# Anionic polymerization of masked disilenes. Regioselective synthesis of monomers, structures of polymers and mechanism of initiation for polysilylenes of the type $(R^1R^2SiSiMe_2)_n$ *,[1]

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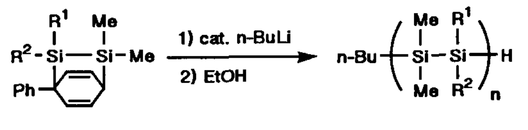
Several masked disilene monomers, i.e. 1-phenyl-7,8-disilabicyclo[2.2.2]octa-2,5-dienes, were prepared regioselectively by the reaction of unsymmetrically substituted dichlorodisilanes with biphenyl radical anions. These monomers gave polysilylenes with highly ordered structures. Important information on the tacticity of polysilylenes was obtained by detailed analysis of n.m.r. spectra. The mechanism of monomer formation as well as the polymerization mechanism are discussed.

**(Keywords: polysilylene; masked disilene; anionic polymerization)**

## INTRODUCTION

Polysilylenes have been investigated extensively in the past decade because of their potential applications in the field of materials science[2,3]. Recent applications of polysilylenes as SiC precursors[4–7], in microlithography[8,9], as photoinitiators[10] and in reprography[11] show that polysilylenes are very promising as advanced materials for the high technology of the next generation.

Polysilylenes are usually prepared by the Wurtz-type reductive coupling of dichlorosilanes with alkali metals. Although many kinds of polysilylenes have been prepared by this method, the structure of the polymers is difficult to control[12,13]. Molecular weight and polydispersity are also unmanageable[14]. Recently, we have reported the anionic polymerization of masked disilenes, i.e. 1-phenyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene derivatives, as a new method for preparing polysilylenes with highly controlled structures[15]. Indeed, a highly ordered alternating polysilylene copolymer, poly(1,1-dihexyl-2,2-dimethyldisilene) $(SiHex_2SiMe_2)_n$, has been synthesized for the first time by this method[16]. An interesting thermochromism was observed for the alternating polysilylene copolymer which possessed a highly ordered structure.



(1)

Masked disilene monomers with unsymmetrically substituted disilene moieties have, in principle, two regioisomers. The isomer ratio of the monomer affects the structural regularity of the resulting polymer. Therefore, regioselective synthesis of masked disilenes is quite important. In this paper we report the regioselective synthesis of a series of masked disilenes and structural characteristics of the polymers together with the mechanism of monomer formation. The mechanism of initiation of the polymerization will also be discussed.

## EXPERIMENTAL

### *Preparation of monomers*

The monomer **1** has been described previously. Monomers **2–5** were synthesized by the method of Roark and Peddle[17]. Reaction of the appropriate dichlorodisilanes with lithium biphenylide in tetrahydrofuran (THF) at −78°C gave monomers in the yields listed in *Table 1*. The monomers were purified by distillation and subsequently used for polymerization.

$^1H$, $^{13}C$ and $^{29}Si$ n.m.r. spectra were recorded on a Bruker AC300 spectrometer. Mass spectral analyses were performed with a JEOL JMS-D300 spectrometer with ionizing potential of 70 eV. U.v. and i.r. spectra were recorded on a Shimadzu UV2100 spectrometer and a JEOL JIR-3505/3510 *FT*i.r. spectrometer, respectively. Molecular weights were determined with LC-08 and LC-908 liquid chromatographs (Japan Analytical Industry) with Shodex AC80M and 804 columns.

### *Physical properties of the major isomers*

1-Phenyl-7,7-dipropyl-8,8-dimethyl-7,8-disilabicyclo-[2.2.2]octa-2,5-diene (**2**): pale yellow oil; b.p. 100–120°C

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**Table 1** Preparation and anionic polymerization of masked disilene, 1-phenyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene

| Monomer | $R^1$, $R^2$ | Monomer yield (%) | **a**:**b**[a] | Polymer (yield %)[b] | $\overline{M}_n$[c] ($\times 10^4$) | [H-T]/[H-H][d] |
|---|---|---|---|---|---|---|
| **1** | (n-Bu, Me) | 61 | 60:40 | **6** (79) | 11 | 6:4 |
| **2** | (n-Pr, n-Pr) | 48 | 85:15 | **7** (68) | –[e] | – |
| **3** | (n-Hex, n-Hex) | 50 | 89:11 | **8** (56) | 6.1 | 9:1 |
| **4** | (i-Bu, Me)[f] | 53 | 89:11 | **9** (70) | 11 | 9:1 |
| **5** | (i-Bu, i-Bu)[f] | 24 | 96:4 | (0)[g] | – | – |

[a] Determined by $^1$H n.m.r. NOE difference spectra

[b] Polymerization was carried out in THF at −78°C with n-BuLi as an initiator. See Experimental for details. Polymer yields are those after reprecipitation and freeze-drying

[c] From g.p.c. elution volume relative to polystyrene. The molecular weight dispersions ($\overline{M}_w/\overline{M}_n$) of the polymers were 1.3–1.6

[d] Sequence regularity: ratio of head-to-tail [H-T] and head-to-head [H-H] connections of the disilene units determined by $^{13}$C n.m.r. See text

[e] Insoluble polysilylene copolymer was obtained

[f] i-Bu = 2-methylpropyl

[g] No polymer was obtained

(0.3 mmHg); $^1$H n.m.r. (300 MHz, $CDCl_3$, $\delta$) 0.16 (s, 6 H, $Si{-}C\underline{H}_3$), 0.50 (m, 4 H, $Si{-}C\underline{H}_2{-}$), 0.84 (t, $J = 7$ Hz, 6 H, $-(CH_2)_2{-}C\underline{H}_3$), 1.10–1.30 (m, 2 H, $CH_2{-}C\underline{H}_2{-}CH_3$), 2.95 (dd, $J = 7$ Hz, $J = 7$ Hz, 1 H), 5.97 (dd, $J = 7$ Hz, $J = 7$ Hz, 2 H), 6.17 (d, $J = 7$ Hz, 2 H), 7.05–7.65 (m, 5 H, Ph); $^{13}$C n.m.r. (75.5 MHz, $CDCl_3$, $\delta$) −2.11, 15.34, 18.55, 18.68, 34.86, 47.52, 124.30, 125.45, 126.87, 128.19, 128.38, 143.31; $^{29}$Si n.m.r. (59 MHz, $CDCl_3$, $\delta$) −16.48, −16.27; m.s. (70 eV) *m/e* (%) 326 ($M^+$, 1.7), 172 ($Pr_2Si{=}SiMe_2$, 78), 130 (100).

1-Phenyl-7,7-dihexyl-8,8-dimethyl-7,8-disilabicyclo-[2.2.2]octa-2,5-diene (**3**): pale yellow oil; b.p. 180–200°C (0.2 mmHg); $^1$H n.m.r. (300 MHz, $CDCl_3$, $\delta$) 0.17 (s, 6 H, $Si{-}C\underline{H}_3$), 0.46–0.56 (m, 4 H, $Si{-}C\underline{H}_2{-}$), 0.85 (t, $J = 7$ Hz, 6 H, $-(CH_2)_5{-}C\underline{H}_3$), 1.05–1.40 (m, 16 H, $CH_2{-}(C\underline{H}_2)_4{-}CH_3$), 2.94 (dd, $J = 6.5$ Hz, $J = 6.5$ Hz, 1 H), 5.96 (dd, $J = 6.5$ Hz, $J = 7$ Hz, 2 H), 6.17 (d, $J = 7$ Hz, 2 H), 7.10–7.65 (m, 5 H, Ph); $^{13}$C n.m.r. (75.5 MHz, $CDCl_3$, $\delta$) −2.07, 12.57, 14.09, 22.57, 24.89, 31.41, 33.62, 34.87, 47.59, 124.30, 125.44, 126.86, 128.19, 128.40, 143.30; $^{29}$Si n.m.r. ($CDCl_3$, $\delta$) −16.54, −13.51; m.s. (70 eV) *m/e* (%) 410 ($M^+$, 3.0), 172 (100); h.r.m.s. calc. for $C_{26}H_{42}Si_2$, 410.2825, found 410.2825.

1-Phenyl-7-(2-methylpropyl)-7,8,8-trimethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (**4**): pale yellow oil; b.p. 100–120°C (0.3 mmHg); $^1$H n.m.r. (300 MHz, $CDCl_3$, $\delta$) 0.01 (s, 3 H), 0.14 (s, 3 H), 0.18 (s, 3 H), 0.42 (m, 2 H, $Si{-}C\underline{H}_2{-}$), 0.75 (d, $J = 7$ Hz, 3 H), 0.80 (d, $J = 7$ Hz, 3 H), 1.50 (qqt, $J = 7$ Hz, $J = 7$ Hz, $J = 7$ Hz, 1 H), 2.98 (dd, $J = 7$ Hz, $J = 7$ Hz, 1 H), 5.97 (m, 2 H), 6.10 (m, 1 H), 6.23 (m, 1 H), 7.10–7.70 (m, 5 H, Ph); $^{13}$C n.m.r. (75.5 MHz, $CDCl_3$, $\delta$) −4.82, −2.99, −2.35, 23.00, 25.42, 26.03, 26.27, 34.82, 47.11, 124.3, 125.5, 127.0, 127.4, 128.2, 129.0, 142.8; $^{29}$Si n.m.r. (59 MHz, $CDCl_3$, $\delta$) −16.51, −16.32; m.s. (70 eV) *m/e* (%) 312 ($M^+$, 1.7), 158 ($BuMeSi{=}SiMe_2$, 34), 154 (Ph–Ph, 24), 102 (100); h.r.m.s. calc. for $C_{19}H_{28}Si_2$ 312.1728, found 312.1722.

1-Phenyl-7,7-di(2-methylpropyl)-8,8-dimethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (**5**): pale yellow oil; b.p. 110–120°C (0.4 mmHg); $^1$H n.m.r. (300 MHz, $CDCl_3$, $\delta$) 0.19 (s, 6 H, $Si{-}Me_2$), 0.54 (dd, $J_{gem} = 15$ Hz, $J = 7$ Hz, 4 H, $C\underline{H}_2$), 0.79 (d, $J = 6$ Hz, 6 H), 0.81 (d, $J = 6$ Hz, 6 H), 1.65 (tqq, $J = 7$ Hz, $J = 6$ Hz, $J = 6$ Hz, 2 H), 2.93 (dd, $J = 7$ Hz, $J = 7$ Hz, 1 H), 5.95 (dd, $J = 7$ Hz, $J = 8$ Hz, 2 H), 6.10 (d, $J = 8$ Hz, 2 H), 7.10–7.50 (m, 5 H, Ph); $^{13}$C n.m.r. (75.5 MHz, $CDCl_3$, $\delta$) −1.26, 24.00, 25.46, 26.30, 26.58, 35.07, 47.61, 124.5, 126.3, 126.8, 128.1, 128.6, 143.7; $^{29}$Si n.m.r. (59 MHz, THF-$d_8$, $\delta$) −17.02, −14.43; m.s. (70 eV) *m/e* (%) 354 ($M^+$, 0.4), 200 (34, $Bu_2Si{=}SiMe_2$), 154 (100); h.r.m.s. calc. for $C_{22}H_{34}Si_2$ 354.2200, found 354.2206.

### *Anionic polymerization*

Polymerizations were carried out in a 50 ml two-necked flask, equipped with a magnetic stirrer, a rubber septum, and a three-way stopcock under dry argon. A solution of monomer in THF, freshly distilled from sodium, was placed in the flask. A hexane solution of n-BuLi was added to the solution at −78°C. The colour of the solution turned red immediately. The mixture was stirred after removing the cooling bath for 30 min. A few drops of ethanol were added to the mixture. The polymers were purified by removal of the solvent, precipitation, and further cycles of dissolving–precipitation followed by freeze-drying.

Polymer **9**: translucent solid (soluble in THF and chloroform, slightly soluble in benzene); $\overline{M}_n = 1.1 \times 10^5$, $\overline{M}_w = 1.7 \times 10^5$, $\overline{M}_w/\overline{M}_n = 1.6$ (g.p.c. polystyrene standard); $^1$H n.m.r. (300 MHz, $CDCl_3$, $\delta$) 0.24 (br), 0.82 (br, $C\underline{H}_2$), 0.94 (d, $J = 6$ Hz, $-CH{-}(C\underline{H}_3)_2$), 1.76 (br, $C\underline{H}$); $^{13}$C n.m.r. (75.5 MHz, $CDCl_3$, $\delta$) −4.22 (minor, $-SiBuMe{-}SiMe_2{-}SiBu\underline{Me}{-}SiMe_2{-}SiMe_2{-}SiBuMe{-}$), −4.00 (major, $-SiBuMe{-}SiMe_2{-}SiBu\underline{Me}{-}SiMe_2{-}SiBuMe{-}SiMe_2{-}$), −2.58 (minor, $-SiBuMe{-}Si\underline{Me}_2{-}Si\underline{Me}_2{-}SiBuMe{-}$), −2.19 (major, $-SiBuMe{-}Si\underline{Me}_2{-}SiBuMe{-}$), 24.50 ($C\underline{H}_2$), 26.73, 26.79 ($C\underline{H}_3$), 27.47 ($C\underline{H}$); $^{29}$Si n.m.r. (59 MHz, $CDCl_3$, $\delta$) −36.5 (m, $SiMe_2$), −32.7 (m, SiBuMe); u.v. (hexane) $\lambda_{max} = 301.4$ nm (rt, $\varepsilon$(Si–Si) = 5500).

Polymer **11**: white grease; $\overline{M}_n = 6.0 \times 10^3$, $\overline{M}_w = 1.3 \times 10^4$, $\overline{M}_w/\overline{M}_n = 2.2$ (g.p.c. polystyrene standard); $^1$H n.m.r. (300 MHz, $CDCl_3$, $\delta$) 0.06 (br, MeSi), 0.25 (br, MeSi), 0.82 (br, $CH_2$), 0.94 (d, $J = 6$ Hz, $CH_3$), 1.76 (br, CH); $^{13}$C n.m.r. (75.5 MHz, $CDCl_3$, $\delta$) −4.22, −4.00 (BuSiMe), −3.69, −3.53 (BuSiMe), −2.77, −2.56 ($SiMe_2$), −2.14 ($SiMe_2$), 1.03 (Si–O–Si), 24.7, 26.68, 26.81, 27.54; $^{29}$Si n.m.r. (59 MHz, $CDCl_3$, $\delta$) −36.8 (br, $SiMe_2$), −32.7 (br, SiMeBu); u.v. (hexane) $\lambda_{max} = 292.6$ nm (rt, $\varepsilon$(Si–Si) = 3500); i.r. (NaCl, $cm^{-1}$) 1033 (Si–O–Si).

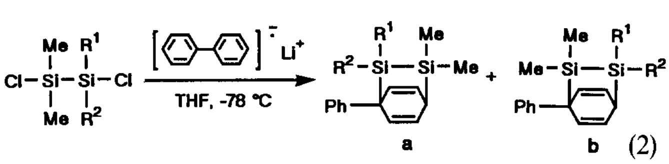
Polymer **12**: white grease; $\overline{M}_n = 7.7 \times 10^3$, $\overline{M}_w = 1.4 \times 10^4$, $\overline{M}_w/\overline{M}_n = 1.8$ (g.p.c. polystyrene standard); $^1$H n.m.r. (300 MHz, $CDCl_3$, $\delta$) 0.24 (br, MeSi), 0.82 (br), 0.94 (br), 1.77 (br); $^{13}$C n.m.r. (75.5 MHz, $CDCl_3$, $\delta$) $-4.4 \sim -1.5$, 24.79, 26.73, 26.84, 27.56; $^{29}$Si n.m.r. (59 MHz, $CDCl_3$, $\delta$) $-36.8$ (br, $SiMe_2$), $-32.5$ (br, SiMeBu); u.v. (hexane) $\lambda_{max} = 298.4$ nm (rt, $\varepsilon$(Si–Si) = 5000).

1,1,1-Trimethyl-2,2-di(2-methylpropyl)disilane (**13**): colourless oil; $^1$H n.m.r. (300 MHz, $CDCl_3$, $\delta$) 0.09 (s, 9 H, $Me_3Si$), 0.64 (m, 4 H, $CH_2$), 0.93 (d, $J = 6.6$ Hz, 12 H, $Me_2CH$-), 1.71 (qqt, $J = 6.6$ Hz, $J = 6.6$ Hz, $J = 6.6$ Hz, 2 H, CH), 3.56 (quint, $J = 4.2$ Hz, 1 H, SiH); $^{13}$C n.m.r. (75.5 MHz, $CDCl_3$, $\delta$) $-1.03$ ($Me_3Si$), 20.99 ($CH_2$), 25.70, 25.89 ($CH_3$), 26.32 (CH); $^{29}$Si n.m.r. (59 MHz, $CDCl_3$, $\delta$) $-36.3$ ($Bu_2HSi$), $-18.9$ ($Me_3Si$); m.s. (70 eV) *m/e* (%) 216 ($M^+$, 10), 86 (100), 73 (99); h.r.m.s. calc. for $C_{11}H_{28}Si_2$ 216.1730, found 216.1737.

1,1,1,3,3-Pentamethyl-2,2,4,4-tetra(2-methylpropyl)-tetrasilane (**14**): colourless oil; $^1$H n.m.r. (300 MHz, $CDCl_3$, $\delta$) 0.14 (s, 9 H, $Me_3Si$), 0.19 (s, 6 H, $Me_2Si$), 0.67 (dd, $J = 6.8$ Hz, $J = 4.1$ Hz, 4 H, $-CH_2SiH$), 0.78 (d, $J = 6.8$ Hz, 4 H, $CH_2$), 0.90–1.00 (m, 24 H, $Me_2CH$-), 1.74 (qqt, $J = 6.8$ Hz, $J = 6.8$ Hz, $J = 6.8$ Hz, 4 H, -CH-), 3.75 (quint, $J = 4.1$ Hz, SiH); $^{13}$C n.m.r. (75.5 MHz, $CDCl_3$, $\delta$) $-3.51$, 0.48, 21.79, 22.93, 25.44, 26.17, 26.35, 26.56, 26.74, 27.19; $^{29}$Si n.m.r. (59 MHz, $CDCl_3$, $\delta$) $-44.42$, $-38.49$, $-33.62$, $-15.31$; m.s. (70 eV) *m/e* (%) 416 ($M^+$, 4.8), 343 ($M^+$-73, 9.0), 103 (100), 73 (99).

## RESULTS AND DISCUSSION

The masked disilene monomers **1**–**5** were synthesized by reactions of dichlorodisilanes of the type $ClSiR^1R^2SiMe_2Cl$ with the biphenyl anion radical as described before resulting in a mixture of two regio isomers, **a** and **b**. The predominant isomer was **a** as determined by $^1$H n.m.r. NOE difference spectra.



(2)

As a typical example, *Figure 1* shows the $^1$H n.m.r. NOE difference spectra of monomer **5**, 1-phenyl-7,7-di(2-methylpropyl)-8,8-dimethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene. Irradiation of the methyl peak on silicon of the major isomer enhanced the peak intensities of the methine ($H_a$) and two vinylic hydrogens ($H_b$). This fact clearly indicates that the major isomer has a structure as depicted by **5a**. The isomer ratio (96:4) was calculated from the relative area of methyl peaks. In a similar way, structures and isomer ratios were determined for all the monomers. *Table 1* lists the results. Apparently, the ratio of the isomers **a**/**b** increases with increasing steric hindrance of the alkyl substituents on the dichlorodisilanes, reaching 96/4 for the di(2-methylpropyl)-dimethyl-substituted derivative **5**.

It is curious that the major isomers have a larger intramolecular steric repulsion between the phenyl group at the 1-position and alkyl substituents than the minor isomer. However, the result can be explained on the basis of the mechanism shown in *Figure 2*. The first step of the reaction of a dichlorodisilane with the biphenyl anion

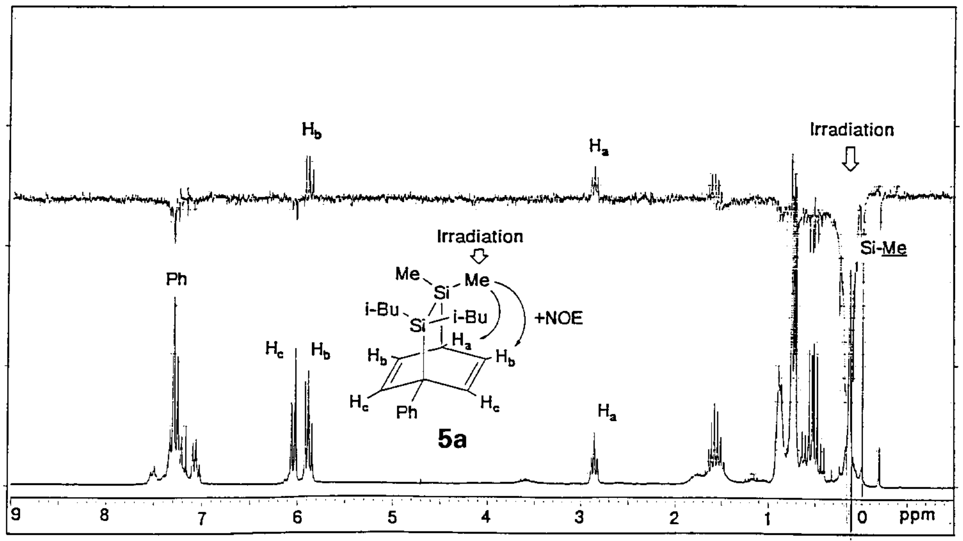


**Figure 1** $^1$H n.m.r. NOE difference spectra of monomer **5**

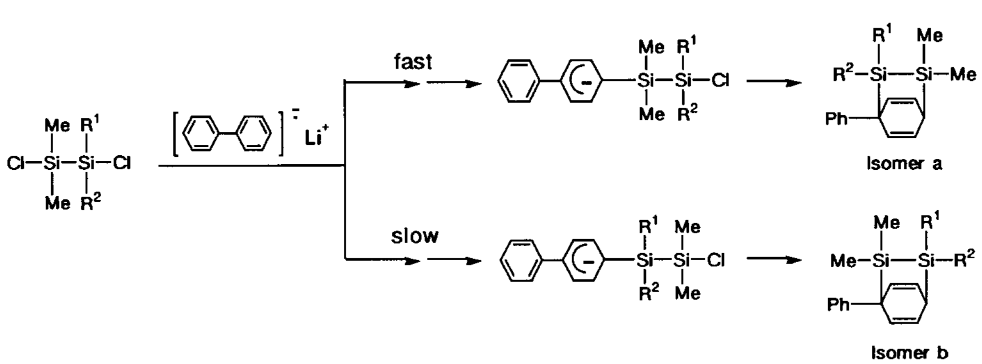
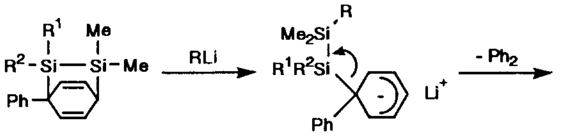


**Figure 2** Synthetic route for the preparation of 1-phenyl-8,8-dimethyl-7,8-disilabicyclo[2.2.2]octa-2,5-dienes (masked disilenes)

radical should be the formation of a C–Si bond at the *para* position of biphenyl to give a cyclohexadienyl anion radical stabilized by the phenyl group. The intermediate then forms the second C–Si bond to give the masked disilene monomer. According to *Figure 2*, the isomer ratio of the monomer depends on the regioselectivity of the first step, and the difference in steric repulsion of this step is solely responsible for the predominant formation of isomer **a**.

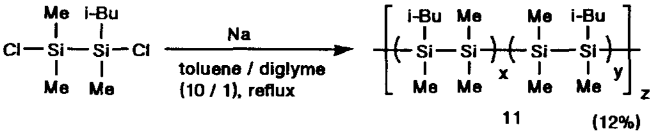
The monomers were then subjected to anionic polymerization without separation of the two isomers. The reaction of monomers **1**–**4** with n-butyllithium (10 mol%) afforded polysilylenes **6**–**9**, respectively. Structures of these polymers, except for **7**, were elucidated by $^1$H, $^{13}$C and $^{29}$Si n.m.r., u.v. and i.r. spectra. In $^{13}$C n.m.r., two kinds of dimethylsilylene signals were observed for these copolymers. As described before[16], the signals can be assigned to those of dimethylsilylenes having head-to-tail [H-T] and head-to-head [H-H] connections of the disilene units. Thus the sequence regularity of the polymers is represented by the ratio of these methyl signals (see below). The results are summarized in *Table 1*. It is clear that highly ordered alternating copolymers were obtained when monomers having high isomeric purity were used for the polymerization. Therefore, the sequence regularities were directly dependent on the isomer ratio of the masked disilenes. Thus monomers with isomeric ratio of 89:11 (**3** and **4**) gave polymers with sequence regularities of 9:1. These facts indicate that the propagation of the polymerization is regiospecific.



$$\text{R-SiMe}_2\text{-SiR}^1\text{R}^2\text{Li} \longrightarrow \longrightarrow \longrightarrow \text{R-(SiMe}_2\text{-SiR}^1\text{R}^2\text{)}_n\text{Li} \qquad (3)$$

As described in a previous paper, anionic polymerization of monomer **3** with n-BuLi in THF followed by quenching with ethanol afforded polymer **8** in 56% yield. Polymer **7** derived from monomer **2**, which possesses two relatively small propyl groups, was an insoluble white solid. This is rather interesting because polymer **10** of a similar structure, prepared by sodium coupling of 1,2-dichloro-1,1-dimethyl-2,2-dipropyldisilane is soluble[18,19]. The structure of **7** can be compared with that of **10** by i.r. spectra. Both polymers **7** and **10** have the same composition but the former shows the structure of an ordered alternating polysilylene copolymer as expected from the predominant regiochemical isomer of monomer **2** and the mechanism of polymerization, while the latter is completely random in sequence regularity as determined by $^{13}$C and $^{29}$Si n.m.r. The insolubility of **7** can be ascribed to the high crystallinity owing to it regular structure.

Monomer **4** was obtained with the same isomer ratio as that of **3** (89:11). It was thus expected that a polysilylene with a regular structure could be obtained. Anionic polymerization of **4** gave polymer **9** in 70% yield. Polymer **9** was soluble in THF and chloroform but was barely soluble in benzene. $\overline{M_n}$ and $\overline{M_w}$ values determined by g.p.c. with polystyrene standard were $1.1 \times 10^5$ and $1.7 \times 10^5$, respectively. With the highly ordered alternating polysilylene copolymer Bu–[SiMe$_2$–SiMe(2-methylpropyl)]$_n$–H being formed, one can expect the presence of tacticity due to the chiral methyl(2-methylpropyl)silylene units. This is an extremely interesting problem in polysilylene chemistry so that the structure of **9** was investigated in detail by n.m.r. together with related polymers **11** and **12**. Both **11** and **12** were prepared by Wurtz-type homo coupling of 1,2-dichloro-1,1,2-trimethyl-3-(2-methylpropyl)disilane and mixed coupling of dimethyldichlorosilane and methyl(2-methylpropyl)-dichlorosilane, respectively.



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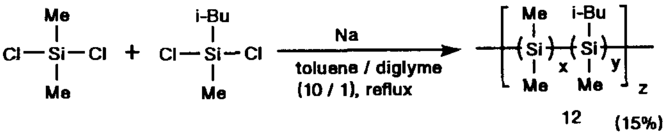

(5)

*Figure 3* shows $^{13}$C n.m.r. spectra of **9**, **11** and **12**. In the region of the 2-methylpropyl peaks, the three polymers gave almost identical spectra, although those of **11** and **12** are somewhat broader than those of **9**. However, a dramatic difference can be seen in the methyl peak regions. An expanded spectrum for the +5 to −10 ppm region is shown in *Figure 4*. Basically two methyl peaks are observed for each polymer, Si($\underline{C}$H$_3$)$_2$

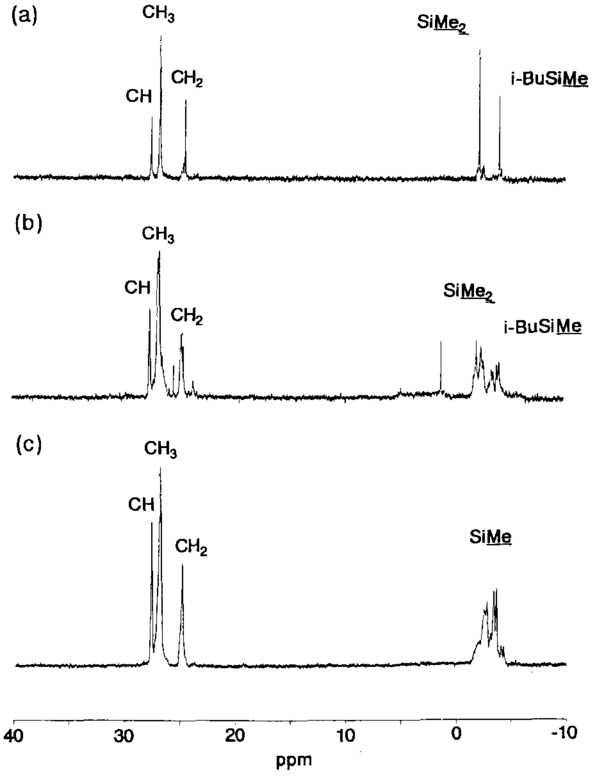

**Figure 3** $^{13}$C n.m.r. spectra of polysilylene copolymers: (a) **9**; (b) **11**; (c) **12**

signals at lower field and Si(2-methylpropyl) ($\underline{C}H_3$) signals at higher field. Two very sharp peaks are observed for polymer **9** at −2.19 and −4.00 ppm. These signals can be assigned to the methyl groups of the [H-T] units (unit A) by an argument analogous to that for polymer **8**[16]. These signals are accompanied by minor signals which may be assigned for the methyl groups of [H-H] units (unit B). Polymer **11** shows several other peaks in addition to those found for **9**. The peak intensities of units A and B are almost the same indicating that **11** has [H-T] and [H-H] structures with equal probability. Furthermore, each methyl peak of **11** splits into two or more peaks. This fact suggests that $^{13}C$ chemical shifts are affected by remote arrangements of the polymer which should be more random than that of **9**. The polysilylene **12**, prepared from the 1:1 mixture of two monomers, shows continuous methyl peaks indicating the absence of ordered structures.

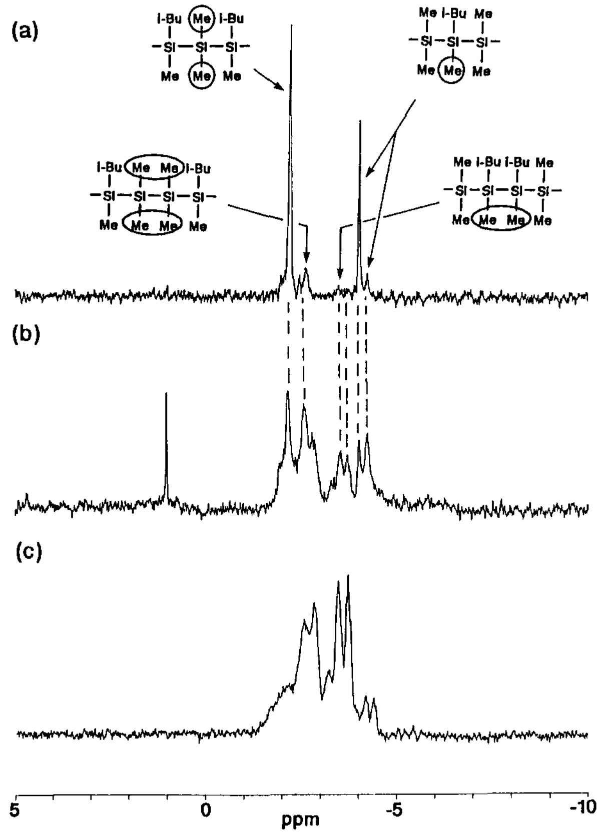

**Figure 4** SiMe regions of $^{13}C$ n.m.r. spectra of polysilylene copolymers: (a) **9**; (b) **11**; (c) **12**

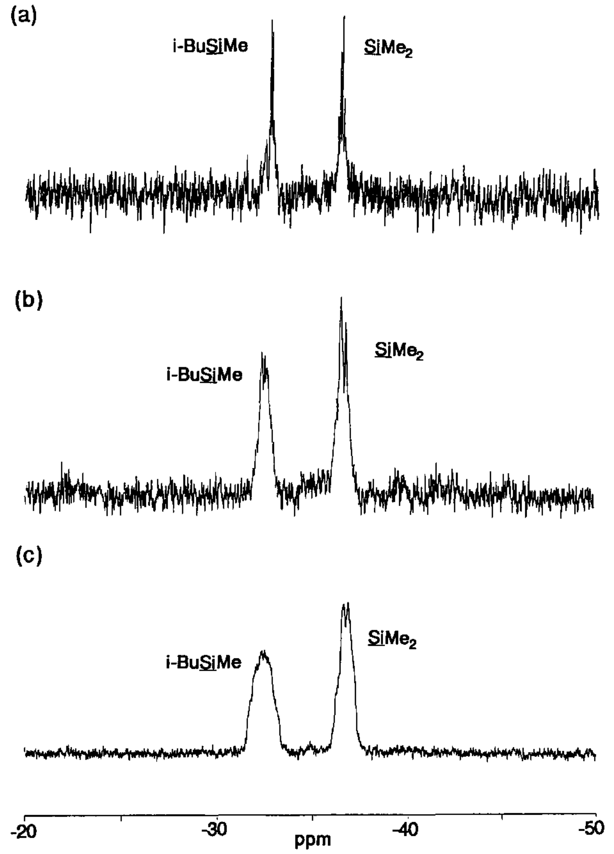

**Figure 5** $^{29}Si$ n.m.r. spectra of polysilylene copolymers: (a) **9**; (b) **11**; (c) **12**

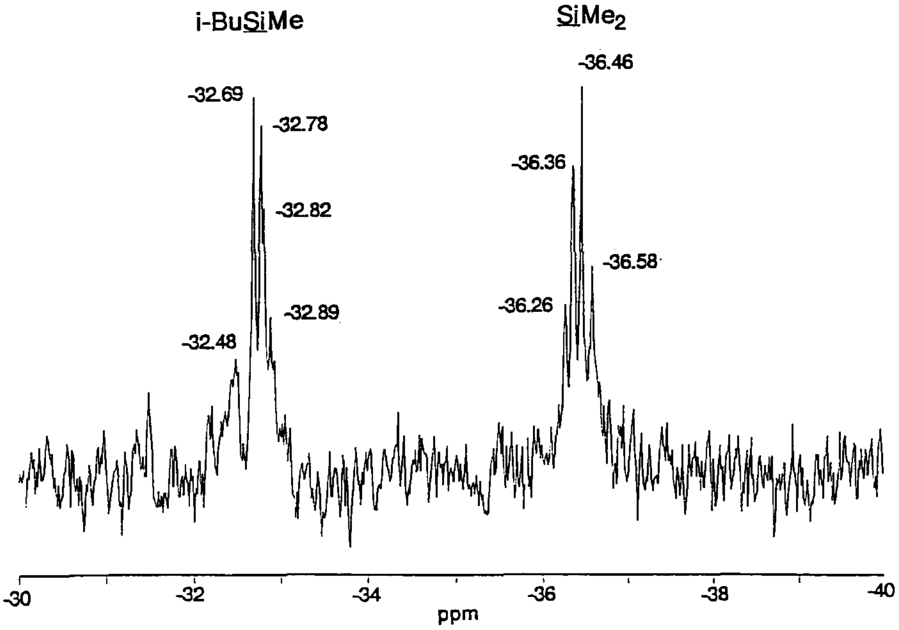

**Figure 6** Expanded $^{29}Si$ n.m.r. spectrum of polysilylene copolymer **9**

*Figure 5* shows the $^{29}$Si n.m.r. spectra for **9**, **11** and **12** in which $\underline{\mathrm{Si}}\mathrm{Me}_2$ and $\underline{\mathrm{Si}}\mathrm{Me(C_4H_9)}$ signals appear at high and low fields. Clearly the signals from both **11** and **12** are much broader than those from **9**, again indicating a much more highly ordered structure for **9**. *Figure 6* is an expanded $^{29}$Si n.m.r. spectrum for polymer **9**. Interestingly, each peak shows very small splitting ($<0.1$ ppm). Since the sequence regularity of 9 is very high, these small splittings are not ascribed to the irregular main-chain sequence but to the main-chain tacticity.

The tacticity of polysilylenes has been studied by $^{29}$Si n.m.r. for various homopolymers and copolymers[20]. In previous studies, all the polymers were prepared by Wurtz coupling and showed much broader peaks than observed in the present study, especially for copolymers. Therefore, $^{29}$Si n.m.r. signals of polymers of the previous studies are probably broadened not only by tacticity but also by irregular arrangement of substituents in the main chain.

How many $^{29}$Si n.m.r. peaks should be observed for **9**? For the dimethylsilylene unit, possible configurations for diad and tetrad structures are indicated in *Figure 7*. The diad should give only two peaks so that one must consider at least tetrad structures. Theoretically, there are six possible tetrads which should give rise to six peaks with an intensity ratio of 1:2:1:1:2:1, if each structure gives the same peak intensity, but in reality only four peaks are observable. This may be due to the limitation of peak resolution or due to some mechanism of stereoselection during the polymerization. Triad or pentad structure may be taken into account for the peak numbers of $^{29}$Si n.m.r. spectra for the methyl(2-methylpropyl)silylene units (*Figure 8*). The triads and pentads should give rise to three and 10 peaks, respectively; at least five peaks were observed.

Since many $^{29}$Si n.m.r. peaks are observed, the polysilylene copolymer **9** should possess an atactic structure. This is a simple consequence of monomer **4** being racemic. It is thus a challenging problem to synthesize optically active monomers for possible isotactic and syndiotactic polysilylenes, provided that propagation of the anionic polymerization would be strictly stereospecific.

Although monomer **5** of the highest isomeric purity did not undergo anionic polymerization because of large steric hindrance, it gave useful information about the mechanism of the initiation. Thus, the reaction of **5** with 1 equivalent of methyllithium, followed by quenching with ethanol, gave 1,1,1-trimethyl-2,2-di(2-methylpropyl)-disilane **13** and 1,1,1,3,3-pentamethyl-2,2,4,4-tetra(2-methylpropyl)tetrasilane **14** as the two main products. These products contained no regioisomers. Deuteriosilanes **13**-d$_1$ and **14**-d$_1$ were also obtained from a similar reaction, but quenched by deuterium oxide. These products were derived by protonation of the disilanyl and tetrasilanyl anions **15** and **16** (*Figure 9*). The important structural characteristic of the products is the existence of trimethylsilyl and di(2-methylpropyl)hydrosilyl groups for both **13** and **14**. The structures of the products clearly indicate that both initiation and propagation steps of the polymerization proceed by the attack of anionic species on a silicon atom at the 8-position of the monomer

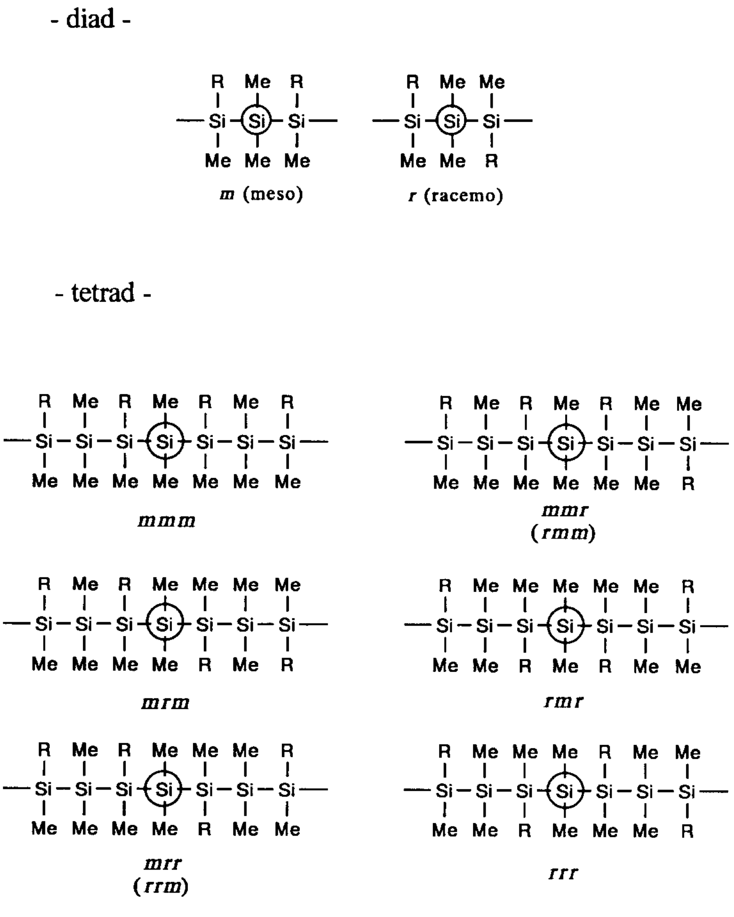

**Figure 7** List of diad and tetrad structures for the dimethylsilylene unit

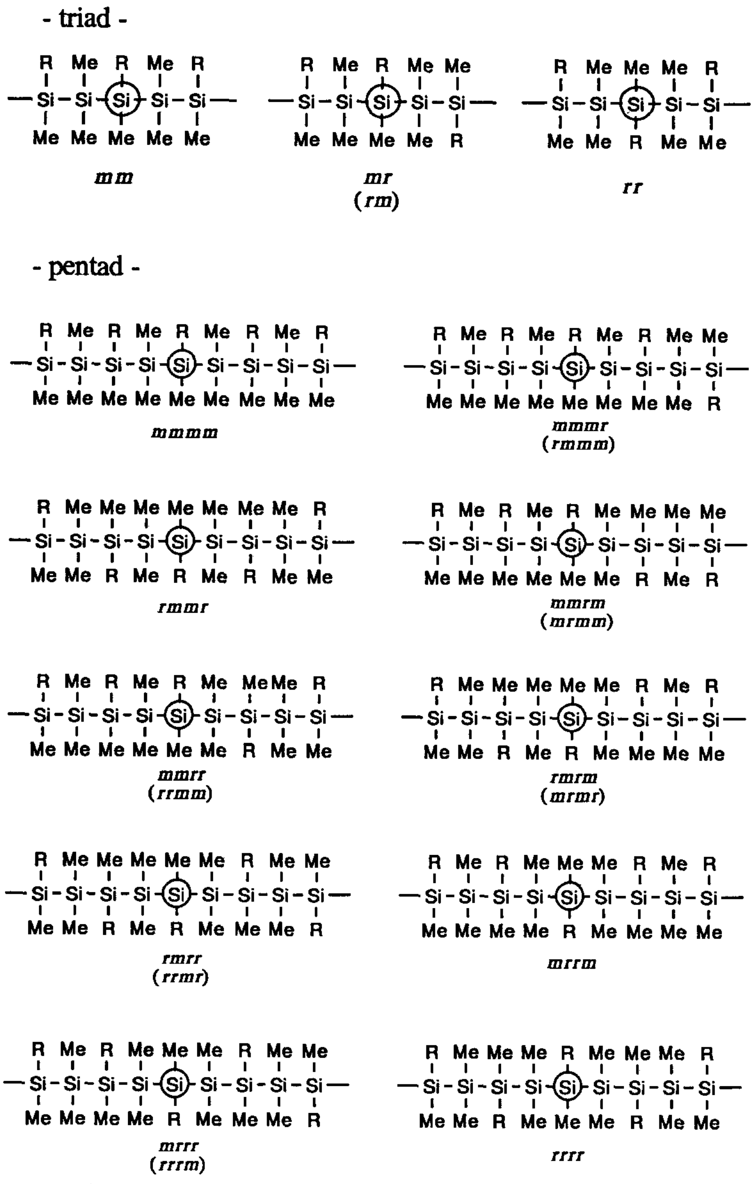

**Figure 8** List of triad and pentad structures for the methyl(2-methylpropyl)silylene unit (R = 2-methylpropyl)

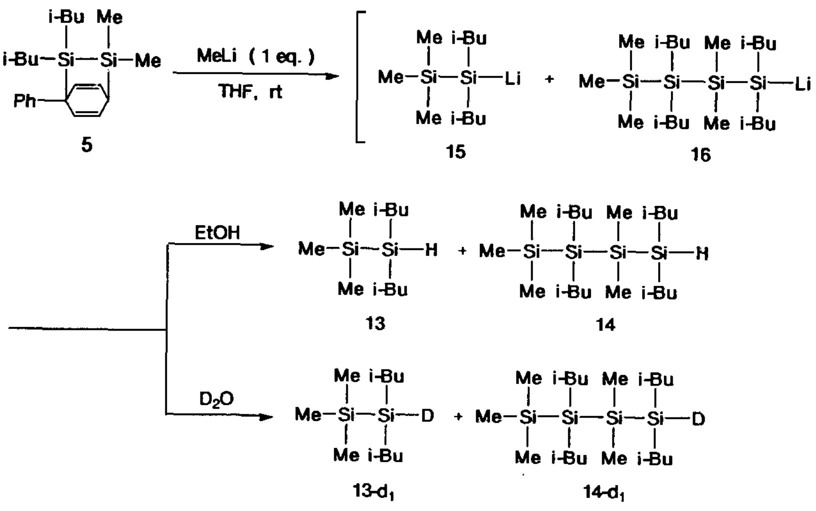

**Figure 9** Reaction of 5 with methyllithium

exclusively. Steric protection by the phenyl group at the 1-position should be the origin of the regioselectivity of the anionic polymerization process.

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