Synthesis and Properties of Novel $\sigma-\pi$-Conjugated Polymers with Alternating Organosilicon and [2.2]Paracyclophane Units in the Main Chain

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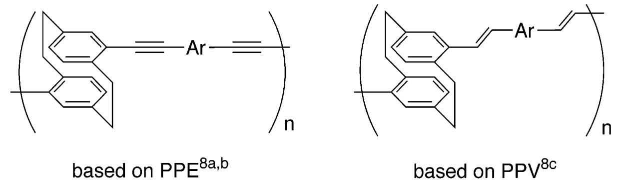
Novel $\sigma-\pi$-conjugated polymers (**8a**−**c**) that have alternating organosilicon and [2.2]paracyclophane units in the polymer backbone were synthesized by polycondensation of dichlorodisilanes (**5a**,**b**) or dichlorosilane (**5c**) with bifunctional lithium acetylide derived from 4,16-diethynyl[2.2]paracyclophane (**4**) and butyllithium, and their optical and thermal properties were investigated. A self-standing thin film of the polymer was obtained easily by casting from a $CHCl_3$ solution. All polymers were thermally stable in the solid state. The polymers showed delocalization of the π-electron through the Si−Si bonds and the through-space of the [2.2]paracyclophane moiety. $\sigma-\pi$ Conjugation between the disilanylene unit and the π-electron system with a paracyclophane core was not significantly effective, which suggests sufficient delocalization of the π-electron along the diethynyl[2.2]paracyclophane unit.

Introduction

During the past decade, there has been a great deal of interest in the synthesis of novel conjugated polymers[1] due to their intriguing properties, including electrical conductivity,[2] electroluminescence,[3] liquid crystallinity,[4] third-order nonlinear optical properties,[5] and chemical sensing.[6] One of the most well-established classes of conjugated polymers are poly(*p*-phenylene-ethynylene)s, PPEs,[7] which are a promising candidate for the molecular wire used as active components in polymer-based electronic and photonic devices. In addition, current research interests in conjugated polymers including PPEs focus on tuning their spectral and electrical properties. Recently, we reported the first preparation and the physical properties of novel π-conjugated polymers based on PPE[8a,b] and poly(*p*-phenylenevinylene), PPV,[8c] using the longitudinal $\pi-\pi$ interaction of [2.2]paracyclophane (Chart 1). These polymers showed an extension of π-delocalization via the through-space with $\pi-\pi$ stacking according to the UV−vis absorption spectra and also exhibited an intense luminescence in solution.

Chart 1



On the other hand, the chemical and physical properties of organosilicon polymers composed of a Si−Si σ-bond and a π-electron unit in the polymer backbone are subjects of current interest in view of their great potential for use in advanced materials such as photoconductors, photoresistors, nonlinear optical materials, and hole-transporting materials.[9] Previously, our group reported the synthesis of alternating copolymers containing disilanylene (Si−Si σ-bond) units and thioketene dimers, in which effective $\sigma-\pi$ conjugations induce the unique charge transfer from the thioketene dimer to the

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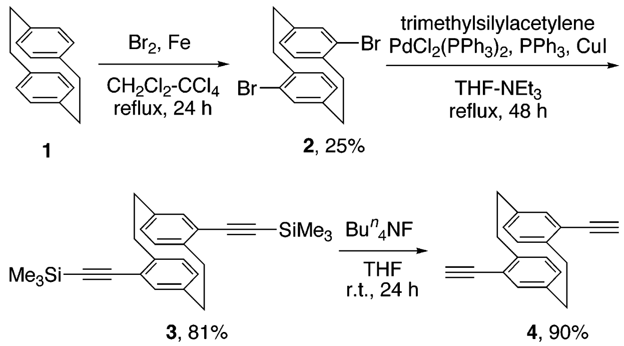
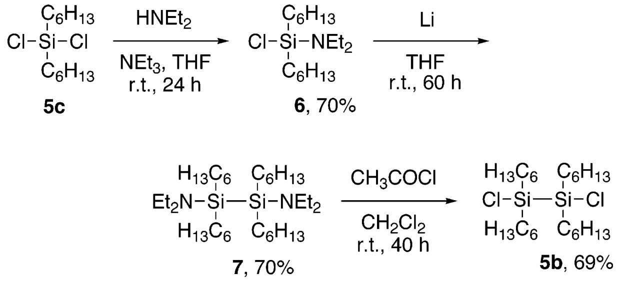
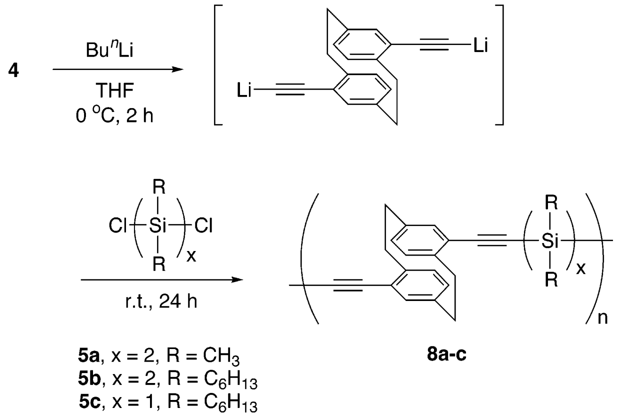
Scheme 1



Scheme 2



Scheme 3



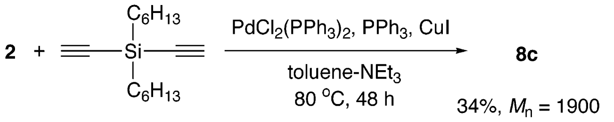
disilanylene units (which act as an acceptor).[10] These observations prompted us to construct a novel σ–π-conjugated system in combination with a π-conjugated system via the through-space. Here, we report the synthesis of novel σ–π-conjugated polymers based on PPEs having organosilicon and [2.2]paracyclophane units in the main chain by polycondensation of dichlorodisilanylenes with bifunctional lithium acetylide derived from 4,16-diethynyl[2.2]paracyclophane and butyllithium (Scheme 3).

Table 1. Synthesis and Optical Properties of the Polymers (8a–c)

run	polymer	yield[a]/%	M_n[b] (M_w/M_n)	UV λ_{max}[c]/ nm	PL λ_{max}[c,d]/ nm
1	**8a**	13	3600 (1.9)	275	385
2	**8b**	91	10 700 (1.6)	276	384
3	**8c**	84	6100 (2.7)	271	403

[a] Isolated yields after reprecipitation into MeOH. [b] GPC (CHCl$_3$), polystyrene standards. [c] Absorption and emission spectra were recorded in dilute CHCl$_3$ solutions at room temperature. [d] The sample solutions were excited at 270 nm.

Scheme 4



Results and Discussion

We initially examined the polycondensation of 4,16-diethynyl[2.2]paracyclophane (**4**) with dichlorotetraalkyldisilanes (**5a**,**b**). The synthesis of the 4,16-diethynyl[2.2]paracyclophane (**4**) was initiated using commercially available [2.2]paracyclophane (**1**) (Scheme 1). Iron-catalyzed electrophilic dibromination of **1** and recrystallization afforded only 4,16-dibromo[2.2]paracyclophane (**2**) in 25% isolated yield.[11] PdCl$_2$(PPh$_3$)$_2$/CuI-catalyzed cross-coupling[12] of **2** and trimethylsilylacetylene provided **3** (81%), which was then converted to the monomer (**4**) by Bu$^n_4$NF-promoted desilylation in 90% yield. Dichlorotetrahexyldisilane (**5b**) was prepared by the following procedure described in Scheme 2. After commercially available dichlorodihexylsilane (**5c**) was converted into silylamide, lithium-mediated homocoupling and chlorination using acetyl chloride were carried out to give the dichlorotetrahexyldisilane (**5b**) in a total yield of 34%.

Synthesis of the polymers (**8a**,**b**) was performed as shown in Scheme 3, and the results are listed in Table 1. Treatment of **4** in THF solution at 0 °C with 2.0 equiv of butyllithium resulted in quantitative lithium–hydrogen exchange to give lithiated paracyclophane, to which was subsequently added 2.0 equiv of **5b** ($x = 2$, R = C$_6$H$_{13}$) to give the corresponding polymer **8b** in 91% yield after workup (run 2). The molecular weight measurements were performed by gel permeation chromatography (GPC) in CHCl$_3$ eluent using a calibration curve of polystyrene standards. For example, the polymer **8b** (x = 2, R = C$_6$H$_{13}$) had a number-average molecular weight (M_n) of 10 700 with M_w/M_n of 1.6, which corresponds to a degree of polymerization of 16. The polymers obtained were soluble in common organic solvents such as THF, CH$_2$Cl$_2$, CHCl$_3$, toluene, and DMF. Further, we synthesized the polymer **8c**, which has a dihexylsilylene chain (x = 1, R = C$_6$H$_{13}$), by a similar reaction from **4** with **5c**. **8c** was obtained in 84% yield, M_w = 16 600 and M_n = 6100 (run 3).

On the other hand, an appropriate polymerization system was critically important for successful gains in the high molecular weight polymers. The typical Heck–Sonogashira coupling condition[12] was not effective for this reaction. Using the catalyst system of PdCl$_2$(PPh$_3$)$_2$/PPh$_3$/CuI, the reaction of 4,16-dibromo[2.2]paracyclophane (**2**) with diethynyldihexylsilane in toluene–NEt$_3$ at 80 °C for 48 h gave the corresponding polymers (**8c**) with low molecular weight (M_n = 1900, Scheme 4). Dibromo[2.2]paracyclophane (**2**) is relatively inert against the oxidative addition to palladium complex due to the

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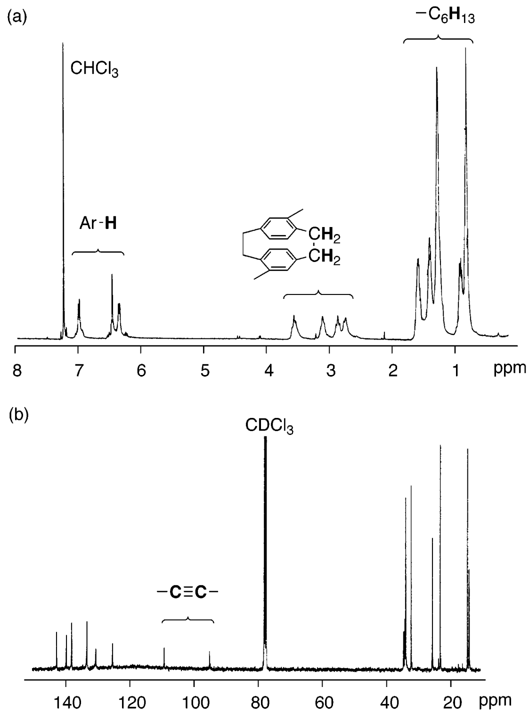


Figure 1. ^1H NMR (a) and ^{13}C NMR (b) spectra of **8b** in $CDCl_3$.

lower reactivity of aryl bromide, the steric hindrance, and the electron-rich feature of the [2.2]paracyclophane moiety.

These polymers (**8a**−**c**) were characterized by ^1H, ^{13}C NMR, and IR spectra. In the ^1H NMR spectrum of **8b** in $CDCl_3$ (Figure 1a), the peak corresponding to the alkyne proton at 3.27 ppm of the monomer **4** almost disappeared. The signals of phenyl protons and bridged methylene protons of a [2.2]paracyclophane unit were found at 6.3−7.1 and 2.6−3.7 ppm, respectively. In the ^{13}C NMR spectrum of **8b** (Figure 1b), the sharp signals of the alkyl side chains dominated in the region of 15−35 ppm and were overlapped with bridged methylene carbons. Typical signals for acetylenic carbons were found at 94.5 and 108.8 ppm. The IR spectrum of **8b** in the film state exhibited a sharp absorption peak at 2140 cm^{-1} due to stretching vibrations of a carbon−carbon triple bond.

The optical properties of the polymers **8a**−**c** are also summarized in Table 1. The absorption spectrum of the polymer **8b**, as a typical representative example, and that of the model compound **9** are shown in Figure 2. The maxima of the absorption spectra of the polymers **8a**−**c** in the $CHCl_3$ solution at room temperature were around 270 nm (Table 1). The polymers **8a** and **8b** showed absorption peaks at 275 and 276 nm, respectively. The peak and shape of the absorption spectra of the polymer films were almost the same as in the solution, e.g., $\lambda_{max} = 276$ nm for **8b**. Changing the side chain on the Si backbone had little effect on the photoproperties of the polymers. The polymer **8c** with a silylene chain length had a spectrum similar to that of **8b** with a disilanylene chain and an absorption maximum at 271 nm, which was slightly blue-shifted compared with that of **8b**. In addition, the compounds **3** and **9** showed an absorption maximum at 265 and 257 nm, respectively. These results indicate the delocalization of π-electrons through the Si−Si bonds and the through-space of the [2.2]paracyclophane moiety. However, σ−π conjugation between the disilanylene unit and the π-electron system with a [2.2]paracyclophane core is not significantly effective in the present polymers due to the expansion of π-conjugation between ethynylene and cyclophane units.[9d,13] On the other hand, the fluorescence maxima of the polymers in dilute $CHCl_3$ solutions were observed in the visible blue region with an excitation wavelength at 270 nm. The fluorescence emission spectrum of the polymer **8b** is also shown in Figure 2. Using 9-anthracenecarboxylic acid in CH_2Cl_2 as a standard ($\Phi = 0.442$), the polymers showed weak quantum efficiencies of <0.10 in $CHCl_3$.[14] In the film state of **8b**, the very weak peak was observed at around 410 nm, which was slightly red-shifted in comparison with the polymer solution.

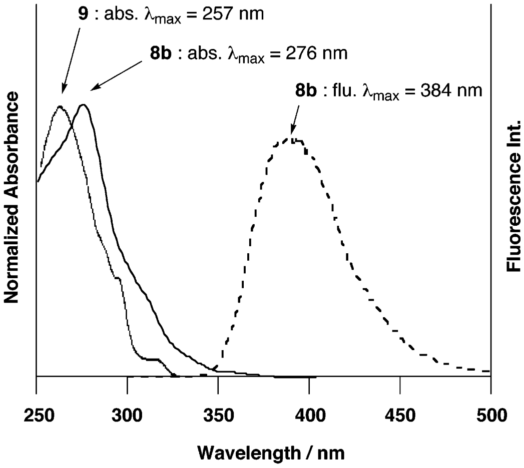
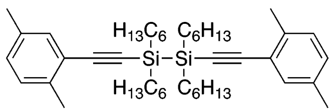


Figure 2. UV−vis absorption spectra of the polymer **8b** and the model compound **9** in $CHCl_3$ solution, and fluorescence emission spectrum of **8b** in $CHCl_3$ solution (270 nm excitation).



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A self-standing thin film of the polymer was obtained easily by casting from a $CHCl_3$ solution. In addition, all polymers were thermally stable in the solid state. The thermal stability of the polymers was investigated by thermogravimetric analysis (TGA), the results of which are shown in Figure 3. For example, **8b** sustained a 10% weight loss at a temperature of 400 °C under both air and nitrogen, respectively, at a heating rate of 10 °C/min, and the weight loss was completed at 500 °C under nitrogen. Under air, the decomposition of the polymer **8b** involved two steps. The first step, which started at 400 °C, may be assigned to thermal decomposition of the alkyl side chain of the polymer, and the second step,

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(14) The quantum efficiency (Φ_{unk}) of an unknown sample was calculated by the following equation: $\Phi_{unk} = \Phi_{std}[A_{std}F_{unk}/A_{unk}F_{std}][n_{D,unk}/n_{D,std}]^2$ where A_{std} and A_{unk} are the absorbance of the standard and unknown sample, respectively, F_{std} and F_{unk} are the corresponding relative integrated fluorescence intensities, and n_D is the refractive index [CH_2Cl_2 ($n_D = 1.424$) and $CHCl_3$ ($n_D = 1.446$) were used].

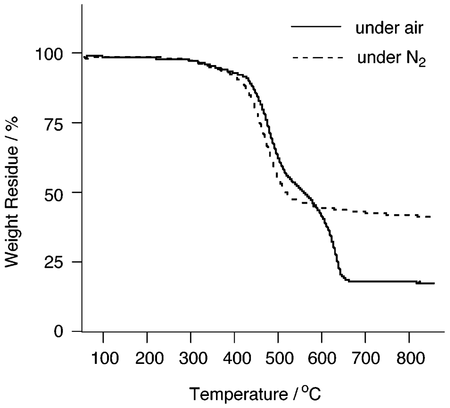

Figure 3. TGA traces (10 °C/min) of **8b** under air and nitrogen.

which started at 550 °C and was completed at 650 °C, may be attributed to the decomposition of the polymer backbone.

In conclusion, novel $\sigma-\pi$-conjugated polymers having organosilicon and [2.2]paracyclophane units in the main chain have been designed, synthesized, and characterized. The polymers showed delocalization of the π-electron through the Si−Si bonds and the through-space of the [2.2]paracyclophane moiety. $\sigma-\pi$ Conjugation between the disilanylene unit and the π-electron system with a paracyclophane core was not significantly effective, which suggests sufficient delocalization of the π-electron along the diethynyl[2.2]paracyclophane unit. The investigated polymers showed high thermal stability and good film formation and are therefore considered promising candidates for use in electronic devices. Further studies on the preparation of organosilicon-containing cyclophane polymers and their application as hole-transporting materials as well as conductive materials are now in progress.

Experimental Section

General Procedures. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX270 instrument at 270 and 67.5 MHz, respectively. ^{29}Si NMR spectra were recorded on a JEOL JNM-A400 instrument at 79.3 MHz. All samples were analyzed in CDCl$_3$, and the chemical shift values were expressed relative to Me$_4$Si as an internal standard. IR spectra were obtained on a Perkin-Elmer 1600 spectrometer. UV−vis spectra were obtained on a JASCO V-530 spectrophotometer, and samples were analyzed in CHCl$_3$ at room temperature. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer, and samples were analyzed in CHCl$_3$ at room temperature. Gel permeation chromatography was carried out on a TOSOH UV-8011 and RI-8000 (Shodex K-803L column) using THF as an eluent after calibration with standard polystyrene. Thermogravimetric analysis (TGA) was made on a Seiko EXSTAR 6000 instrument (10 °C/min). Analytical thin-layer chromatography (TLC) was performed with silica gel 60 Merck F$_{254}$ plates. Column chromatography was performed with Wakogel C-300 silica gel. Low-resolution mass spectra (LRMS) and high-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A spectrometer. Elemental analysis was performed at the Microanalytical Center of Kyoto University.

Materials. THF was distilled from sodium benzophenone ketyl. HNEt$_2$ and NEt$_3$ were distilled from KOH. CH$_2$Cl$_2$ was distilled from CaCl$_2$. [2.2]Paracyclophane (**1**), 1,2-dichloro-1,1,2,2-tetramethydisilane (**5a**), dichlorodihexylsilane (**5c**), acetyl chloride, and 1.6 M Bu^{n}Li in hexane were obtained commercially and used without further purification. Li (dispersion in mineral oil) was purchased and used after removal of mineral oil by washing with hexane and THF. 4,16-Dibromo-[2.2]paracyclophane (**2**) was prepared as described in the literature.[11] 1,2-Dichloro-1,1,2,2-tetrahexyldisilane (**5b**) was prepared as described in the literature with a minor modification.[15] All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. New compounds are characterized below.

4,16-Bis[(trimethylsilyl)ethynyl][2.2]paracyclophane (3). 4,16-Dibromo[2.2]paracyclophane (**2**) (3.5 g, 9.7 mmol), trimethylsilylacetylene (10 mL), PdCl$_2$(PPh$_3$)$_2$ (0.70 g, 1.0 mmol), PPh$_3$ (0.52 g, 2.0 mmol), and CuI (0.20 g, 1.0 mmol) were dissolved in 70 mL of THF−NEt$_3$ (v/v = 5:2). The solution was stirred at 75 °C for 2 days under a nitrogen atmosphere. Precipitated ammonium salts were filtered off, and the filtrate was evaporated under vacuum. The residue was subjected to column chromatography on SiO$_2$ with hexane−CHCl$_3$ (v/v = 2:1, $R_f = 0.15$) as an eluent to give the compound **3** (2.7 g, 6.8 mmol, 81%) as a white powder. ^{1}H NMR (CDCl$_3$, 270 MHz): δ 0.31 (s, 18H), 2.80 (m, 2H), 2.97 (m, 2H), 3.14 (m, 2H), 3.57 (m, 2H), 6.44 (d, $J = 7.8$ Hz, 2H), 6.49 (s, 2H), 7.98 (d, $J = 7.8$ Hz, 2H). ^{13}C NMR (CDCl$_3$, 67.5 MHz): δ 0.13, 33.5, 34.0, 97.5, 105.8, 124.6, 130.1, 133.0, 137.4, 139.3, 142.6. IR (Nujol): 2146 cm^{-1}. UV (CHCl$_3$): $\lambda_{\max} = 265$ nm, log $\epsilon = 4.23$. LRMS (EI) m/z (rel intensity) = 400 (M$^+$, 75), 200 (100), 185 (70). Anal. Calcd for $C_{26}H_{32}Si_2$: C 77.93, H 8.05. Found: C 77.82, H 8.02.

4,16-Diethynyl[2.2]paracyclophane (4). To a solution of **3** (2.0 g, 5.0 mmol) in 50 mL of THF was added Bu$^n_4$NF (10 mL, 1.0 M solution in THF). The reaction mixture was stirred at room temperature for 20 h under a nitrogen atmosphere. The solution was evaporated under vacuum, and the residue was subjected to column chromatography on SiO$_2$ with hexane−CHCl$_3$ (v/v = 2:1, $R_f = 0.55$) as an eluent to give the compound **4** (1.1 g, 4.5 mmol, 90%) as a white powder. ^{1}H NMR (CDCl$_3$, 270 MHz): δ 2.92 (m, 4H), 3.19 (m, 2H), 3.27 (s, 2H), 3.59 (m, 2H), 6.44 (d, $J = 7.0$ Hz, 2H), 6.56 (s, 2H), 7.00 (d, $J = 7.0$ Hz, 2H). ^{13}C NMR (CDCl$_3$, 67.5 MHz): δ 33.7, 33.8, 80.2, 83.9, 123.5, 130.6, 133.2, 137.8, 139.5, 142.6. IR (KBr): 3298, 2098 cm^{-1}. UV (CHCl$_3$): $\lambda_{\max} = 252$ nm, log $\epsilon = 4.28$. LRMS (EI) m/z (rel intensity) = 256 (M$^+$, 88), 241 (35), 128 (100). Anal. Calcd for $C_{20}H_{16}$: C 93.71, H 6.29. Found: C 93.45, H 6.26.

Diethylaminodihexylchlorosilane (6). To a solution of **5c** (4.2 g, 16 mmol) and NEt$_3$ (2.8 mL) in 9.0 mL of THF was added HNEt$_2$ (1.3 g, 18 mmol) dropwise at 0 °C. The reaction mixture was warmed to room temperature and stirred for 24 h under a nitrogen atmosphere. The precipitated ammonium salts were filtered off, and the filtrate was evaporated under reduced pressure. The residue was distilled under vacuum using Kugelrohr to give the compound **6** (3.4 g, 11 mmol, 70%): colorless oil, bp 120−125 °C (3.0 mmHg, Kugelrohr). ^{1}H NMR (CDCl$_3$, 270 MHz): δ 0.88 (m, 10H), 1.03 (t, $J = 7.0$ Hz, 6H), 1.29 (m, 16H), 2.87 (q, $J = 7.0$ Hz, 4H). ^{13}C NMR (CDCl$_3$, 67.5 MHz): δ 14.1, 15.1, 16.1, 22.6, 23.1, 31.4, 32.8, 39.5. ^{29}Si NMR (CDCl$_3$, 79.3 MHz): δ 13.4. IR (neat): 2961, 2925, 2858, 1466, 1377, 1206, 1167, 1030 cm^{-1}. LRMS (EI) m/z (rel intensity) = 305 (M$^+$, 10), 290 (100), 220 (34) 206 (55). Anal. Calcd for $C_{16}H_{36}SiNCl$: C 62.80, H 11.86, N 4.58. Found: C 62.95, H 11.98, N 4.40.

1,2-Bis(diethylamino)-1,1,2,2-tetrahexyldisilane (7). Li (dispersion in mineral oil) was placed in a 30 mL flask under a flow of nitrogen and washed with hexane (10 mL × 2) and THF (10 mL × 1). To a solution of the above Li in 5.0 mL of THF was added **6** (3.4 g, 11 mmol) dropwise at room temperature, and the mixture was stirred for 60 h. The inorganic impurities were filtered off, and the filtrate was evaporated under reduced pressure. The residue was distilled under

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vacuum using Kugelrohr to give the compound **7** (2.2 g, 4.0 mmol, 70%): colorless oil, bp 200−210 °C (2.5 mmHg, Kugelrohr). ^{1}H NMR (CDCl$_3$, 270 MHz): δ 0.57 (m, 8H), 0.82 (m, 12H), 0.90 (t, J = 7.2 Hz, 12H), 1.22 (m, 32H), 2.73 (q, J = 7.2 Hz, 8H). ^{13}C NMR (CDCl$_3$, 67.5 MHz): δ 14.1, 15.4, 16.5, 22.7, 24.1, 31.6, 33.8, 40.8. ^{29}Si NMR (CDCl$_3$, 79.3 MHz): δ −2.7. IR (neat): 2923, 2856, 1465, 1375, 1173, 1023 cm^{-1}. LRMS (EI) m/z (rel intensity) = 540 (M$^+$, 6), 382 (10), 270 (100). HRMS (EI) calcd for $C_{32}H_{72}N_2Si_2$, 540.5237; found, 540.5240.

1,2-Dichloro-1,1,2,2-tetrahexyldisilane (5b). To a solution of **7** (2.1 g, 3.9 mmol) in 3.0 mL of CH$_2$Cl$_2$ was added acetyl chloride (6.0 mL, 84 mmol) dropwise slowly at 0 °C, and the mixture was stirred for 40 h at room temperature. The solution was evaporated, and the residue was distilled under vacuum using Kugelrohr to give the compound **5b** (1.3 g, 2.7 mmol, 69%): colorless oil, bp 200−205 °C (2.0 mmHg, Kugelrohr). ^{1}H NMR (CDCl$_3$, 270 MHz): δ 0.89 (t, J = 7.2 Hz, 12H), 0.99 (q, J = 7.2 Hz, 8H), 1.36 (m, 32H). ^{13}C NMR (CDCl$_3$, 67.5 MHz): δ 14.1, 16.8, 22.6, 23.2, 31.4, 32.8. ^{29}Si NMR (CDCl$_3$, 79.3 MHz): δ 19.5. IR (neat): 2927, 2856, 1466, 1405, 1378, 1183 cm^{-1}. LRMS (EI) m/z (rel intensity) = 466 (M$^+$, 16), 381 (14), 297 (29), 233 (79), 198 (100), 170 (96), 149 (79), 113 (88). HRMS (EI) calcd for $C_{24}H_{52}Cl_2Si_2$, 466.2985; found, 466.2985.

1,2-Bis[(2,5-dimethylphenyl)ethynyl]-1,1,2,2-tetrahexyldisilane (9). The model compound **9** was prepared from 2-ethynyl-*p*-xylene and **5b**. To a solution of 2-ethynyl-*p*-xylene (161 mg, 1.2 mmol) in THF (1.2 mL) was added 0.85 mL of a 1.6 M Bu^{n}Li solution in hexane (1.4 mmol) at 0 °C over a period of 20 min. The solution was allowed to warm to room temperature and stirred for 2 h. Then, **5b** (290 mg, 0.62 mmol) was added at room temperature over a period of 30 min, and the mixture was stirred for 24 h. The reaction mixture was quenched with water. The organic layer was washed several times with water and dried over MgSO$_4$. The solvent was evaporated, and the crude product was subjected to column chromatography on SiO$_2$ with CH$_2$Cl$_2$−hexane (v/v = 1:3) as an eluent to give the compound **9** (314 mg, 0.48 mmol, 77%) as a colorless oil. ^{1}H NMR (CDCl$_3$, 270 MHz): δ 0.83−0.95 (m, 20H), 1.27−1.42 (m, 24H), 1.51 (m, 8H), 2.25 (s, 6H), 2.41 (s, 6H), 7.03 (d, J = 7.8 Hz, 2H), 7.08 (d, J = 7.8 Hz, 2H), 7.22 (s, 2H). ^{13}C NMR (CDCl$_3$, 67.5 MHz): δ 13.4, 14.2, 20.3, 20.7, 22.6, 24.9, 31.6, 33.3, 95.0, 107.4, 123.2, 129.1, 129.2, 132.6, 134.8, 137.4. ^{29}Si NMR (CDCl$_3$, 79.3 MHz): δ −33.0. IR (neat): 2142 cm^{-1}. LRMS (EI) m/z (rel intensity) = 654 (M$^+$, 45), 639 (62), 570 (100), 317 (42), 159 (64). Anal. Calcd for $C_{44}H_{70}Si_2$: C 80.66, H 10.77. Found: C 80.76, H 10.87.

Polymerization. A typical procedure is as follows. To a solution of **4** (128 mg, 0.50 mmol) in THF (5.0 mL) was added 0.70 mL of a 1.6 M Bu^{n}Li solution in hexane (1.10 mmol) at 0 °C. The solution was allowed to warm to room temperature and stirred for 2 h. Then, **5** (0.50 mmol) was added at room temperature over a period of 20 min, and the mixture was stirred for 24 h. The reaction mixture was quenched with water. The organic layer was washed several times with water and dried over MgSO$_4$. After filtration of MgSO$_4$, the solvent was concentrated and dissolved in CHCl$_3$, followed by reprecipitation into a large amount of MeOH. The obtained precipitate was washed with MeOH several times. After the product was dried under reduced pressure, a white polymer (**8**) was obtained.

8a. Yield: 24 mg, 13%. ^{1}H NMR (CDCl$_3$, 270 MHz): δ 0.35−0.4 (m, 12H), 2.80 (m, 2H), 2.90 (m, 2H), 3.14 (m, 2H), 3.62 (m, 2H), 6.42 (d, J = 5.2 Hz, 2H), 6.46 (s, 2H), 7.05 (d, J = 5.2 Hz, 2H). ^{13}C NMR (CDCl$_3$, 67.5 MHz): δ 1.6, 33.4, 34.3, 94.6, 107.8, 124.0, 129.7, 133.1, 137.4, 140.0, 142.5. ^{29}Si NMR (CDCl$_3$, 79.3 MHz): −34.4. IR (film): 2141 cm^{-1}.

8b. Yield: 296 mg, 91%. ^{1}H NMR (CDCl$_3$, 270 MHz): δ 0.90−1.00 (m, 20H), 1.38−1.72 (m, 32H), 2.79 (m, 2H), 2.95 (m, 2H), 3.15 (m, 2H), 3.58 (m, 2H), 6.37 (d, J = 4.8 Hz, 2H), 6.46 (s, 2H), 7.02 (d, J = 4.8 Hz, 2H). ^{13}C NMR (CDCl$_3$, 67.5 MHz): δ 13.6, 14.2, 22.7, 25.1, 31.7, 33.4, 94.5, 108.8, 124.9, 130.2, 133.0, 137.6, 139.3, 142.3. ^{29}Si NMR (CDCl$_3$, 79.3 MHz): δ −32.7. IR (film): 2140 cm^{-1}.

8c. Yield: 190 mg, 84%. ^{1}H NMR (CDCl$_3$, 270 MHz): δ 0.88−1.02 (m, 10H), 1.34−1.70 (m, 16H), 2.83−2.99 (m, 4H), 3.13 (m, 2H), 3.50 (m, 2H), 6.40 (br, 2H), 6.46 (s, 2H), 7.00 (br, 2H). ^{13}C NMR (CDCl$_3$, 67.5 MHz): δ 13.5, 14.1, 22.7, 25.0, 31.1, 33.4, 93.8, 106.0, 124.7, 130.1, 133.0, 137.8, 140.1, 142.3. ^{29}Si NMR (CDCl$_3$, 79.3 MHz): δ −36.9. IR (film): 2142 cm^{-1}.

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