Polymeric Organosilicon Systems. 27. Preparation and Reactions of Poly[(ethoxysilylene)phenylenes] and Thermal Properties of the Resulting Polymers

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ABSTRACT: Treatment of (4-bromophenyl)diethoxymethylsilane with magnesium in THF gave poly[*p*-(ethoxymethylsilylene)phenylene] (**1a**) in 58% yield. Similar reactions of (4-bromophenyl)triethoxysilane and (3-bromophenyl)diethoxymethylsilane with magnesium afforded poly[*p*-(diethoxysilylene)phenylene] (**1b**) and poly[*m*-(ethoxymethylsilylene)phenylene] (**1c**) in 61% and 27% yields, respectively. The Si−OEt bonds of polymer **1a** could be readily transformed into the Si−Cl bonds, by treating the polymer with excess acetyl chloride, while polymer **1b** did not react with acetyl chloride. Treatment of polymers **1a**−**c** with lithium aluminum hydride produced the respective polymers having an Si−H bond. The polymers having an Si−OEt and Si−Cl bond readily reacted with a variety of nucleophiles, including Grignard reagents and organolithium reagents, to afford substitution products. The thermal properties of the polymers thus obtained were investigated by thermogravimetric analysis in a nitrogen atmosphere.

Introduction

Polymers having a regular alternating arrangement of a π-electron system and an organosilicon moiety in their backbone are of current interest, because they can be used as functionality materials such as semiconducting materials, precursors of silicon carbide, and heat-resistant materials.[1] Many papers concerning the synthesis and properties of this type of polymers have been published to date. The methods for the synthesis of these polymers reported so far include four types of reactions, Wurtz-type condensation of bis(chlorosilyl)-substituted compounds with alkali metals,[2] reactions of dichlorosilanes with organodilithium reagents,[3] transition-metal-catalyzed coupling reactions of organosilicon compounds,[4] and ring-opening polymerization of silicon-containing strained ring systems.[5]

However, these studies have been limited to polymers with simple substituents, such as phenyl, ethyl, and methyl groups on the silicon atom, and the development of the synthesis of silicon-containing polymers involving the functional groups on the silicon atoms, which can be readily transformed into the other substituents is expected to offer a convenient route to a wide range of the silicon polymers. Although some papers concerning the synthesis of the polymers bearing a functional group on the silcion atoms in the polymer backbone have been published,[1] no convenient methods to prepare the polymers composed of an alternating arrangement of a functionalized silicon moiety and π-electron system have been reported until recently.

Recently, we have demonstrated that the reactions of *p*- and *m*-dilithiobenzene with dichlorohydrosilanes afford poly[(hydrosilylene)phenylenes] which can readily introduce various organic substituents on the silicon atom by platinum-catalyzed hydrosilylation with acetylenes and olefins.[6] However, the Si−H bond of these polymers did not react with nucleophiles, and all attempts to introduce an organic substituent by the reactions with organometallic reagents were unsuccessful. Uhlig et al.[7] have reported that treatment of poly[(allylsilylene)diethynylenes] and poly[(phenylsilylene)diethynylenes] with trifluoromethanesulfonic acid in ether affords polymers bearing a silyl−trifluoromethanesulfonate bond (Si−OTf).[7] Although the Si−OTf bond thus formed reacts readily with nucleophiles to give the substitution products, this bond is highly sensitive to moisture, and therefore these polymers cannot be isolated. More recently, Tanaka and his co-workers have reported that the ruthenium-catalyzed desilylating coupling reactions of bis(trihydrosilyl)benzenes produce poly[(dihydrosilylene)phenylenes] whose Si−H bond can be transformed into an Si−alkoxy bond by treatment of the polymers with alcohols in the presence of the ruthenium catalyst.[8] However, this method involves the formation of hazardous silane gas which is unavoidable.

In this paper, we report the synthesis and reactions of poly[(ethoxysilylene)phenylenes], which offer a convenient method to prepare poly[(silylene)phenylenes] having various substituents on a silicon atom in the backbone.

We also investigated thermal properties of the polymers obtained from the reactions of poly[(ethoxysilylene)phenylenes] by thermogravimetric analysis in a nitrogen atmosphere, in order to learn how the substituent attached to the silicon atom influences the thermal properties of the polymers, which would give important information for the design of silicon-based heat-resistant materials and efficient precursors of silicon carbide.

Results and Discussion

Preparation of Poly[(ethoxysilylene)phenylenes]. The reaction of (4-bromophenyl)diethoxymethylsilane with 1 equiv of magnesium in refluxing THF for 64 h, followed by reprecipitation of the resulting organic products from chloroform−ethanol gave poly[*p*-(ethoxymethylsilylene)phenylene] (**1a**) in 58% yield, as shown

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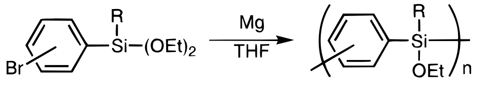
Scheme 1



1a, *p*-, R = Me
1b, *p*-, R = OEt
1c, *m*-, R = Me

in Scheme 1. The structure of polymer **1a** was verified by spectrometric and elemental analysis. The IR spectrum of **1a** shows an absorption band at 1021 cm^{-1} due to the stretching frequencies of an Si–O bond. Its ^{29}Si NMR spectrum reveals only one sharp signal at −3.4 ppm. The ^{1}H and ^{13}C spectra of **1a** are also consistent with the regular alternating ethoxymethylsilylene-*p*-phenylene structure (see Experimental Section). Similarly, (4-bromophenyl)triethoxysilane polymerized to give poly[*p*-(diethoxysilylene)phenylene] (**1b**) under the same conditions in 61% yields. The reaction of (3-bromophenyl)diethoxymethylsilane with magnesium in THF again proceeded smoothly at 170 °C to afford poly[*m*-(ethoxymethylsilylene)phenylene] (**1c**) in 27% yield. The structures of polymers **1b** and **1c** were also verified by NMR and IR spectrometry, and elemental analysis (see Experimental Section). For polymer **1c**, weak signals at 1.17–1.22 and 3.67–3.74 ppm, probably due to the terminal diethoxymethylsilyl groups are also observed in its ^{1}H NMR spectrum, in addition to major signals due to the ethoxymethylsilylene–*m*-phenylene structure. The Si–OEt bond in these polymers is stable toward atmospheric moisture and can be handled in air but reacts slowly with water to produce a cross-linking siloxane unit and therefore hydrolytic workup must be avoided to obtain pure polymers.

Some properties of polymers **1a–c** are summarized in Table 1. Polymers **1a** and **1b** are white solids and melt without decomposition, while polymer **1c** is the viscous oil. Polymers **1a–c** are soluble in chlorocarbons, hydrocarbons, and ethers, but insoluble in alcohols. Molecular weights of the polymers were determined to be $M_w = 10\,000–30\,000$ by GPC, relative to polystyrene standards. Molecular weights of **1a** and **1b** were also determined by osmometry to be $M_n = 8900$ and 15 000, respectively, in good agreement with those obtained by GPC, as can be seen in Table 1. The lower yield of polymer **1c** than those of polymers **1a** and **1b** may be ascribed to the formation of oligomers which are soluble in ethanol. Severe conditions at 170 °C in an autoclave are required to obtain polymer **1c** with high molecular weight in high yield. In fact, reaction conditions similar to those used for the preparation of **1a** and **1b** lead to the formation of **1c** with low molecular weight in low yield. Thus, when the reaction of (3-bromophenyl)diethoxymethylsilane with magnesium was carried out in refluxing THF, polymer **1c** with molecular weight of $M_w = 6200$ was obtained only in 16% yield.

Reactions of Polymers 1a–c with Acetyl Chloride and LiAlH$_4$. The Si–OEt bond in polymer **1a** can be readily replaced by an Si–Cl bond by treating with acetyl chloride (Scheme 2 and Table 2). Thus, when a solution of polymer **1a** ($M_w = 17\,000$; $M_w/M_n = 1.8$) in acetyl chloride was stirred at room temperature and the progress of the reaction was monitored by IR spectrometry, the absorption band at 1021 cm^{-1} due to the stretching frequencies of the Si–O bond in **1a** decreased gradually and finally disappeared after 5 days reaction. Evaporation of excess acetyl chloride and the resulting ethyl acetate gave poly[*p*-(chloromethylsilylene)phenylene] (**2a**) in 80% yield. Polymer **2a** is white solids and soluble in chlorocarbons and ethers, but hardly soluble in aromatic hydrocarbons and insoluble in saturated hydrocarbons. Polymer **2a** was found to exhibit reactivities toward water higher than those of **1a**, and standing it in air resulted in the formation of a cross-linking siloxane unit in the polymer backbone. As shown in Table 2, the molecular weight of **2a** was determined to be slightly smaller than the theoretical value, indicating that cleavage of the Si–phenylene bonds also occurred to some extent. In contrast to **1a**, polymer **1b** did not react with acetyl chloride even at the refluxing temperature. In this reaction, polymer **1b** was recovered unchanged.

The Si–Cl bond in polymer **2a** can be further transformed into an Si–F bond (Scheme 2). Thus, when polymer **2a** was treated with a slight excess of SbF$_3$ in ether, the resulting inorganic salts and insoluble polymers were filtered off, and then polymer which is soluble in ether was reprecipitated from chloroform-hexane, poly[*p*-(fluoromethylsilylene)phenylene] (**3a**) was obtained in 20% yield. The ^{29}Si NMR spectrum of **3a** shows a doublet with a coupling constant of $J_{\text{Si–F}} = 280.7$ Hz. No other signals are observed in this spectrum. ^{1}H and ^{13}C NMR spectra are also consistent with the structure proposed for **3a** (see Experimental Section). The low yield and lower molecular weight of polymer **3a** than calculated from the molecular weight of the starting **2a** may be due to the formation of a large amount of an insoluble polymer which was filtered off with inorganic products. All attempts to separate the insoluble polymer from the inorganic salts were unsuccessful, and therefore we have not yet obtained any information about the structure. Presumably, high crystallinity of the polymer and/or the presence of a cross-linking siloxane unit which may be formed by the hydrolysis of the Si–F bond during work up, are responsible for the formation of the insoluble polymer.

Polymers **1a–c** reacted also with lithium aluminum hydride (LiAlH$_4$) in THF to give the respective Si–H containing polymers (**4a–c**) in moderate yields, as shown in Scheme 3 and Table 2. Polymer **1a** reacted cleanly with $^1/_4$ equiv of LiAlH$_4$ to give **4a**. For complete transformation of **1c** to **4c**, however, it was necessary to use $^1/_2$ equiv of LiAlH$_4$. When **1c** was treated with $^1/_4$ equiv of LiAlH$_4$, the polymer in which only 50% of the EtO–Si bonds was replaced by an Si–H bond was obtained in 65% yield. This may be ascribed to the steric hindrance due to the meta substitution on the phenylene ring. Polymers **4a** and **4c** are soluble in chlorocarbons and aromatic hydrocarbons and can be purified by reprecipitation from chloroform–ethanol. As shown in Table 2, the molecular weight of polymer **4a** was slightly higher than the expected value, indicating that some cross-linking reactions occurred in this reaction. Although evidence for the presence of cross-linked units in **4a** has not yet been obtained, this may be ascribed to the hydrolysis of a trace of the Si–OEt bond remaining in the polymer chain giving a cross-linking siloxane bridge. A similar reaction of polymer **1b** with LiAlH$_4$ gave poly[*p*- (silylene)phenylene] (**4b**); however, **4b** thus obtained was insoluble in common organic solvents, in marked contrast to the polymer prepared from the reaction of 1,4-dilithiobenzene and 1,4-bis(chlorosilyl)benzene, which was soluble in benzene, chlorocarbons, and ethers.[6] Presumably, again a cross-linking reaction took place, as in the case of **4a**.

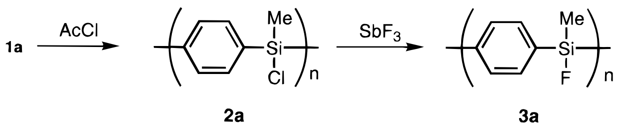
Nucleophilic Substitution. Next, we examined the reactions of polymers **1a–c** and **2a** with nucleophiles, as shown in Schemes 4 and 5. The results are summarized in Table 3. The reactions of polymers **1a** and **1b** with a slight excess of *n*-butyllithium in refluxing

Table 1. Properties of Polymer 1a−c

				TGA		
polymer	yield (%)[a]	M_w (M_w/M_n)[b]	M_n[c]	mp (°C)	Td$_5$[d]	weight loss (%)[e]
1a	58	17 000 (1.8)	8 900	86−95	465	42
1b	61	30 000 (1.6)	15 000	64−73	450	50
1c	27	10 000 (1.7)		viscous oil		

[a] After reprecipitation. [b] Determined by GPC, relative to polystyrene standards. [c] Determined by osmometry. [d] Temperature of 5% weight loss. [e] Weight loss at 1000 °C.

Scheme 2



THF gave poly[*p*-(butylmethylsilylene)phenylene] (**5a**) and poly[*p*-(dibutylsilylene)phenylene] (**5b**) in 80 and 57% yields, respectively, after reprecipitation of the polymers from chloroform−ethanol. Treatment of polymer **1b** with 1 equiv of *n*-butyllithium gave a monobutylated product, poly[*p*-(butylethoxysilylene)phenylene] (**5b′**) in 72% yield. The ^{1}H, ^{13}C, and ^{29}Si NMR spectrometric analyses of **5b′** clearly show that one of the Si−OEt bonds in the diethoxysilylene moiety of polymer **1b** was replaced selectively by an Si−Bu bond (see Experimental Section). No signals due to diethoxysilylene and dibutylsilylene units are observed in these spectra. Polymer **1c** also reacted with *n*-butyllithium to give poly[*m*-(butylmethylsilylene)phenylene] (**5c**) as a viscous oil in 93% yield. Treatment of **1a** with phenyllithium in ether at room temperature gave poly[*p*-(methylphenylsilylene)phenylene] (**6a**) with a molecular weight of 16 000 (M_w/M_n = 1.6) in 56% yield. In similar reactions of **1b** with phenyllithium, a mono-phenylated product, poly[*p*-(ethoxyphenylsilylene)phenylene] (**6b**), was always obtained, even when a large excess of phenyllithium was used.

The reactions of **1a** and **1b** with phenyllithium in refluxing THF, however, led to cleavage of the polymer backbone to give the respective phenylated polymers with low molecular weights. For example, treatment of **1a** with 1 equiv of phenyllithium in refluxing THF gave polymer **6a** with a molecular weight of M_w = 1900 (M_w/M_n = 1.2) in 61% yield. It was found that the reaction must be carried out in ether at low temperatures to suppress this cleavage reaction.

The functional-group-substituted phenyl groups can also be introduced into the silicon atoms in the polymer backbone. Thus, the reactions of **1a** with (4-chlorophenyl)lithium, 4-(bromophenyl)lithium, and [4-[(trimethylsilyl)ethynyl]phenyl]lithium proceeded cleanly to give poly{*p*-[(4-chlorophenyl)methylsilylene]phenylene} (**7a**), poly{*p*-[(4-bromophenyl)methylsilylene]phenylene} (**8a**), and poly{*p*-{methyl[4-[(trimethylsilyl)ethynyl]phenyl]silylene}phenylene} (**9a**), respectively.

Next, we prepared poly{*p*-{[2-[(dimethylamino)methyl]phenyl]methylsilylene}phenylene} (**10a**) and poly{*p*-{ethoxy[2-[(dimethylamino)methyl]phenyl]silylene}phenylene} (**10b**), by treatment of the respective polymers **1a** and **1b** with [2-[(dimethylamino)methyl]phenyl]lithium, in the hope that the amino group coordinates to the silicon atom to form the high-coordinated silicon moiety. Introduction of a high-coordinated silicon moiety is expected to cause significant changes in the electronic states and bonding structures of the polymers.[9,10] It is well-known that high-field shift is observed in the ^{29}Si NMR signal when the coordination number of the silicon atom becomes higher than 4.[11] ^{29}Si NMR signals for **10a** and **10b** appear at −12.2 and −16.7 ppm, respectively, which are slightly high field shifted relative to those for **6a** (−11.4 ppm) and **6b** (−13.8 ppm). A larger high-field shift for polymer **10b** than that for **10a**, relative to **6a** and **6b**, may be attributed to the presence of an electron-withdrawing ethoxy group on the silicon atom in **10b**, which would stabilize the Si−N coordination leading to the higher coordination in **10b** than in **10a**.[9] However, the degree of the high-field shift is small even for **10b**, indicating that the coordination of the amino group to the silicon atom is weak. Attempts to determine molecular weights of polymers **10a** and **10b** by GPC resulted in decomposition of the polymers to give low molecular weight products, and therefore their molecular weights were determined by osmometry. When the decomposition products obtained from treatment of polymer **10a** with GPC eluting with THF were analyzed by IR spectrometry, new absorption bands at 3400 and 1100 cm^{-1} probably due to the stretching frequencies of an O−H and Si−O bond were observed, indicating that hydrolysis of the Si-phenylene bond by a trace of water in THF occurred. Since polymers **6a** and **6b** having no amino group on the phenyl ring were satisfactorily analyzed by GPC, it seems likely that the weak Si−N interaction in **10a** and **10b** facilitates the hydrolysis of the Si−phenylene bond.[9]

In contrast to the reactions with organolithium reagents, the Si−OEt bond in the polymers reacted with Grignard reagents very slowly to give substituted polymers. For example, in the reaction of polymer **1a** with an excess of methylmagnesium chloride in refluxing THF for 39 h, only 40% of the Si−OEt bond was replaced by an Si−Me bond. The reaction of (chloromethylsilylene)phenylene polymer **2a** with n-butylmagnesium bromide again proceeded slowly to afford polymer **5a′**, in which approximately two-thirds of the Si−Cl bonds in the starting polymer **2a** were transformed into Bu−Si bonds. The Si−Cl bonds remaining in **5a′** were converted into Si−OH and Si−O−Si bonds during workup. However, with sterically less hindered Grignard reagents, [(trimethylsilyl)ethynyl]magnesium bromide and vinylmagnesium bromide, polymer **2a** gave the coupling products, poly{*p*-[methyl[(trimethylsilyl)ethynyl]silylene]phenylene} (**11a**) and poly[*p*-(methylvinylsilylene)phenylene] (**12a**) in good yields, as shown in Table 3.

The reaction of **2a** with sodium acetylide also gave a coupling product, poly[*p*-(ethynylmethylsilylene)phenylene] (**13a**), in good yield. Polymer **13a** is insoluble in common organic solvents but can be characterized by IR spectrometry which shows strong absorptions at 3272 and 2037 cm^{-1}, due to the stretching frequencies of a terminal ethynyl C−H bond and a C≡C bond, respectively. In this spectrum, a weak absorption band at 1086 cm^{-1} is also observed, indicating the presence of siloxane bonds in the polymer, which may be formed by hydrolysis of the Si−Cl bonds remaining in the coupling reaction, during workup.

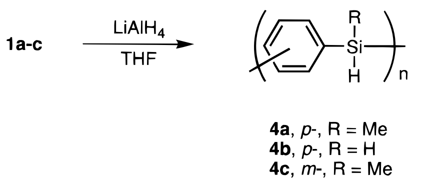
Treatment of **2a** with Cp(CO)$_2$FeNa in THF gave polymer **14a**, which involves an Si−Fe bond, in 51%

Table 2. Reactions of Polymers 1a–c and 2a with Acetyl Chloride, SbF_3, and $LiAlH_4$

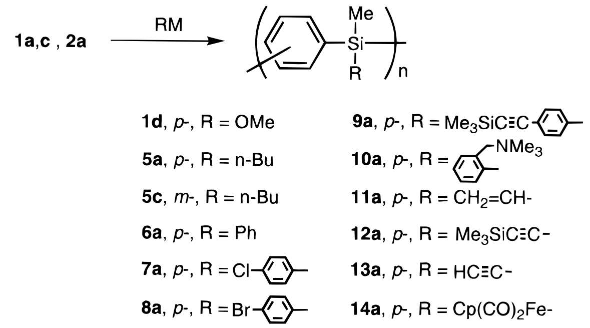
polymer	M_w (M_w/M_n)[a]	reagent	product	yield (%)[b]	M_w (M_w/M_n)[a]
1a	17 000 (1.8)	AcCl	**2a**	80	11 000 (1.9)
	14 000 (1.5)	$LiAlH_4$	**4a**	77	19 000 (1.9)
2a	11 000 (1.9)	SbF_3	**3a**	20	8500 (1.4)
1b	30 000 (1.6)	AcCl	no reacn		
	30 000 (1.6)	$LiAlH_4$	**4b**	quantitative	insoluble
1c	7 300 (1.3)	$LiAlH_4$	**4c**	79	6800 (1.7)

[a] Determined by GPC, relative to polystyrene standards. [b] After reprecipitation, except for **2a** and **4b**.

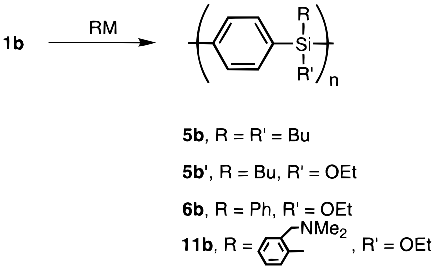
Scheme 3



Scheme 4



Scheme 5



yield. All spectral data obtained for polymer **14a** are wholly consistent with the proposed structure. The ^{29}Si NMR spectrum of **14a** shows only one signal at 33.9 ppm, characteristic of metal-substituted silicons.[11] GPC analysis of polymer **14a** indicates a bimodal molecular weight distribution which consists of two fractions corresponding to M_w = 640 000 and 20 000 in an approximate integral ratio of 6:4. The fraction with higher molecular weight distribution probably involves partly cross-linked units in the polymer backbone, while, the reaction of **2a** with $Cp(CO)_2FeK$ under the same conditions gave a 72% yield of polymer **14a** whose GPC shows monomodal molecular weight distribution with M_w = 41 000 (M_w/M_n = 4.1).

Polymer **14a** is electrochemically active. A cyclic voltammogram (CV) of a thin solid film of polymer **14a** prepared from the reaction of **2a** with $Cp(CO)_2FeK$, in a range of −0.2 to +0.7 V vs SCE reveals a couple of anodic and cathodic peaks at 0.42 and 0.30 V, respectively, presumably due to the Fe(II)–Fe(III) cycle. During repetitive scanning, the polymer film became brittle and the anodic and cathodic peak currents were reduced gradually to approximately three-quarters of their initial values at the 10th cycle. However, no obvious changes in IR spectroscopy and the GPC profile were observed for the polymer after 10 times scanning.

We also carried out CV measurements for polymers **1a**, **5a**, and **10a**, but they were found to be electrochemically inactive in a range of −0.2 to +1.2 V vs SCE.

Poly[*p*-(methoxymethylsilylene)phenylene] (**1d**) was obtained by treatment of **1a** with an excess of methanol in 91% yield, as an insoluble polymer in common organic solvents. The structure of **1d** was confirmed by IR spectrometric and elemental analysis (see Experimental Section).

To learn the chemical properties of the functional-group-substituted polymers, we carried out some reactions of polymers **8a** and **9a**. Thus, treatment of polymer **8a** with (trimethylsilyl)acetylene in the presence of a $Pd(PPh_3)_4$/CuI catalyst in a triethylamine/THF solution at room temperature gave polymer **9a′** whose NMR spectrometry indicates that two-thirds of bromophenyl group was replaced with a 4-[(trimethylsilyl)-ethynyl]phenyl group, in 79% yield (Scheme 6). On the contrary, the chlorophenyl group in polymer **7a** did not react with (trimethylsilyl)acetylene under the same conditions. In this reaction, polymer **7a** was recovered unchanged. Methanolysis of polymer **9a** afforded desilylated product **15a** in 67% yield (Scheme 7, Table 4). Further transformation by treating **15a** with *n*-butyllithium produced the corresponding lithiated polymer, which reacted readily with chlorodimethylsilane to afford polymer **16a**.

Thermal Properties of the Polymers. Thermal properties of some of the polymers thus obtained were examined by thermogravimetric analysis (TGA) in a nitrogen atmosphere. The results are summarized in Tables 1, 3, and 4. Figure 1 represents a TGA profile for polymers **5a**, **11a**, **13a**, and **15a** as a typical example. As shown in Tables 1, 3, and 4, TGA of polymers having ethoxy, butyl, and phenyl groups on the silicon atoms reveals rapid weight loss in the range of temperature 440–550 °C and the total weight loss at 1000 °C was calculated to be 42–62% based on the initial weight. TGA of polymers **10a** and **10b** having a 2-[(dimethylamino)methyl]phenyl group at the silicon atom shows that the weight loss starts at a lower temperature than those observed for phenyl-substituted polymers **6a** and **6b**. Interaction of the dimethylamino group with the silicon atom in their backbone, as indicated by upfield shifts of the ^{29}Si NMR signals, would decrease the thermal stability of the Si–phenylene bond. Polymer **14a** was found to decompose at a much lower temperature than the others, reflecting the presence of a weak Si–Fe bond. Polymers bearing a vinyl or ethynyl group **9a**, **11–13a**, **15a**, and **16a** were observed to decompose with continuous weight loss in the range of 350–800 °C including rather rapid weight loss at around 600 °C. The total weight loss of the vinyl- and ethynyl-substituted polymers at 1000 °C was determined to be 17–38% of the initial weight of the respective polymers, lower than those of the polymers having no vinyl and ethynyl groups.

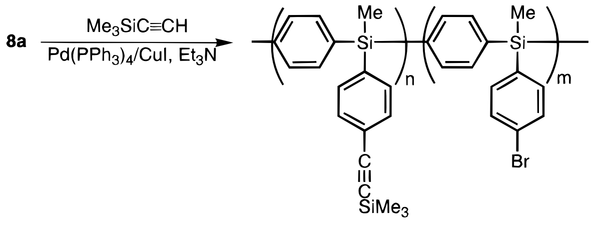
Previously, we have demonstrated that the pyrolysis of poly[(dimethylsilylene)phenylenes] proceeds with homolytic scission of the Si–phenylene bond, leading to

Table 3. Reactions of Polymers 1a–c and 2a with Nucleophiles

polymer	$M_w(M_w/M_n)^a$	reagent	product	yield(%)^b	M_w $(M_w/M_n)^a$	TGA	
						Td$_5$^{g}	weight loss (%)^h
1a	29 000 (1.7)	*n*-BuLi	**5a**	80	31 000 (1.8)	453	55
	17 000 (1.8)	PhLi	**6a**	56	16 000 (1.6)	495	47
	16 000 (2.1)	4-ClPhLi	**7a**	93	22 000 (2.9)		
	7 300 (1.6)	4-BrPhLi	**8a**	51	12 000 (2.6)		
	9 800 (1.7)	4-$Me_3SiC\equiv CPhLi$	**9a**	75	9 800 (1.5)	463	28
	13 000 (1.3)	2-$(Me_2NCH_2)PhLi$	**10a**	77	15 000^e	394	62
	17 000 (1.8)	MeONa/MeOH	**1d**	91	insoluble		
2a	3 400 (1.9)	*n*-BuMgBr	**5a′**	54^c	20 000 (1.5)		
	5 000 (1.5)	$CH_2{=}CHMgBr$	**11a**	75	18 000 (1.7)	486	29
	6 000 (1.8)	$Me_3SiC\equiv CMgBr$	**12a**	73	30 000 (2.2)	382	38
	2 100 (1.4)	$HC\equiv CNa$	**13a**	82	insoluble	452	19
	8 000 (2.4)	$Cp(CO)_2FeNa$	**14a**	51	640 000 (3.5)^f 20 000 (1.2)^f	284	29
	8 000 (2.4)	$Cp(CO)_2FeK$	**14a**	72	41 000 (4.1)	276	36
1b	16 000 (1.5)	*n*-BuLi (excess)	**5b**	57	15 000 (1.5)	437	62
	30 000 (1.6)	*n*-BuLi (1 equiv)	**5b′**	72^d	25 000 (1.7)		
	30 000 (1.6)	PhLi	**6b**	82^d	20 000 (1.8)	441	45
	30 000 (1.6)	2-$(Me_2NCH_2)PhLi$	**11b**	62^d	24 000^e	365	60
1c	7 300 (1.3)	*n*-BuLi	**5c**	93	9 900 (1.4)		

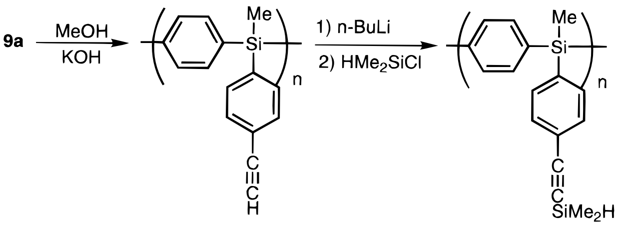
[a] Determined by GPC, relative to polystyrene standards, except for **11a** and **11b**. [b] After reprecipitation except for insoluble polymers. [c] Partial butylation product. [d] Monosubstitution product. [e] M_n determined by osmometry. [f] Bimodal distribution. [g] Temperature of 5% weight loss. [h] Weight loss at 1000 °C.

Scheme 6



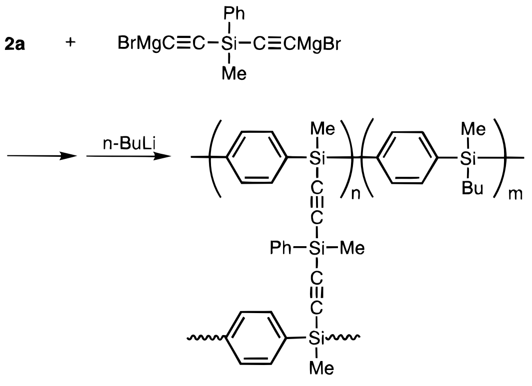
9a′ n/m = 2/1

Scheme 7



15a **16a**

Scheme 8



17a (n/m = 7/93)

the formation of silyl and phenyl radicals.[6] For the vinyl- and ethynyl-substituted polymers, the silyl and phenyl radicals are probably produced in their pyrolysis and add across the vinyl and ethynyl bond, leading to the formation of cross-linked units, which may be responsible for the low weight loss of these polymers at 1000 °C. In fact, when the pyrolysis of polymer **13a** was carried out at 500 °C for 10 min in vacuo and the resulting residue was analyzed by IR spectrometry, the absorption bands due to the stretching frequencies of an H–C≡ and C≡C bond of **13a** completely disappeared and a new absorption band at 1604 cm^{-1} probably attributed to the stretching frequencies of a silyl-substituted C=C bond[12] was observed. The present findings are in accordance with those reported by Corriu and his co-workers[13] and Barton et al.[4i] They have reported that introduction of the unsaturated groups into poly(carbosilane)s leads to the high char yields when the polymers are pyrolyzed. Recently, we have demonstrated that the presence of an Si–H bond in poly[(silylene)phenylene] also leads to an increase of the char yield.[6] However, TGA on polymer **16a** having both unsaturation and an Si–H bond shows even higher weight loss at 1000 °C than **15a** which has no Si–H bond but involves a terminal acetylene unit.

Preparation and Thermal Properties of Branched Polymers. Treatment of polymer **2a** with the di-Grignard reagent of diethynylmethylphenylsilane, followed by butyllithium gave branched polymers, as shown in Scheme 8. The properties of branched polymers prepared from the reactions of **2a** with the di-Grignard reagent with different stoichiometries are summarized in Table 4. When polymer **2a** was treated with 5% of the di-Grignard reagent, followed by treatment of the resulting mixture with *n*-butyllithium, a soluble branched polymer (**17a**) was obtained in 35% yield, after reprecipitation of the products from chloroform–ethanol. The ^1H NMR spectrum of polymer **17a** shows two singlet signals at 0.61 and 0.66 ppm in the Me–Si region, which are assignable to an Me–SiBu and Me–SiC≡C– unit, respectively, by comparison of their chemical shifts with those of polymers **5a** and **12a**. The content of the branched units in the polymer backbone was calculated to be approximately 7% by ^1H NMR spectrometric analysis of **17a**. All polymers obtained from the reactions of **2a** with more than 10% of the diGrignard reagent were shown to be insoluble in organic solvents.

As expected, TGA of the branched polymers indicates that the total weight loss of the polymers at 1000 °C decreases with the increasing degree of branches in the

Table 4. Reactions of Polymers 9a and 15a

reaction	product	yield (%)[a]	M_w (M_w/M_n)[b]	TGA Td_5[c]	 weight loss (%)[d]
9a + KOH/MeOH	**15a**	67	7000 (1.6)	568	17
15a + (1) BuLi, (2) HMe_2SiCl	**16a**	30	9800 (1.6)	490	23

[a] After reprecipitation. [b] Determined by GPC, relative to polystyrene standards. [c] Temperature of 5% weight loss. [d] Weight loss at 1000 °C.

Table 5. Properties of Branched Polymers

amt of $PhMeSi(C{\equiv}CMeBr)_2$ (mol%)	yield (%)	M_w (M_w/M_n)[b]	mp (°C)	TGA Td_5[c]	 weight loss (%)[d]
5	35[a]	73,000 (3.7)	>300	285	54
10	84	insoluble	>300	312	42
20	90	insoluble	>300	292	34

[a] After reprecipitation. [b] Determined by GPC, relative to polystyrene standards. [c] Temperature of 5% weight loss. [d] Weight loss at 1000 °C.

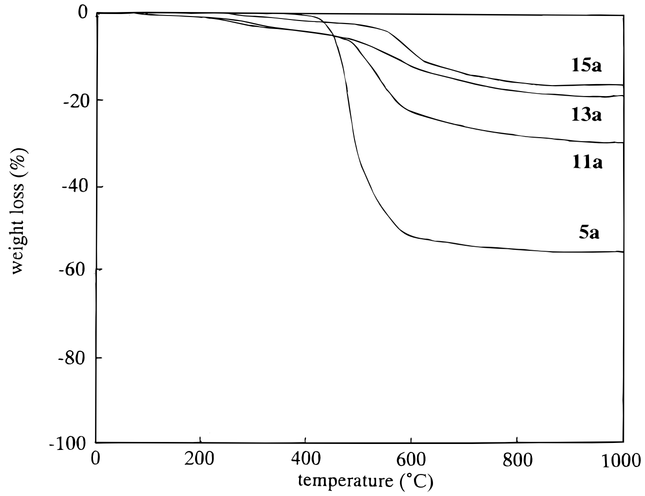


Figure 1. TGA profile for **5a**, **11a**, **13a**, and **15a** in a nitrogen atmosphere.

polymers (Table 4).

Conclusions

We have demonstrated the usefulness of poly[(ethoxy- and chlorosilylene)phenylenes] as a new class of the starting materials for the synthesis of a variously substituted poly[(silylene)phenylenes].

We have also studied thermal properties of the present polymers thus obtained by TGA and found that introduction of an unsaturated substituent as well as branching unit lead to a decrease in the weight loss at 1000 °C. The minimum weight loss at 1000 °C among the polymers is 17% of the initial weight for polymer **15a**. Further studies to evaluate detailed chemical and physical properties of the polymers and to obtain polymers with higher heat resistance are in progress.

Experimental Section

General Procedures. 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 Shimadzu QP-1000 spectrometer. TGA was carried out using a SEIKO TGA30 thermobalance.

Materials. Ether and THF were dried over sodium−potassium alloy and distilled just before use. Diethynylmethylphenylsilane was prepared as reported in the literature.[4a]

Preparation of (4-Bromophenyl)diethoxymethylsilane. To a mixture of 178.0 g (1.20 mol) of triethoxymethylsilane and 200 mL of ether was added dropwise a solution of (4-bromophenyl)magnesium bromide prepared from 235.9 g (1.00 mol) of 1,4-dibromobenzene and 24.3 g (1.00 mol) of magnesium in 700 mL of ether, over a period of 30 min at 0 °C. The resulting mixture was stirred overnight at room temperature. To the mixture was added 500 mL of hexane to precipitate magnesium salts, and then the magnesium salts were filtered off. After evaporation of the solvents, the residue was distilled under reduced pressure to give 125.2 g (43% yield) of (4-bromophenyl)diethoxymethylsilane: bp 78 °C (0.5 mmHg); MS m/z 288 (M^+); ^1H NMR (δ in $CDCl_3$) 0.33 (s, 3H, MeSi), 1.23 (t, 6H, J = 6.93 Hz, CH_3CH_2), 3.80 (q, 4H, J = 6.93 Hz, CH_2CH_3), 7.50 (s, 4H, phenylene); ^{13}C NMR (δ in $CDCl_3$) −4.4 (MeSi), 18.2 (CH_3CH_2), 58.4 (CH_2CH_3), 124.8, 130.9, 133.5, 135.5 (phenylene); IR ν_{Si-O} 1071 cm^{-1}. Anal. Calcd for $C_{11}H_{17}SiBrO_2$: C, 45.68; H, 5.92. Found: C, 45.50; H, 5.90.

Preparation of (4-Bromophenyl)triethoxysilane. To a solution of 208.3 g (1.00 mol) of tetraethoxysilane in 200 mL of ether was added dropwise a solution of (4-bromophenyl)magnesium bromide prepared from 235.9 g (1.00 mol) of 1,4-dibromobenzene and 24.3 g (1.00 mol) of magnesium in 700 mL of ether, over a period of 30 min at 0 °C. The resulting mixture was stirred overnight at room temperature. To the mixture 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 86.3 g (27% yield) of (4-bromophenyl)diethoxymethylsilane: bp 83−86 °C (0.6 mmHg); MS m/z 318 (M^+); ^1H NMR (δ in $CDCl_3$) 1.21 (t, 9H, J = 7.03 Hz, CH_3CH_2), 3.84 (q, 6H, J = 7.03 Hz, CH_2CH_3), 7.50 (s, 4H, phenylene); ^{13}C NMR (δ in $CDCl_3$) 18.1 (CH_3CH_2), 58.7 (CH_2CH_3), 125.2, 130.0, 130.9, 136.2 (phenylene); IR ν_{Si-O} 1076 cm^{-1}. Anal. Calcd for $C_{12}H_{19}SiBrO_3$: C, 45.14; H, 6.00. Found: C, 45.04; H, 6.25.

Preparation of (3-Bromophenyl)diethoxymethylsilane. To a solution of 44.9 g (0.252 mol) of triethoxymethylsilane in 200 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 150 mL of ether, over a period of 30 min at 0 °C. The resulting mixture was stirred overnight at room temperature. To the mixture 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 29.1 g (48% yield) of (3-bromophenyl)diethoxymethylsilane: bp 83 °C (1 mmHg); MS m/z 288 (M^+); ^1H NMR (δ in $CDCl_3$) 0.34 (s, 3H, MeSi), 1.23 (t, 6H, J = 6.93 Hz, CH_3CH_2), 3.80 (q, 4H, J = 6.93 Hz, CH_2CH_3), 7.24 (t, 1H, J = 7.59 Hz, phenylene H on C_5), 7.53 (br d, 2H, J = 7.59 Hz, phenylene H on C_4 and C_6), 7.73 (br s, 1H, phenylene H on C_2); ^{13}C NMR (δ in $CDCl_3$) −4.3 (MeSi), 18.3 (CH_3CH_2), 58.6 (CH_2CH_3), 122.9, 129.6, 132.3, 132.9, 136.7, 138.0 (phenylene); IR ν_{Si-O} 1079 cm^{-1}. Anal. Calcd for $C_{11}H_{17}SiBrO_2$: C, 45.68; H, 5.92. Found: C, 45.52; H, 5.86.

Preparation of Polymer 1a. In a 100 mL two-necked flask was placed 1.50 g (62.0 mmol) of magnesium and 30 mL of THF, and the flask was cooled at 0 °C. To this was added dropwise 16.2 g (56.0 mmol) of (4-bromophenyl)diethoxymethylsilane at 0 °C over a period of 30 min. The resulting mixture was heated to reflux for 64 h. To this mixture was added 60 mL of hexane to precipitate magnesium salts, and then the magnesium salts were filtered off. The solvent was evaporated, and the resulting residue was reprecipitated twice from chloroform−ethanol to give 5.3 g (58% yield) of polymer **1a**: mp 86−95 °C; $M_w = 17\,000$; $M_n = 9400$; ^{1}H NMR (δ in $CDCl_3$) 0.63 (s, 3H, MeSi), 1.22 (t, 3H, $J = 6.93$ Hz, CH_3CH_2), 3.77 (q, 2H, $J = 6.93$ Hz, CH_2CH_3), 7.60 (s, 4H, phenylene); ^{13}C NMR (δ in $CDCl_3$) −3.1 (MeSi), 18.4 (CH_3CH_2), 59.2 (CH_2CH_3), 133.5, 137.7 (phenylene); ^{29}Si NMR (δ in $CDCl_3$) −3.4; IR ν_{Si-O} 1021 cm^{-1}. Anal. Calcd for $(C_9H_{12}SiO)_n$: C, 65.80; H, 7.36. Found: C, 65.80; H, 7.29.

Preparation of Polymer 1b. To a mixture of 7.16 g (295.0 mmol) of magnesium and 150 mL of THF was added dropwise 85.2 g (268.0 mmol) of (4-bromophenyl)triethoxysilane at 0 °C over a period of 2 h. The resulting mixture was heated to reflux for 40 h. To this mixture was added 700 mL of hexane to precipitate magnesium salts, and the magnesium salts were filtered off. The solvent was evaporated, and the resulting residue was reprecipitated twice from chloroform−ethanol to give 31.6 g (61% yield) of polymer **1b**: mp 64−73 °C; $M_w = 30\,000$; $M_n = 19\,000$; ^{1}H NMR (δ in $CDCl_3$) 1.25 (t, 6H, $J = 7.03$ Hz, CH_3CH_2), 3.87 (q, 4H, $J = 7.03$ Hz, CH_2CH_3), 7.66 (s, 4H, phenylene); ^{13}C NMR (δ in $CDCl_3$) 18.3 (CH_3CH_2), 59.0 (CH_2CH_3), 134.0, 135.0 (phenylene); ^{29}Si NMR (δ in $CDCl_3$) −32.7; IR ν_{Si-O} 1079 cm^{-1}. Anal. Calcd for $(C_{10}H_{14}SiO_2)_n$: C, 61.82; H, 7.26. Found: C, 61.94; H, 7.26.

Preparation of Polymer 1c. To a mixture of 2.02 g (83.0 mmol) of magnesium and 50 mL of THF was added dropwise 20.0 g (69.2 mmol) of (3-bromophenyl)diethoxymethylsilane at room temperature over a period of 1 h. The resulting mixture was stirred at room temperature for 4 h, until almost all of (3-bromophenyl)diethoxymethylsilane was consumed. The mixture was then placed in an autoclave under an argon atmosphere and heated at 170 °C for 42 h. To the mixture was added 150 mL of hexane to precipitate magnesium salts, and the magnesium salts were filtered off. The solvent was evaporated, and the resulting residue was reprecipitated twice from chloroform−ethanol to give 3.08 g (27% yield) of polymer **1c** as viscous oil: $M_w = 10\,000$; $M_n = 5900$; ^{1}H NMR (δ in $CDCl_3$) 0.60 (s, 3H, MeSi), 1.15 (t, 3H, $J = 6.93$ Hz, CH_3CH_2), 3.72 (q, 2H, $J = 6.93$ Hz, CH_2CH_3), 7.33 (t, 1H, phenylene, $J = 7.26$ Hz), 7.58 (d, 2H, phenylene, $J = 7.26$ Hz), 7.89 (br s, 1H, phenylene); ^{13}C NMR (δ in $CDCl_3$) −2.8 (MeSi), 18.3 (CH_3-CH_2), 59.2 (CH_2CH_3), 127.1, 135.3, 135.8, 140.1 (phenylene); ^{29}Si NMR (δ in $CDCl_3$) −3.0; IR ν_{Si-O} 1084 cm^{-1}. Anal. Calcd for $(C_9H_{12}SiO)_n$: C, 65.80; H, 7.36. Found: C, 64.23; H, 7.37.

Reaction of Polymer 1a with Acetyl Chloride. A mixture of 2.23 g of polymer **1a** ($M_w = 17\,000$; $M_n = 9400$) and 90 mL of acetyl chloride was stirred at room temperature for 5 days. An excess of acetyl chloride and the resulting ethyl acetate were removed under reduced pressure to give 1.75 g (80% yield) of polymer **2a**: mp >300 °C; $M_w = 11\,000$; $M_n = 5800$; ^{1}H NMR (δ in $CDCl_3$) 0.92 (s, 3H, MeSi), 7.64 (s, 4H, phenylene); ^{13}C NMR (δ in $CDCl_3$) 0.55 (MeSi), 133.5, 136.9 (phenylene); ^{29}Si NMR (δ in $CDCl_3$) 9.9. Anal. Calcd for $(C_7H_7SiCl)_n$: C, 54.36; H, 4.56. Found: C, 54.28; H, 4.54.

Reaction of Polymer 2a with SbF$_3$. A mixture of 1.75 g of polymer **2a**, 1.00 g (5.7 mmol) of SbF_3, and 30 mL of ether was stirred at room temperature for 89 h. Insoluble polymers and antimony salts were filtered off and the solvent was evaporated. Reprecipitation of the residue from chloroform−hexane gave 0.32 g (20% yield) of polymer **3a**; mp 129−131 °C; $M_w = 8500$; $M_n = 6100$; ^{1}H NMR (δ in $CDCl_3$) 0.73 (d, 3H, $J_{H-F} = 7.26$ Hz, MeSi), 7.61 (s, 4H, phenylene); ^{13}C NMR (δ in $CDCl_3$) 2.6 (d, $J_{C-F} = 14.7$ Hz, MeSi), 133.3 (CH−phenylene), 136.7 (d, $J_{C-F} = 17.1$ Hz, q-C-phenylene); ^{29}Si NMR (δ in $CDCl_3$) 7.96 (d, $J_{Si-F} = 280.7$ Hz). Anal. Calcd for $(C_7H_7SiF)_n$: C, 60.83; H, 5.16. Found: C, 57.22; H, 5.10.[14]

Reaction of Polymer 1a with LiAlH$_4$. A mixture of 0.870 g of polymer **1a** ($M_w = 14\,000$; $M_n = 9300$), 0.060 g (1.59 mmol) of $LiAlH_4$, and 20 mL of THF was stirred at room temperature for 18 h. The resulting mixture was 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 magnesium sulfate. After evaporation of the solvents, the residue was reprecipitated from chloroform−ethanol to give 0.500 g (77% yield) of polymer **4a**: $M_w = 19\,000$; $M_n = 10\,000$. All spectral data obtained for polymer **4a** were identical with those of the authentic sample.[6]

Reaction of Polymer 1b with LiAlH$_4$. A mixture of 2.04 g of polymer **1b** ($M_w = 30\,000$; $M_n = 19\,000$), 0.240 g (6.30 mmol) of $LiAlH_4$, and 20 mL of THF was stirred at room temperature for 41 h. The resulting mixture was hydrolyzed with water, and the resulting precipitates were separated and washed twice with 1 N hydrochloric acid and then with ethanol. The precipitates were collected and dried under reduced pressure to give a quantitative yield of polymer **4b**. Polymer **4b** thus obtained was insoluble in common organic solvents. The IR spectrum obtained for polymer **4b** was identical with that of the authentic sample.[6]

Reaction of Polymer 1c with LiAlH$_4$. A mixture of 0.576 g of polymer **1c** ($M_w = 7300$; $M_n = 5600$), 0.068 g (1.80 mmol) of $LiAlH_4$, and 20 mL of THF was stirred at room temperature for 48 h. The resulting mixture was 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 magnesium sulfate. After evaporation of the solvents, the residue was reprecipitated from chloroform−ethanol to give 0.334 g (79% yield) of polymer **4c**: $M_w = 6800$; $M_n = 4000$. All spectral data obtained for polymer **4a** were identical with those of the authentic sample.[6]

Reaction of Polymer 1a with n-Butyllithium. To a solution of 0.775 g of polymer **1a** ($M_w = 29\,000$; $M_n = 17\,000$) in 10 mL of THF was added 4.3 mL (7.1 mmol) of a 1.64 M *n*-butyllithium-hexane solution. The resulting mixture was heated to reflux for 80 h and 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 magnesium sulfate. After evaporation of the solvents, the residue was reprecipitated from chloroform−isopropyl alcohol to give 0.667 g (80% yield) of polymer **5a**: mp 68−77 °C; $M_w = 31\,000$; $M_n = 17\,000$; ^{1}H NMR (δ in $CDCl_3$) 0.50 (s, 3H, MeSi), 1.03 (br t, 3H, $J = 6.26$ Hz, CH_3−Bu), 1.03−1.06 (m, 2H, CH_2−Bu), 1.32−1.34 (m, 4H, CH_2−Bu), 7.46 (s, 4H, phenylene); ^{13}C NMR (δ in $CDCl_3$) −4.7 (MeSi), 13.7, 13.8, 26.0, 26.6 (Bu), 133.7, 138.2 (phenylene); ^{29}Si NMR (δ in $CDCl_3$) −7.6. Anal. Calcd for $(C_{11}H_{16}Si)_n$: C, 74.93; H, 9.15. Found: C, 74.92; H, 9.18.

Reaction of Polymer 1a with Phenyllithium. To a solution of 0.655 g of polymer **1a** ($M_w = 17\,000$; $M_n = 9400$) in 40 mL of ether was added 4.4 mL (4.4 mmol) of a 1.00 M phenyllithium−cyclohexane solution, and the resulting mixture was stirred at room temperature for 67 h and 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 magnesium sulfate. After evaporation of the solvents, the residue was reprecipitated from chloroform−isopropyl alcohol to give 0.442 g (56% yield) of polymer **6a**: mp 218−224 °C; $M_w = 16\,000$; $M_n = 10\,000$; ^{1}H NMR (δ in $CDCl_3$) 0.79 (s, 3H, MeSi), 7.25−7.47 (m, 9H, phenyl and phenylene); ^{13}C NMR (δ in $CDCl_3$) −3.3 (MeSi), 127.8, 129.3, 134.5, 135.2, 135.8, 137.1 (phenyl and phenylene); ^{29}Si NMR (δ in $CDCl_3$) −11.4. Anal. Calcd for $(C_{13}H_{12}Si)_n$: C, 79.53; H, 6.16. Found: C, 79.49; H, 6.25.

Reaction of Polymer 1a with (4-Chlorophenyl)lithium. To a solution of 2.00 g of polymer **1a** ($M_w = 16\,000$; $M_n = 7600$) in 20 mL of ether was added dropwise (4-chlorophenyl)lithium prepared from 13.9 g (72.7 mmol) of 4-chloroiodobenzene and 1 equiv of butyllithium in 30 mL of ether at room temperature over a period of 2 h. The mixture was stirred at room temperature for 24 h and 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 magnesium sulfate. After evaporation of the solvents, the residue was reprecipitated from chloroform−ethanol to give 2.85 g (93% yield) of polymer **7a**: mp 215−224 °C; $M_w = 22\,000$; $M_n = 7500$; ^{1}H NMR (δ in $CDCl_3$) 0.80 (s, 3H, MeSi), 7.32−7.66 (m, 8H, phenylene); ^{13}C NMR (δ in $CDCl_3$) −3.6 (MeSi), 128.3, 134.0, 134.5, 136.0, 136.6, 136.9 (phenylene); ^{29}Si NMR (δ in $CDCl_3$) −11.1. Anal. Calcd for $(C_{13}H_{11}SiCl)_n$: C, 67.66; H, 4.80. Found: C, 67.51; H, 5.01.

Reaction of Polymer 1a with (4-Bromophenyl)lithium. To a solution of 5.85 g of polymer **1a** ($M_w = 7300$; $M_n = 4500$)

in 20 mL of ether was added dropwise (4-bromophenyl)lithium prepared from 8.14 g (49.9 mmol) of 4-bromoiodobenzene and 1 equiv of butyllithium in 30 mL of ether at room temperature over a period of 30 min. The mixture was stirred at room temperature for 15 h and 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 magnesium sulfate. After evaporation of the solvents, the residue was reprecipitated twice from chloroform−ethanol to give 5.34 g (51% yield) of polymer **8a**: mp 205−214 °C; $M_w = 12\,000$; $M_n = 4600$; ^{1}H NMR (δ in $CDCl_3$) 0.82 (s, 3H, MeSi), 7.36−7.45 (m, 8H, phenylene); ^{13}C NMR (δ in $CDCl_3$) −3.7 (MeSi), 124.5, 131.1, 131.2, 134.5, 136.8 (2C) (phenylene); ^{29}Si NMR (δ in $CDCl_3$) −10.9. Anal. Calcd for $(C_{13}H_{11}SiBr)_n$: C, 56.73; H, 4.03. Found: C, 56.80; H, 4.00.

Preparation of Bromo-4-[(trimethylsilyl)ethynyl]benzene. A mixture consisting of 25.30 g (89.43 mmol) of 4-bromoiodobenzene, 9.70 g (98.76 mmol) of (trimethylsilyl)acetylene, 100 mL of triethylamine, 52 mg of copper iodide (I), 104 mg of terakis(triphenylphosphine)palladium(0) was stirred at room temperature for 1 h. The resulting precipitates were filtered off, the solvent was evaporated, and then the residue was chromatographed on a silica gel column eluting with hexane to give 22.07 g (97% yield) of bromo-4-[(trimethylsilyl)ethynyl]benzene: mp 55−57 °C; MS m/z 252 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.24 (s, 9H, Me_3Si), 7.29−7.43 (m, 4H, phenylene); ^{13}C NMR (δ in $CDCl_3$) −0.1 (Me_3Si), 95.5, 103.8 ($C{\equiv}C$), 122.0, 122.7, 131.4, 133.3 (phenylene). Anal. Calcd for $(C_{15}H_{15}BrSi)_n$: C, 52.18; H, 5.17. Found: C, 51.80; H, 5.06.

Reaction of Polymer 1a with [4-[(Trimethylsilyl)ethynyl)phenyl]lithium. To a solution of [4-[(trimethylsilyl)ethynyl]phenyl]lithium prepared from 2.10 g (8.29 mmol) of bromo-4-(trimethylsilyl)benzene and 1 equiv of *tert*-butyllithium in 30 mL of ether was added dropwise a solution of 1.41 g of polymer **1a** ($M_w = 9800$; $M_n = 5800$) in 20 mL of ether at room temperature over a period of 30 min. The mixture was stirred at room temperature for 15 h and 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 magnesium sulfate. After evaporation of the solvents, the residue was reprecipitated twice from benzene−ethanol to give 1.41 g (75% yield) of polymer **9a**: mp 108−117 °C; $M_w = 11\,900$; $M_n = 8400$; ^{1}H NMR (δ in $CDCl_3$) 0.09 (s, 9H, Me_3Si), 0.80 (s, 3H, MeSi), 7.44 (br s, 8H, phenylene); ^{13}C NMR (δ in $CDCl_3$) −3.7 (MeSi), −0.0 (Me_3Si), 95.2, 105.0 ($C{\equiv}C$), 124.1, 131.1, 134.5, 135.0, 136.5, 136.9 (phenylene); ^{29}Si NMR (δ in $CDCl_3$) −17.7, −11.1; IR $\nu_{C\equiv C}$ 2158 cm^{-1}. Anal. Calcd for $(C_{18}H_{20}Si_2)_n$: C, 73.91; H, 6.89. Found: C, 72.56; H, 6.90.

Reaction of Polymer 1a with [2-[(Dimethylamino)methyl]phenyl]lithium. To a solution of 0.820 g of polymer **1a** ($M_w = 13\,000$; $M_n = 8700$) in 30 mL of ether was added dropwise [2-[(dimethylamino)methyl]phenyl]lithium prepared from 1.0 g (7.50 mmol) of *N*,*N*-dimethylbenzylamine and 1 equiv of *n*-butyllithium in 20 mL of ether at 0 °C. The resulting mixture was stirred at room temperature for 24 h and hydrolyzed with aqueous ammonium chloride. The organic layer was separated, and the aqueous layer was extracted with chloroform. The organic layer and the extracts were combined and dried over magnesium sulfate. After evaporation of the solvents, the residue was reprecipitated from chloroform−ethanol to give 0.98 g (77% yield) of polymer **10a**: mp 144−152 °C; $M_n = 15\,000$; ^{1}H NMR (δ in $CDCl_3$) 0.84 (s, 3H, MeSi), 1.80 (s, 6H MeN), 3.26 (s, 2H, CH_2N), 7.08−7.41 (m, 4H, Ph), 7.44 (s, 4H, phenylene), 7.70−7.78 (m, 1H, Ph); ^{13}C NMR (δ in $CDCl_3$) −2.3 (MeSi), 44.9 (MeN), 64.4 (CH_2N), 126.1, 128.7, 129.6, 134.1, 134.7, 137.6, 138.2, 146.3 (ring carbons); ^{29}Si NMR (δ in $CDCl_3$) −12.2. Anal. Calcd for $(C_{14}H_{21}SiON)_n$: C, 75.83; H, 7.56; N, 5.53. Found: C, 75.63; H, 7.58; N, 5.33.

Reaction of Polymer 1a with MeOH. A mixture of 1.63 g of polymer **1a** ($M_w = 17\,000$; $M_n = 9400$), 25 mL of THF, and 25 mL of methanol was heated to reflux for 19 h. The resulting white precipitates were collected, washed with methanol, and then dried under reduced pressure to give 1.36 g (91% yield) of polymer **1d**: mp >300 °C; IR ν_{Si-O} 1085 cm^{-1}. Anal. Calcd for $(C_8H_{10}SiO)_n$: C, 63.95; H, 6.71. Found: 64.07; H, 6.58.

Reaction of Polymer 1b with an Excess of *n*-Butyllithium. To a solution of 0.270 g of polymer **1b** ($M_w = 16\,000$; $M_n = 10\,000$) in 20 mL of THF was added 3.3 mL (5.4 mmol) of a 1.64 M *n*-butyllithium−hexane solution. The resulting mixture was heated to reflux for 95 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 magnesium sulfate. After evaporation of the solvents, the residue was reprecipitated from chloroform−isopropyl alcohol to give 0.170 g (57% yield) of polymer **5b**: mp 55−59 °C; $M_w = 15\,000$; $M_n = 10\,000$; ^{1}H NMR (δ in $CDCl_3$) 0.84 (br s, 6H, CH_3−Bu), 1.04−1.06 (m, 4H, CH_2-Bu), 1.33 (br s, 8H, CH_2−Bu), 7.46 (s, 4H, phenylene); ^{13}C NMR (δ in $CDCl_3$) 12.2, 13.7, 25.9, 26.7 (Bu), 134.0, 137.3 (phenylene); ^{29}Si NMR (δ in $CDCl_3$) −7.2. Anal. Calcd for $(C_{14}H_{22}Si)_n$: C, 76.99; H, 10.15. Found: C, 76.89; H, 10.10.

Reaction of Polymer 1b with 1 equiv of *n*-Butyllithium. To a solution of 1.20 g of polymer **1b** ($M_w = 30\,000$; $M_n = 19\,000$) in 30 mL of ether was added 3.8 mL (6.2 mmol) of 1.64 M *n*-butyllithium−hexane solution. The mixture was stirred at room temperature for 21 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 magnesium sulfate. After evaporation of the solvents, the residue was reprecipitated from chloroform−ethanol to give 0.920 g (72% yield) of polymer **5b′**: mp 62−70 °C; $M_w = 25\,000$; $M_n = 15\,000$; ^{1}H NMR (δ in $CDCl_3$) 0.84 (br t, 3H, $J = 6.27$ Hz, CH_3−Bu), 1.09−1.15 (m, 2H, CH_2−Bu), 1.33−1.36 (m, 4H, CH_2−Bu), 1.19 (t, 3H, $J = 6.93$ Hz, CH_3CH_2O), 3.76 (q, 2H, $J = 6.93$ Hz, OCH_2-CH_3), 7.57 (s, 4H, phenylene); ^{13}C NMR (δ in $CDCl_3$) 13.6, 13.7, 25.1, 26.5 (Bu), 18.4 (CH_3CH_2O), 59.3 (OCH_2CH_3), 133.8, 136.9 (phenylene); ^{29}Si NMR (δ in $CDCl_3$) −4.2; IR ν_{Si-O} 1079 cm^{-1}. Anal. Calcd for $(C_{12}H_{18}SiO)_n$: C, 69.85; H, 8.79. Found: C, 69.81; H, 8.78.

Reaction of Polymer 1b with Phenyllithium. To a solution of 0.740 g of polymer **1b** ($M_w = 30\,000$; $M_n = 19\,000$) in 30 mL of ether was added 4.0 mL (4.0 mmol) of a 1.00 M phenyllithium−cyclohexane solution. The mixture was stirred at room temperature for 24 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 magnesium sulfate. After evaporation of the solvents, the residue was reprecipitated from chloroform−ethanol to give 0.710 g (82% yield) of polymer **6b**: mp 189−194 °C; $M_w = 20\,000$; $M_n = 11\,000$; ^{1}H NMR (δ in $CDCl_3$) 1.20 (t, 3H, $J = 6.98$ Hz, CH_3CH_2), 3.84 (q, 2H, $J = 6.98$ Hz, CH_2CH_3), 7.37 (br s, 5H, phenyl), 7.62 (s, 4H, phenylene); ^{13}C NMR (δ in $CDCl_3$) 18.4 (CH_3CH_2), 59.8 (CH_2-CH_3), 127.8, 134.0, 134.6, 135.4, 135.9, 136.1 (phenyl and phenylene); ^{29}Si NMR (δ in $CDCl_3$) −13.8; IR ν_{Si-O} 1080 cm^{-1}. Anal. Calcd for $(C_{14}H_{14}SiO)_n$: C, 74.29; H, 6.23. Found: C, 74.28; H, 6.18.

Reaction of Polymer 1b with [2-[(Dimethylamino)methyl]phenyl]lithium. To a solution of 0.608 g of polymer **1b** ($M_w = 30\,000$; $M_n = 19\,000$) in 30 mL of ether was added dropwise [2-[(dimethylamino)methyl]phenyl]lithium prepared from 0.474 g (3.50 mmol) of *N*,*N*-dimethylbenzylamine and 1 equiv of *tert*-butyllithium in 20 mL of ether at 0 °C. The mixture was stirred at 0 °C for 4 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 magnesium sulfate. After evaporation of the solvents, the residue was reprecipitated from chloroform−ethanol to give 0.58 g (62% yield) of polymer **10b**: mp 132−138 °C; $M_n = 24\,000$; ^{1}H NMR (δ in $CDCl_3$) 1.13 (br t, 3H, CH_3CH_2, $J = 6.93$ Hz), 1.75 (s, 6H, MeN), 3.47 (s, 2H, CH_2N), 3.70 (br q, 2H, CH_2CH_3, $J = 6.93$ Hz), 7.35−7.56 (m, 3H, Ph), 7.60 (s, 4H, phenylene), 7.70−7.78 (m, 1H, Ph); ^{13}C NMR (δ in $CDCl_3$) 18.2 (CH_3CH_2), 43.9 (MeN), 59.4 (CH_2CH_3), 63.5 (CH_2N), 126.2, 128.3, 129.9, 134.0, 134.1, 136.7, 137.2, 146.5 (phenylene); ^{29}Si NMR (δ in $CDCl_3$) −16.7. Anal. Calcd for $(C_{16}H_{21}SiON)_n$: C, 72.04; H, 7.47; N, 4.94. Found: C, 72.10; H, 7.69; N, 4.79.

Reaction of Polymer 2a with *n*-Butylmagnesium Bromide. To a solution of 0.76 g of polymer **2a** ($M_w = 3400$; $M_n = 1800$) in 20 mL of THF was added 7.4 mmol of butylmagnesium bromide in 10 mL of THF. The mixture was stirred at room temperature for 24 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 magnesium sulfate. After evaporation of the solvents, the residue was reprecipitated from chloroform−isopropyl alcohol to give 0.437 g (54% yield) of polymer **5a′**: mp 64−80 °C; $M_w = 20\,000$; $M_n = 13\,000$; ^{1}H NMR (δ in $CDCl_3$) 0.51 (s, 2H, MeSiBu), 0.63 (s, 1H, MeSiO), 0.85−1.30 (m, 7.2H, Bu), 1.20 (t, 0.5H, $J = 6.93$ Hz, CH_3CH_2O), 3.70 (q, 0.3H, $J = 6.93$ Hz, CH_2O), 7.47−7.55 (m, 4H, phenylene); ^{13}C NMR (δ in $CDCl_3$) −4.7 (MeSi), −1.3 (MeSi), 13.7, 13.8, 26.0, 26.6 (Bu), 132.9, 133.1, 133.5, 133.7, 133.8, 134.4, 137.6, 138.2 (phenylene); IR ν_{O-H} 3255, ν_{Si-O} 1078 cm^{-1}.

Reaction of Polymer 2a with Vinylmagnesium Bromide. In a 200 mL two-necked flask was placed 0.40 g of polymer **2a** ($M_w = 4900$; $M_n = 3300$) and 20 mL of THF. To this was added dropwise a solution of 3.9 mmol of vinylmagnesium bromide in 3.9 mL of THF at room temperature. The resulting mixture was stirred for 15 h at room temperature and 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. Evaporation of the solvent gave viscous oil. The oil was reprecipitated from chloroform−ethanol to give 0.280 g (75% yield) of polymer **11a**: mp 170−180 °C; $M_w = 18\,000$; $M_n = 11\,000$; ^{1}H NMR (δ in $CDCl_3$) 0.60 (s, 3H, MeSi), 5.78 (dd, 1H, vinyl, $J = 20.1$, 2.6 Hz), 6.17 (dd, 1H, vinyl, $J = 14.7$, 2.6 Hz), 6.44 (dd, 1H, vinyl, $J = 20.1$, 14.7 Hz), 7.50 (br s, 4H, phenylene); ^{13}C NMR (δ in $CDCl_3$) −4.3 (MeSi), 134.1, 137.2 (phenyl and phenylene), 135.0 ($CH_2{=}C$), 135.5 ($CH{=}C$); ^{29}Si NMR (δ in $CDCl_3$) −14.8. Anal. Calcd for $(C_9H_{10}Si)_n$: C, 73.91; H, 6.89. Found: C, 64.62; H, 6.79.[14]

Reaction of Polymer 2a with [(Trimethylsilyl)ethynyl]magnesium Bromide. In a 200 mL two-necked flask was placed a solution of polymer **2a** ($M_w = 6000$; $M_n = 3300$) prepared from 1.00 g of polymer **1a** with acetyl chloride in 30 mL of THF. To this was added dropwise a solution of 8.53 mmol of [(trimethylsilyl)ethynyl]magnesium bromide in 120 mL of THF at room temperature. The resulting mixture was stirred overnight at room temperature 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. Evaporation of the solvent gave a viscous oil. The oil was reprecipitated from chloroform−ethanol to give 0.638 g (45% yield from polymer **1a**) of polymer **12a**: mp 156−168 °C; $M_w = 11\,300$; $M_n = 8100$; ^{1}H NMR (δ in $CDCl_3$) 0.21 (s, 9H, Me_3Si), 0.65 (s, 3H, MeSi), 7.62 (br s, 4H, phenylene); ^{13}C NMR (δ in $CDCl_3$) −2.2 (MeSi), −0.2 (Me_3Si), 108.9, 118.2 ($C{\equiv}C$), 133.8, 136.6 (phenylene); ^{29}Si NMR (δ in $CDCl_3$) −27.1, −18.2; IR $\nu_{C\equiv C}$ 2089 cm^{-1} (weak). Anal. Calcd for $(C_{12}H_{16}Si_2)_n$: C, 66.60; H, 7.45. Found: C, 66.80; H, 7.32.

Reaction of Polymer 2a with Sodium Acetylide. In a 50 mL Schlenk tube was placed a solution of 0.892 g of polymer **2a** ($M_w = 2100$; $M_n = 1500$) in 30 mL of THF. To this was added dropwise a solution of 8.16 mmol of sodium acetylide in 10 mL of toluene at room temperature. The resulting mixture was stirred for 45 h at room temperature and then hydrolyzed with water. The resulting precipitates were collected and washed three times with methanol to give 0.642 g (82% yield) of polymer **13a**. Polymer **13a** thus formed was insoluble in organic solvents: mp >300 °C; IR $\nu_{H-C\equiv}$ 3272, $\nu_{C\equiv C}$ 2037, ν_{Si-O} 1086 cm^{-1} (weak). Anal. Calcd for $(C_9H_8Si_2)_n$: C, 74.94; H, 5.59. Found: C, 67.42; H, 5.74.[14]

Reaction of Polymer 2a with $Cp(CO)_2FeNa$. To a solution of 0.32 g of polymer **2a** ($M_w = 8000$; $M_n = 3300$) in 10 mL of THF was added $Cp(CO)_2FeNa$[16a] prepared from 0.55 g (1.55 mmol) of $[Cp(CO)_2Fe]_2$ and 0.10 g (4.35 mmol) of sodium in 20 mL of THF. The resulting mixture was stirred at room temperature for 40 h and then hydrolyzed with saturated aqueous ammonium chloride. The organic layer was separated, and the aqueous layer was extracted with chloroform. The organic layer and the extracts were combined and dried over magnesium sulfate. After evaporation of the solvents, the residue was reprecipitated from chloroform−isopropyl alcohol to give 0.31 g (51% yield) of polymer **14a**: mp >300 °C; $M_w = 640\,000$, 20 000; $M_n = 180\,000$, 16 000; ^{1}H NMR (δ in $CDCl_3$) 0.85 (br s, 3H, MeSi), 4.60 (br s, 5H, Cp), 7.51 (s, 4H, phenylene); ^{13}C NMR (δ in $CDCl_3$) 4.9 (MeSi), 84.4 (Cp), 133.1, 143.7 (phenylene), 215.3 (CO); ^{29}Si NMR (δ in $CDCl_3$) 33.9. Anal. Calcd for $(C_{14}H_{12}SiFeO_2)_n$: C, 56.77; H, 4.08. Found: C, 53.39; H, 4.08.[14]

Reaction of Polymer 2a with $Cp(CO)_2FeK$. To a solution of 0.32 g of polymer **2a** ($M_w = 8000$; $M_n = 3300$) in 5 mL of THF was added $Cp(CO)_2FeK$[16b] prepared from 0.62 g (1.74 mmol) of $[Cp(CO)_2Fe]_2$ and 0.63 g (13.4 mmol) of $Na/K_{2.8}$ in 20 mL of THF. The resulting mixture was stirred at room temperature for 16 h and then hydrolyzed with saturated aqueous ammonium chloride. The organic layer was separated, and the aqueous layer was extracted with chloroform. The organic layer and the extracts were combined and dried over magnesium sulfate. After evaporation of the solvents, the residue was reprecipitated from chloroform−ethanol to give 0.44 g (72% yield) of polymer **14a** ($M_w = 41\,000$; $M_n = 11\,000$). All spectral data obtained for the polymer are identical with those of polymer **14a** prepared from the reaction of **2a** with $Cp(CO)_2FeNa$.

Reaction of Polymer 1c with *n*-Butyllithium. To a solution of 0.444 g of polymer **1c** ($M_w = 7300$; $M_n = 5600$) in 20 mL of THF was added 4.1 mL (6.7 mmol) of a 1.64 M *n*-butyllithium−hexane solution. The mixture was stirred at room temperature for 42 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 magnesium sulfate. Evaporation of the solvents gave 0.447 g (93% yield) of polymer **5c** as a viscous oil: $M_w = 9900$; $M_n = 7000$; ^{1}H NMR (δ in $CDCl_3$) 0.49 (s, 3H, MeSi), 0.84−1.31 (m, 9H, Bu), 7.26 (t, 1H, $J = 7.26$ Hz, H on C5), 7.46 (d, 2H, $J = 7.26$ Hz, H on C4 and C6), 7.71 (s, 1H, H on C2); ^{13}C NMR (δ in $CDCl_3$) −4.4 (MeSi), 13.7, 14.0, 26.0, 26.5 (Bu), 127.0, 134.8, 136.3, 140.4 (phenylene); ^{29}Si NMR (δ in $CDCl_3$) −7.4. Anal. Calcd for $(C_{11}H_{16}Si)_n$: C, 74.93; H, 9.15. Found: 74.85; H, 9.18.

Preparation of Polymer 9a′. A mixture consisting of 5.02 g of polymer **8a** ($M_w = 12\,000$; $M_n = 4600$), 6.07 g (61.8 mmol) of (trimethylsilyl)acetylene, 104.0 mg (0.090 mmol) of $Pd(PPh_3)_4$, 50.0 mg (0.26 mmol) of CuI, 50 mL of THF, and 80 mL of triethylamine was stirred at room temperature for 24 h. The resulting salts were filtered off. After evaporation of THF and triethylamine under reduced pressure, the residue was reprecipitated from chloroform−methanol to give 4.07 g (79% yield) of polymer **9a′**. ^{1}H and ^{13}C NMR spectra of polymer **9a′** indicate that this polymer is composed of a [*p*-(4-bromophenyl)methylsilylene]phenylene unit and *p*-{[4-[(trimethylsilyl)ethynyl]phenyl]methylsilylene}phenylene unit in an approximate ratio of 1:2.

Preparation of Polymer 15a. A mixture consisting of 0.514 g of polymer **9a** ($M_w = 11\,900$; $M_n = 8400$), 0.250 g (4.46 mmol) of KOH, 10 mL of methanol, and 15 mL of THF was stirred at room temperature for 24 h. After evaporation of THF and an excess of MeOH under reduced pressure, the residue was reprecipitated from chloroform−methanol to give 0.346 g (67% yield) of polymer **15a**: mp >300 °C; $M_w = 7000$; $M_n = 4300$; ^{1}H NMR (δ in $CDCl_3$) 0.82 (s, 3H, MeSi), 3.10 (s, 1H, $HC{\equiv}C$), 7.47 (br s, 8H, phenylene); ^{13}C NMR (δ in $CDCl_3$) −3.7 (MeSi), 78.1, 83.6 ($C{\equiv}C$), 123.1, 131.3, 133.3, 134.5, 135.1, 136.8 (phenylene); ^{29}Si NMR (δ in $CDCl_3$) −11.0; IR $\nu_{H-C\equiv C}$ 3298, $\nu_{C\equiv C}$ 2107 cm^{-1}. Anal. Calcd for $(C_{15}H_{12}Si)_n$: C, 81.76; H, 5.49. Found: C, 68.24; H, 5.49.[14]

Preparation of Polymer 16a. To a mixture of 50.0 mg of polymer **9a** ($M_w = 11\,900$; $M_n = 8400$) and 10 mL of ether was added slowly 0.2 mL (0.340 mmol) of a 1.7 M *n*-butyllithium−hexane solution at −78 °C. After the mixture was stirred for 3 h at room temperature, 32.2 mg (0.340 mmol) of chlorodimethylsilane was added to the mixture. The resulting mixture was stirred for 18 h and hydrolyzed with aqueous ammonium chloride. The organic layer and the extracts were combined and dried over magnesium sulfate. After evaporation of the solvent, the residue was reprecipitated from chloroform−methanol to give 18.9 mg (30% yield) of polymer **16a**: mp 209−

217 °C; $M_w = 9800$; $M_n = 6000$; ^{1}H NMR (δ in $CDCl_3$) 0.32 (br s, 6H, MeSiH), 0.81 (s, 3H, MeSi), 4.27 (br sept, 1H, HSi), 7.43−7.46 (m, 8H, phenylene); ^{13}C NMR (δ in $CDCl_3$) −3.7 (MeSi), −3.0 (MeSiH), 92.1, 106.3 (C≡C), 123.8, 131.1, 134.5, 134.98, 135.02, 136.8; ^{29}Si NMR (δ in $CDCl_3$) −37.4, −11.1; IR ν_{H-Si} and $\nu_{C\equiv C}$ 2160, 2140 cm^{-1}. Anal. Calcd for $(C_{17}H_{18}Si_2)_n$: C, 73.32; H, 6.51. Found: C, 65.96; H, 6.29.[14]

Preparation of a Soluble Branched Polymer (17a). To a solution of 0.38 g of **2a** ($M_w = 6000$; $M_n = 4000$) in 10 mL of THF was added dropwise 10 mmol of di-Grignard reagent prepared from 1.7 g (10 mmol) of diethynylmethylphenylsilane and an equimolar amount of ethylmagnesium bromide at room temperature. The resulting mixture was stirred at room temperature for 40 h, and to this was added 2.4 mL (3.9 mmol) of a 1.64 M *n*-butyllithium−hexane solution at 0 °C. The mixture was stirred for 2 h at the same temperature and then hydrolyzed with aqueous ammonium chloride. The organic layer and the extracts were combined and dried over magnesium sulfate. After evaporation of the solvent, the residue was reprecipitated from chloroform−ethanol to give 0.15 g (35% yield) of polymer **17a**: $M_w = 73\,000$; $M_n = 20\,000$; ^{1}H NMR (δ in $CDCl_3$) 0.49 (s, 3H, MeSiBu), 0.61 (s, 0.25H, MeSiC≡C), 0.66 (s, 0.13H, MeSiPhC≡C), 0.84−1.30 (m, 9H, Bu), 7.40−7.50 (m, 4.2H, ring protons); IR $\nu_{C\equiv C}$ 2036 cm^{-1}.

Other branched polymers were prepared by a method similar to that for **17a**.

Measurement of a Cyclic Voltammogram for Polymer 14a. CV measurement was carried out using a three-electrode system in a mixed solvent of acetonitrile:water = 1:1 containing 1 mmol % of lithium perchlorate as a supporting electrolyte. A thin solid film of polymer **14a** was prepared on the platinum working electrode by casting its chloroform solution. A saturated calomel electrode (SCE) and Pt plate were used as the reference and counter electrode, respectively. Potential was given with respect to the SCE, and the sweep rate was 10 mV/S. The current−voltage curve was measured by a Hokuto Denko HAB-151 potentiostat/galvanostat.

Thermogravimetric Analysis of the Polymers. On a platinum plate was placed 5−10 mg of a polymer, and the plate was heated from room temperature to 1000 °C at a rate of 10 °C/min in a nitrogen atmosphere. The results are shown in Tables 1 and 3−5 and Figure 1.

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