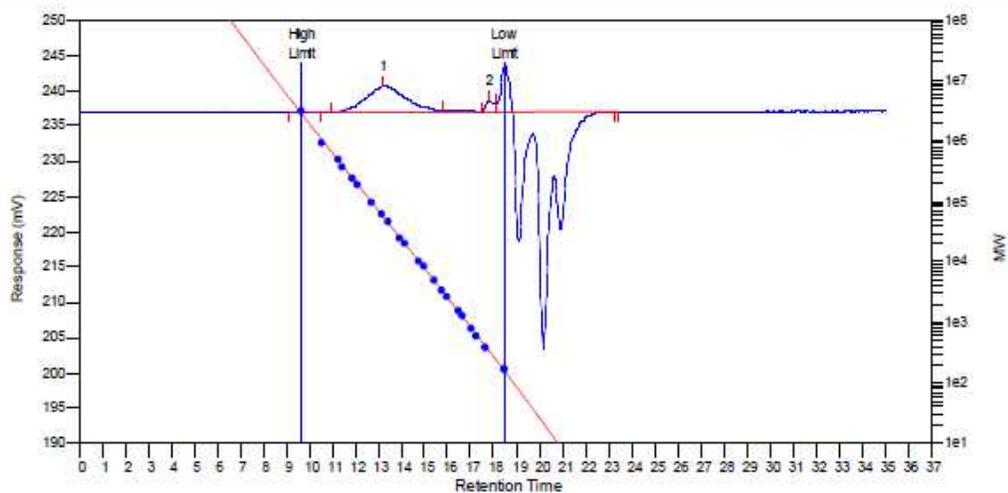
<i>compound 1</i>			<i>Polysiloxane</i>		<i>Diphenyliodonium Triflate</i>				
<i>Initial weight [mg]</i>	<i>mmol</i>	<i>mol%</i>	<i>Initial weight [g]</i>	<i>mmol</i>	<i>Initial weight [mg]</i>	<i>mmol</i>	<i>mol %</i>	<i>Mw</i>	<i>PDI</i>
0	0	0	4	1.77	10	0.023	1.30	0	0
0	0	0	4	1.77	20	0.046	2.60	70000	2
0	0	0	4	1.77	30	0.070	3.94	15000	2.4
20	0.088	5	4	1.77	10	0.023	1.30	127000	2.17
20	0.088	5	4	1.77	20	0.046	2.60	150000	2.5
20	0.088	5	4	1.77	30	0.070	3.94	400000	3.5

**SI Table 2.** Copolymerization parameters/ Triphenylsulfonium triflate

<i>compound 1</i>			<i>Polysiloxane</i>		<i>Triphenylsulfonium Triflate</i>				
<i>Initial weight [mg]</i>	<i>mmol</i>	<i>mol%</i>	<i>Initial weight [g]</i>	<i>mmol</i>	<i>Initial weight [mg]</i>	<i>mmol</i>	<i>mol %</i>	<i>Mw</i>	<i>PDI</i>
0	0	0	4	1.77	9	0.023	1.30	70050	3
0	0	0	4	1.77	19	0.046	2.60	30000	2
0	0	0	4	1.77	29	0.070	3.94	100000	2
20	0.088	5	4	1.77	9	0.023	1.30	220000	3.5
20	0.088	5	4	1.77	19	0.046	2.60	304000	4.4
20	0.088	5	4	1.77	29	0.070	3.94	X	X

## Size exclusion chromatographie

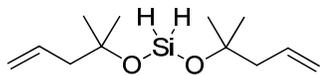
This chromatogram is an exemplary size exclusion chromatogram of the obtained copolymers.



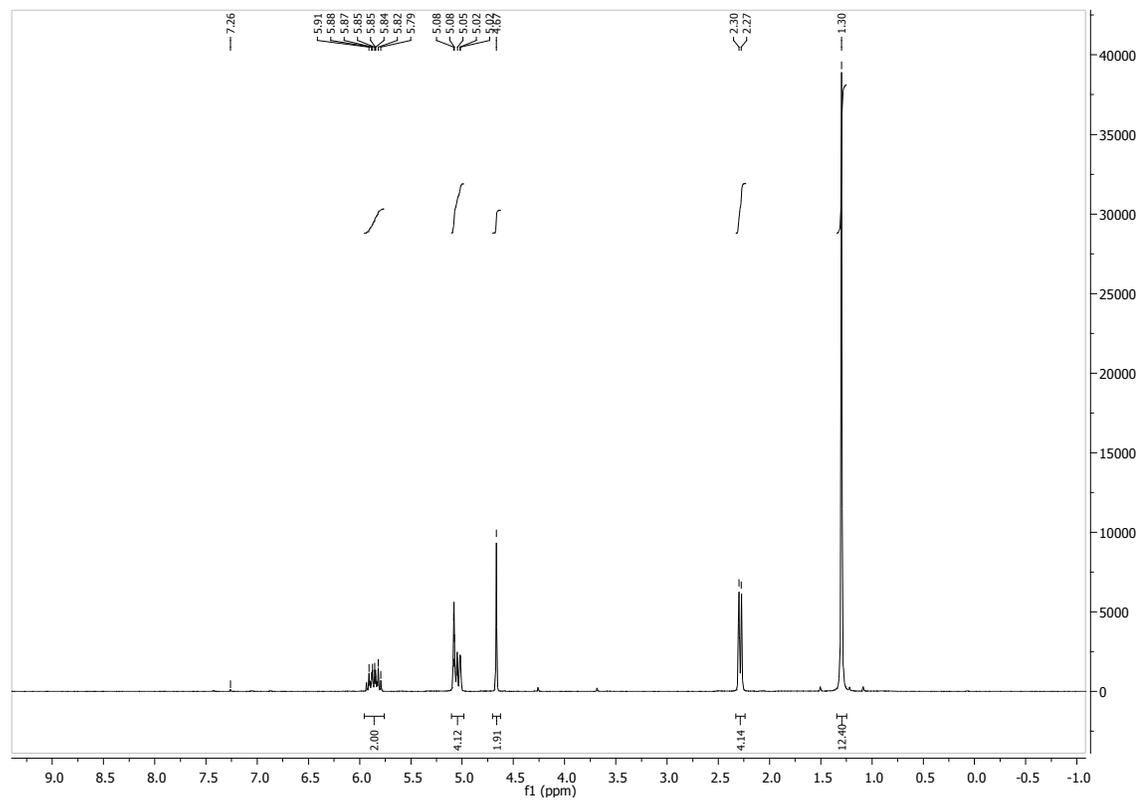
### MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	56794	28621	70688	150237	259798	62401	2.46979
2	342	334	312	335	343	305	0.934132

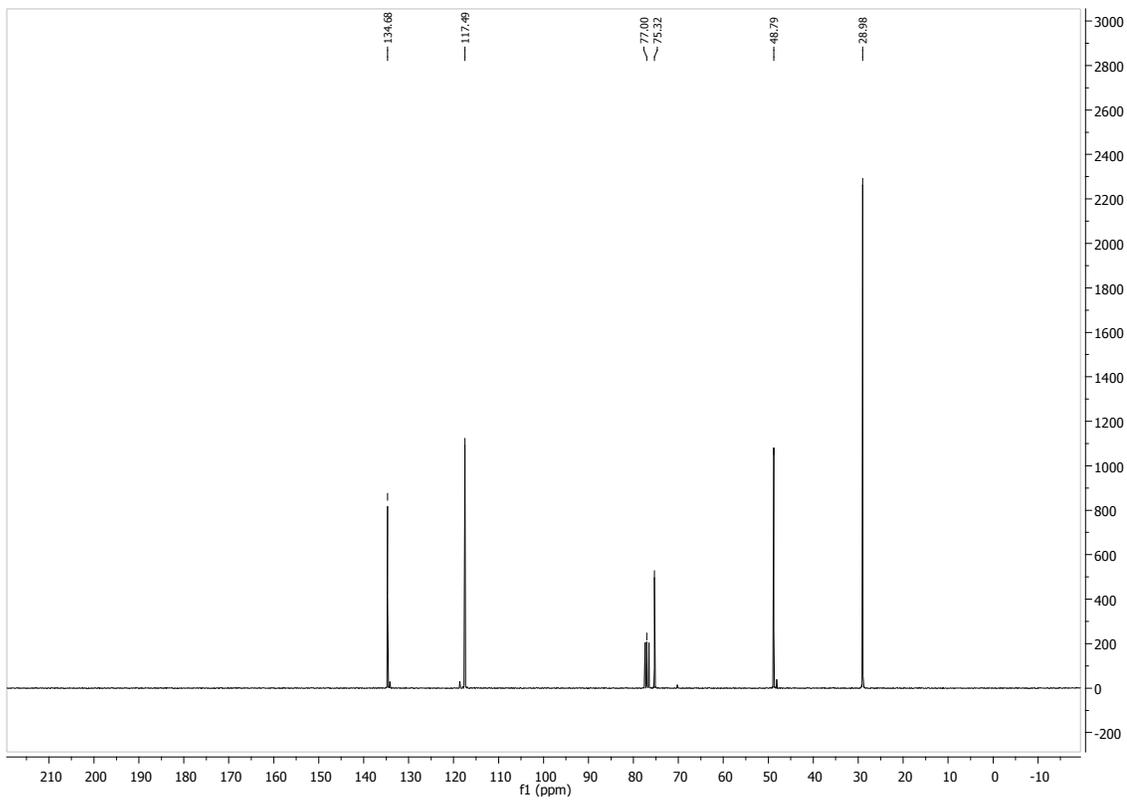
### 3. Spectra



Bis(2-methylpent-4-en-2-yl)oxy)silane

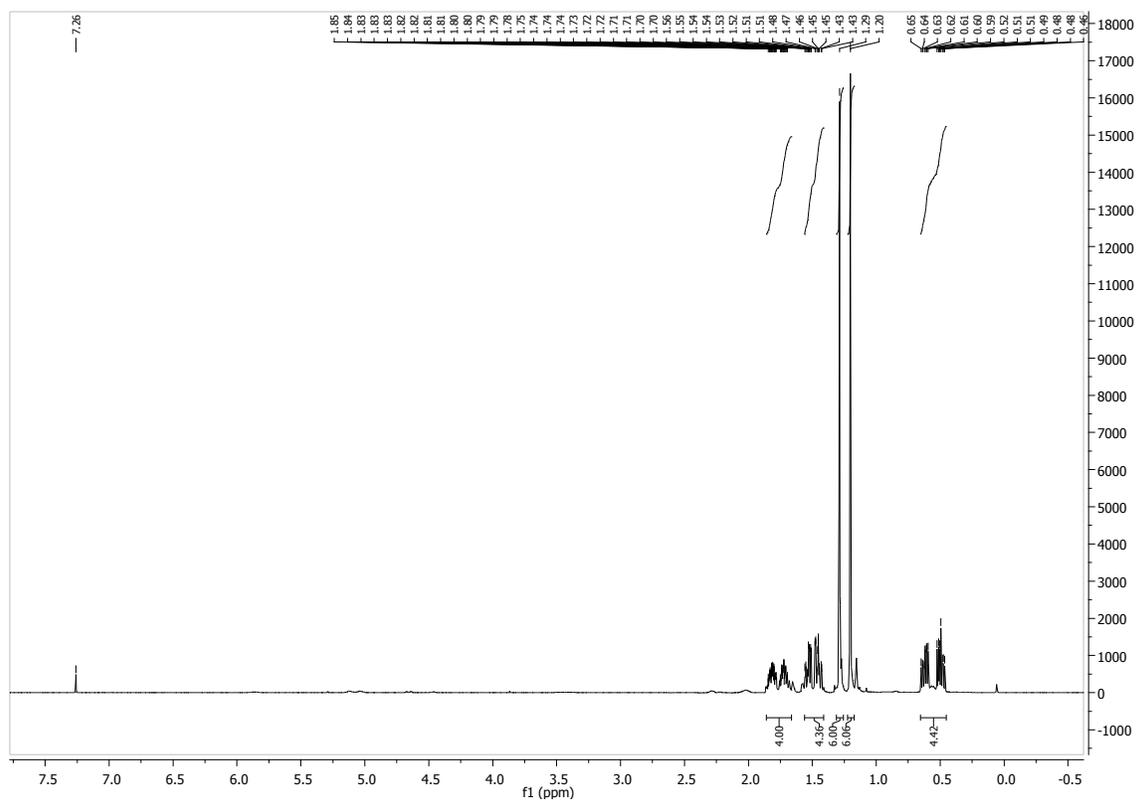
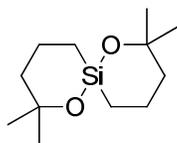


SI Figure 2a.  $^1\text{H}$ -spectrum of the spiro compound precursor bis(2-methylpent-4-en-2-yl)oxy)silane.

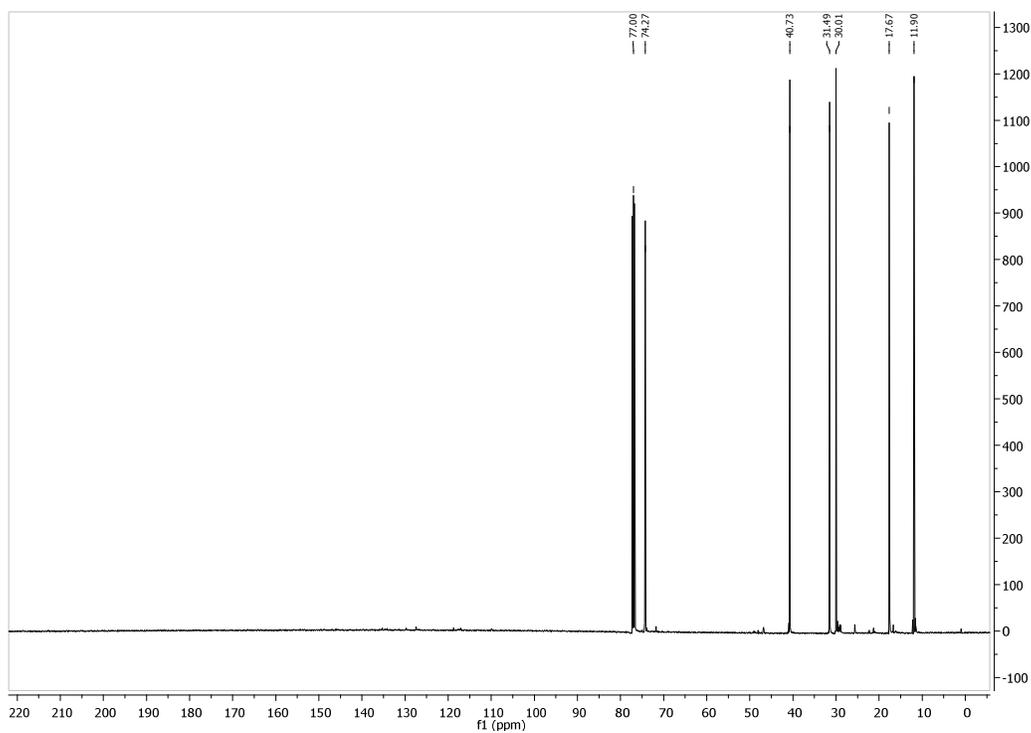


**SI Figure 2b.** Proton decoupled  $^{13}\text{C}$ -spectrum of bis(2-methylpent-4-en-2-yl)oxy silane.

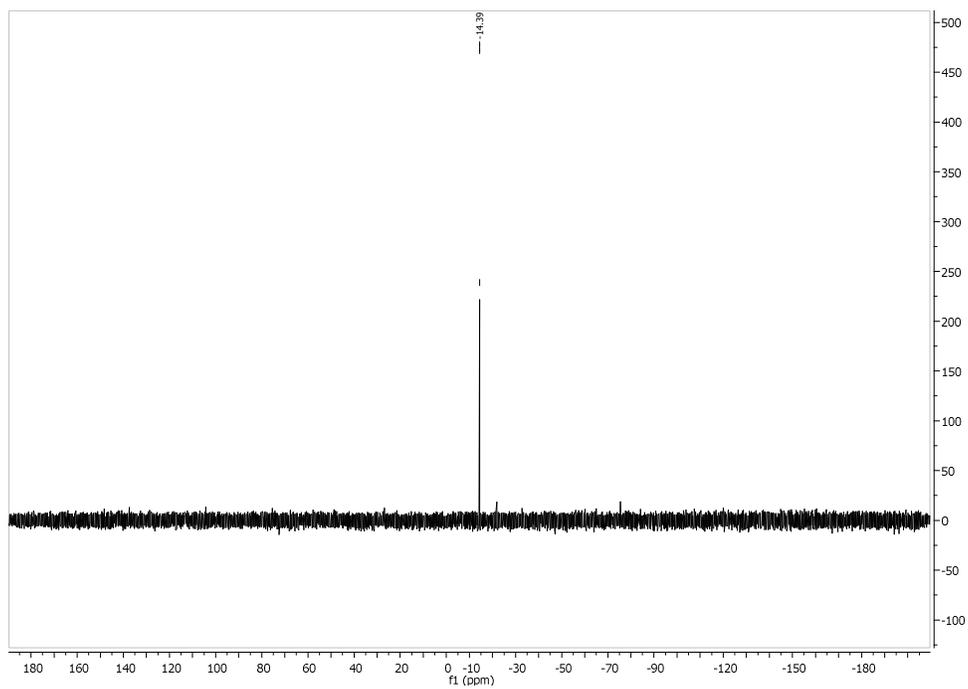
**2,2,8,8-Tetramethyl-1,7-dioxaspiro[5.5]undecane (compound 1)**



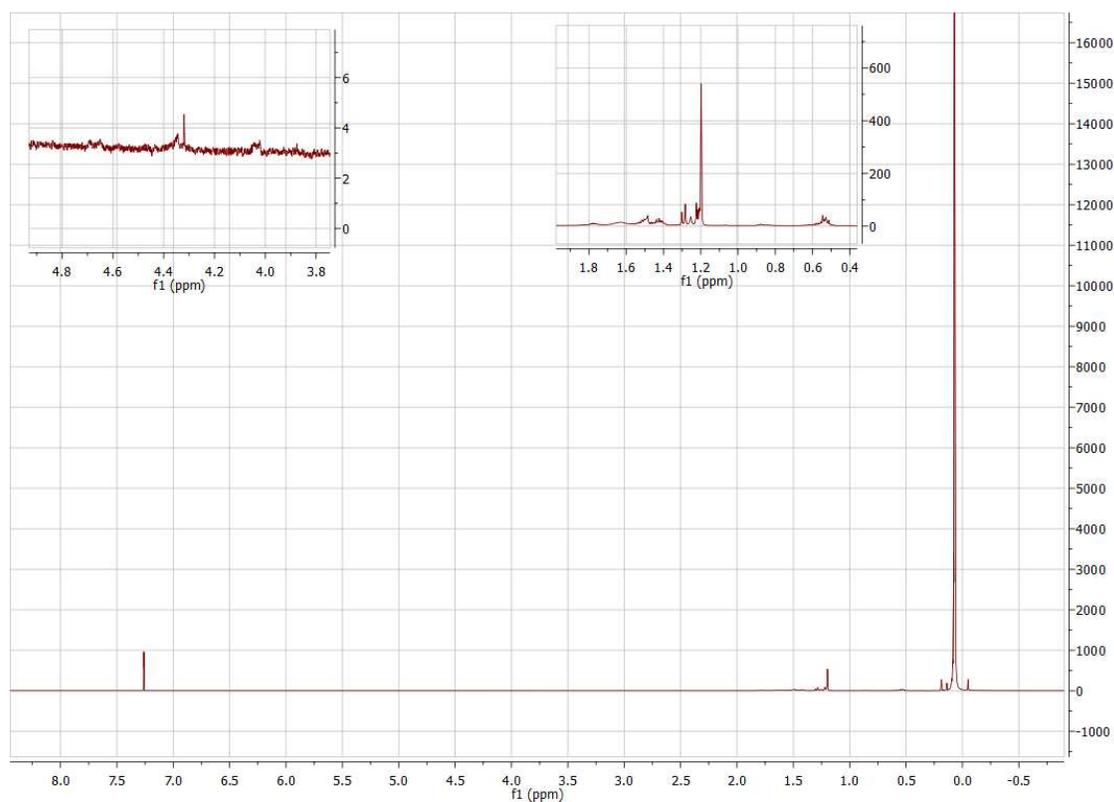
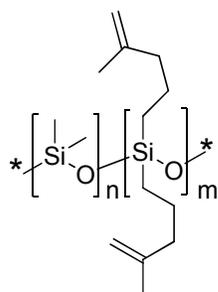
**SI Figure 3a.**  $^1\text{H}$ -spectrum of the spiro compound **1**



SI Figure 3b. Proton decoupled  $^{13}\text{C}$ -spectrum of the spiro compound **1**



SI Figure 3c.  $^{29}\text{Si}$ -NMR of the spiro compound **1**



SI-Figure 4 -  $^1\text{H}$  NMR spectrum of the obtained copolymer

The  $^1\text{H}$  NMR spectrum shows mainly the backbone of polydimethylsiloxane. By 1.8 – 1.2 the polymerized spirocycle can be detected. By 4.8 – 3.9 the not well resolved double bonds are detected.

<sup>1</sup> Taillier, C ; Hameury, T; Bellosta, V.; Cossy, J. *Tetrahedron*, **2007**, *63*, 4472-4490.

<sup>2</sup> Lehmann, M.; Schulz, A.; Villinger, A. *Angew. Chem. Int. Ed.*, **2009**, *48*, 7444-7447.