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Heterosubstituted Polysilanes

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ABSTRACT: The reaction of phenylalkylpolysilanes $(PhRSi)_n$ (R = Me, Pr, Hex, Oct) with acetyl chloride/aluminum chloride or acetyl bromide/aluminum bromide yielded the new halogen-substituted polysilanes $SiX_2R-(SiXR)_n-SiX_2R$ (X = Cl, Br). These were further converted into alkoxy- or thioalkyl-substituted polysilanes, providing the first method for synthesizing such polymers. The halogenated polysilanes were also hydrogenated with $LiAlH_4$ to form hydropolysilanes $SiH_2R-(SiHR)_n-SiH_2R$. All polysilanes were characterized by ^1H, ^{13}C, ^{29}Si NMR, GPC, and UV. The phenylalkylpolysilanes and *p*-methoxyphenylhexylpolysilane showed strong fluorescence in the near-UV.

I. Introduction

Polysilanes are a unique class of polymers, containing linear Si−Si catenation in the main chain with two organic substituents at each silicon.[1] σ-Electrons in the main chain of polysilanes are strongly delocalized. Despite great efforts to find alternative synthetic routes to polysilanes,[2] the Wurtz coupling reaction of dichlorosilanes is still the most widely employed approach. The harsh reaction conditions allow only simple alkyl or aryl substituents as side chains. The only functional group that could be introduced into polysilanes so far is an ether oxygen atom.[3] On the other hand, it should be possible to do substitution reactions on an already prepared polysilane. Most promising is the dearylation of aryl groups, e.g. in $(PhMeSi)_n$. Attempts to cleave the Si−Ph bonds in $(PhMeSi)_n$ with HCl in the presence of $AlCl_3$ led only to a partial substitution and a polymer of the composition $[(PhMeSi)_{0.3}(SiClMe)_{0.7}]_n$.[4] Another possibility is cleavage with trifluoromethanesulfonic acid (HOTf). This reaction works quite well in the synthesis of substituted oligosilanes, but in $(PhMeSi)_n$ only 50%[5] or 80%[6] of the phenyl groups could be replaced without significant cleavage of the Si−Si chain, leading to a copolymer of the type $[(PhMeSi)_x(MeSiOTf)_y]_n$. Even with an excess of HOTf 10% of the phenyl groups remained attached to the polysilane backbone.

Recent syntheses of chloro-substituted and bromo-substituted silanes starting from phenyl-substituted silanes with acetyl chloride and aluminum chloride or acetyl bromide and aluminum bromide showed that, under these conditions, phenyl and methyl groups can be replaced quite efficiently without cleavage of Si−Si bonds.[7] We have applied these reactions to poly(alkylaryl)silanes and found that they lead to complete replacement of the aryl substituents (Ar = aryl; R = alkyl; Ac = MeCO; X = Cl, Br):

$$(ArSiR)_n + nAcX + nAlX_3 \rightarrow (XSiR)_n + nAcAr\cdot AlX_3$$

Some cleavage of the polysilane chain also took place. Further substitution of the chloro- or bromo-substituted polymers with nucleophiles, alcohols, amines, or mercaptans provided an approach to a great variety of heterosubstituted polysilanes $(YSiR)_n$ (Y = OR, NR_2, SR, ...) which were previously unknown.

II. Experimental Section

Synthesis of Phenylalkyldichlorosilanes, $PhSiRCl_2$ (R = *n*-Propyl, *n*-Hexyl, *n*-Octyl, and *p*-$MeOC_6H_4SiHexCl_2$). The dichlorosilanes were prepared by reaction of phenylmagnesium bromide with the commercially available alkyltrichlorosilanes. In a typical reaction a phenylmagnesium bromide solution was prepared from 15 g (0.62 mol) of Mg and 70.6 g (0.45 mol) of bromobenzene in 150 mL of diethyl ether. The Grignard solution was syringed into a solution of 110 g (0.5 mol) of $HexSiCl_3$ in 100 mL of diethyl ether under intensive stirring. After stirring overnight the solution was filtered from precipitated magnesium salts and distilled in a vacuum to give 62 g of pure $PhHexSiCl_2$, bp (0.5 Torr) 90−100 °C.

Similar reactions with $PrSiCl_3$ yielded $PhPrSiCl_2$, bp (0.5 Torr) 58 °C, and with $OctSiCl_3PhOctSiCl_2$, bp (0.5 Torr): 105−115 °C.

$PhPrSiCl_2$. ^1H NMR: 0.98 ppm (3H, $^3J_{HH}$ = 7.2 Hz), 1.29 ppm (Si−CH_2, $^3J_{HH}$ = 8.2 Hz), 1.56 ppm (2H), 7.37−7.43 ppm (3H, meta + para), 7.69 (2H, ortho, $^3J_{HH}$ = 7.8 Hz). ^{13}C NMR: 16.2 ppm, 17.15 ppm, 23.05 ppm ($^1J_{SiC}$ = 71 Hz), 128.3 ppm (ortho), 131.5 ppm (para), 132.7 ppm (ipso), 133.3 ppm (meta). ^{29}Si NMR: 18.9 ppm.

$PhHexSiCl_2$. ^1H NMR: 0.85 ppm (3H, $^3J_{HH}$ = 6.6 Hz), 1.22−1.36 ppm (8 H), 1.54 ppm (2 H), 7.32−7.40 (3 H, meta + para), 7.68 ppm (2 H, ortho, $^3J_{HH}$ = 7.8 Hz). ^{13}C NMR: 14.05 ppm (CH_3), 20.8 ppm (C^α, $^1J_{SiC}$ = 71 Hz), 22.46 ppm (C^β), 22.49 ppm (C^ϵ), 31.3 ppm (C^δ), 32.1 ppm (C^γ), 128.3 ppm (ortho), 131.5 ppm (para), 132.8 ppm (ipso), 133.3 ppm (meta). ^{29}Si NMR: 19.3 ppm.

$PhOctSiCl_2$. ^1H NMR: 0.85 ppm (3H, $^3J_{HH}$ = 6.6 Hz), 1.22−1.36 ppm (8 H), 1.54 ppm (2 H), 7.32−7.40 (3 H, meta + para), 7.68 ppm (2 H, ortho, $^3J_{HH}$ = 7.8 Hz). ^{13}C NMR: 14.1 ppm (CH_3), 20.75 ppm (C^α, $^1J_{SiC}$ = 71 Hz), 22.5 ppm, 22.7 ppm, 29.1 ppm, 29.15 ppm, 31.9 ppm, 32.45 ppm, 128.3 ppm, 131.5 ppm, 132.8 ppm, 133.3 ppm. ^{29}Si NMR: 19.2 ppm.

p-$MeOC_6H_4SiHexCl_2$ was synthesized from a Grignard solution made from 50 g (0.267 mol) of *p*-MeO−C_6H_4−Br and 7.3 g (0.3 mol) of Mg in diethyl ether and 76 g (0.35 mol) of hexyltrichlorosilane. Fractional distillation in a vacuum yielded 32 g of *p*-$MeOC_6H_4SiHexCl_2$, bp (0.5 Torr): 125−130 °C. ^1H NMR: 0.87 ppm (3H, $^3J_{HH}$ = 6.7 Hz), 1.25−1.35 ppm (8 H), 1.52 ppm (2 H), 3.77 ppm (CH_3O−), 6.94 ppm (2H, $^3J_{HH}$ = 8.7 Hz), 7.63 ppm (2H). ^{13}C NMR: 14.1 ppm (CH_3), 20.95 ppm ($^1J_{SiC}$ = 71 Hz), 22.5 ppm ($C^\beta + C^\epsilon$), 31.3 ppm (C^δ), 32.1 ppm (C^γ), 55.1 ppm (MeO), 114.0 ppm, 123.7 ppm (C−Si), 135.2 ppm, 162.3 ppm (C−O). ^{29}Si NMR: 19.3 ppm.

Wurtz Coupling Reactions. In a typical experiment 10 g (0.435 mol) of Na and 100 mL of toluene were heated to 110 °C and stirred under Ar. $PhHexSiCl_2$ (54.8 g, 0.21 mol) was added to this dispersion over 50 min. The sodium turned pink and later deep blue. After 1 h of vigorous stirring at 110 °C the mixture was allowed to cool to room temperature, where-

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upon 300 mL of methanol was added carefully. The light blue residue of polysilane and NaCl was extracted with 100 mL of toluene. The solution was filtered from the light blue NaCl, and the polymer was precipitated by adding of 100 mL of methanol. Finally the polymer was dried in a vacuum to give 6.5 g (16.5%) of a white, highly viscous polysilane.

$(PhMeSi)_n$ (yield 42%) and $(PhPrSi)_n$ (yield 6%) are white powders, $(PhHexSi)_n$ and $(p\text{-}MeO{-}C_6H_4SiHex)_n$ (yield 5%) are highly viscous and milky, and $(PhOctSi)_n$ (yield 30%) is viscous but transparent.

After complete removal of all solvent in a vacuum the polysilanes $(PhHexSi)_n$ and $(p\text{-}MeO{-}C_6H_4SiHex)_n$ showed a visible blue fluorescence.

Reactions with Acetyl Chloride/Aluminum Chloride or Acetyl Bromide/Aluminum Bromide. In a typical experiment, 1 g of $(PhMeSi)_n$ was dissolved in 10 mL of dry hexane and 2 g (15 mmol) of anhydrous $AlCl_3$ was added. Under stirring in an ice bath 1.2 g (15 mmol) of acetyl chloride was added dropwise. The reaction mixture turned dark brown immediately. After stirring for several hours at 0 °C and then at room temperature and standing overnight, the upper layer was separated and the dark brown residue extracted twice with 15 mL of hexane. The combined hexane solutions of $SiCl_2Me{-}(SiClMe)_n{-}SiCl_2Me$ were concentrated in a vacuum to give a semisolid slightly yellow residue of the polysilane in ca. 70% yield.

The reaction procedure with acetyl bromide and aluminum bromide was essentially the same as described above, but 4 g (15 mmol) of $AlBr_3$ and 1.85 g (15 mmol) of acetyl bromide were used instead.

In the cases of polysilanes with longer alkyl chains (propyl through octyl) the reaction was started at room temperature and after 1 h heated to 50 °C for 1 h to achieve a complete substitution of the phenyl groups.

Reaction with Alcohols or Mercaptans. A hexane solution of $SiX_2R{-}(SiXR)_n{-}SiX_2R$ (X = Cl, Br; R = Me, Pr, Hex, Oct) as obtained in the synthesis above was treated with 15 mmol of the desired alcohol (MeOH, EtOH, *n*-BuOH, *i*-PrOH, *t*-BuOH) or mercaptan (EtSH, *n*-BuSH) and 1.5 g (15 mmol) of NEt_3. After stirring for 2 h the solution was separated from precipitated $Et_3N{\cdot}HCl$, and the hexane and excess alcohol or mercaptan and triethylamine were removed in a vacuum to give the alkoxy- or thioalkyl-substituted polysilanes as colorless highly viscous oils.

Hydrogenation with $LiAlH_4$. $LiAlH_4$ (0.57 g, 15 mmol) was dissolved in 10 mL of dried diethyl ether, and a solution of the chloro-substituted polysilane as obtained in the synthesis above in 5 mL of hexane was added. After stirring for 2 h at room temperature the solution was hydrolyzed carefully with dilute HCl/ice. The ether layer was separated and dried over Na_2SO_4, and the solvent was removed in a vacuum to yield $SiH_2R{-}(SiHR)_n{-}SiH_2R$ polymers as colorless viscous oils.

NMR, UV, GPC, and Fluorescence Measurements. All NMR measurements were performed on a Bruker AM 360 spectrometer. $CDCl_3$ was used as solvent and Me_4Si as internal reference for ^1H (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. A total of 2000 scans were necessary to get a sufficient signal-to-noise ratio if approximately 0.5 g of the polymer was used. 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 with 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 either as thin films on black paper or in hexane solution.

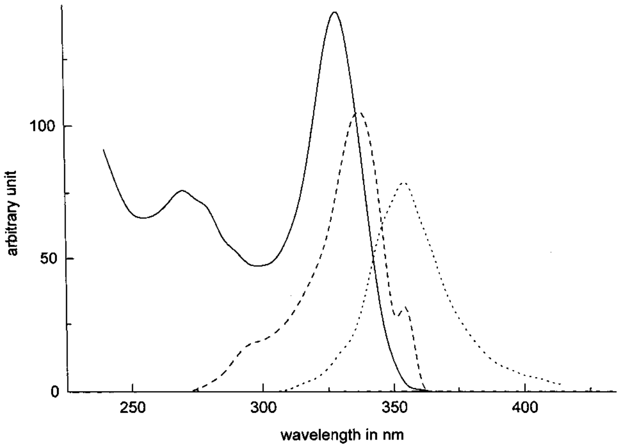

Figure 1. Electronic spectra of $[PrSiPh]_n$ in *n*-hexane: (—) UV absorption; (···) fluorescence emission (excitation at 300 nm); (- - -) excitation spectrum (emission at 355 nm).

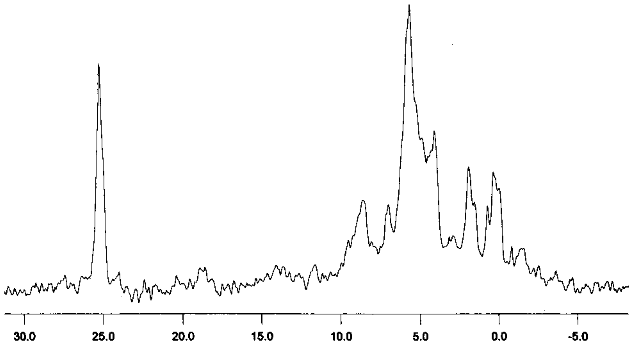

Figure 2. ^{29}Si NMR spectrum of $SiCl_2Me{-}(SiClMe)_n{-}SiCl_2Me$ in $CDCl_3$.

III. Results and Discussion

The Wurtz coupling reaction of the alkylaryldichlorosilanes $PhMeSiCl_2$, $PhPrSiCl_2$, $PhHexSiCl_2$, $PhOctSiCl_2$, and $p\text{-}MeOC_6H_4HexSiCl_2$ yielded the desired poly(arylalkyl)silanes. All of these polymers showed strong fluorescence in the near-UV in the solid state as well as in hexane solution. A significant shift of the UV absorption as well as the fluorescence to longer wavelength was observed for the $[p\text{-}MeOC_6H_4SiHex]_n$ polymer compared with $[PhSiHex]_n$. Similar bathochromic shifts upon *p*-methoxy substitution have been observed for poly(arylmethyl)silanes.[8] Although the electronic spectra of poly(arylalkyl)silanes are not fully understood, the observed shift may be explained by electron donation from the *p*-methoxy group, raising the energy of the aromatic ring π orbitals which mix with the polysilane σ HOMO.

The excitation spectra show clearly that the excitation corresponds to the UV absorption band of the delocalized Si−Si σ-electrons. Figure 1 shows the UV, fluorescence emission, and excitation spectrum of $[PhSiPr]_n$ as one example. Due to the workup in methanol, the end groups in all polymers are −SiPhR(OMe). This allowed the determination of the average chain length and molecular weight (M_n) from the ^{29}Si NMR spectra, which can be compared with the results of the GPC measurements. Table 1 summarizes the UV, fluorescence, and GPC results, and Tables 2 and 3 give the NMR chemical shifts of the polymers.

The reaction of the poly(phenylalkyl)silanes with acetyl chloride/aluminum chloride and acetyl bromide/aluminum bromide yielded the halogen-substituted

Table 1. UV, Fluorescence Emission and Excitation Spectra and GPC Data of the Polymers (ArSiR)$_n$; Ar = Ph, p-MeOC$_6$H$_4$; R = Me, ^{n}Pr, ^{n}Hex, ^{n}Oct

		thin film		hexane solution		
polymer	GPC M_w (g/mol)	UV (σ Si) (nm)	fluor EM[a] (nm)	UV (σ Si) (nm)	fluor EM[a] (nm)	fluor EX[b] (nm)
(PhSiMe)$_n$	5000 (85%), 300000 (15%)	334	367	328	350.5	335
(PhSi^{n}Pr)$_n$	6500	322	368.5	330	354	337
(PhSi^{n}Hex)$_n$	4500 (95%), 130000 (5%)	326	365	330	358.5	348
(PhSi^{n}Oct)$_n$	5000 (95%), 50000 (5%)	324	358	326	357	343.5
(p-MeO−C$_6$H$_4$Si^{n}Hex)$_n$	5500	346	375.5	350	368	354.5

[a] Peak position in the emission spectrum. [b] Peak position in the excitation spectrum.

Table 2. ^{29}Si NMR Data of the Polymers (ArSiR)$_n$; Ar = Ph, p-MeOC$_6$H$_4$; R = Me, ^{n}Pr, ^{n}Hex, ^{n}Oct

polymer	δ_{Si} (ppm) middle units −SiArR−	δ_{Si} (ppm) terminal units −SiArR(OMe)	av chain length (^{29}Si NMR)	M_n (^{29}Si NMR) (g/mol)
(PhSiMe)$_n$	−39.4, −40.1, −41.4	8.3	40	4900
(PhSi^{n}Pr)$_n$	−30.2, −32.4, −39.2	8.5	19	2900
(PhSi^{n}Hex)$_n$	−32.0, −35.0, −38.9	8.7	16	3100
(PhSi^{n}Oct)$_n$	−32.0, −34.8, −38.8	8.7	17	3800
(p-MeO−C$_6$H$_4$Si^{n}Hex)$_n$	−29.8, −32.4, −35.6	8.3	20	4400

Table 3. ^{1}H and ^{13}C NMR Data of the Polymers (ArSiR)$_n$; Ar = Ph, p-MeOC$_6$H$_4$; R = Me, ^{n}Pr, ^{n}Hex, ^{n}Oct

polymer	^{1}H NMR (ppm)	^{13}C NMR (ppm)
(PhSiMe)$_n$	Me: 0 to −0.9	Me: −6.6
Ph: 6.25−7.25	Ph: 127.2, 134.9	
OMe: 3.05[a]	OMe: 51.5[a]	
(PhSi^{n}Pr)$_n$	Pr: 0−1.1	Pr: 16.2 (α), 19.8 (β), 18.5 (CH$_3$)
Ph: 6.5−7.3	Ph: 127.3, 134.0, 136.0	
OMe: 3.15[a]	OMe: 51.5[a]	
(PhSi^{n}Hex)$_n$	Hex: 0.81 (CH$_3$), 0.9−1.2	Hex: 12.5 (α), 26.4 (β), 33.7 (γ), 31.3 (δ), 22.6 (ϵ), 14.1 (CH$_3$)
Ph: 6.8−7.4	Ph: 127.4, 134.1, 136.1, 136.6	
OMe: 3.15[a]	OMe: 51.5[a]	
(PhSi^{n}Oct)$_n$	Oct: 0.85 (CH$_3$), 0.9−1.4	Oct: 12.6 (α), 26.4 (β), 33.9 (γ), 32.0 (δ), 29.2 (ϵ and ζ), 22.7 (η), 14.2 (CH$_3$)
Ph: 6.8−7.5	Ph: 127.4, 134.0, 136.0	
OMe: 3.15[a]	OMe: 51.6[a]	
(p-MeO−C$_6$H$_4$Si^{n}Hex)$_n$	Hex: 0.84 (CH$_3$), 0.9−1.4	Hex: 12.6 (α), 26.4 (β), 33.8 (γ), 31.5 (δ), 22.6 (ϵ), 14.1 (CH$_3$)
C$_6$H$_4$: 6.2−7.5	C$_6$H$_4$: 115, 135, 162	
OMe: 3.72	OMe: 55.1	

[a] Terminal units −SiArR(OMe).

Table 4. GPC, UV, and ^{29}Si NMR Data of the Polymers SiX$_2$R−[SiXR]$_n$−SiX$_2$R; X = Cl, Br, H; R = Me, ^{n}Pr, ^{n}Hex, ^{n}Oct

X	R	GPC M_w (g/mol)	PD	UV (nm)	δ_{Si} (ppm) middle units	term. units	chain length (Si NMR)
Cl	Me	4000	1.3	300	0.3, 1.8, 4.0, 5.5 (main), 8.4	25.1	25
Cl	Pr	5000	1.1	302	1.5, 3.6, 7.9 (main), 11.7	25.0	14
Cl	Hex	5000	1.1	300	1.5, 4.3, 7.9 (main), 10.2	25.2	13
Cl	Oct	5200	1.2	304	1.5, 4.3, 7.8 (main), 11.6	25.1	12
Br	Me			310	−2.6, −8.0, −9.3 (main), −11.0, −13.0	9.2	11
Br	Hex			310	−11.6, −8.8, −7.5, −5.5 (main), −3.8	12.6[a]	10
Br	Oct			304	−11.6, −8.8, −7.4, −6.9, −5.9 (main), −4.0	12.4[b]	9
H	Me	2500	1.1	254	−70.5, −69.5 (main), −68.2	−64.6	27
H	Pr	4500	1.2	257	−70.2, −66.1	−61.0	15
H	Hex	4500	1.1	250	−69.0, −65.4	−59.9	14
H	Oct	4700	1.1		−69.0, −65.6	−59.9	15

[a] Additional signals at 5.1 ppm (SiBr$_2$Hex−SiBr$_2$Hex) and −14.3 ppm (1 Si) and 10.3 ppm (2 Si) (SiBr$_2$Hex−SiBrHex−SiBr$_2$Hex).
[b] Additional signals at 5.1 ppm (SiBr$_2$Oct−SiBr$_2$Oct) and −14.3 ppm (1 Si) and 10.3 ppm (2 Si) (SiBr$_2$Oct−SiBrOct−SiBr$_2$Oct).

polysilanes SiX$_2$R−[SiXR]$_n$−SiX$_2$R (R = Me, Pr, Hex, Oct; X = Cl, Br). In the cases where the alkyl chains R were longer than methyl, higher reaction temperatures were necessary to achieve a complete substitution of the phenyl groups. According to the integration of the ^{1}H NMR spectra, only approximately 1% of the phenyl groups remained, that is, much less than one per polysilane molecule. The reaction with acetyl chloride and aluminum bromide yielded in general polymers with shorter chain lengths than the reaction with acetyl chloride/aluminum chloride. In both cases, however, some Si−Si bond cleavage occurred, yielding products with chain lengths of 9−27 Si units (Table 4). In the cases of longer alkyl chains (Hex, Oct) even the small oligosilanes SiBr$_2$R−SiBr$_2$R and SiBr$_2$R−SiBrR−SiBr$_2$R (R = Hex, Oct) could be detected by ^{29}Si NMR in the products.[9] For that reason the chloro-subsituted polysilanes were used for further synthesis of heterosubstituted polymers.

The average chain lengths and calculated molecular weights determined from the ^{29}Si NMR spectra are somewhat smaller that the values observed by GPC, even taking into account the fact that the NMR results yield M_n values and the GPC reports M_w. The polydispersities M_w/M_n derived from the GPC results are in the range from 1.1 to 1.3, a remarkably low value. This

Table 5. GPC, UV and ^{29}Si NMR Data of the Polymers SiY_2R-$[SiYR]_n$-SiY_2R; Y = OMe, OEt, O^{n}Bu, O^{i}Pr, O^{t}Bu, SEt, SBu; R = Me, ^{n}Pr, ^{n}Hex, ^{n}Oct

Y	R	GPC M_w (g/mol)	UV (nm)	δ_{Si} (ppm) middle units	term. units	chain length (Si NMR)
OMe[a]	Me	2800	303	5.1, 5.9, 6.3, 10.8, 11.5, 12.1	−1.2	23
OMe[b]	Me	2100		5.1, 5.9, 6.3, 10.8, 11.5, 12.1	−1.2	16
OMe	Pr	4500	302	7.8, 9.1, 14.8, 16.2	−2.3	16
OMe	Hex	4500	298	8.0, 9.4, 11.1, 14.8, 16.3	−2.1	13
OMe	Oct	5200		8.5, 9.4, 11.1, 14.8, 16.3	−2.1	12
OEt	Me	3000	304	2.7, 7.3, 7.9, 8.6, 9.2	−4.9	18
OEt	Hex	5000	298	4.6, 5.8, 7.7, 9.9, 11.6, 13.7	−5.7	14
OEt	Oct	4800		4.5, 5.8, 7.7, 9.9, 11.8, 13.7	−5.7	12
O^{i}Pr	Me	3500	292	−1.4, 4.4, 5.6	−9.2	14
O^{i}Pr	Hex	4800	304	1.0, 1.4, 1.8, 2.7, 4.3, 8.7, 9.9	−11.1	12
O^{n}Bu	Me	4700	296	2.6, 7.3, 7.7, 8.4, 9.1	−5.0	13
O^{t}Bu/Cl	Me	4500	290	−2 (line width 20 ppm)		
SEt	Me	3200	316	−22.0, −19.0, −15.1	12.4	16
SBu	Me	3800	316	−19.1, −15.3 (main)	12.6	14
NEt_2/Cl	Me	4000	305	NEt_2: −8.4 (line width 3 ppm) Cl: 5.5 (line width 5 ppm)		

[a] Prepared from $(SiClMe)_n$. [b] Prepared from $(SiBrMe)_n$.

Table 6. ^{1}H and ^{13}C NMR Data of the Polymers $SiY_2R-[SiYR]_n-SiY_2R$; Y = Cl, Br, H, OMe, OEt, O^{n}Bu, O^{i}Pr, O^{t}Bu, SEt, SBu; R = Me, ^{n}Pr, ^{n}Hex, ^{n}Oct

Y	R	δ_H (ppm)	δ_C (ppm)
Cl	Me	0.87, 0.89, 0.91, 0.95, 1.03*	−1.0, 0.5, 7.0[a]
Br	Me	0.86, 0.88	−1.0, 0.5, 8.5[a]
H	Me	0.25,[a] 0.29, 3.55/3.61 (Si−H)	−10.8 (main), −10.3
OMe	Me	0.28, 3.57 (OMe)	−1.9, −1.6, 1.0,[a] 53.1 (OMe)
OEt	Me	0.27, 1.22 (O∼CH_3), 3.8(OCH_2)	−1.3, −0.7,[a] 18.5 (O∼CH_3), 61.2 (OCH_2)
OBu	Me	0.25; Bu: 0.93, 1.39, 1.55, 3.65	−1.2, −0.8;[a] Bu: 13.9, 19.0, 35.0, 65.5
O^{i}Pr	Me	0.28, 1.19 (O∼CH_3), 4.1 (OCH)	0.2, 25.9 (O∼CH_3), 67.8 (O−CH<)
SEt	Me	0.78, 1.32 (S∼CH_3), 2.7 (SCH_2)	−1.6, 1.5,[a] 18.3 (S∼CH_3), 23.4 (S−CH_2)
SBu	Me	0.74; Bu: 0.90, 1.43, 1.60, 2.7	−1.8, 1.5;[a] Bu: 13.7, 21.9, 28.8, 34.8
NEt_2/Cl	Me	NEt_2: 0.67; Et: 1.02, 2.90 Cl: 0.87	NEt_2: −2.3 (SiMe); Et: 15.5, 39.7/42.3 Cl: 2 (SiMe)
Cl	Pr	1.06 (CH_3), 1.34 (Si−CH_2), 1.62	17.2/18.3 (α), 20.3 (β), 18.0 (CH_3)
H	Pr	0.88 (Si−CH_2), 1.49 (Si∼CH_2), 0.99 (CH_3), 3.55 (Si−H)	10.5/11.5 (α), 21.7 (β), 17.8 (CH_3)
OMe	Pr	0.99 (CH_3), 0.7−1.6 (CH_2), 3.57 (OMe)	16.0 (α), 19.2 (β), 18.6 (CH_3), 53.5 (OMe)
Cl	Hex	0.90 (CH_3), 1.0−1.7 (CH_2)	17.0/18.0 (α), 24.6 (β), 32.8 (γ), 31.3 (δ), 22.5 (ϵ), 14.0 (CH_3)
Br	Hex	0.89 (CH_3), 1.2−1.6 (CH_2)	16.6/17.7 (α), 24.7/25.6 (β), 32.8 (γ)[b]
H	Hex	0.88, 1.1−1.5 (CH_2), 3.55 (Si−H)	8.2 (α*), 9.8 (α), 28.48 (β), 32.9 (γ)[b]
OMe	Hex	0.89, 1.2−1.5 (CH_2), 3.53 (OMe)	16.8 (α), 24.8 (β), 33.6 (γ),[b] 53.3 (OMe)
OEt	Hex	0.89 (CH_3), 1.2−1.6 (CH_2); 1.21 (O∼CH_3), 3.8 (O−CH_2)	17.4 (α), 25.0/25.4 (β), 33.7 (γ),[b] 18.5 (O∼CH_3), 61.2 (O−CH_2)
O^{i}Pr	Hex	0.88 (CH_3), 1.0−1.6 (CH_2), 1.20 (O∼CH_3), 4.24 (O−CH)	18.2 (α), 24.8/25.4 (β), 33.7 (γ),[a] 26.0 (O∼CH_3), 68.2 (O−CH)
Cl	Oct	0.89 (CH_3), 1.2−1.7 (CH_2)	16.9/17.9 (α), 24.6 (β), 33.2 (γ), 31.9 (δ), 29.2 (ϵ and ζ), 22.7 (η), 14.1 (CH_3)
Br	Oct	0.89 (CH_3), 1.2−1.7 (CH_2)	16.6/17.6 (α), 24.8/25.7 (β), 33.1 (γ)[b]
H	Oct	0.88 (CH_3), 1.2−1.5, 3.55 (Si−H)	8.5 (α), 28.8 (β), 33.4 (γ)[b]
OMe	Oct	0.88 (CH_3), 1.2−1.6, 3.57 (OMe)	17.0 (α), 25.0 (β), 34.1 (γ),[b] 53.2 (OMe)
OEt	Oct	0.88 (CH_3), 1.0−1.6 (CH_2), 1.2 (O∼CH_3), 3.83 (O−CH_2)	17.6 (α), 25.1/26.4 (β), 34.1 (γ),[b] 18.6 (O∼CH_3), 61.4 (O−CH_2)

[a] In terminal units. [b] δ_C of C^δ, C^ϵ, ..., CH_3 of Hex or Oct is in all polysilanes unchanged.

could be explained by the polysilane model of Jones and co-workers,[11] in which all-anti regions of similar length are broken by sharp gauche turns. If chain cleavage takes place at these gauche conformations, it could lead to chain lengths of nearly uniform size, resulting in a low polydispersity.

If the polymer $(p\text{-}MeOC_6H_4SiHex)_n$ was used as the starting material instead of $(PhSiHex)_n$, no increased reactivity toward acetyl halide/aluminum halide was observed, nor was the length of the halogen-substiuted polymer chains increased, despite the expected higher reactivity of the (p-$MeOC_6H_4$) group compared with phenyl.[12]

The reaction of $SiCl_2Me-[SiClMe]_n-SiCl_2Me$ with the alcohols MeOH, EtOH, n-BuOH, and i-PrOH in the presence of NEt_3 yielded the completely alkoxy-substituted polysilanes:

$$SiCl_2Me-[SiClMe]_n-SiCl_2Me + (n + 4)(ROH + NEt_3) \rightarrow SiMe(OR)_2-[SiMe(OR)]_n-SiMe(OR)_2 + (n + 4)NEt_3{\cdot}HCl\downarrow$$

Only with t-BuOH was the alkoxy group too bulky to give complete substitution, leading to a “mixed” polymer, $MeSiY_2-(MeSiY)_n-MeSiY_2$, Y = Cl, t-BuO. In contrast to all other alkoxypolysilanes in this case Cl^- could be detected with $AgNO_3$ after hydrolysis of the polymer in H_2O. In the series with OMe, OEt, O-i-Pr, and O-t-Bu as side groups, the ^{29}Si NMR chemical shifts of the middle as well as the terminal units show a significant high field shift with increasing branching.

On the other hand, the ^{29}Si NMR spectra of the OEt- and O-*n*-Bu-substituted polysilanes are almost identical. Some of these experiments were repeated with the other chloro-substituted polysilanes, especially R = Hex, but gave analogous results.

Similar reactions with thiols (EtSH, BuSH) yielded the thioalkyl-substituted polysilanes $SiMe(SR)_2-[SiMe(SR)]_n-SiMe(SR)_2$. Attempts to prepare an amino-substituted polysilane by reacting the chloro-substituted polysilane with excess $HNEt_2$ gave only a partially substituted product. Further treatment with $LiNEt_2$ in hexane gave not much improvement.

In the UV spectra most of the polymers show an absorption between 300 and 304 nm for the Si−Si σ-bonds (see Tables 4 and 5). As expected, this absorption is shifted to longer wavelengths for bromo-substituted and even more for thioalkyl-substituted polysilanes, which indicates that the Si−Br and Si−S σ-electrons take part in the delocalization along the main chain to some extent.[13]

Finally, the hydrogenation of the chloro-substituted polymers with $LiAlH_4$ in diethyl ether produced the hydropolysilanes $SiH_2R-[SiHR]_n-SiH_2R$ (R = Me, Pr, Hex, Oct). In contrast to the formation of such polymers by the dehydrogenative polymerization of alkylsilanes with transition-metal complexes, these products contain no branching or cyclic oligomers. The UV spectra of the hydropolysilanes show an absorption for the Si−Si σ-electrons at relatively short wavelengths of only 250−257 nm, consistent with earlier observations on such polymers[1c] and with theoretical calculations.[14]

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(9) The observed ^{29}Si NMR chemical shifts are in good agreement with the previously reported chemical shifts of 2.8 ppm in $Br_2SiMe-SiMeBr_2$[7b] and of −15.2 ppm (1 Si) and 8.7 ppm (2 Si) in $SiBrMe(SiMeBr_2)_2$.[10]

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