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# Polymeric organosilicon systems. XXIX. Thermal properties of poly[(disilanylene)oligophenylenes]

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**Abstract**

Thermal properties of variously substituted poly[(disilanylene)oligophenylenes], $[(SiR^1R^2SiR^1R^2)(p\text{-}C_6H_4)_m]_n$ ($R^1 = R^2 = Me$, $R^1 = R^2 = Et$, and $R^1 = Ph$, $R^2 = Me$, $m = 1$–$4$) were investigated. The thermogravimetric analysis of the polymers in the range of 20–1000°C showed rapid weight loss starting from about 400°C. The total weight loss of the polymers at 1000°C was calculated to be 54.5–75.5% based on the initial weight of the polymers. GC-MS analysis of the volatile products obtained from the pyrolysis of the polymers with $R^1 = R^2 = Me$, $m = 2$ and $R^1 = R^2 = Et$, $m = 1$–$4$ at 500°C indicated the formation of silicon-containing oligomers arising from the Si–Si and Si–phenylene bond cleavage, mainly. The formation of oligophenylenes, $H(C_6H_4)_lH$ ($l = 1$–$4$), was also observed in the pyrolysis of the polymers with $m = 3$ and 4. A model reaction for the polymer degradation was also examined, using 1,2-diphenyltetramethyldisilane. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Organosilicon polymer; Oligophenylene; Pyrolysis

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## 1. Introduction

Polycarbosilanes composed of organosilicon units linked by a hydrocarbon bridge are of current interest, since they may be used for the precursors of silicon carbide [1,2]. However, the ceramic yields from the pyrolysis of $sp^3$-hybridized polycarbosilanes are usually low, unless they have a functional group, such as an Si–H bond at the silicon atom [3–6]. Recently, it has been demonstrated that introduction of a $\pi$-electron system, such as an ethenylene [7,8] or ethynylene group [9,10] as the bridging unit into the polymer main chain leads to high char yield, even though the polymers have no functional groups at the silicon atom. This seems to be due to radical cross-linking reactions across the $\pi$-electron system during the pyrolysis and also due to the presence of thermodynamically more stable Si–ethenylene and Si–ethynylene bonds relative to Si–alkyl bonds. Recently, Itoh and his coworkers have reported that poly[(silylene)ethynylene(phenylene)ethynylenes] having both unsaturated hydrocarbon bridge and Si–H bond exhibit high thermal stability, and thermogravimetric analysis of the polymer in an inert atmosphere reveals only 3–12% weight loss at 1000°C, depending on the orientation of the phenylene ring and the nature of substituents on the silicon atom [11]. We have also reported that substitution on the silicon atom in poly[(silylene)phenylenes] with an Si–H bond [12] or a terminal ethynyl group [13] leads to high char yields upon pyrolysis of the polymers. However, no systematic

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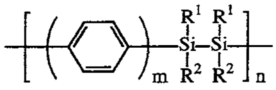
studies to clarify the relationship between the thermal properties of the polymers and the structures of the bridging $\pi$-electron system have been reported.

Recently, we have prepared a series of poly[(disilanylene)oligophenylenes] (**2a**–**4a**, **1b**–**4b**, and **1c**–**4c**) and examined them with regard to the UV absorptions and photochemical properties [14]. It was found that the photoactivities of these polymers decrease with the increasing number of phenylene units in a repeating unit from $m = 1$–4. This is in good agreement with the results of molecular orbital calculations on a series of simplified model polymers using the SCF-CO method, which predict that the nature of both HOCO and LUCO interchanges from $\sigma$-type to $\pi$-type as the number of phenylene groups increases.



**1b** $m = 1$ $R^1 = R^2 = Et$
**1c** $m = 1$ $R^1 = Ph, R^2 = Me$
**2a** $m = 2$ $R^1 = R^2 = Me$
**2b** $m = 2$ $R^1 = R^2 = Et$
**2c** $m = 2$ $R^1 = Ph, R^2 = Me$
**3a** $m = 3$ $R^1 = R^2 = Me$
**3b** $m = 3$ $R^1 = R^2 = Et$
**3c** $m = 3$ $R^1 = Ph, R^2 = Me$
**4a** $m = 4$ $R^1 = R^2 = Me$
**4b** $m = 4$ $R^1 = R^2 = Et$
**4c** $m = 4$ $R^1 = Ph, R^2 = Me$

In order to learn how the structure of the $\pi$-electron system in the polymer chain affects the thermal properties of the polymers, we investigated those for poly[(disilanylene)oligophenylenes].

## 2. Results and discussion

### 2.1. Thermogravimetric analysis of the polymers

The thermal properties of poly[(disilanylene)oligophenylenes] were examined by thermogravimetric analysis (TGA) in the range of 20–1000°C in a nitrogen atmosphere, the results are presented in Fig. 1. The total weight loss at 1000°C and the temperature of 10% weight loss ($T_d^{10}$) are summarized in Table 1, together with some properties of the polymers. As shown in Fig. 1, TGA curves for polymers **2a**, **3a**, **1b**, **2b**, and **1c**–**4c** reveal that the weight of the polymers rapidly decreases from about 400°C in one step. While, polymers **4a**, **3b**, and **4b** decompose with two distinguishing steps. One is continuous weight loss at 300–400°C, and the other comprises rapid weight loss at 400–600°C. Polymers **1c**–**4c** bearing a phenyl group on the silicon atom, always show the highest $T_d^{10}$ among the polymers with the same number of phenylenes between disilanylene units, reflecting the thermal stability of the Si–Ph bond relative to Si–alkyl bond. At temperature of 1000°C, however, no obvious relationship between the substituents at the silicon atoms and the total weight loss is observed. The total weight loss at 1000°C for the polymers was calculated to be 54.5–75.5% on the basis of the initial weight, which is lower than that for poly[$p$-(dimethylsilylene)phenylene] reported previously (87%) [12], in spite of the fact that an Si–Si bond is usually thermodynamically less stable than an Si–C bond [15]. Among the polymers having the same substituents on the silicon atom, polymers with $m = 1$ (**1b** and **1c**) show the highest weight loss at 1000°C. The total weight loss for phenylated polymers **1c**–**4c** has a tendency to decrease with increasing the number of phenylenes ($m$). However, this is not evident for peralkylated polymers **2a**–**4a** and **1b**–**4b**.

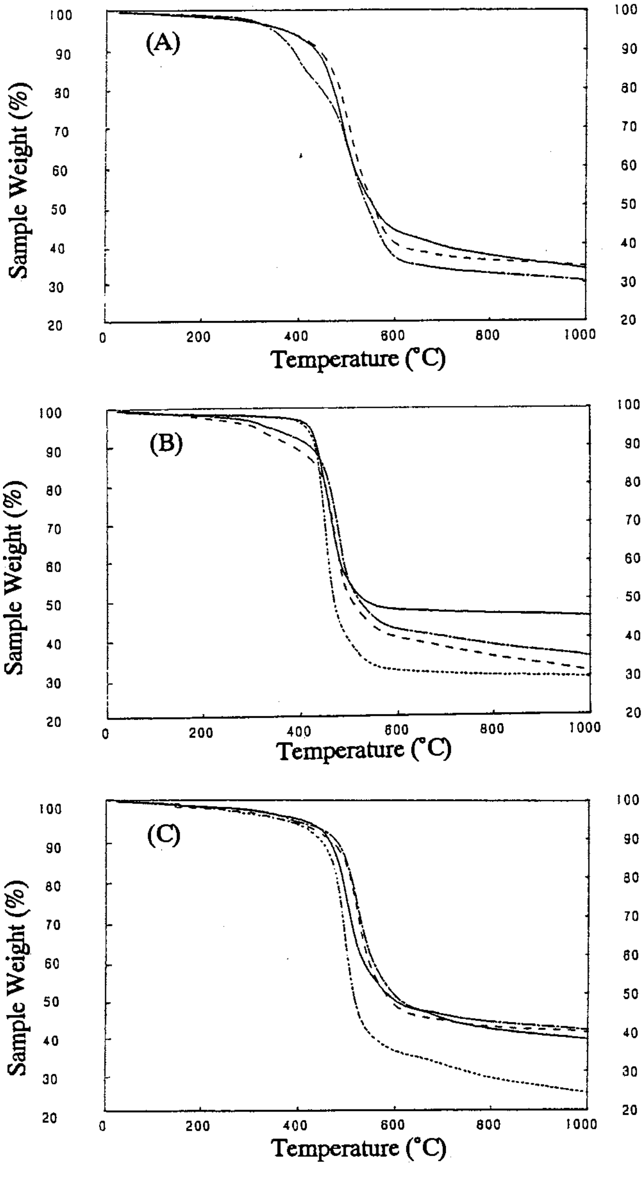


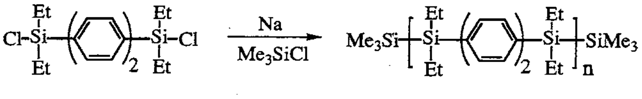
Fig. 1. TGA profile for (A) polymers **2a** (—), **3a** (---), and **4a** (–––), (B) **1b** (----), **2b** (—), **3b** (---), and **4b** (–––), and (c) **1c** (-----), and **2c** (—), and **3c** (---), and **4c** (–––).

Table 1
Properties of polymers

| Polymer | $m$ | $R^1$ | $R^2$ | m.p. (°C) | Mw (Mn)[a] | TGA | |
|---|---|---|---|---|---|---|---|
| | | | | | | weight loss (%)[b] | $T_d^{10}$ (°C)[c] |
| **2a** | 2 | Me | Me | 192–202 | 17 000 (6000) | 66.3 | 435 |
| **3a** | 3 | Me | Me | 113–126 | 9500 (4900) | 65.9 | 444 |
| **4a** | 4 | Me | Me | 120–138 | 5800 (4000) | 69.5 | 394 |
| **1b** | 1 | Et | Et | 192–216 | 11 000 (5800) | 70.8 | 435 |
| **2b** | 2 | Et | Et | 122–134 | 27 000 (10 000) | 54.5 | 435 |
| | | | | 154–159 | 15 700 (8 000) | 51.8 | 440 |
| | | | | 118–123 | 5300 (3400) | 53.9 | 435 |
| **3b** | 3 | Et | Et | 99–110 | 8500 (4000) | 68.7 | 391 |
| **4b** | 4 | Et | Et | 104–127 | 7000 (4500) | 64.8 | 425 |
| **1c** | 1 | Ph | Me | 96–100 | 8900 (3800) | 75.5 | 449 |
| **2c** | 2 | Ph | Me | 169–183 | 14 000 (5800) | 61.7 | 461 |
| **3c** | 3 | Ph | Me | 143–161 | 7000 (3600) | 59.8 | 459 |
| **4c** | 4 | Ph | Me | 180–199 | 6900 (3400) | 59.2 | 476 |

[a] Determined by GPC, relative to polystyrene standards.
[b] Total weight loss at 1000°C.
[c] Temperature of 10% weight loss based on the initial weight.

To know how the molecular weight influences the thermal properties of polymers, we prepared two samples of polymer **2b** with low molecular weights (Mw = 15700 and 5300) by sodium condensation of bis(chlorodiethylsilyl)biphenyl in the presence of 5 mol% of chlorotrimethylsilane as a terminating reagent (Eq. 1), and compared their thermal properties with that of **2b** (Mw = 27000) obtained from the similar reaction in the absence of chlorotrimethylsilane as reported in the literature [14]. As shown in Table 1, polymers with different molecular weights exhibit an almost identical TGA profile, indicating that the thermal properties of the polymers are little affected by the molecular weight, compatible with the results reported by Corriu et al. for poly[(dimethylsilylene)diethynylene] [9]



**2b** (Mw = 15,700 and 5,300)

(1)

## 2.2. GC-MS analysis of the volatile products from the pyrolysis of polymers 2a and 1b–4b

Next, we carried out pyrolysis of the polymers at 500°C and analyzed volatile products by GC-MS. The results are shown in Fig. 2 for **1b** and Table 2 for **2a** and **2b**–**4b**. The Mass spectra of some of the products are consistent with those of the authentic samples. The other products were tentatively assigned by careful comparison of the spectra with those of related compounds (Table 3). For example, products derived from the pyrolysis of **1b** were assigned to be those shown in Fig. 2. The mass spectral fragmentation for the products with ethyl substituents obeys a general sequence. Namely, an $[ArSiEt_2]^+$ ion which is produced by loss of R radical from a molecular ion $[ArSiEt_2R]^{+\bullet}$ (R = alkyl, silyl group, or hydrogen), fragments further to smaller ions such as $[ArSiHEt]^+$ and $[ArSiH_2]^+$ via subsequent elimination of ethylene molecules. Thus, the fragmentation pattern of $H_2EtSi(C_6H_4)SiEt_2H^{+\bullet}$ ($m/z$ 222) closely resembles that of $HEt_2Si(C_6H_4)SiEt_2H^{+\bullet}$ ($m/z$ 250) whose spectrum is consistent with that of the authentic sample, in the region of $m/z$ from 100 to 200 with one exception for the presence of a signal at $m/z$ 165 probably due to $H_2EtSi(C_6H_4)SiH_2^+$. Mass spectra of $MeEt_2Si(C_6H_4)SiEt_2H$ and $Et_3Si(C_6H_4)SiEt_2H$ also show a similar pattern to that of $HEt_2Si(C_6H_4)SiEt_2H$ in this region. Moreover, the fragmentation for these products observed in the region over $m/z$ 200 is quite similar to that of $HEt_2Si(C_6H_4)SiEt_2H$ which shows signals due to $[M\text{-}29]^+$ and $[M\text{-}57]^+$ with high intensities. These facts clearly indicate that these products have the same $-(C_6H_4)SiEt_2H$ moiety. Assignment of longer oligomers was also performed, based on similar consideration. Another example involves assignment of a product with the parent signal at $m/z$ 316, obtained from polymers **3b** and **4b**. The mass spectrum disagrees with that of $Ph(C_6H_4)SiEt_2Ph$ prepared independently, and therefore we assigned it as $Ph(C_6H_4)_2SiEt_2H$.

As shown in Fig. 2 and Table 2, the polymers readily decomposed at 500°C to give silicon-containing oligomers, mainly. A possible mechanistic interpretation for the observed reactions of the polymers is

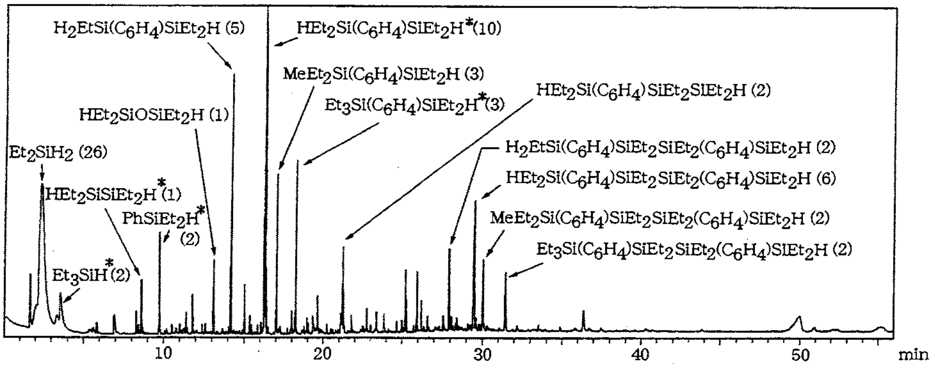


Fig. 2. TIC profile for the volatile products obtained from the pyrolysis of polymer **1b** at 500°C with tentative assignment of the signals. Asterisks indicate products whose mass spectra are constitent with the authenic samples.

presented in Scheme 1. From the pyrolysis of polymer **1b**, hydrosilanes arising from homolytic scission of an Si–Si bond, followed by abstraction of hydrogen by the resulting silyl radicals from any hydrogen sources available, are produced as the major products. In addition, the formation of $Et_2SiH_2$ and $PhSiEt_2H$ clearly indicates the occurrence of Si–phenylene bond cleavage. Products having an $H_2EtSi$– unit suggest that Si–Et bond cleavage is also involved in this pyrolysis. The formation of a $MeEt_2Si$– and $Et_3Si$– group in products may be explained in terms of redistribution reactions via silyl radical intermediates and/or alkyl migration in a tetraethyldisilanylene unit.

The pyrolysis of polymers **2b**–**4b** proceeds in a similar fashion to that of **1b** to afford products arising from cleavage of Si–Si, Si–phenylene, and Si–Et bonds in a radical fashion mainly. In contrast to the pyrolysis of **1b** and **2b** which gave no major volatile products arising from phenylene–phenylene bond cleavage, polymer **3b** gave bis(silyl)-biphenyls presumably derived from phenylene extrusion from the terphenylene unit. Small amounts of benzene and terphenylene were also found to be produced. The pyrolysis of polymer **4b** produced phenylene-contraction products, bis(silyl)-substituted biphenyls and terphenylenes, as observed for polymer **3b**. The formation of oligophenylenes $H(C_6H_4)_lH$ ($l=1-4$) occurred to a higher extent in the pyrolysis of polymer **4b** than that of **3b**.

In contrast to **1b**–**4b** which gave products from Si–Et bond cleavage, permethylated polymer **2a** afforded no major volatile products arising from Si–Me bond cleavage. The formation of only small amounts of products bearing an $SiMe_3$ substituent suggests that the Si–Me bond cleavage is a minor pathway, even if it is involved. This may be explained by the enhanced steric hindrance of ethyl-substituted silyl radicals than methyl-substituted ones and/or formation of thermodynamically more favored ethyl radical than methyl radical. The sterically hindered ethyl-substituted silyl radicals may undergo abstraction of a hydrogen atom or a methyl group, in preference to addition across the phenylene unit to form a cross-linked unit which would be involved in the nonvolatile products (Scheme 1).

Radicals arising from the homolytic scission of the main chain and the Si–Et bond would undergo two different kinds of reactions. One is hydrogen abstraction as described above. While, the other comprises addition of the radicals across the phenylene unit to

Table 2
Assignment of the volatile products from the pyrolysis of polymers **2a**, **2b**–**4b** at 500°C by GC-MS analysis

| Polymer | Product (area % in TIC) |
|---|---|
| **2a** | $PhSiMe_3^*$ (1), $H(C_6H_4)_2H^*$ (2), $Ph(C_6H_4)SiMe_2H^*$ (17), $Ph(C_6H_4)SiMe_2SiMe_2H$ (9), $HSiMe_2(C_6H_4)_2SiMe_2H^*$ (11), $[2(C_6H_4)+SiMe_2+SiMe_3+H]$ (3), $[2(C_6H_4)+3SiMe_2+2H]$ (2), $[2(C_6H_4)+3SiMe_2+2H]$ (7), $[2(C_6H_4)+2SiMe_2+SiMe_3+H]$ (3), $[2(C_6H_4)+4SiMe_2+2H]$ (3), $[2(C_6H_4)+4SiMe_2+2H]$ (2), $[3(C_6H_4)+2SiMe_2+2H]$ (1), $[4(C_6H_4)+SiMe_2+2H]$ (1), $[4(C_6H_4)+2SiMe_2+2H]$ (6), $[4(C_6H_4)+3SiMe_2+2H]$ (4) |
| **2b** | $Et_2SiH_2$ (34), $HSiEt_2SiEt_2H^*$ (1), $Ph(C_6H_4)SiEtH_2$ (2), $Ph(C_6H_4)SiEt_2H^*$ (3), $H_2EtSi(C_6H_4)_2SiEt_2H$ (9), $HEt_2Si(C_6H_4)_2SiEt_2H^*$ (14), $MeEt_2Si(C_6H_4)_2SiEt_2H$ (2), $Et_3Si(C_6H_4)_2SiEt_2H^*$ (3), $[2(C_6H_4)+3SiEt_2+2H]$ (3) |
| **3b** | $Et_2SiH_2$ (10), $C_6H_6^*$ (5), $PhSiEtH_2$ (2), $PhSiEt_2H^*$ (7), $Br(C_6H_4)SiEt_2H$ (2), $Ph(C_6H_4)SiEtH_2$ (4), $Ph(C_6H_4)SiEt_2H^*$ (9), $H(C_6H_4)_3H^*$ (2), $H_2EtSi(C_6H_4)_2SiEt_2H$ (3), $Ph(C_6H_4)_2SiEt_2H$ (5), $HEt_2Si(C_6H_4)_2SiEt_2H^*$ (5), $HEt_2Si(C_6H_4)_3SiEt_2H$ (5) |
| **4b** | $Et_2SiH_2$ (12), $C_6H_6^*$ (8), $PhSiEtH_2$ (2), $PhSiEt_2H^*$ (10), $PhSiEt_2Me$ (1), $H(C_6H_4)_2H^*$ (4), $Ph(C_6H_4)SiEt_2H^*$ (3), $H(C_6H_4)_3H^*$ (6), $H_2EtSi(C_6H_4)_2SiEt_2H$ (2), $HEt_2Si(C_6H_4)_2SiEt_2H^*$ (4), $Ph(C_6H_4)_2SiEtH_2$ (2), $Ph(C_6H_4)_2SiEt_2H$ (8), $H(C_6H_4)_4H$ (6) |

* Compounds whose mass spectra are identical with those of the authentic samples.

Table 3
Mass spectral data for volatile products from the pyrolysis of polymers **2a** and **lb-4b**

| Compound | $m/z$ (relative intensity/%)[a] |
|---|---|
| $PhSiMe_3$ | 150 (34), 135 (100), 58 (59), 43 (88) |
| $H(C_6H_4)_2H$ | 154 (100), 128 (6), 115 (6), 102 (5), 76 (23), 63 (13), 51 (25), 39 (16) |
| $Ph(C_6H_4)SiMe_2H$ | 212 (36), 197 (100), 181 (9), 165 (9), 152 (5), 98 (8), 58 (41), 53 (13), 43 (45) |
| $Ph(C_6H_4)SiMe_2SiMe_2H$ | 270 (8), 211 (100), 195 (16), 181 (5), 165 (5), 59 (5), 45 (5), 43 (19) |
| $HSiMe_2(C_6H_4)_2SiMe_2H$ | 270 (18), 255 (19), 211 (100), 195 (13), 181 (5), 165 (6), 59 (27), 43 (20) |
| $[2(C_6H_4)+SiMe_2+SiMe_3+H]$ | 284 (30), 269 (100), 211 (59), 195 (15), 181 (7), 165 (8), 134 (5), 127 (13), 73 (23), 59 (34), 45 (18), 43 (23) |
| $[2(C_6H_4)+3SiMe_2+2H]$ | 328 (3), 211 (45), 195 (37), 181 (8), 165 (5), 116 (100), 73 (27), 59 (10), 45 (12), 43 (22) |
| $[2(C_6H_4)+3SiMe_2+2H]$ | 328 (6), 269 (100), 195 (11), 73 (6), 59 (31), 45 (5), 43 (12) |
| $[2(C_6H_4)+2SiMe_2+SiMe_3+H]$ | 342 (10), 283 (100), 269 (25), 195 (11), 134 (17), 73 (52), 59 (13), 45 (19), 43 (13) |
| $[2(C_6H_4)+4SiMe_2+2H]$ | 386 (3), 269 (27), 253 (5), 195 (13), 116 (100), 73 (22), 59 (27), 45 (6), 43 (9) |
| $[2(C_6H_4)+4SiMe_2+2H]$ | 386 (3), 327 (36), 269 (20), 253 (5), 195 (9), 134 (13), 116 (100), 73 (19), 59 (22), 45 (6), 43 (13) |
| $[3(C_6H_4)+2SiMe_2+2H]$ | 346 (33), 331 (100), 287 (5), 273 (8), 211 (22), 195 (8), 165 (10), 158 (13), 135 (22), 105 (9), 59 (28), 43 (26) |
| $[4(C_6H_4)+SiMe_2+2H]$ | 364 (29), 349 (100), 195 (18), 181 (8), 174 (19), 165 (12), 53 (6), 43 (15) |
| $[4(C_6H_4)+2SiMe_2+2H]$ | 422 (35), 407 (100), 363 (7), 349 (9), 211 (27), 196 (33), 181 (11), 165 (12), 59 (35), 43 (22) |
| $[4(C_6H_4)+3SiMe_2+2H]$ | 480 (17), 421 (17), 407 (8), 269 (89), 211 (100), 195 (23), 181 (9), 165 (8), 59 (39), 43 (27) |
| $Et_2SiH_2$ | 88 (8), 86 (9), 58 (100), 43 (35), 31 (44) |
| $HSiEt_2SiEt_2H$ | 174 (24), 145 (28), 117 (42), 86 (84), 59 (100), 43 (23), 31 (38) |
| $Ph(C_6H_4)SiEtH_2$ | 212 (33), 183 (100), 155 (11), 134 (13), 105 (11), 91 (18), 77 (5), 53 (15), 43 (5) |
| $Ph(C_6H_4)SiEt_2H$ | 240 (20), 211 (44), 183 (100), 155 (8), 105 (8), 91 (27), 58 (10) |
| $H_2EtSi(C_6H_4)_2SiEt_2H$ | 298 (23), 269 (21), 241 (100), 211 (35), 181 (53), 155 (9), 106 (42), 59 (16), 53 (11), 31 (9) |
| $HEt_2Si(C_6H_4)_2SiEt_2H$ | 326 (23), 297 (16), 269 (100), 239 (34), 211 (41), 181 (38), 155 (5), 120 (31), 106 (94), 59 (41), 53 (8), 31 (7) |
| $MeEt_2Si(C_6H_4)_2SiEt_2H$ | 340 (18), 311 (50), 283 (86), 226 (13), 195 (8), 181 (11), 127 (23), 113 (100), 73 (5), 59 (17), 43 (8) |
| $Et_3Si(C_6H_4)_2SiEt_2H$ | 354 (17), 325 (52), 297 (52), 269 (80), 212 (23), 181 (27), 134 (33), 120 (51), 106 (100), 87 (7), 59 (25) |
| $[2(C_6H_4)+3SiEt_2+2H]$ | 412 (10), 325 (86), 297 (66), 269 (100), 240 (5), 212 (26), 181 (34), 149 (5), 135 (20), 120 (31), 106 (36), 87 (9), 59 (45), 31 (7) |
| $PhSiEtH_2$ | 136 (35), 107 (100), 81 (9), 58 (22), 53 (23), 43 (13) |
| $PhSiEt_2H$ | 164 (17), 135 (47), 107 (100), 86 (13), 81 (7), 58 (9), 53 (12), 43 (5) |
| $Br(C_6H_4)SiEt_2H$[b] | 242 (14), 213 (81), 187 (97), 164 (5), 133 (5), 105 (64), 91 (10), 79 (9), 53 (17) |
| $H(C_6H_4)_3H$ | 230 (100), 152 (5), 115 (22) |
| $Ph(C_6H_4)_2SiEt_2H$ | 316 (34), 287 (31), 259 (89), 230 (8), 129 (100), 102 (5), 86 (8), 58 (11), 53 (6) |
| $HEt_2Si(C_6H_4)_3SiEt_2H$ | 402 (15), 345 (32), 315 (13), 287 (19), 259 (17), 158 (13), 144 (100), 59 (16) |
| $PhSiEt_2Me$ | 178 (18), 149 (37), 121 (100), 105 (6), 86 (9), 58 (8), 53 (8), 43 (11) |
| $Ph(C_6H_4)_2SiEtH_2$ | 288 (73), 259 (100), 230 (59), 202 (5), 181 (14), 152 (5), 134 (13), 129 (80), 115 (10), 105 (11), 53 (14) |
| $H(C_6H_4)_4H$ | 306 (100), 289 (7), 153 (35), 138 (5) |

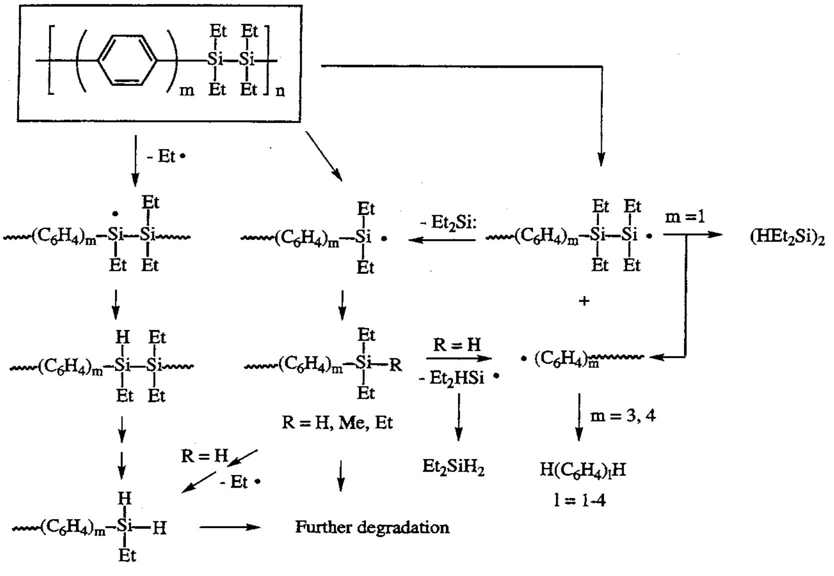
[a] Parent ion and ion with a relative intensity $\geq 5\%$.
[b] Ion for $Br^{79}$.

produce cross–linked unit, which seems to be responsible for the higher char yields in the pyrolysis of polymers with extended oligophenylene units ($m \geq 2$). It is likely that polymers with an extended oligophenylene unit favor addition reactions with the radicals, due to its high-lying HOMO and low steric hindrance, relative to disilanylene-phenylene polymers **1b** and **1c**. For phenylated polymers **1c**–**4c**, radical cross-linking would also occur at phenyl substituents.

The formation of an Si–H bond was also detected in the non volatile products from the pyrolysis of the polymers. For example, when **2b** was heated at 450°C for 5 min in vacuo and the residue was analyzed by IR spectrometry, an absorption band due to the stretching frequencies of an Si–H bond was observed at 2100 $cm^{-1}$. The residue is insoluble in organic solvents, in contrast to the starting polymer, indicating that the cross-linking reactions apparently took place during the pyrolysis.

### 2.3. Pyrolysis of a model compound

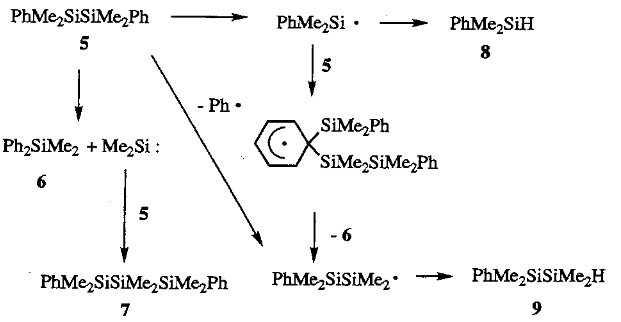
When a model compound, 1,1,2,2-tetramethyldiphenyldisilane (**5**) was heated at 400°C for 16 h in a sealed glass tube, dimethyldiphenylsilane (**6**), 1,1,2,2,3,3-hexamethyldiphenyltrisilane (**7**), dimethylphenylsi-



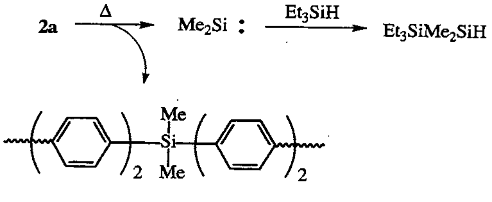
Scheme 1.

lane (**8**), and 1,1,2,2-tetramethylphenyldisilane (**9**) were obtained in 14, 4, 3, and 1% yields, respectively, in addition to many products in less than 1% yields and 58% of the starting disilane (Scheme 2). The formation of compounds **6** and **7** can be understood in terms of extrusion of dimethylsilylene from **5**, followed by insertion of the resulting silylene into the Si–Si bond of the starting disilane **5**. For the formation of **8** and **9**, it seems likely that homolytic scission of the Si–Si and Si–Ph bonds leading to the respective silyl and disilanyl radical, is involved in this pyrolysis. The silyl radicals would abstract a hydrogen atom from any sources available in the reaction mixture. The formation of **6** and **9** can be also explained by the redistribution reaction of dimethylphenylsilyl radical and **5**, as shown in Scheme 2.

In order to know more about the silylene formation from poly[(disilanylene)oligophenylenes], we carried out the pyrolysis of polymer **2a** at 400°C for 16 h in the presence of triethylsilane as the silylene trapping reagent. GLC analysis of the resulting mixture shows the formation of a dimethylsilylene-trapped product 1,1,1-triethyldimethyldisilane in 6% yield (Scheme 3). In this pyrolysis two unidentified volatile products whose parent signals appear at *m*/*z* 356 and 384 in the mass spectra were also produced in both 2% yields. Regarding the non volatile products, GPC analysis of the mixture shows the formation of an oligomer with the molecular weight of Mw = 8500; Mn = 720. The oligomer was divided into two fractions by reprecipitation; ethanol-soluble viscous pale yellow oil (Mw = 2300; Mn = 490) and ethanol-insoluble white solids (Mw = 9300; Mn = 1700). Each fraction was examined with respect to the IR, and $^1H$ and $^{13}C$-NMR spectra which indicate the existence of phenylene, H–Si, EtSi, and MeSi groups. The spectra for each fraction are essentially the same, although they exhibit that relatively smaller amounts of H–Si and EtSi units are involved in the ethanol-insoluble oligomer with higher molecular weight. The $^1H$-NMR spectrum of the ethanol-soluble oligomer reveals two septet H–Si signals at 3.74 and 4.57 ppm which were found to couple with MeSi signals at 0.14 and 0.37 ppm, respectively, by the homo-decoupling experiments. They are assignable to an $HSiMe_2SiMe_2$– and $HSiMe_2$–$(C_6H_4)$– group, respectively, on the basis of the comparison of the chemical shifts with those of related compounds **9** and



Scheme 2.



Scheme 3.

Ph($p$-$C_6H_4$)$SiMe_2H$ (see Section 4). Although the $^1H$-NMR spectrum for the ethanol-insoluble oligomer shows two septets of H–Si at the same chemical shifts, homodecoupling experiments could not be carried out due to their low intensities.

## 3. Conclusion

Introduction of a phenyl substituent on the silicon atom of poly[(disilanylene)oligophenylenes] led to higher heat-resistance, relative to those having only alkyl substituents. Polymers with two or more phenylene groups in a unit ($m \geq 2$) show higher heat-resistance than monophenylene-containing polymers ($m = 1$). Polymer **2b** exhibited the smallest weight loss at 1000°C and highest $T_d10$ among the present polymers, although the origin of the high thermal stability of **2b** is still unclear. The volatile products from the pyrolysis of polymers **2a** and **1b**–**4b** were analyzed by GC-MS which showed that the polymers decomposed by the homolytic scission of both Si–Si and Si–phenylene bonds mainly. In addition, phenylene–phenylene bond cleavage was also observed for polymers **3b** and **4b** with $m \geq 3$. The degree of the phenylene–phenylene bond cleavage relative to Si–phenylene and Si–Si bond cleavage in the pyrolysis of the polymers seems to be higher for **4b** than for **3b**. The cleavage of the Si–Et bond was always observed as the major degradation pathway for ethylated polymers **1b**–**4b**, while no major volatile products arising from Si–Me bond cleavage were obtained in the pyrolysis of permethylated polymer **2a**.

Products from the model reaction using **5** suggest that silylene extrusion and Si–Si bond cleavage occurred mainly in these pyrolyses. In addition, product **9** from Si–phenylene bond cleavage was obtained in low yield.

## 4. Experimental

### 4.1. General

Poly[(disilanylene)-$p$-oligophenylenes] were synthesized as reported in the literature [14]. All reactions were carried out under an atmosphere of purified argon. NMR spectra were recorded on a JEOL EX-270 spectrometer using tetramethylsilane as an internal standard. IR spectra were measured on a Perkin-Elmer FT1600 spectrophotometer. Mass spectra were measured on a Hitachi M-80B spectrometer, except for the products obtained from the pyrolysis of the polymers. GC-MS analysis for the volatile products from the pyrolysis of the polymers were carried out with a Frontier Lab PY-2010D pyrolyzer attached to a Shimadzu GC-MS QP5000 spectrometer. TGA was carried out using a SEIKO TGA30 thermobalance.

### 4.2. Preparation of polymer **2b** with low molecular weight

In a 200 ml two-necked flask were placed 0.40 g (17.4 mmol) of sodium dispersion and 100 ml of dry toluene. To this was added a mixture of 2.43 g (6.14 mmol) of 4,4′-bis(chlorodiethylsilyl)biphenyl and 0.040 ml (0.307 mmol) of chlorotrimethylsilane in 20 ml of toluene at room temperature (r.t.). The mixture was stirred at r.t. for 30 min, and then heated to reflux. After refluxing for 6 h, the resulting mixture was hydrolyzed with water. The organic layer was separated and dried over magnesium sulfite. The solvent was evaporated, the residue was reprecipitated from hexane–chloroform, and the resulting polymer **2b** with molecular weight of Mw = 15700; Mn = 8000 was filtered out as white solids (0.989 g, 50% yield). After evaporation of the solvent from the filtrate, reprecipitation of the residue from acetone–chloroform gave **2b** with molecular weight of Mw = 5300; Mn = 3400 (0.670 g, 34% yield). NMR and IR spectra for the polymers are identical with those of the polymer with high molecular weight prepared as reported previously, except for the presence of a weak signal due to a trimethylsilyl unit at the polymer end, which was observed at 0.13 ppm in their $^1H$ spectra.

### 4.3. Thermogravimetric analysis of the polymers

In a platinum pot was placed 4–5 mg of a polymer, and the pot was heated from r.t. to 1000°C at a rate of 10°C/min under a nitrogen atmosphere. The results are shown in Fig. 1 and Table 1.

### 4.4. Pyrolysis of the polymers at 500°C

In a quartz sample tube was placed ca. 10 mg of a polymer and the tube was heated at 500°C under reduced pressure ($2 \times 10^{-7}$ mmHg), and the gas, evolved was directly introduced into a GC-MS spectrometer. The results are shown in Fig. 2 and Table 2. Table 3 summarizes the mass spectral data of the volatile products. Mass spectra of some of the products were identical with those of the authentic samples. Compounds $HSiEt_2(C_6H_4)SiEt_2H$ and $HR_2Si(C_6H_4)_2SiR_2H$ (R = Me, Et) were prepared as described in the literature [14]. Oligophenylenes, $H(C_6H_4)_lH$ ($l = 1$–3), were purchased from Wako Chemical Co. Ltd. Silicon compounds $Et_3SiH$ and $PhSiMe_3$ were purchased from Shin-Etsu Co. Ltd. The other authentic samples were prepared as follows.

### 4.5. Preparation of $p$-Ph($C_6H_4$)$SiMe_2H$

To a solution of Ph($C_6H_4$)Li in 20 ml of ether, prepared by the reaction of 0.50 g (2.15 mmol) of 4-bromobiphenyl and an equimolar amount of $n$-butyllithium, was added 0.22 g (2.20 mmol) of chlorodimethylsilane at r.t. After stirring for 3 h, the mixture was hydrolyzed with water, and the organic layer was separated and dried over magnesium sulfate. After evaporation of the solvent, Kügel-rohr distillation of the residue under reduced pressure gave 0.369 g (81% yield) of $Ph(C_6H_4)SiMe_2H$: b.p. 100–104°C (1 mmHg); MS $m/z$ 212 ($M^+$); $^1$H-NMR (in $C_6D_6$) $\delta = 0.50$ (d, 6H, MeSi, $J = 3.7$ Hz), 4.62 (sept, 1H, HSi, $J = 3.7$ Hz), 7.45–7.75 (m, 9H, Ph and phenylene); $^{13}$C-NMR (in $C_6D_6$) $\delta = -3.7$, 126.6, 127.1, 127.4, 128.8, 134.5, 136.1, 141.0, 142.0. Anal. Found: C, 79.27; H, 7.61. Calc. for $C_{14}H_{16}Si$: C, 79.18; H, 7.59%.

### 4.6. Preparation of *p*-$Ph(C_6H_4)SiEt_2H$

To a solution of $Ph(C_6H_4)Li$ in 20 ml of ether, prepared by the reaction of 0.50 g (2.15 mmol) of 4-bromobiphenyl and 1.4 ml (2.19 mmol) of a 1.57 M *n*-butyllithium/hexane solution, was added 0.26 g (2.14 mmol) of chlorodiethylsilane at r.t. After stirring for 1 day, the mixture was hydrolyzed with water, and the organic layer was separated and dried over magnesium sulfate. After evaporation of the solvent, the residue was chromatographed on silica gel eluting with hexane, then treated with preparative GPC eluting with benzene to give 0.42 g (81% yield) of $Ph(C_6H_4)SiEt_2H$: MS $m/z$ 240 ($M^+$); $^1$H-NMR (in $CDCl_3$) $\delta = 0.86$–$0.98$ (m, 4H, $CH_2Si$), 1.09 (t, 6H, $CH_3$, $J = 7.8$ Hz), 4.30 (quintet, 1H, HSi, $J = 3.3$ Hz), 7.34–7.42 (m, 1H, Ph), 7.43–7.51 (br. t, 2H, Ph, $J = 7.3$ Hz), 7.60–7.68 (m, 6H, Ph and phenylene); $^{13}$C-NMR (in $CDCl_3$) $\delta = 3.47$, 8.12, 126.5, 127.1, 127.3, 128.8, 134.3, 135.1, 141.0, 141.9; $^{29}$Si NMR (in $CDCl_3$) $\delta = -5.23$; IR 2107 cm$^{-1}$ (Si–H). Anal. Found: C, 79.93; H, 8.38. Calc. for $C_{16}H_{20}Si$: C, 79.90; H, 8.44%.

### 4.7. Preparation of *p*-$Ph(C_6H_4)SiEt_2Ph$

To a solution of $Ph(C_6H_4)Li$ in 20 ml of ether, prepared by the reaction of 0.50 g (2.15 mmol) of 4-bromobiphenyl and 1.4 ml (2.19 mmol) of a 1.57 M *n*-butyllithium/hexane solution, was added 0.43 g (2.16 mmol) of chlorodiethylphenylsilane at r.t. After stirring for 1 day, the mixture was hydrolyzed with water and the organic layer was separated and dried over magnesium sulfate. After evaporation of the solvent, the residue was chromatographed on silica gel eluting with hexane to give 0.54 g (79% yield) of $Ph(C_6H_4)SiEt_2Ph$: MS $m/z$ 316 ($M^+$); $^1$H-NMR (in $CDCl_3$) $\delta = 1.03$–$1.20$ (m, 10H, EtSi), 7.36–7.68, (m, 14H, Ph and phenylene); $^{13}$C-NMR (in $CDCl_3$) $\delta = 3.90$, 7.44, 126.4, 127.1, 127.3, 128.7, 135.0, 135.4, 141.0, 141.7, 127.8, 129.1, 134.9, 136.1; $^{29}$Si-NMR (in $CDCl_3$) $\delta = -3.91$. Anal. Found: C, 83.48; H, 7.64. Calc. for $C_{22}H_{24}Si$: C, 83.25; H, 7.61%.

### 4.8. Preparation of *p*-$Br(C_6H_4)SiEt_3$

To a solution of $Br(C_6H_4)Li$ in 150 ml of ether, prepared by the reaction of 11.80 g (50.0 mmol) of 1,4-dibromobenzene and 55 ml (88.0 mmol)of a 1.6 M *n*-butyllithium/hexane solution, was added 7.0 g (2.20 mmol) of chlorotriethylsilane at r.t. After stirring for 3 h, the mixture was hydrolyzed with water and the organic layer was separated and dried over magnesium sulfate. After evaporation of the solvent, the residue was distilled under a reduced pressure to give 3.3 g (24% yield) of $Br(C_6H_4)SiEt_3$: b.p. 67°C (0.1 mmHg); MS $m/z$ 270 ($M^+$ for $Br^{79}$); $^1$H-NMR (in $C_6D_6$) $\delta = 0.81$ (q, 6H, $CH_2Si$, $J = 8.0$ Hz), 0.98 (t, 9H, $CH_3$, $J = 8.0$ Hz), 7.38 (d, 2H, phenylene, $J = 8.2$ Hz), 7.51 (d, 2H, phenylene, $J = 8.2$ Hz); $^{13}$C-NMR (in $C_6D_6$) $\delta = 3.2$, 7.3, 123.5, 130.8, 135.7, 136.1. Anal. Found: C, 53.06; H, 7.14. Calc. for $C_{12}H_{19}SiBr$: C, 53.13; H, 7.06%.

### 4.9. Preparation of *p*-$Et_3Si(C_6H_4)SiEt_2H$

To a solution of $Et_3Si(C_6H_4)Li$ in 4 ml of ether, prepared by the reaction of 0.537 g (1.98 mmol) of $Br(C_6H_4)SiEt_3$ and 1.8 ml (2.8 mmol) of a 1.54 M *n*-butyllithium/hexane solution, was added 0.30 g (2.00 mmol) of chlorotriethylsilane at r.t. After stirring for 3 h, the mixture was hydrolyzed with water and the organic layer was separated and dried over magnesium sulfate. After evaporation of the solvent, the residue was treated with preparative GPC eluting with benzene to give 0.22 g (32% yield) of $Et_3Si(C_6H_4)SiEt_2H$: MS $m/z$ 278 ($M^+$); $^1$H-NMR (in $C_6D_6$) $\delta = 0.83$ (q, 6H, $CH_2Si$, $J = 8.1$ Hz), 0.90 (qd, 4H, $CH_2$SiH, $J = 7.9$, 3.1 Hz), 1.01 (t, 9H, $CH_3$, $J = 8.1$ Hz), 1.07 (t, 6H, $CH_3$, $J = 7.9$ Hz), 4.24 (quint, 1H, HSi, $J = 3.1$ Hz), 7.51 (d, 2H, phenylene, $J = 7.3$ Hz), 7.54 (d, 2H, phenylene, $J = 7.3$ Hz); $^{13}$C-NMR (in $C_6D_6$) $\delta = 3.3$, 3.4, 7.4, 8.2, 133.5, 133.8, 135.9, 138.5. Anal. Found: C, 69.02; H, 10.88. Calc. for $C_{16}H_{30}Si_2$: C, 68.98; H, 10.85%.

### 4.10. Pyrolysis of compound **5** at 400°C

In a sealed glass tube was placed 104.7 mg (0.388 mmol) of $PhMe_2SiSiMe_2Ph$ (**5**), and the tube was heated at 400°C for 16 h. The resulting mixture was analyzed by GLC using 13.0 mg (0.0663 mmol) of tridecane as an internal standard as being $Ph_2Me_2Si$ (**6**) (14% yield), $Ph(Me_2Si)_3Ph$ (**7**) (4%), $PhMe_2SiH$ (**8**) (3%), and $PhMe_2SiSiMe_2H$ (**9**) (1%), along with 58% of $PhMe_2SiSiMe_2Ph$. GLC retention times and the mass spectra for the products were identical with those of the authentic samples. Authentic samples of **6** and **8** were purchased from Shin-Etsu Co. Ltd. Compounds **7** and **9** were prepared as follows.

### 4.11. Preparation of **7** [16]

To a solution of 0.30 ml (2.49 mmol) of $Me_2SiCl_2$ in 5 ml of THF was added a solution of $PhMe_2SiLi$ prepared from 1.0 g (5.9 mmol) of $PhMe_2SiCl$ and 0.17 g (27 mmol) of lithium in 10 ml of THF, at 0°C. The resulting mixture was stirred overnight at r.t. The mixture was hydrolyzed with water, and the organic layer was separated and dried over magnesium sulfate. After evaporation of the solvent, Kügel-rohr distillation of the residue under a reduced pressure gave 0.697 g (36% yield) of $Ph(Me_2Si)_3Ph$: b.p. 190°C (3 mmHg); MS $m/z$ 328 ($M^+$); $^1$H-NMR (in $C_6D_6$) $\delta = 0.17$ (s, 6H, MeSi), 0.32 (s, 12H, MeSi), 7.20–7.49 (m, 10H, ring protons); $^{13}$C-NMR (in $C_6D_6$) $\delta = -6.5$, $-3.1$, 128.0, 128.7, 134.0, 139.6. Anal. Found: C, 65.67; H, 8.59. Calc. for $C_{13}H_{28}Si_3$: C, 65.78; H, 8.59%.

### 4.12. Preparation of **9** [17]

To a solution of 0.70 ml (6.4 mmol) of $HMe_2SiCl$ in 5 ml of THF was added a $PhMe_2SiLi$ solution prepared from 1.0 g (5.9 mmol) of $PhMe_2SiCl$ and 0.17 g (27 mmol) of lithium in 10 ml of THF at 0°C. The resulting mixture was stirred overnight at r.t. The mixture was hydrolyzed with water, and the organic layer was separated and dried over magnesium sulfate. After evaporation of the solvent, Kügel-rohr distillation of the residue under a reduced pressure gave 0.680 g (60% yield) of $Ph(Me_2Si)_2H$: b.p. 150°C (13 mmHg); MS $m/z$ 194 ($M^+$); $^1$H-NMR (in $C_6D_6$) $\delta = 0.01$ (d, 6H, *Me*SiH, $J = 4.62$ Hz),0.32 (s, 6H, MeSi), 4.01 (sept, 1H, HSi, $J = 4.62$ Hz), 7.16–7.23 (m, 3H, ring protons), 7.46 (dd, 2H, ring protons, $J = 7.26$, 1.98 Hz); $^{13}$C-NMR ($CDCl_3$) $\delta = -6.6$, $-3.5$, 128.2, 128.9, 134.1, 139.0; IR: 2092 cm$^{-1}$ ($\nu_{Si-H}$). Anal. Found: C, 61.50; H, 9.21. Calc. for $C_{10}H_{18}Si_2$: C, 61.78; H, 9.33%.

### 4.13. Pyrolysis of polymer **2a** in the presence of $Et_3SiH$

A mixture of 50 mg of polymer **2a** (Mw = 17000; Mn = 6000) and 22 mg (1.9 mmol) of $Et_3SiH$ was heated at 400°C for 16 h in a degassed sealed glass tube. The resulting mixture was analyzed by GLC using *n*-dodecane as an internal standard as being $Et_3SiSiMe_2H$ in 6% yields, together with unidentified products whose mass spectra reveal the parent signal at $m/z$ 356 and 384, respectively, both in 2% yields. After removal of excess $Et_3SiH$ and the resulting $Et_3SiSiMe_2H$ under a reduced pressure, the residue was reprecipitated from chloroform-ethanol. The resulting precipitates were collected by filtration to give 32 mg of an oligomer as white solids. The solvent was evaporated from the filtrate to give 16 mg of pale yellow viscous oil. For the solids: Mw = 9300; Mn = 1700; $^1$H-NMR (in $CDCl_3$) $\delta = 0.10$–0.20, 0.35–0.45, 0.55–0.70 (m, MeSi, relative integration = 100), 0.78–1.07 (m, EtSi, 23), 3.74 (sept, HSi, 1, $J = 4.71$ Hz), 4.47 (sept, HSi, 1, $J = 4.44$ Hz), 7.41–7.78 (m, phenylene, 74); $^{13}$C-NMR ($CDCl_3$) $\delta = -3.8$, $-3.2$, $-2.3$ (Me), 3.4, 7.4 (Et), 126.4, 126.5, 126.6, 127.2, 133.5, 134.2, 134.4, 134.7, 137.1, 138.0, 141.2, 141.8; IR: 2117 cm$^{-1}$ ($\nu_{Si-H}$). For the oil: Mw = 2300; Mn = 490; $^1$H-NMR (in $CDCl_3$) $\delta = 0.05$–0.15, 0.35–0.45, 0.55–0.65 (m, MeSi, relative integration = 100), 0.78–1.07 (m, EtSi, 49), 3.74 (sept, HSi, 2, $J = 4.71$ Hz), 4.47 (sept, HSi, 2, $J = 4.44$ Hz), 7.32–7.71 (m, phenylene, 71); $^{13}$C-NMR ($CDCl_3$) $\delta = -3.8$, $-3.2$, $-2.3$ (Me), 3.4, 7.4 (Et), 126.4, 126.5, 126.6, 127.2, 133.5, 134.2, 134.4, 134.7, 137.1, 138.0, 141.2, 141.8; IR: 2116 cm$^{-1}$ ($\nu_{Si-H}$).

GLC retention time and mass spectrum for $Et_3SiSiMe_2H$ are identical with those of the authentic sample.

### 4.14. Preparation of $Et_3SiSiMe_2H$

Through a vigorously stirred mixture of 0.58 g (2.34 mmol) of $Et_3SiSiMe_2Ph$ [18] and 20 mg of $AlCl_3$ in 5 ml of benzene was passed HCl gas in a rate of ca. 20 ml/min. Monitoring the reaction progress by GLC indicated complete consumption of the starting disilane and the formation of $Et_3SiSiMe_2Cl$ after 2 h reaction. To this was added 5 ml of acetone to deactivate the aluminum catalyst and the resulting precipitates were filtered off. After the solvent was removed under a reduced pressure, the residue was dissolved in 2 ml of ether and the solution was added dropwise to a mixture of 24 mg (0.63 mmol) of $LiAlH_4$ in 4 ml of ether. The resulting mixture was stirred overnight at r.t. and hydrolyzed with water. The organic layer was separated and dried over magnesium sulfate. After evaporation of the solvent, the residue was distilled under a reduced pressure and the fraction boiling at 65–67°C (18 mmHg) was collected. The distillate was then treated with recycling preparative GPC eluting with benzene to give 0.26 g (65% yield) of $Et_3SiSiMe_2H$: MS $m/z$ 174 (relative intensity 9, $M^+$), 145 (9), 116 (77), 87 (100), 73 (7), 59 (52); $^1$H-NMR (in $CDCl_3$) $\delta = 0.15$ (d, 6H, *Me*SiH, $J = 4.6$ Hz), 0.63 (q, 6H, $CH_2CH_3$, $J = 7.9$ Hz), 0.96 (t, 9H, $CH_2CH_3$, $J = 7.9$ Hz), 3.70 (sept, 1H, HSi, $J = 4.6$ Hz); $^{13}$C-NMR ($CDCl_3$) $\delta = -5.8$, 3.3, 8.2; $^{29}$Si-NMR ($CDCl_3$) $\delta = -7.6$, $-42.1$; IR: 2089 cm$^{-1}$ ($\nu_{Si-H}$). Anal. Found: C, 55.09; H, 12.71.

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