Polymerization of in situ generated disilenes [1]

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Abstract

Polymerization of in situ generated disilene as a novel method of preparation of polysilylenes was investigated. The reactions of a number of dichlorodisilanes with 3,3',5,5'-tetramethylbiphenyl anion radical at $-78°C$ gave the corresponding polysilylenes in moderate yields. For successful reaction the presence of the four methyl groups on the reductant was necessary to prevent the formation of the masked disilene derivatives by both steric and electronic effects. A comparison of the various reductants used and the unique difference in reactivity between dichlorodisilane and dichlorosilane under the reaction conditions are also described.

Keywords: Silicon; Disilene; Polysilylenes; Polysilanes; Anion radicals; Masked disilene

1. Introduction

Up to now the conventional Wurtz-type reductive coupling method has been widely employed for the synthesis of polysilylenes [1]. Although many dichloro(mono)silanes are used as monomers for the polycondensation reactions, dichlorodisilanes have not been used for this purpose, except 1,2-dichloro-1,1,2-trimethylphenyldisilane, which has occasionally been used [2].

However, the reaction of dichlorodisilanes with aromatic anion radicals is known to afford 7,7-disila-[2.2.2]bicyclooctadienes [3] or isolable disilenes [4]. In the latter case the presence of bulky substituents on silicon is necessary to stabilize kinetically the free
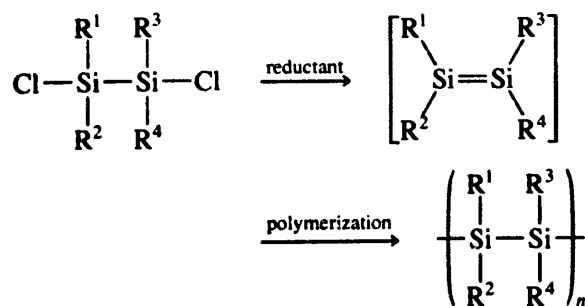
disilenes generated. Recently, we used 7,7-disila[2.2.2]bicyclooctadienes as masked disilenes for anionic polymerization to give high molecular weight polysilylenes [5].

(1)

(Ar = 2,4,6-triisopropylphenyl)

(2)
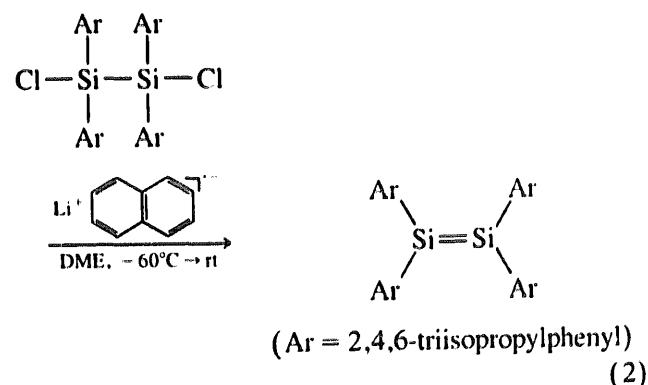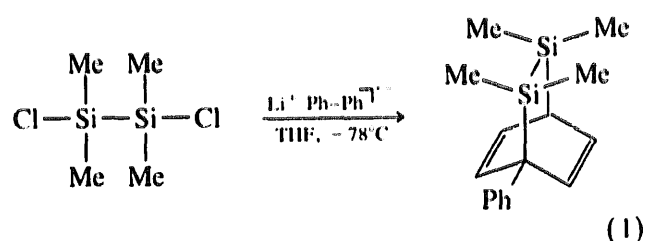
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[1] Dedicated to Professor Robert Corriu in recognition of his outstanding contributions to organosilicon chemistry. This paper is No. 331 in the series Chemistry of Organosilicon Compounds.

We describe below the novel application of dichloro-disilanes in the preparation of polysilylenes based on polymerization of in situ generated disilenes.

$$Cl-\underset{\underset{R^2}{|}}{\overset{\overset{R^1}{|}}{Si}}-\underset{\underset{R^4}{|}}{\overset{\overset{R^3}{|}}{Si}}-Cl \quad\xrightarrow{reductant}\quad \left[\underset{\underset{R^2}{\diagdown}}{\overset{\overset{R^1}{\diagup}}{Si}}=\underset{\underset{R^4}{\diagup}}{\overset{\overset{R^3}{\diagdown}}{Si}}\right]$$

$$\xrightarrow{polymerization}\quad \left(\underset{\underset{R^2}{|}}{\overset{\overset{R^1}{|}}{Si}}-\underset{\underset{R^4}{|}}{\overset{\overset{R^3}{|}}{Si}}\right)_n$$
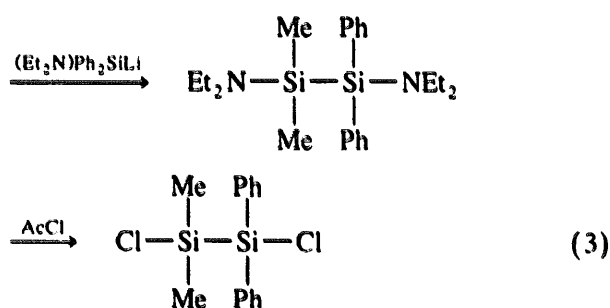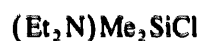
In polymerization of in situ generated disilenes, bulky substituents on silicon are detrimental but it is necessary to prevent the coupling of dichlorodisilanes with the reductant. Use of steric effects of substituents on the reductant seemed to offer a solution. Thus we have used 3,3′,5,5′-tetramethylbiphenyl anion radical as a reducing agent, which shows a remarkable chemoselectivity in the polymerization reaction.
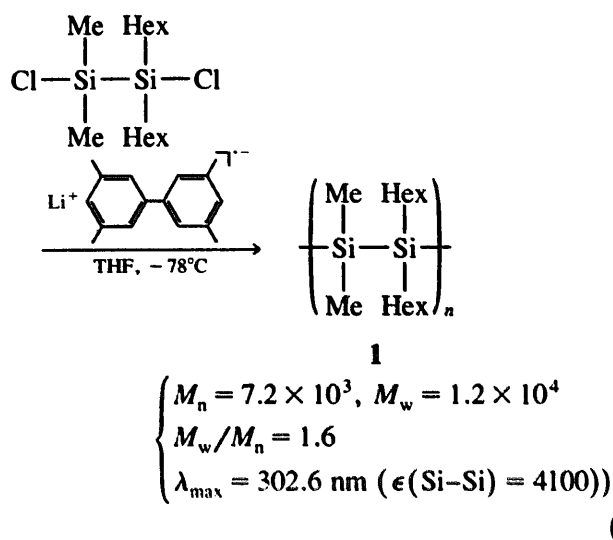
2. Results and discussion

2.1. Preparation of dichlorodisilanes

Dichlorodisilane monomers were prepared by previously reported procedures except in the case of 1,2-dichloro-1,1-dimethyl-2,2-diphenyldisilane. This new dichlorodisilane was made by the sequence shown in Eq. (3). (Use of amino-substituted disilanes has recently been described by Tamao et al. [6].)

$(Et_2N)Me_2SiCl$

$$\xrightarrow{(Et_2N)Ph_2SiLi}\quad Et_2N-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-\underset{\underset{Ph}{|}}{\overset{\overset{Ph}{|}}{Si}}-NEt_2$$

$$\xrightarrow{AcCl}\quad Cl-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-\underset{\underset{Ph}{|}}{\overset{\overset{Ph}{|}}{Si}}-Cl \qquad (3)$$

2.2. Polymerization of in situ generated disilene

The reaction of 1,2-dichloro-1,1-dihexyl-2,2-dimethyldisilane with the 3,3′,5,5′-tetramethylbiphenyl anion radical at −78°C gave the corresponding polysilylene 1 in 42% yield.

$$Cl-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-\underset{\underset{Hex}{|}}{\overset{\overset{Hex}{|}}{Si}}-Cl$$

$$\underset{Li^+}{\overset{}{}}\quad \xrightarrow[THF,\ -78°C]{}\quad \left(\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-\underset{\underset{Hex}{|}}{\overset{\overset{Hex}{|}}{Si}}\right)_n$$

1

$$\begin{cases} M_n = 7.2\times10^3,\ M_w = 1.2\times10^4 \\ M_w/M_n = 1.6 \\ \lambda_{max} = 302.6\ nm\ (\epsilon(Si-Si) = 4100) \end{cases}$$

$$(4)$$

The molecular weight distribution of the polymer **1** was determined by gel permeation chromatography (GPC), with calibration by use of polystyrene standards with chloroform as eluant; $M_n = 7.2\times10^3$, $M_w = 1.2\times10^4$, and $M_w/M_n = 1.6$. The molecular weights of the polymer **1** are lower than those of the corresponding polysilylenes prepared by anionic polymerization of a masked disilene or condensation of an appropriate dichlorodisilane [7]. It is also noteworthy that the dispersion factor for molecular weight distribution (M_w/M_n) of the polymer **1**, i.e. 1.6, is much smaller than that of the polysilylene prepared by the Wurtz coupling method, i.e. 3.8 [7]. Other polysilylenes **2–6** were made by similar procedures. The results are listed in Table 1.

It was found that various polysilylenes were formed under lower temperature reaction conditions than those used in the conventional condensation method. However, the molecular weights and yields of all the phenyl-substituted polysilylenes **4**, **5**, and **6** were lower than those of alkyl-substituted polysilylenes **1**, **2**, and **3**. It is probable that stabilization of silyl anions by the phenyl group results in facile cleavage of silicon–silicon bonds of the intermediate polysilylene oligomers under the reaction conditions, even at −78°C. This may be the reason for the rather low molecular weight of the phenyl-substituted polysilylenes.

2.3. Structure of the polysilylene

Fig. 1 shows the methyl region of the ^{13}C NMR spectra of three poly(dihexylsilylene-co-dimethylsilylene) compounds, **7**, **8**, and **1**, derived by different methods, respectively anionic polymerization of a masked disilene, Wurtz-type coupling of a dichlorodisilane, and polymerization of an in situ generated disilene. The spectral features of the former two polysilylenes have already been discussed in detail [7,8]. The ^{13}C NMR spectra of **1** are somewhat complicated. Two peaks with almost the same intensity are observed, at

Table 1

Reactions of various 1,2-dichlorodisilanes with the anion radical of 3,3',5,5'-tetramethylbiphenyl

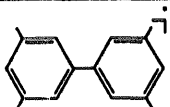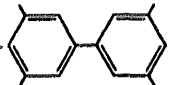| Entry	Dichlorodisilane	Yield of polysilylene (%)	M_n [a] $\times 10^{-3}$	M_w [a] $\times 10^{-3}$	M_w/M_n
1	Me Hex | | Cl–Si–Si–Cl | | Me Hex	42	7.2	12	1.6
2	Me iBu | | Cl–Si–Si–Cl | | Me iBu	60	5.6	8.4	1.5
3	Bu Bu | | Cl–Si–Si–Cl | | Me Me	51	5.4	8.4	1.6
4	Ph Me | | Cl–Si–Si–Cl | | Me Me	13	2.4	4.4	1.8
5	Ph Ph | | Cl–Si–Si–Cl | | Me Me	38	3.8	7.1	1.9
6	Me Ph | | Cl–Si–Si–Cl | | Me Ph	38	2.7	4.2	1.5

[a] Determined by GPC.

−0.66 and −1.66 ppm, for the polymer 1 together with small signals at higher field. These two peaks can be assigned to the methyl group of SiHex$_2$–SiMe$_2$–SiHex$_2$ (the head-to-tail unit A) and that of SiHex$_2$–SiMe$_2$–SiHex$_2$ (the head-to-head unit B) respectively. The other small high-field methyl peaks must come from the poly(dimethylsilylene) part SiHex$_2$–(SiMe$_2$)$_n$–SiHex$_2$ (the unit C). Redistribution of the polymer end may take place even at low temperature under the conditions used. Judging from these results, the polymerization process appears to proceed in a completely random fashion. It is noteworthy however, that no disiloxane peak is observed for polymer 1, whereas it is clearly observed in the polysilylene 8 prepared by Wurtz-type condensation of the corresponding dichlorodisilane.

More complicated ^{13}C NMR spectra were observed for the phenyl-substituted polysilylenes 4–6, indicating

Table 2

Polymerization of 1,2-dichlorodisilane by various reductants

Me Hex   / Me Hex \
\| \| reductant (\| \|)
Cl–Si–Si–Cl ⟶   (+Si–Si+)
\| \| THF, −78°C (\| \|)
Me Hex   \ Me Hex /$_n$

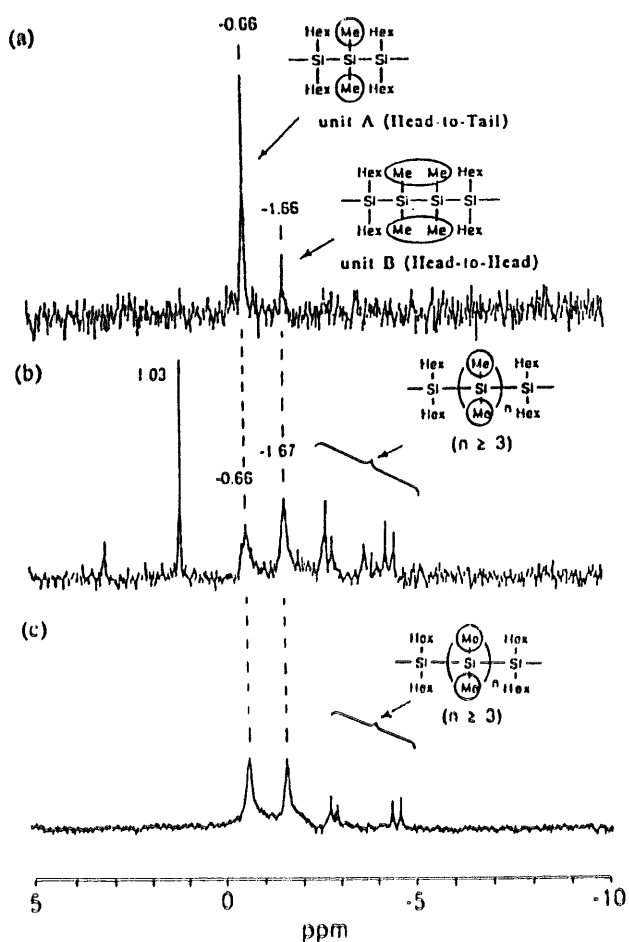| Polymer	Reductant	Yield of polymer (%)	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	λ_{max} (nm) (ϵ(Si–Si)) [a]
1	Li⁺ [biphenyl anion radical]	42	7.2	12	1.6	302.6 (4100)
9	Li + [biphenyl] (10 mol.%)	52	7.6	27	3.6	273.6 (1600)
10	Li (powder)	25	4.3	8.8	2.0	268.2 (1800)

[a] In hexane.

Fig. 1. ^{13}C NMR spectra (Si-Me region) of poly(dihexylsilylene-co-dimethylsilylene). (a) Anionic polymerization of masked disilene (7); (b) Na condensation of dichlorodisilane (8); (c) this work (9).

that frequent redistribution occurred during the polymerization, and this was the reason not only for the relatively low molecular weight but also for the complicated structure of the phenyl-substituted polysilylenes.

2.4. Comparison of reductants

It is of interest that the reactions of 1,2-dichloro-1,1-dihexyl-2,2-dimethyldisilane with a catalytic amount of 3,3′,5,5′-tetramethylbiphenyl anion radical or with lithium metal in the absence of the reductant also gave the polymers 9 and 10. The results are shown in Table 2.

Although the molecular weights of these polysilylenes were similar to that of the polymer 1, the absorption maxima were at high energies (9 λ_{max} = 274 nm; 10 λ_{max} = 268 nm). Broad peaks ascribed to the Si-O-Si stretching were present in the IR spectra of both polymers.

These results clearly indicate that the polymers 9 and 10 are not pure polysilylenes; they are probably polysilylene–polysiloxane copolymers. This remarkable difference in reactivity between the reductants demonstrates that electron transfer to dichlorodisilanes from the reductant is a key step in the generation of disilenes and the subsequent polymerization. Thus, high reducing power is necessary for the polymerization. The presence of four methyl groups on biphenyl enhances the ratio of reduction to substitution by both steric and electronic effects.
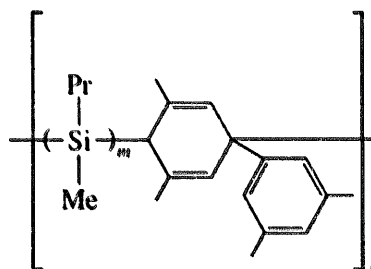
2.5. Reaction of the dichlorosilane with the reductant

In the light of the results described above, generation and polymerization of disilenes may be provisionally assumed. However, simple reductive (dechlorinative) coupling of dichlorodisilane cannot be rigorously excluded. Accordingly, the reaction of dichlorosilanes is interesting because a dichlorosilane formally affords only a silylene, not a disilene. Thus the reaction of propylmethyldichlorosilane with 3,3′,5,5′-tetramethylbiphenyl anion radical was examined, and was found to give the polymer 11 in 26% yield.

$$\text{PrMeSiCl}_2 \xrightarrow[\text{26\%}]{\text{THF, }-78°C} \text{polymer A} \qquad (5)$$
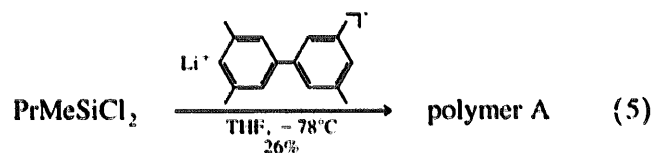
$$\begin{cases} M_n = 4.9 \times 10^3, \ M_w/M_n = 1.8 \\ \lambda_{max} = 302.8 \text{ nm} \ (\epsilon(\text{Si-Si}) = 1800)) \end{cases}$$

Polymer 11 shows an absorption maximum at 303 nm, which in itself would be consistent with a normal polysilylene. However, the ^{1}H NMR spectrum presented a complicated pattern. There are many signals that could not be attributed to a poly(propylmethylsilylene) homopolymer, being indicative of incorporation of reduced tetramethylbiphenyl units into the polymer structure. It is evident that some tetramethylbiphenyl is present in the backbone of polymer 11, the possible structure of which may be described as shown below.

Interestingly, a similar conclusion was previously reached by Shiina and Minoura [9] in the case of the

reaction of dimethyldichlorosilane with sodium naph-thalenide.

(6)
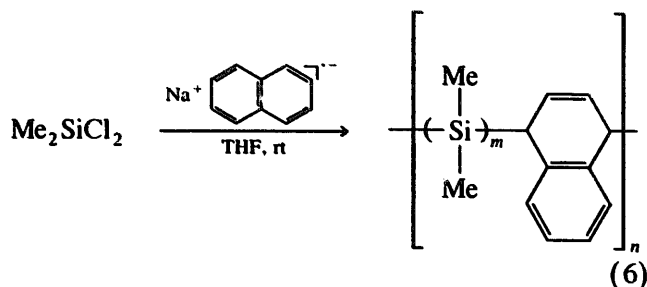
It is noteworthy that the molecular weight of the polysilylene derived from a dichlorodisilane is much higher than that of the polysilylene derived from a dichlorosilane even in the case of electroreductive synthesis.

2.6. Possible mechanism of polymerization

It was found that polymerization of dichlorodisilanes by the 3,3',5,5'-tetramethylbiphenyl anion radical took place readily even at very low temperatures. This reaction was specific to dichlorodisilanes. The difference in reactivity between dichlorodisilanes and dichlorosilanes may be attributed to facile generation of disilene from dichlorodisilane as a result of β-elimination of chlorine atoms, silylenes being unlikely to be generated under the reductive condition without activation. Since nucleophilic attack of the silyl anion on the chlorosilane, which is the main reaction in the Wurtz coupling method, is very slow at −78°C, the propagation step in this polymerization may be similar to that established for a carbon monomer, such as styrene, as shown in Scheme 1. Thus, α,ω-dilithiopolysilylene appears to be generated as an intermediate in the reaction.
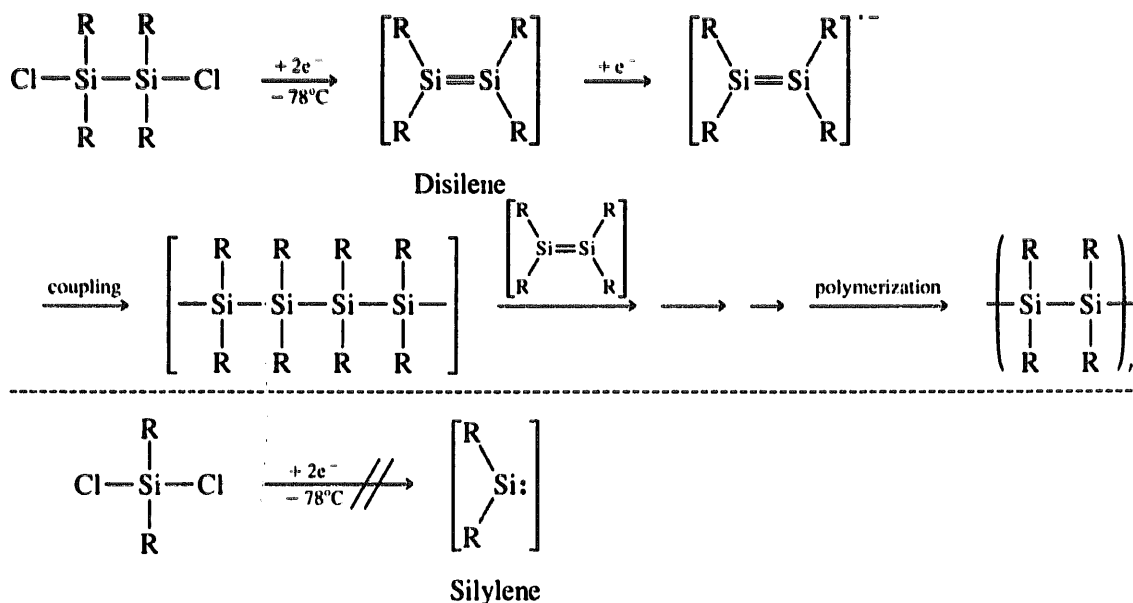
3. Experimental

3.1. General

^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker AC-300P FT-NMR spectrometer at 300, 75.4, and 59 MHz respectively. Chemical shifts are relative to the residual solvent resonances, except for ^{29}Si NMR (external TMS). Some of the ^{1}H NMR and NOE spectra were recorded on a Bruker AM-600 or a JEOL JNM-GX400 FT-NMR spectrometer at 600 and 400 MHz respectively. Mass spectra, including high resolution spectra, were obtained with a Jeol JMS D-300 mass spectrometer. Electronic absorption spectra were recorded on a Shimadzu UV-2100 spectrometer. For gas–liquid chromatography (GLC) a Shimadzu GC-8A gas chromatograph was used. The molecular weight distribution of polysilylenes was measured by use of a JAI LC-908 gel permeation chromatograph with calibrated polystyrene standards, chloroform being used as eluant.

3.2. Materials

Methylpropyldichlorosilane, lithium powder, methanol and spectrograde hexane were commercially available. Tetrahydrofuran and diethyl ether were dried and distilled from sodium benzophenone ketyl immediately before use. 1,2-Dichloro-1,1-dihexyl-2,2-dimethyldisilane and 1,2-dichloro-1,1-isobutyl-2,2-dimethyldisilane were prepared as described previously [7,8]. 1,2-Dichloro-1,2-dimethyl-1,2-dibutyldisilane, 1,2-dichloro-1-phenyl-1,2,2-trimethyldisilane [9], and 1,2-dichloro-1,2-diphenyl-1,2-dimethyldisilane [10], (diethylamino)-dimethylchlorosilane [11], (diethylamino)diphenylchlo-

Disilene

Silylene

Scheme 1.

rosilane [10] and (diethylamino)diphenylsilyllithium [6] were synthesized by previously reported procedures.

3.3. Preparation of 1,2-bis(diethylamino)-1,1-dimethyl-2,2-diphenyldisilane

To a solution containing 10.4 g (62.7 mmol) of (diethylamino)dimethylchlorosilane in 150 ml of THF was quickly added at 0°C 200 ml of a THF solution of (diethylamino)diphenylsilyllithium prepared by reaction of 20.9 g (72.1 mmol) of (diethylamino)diphenylchlorosilane with 1.70 g (245 mmol) of lithium powder. When the addition was complete, the solution was stirred for 14 h, after which the THF was evaporated off in vacuo, 200 ml of hexane was added to the residue and the salt was filtered off. The solvent was evaporated from the filtrate under reduced pressure. Distillation of the residue gave 1,2-bis(diethylamino)-1,1-dimethyl-2,2-diphenyldisilane(23.4 g, 60.8 mmol) in 84% yield as a colorless oil; b.p. 160–170°C (0.4 mmHg). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 0.26 (s, 6H), 0.84 (d, $J = 7.1$ Hz, 6H), 1.03 (t, $J = 7.1$ Hz, 6H), 2.73 (q, $J = 7.1$ Hz, 4H), 3.06 (q, $J = 7.1$ Hz, 4H), 7.30–7.42 (m, 6H), 7.52–7.68 (m, 4H). ^{13}C NMR (CDCl$_3$, 75.4 MHz): δ 0.88, 14.92, 15.47, 40.75, 41.10, 127.49, 128.49, 135.29, 138.95. ^{29}Si NMR (CDCl$_3$, 59 MHz): δ −13.48, −5.65. MS (70 eV) m/z (%): 384 (M$^+$, 10.6), 254 (Ph$_2$(Et$_2$N)Si, 81), 183 (59), 130 (Me$_2$(Et$_2$N)Si, 100).

3.4. Preparation of 1,2-Dichloro-1,1-dimethyl-2,2-diphenyldisilane

To a solution of 23.4 g (62.7 mmol) of 1,2-bis(diethylamino)-1,2-dimethyl-1,2-diphenyldisilane in 120 ml of ether at 0°C was added 10.5 g (134 mmol) of acetyl chloride. When the addition was complete, the solution was stirred for 2 h at 0°C. The solvent was then evaporated off in vacuo and the residue distilled to give 1,2-dichloro-1,1-dimethyl-2,2-diphenyldisilane 17.2 g (55.2 mmol) in 91% yield as a colorless oil; b.p. 100–120°C (0.4 mmHg). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 0.68 (s, 6H), 7.30–7.55 (m, 6H), 7.66–7.82 (m, 4H). ^{13}C NMR (CDCl$_3$, 75.4 MHz): δ 1.89, 128.35, 130.73, 132.29, 134.54. ^{29}Si NMR (CDCl$_3$, 59 MHz): δ −3.16, 17.05.

3.5. Polymerization of 1,2-dichloro-1,1-dihexyl-2,2-dimethyldisilane by the 3,3',5,5'-tetramethylbiphenyl anion radical

A mixture of 7.51 g (35.7 mmol) of 3,3',5,5'-tetramethylbiphenyl and 0.100 g (14.3 mmol) of lithium powder in 40 ml of THF was stirred overnight. At this stage, the presence of the 3,3',5,5'-tetramethylbiphenyl anion radical was indicated by the dark green color. A solution of 1.64 g (5.00 mmol) of 1,2-dichloro-1,1-di-

hexyl-2,2-dimethyldisilane in 40 ml of THF was added at −70°C during 2 h. When the addition was complete, the color of the solution had changed to yellow. After hydrolysis of the solution, the organic layer was separated, washed with water, and dried over anhydrous sodium sulfate. A small amount of cyclotetrasilane was detected by GC-MS analysis of the solution. After removal of the solvent, the residue was dissolved in benzene and the polymer was reprecipitated by pouring the solution into methanol. A second cycle of dissolution–precipitation, followed by freeze-drying, gave 0.541 g of poly(1,1-dihexyl-2,2-dimethyldisilanylene) in 42% yield; white solid; $M_n = 7.2 \times 10^3$, $M_w = 1.2 \times 10^4$, $M_w/M_n = 1.6$ (determined by GPC, polystyrene standard); UV (hexane) $\lambda_{max} = 303$ nm (rt, ε(Si–Si) = 4100)).

3.6. Polymerization of 1,2-dichloro-1,1-diisobutyl-2,2-dimethyldisilane by the 3,3',5,5'-tetramethylbiphenyl anion radical

The same procedure, starting from 1.68 g (6.18 mmol) of 1,2-dichloro-1,1-diisobutyl-2,2-dimethyldisilane, gave 0.706 g of poly(1,1-diisobutyl-2,2-dimethyldisilanylene) in 60% yield; white solid; $M_n = 5.6 \times 10^3$, $M_w = 8.4 \times 10^3$, $M_w/M_n = 1.5$ (determined by GPC, polystyrene standard).

3.7. Polymerization of 1,2-dibutyl-1,2-dichloro-1,2-dimethyldisilane by the 3,3',5,5'-tetramethylbiphenyl anion radical

The same procedure, starting from 1.87 g (6.89 mmol) of 1,2-dibutyl-1,2-dichloro-1,2-dimethyldisilane, gave 0.706 g of poly(1,2-dibutyl-1,2-dimethyldisilanylene) in 51% yield; white solid; $M_n = 5.4 \times 10^3$, $M_w = 8.4 \times 10^3$, $M_w/M_n = 1.6$ (determined by GPC, polystyrene standard).

3.8. Polymerization of 1,2-dichloro-1-phenyl-1,2,2-trimethyldisilane by the 3,3',5,5'-tetramethylbiphenyl anion radical

The same procedure, starting from 1.48 g (5.92 mmol) of 1,2-dichloro-1-phenyl-1,2,2-trimethyldisilane, gave 0.141 g of poly(1-phenyl-1,2,2-trimethyldisilanylene) in 13% yield; white solid; $M_n = 2.4 \times 10^3$, $M_w = 4.4 \times 10^3$, $M_w/M_n = 1.8$ (determined by GPC, polystyrene standard).

3.9. Polymerization of 1,2-dichloro-1,2-dimethyl-1,2-diphenyldisilane by the 3,3',5,5'-tetramethylbiphenyl anion radical

The same procedure, starting from 1.35 g (4.34 mmol) of 1,2-dichloro-1,2-dimethyl-1,2-diphenyldis-

ilane, gave 0.399 g of poly(1,2-dibutyl-1,2-dimethyldis-ilanylene) in 38% yield; white solid; $M_n = 3.8 \times 10^3$, $M_w = 7.1 \times 10^3$, $M_w/M_n = 1.9$ (determined by GPC, polystyrene standard).

3.10. Polymerization of 1,2-dichloro-1,1-dimethyl-2,2-diphenyldisilane by the 3,3′,5,5′-tetramethylbiphenyl anion radical

The same procedure, starting from 1.46 g (4.69 mmol) of 1,2-dichloro-1,1-dimethyl-2,2-diphenyldis-ilane, gave 0.433 g of poly(1,1-dimethyl-2,2-diphenyl-disilanylene) in 38% yield; white solid; $M_n = 2.7 \times 10^3$, $M_w = 4.2 \times 10^3$, $M_w/M_n = 1.5$ (determined by GPC, polystyrene standard).

3.11. Reaction of 1,2-dichloro-1,1-dihexyl-2,2-dimethyl-disilane and lithium in the presence of a catalytic amount of 3,3′,5,5′-tetramethylbiphenyl

A mixture of 0.606 g (2.88 mmol) of 3,3′,5,5′-tetra-methylbiphenyl and 0.200 g (28.8 mmol) of lithium powder in 40 ml of THF was stirred overnight, after which the presence of the 3,3′,5,5′-tetramethylbiphenyl anion radical was evident from the dark green color. A solution of 3.54 g (4.69 mmol) of 1,2-dichloro-1,1-di-hexyl-2,2-dimethyldisilane in 40 ml of THF was added at −78°C during 1.5 h. When the addition was complete, the color of the solution had changed to yellow. After hydrolysis of the solution, the organic layer was separated, washed with water, and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was dissolved in benzene and polymer was reprecipitated by pouring the solution into methanol. A second cycle of dissolution–precipitation, followed by freeze-drying, gave 1.44 g of poly(1,1-dimethyl-2,2-diphenyl-disilanylene) in 52% yield; pale yellow sticky solid; $M_n = 7.6 \times 10^3$, $M_w = 27 \times 10^3$, $M_w/M_n = 3.6$ (determined by GPC, polystyrene standard); UV (hexane) $\lambda_{max} = 274$ nm (rt, ε(Si–Si) = 1600)).

3.12. Polycondensation of 1,2-dichloro-1,1-dihexyl-2,2-dimethyldisilane by lithium metal

Condensation of 4.00 g (4.69 mmol) of 1,2-dichloro-1,1-dihexyl-2,2-dimethyldisilane with 0.226 g (32.6 mmol) of lithium powder in THF gave 0.768 g of poly(1,1-dimethyl-2,2-diphenyldisilanylene) in 52% yield; colorless sticky solid; $M_n = 4.3 \times 10^3$, $M_w = 8.8 \times 10^3$, $M_w/M_n = 2.0$ (determined by GPC, polystyrene standard); UV (hexane) $\lambda_{max} = 268$ nm (rt, ε(Si–Si) = 1800)); IR (NaCl, cm^{-1}) 1031 (Si–O–Si).

3.13. Polymerization of propylmethyldichlorosilane by the 3,3′,5,5′-tetramethylbiphenyl anion radical

The reaction of the 3,3′,5,5′-tetramethylbiphenyl anion radical, prepared from 3.50 g (16.6 mmol) of 3,3′,5,5′-tetramethylbiphenyl and 0.116 g (16.6 mmol) of lithium powder with 1.30 g (8.30 mmol) of propyl-methyldichlorosilane in 40 ml of THF at −78°C gave 0.183 g of polymer in 38% yield; white solid; $M_n = 4.9 \times 10^3$, $M_w = 8.8 \times 10^3$, $M_w/M_n = 1.8$ (determined by GPC, polystyrene standard); UV (hexane) $\lambda_{max} = 303$ nm (rt, ε(Si–Si) = 1800)).

References

[1] F.S. Kipping, J. Chem. Soc., 125 (1924) 2291; C.A. Burkhard, J. Am. Chem. Soc., 71 (1949) 963; R. West, L.D. David, K.L. Stearly, K.S.V. Srinvasan and H. Yu, J. Am. Chem. Soc., 103 (1981) 7352; H.K. Kim and K. Matyjaszewski, J. Am. Chem. Soc., 110 (1988) 3321; R.D. Miller, D. Thompson, R. Sooriyakumaran and G.N. Ficks, J. Polym. Sci., Part A, Polym. Chem., 39 (1991) 813. However, see R.G. Jones, R.E. Benfield, R.H. Cragg, P.J. Evans and A.C. Swain, Polymer, 35 (1994) 4924.
[2] H. Watanabe, Y. Akutsu, A. Shinohara, S. Shinohara, Y. Yam-aguchi, A. Ohta, M. Onozuka and Y. Nagai, Chem. Lett., (1988) 1883; A.R. Wolff, I. Nozue, J. Maxka and R. West, J. Polym. Sci., Polym. Chem. Ed., 26 (1988) 701; T. Shono, S. Kashiwa-mura, M. Ishifune and R. Nishida, J. Chem. Soc., Chem. Commun., (1990) 1477.
[3] G.J.D. Peddle, D.N. Roark, A.M. Good and S.G. McGeachin, J. Am. Chem. Soc., 91 (1969) 2807; D.N. Roark and G.J.D. Peddle, J. Am. Chem. Soc., 94 (1972) 5837.
[4] H. Watanabe, K. Takeuchi, K. Nakajima, Y. Nagai and M. Goto, Chem. Lett., (1988) 1343.
[5] H. Sakurai, K. Sakamoto, Y. Funada and M. Yoshida, Inorganic and Organometallic Polymers II, ACS Symp. Ser., Vol. 572, 1994, p. 8.
[6] K. Tamao, A. Kawachi and Y. Ito, J. Am. Chem. Soc., 114 (1992) 3898.
[7] K. Sakamoto, M. Yoshida and H. Sakurai, Macromolecules, 23 (1990) 4494.
[8] K. Sakamoto, M. Yoshida and H. Sakurai, Polymer, 35 (1994) 4990.
[9] K. Shiina and Y. Minoura, Proc. 17th Annual Meet. of the Chemical Society of Japan, 1964, Abstr. 31P16.
[10] K. Tamao, M. Kumada and M. Ishikawa, J. Organomet. Chem., 31 (1971) 17.
[11] K. Tamao, E. Nakajo and Y. Ito, Tetrahedron, 44 (1988) 3997.