# Polysilanes Bearing a Phenoxypropyl Side Chain

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**Abstract.** A series of polysilanes bearing a 3-phenoxypropyl side chain was prepared applying the Wurtz coupling reaction of dichlorosilanes. All prepared polymers ([R-Si(CH$_2$)$_3$OPh]$_n$, R = Me, Pent, Hex, Hept, (CH$_2$)$_3$OPh, Ph) were investigated by GPC, UV, fluorescence, and $^1$H, $^{13}$C, $^{29}$Si NMR spectroscopy. Among these polysilanes only [HeptSi(CH$_2$)$_3$OPh]$_n$ (**3d**) exhibits a thermochromic behaviour showing at least two transitions.

Polysilanes are due to the σ-electron delocalization in the main chain a unique class of polymers [1]. So far the most widely employed approach to this class of polymers is the Wurtz coupling reaction of dichlorosilanes with alkaline metals [2]. The harsh reaction conditions allow only simple alkyl or aryl substituents as side chains. The only functional group introduced so far are ether oxygen atoms in polysilanes like [MeSi(CH$_2$)$_x$O(CH$_2$)$_y$CH$_3$]$_n$ [3]. Polysilanes bearing longer alkyl side chains show an interesting thermochromic behaviour in the near UV which corresponds to phase transitions of the polymer. Very likely a rod-like ordering of the alkyl side chains with decreasing temperature forces the polysilane main chain in different conformations. The extend of the σ-electron delocalization along the main chain depends on the torsion angles, and this yields changes in the UV spectrum with temperature. This effect is well investigated for symmetrical dialkylpolysilanes, especially [Hex$_2$Si]$_n$ [4], or alkylmethylpolysilanes [RMeSi]$_n$ (R = Bu, Pent, ..., Dodec) [5]. Polysilanes bearing an ether side chain, *e.g.* the series [MeSi(CH$_2$)$_6$OMe]$_n$, [MeSi(CH$_2$)$_5$OEt]$_n$, [MeSi(CH$_2$)$_4$OPr]$_n$ (constant overall chain length) show a very similar behaviour to the polymers [MeSiHex]$_n$, [MeSiPent]$_n$, [MeSiBu]$_n$ because the angle C–O–C is very flexible even at lower temperature [6]. That means that the substituent behind the oxygen atom has no influence to the thermochromic behaviour. The aim of this work was to prepare and investigate polysilanes bearing a 3-phenoxypropyl side chain in order to extend the substitution pattern of known ethersubstituted polysilanes. So far no polysilanes bearing a side chain Ph–O-(CH$_2$)$_n$- are described in the literature.

## Results and Discussion

The hydrosilylation of allyl phenyl ether with Si–H containing dichlorosilanes yielded the phenoxypropyl substituted dichlorosilanes in good yields:



(1)
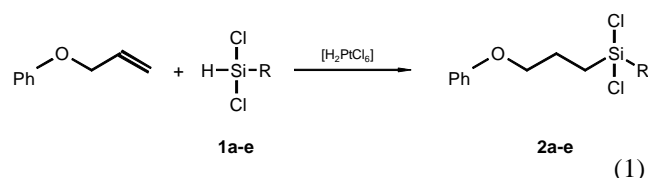
R = Me (**a**), Pent (**b**), Hex (**c**), Hept (**d**), Ph (**e**)



(2)
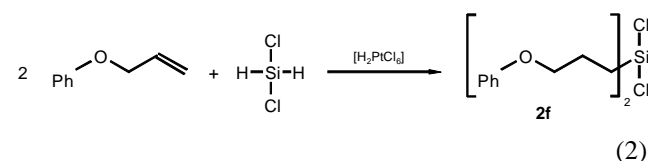
The alkyldichlorosilanes PentSiHCl$_2$ (**1b**), HexSiHCl$_2$ (**1c**) and HeptSiHCl$_2$ (**1d**) could be obtained by hydrosilylation of one equivalent pent-1-ene, hex-1-ene or hept-1-ene, respectively, with dichlorosilane:



(3)

$^{1}$H and $^{13}$C NMR spectra of the obtained product mixtures showed beside approximately 80% of the desired monoaddition 10% of starting $H_2SiCl_2$ and 10% of the dialkyldichlorosilanes $R_2SiCl_2$ (R = Pent, Hex or Hept) which could be separated very easily by fractional distillation.

Wurtz coupling of the dichlorosilanes under standard conditions and fractionated precipitation of the polysilane with isopropanol from a toluene solution gave all desired polysilanes in satisfactory yields.



(4)
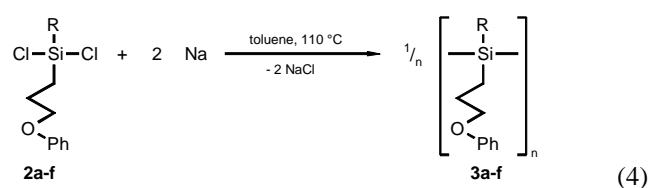
The $^{29}$Si NMR spectra (table 2) of all polysilanes showed in CDCl$_3$ solution only one peak in the expected region for polysilanes. No signals due to terminal groups could be detected confirming a high molecular weight as determined by GPC, see table 1.

The $^{1}$H and $^{13}$C NMR spectra in CDCl$_3$ solution are consistent with the expected structures of the side chains (table 2). Especially in the $^{13}$C NMR spectra the signals are more and more broadened as one approaches the silicon main chain, see fig. 1.

This can be explained by a hindered motion or by a splitting of these signals due to different tacticities of the main chain. Usually the tacticity along the main chain of polysilanes of the structure [RSiR']$_n$ made by Wurtz coupling can be described with Bernoullian statistics with p$_m$ values between 0.6 and 0.8 [7].

All polysilanes show in solution as well as in solid state (thin film) a UV absorption which is in the expected range for methylalkylpolysilanes (300···310 nm), dialkylpolysilanes (314···330 nm) and alkylarylpolysilanes (330···350 nm) [1]. Besides UV fluorescence emission and excitation spectra were recorded. All polysilanes exhibit a strong fluorescence in the near UV. The excitation spectra show a good correlation of the excitation maxima and the UV absorption of the Si–Si $\sigma$-electrons. In all cases the peaks in the excitation spectra are shifted 6.5 to 13 nm to longer wavelengths compared to the peak positions in the UV spectra, see fig. 2.

**Table 1** GPC, UV and fluorescence data of the polysilanes [PhO(CH$_2$)$_3$SiR]$_n$ (**3a**–**f**)

| polymer R | M$_w$ (GPC) (g/mol) | UV (room temp.) thin film (nm) | in hexane (nm) | excitation in hexane (nm) | fluorescence in hexane (nm) |
|---|---|---|---|---|---|
| Me (**3a**) | 200 000 | 304 | 303 | 316 | 335 |
| Pent (**3b**) | 300 000 | 318 | 316 | 326 | 344.5 |
| Hex (**3c**) | 350 000 | 326 | 328 | 334.5 | 347 |
| Hept (**3d**) | 450 000 | 316/356 [a] | 318 | 326 | 345 |
| Ph (**3e**) | 4500 | 336 | 332 | 345 | 361 |
| PhO(CH$_2$)$_3$ (**3f**) | 120 000 | 314 | 316 | 323 | 346.5 |

[a] phase transition at room temperature

**Table 2** $^{29}$Si, $^{1}$H and $^{13}$C NMR chem. shifts (in ppm) of the polysilanes [PhOC$^{C}$H$_2$–C$^{B}$H$_2$–C$^{A}$H$_2$–SiR]$_n$ (**3a**–**f**) [$\alpha$–$\eta$: Si–C$^{\alpha}$H$_2$–C$^{\beta}$H$_2$–C$^{\gamma}$H$_2$–C$^{\delta}$H$_2$...–CH$_3$; i', o', m' and p': Si-Ph signals]

| R | $^{29}$Si | $^{1}$H | $^{13}$C |
|---|---|---|---|
| Me (**3a**) | −31.5 | A: 1.03 B: 1.84, C: 3.82, $\alpha$: 0.38 ArH: o: 6.74, m: 7.12, p: 6.83 | A: 10.7, B: 26.7, C: 70.2, $\alpha$: −4.1, i: 159.0, o: 129.4, m: 114.5, p: 120.5 |
| Pent (**3b**) | −24.2 | A+ $\alpha$: 0.74, B: 1.90, C: 3.77, $\beta$ + $\gamma$+ $\delta$: 1.23 and 1.43, $\varepsilon$: 1.04, ArH: o: 6.68, m: 7.09, p: 6.82 | A: 14.9, B: 27.4, C: 70.2, $\alpha$: 10.6, $\beta$: 27.2, $\gamma$: 36.8, $\delta$: 22.5, $\varepsilon$: 14.1 (CH$_3$), i: 158.9, o: 129.3, m: 114.3, p: 120.3 |
| Hex (**3c**) | −23.7 | A+a: 0.74, B: 1.90, C: 3.78, $\beta$ + $\gamma$+ $\delta$ + $\varepsilon$: 1.20 and 1.4, $\xi$: 1.05 ArH: o: 6.68, m: 7.07, p: 6.80 | A: 15.1, B: 27.3, C: 70.3, $\alpha$: 10.8, $\beta$: 27.7, $\gamma$: 34.4, $\delta$: 31.8, $\varepsilon$: 22.8, $\xi$: 14.0 (CH$_3$), i: 159.1, o: 129.3, m: 114.4, p: 120.4 |
| Hept (**3d**) | −24.1 | A+$\alpha$: 0.75, B: 1.90, C: 3.77, $\beta$ - $\xi$: 1.23 and 1.43, $\eta$: 1.05, ArH: o: 6.68, m: 7.08, p: 6.81 | A: 15.1, B: 27.3, C: 70.3, $\alpha$: 10.7, $\beta$: 27.8, $\gamma$: 34.8, $\delta$: 32.1, $\varepsilon$: 29.5, $\xi$: 22.7, $\eta$: 14.1 (CH$_3$), i: 159.0, o: 129.3, m: 114.3, p: 120.3 |
| Ph (**3e**) | − 32.0 | A: 0.75 [a], B: 1.47 [a], C: 3.52 [a], ArH: 6.7 [a], 6.9 [a], 7.2 [a]) | A: 9.3, B: 25.8, C: 69.9, i: 159.0, o: 129.3, m: 114.4, p: 120.3, o': 135.8, m': 127.8, p': 134.0 |
| PhO(CH$_2$)$_3$ (**3f**) | − 23.0 | A: 1.28 [a], B: 1.92, C: 3.69, ArH: o: 6.69, m: 7.07, p: 6.80 | A: 8.1 [a] and 10.1 [a], B: 26.6 [a] and 22.9 [a], C: 70.0, i: 159.0, o: 129.4, m: 114.5, p: 120.5 |

[a] broad signals
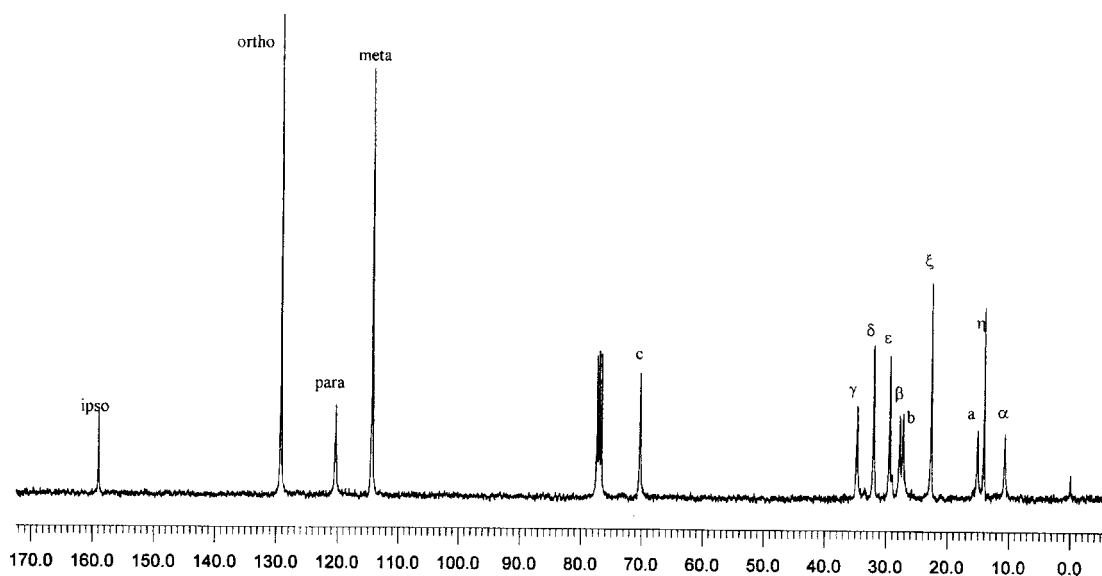
**Fig. 1** $^{13}C$ NMR spectrum of [Hept Si $(CH_2)_3$ OPh]$_n$ (**3d**) in CDCl$_3$
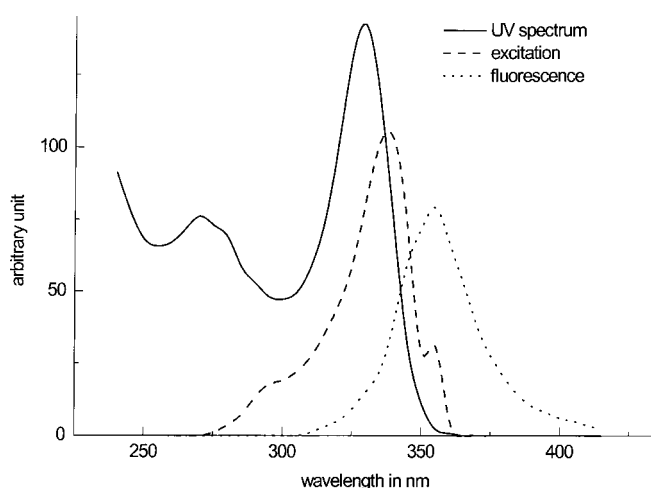


**Fig. 2** UV, excitation and fluorescence spectrum of [Hept Si $(CH_2)_3$ OPh] (**3d**) in *n*-hexane solution

The polymer **3c** seems to be an exception in the series [PhO(CH$_2$)$_3$SiR]$_n$ (R = Pent, Hex, Hept) (**3b–d**) in solution since the $^{29}$Si NMR signal in CDCl$_3$ is shifted to lower field compared with the other two polysilanes, and the UV and excitation peaks are shifted approximately by 10 nm to longer wavelengths. Probably it adopts a different conformation in solution at room temperature.

In the polymer **3e** all spectra are shifted towards longer wavelengths showing, that the phenyl substituent at the silicon takes part in the Si–Si σ-electron delocalization as this is well known for [PhSiMe]$_n$. In order to verify any significance of the phenyl ring in the phenoxypropyl side chain for the fluorescence, dipentylpolysilane (made by Wurtz coupling from Pent$_2$SiCl$_2$) was measured as well. This polymer gave in hexane

solution a UV peak at 316 nm, a peak in the excitation spectrum at 325 nm and in the fluorescence spectrum at 345 nm which is almost identical with the polymers **3b**, **3d** and **3f**. That means that the phenoxy group has no influence towards the Si–Si σ-electrons.

The polymers **3a**, **3e** and **3f** showed no thermochromic behaviour between – 60 and + 30 °C. If one can neglect the phenoxy group because of the very flexible angle at the oxygen atom, these polysilanes should behave like the known polysilanes [PrSiMe]$_n$ [8], [PrSiPh]$_n$ [9] and [Pr$_2$Si]$_n$ [10], where no thermochromism was observed. The alkyl chains are too short to introduce any forces into the main chain.

The polysilanes **3b** and **3c** show some little change in the UV spectra with temperature but no significant phase transition (Fig. 3). The polymer **3d** on the other hand exhibits at least two drastic changes in its UV spectrum with increasing temperature. The first phase transition occures in the relatively broad temperature range between – 15 °C and + 10 °C whereas the second transition takes place in the very narrow range between + 25 °C and + 28 °C.

In order to get more information about the formed phases temperature dependent solid state $^{29}$Si NMR and X-ray diffraction spectra were recorded.

Unfortunately, the $^{29}$Si NMR spectra (Fig. 4)are not very well resolved, but one can assign the relatively narrow signal of the hexagonal columnar mesophase at – 24.4 ppm [3a, 11] in the spectrum at 40 °C. At 15 °C, below the upper phase transition, the peak is broadened and unsymmetric and consists very likely of a new broad peak at approximately – 25.7 ppm, called phase II, and the narrow peak due to the hexagonal columnar mesophase at – 24.4 ppm. At – 20 °C, below the lower phase transition, the peak is even more broadened and shifted
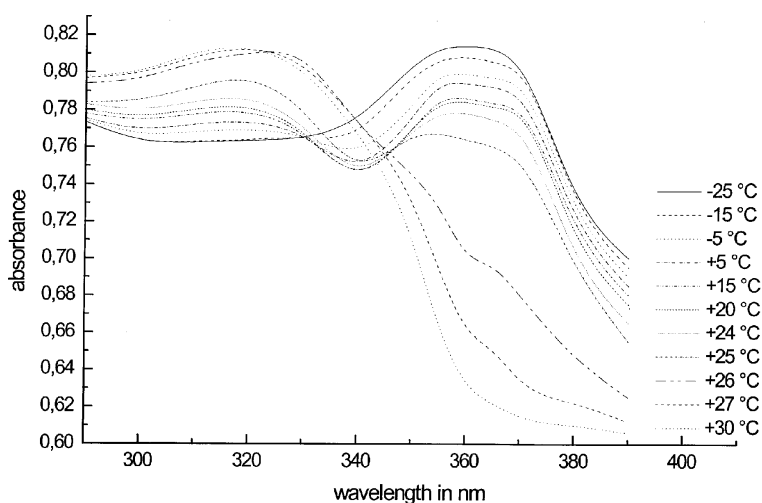
**Fig. 3** UV spectrum of [Hept Si (CH$_2$)$_3$ OPh]$_n$ (**3d**) as thin film on a quartz plate as function of temperature
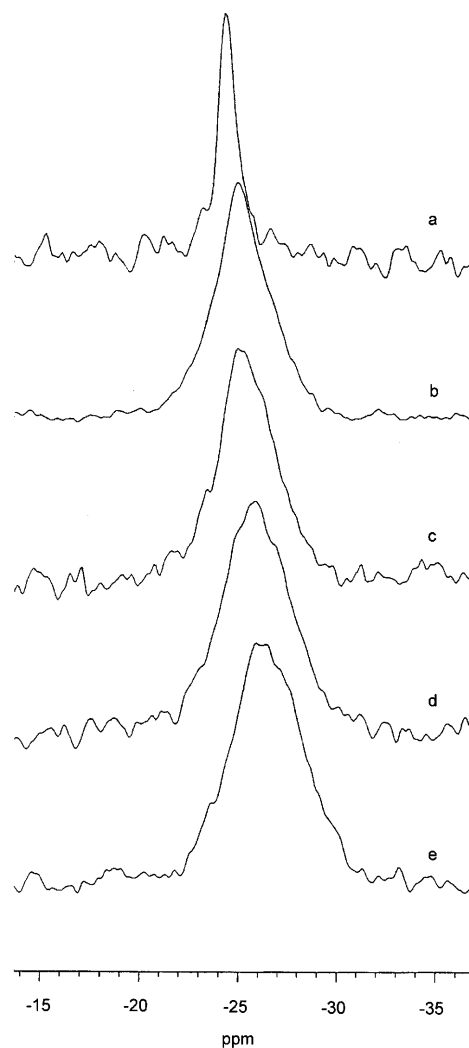


**Fig. 4** $^{29}$Si MAS NMR spectra of [Hept Si (CH$_2$)$_3$ OPh]$_n$ (**3d**) at different temperatures: a) 40 °C, b) 24.5 °C, c) 15 °C, d) 0 °C, e) −20 °C

to higher field. One can assume now two peaks at −25.7 ppm (phase II) and −27.2 ppm (phase III). So far the nature of these two phases is unclear but it is possible that phase III possesses an all-transoid Si–Si main chain. The X-ray diffraction spectra show reflexes at $2\theta = 13.6°$, 13.9°, 18° and 19.5°. All reflexes disappear at temperatures above the upper transition temperature (40 °C). The X-ray spectra at 24 °C and −11 °C are almost identical. It should be mentioned, that the same temperature dependent changes in the UV spectra were observed during cooling and heating of the sample.

**Experimental**

All NMR measurements in solution were performed on a Bruker AM 360 spectrometer. CDCl$_3$ was used as solvent and Me$_4$Si as internal reference for $^1$H (360 MHz), $^{13}$C (90.55 MHz), and $^{29}$Si (71.55 MHz) in 10 mm sample tubes. The $^{29}$Si NMR spectra were recorded using an IGATED pulse sequence and a relaxation delay of 30 s to get quantitative spectra. $^{29}$Si MAS NMR spectra were recorded on a Bruker MSL 300 spectrometer at 59.588 MHz, spinning frequency: 2 kHz. GPC was performed using a Waters Associates Model 6000A Liquid Chromatograph equipped with three American Polymer Standards Co. Ultrastyragel columns in series with porosity indices of 10$^3$, 10$^4$ and 10$^5$ Å, and THF as eluant. The polysilanes were detected with a Waters Model 440 UV Absorbance Detector at a wavelength of 254 nm. Molecular weights were determined relative to calibration with polystyrene standards. UV absorption spectra were recorded on a HP 8452 Diode Array Spectrophotometer. Thin films of the polysilanes were cast on a quartz plate and measured under Ar. Fluorescence emission and excitation spectra were measured on a Hitachi F-4500 Fluorescence Spectrophotometer in $n$-hexane solution.

## Preparation of Dichlorosilanes by Hydrosilylation

*Phenoxypropyl-methyldichlorosilane* (**2a**)

Under nitrogen 9.15 g (68 mmol) allyl phenyl ether were mixed with 9.1 g (79 mmol) $MeSiHCl_2$ and 2 drops of a solution of 20 mg $H_2PtCl_6 \cdot 6H_2O$ in isopropanol were added. After stirring over night the product was distilled *in vacuo* to give at first some $MeSiHCl_2$, 1 ml unchanged allyl phenyl ether (40 °C/0.5 torr) and 12 g (71%) **2a** (*Kp*. 85–110 °C/0.5 torr). 1 ml black oily residue remained.
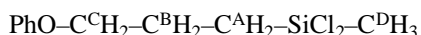
$PhO–C^CH_2–C^BH_2–C^AH_2–SiCl_2–C^DH_3$
$^1$H NMR:  A: 1.24 ppm ($^3J_{HH}$: 8.3 Hz, $^2J_{SiH}$: 7.6 Hz),
 B: 1.94 ppm, C: 3.90 ppm ($^3J_{HH}$: 6.3 Hz),
 D: 0.76 ppm ($^3J_{HH}$: 7.3 ppm), ArH: o: 6.86 ppm
 ($^3J_{HH}$: 8 Hz), m: 7.25 ppm, p: 6.91 ppm ($^3J_{HH}$:
 7.5 Hz)
$^{13}$C NMR:  A: 18.1 ppm ($^1J_{CH}$: 122 Hz), B: 22.6 ppm ($^1J_{CH}$:
 128 Hz) C: 68.6 ppm ($^1J_{CH}$: 144 Hz), D: 5.1 ppm
 ($^1J_{CH}$: 123 Hz, $^1J_{SiC}$: 66.8 Hz) i: 158.7 ppm
 ($^2J_{CH}$: 8.7 Hz), o: 129.4 ppm ($^1J_{CH}$: 157 Hz,
 $^2J_{CH}$: 8.7 Hz) m: 114.4 ppm ($^1J_{CH}$: 153 Hz),
 *p*: 120.7 ppm ($^1J_{CH}$: 163 Hz, $^2J_{CH}$: 7.3 Hz)
$^{29}$Si NMR: 32.9 ppm.

*Pentyldichlorosilane* (**1b**)

51 g of a 25% solution of $H_2SiCl_2$ in xylene (contains 12.75 g/0.126 mol $H_2SiCl_2$) were mixed with 8.76 g (0.125 mol) pent-1-ene under Ar, and 2 drops of a solution of $H_2PtCl_6$ in isopropanol were added. After stirring over night all pent-1-ene was consumed as checked by $^1$H and $^{13}$C NMR. Fractionated distillation yielded 48.7 g of a fraction containing 31.6 mass-% **1b** (0.090 mol) beside xylene, as checked by $^1$H NMR, and 1 ml residue of dipentyldichlorosilane.
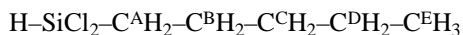
$H–SiCl_2–C^AH_2–C^BH_2–C^CH_2–C^DH_2–C^EH_3$
$^1$H NMR:  Si–H: 5.43 ppm, A: 1.05 ppm ($^3J_{HH}$: 7.9 Hz),
 B: 1.44 ppm, C and D: 1.28 ppm, E: 0.87 ppm
$^{13}$C NMR:  A: 20.2 ppm, B: 22.3 ppm, C: 34.3 ppm,
 D: 21.5 ppm, E: 13.9 ppm.

*Phenoxypropyl-pentyldichlorosilane* (**2b**)

The mixture of **1b** and xylene as obtained was mixed with 12.1 g (0.09 mol) allyl phenyl ether, and 2 drops of a solution of $H_2PtCl_6$ in isopropanol were added. After stirring over night the reaction was complete and fractional distillation gave 16.1 g (0.053 mol) of the desired phenoxypropyl-pentyldichlorosilane which was essentially pure as checked by $^1$H and $^{13}$C NMR.
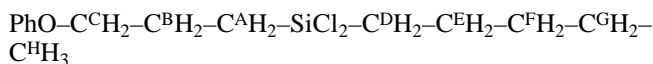
$PhO–C^CH_2–C^BH_2–C^AH_2–SiCl_2–C^DH_2–C^EH_2–C^FH_2–C^GH_2–C^HH_3$
$^1$H NMR:  A: 1.255 ppm ($^3J_{HH}$: 8.3 Hz), B: 1.98 ppm,
 C: 3.95 ppm ($^3J_{HH}$: 6.2 Hz), D: 1.11 ppm ($^3J_{HH}$:
 8.1 Hz), E: 1.50 ppm, F and G: 1.32 ppm,
 H: 0.89 ppm ($^3J_{HH}$: 7.2 Hz), ArH: o: 6.89 ppm
 ($^3J_{HH}$: 8 Hz), m: 7.26 ppm, p: 6.93 ppm
 ($^3J_{HH}$: 7.2 Hz)
$^{13}$C NMR: A: 16.8 ppm ($^1J_{SiC}$: 66.8 Hz), B: 22.6 ppm,
 C: 68.8 ppm, D: 20.3 ppm ($^1J_{SiC}$: 67.4 Hz),
 E: 22.1 ppm, F: 34.6 ppm, G: 22.0 ppm,
 H: 13.9 ppm, i: 158.8 ppm, o: 129.5 ppm,
 *m*: 114.5 ppm, p: 120.8 ppm

*Hexyldichlorosilane* (**1c**) *and phenoxypropyl-hexyldichlorosilane* (**2c**)

were prepared essentially *via* the same route as described for **2b**. The reaction of 15 g (0.15 mol) $H_2SiCl_2$ (as 25% solution in xylene) with 12 g (0.14 mol) hex-1-ene yielded after distillation 53.1 g of a fraction containing 20.7 g (0.112 mol) **1c** and xylene, as checked by $^1$H NMR. This mixture was used without further purification. The reaction with 15 g (0.112 mol) allyl phenyl ether yielded after distillation 29.5 g (0.092 mol) pure **2c**.
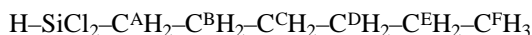
$H–SiCl_2–C^AH_2–C^BH_2–C^CH_2–C^DH_2–C^EH_2–C^FH_3$
$^1$H NMR:  Si–H: 5.43 ppm ($^3J_{HH}$: 1.8 Hz), A: 1.05 ppm
 ($^3J_{HH}$: 8.0 Hz), B: 1.44 ppm, C, D and
 E: 1.27 ppm, F: 0.88 ppm ($^3J_{HH}$: 6.9 Hz)
$^{13}$C NMR:  A: 20.3 ppm ($^1J_{SiC}$: 68.7 Hz) , B: 22.6 ppm,
 C and D: 31.4 and 31.8 ppm, E: 21.9 ppm,
 F: 14.1 ppm
$^{29}$Si NMR: 11.5 ppm ($^1J_{SiH}$: 276.0 Hz, $^2J_{SiH} \approx ^3J_{SiH}$: 7.4 Hz)
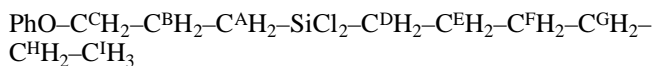
$PhO–C^CH_2–C^BH_2–C^AH_2–SiCl_2–C^DH_2–C^EH_2–C^FH_2–C^GH_2–C^HH_2–C^IH_3$
$^1$H NMR:  A: 1.27 ppm, B: 1.97 ppm, C: 3.93 ppm ($^3J_{HH}$:
 6.2 Hz), D: 1.11 ppm ($^3J_{HH}$: 8.1 Hz), E: 1.49 ppm,
 F, G and H: 1.27 ppm, I: 0.89 ppm
 ($^3J_{HH}$: 6.6 Hz), ArH: o: 6.87 ppm ($^3J_{HH}$: 8.2 Hz),
 *m*: 7.26 ppm, *p*: 6.92 ($^3J_{HH}$: 7.2 Hz)
$^{13}$C NMR:  A: 16.8 ppm ($^1J_{SiC}$: 67.4 Hz), B: 22.6 ppm,
 C: 68.8 ppm, D: 20.3 ppm ($^1J_{SiC}$: 67.4 Hz),
 E: 22.5 ppm, F : 32.1 ppm, G: 31.3 ppm,
 H: 22.3 ppm, I: 14.1 ppm, i: 158.8 ppm,
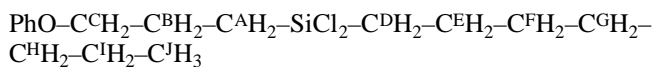 *o*: 129.4 ppm, *m*: 114.5 ppm, *p*: 120.8 ppm

*Heptyldichlorosilane* (**1d**) *and Phenoxypropyl-heptyldichlorosilane* (**2d**)

were prepared essentially via the same route as described for **1b** and **2b**. The reaction of 15 g (0.15 mol) $H_2SiCl_2$ (as 25% solution in xylene) with 14 g (0.14 mol) hept-1-ene yielded after distillation at 35–60 °C and 0.5 torr 40 g of a fraction containing 21 g (0.105 mol) **1d** and xylene, as checked by $^1$H NMR and 2 g of a residue of diheptyldichlorosilane. The mixture with xylene was used without further purification. The reaction with 14.7 g (0.11 mol) allyl phenyl ether yielded after distillation 29.5 g (0.089 mol) pure **2d**.
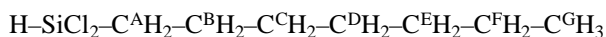
$H–SiCl_2–C^AH_2–C^BH_2–C^CH_2–C^DH_2–C^EH_2–C^FH_2–C^GH_3$
$^1$H NMR:  Si-H: 5.45 ppm ($^1J_{SiH}$: 275.8 Hz, $^3J_{HH}$: 1.8 Hz),
 A: 1.08 ppm ($^3J_{HH}$: 7.8 Hz), B: 1.47 ppm,
 C, D E and F: 1.27 ppm, G: 0.89 ppm
 ($^3J_{HH}$: 6.6 Hz)
$^{13}$C NMR:  A: 20.3 ppm ($^1J_{SiC}$: 68.8 Hz) , B: 22.8 ppm,
 C: 32.2 ppm, D: 31.8 ppm, E: 28.9 ppm,
 F: 21.9 ppm, G: 14.1 ppm.

$PhO–C^CH_2–C^BH_2–C^AH_2–SiCl_2–C^DH_2–C^EH_2–C^FH_2–C^GH_2–C^HH_2–C^IH_2–C^JH_3$
$^1$H NMR:  A: 1.27 ppm, B: 1.98 ppm, C: 3.95 ppm
 ($^3J_{HH}$: 6.3 Hz), D: 1.12 ppm ($^3J_{HH}$: 8.1 Hz),
 E: 1.50 ppm, F, G, H and I: 1.28 ppm,
 J: 0.89 ppm ($^3J_{HH}$: 6.3 Hz), ArH: o: 6.88 ppm
 ($^3J_{HH}$: 8.1 Hz), m: 7.26 ppm, p: 6.92 ppm
$^{13}$C NMR:  A: 16.8 ppm ($^1J_{SiC}$: 67 Hz), B: 22.6 ppm,

C: 68.8 ppm, D: 20.4 ppm ($^1J_{SiC}$: 68 Hz),
E: 22.7 ppm, F : 32.4 ppm, G: 31.7 ppm,
H: 28.8 ppm, I: 22.4 ppm, J: 14.1 ppm,
*i*: 158.8 ppm, *o*: 129.5 ppm, *m*: 114.5 ppm,
*p*: 120.8 ppm

*Phenoxypropyl-phenyldichlorosilane* (**2e**)

Under nitrogen 16.0 g (0.12 mol) allyl phenyl ether were mixed with 17.7 g (0.10 mol) PhSiHCl$_2$, and 2 drops of a solution of 20 mg H$_2$PtCl$_6$ · 6H$_2$O in isopropanol were added. After stirring over night the reaction mixture turned black, and the fractionated distillation *in vacuo* gave at first 4 g allyl phenyl ether and than 26.7 g (86%) **2e** at 165–190 °C/ 0.5 torr). 1 ml black oily residue remained.

Ph$^b$O–C$^C$H$_2$–C$^B$H$_2$–C$^A$H$_2$–SiCl$_2$–Ph$^a$
$^1$H NMR:  A: 1.48 ppm ($^3J_{HH}$: 8.3 Hz), B: 1.98 ppm,
C: 3.89 ppm ($^3J_{HH}$: 6.3 Hz, $^1J_{CH}$: 142 Hz),
Ph$^a$: o: 7.70 ppm ($^3J_{HH}$: 7.6 Hz), m: 7.39 ppm,
p: 7.43 ppm ($^3J_{HH}$: 7.2 Hz), Ph$^b$: o: 6.83 ppm
($^3J_{HH}$: 7.9 Hz), m: 7.23 ppm, p: 6.90 ppm($^3J_{HH}$:
7.2 Hz)
$^{13}$C NMR:  A: 17.1 ppm ($^1J_{SiC}$: 71.2 Hz), B: 22.6 ppm,
C: 68.6 ppm, Ph$^a$: *i*: 132.2 ppm, *o*: 133.3 ppm,
*m*: 128.4 ppm, *p*: 131.7 ppm Ph$^b$: *i*: 158.7 ppm,
*o*: 129.4 ppm, *m*: 114.4 ppm, *p*: 120.7 ppm
$^{29}$Si NMR: 19.15 ppm

*Bis(phenoxypropyl)dichlorosilane* (**2f**)

Under nitrogen 24.5 g (0.183 mol) allyl phenyl ether were mixed with a solution of 9.3 g H$_2$SiCl$_2$ (0.092 mol) in xylene (25 mass-% H$_2$SiCl$_2$), and 2 drops of a solution of 20 mg H$_2$PtCl$_6$ · 6H$_2$O in isopropanol were added. After stirring for two days the product was distilled *in vacuo* to give at first xylene and some allyl phenyl ether, next approximately 5 ml at 120–125 °C/0.5 torr (mainly PhO(CH$_2$)$_3$SiHCl$_2$) and finally 20.5 g (61%) 2f (*Kp.* 180–210 °C / 0.5 torr). 1 ml black oily residue remained.

[PhO–C$^C$H$_2$–C$^B$H$_2$–C$^A$H$_2$-]$_2$SiCl$_2$
$^1$H NMR:  A: 1.26 ppm ($^3J_{HH}$: 8.3 Hz), B: 1.96 ppm,
C: 3.88 ppm ($^3J_{HH}$: 6.1 Hz)
ArH: o: 6.85 ppm ($^3J_{HH}$: 8.6 Hz), m: 7.24 ppm,
p: 6.91 ppm ($^3J_{HH}$: 7.5 Hz)
$^{13}$C NMR:  A: 16.7 ppm ($^1J_{CH}$: 122 Hz, $^2J_{CH}$: 4.0 Hz,
$^1J_{SiC}$: 76.3 Hz), B: 22.5 ppm ($^1J_{CH}$: 129 Hz,
$^2J_{SiC}$: 8.0 Hz), C: 68.6 ppm ($^1J_{CH}$: 143 Hz,
$^2J_{CH}$: 4.0 Hz), i: 158.7 ppm, o: 129.4 ppm
($^1J_{CH}$: 158.5 Hz, $^2J_{CH}$: 8.7 Hz, $^3J_{CH}$: 1.5 Hz),
*m*: 114.4 ppm ($^1J_{CH}$: 158.5 Hz), *p*: 120.7 ppm
($^1J_{CH}$: 160 Hz)
$^{29}$Si NMR: 33.4 ppm
PhO–CH$_2$–CH$_2$–CH$_2$–SiHCl$_2$: $^1$H NMR: SiH: 5.55 ppm
($^3J_{HH}$: 2.0 Hz); $^{29}$Si NMR: 10.7 ppm

## Wurtz Condensation

*Preparation of {[PhO(CH$_2$)$_3$]$_2$Si}$_n$ (**3f**) as a typical example*
2.76 g (0.12 mol) Na and 50 ml toluene were heated until 110°C and stirred under Ar. 20 g (0.054 mol) [PhO(CH$_2$)$_3$]$_2$

SiCl$_2$ were added to this dispersion within 5 min. The sodium turned pink and later deep blue. After 1 h of intensive stirring at 110 °C the mixture was allowed to cool to room temperature before 3 ml isopropanol and finally 250 ml methanol were added carefully. The light blue residue of polymer and NaCl were dissolved in 40 ml toluene. The solution was filtered from the light blue NaCl, and the polymer was precipitated by adding of 100 ml MeOH to yield 5 g crude product. The polymer was redissolved in 40 ml toluene and precipitated with 40 ml MeOH to yield 3.5 g (22%) of a white, almost solid polysilane after drying *in vacuo*.

All other polysilanes were prepared using the same procedure. The yields of polysilanes after fractionation were **3a**: 7.5%, **3b**: 7%, **3c**: 5%, **3d**: 12%, **3e**: 29%.

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