Synthesis of Poly{[bis(ethynylphenyl)silylene]phenylene}s with Highly Heat-Resistant Properties

Joji Ohshita,* Akihiro Shinpo, and Atsutaka Kunai*

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

Received March 2, 1999

ABSTRACT: Poly{bis[(trimethylsilylethynyl)phenyl]silylenephenylene}s (**2a**−**d**) were prepared by the reactions of the respective poly[(diethoxysilylene)phenylene]s with (trimethylsilylethynyl)phenyllithium. Desilylation of the resulting polymers **2a**−**d** with K_2CO_3/MeOH gave poly{[bis(ethynylphenyl)silylene]-phenylene}s (**3a**−**d**). Polymers **3a**−**d** exhibit extremely high heat-resistance and their thermogravimetric analysis (TGA) in a nitrogen atmosphere shows the temperature of 5% weight loss (T_{d_5}) of 651−711 °C. Total weight loss at 1000 °C in TGA was determined to be 8−10% based on the initial weight. Thermal differential analysis (TDA) of the polymers reveals an exothermic peak around 220 °C probably due to cross-linking reactions concerning ethynyl groups. TGA of the polymers shows a high T_{d_5} of 436−566 °C even in air, although the total weight loss at 1000 °C was 76−81% of the initial weight, much higher than that in nitrogen.

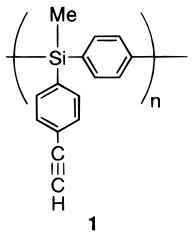
Introduction

Organosilicon polymers composed of an alternating arrangement of an organosilicon unit and π-electron system represent a new class of organometallic polymers which can be used as functionality materials,[1] such as organic semiconductors,[2] hole-transporting materials,[3] and photoresists.[4] In addition, current interest has been focused on this type of polymer regarding their heat-resistant properties.[1c]

Corriu et al. have reported that poly[(silylene)diethynylene]s exhibit remarkable heat-resistant properties, and their thermogravimetric analyses (TGA) in an argon atmosphere reveal no weight loss up to 450 °C.[5] The total weight loss at 1400 °C varies from 13% to 37% based on the initial weight, depending on the substituents at the silicon atom, in marked contrast to that for an analogous saturated polymer, $[(SiMe_2)(CH_2)_4]_n$, whose pyrolysis leads no residue. The high char yields for the diethynylene polymers would be due to the cross-linking reactions with respect to the diethynylene units around 200 °C. Similar to this, poly[(silylene)ethynylene]s have been demonstrated to show high thermal stability.[6] Itoh et al. have reported synthesis of poly-[(hydrosilylene)ethynylene(phenylene)ethynylene]s with excellent heat- and frame-resistant properties.[7] TGA of the polymers in an argon atmosphere reveals only 3−12% weight loss at 1000 °C based on the initial weight, and it has been proposed that the high heat-resistant properties of these polymers be ascribed to the cross-linking reactions concerning the Si−H and C−C triple bonds.

On the other hand, introduction of an ethenylene unit in place of the ethynylene unit usually results in the increase of weight loss upon pyrolysis of the polymers, and TGA on poly[(silylene)ethenylene]s[8] and poly[(disilanylene)ethenylene]s[9] in an inert atmosphere reveals the weight loss at 1000 °C in the ranges 60−83% and 75−88%, respectively. Lower bond energies of C(sp^2)−Si bonds than C(sp)−Si bonds and also lower reactivities of ethenylene units toward cross-linking relative to ethynylene units seem to be responsible for the lower heat-resistance of the ethenylene polymers.

Chart 1



1

To learn how the nature of substituents affects the thermal properties of silicon-based polymers, we have studied thermal properties of variously substituted poly-[(silylene)phenylene]s by TGA in a nitrogen atmosphere and found that introduction of an unsaturated group on the silicon atom leads to high thermal stability of the polymers.[10,11] Of those, poly{[(4-ethynylphenyl)-methylsilylene]-*p*-phenylene} (**1** in Chart 1) exhibits the best heat-resistant properties in a nitrogen atmosphere (T_{d_5} = 568 °C and total weight loss at 1000 °C = 17% of the initial weight), comparable with those of poly-[(silylene)diethynylene]s reported by Corriu et al. despite the fact that the polymer backbone involves C(sp^2)−Si bonds.[11]

In this paper, we report synthesis and thermal properties of poly{[bis(ethynylphenyl)silylene]phenylene}s which were designed as high heat-resistant materials on the basis of the results of our previous studies on poly[(silylene)phenylene]s.[10,11]

Results

Preparation of Poly{[bis(ethynylphenyl)silylene]-phenylene}s. Recently we have demonstrated that nucleophilic substitution on EtO−Si bond of poly-[(ethoxysilylene)phenylene]s with organolithium reagents provides a convenient method to prepare variously substituted poly[(silylene)phenylene]s.[11] When poly[(diethoxysilylene)phenylene]s were treated with *p*- and *m*-(trimethylsilylethynyl)phenyllithium, the corresponding poly{bis[(trimethylsilylethynyl)phenyl]silylene-phenylene}s with different modes of substitution on the

10.1021/ma990314a CCC: $18.00
Published on Web 08/31/1999

Scheme 1

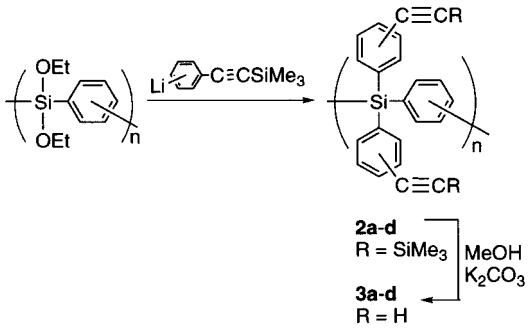


Table 1. Preparation and Substitution Mode of Polymers 2a−d and 3a−d

	substitution of phenylene			
polymer	backbone	pendant	yield/%	M_w (M_w/M_n)[a]
2a	*p*	*p*	53	29 000 (1.4)
2b	*m*	*p*	60	15 000 (1.4)
2c	*p*	*m*	37	26 000 (1.5)
2d	*m*	*m*	84	15 000 (1.4)
3a	*p*	*p*	84	33 000 (2.2)
3b	*m*	*p*	84	13 000 (1.2)
3c	*p*	*m*	56	22 000 (1.8)
3d	*m*	*m*	59	9500 (1.5)

[a] Determined by GPC, relative to polystyrene standards.

Table 2. Thermal Properties of Polymers 2a−d and 3a−d

	TGA[a] in N_2		TGA[a] in air	
polymer	T_{d_5}/°C[b]	wt loss/%[c]	T_{d_5}/°C[b]	wt loss/%[c]
2a	456	25	362	74
2b	501	22	474	66
2c	483	22	488	66
2d	501	20	431	70
3a	655	9	436	76
3b	711	8	524	81
3c	651	9	452	80
3d	676	10	566	80

[a] At a rate of 10 °C/min from 25 to 1000 °C. [b] Temperature of 5% weight loss based on the initial weight. [c] Total weight loss at 1000 °C.

phenylene units in the pendant groups and backbone (**2a−d**) were obtained as shown in Scheme 1 and Table 1. Complete transformation of the EtO−Si bonds to (trimethylsilylethynyl)phenyl−Si bonds was confirmed by NMR and IR spectrometric analysis of the polymers. Further treatment of the resulting polymers **2a−d** with methanol in the presence of a catalytic amount of K_2CO_3 gave desilation products, poly{[bis(ethynylphenyl)silylene]phenylene}s (**3a−d**) as shown in Scheme 1 and Table 1. Again, the reactions proceeded smoothly and no signals due to trimethylsilyl groups were observed in ^{1}H, ^{13}C, and ^{29}Si NMR spectra of **3a−d**.

Polymers **2a−d** and **3a−d** are soluble in aromatic solvents, halocarbons, and ethers, but insoluble in alcohols. In saturated hydrocarbons, polymers **2a−d** are soluble while **3a−d** are barely soluble. They do not melt up to 300 °C.

Thermal Properties of Polymers 2a−d and 3a−d. Thermal properties of polymers **2a−d** and **3a−d** were examined by TGA−TDA. Temperature resulting in a 5% weight loss based on the initial weight (T_{d_5}) and final weight loss at 1000 °C were noted as shown in Table 2. TGA−TDA curves for polymers **2b** and **3b** in nitrogen are depicted in Figure 1 as typical examples. As shown in Table 2, the materials obtained from the polymers

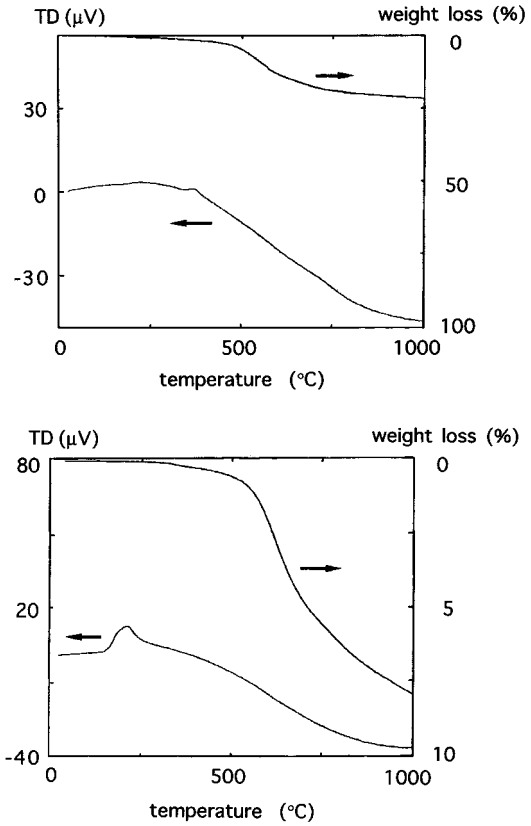


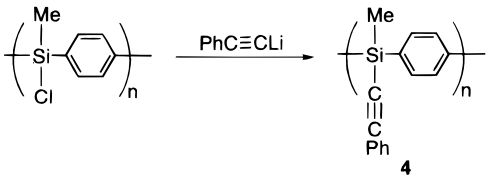
Figure 1. TGA−TDA profile for polymers **2b** (top) and **3b** (bottom) in N_2.

exhibit excellent heat-resistant properties in nitrogen, and TGA of polymer **3b** shows the highest T_{d_5} (711 °C) and the lowest weight loss at 1000 °C (8% of the initial weight). TGA−TDA of the polymers in air, however, show a slight decrease in T_{d_5} and a significant increase in weight loss at 1000 °C. The highest T_{d_5} in air is found for polymer **3d** (566 °C).

Trimethylsilyl-substituted polymers **2a−d** exhibit lower T_{d_5} in nitrogen as well as in air, relative to those of polymers **3a−d**. This is probably due to the steric protection of the ethynyl group in polymers **2a−d** by the trimethylsilyl group which suppresses the cross-linking reactions. In fact, TDA curves for polymers **3a−d** in a nitrogen atmosphere and in air show a strong exothermic peak around 220 °C, while those for **2a−d** reveal only broad and unclear exothermic peak centered at about 210 °C in nitrogen. In air, exothermic peaks at 500−700 °C, probably due to combustion of the polymers, are also observed for all of the present polymers. That the cross-linking reactions concerning the ethynyl groups took place was confirmed by monitoring the reaction progress by IR spectrometry. Thus, when polymer **3a** was heated at 220 °C for 30 min in nitrogen, the polymer became insoluble and the IR spectrum revealed the decrease of the absorptions due to the H−C≡C unit. The intensity ratios of the stretching frequencies of H−C≡ and C≡C at 3282 and 2108 cm^{-1} relative to that of H−C═C at 3050 cm^{-1} decreased from 3.3 and 0.6 to 1.1 and 0.2, respectively, after heating.

The weight loss at 1000 °C in nitrogen for polymers **3a−d** was determined to be lower than that of **2a−d**, compatible with the higher T_{d_5} for **3a−d**. In air, however, polymers **2a−d** exhibit lower weight loss at 1000 °C, probably due to the higher contents of silicon

Scheme 2



atoms which are likely to be converted to the ceramic composite in the residue.

It has been demonstrated that introduction of phenylethynyl substituents on carbon-based polymers gives rise to high heat resistance of the resulting polymers.[12] To know the influence of the regional change in the substituents attached to the silicon atoms, we prepared poly{[methyl(phenylethynyl)silylene]-*p*-phenylene]} (**4**) as shown in Scheme 2 and examined it by TGA in comparison with polymer **1**. TGA of **4** reveals T_{d_5} at 515 °C and the total weight loss at 1000 °C was calculated to be 21% of the initial weight, indicating less thermal stability for **4** relative to **1**. The presence of a terminal ethynyl unit would be important for the high heat-resistant properties of polymers **1** and **3a**−**d**.

Discussion

As evidenced by IR spectroscopy for **3a**, cross-linking reactions between ethynyl groups occur during heat curing, and the degree of the reactions may play an important role on the thermal stability of the present polymers. When the T_{d_5} values for polymers **2a**−**d** and **3a**−**d** are compared, it must be pointed out that meta-arrangement in the phenylene group in the backbone always leads to higher heat resistance than those with the *p*-phenylene backbone, except for **2d** in air whose T_{d_5} in air was determined to be a little lower than that of polymer **2c** with the same pendants on the silicon atom. TDA of the polymers in nitrogen reveals the exothermic peak due to the cross-linking at slightly lower temperature for *m*-phenylene polymers **3b** (217 °C) and **3d** (221 °C), relative to the respective *p*-phenylene polymers **3a** (229 °C) and **3c** (222 °C).

In particular, the polymers with the *m*-phenylene backbone and terminal ethynyl groups exhibit higher thermal stability. Although we have no information on the conformation of the present polymers in solid states, we assume that the polymer chains of **3a**−**d** are composed of several segments with different conformations, as illustrated in Figure 2 as typical examples.[13] In the polymers with *m*-phenylene backbone, a *trans*-linear segment (**A**) is considered to be a stable one. However, the crowded arrangement in **A** may cause considerable steric repulsion between the *m*-phenylene chain and pendant groups, which induces in part a folded or helical segment (**B**), making some of the ethynylphenyl groups closer (**C**). Whereas the ethynylphenyl groups on the edge of **B** jut out from the polymer rod. Thus, the increased irregularity in the polymer chain may facilitate cross-linking reactions across the ethynyl groups in either intramolecular or intermolecular manner. On the other hand, a *trans*-linear segment (**D**) in the *p*-phenylene polymers would be less hindered and hence much more stable, compared to meta isomers. The rigid polymer rod prevents access of the reactive sites, and thus the cross-linking reactions diminish.

The lower T_{d_5} values of the polymers with (silylethynyl)phenyl pendants (**2a**−**d**) than those with ethynylphenyl pendants (**3a**−**d**) seem to be primarily due to the lack of a reactive, easily cross-linkable terminal acetylenic unit. Cross-linking in **2a**−**d** concerning the acetylenic unit would be suppressed by the steric protection over the reactive sites with terminal silyl groups, even if it occurs. There appears, however, to be no clear dependence of the weight loss at 1000 °C on the substitution manner of the phenylene groups in the polymers.

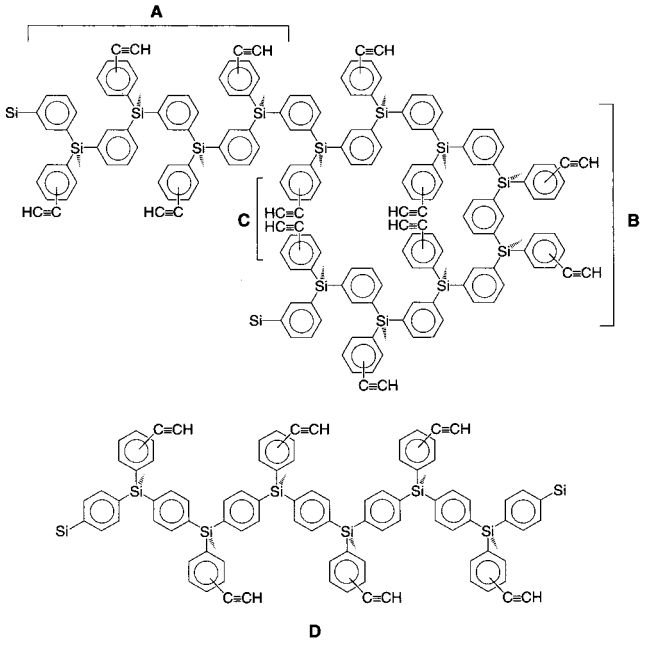


Figure 2. Schematic representation for the conformation of silylene-*m*-phenylene polymer (top) and silylene-*p*-phenylene polymer (bottom).

Conclusions

We prepared poly{[bis(ethynylphenyl)silylene]phenylene}s as the highly heat-resistant materials, which are soluble in organic solvent and processable into solid films by spin coating of the solutions. The high heat resistance of the polymers are ascribed to cross-linking reactions concerning ethynyl groups, which occurs around 220 °C. The present studies suggest that introduction of ethynylphenyl groups is quite effective to increase thermal stability of silicon-based polymers.

Experimental Section

General Data. All reactions were carried out under an atmosphere of dry nitrogen. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on JEOL model JNM-EX 270 and JEOL model JNM-LA 400 spectrometers. Mass spectra were measured with a Hitachi M-80B spectrometer. IR spectra were measured on a Perkin-Elmer FT-IR model 1600 spectrometer. Molecular weights of the polymers were determined by gel-permeation chromatography relative to polystyrene standards, using Shodex 806 and 804 as the column and THF as the eluent.

Materials. Ether and THF were dried over sodium−potassium alloy and distilled just before use. Methanol was dried over magnesium methoxide and distilled just before use. Bromo-4-[(trimethylsilyl)ethynyl]benzene, poly[(diethoxysilylene)-*p*-phenylene], and poly[(chloromethylsilylene)-*p*-phenylene] were prepared as reported in the literature.[11]

Preparation of (3-Bromophenyl)triethoxysilane. To a solution of 44.0 g (0.21 mol) of tetraethoxysilane in 180 mL of ether was added dropwise a solution of (3-bromophenyl)-magnesium bromide prepared from 50.0 g (0.21 mol) of 1,3-dibromobenzene and 5.1 g (0.21 mol) of magnesium in 30 mL

of ether, over a period of 1 h at 0 °C. The resulting mixture was stirred overnight at room temperature. To this was added 500 mL of hexane to precipitate magnesium salts, and the magnesium salts were filtered off. The solvent was evaporated, and the residue was distilled under reduced pressure to give 17.7 g (27% yield) of (3-bromophenyl)triethoxysilane: bp 78 °C (0.5 mmHg); MS *m*/*z* 318 (M^+); ^{1}H NMR (δ in $CDCl_3$) 1.23 (t, 9H, J = 7.0 Hz, CH_3CH_2), 3.85 (q, 6H, J = 7.0 Hz, CH_2-CH_3), 7.22 (t, 1H, J = 7.7 Hz, phenylene H on C5), 7.52 (ddd, 1H, J = 1.1, 2.0, 7.7 Hz, phenylene H on C6), 7.56 (dt, 1H, ^tJ = 1.1 Hz, ^dJ = 7.7 Hz, phenylene H on C4), 7.78 (dt, 1H, ^tJ = 1.1 Hz, ^dJ = 2.0 Hz, phenylene H on C2); ^{13}C NMR (δ in $CDCl_3$) 18.0 (CH_3CH_2), 58.7 (CH_2CH_3), 122.7, 129.5, 132.9, 133.2, 134.2, 137.3 (phenylene); ^{29}Si NMR (δ in $CDCl_3$) −59.9; IR ν_{Si-O} 1078 cm^{-1}. Anal. Calcd for $C_{12}H_{19}SiBrO_3$: C, 45.14; H, 6.00. Found: C, 45.04; H, 6.18.

Preparation of Bromo-3-[(trimethylsilyl)ethynyl]benzene. A mixture consisting of 20.0 g (70.7 mmol) of 3-bromoiodobenzene, 8.0 g (81.5 mmol) of (trimethylsilyl)acetylene, 120 mL of triethylamine, 42 mg of copper(I) iodide, and 104 mg of tetrakis(triphenylphosphine)palladium(0) was stirred at room temperature for 5 h. The resulting precipitates were filtered off, and the solvent was evaporated off. The residue was chromatographed on a silica gel column eluting with hexane to give 15.2 g (73% yield) of bromo-3-[(trimethylsilyl)-ethynyl]benzene: MS *m*/*z* 252 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.28 (s, 9H, Me_3Si), 7.12 (t, 1H, J = 8.0 Hz, phenylene H on C5), 7.38 (d 1H, J = 8.0 Hz, phenylene H on C4), 7.43 (dt, 1H, J = 1.0, 8.0 Hz, phenylene H on C6), 7.63 (s, 1H, phenylene H on C2); ^{13}C NMR (δ in $CDCl_3$) −0.15 (Me_3Si), 95.8, 103.3 (C≡C), 122.0, 125.1, 129.6, 130.3, 131.5, 134.6 (aromatic carbons); ^{29}Si NMR (δ in $CDCl_3$) −17.4 (Me_3Si); IR $\nu_{C\equiv C}$ 2163 cm^{-1}. Anal. Calcd for $C_{11}H_{13}BrSi$: C, 52.18; H, 5.17. Found: C, 52.00; H, 5.24.

Preparation of Poly[(diethoxysilylene)-*m*-phenylene]. To a mixture of 1.71 g (70.5 mmol) of magnesium and 20 mL THF was added dropwise 20.5 g (64.3 mmol) of (3-bromophenyl)triethoxysilane at room temperature over a period of 1.5 h. The resulting mixture was heated to reflux for 41 h. To this was added 500 mL of hexane to precipitate magnesium salts and the magnesium salts were filtered off. The solvent was evaporated, and the residue was reprecipitated twice from chloroform-methanol to give 1.28 g (10% yield) of poly[*m*-(diethoxysilylene)phenylene] as a viscous oil: M_w = 8100 (M_w/M_n = 1.4); ^{1}H NMR (δ in $CDCl_3$) 1.17 (t, 6H, J = 7.0 Hz, CH_3CH_2), 3.80 (q, 4H, J = 7.0 Hz, CH_2CH_3), 7.31 (t, 1H, J = 7.3 Hz, phenylene H on C5), 7.65 (d, 2H, J = 7.3 Hz, phenylene H on C4, C6), 8.01 (s, 1H, J = 7.3 Hz, phenylene H on C2); ^{13}C NMR (δ in $CDCl_3$) 18.2 (CH_3CH_2), 58.9 (CH_2CH_3), 127.1, 132.3, 136.7, 141.2 (aromatic carbons); ^{29}Si NMR (δ in $CDCl_3$) −32.2; IR ν_{Si-O} 1078 cm^{-1}. Anal. Calcd for $(C_{10}H_{14}SiO_2)_n$: C, 61.82; H, 7.26. Found: C, 62.05; H, 7.21.

Preparation of Polymer 2a. To a solution of 4-[(trimethylsilyl)ethynyl]phenyllithium prepared from 1.44 g (5.69 mmol) of bromo-4-[(trimethylsilyl)ethynyl]benzene and 1 equiv of *tert*-butyllithium in 100 mL ether was added dropwise a solution of 0.50 g of poly[(diethoxysilylene)-*p*-phenylene] (M_w = 20 000, M_n = 13 000) in 50 mL of ether. The mixture was stirred at room temperature for 13 h and then hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with chloroform. The organic layer and the extracts were combined and dried over anhydrous magnesium sulfate. After evaporation of the solvents, the residue was reprecipitated twice from chloroform−ethanol to give 515.6 mg (53% yield) of polymer **2a**: mp >300 °C; M_w = 29 000 (M_w/M_n = 1.4); ^{1}H NMR (δ in $CDCl_3$) 0.21 (br s, 18H, Me_3Si), 7.42 (br s, 8H, ethynylphenyl), 7.49 (br s, 4H, phenylene); ^{13}C NMR (δ in $CDCl_3$) −0.07 (Me_3Si), 95.6, 104.8 (C≡C), 124.6, 131.2, 134.0, 135.0, 135.6, 136.0 (aromatic carbons); ^{29}Si NMR (δ in $CDCl_3$) −0.88, −17.6; IR $\nu_{C\equiv C}$ 2158 cm^{-1}. Anal. Calcd for $(C_{28}H_{30}Si_3)_n$: C, 74.60; H, 6.65. Found: C, 74.35; H, 6.40.

Polymers **2b**−**d** were prepared as described for polymer **2a** using appropriate combination of the starting polymer and (trimethylsilylethynyl)phenyllithium.

Data for **2b**: mp >300 °C; M_w = 15 000 (M_w/M_n = 1.4); ^{1}H NMR (δ in $CDCl_3$) 0.20 (br s, 18H, Me_3Si), 7.22 (d, 4H, J = 8.0 Hz, ethynylphenyl H), 7.31 (d, 4H, J = 8.0 Hz, ethynylphenyl H), 7.37 (t, 1H, J = 8.0 Hz, phenylene H on C5), 7.42 (d, 2H, J = 8.0 Hz, phenylene H on C4, C6), 7.59 (s, 1H, phenylene H on C2); ^{13}C NMR (δ in $CDCl_3$) −0.02 (Me_3Si), 95.4, 104.9 (C≡C), 122.4, 127.6, 131.2, 132.7, 134.2, 135.8, 137.5, 143.9 (aromatic carbons); ^{29}Si NMR (δ in $CDCl_3$) −0.85, −17.7; IR $\nu_{C\equiv C}$ 2157 cm^{-1}. Anal. Calcd for $(C_{28}H_{30}Si_3)_n$: C, 74.60; H, 6.65. Found: C, 73.69; H, 6.46.

Data for **2c**: mp >300 °C; M_w = 26 000 (M_w/M_n = 1.5); ^{1}H NMR (δ in $CDCl_3$) 0.16 (br s, 18H, Me_3Si), 7.27 (t, 2H, J = 7.2 Hz, ethynylphenyl H on C5), 7.41 (d, 2H, J = 7.2 Hz, ethynylphenyl H on C4), 7.49 (d, 2H, J = 7.2 Hz, ethynylphenyl H on C6), 7.53 (s, 4H, phenylene), 7.62 (s, 2H, ethynylphenyl H on C2); ^{13}C NMR (δ in $CDCl_3$) −0.05 (Me_3Si), 94.6, 105.1 (C≡C), 122.9, 127.8, 133.5, 133.6, 134.9, 135.7, 136.4, 139.3 (aromatic carbons); ^{29}Si NMR (δ in $CDCl_3$) −0.85, −17.8; IR $\nu_{C\equiv C}$ 2164 cm^{-1}. Anal. Calcd for $(C_{28}H_{30}Si_3)_n$: C, 74.60; H, 6.65. Found: C, 73.01; H, 6.62.

Data for **2d**: mp >300 °C; M_w = 15 000 (M_w/M_n = 1.4); ^{1}H NMR (δ in $CDCl_3$) 0.20 (br s, 18H, Me_3Si), 7.31−7.64 (m, 12H, aromatic protons); ^{13}C NMR (δ in $CDCl_3$) −0.02 (Me_3Si), 94.4, 105.4 (C≡C), 122.8, 127.8, 127.9, 132.2, 133.5, 133.6, 136.8, 137.8, 139.2, 144.0 (aromatic carbons); ^{29}Si NMR (δ in $CDCl_3$) −0.87, −18.1; IR $\nu_{C\equiv C}$ 2161 cm^{-1}. Anal. Calcd for $(C_{28}H_{30}Si_3)_n$: C, 74.60; H, 6.65. Found: C, 72.49; H, 6.48.

Preparation of Polymer 3a. A mixture of 0.49 g of polymer **2a** (M_w = 29 000, M_n = 21 000), 0.406 g (2.94 mmol) of K_2CO_3, 20 mL of methanol, and 30 mL of THF was stirred at room temperature for 3 h. After evaporation of THF and an excess of MeOH under reduced pressure, the residue was reprecipitated from chloroform−methanol to give 0.28 g (84% yield) of polymer **3a**: mp >300 °C; M_w = 33 000 (M_w/M_n = 2.2); ^{1}H NMR (δ in $CDCl_3$) 3.08 (br s, 2H, CH), 7.45 (br s, 12H, aromatic protons); ^{13}C NMR (δ in $CDCl_3$) 78.5, 83.4 (C≡C), 123.6, 131.5, 134.2, 134.7, 135.7, 136.1 (aromatic carbons); ^{29}Si NMR (δ in $CDCl_3$) −14.5; IR $\nu_{C\equiv C}$ 2108 cm^{-1}, $\nu_{H-C\equiv}$ 3282 cm^{-1}. Anal. Calcd for $(C_{22}H_{14}Si)_n$: C, 86.23; H, 4.60. Found: C, 79.79; H, 4.94. The lower carbon content determined by combustion analysis compared with the theoretical value is often observed for organometallic polymers.[10,11,14] This would be due to the formation of silicon-containing ceramics, such as β-SiC during the analysis.

Polymers **3b**−**d** were prepared from polymers **2b**−**d** as described for polymer **3a**.

Data for **3b**: mp >300 °C; M_w = 13 000 (M_w/M_n = 1.2); ^{1}H NMR (δ in $CDCl_3$) 3.10 (s, 2H, CH), 7.24 (d, 4H, J = 7.5 Hz, ethynylphenyl H), 7.32 (d, 4H, J = 7.5 Hz, ethynylphenyl H), 7.40 (t, 1H, J = 7.5 Hz, phenylene H on C5), 7.48 (d, 2H, J = 7.5 Hz, phenylene H on C4, C6), 7.55 (s, 1H, phenylene H on C2); ^{13}C NMR (δ in $CDCl_3$) 78.5, 83.4 (C≡C), 123.5, 127.7, 131.4, 132.7, 134.3, 135.8, 137.5, 144.1 (aromatic carbons); ^{29}Si NMR (δ in $CDCl_3$) −14.5; IR $\nu_{C\equiv C}$ 2108 cm^{-1}, $\nu_{H-C\equiv}$ 3298 cm^{-1}. Anal. Calcd for $(C_{22}H_{14}Si)_n$: C, 86.23; H, 4.60. Found: C, 79.73; H, 4.49.

Data for **3c**: mp >300 °C; M_w = 22 000 (M_w/M_n = 1.8); ^{1}H NMR (δ in $CDCl_3$) 3.02 (br s, 2H, CH), 7.35 (br s, 2H, aromatic protons), 7.59 (br s, 8H, aromatic protons), 7.68 (br s, 2H, aromatic protons); ^{13}C NMR (δ in $CDCl_3$) 77.8, 83.6 (C≡C), 122.0, 128.0, 133.5, 133.6, 134.8, 135.7, 136.6, 139.6 (aromatic carbons); ^{29}Si NMR (δ in $CDCl_3$) −14.6; IR $\nu_{C\equiv C}$ 2110 cm^{-1}, $\nu_{H-C\equiv}$ 3293 cm^{-1}. Anal. Calcd for $(C_{22}H_{14}Si)_n$: C, 86.23; H, 4.60. Found: C, 81.46; H, 4.45.

Data for **3d**: mp >300 °C; M_w = 9500 (M_w/M_n = 1.5); ^{1}H NMR (δ in $CDCl_3$) 3.02 (br s, 2H, CH), 7.12−7.60 (m, 12H, aromatic protons); ^{13}C NMR (δ in $CDCl_3$) 77.7, 83.8 (C≡C), 121.8, 127.9, 128.0, 132.5, 133.4, 133.6, 136.2, 137.6, 139.4, 144.0 (aromatic carbons); ^{29}Si NMR (δ in $CDCl_3$) −14.6; IR $\nu_{H-C\equiv}$ 2108 cm^{-1}, $\nu_{HC\equiv C}$ 3287 cm^{-1}. Anal. Calcd for $(C_{22}H_{14}Si)_n$: C, 86.23; H, 4.60. Found: C, 80.09; H, 4.46.

Preparation of Polymer 4. To a 30 mL THF solution of 1.0 g of poly[(chloromethylsilylene)-*p*-phenylene] was added phenylethynyllithium, prepared from 721 mg (7.06 mmol) of phenylacetylene and 4.4 mL (7.04 mmol) of a 1.6 M hexane

solution of *n*-butyllihtium in 50 mL of THF at 0 °C. The mixture was allowed to warm to room temperature and hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and dried over anhydrous magnesium sulfate. After evaporation of the solvents, the residue was reprecipitated twice from THF−methanol to give 233.7 mg (16% yield) of polymer **4**: mp >300 °C; M_w = 9300 (M_w/M_n = 1.6); ^{1}H NMR (δ in $CDCl_3$) 0.79 (s, 3H, MeSi), 7.33−7.96 (br m, 9H, phenylene and Ph); ^{13}C NMR (δ in $CDCl_3$) −2.2 (MeSi), 89.9, 108.5 (C≡C), 122.7, 128.2, 128.9, 132.1, 133.9, 136.7 (aromatic carbons); ^{29}Si NMR (δ in $CDCl_3$) −25.6; IR $\nu_{C\equiv C}$ 2157 cm^{-1}. Anal. Calcd for $(C_{22}H_{14}Si)_n$: C, 81.76; H, 5.49. Found: C, 80.54; H, 5.47.

References and Notes

(1) For reviews, see: (a) *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, H. K. J., Allcock, R., Eds.; ACS Symposium Series 368; American Chemical Society: Washington, DC, 1988. (b) *Silicon-Based Polymer Science*; Zeigler, J. M., Fearon, F. W. G., Eds.; Advances in Chemistry Series 224; American Chemical Society: Washington, DC, 1990. (c) Ohshita, J.; Kunai, A. *Acta Polym.* **1998**, *49*, 379.

(2) Ishikawa, M.; Ohshita, J. Silicon and Germanium Containing Conductive Polymers. In *Handbook of Organic Conductive Molecules and Polymers*, Nalwa, H. S., Ed.; Wiley: New York, 1997; Vol. 2, Chapter 15.

(3) Adachi, A.; Manhart, S. A.; Okita, K.; Kido, J.; Ohshita, J.; Kunai, A. *Synth. Met.* **1997**, *91*, 333.

(4) Ishikawa, M.; Nate, K. in *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988; Chapter 16. (b) Ohshita, J.; Ishikawa, M. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: New York, 1996; p 892 and references therein.

(5) (a) Corriu, R. J. P.; Gerbier, P.; Guérin, C.; Henner, B. J. L.; Jean, A.; Mutin, P. H. *Organometallics* **1992**, *11*, 2507. (b) Corriu, R.; Gerbier, Ph.; Guérin, C.; Henner, B.; Fourcade, R. *J. Organomet. Chem.* **1993**, *449*, 111. (c) Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Planeix, J.-M.; Vioux, A. *Organometallics* **1993**, *12*, 454.

(6) Ijadi-Maghsoodi, S.; Pang, Y.; Barton, T. J. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 955.

(7) (a) Itoh, M.; Inoue, K.; Iwata, K.; Mitsuzuka, M.; Kakigano, T. *Macromolecules* **1997**, *30*, 694. (b) Itoh, M.; Mitsuzuka, M.; Iwata, K.; Inoue, K. *Macromolecules* **1994**, *27*, 7917.

(8) Pang, Y.; Ijadi-Maghsoodi, S.; Barton, T. J. *Macromolecules* **1993**, *26*, 5671.

(9) Ohshita, J.; Kanaya, D.; Watanabe, T.; Ishikawa, M. *J. Organomet. Chem.* **1995**, *489*, 165.

(10) Ohshita, J.; Ishii, M.; Ueno, Y.; Yamashita, A.; Ishikawa, M. *Macromolecules* **1994**, *27*, 5583.

(11) Ohshita, J.; Yamashita, A.; Hiraoka, T.; Shimpo, A.; Kunai, A.; Ishikawa, M. *Macromolecules* **1997**, *30*, 1540.

(12) Morgan, A. B.; Tour, J. M. *Macromolecules* **1998**, *31*, 2857.

(13) One reviewer suggested that the X-ray diffraction studies would afford information about the polymer conformation. Powder X-ray diffraction analysis for polymer **3b** revealed no characteristic patterns, while a broad and weak peak was observed for **3a** at 2θ = 5−6° (Cu Kα), which might reflect some regularity in the solid state due to rigid rods of **3a**.

(14) Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *Macromolecules* **1991**, *24*, 6843.

MA990314A