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Thermal Ring-Opening Polymerization of [2.2]Paracyclophanes Having Two Disilanylene Bridges

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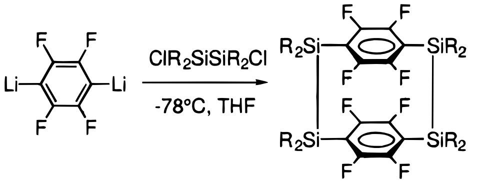
Summary: Novel disilanylene-bridged paracyclophanes, ($SiR_2SiR_2-C_6F_4)_2$, were prepared by the reactions of the corresponding 1,2-dichlorodisilanes with 1,4-dilithiotetrafluorobenzene. Thermolysis of the paracyclophanes at 300 °C gave the corresponding poly(disilanylene-1,4-phenylene) species, ($SiR_2SiR_2-C_6F_4)_n$, via homolytic Si−Si bond cleavage.

Much attention has been focused on silicon-based polymers because of their potential application to photoconductors, photoresists, and nonlinear optical materials.[1] Recently, a number of studies of polymers having a regular alternating arrangement of a silicon−silicon unit and a π-conjugated system such as ethynylene, arylene, and oligoarylene in the polymer backbone have been reported.[2−5] We report here a novel thermal ring-opening polymerization of disilanylene-bridged paracyclophanes, giving the corresponding poly(disilanylene-1,4-phenylene) compounds.

Sakurai *et al.* have first reported the synthesis and the interesting molecular structure of cyclophanes having two disilanylene bridges, but their reactions have received little attention to date.[6,7] We have synthesized novel disilanylene-bridged paracyclophanes, 1,1,2,2,9,9,10,10-octaalkyl-4,5,7,8,12,13,15,16-octafluoro-1,2,9,10-tetrasila[2.2]paracyclophanes **1a**[8] and **1b**[9] in 28% and 4% yield, respectively, by a simple coupling reaction of the corresponding 1,2-dichlorodisilanes with 1,4-dilithiotetrafluorobenzene, which was prepared from 1,4-dibromotetrafluorobenzene and *n*-butyllithium in THF at −78 °C.[10]



(1)

1a, R = Pr 28%
1b, R = Et 4%

When the paracyclophane **1a** was heated for 20 h in an evacuated sealed Pyrex tube at 300 °C, poly(tetrapropyldisilanylene-1,4-tetrafluorophenylene) (**2a**) was obtained in 91% yield.[11] The molecular weight (M_w) of **2a** was determined to be 54 000 with $M_w/M_n = 2.2$ by GPC.[12] The polymer **2a** was highly soluble in chloro-

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[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1997.

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(7) Because of the very low yield synthesis of the disilanylene-bridged paracyclophanes reported by Sakurai et al.,[6c] we have not investigated the thermal reactivity.

(8) Synthesis of **1a**: To a THF (10 mL) solution of 1,4-dibromotetrafluorobenzene (2.04 g, 6.63 mmol) was added *n*-BuLi (9.5 mL of a 1.4 M hexane solution, 13 mmol) with a syringe at −78 °C. After the suspension of 1,4-dilithiotetrafluorobenzene thus formed in the temperature range of −70 to −80 °C was stirred for 60 min, 1,2-dichlorotetrapropyldisilane (1.99 g, 6.65 mmol) in THF (5 mL) was added at −78 °C. The mixture was stirred for 15 min at −78 °C and then at 0 °C for 1.5 h. After hydrolysis with aqueous HCl, the organic layer was separated and dried over magnesium sulfate. Evaporation of the solvent gave a bright yellow solid (2.54 g). Recrystallization of the crude product with *n*-hexane yielded a white solid of **1a** in 28% yield. **1a**: mp 180−181 °C; ^{1}H NMR ($CDCl_3$, δ) 0.95 (m, 8H), 0.96 (t, $J = 7.3$ Hz, 24H), 1.12 (m, 8H), 1.35 (m, 16H); ^{13}C NMR ($CDCl_3$, δ) 14.4, 18.4, 18.6, 116.9 (quintet m, $^2J_{CF}$, $^3J_{CF} = 15.7$ Hz), 146.5−150.3 (dm, $^1J_{CF} = 249.3$ Hz); ^{19}F NMR ($CDCl_3$, δ) −127.3; ^{29}Si NMR ($CDCl_3$, δ) −12.0; MS (13 eV) *m/z* 752 (M^+, 20), 231 (17), 154 (15), 57 (21), 44 (100); UV−vis (*n*-hexane) λ_{max} (ϵ), 222 nm (22 700), 269 nm (28 600). Anal. Calcd for $C_{36}H_{56}F_8Si_4$: C, 57.41; H, 7.49. Found: C, 57.63; H, 7.37.

(9) **1b**: 4% yield; ^{1}H NMR ($CDCl_3$, δ) 1.00−1.10 (m, 32H), 1.23−1.32 (m, 8H); ^{13}C NMR ($CDCl_3$, δ) 3.3, 8.3, 115.9−117.3 (m), 146.6−150.2 (dm, $^1J_{CF} = 243.8$ Hz); ^{19}F NMR ($CDCl_3$, δ) −127.3; ^{29}Si NMR ($CDCl_3$, δ) −7.9; MS *m/z* (relative intensity) 640 (M^+, 6), 217 (24), 145 (30), 142 (35), 98 (26), 77 (100); UV−vis (*n*-hexane) λ_{max} (ϵ) 222 nm (18 300), 268 nm (23 900). Anal. Calcd for $C_{28}H_{40}F_8Si_4$: C, 52.47; H, 6.29. Found: C, 52.22; H, 6.56.

(10) McDonald, R.; Sturge, K. C.; Hunter, A. D.; Shilliday, L. *Organometallics* **1992**, *11*, 893 and references cited therein.

(11) The starting **1a** was recovered in 20% yield. Since **1a** is quite insoluble in methanol, simple precipitation could not be used for purification; **1a** was separated from the product mixture by preparative GPC.[12] The yield of **2a** is based on the consumed amount of **1a**. Polymer **2a**: ^{1}H NMR ($CDCl_3$, δ) 0.92−1.36 (m); ^{13}C NMR ($CDCl_3$, δ) 14.8, 18.1, 18.3, 115.6−116.8 (m), 146.5−150.6 (dm, $^1J_{CF} = 262.4$ Hz); ^{19}F NMR ($CDCl_3$, δ) −127.4; ^{29}Si NMR ($CDCl_3$, δ) −16.7; UV−vis (*n*-hexane) λ_{max} (ϵ) 264 nm (15 100 per disilanylenephenylene unit).

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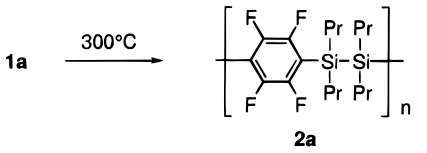
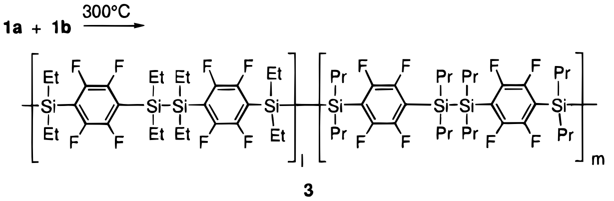


(2)

form, benzene, and THF, suggesting that no appreciable cross-linking took place during the thermolysis. The UV−vis spectrum of **2a** in hexane showed an absorption maximum at 264 nm (ϵ 15 100 per disilanylenephenylene unit), which is slightly longer than that of *p*-bis(pentamethyldisilanyl)tetrafluorobenzene (λ_{max} 250 nm, ϵ 18 600).[13] The IR spectrum of **1a** showed no absorption bands at around 1050 cm^{-1}, indicating the absence of Si−O bonds in the polymer chain. A relatively sharp singlet ^{29}Si NMR signal observed at −16.7 ppm (Figure 1a) as well as the ^{13}C and ^{19}F NMR spectra are indicative of the regular repetition of a disilanylene-1,4-phenylene unit in **2a**.

Thermal copolymerization of a 1:1 mixture of the cyclophanes **1a** and **1b** was performed in an evacuated sealed Pyrex tube at 300 °C. A random copolymer of **1a** and **1b** (the polymer **3**) was isolated by GPC in 92% yield;[12,14] M_w = 14 000 (M_w/M_n = 1.6), with the ratio l/m = 0.72.



(3)

The structure of **3** was determined by comparing the ^{13}C, ^{19}F, and ^{29}Si NMR spectra. As shown in Figure 1b, the ^{29}Si NMR spectrum of **3** showed two resonances at −12.6 and −12.9 ppm due to SiEt$_2$ silicons and two resonances at −16.7 and −16.9 ppm due to SiPr$_2$ silicons.

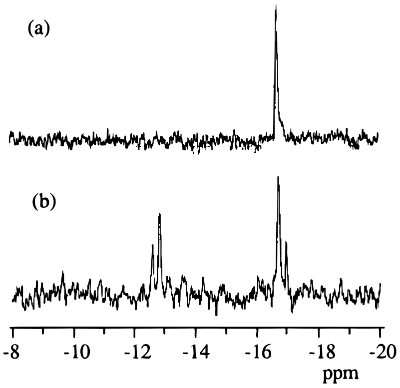
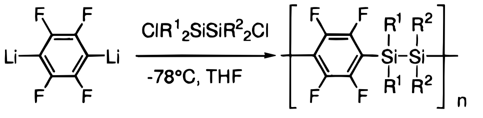


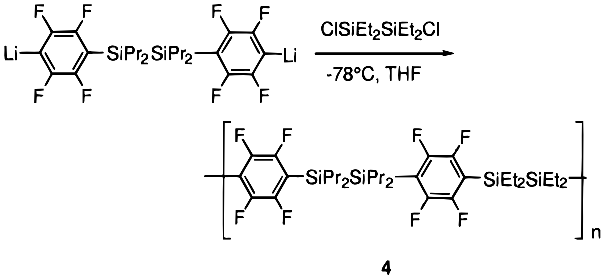
Figure 1. ^{29}Si NMR spectra in CDCl$_3$ of (a) polymer **2a** and (b) **3** obtained by thermal ring opening of disilanylene-bridged paracyclophanes.

In order to characterize the detailed structure of **3**, **2a** and related polymers (**2b**−**d**) were prepared by the usual coupling of the corresponding 1,2-dichlorodisilanes with 1,4-dilithiotetrafluorobenzene in THF at −78 °C, *using high concentrations of the substrates.*[15] Although the molecular weight of **2a** (M_w = 13 000, M_w/M_n = 1.6) obtained in the coupling reaction was lower than that of **2a** derived from the ring opening of **1a**, all the spectral features were the same between these polymers. The copolymer **4** was obtained by a similar coupling reaction (eq 5).[16] The ^{29}Si resonances for SiPr$_2$ in **2a**, **2d**, and **4** were found at −16.7, −16.9, and −16.7 ppm, respectively, while the resonances for SiEt$_2$ in **2b**, **2d**, and **4** were at −12.8, −12.6, and −12.9 ppm, respectively. By comparison of the ^{29}Si resonances among these polymers, the resonances at −12.6 and −16.9 ppm in **3** are assigned to SiEt$_2$ and SiPr$_2$ of SiEt$_2$-SiPr$_2$ segments, respectively, while the resonances at −12.9 and −16.7 ppm in **3** are to those of SiEt$_2$SiEt$_2$ and SiPr$_2$SiPr$_2$ segments, respectively. Thus, the polymer **3** should have three types of disilanylene segments, SiEt$_2$SiEt$_2$, SiPr$_2$SiPr$_2$, and SiEt$_2$SiPr$_2$, in a molecule.



(4)

2a, R^1 = R^2 = Pr; **2b**, R^1 = R^2 = Et;
2c, R^1 = R^2 = Me; **2d**, R^1 = Pr, R^2 = Et.



(5)

The thermal ring-opening polymerization of 1,2,5,6-tetrasilacycloocta-3,7-diynes has been reported by Ishikawa et al.[2g] to involve homolytic scission of an ethynyl carbon−silicon bond as the initial step. In contrast, the ring-opening polymerization of **1a** should involve the scission of at least one Si−Si bond, because the copolymerization of **1a** and **1b** gives a polymer having three

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(12) Preparative GPC was conducted using a JAI (Japan Analytical Instruments, Co. Ltd.) Model LC908 instrument with a series of JAIGEL 1H and 2H columns (2 cm × 60 cm each). Chloroform was used as an eluent. Molecular weight distribution was determined relative to polystyrene standards by the chromatograph with a JAIGEL MH-A column.

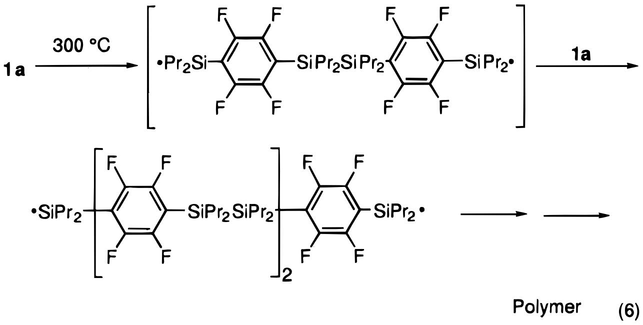
(13) Kira, M.; Tokura, S. *Chem. Lett.* **1994**, 1459.

(14) The yield was based on the consumed amount of a mixture of **1a** and **1b** (65%). Polymer **3**: ^{1}H NMR (CDCl$_3$, δ) 0.60−1.42 (m); ^{13}C NMR (CDCl$_3$, δ) 3.8 (m), 7.9 (m), 14.8 (m), 18.1, 18.3, 115.9 (m), 146.6−150.4 (dm, $^1J_{CF}$ = 249.0 Hz); ^{19}F NMR (CDCl$_3$, δ) −127.4 (m); ^{29}Si NMR (CDCl$_3$, δ) −16.9, −16.7, −12.9, −12.6.

(15) The physical properties of polymers obtained by the coupling reactions are as follows. **2a**: 39% yield; M_w = 13 000 (M_w/M_n = 1.6); mp 80−81 °C. The spectral data are the same as **2a** prepared by thermolysis of **1a**. Anal. Calcd for $C_{36}H_{56}F_8Si_4$: C, 57.41; H, 7.49. Found: C, 57.69; H, 7.62. **2b**: 34% yield; M_w = 2600 (M_w/M_n = 1.3); ^{1}H NMR (CDCl$_3$, δ) 0.89−1.14 (m); ^{13}C NMR (CDCl$_3$, δ) 3.7, 7.9, 115.1−116.4 (m), 146.6−150.4 (dm, $^1J_{CF}$ = 247.9 Hz); ^{19}F NMR (CDCl$_3$, δ) −127.6; ^{29}Si NMR (CDCl$_3$, δ) −12.8; UV−vis (*n*-hexane) λ_{max} (ϵ) 260 nm (13 100 per disilanylenephenylene unit). **2c**: 53% yield; M_w = 37 000 (M_w/M_n = 2.8); ^{1}H NMR (CDCl$_3$, δ) 0.48 (s); ^{13}C NMR (CDCl$_3$, δ) −3.0, 116.8−117.6 (m), 146.5−150.2 (dm, $^1J_{CF}$ = 248.9 Hz); ^{19}F NMR (CDCl$_3$, δ) −127.5; ^{29}Si NMR (CDCl$_3$, δ) −19.5; UV−vis (*n*-hexane) λ_{max} (ϵ) 253 nm (12 700 per disilanylenephenylene unit). **2d**: 25% yield; M_w = 3000 (M_w/M_n = 1.3); ^{1}H NMR (CDCl$_3$, δ) 0.82−1.11 (m, 20H); 1.21−1.42 (m, 4H); ^{13}C NMR (CDCl$_3$, δ) 3.7, 8.0, 14.7, 18.1, 18.3, 115.9 (m), 146.6−150.4 (dm, $^1J_{CF}$ = 249.0 Hz); ^{19}F NMR (CDCl$_3$, δ) −127.5; ^{29}Si NMR (CDCl$_3$, δ) −16.9, −12.6.

(16) **4**: 62% yield; M_w = 14 000 (M_w/M_n = 1.4); ^{1}H NMR (CDCl$_3$, δ) 0.92−1.39 (m); ^{13}C NMR (CDCl$_3$, δ) 3.7, 7.9, 14.8, 18.1, 18.3, 115.8−117.5 (m), 146.6−150.5 (dm, $^1J_{CF}$ = 247.3 Hz); ^{19}F NMR (CDCl$_3$, δ) −127.4; ^{29}Si NMR (CDCl$_3$, δ) −16.7, −12.9. Anal. Calcd for $C_{32}H_{48}F_8Si_4$: C, 55.14; H, 6.94. Found: C, 55.91; H, 6.93.

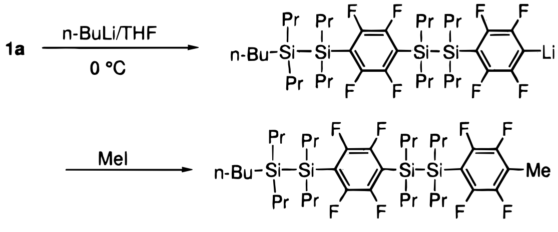
types of disilanylene segments. Since thermolysis of [2.2]paracyclophane at 600 °C has been known to give a polymer via 1,4-quinodimethane,[17] the thermolysis of **1a** may give the corresponding 1,4-disila-1,4-quinodimethane as the key intermediates in the polymerization. However, the relative amount of $SiEt_2SiPr_2$ segments in **3** is much smaller than that expected from the random recombination of the two 1,4-disila-1,4-quinodimethane fragments.[18] The thermal polymerization of **1a** would occur *via* only one Si−Si bond cleavage of the cyclophane to give an α,ω-disilyl diradical followed by the S_H2 attack of a silyl radical center at the disilanylene bridge. Since **1a** is intact when heated to 150−200 °C in the presence of di-*tert*-butyl peroxide (10 mol %) and triethylsilane (20 mol %), the Si−Si bond cleavage via the S_H2 attack would proceed only at high temperatures such as 300 °C.



(6)

Irradiation of the polymer **2a** (12 mg, M_w = 13 000, M_w/M_n = 1.6) in cyclohexane (1 mL) with a 110 W low-pressure Hg arc lamp for 20 min showed significant degradation of the polymer chain to give a polymer with a monomodal distribution of the molecular weight (M_w = 7000, M_w/M_n = 1.8). The ^1H NMR spectrum of the product showed resonances at 4.46 (m) and 0.85−1.60 (m) ppm due to Si−H and Si−Pr protons, respectively, with the intensity ratio of 1.2:100. The IR analysis revealed a signal at 2154 cm^{-1} due to Si−H stretching but no signals due to Si−OH or SiOSi. Similar photolysis of a mixture of **2a** (12 mg), ethanol (0.1 mL), and cyclohexane (1 mL) for 20 min afforded a product with an M_w value of 1400 (M_w/M_n = 1.3). The NMR and IR analysis of the product showed the existence of Si−H and $SiOCH_2CH_3$ groups. As shown by Ishikawa et al.,[2s] homolytic scission of Si−Si bonds followed by disproportionation of the generated silyl radical pair would cause photochemical degradation of the polymer **2a**. The polymer **2a** (M_w = 13 000) exhibited a 5% weight loss (TG5) at 400 °C with a ceramic yield of 16.7% at >650 °C.

Attempted anionic polymerization of **1a** failed. When **1a** in THF was treated with a catalytic amount (5 mol %) of *n*-butyllithium in hexane at 0 °C, no polymerization took place, while the reaction of **1a** in THF with *n*-butyllithium (1.2 equiv) at 0 °C followed by addition of excess methyl iodide gave **5**[19] in 45% yield. The results indicate that the ring opening by nucleophilic attack of *n*-butyllithium occurs to give the corresponding phenyl anion, which is not sufficiently reactive to open the ring of **1a**.



(7)

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Related work is in progress.

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[17] Pyrolysis of [2.2]paracyclophane at 400 °C leads to the formation of 4,4′-dimethylenebibenzyl radical. For reviews, see: (a) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1971**, *4*, 204. (b) Vögtle, F. *Cyclophane Chemistry: Synthesis, Structures, and Reactions*; translated in English by Jones, P. R., Wiley: Chichester, U.K., 1993; Chapter 2, and references cited therein.

[18] The ratio of $Et_2SiSiPr_2$ to $Et_2SiSiEt_2$ to $Pr_2SiSiPr_2$ in **3** is expected to be 2:1:1 for the 1,4-disilaquinodimethane mechanism, while the ratio should be 1:2:2 for one Si−Si bond cleavage mechanism. As seen in Figure 1b, a rough estimation of the ratio based on the ^{29}Si NMR favors the latter mechanism.

[19] **5**: a colorless oil; ^1H NMR ($CDCl_3$, δ) 0.58−0.64 (m, 8H), 0.81−1.44 (m, 57H), 2.25 (t, $^4J_{HF}$ = 2.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, δ) 7.9 (t, $^3J_{CF}$ = 2.1 Hz), 12.0, 13.6, 14.8 (t, $^4J_{CF}$ = 2.5 Hz), 14.9 (t, $^4J_{CF}$ = 3.3 Hz), 15.1, 15.5 (t, $^4J_{CF}$ = 3.3 Hz), 18.1, 18.16, 18.20, 18.36, 18.39, 18.41, 18.6, 18.7, 26.7, 26.8, 111.1 (t, $^2J_{CF}$ = 32.7 Hz), 115.5 (t, $^2J_{CF}$ = 31.7 Hz), 117.5 (t, $^2J_{CF}$ = 19.4 Hz), 117.9 (t, $^2J_{CF}$ = 33.3 Hz), 142.8−143.2 (m), 146.7−146.5 (m), 146.6−147.1 (m), 149.7−150.2 (m); ^{19}F NMR ($CDCl_3$, δ) −144.2 to −144.0 (m, 4F), −128.8 to −127.8 (m, 2F), −127.6 to −127.5 (m, 2F); ^{29}Si NMR ($CDCl_3$, δ) −16.7, −16.6, −16.5, −13.6; MS *m/z* (relative intensity) 822 (17, M$^+$), 376 (37), 242 (68), 208 (78), 169 (80), 106 (100), 71 (91), 63 (91). Anal. Calcd for $C_{41}H_{68}F_8Si_4$: C, 59.67; H, 8.30. Found: C, 59.95; H, 8.30.