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Polymeric Organosilicon Systems. 20. Synthesis and Some Reactions of Functionalized Organosilicon Polymers, Poly[(silylene)phenylenes]

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ABSTRACT: Poly[*p*- and *m*-(methylsilylene)phenylenes] were prepared from the reaction of dichloromethylsilane with *p*- and *m*-dilithiobenzene in 11% and 31% yields, respectively. The reaction of dichlorophenylsilane with *p*-dilithiobenzene afforded poly[*p*-(phenylsilylene)phenylene] in 58% yield, while treatment of bis(chlorosilyl)benzene with *p*-dilithiobenzene gave poly[*p*-(silylene)phenylene] in 15% yield. These polymers readily react with olefins and acetylenes in the presence of a platinum catalyst to give hydrosilation products. Thermal behavior of the polymers and poly[*p*-(dimethylsilylene)phenylene] prepared from *p*-phenylenedimagnesium dibromide with dichlorodimethylsilane was also investigated by thermogravimetric analysis in air as well as in a nitrogen atmosphere.

Introduction

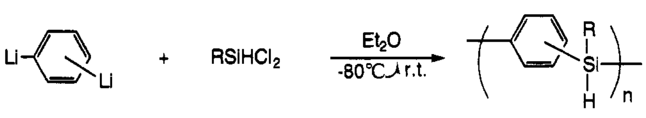
Polymers composed of an alternating arrangement of an organosilicon unit and a π-electron system are of current interest because they can be used as functionality materials, such as precursors of β-silicon carbide, unusual optical materials, and semiconducting materials.[1] Many papers concerning the preparation of these polymers have been published. The methods reported to date involve sodium condensation reactions of bis(chlorosilyl)-substituted compounds,[2] coupling reactions of dichlorosilanes with organodilithium reagents,[3] transition-metal-catalyzed reactions of organosilicon compounds,[4] and ring-opening polymerization of strained polysilacycles.[5] However, no conventional method which can be used for the preparation of the polymers composed of an organosilicon unit bearing a functional group on the silicon atom and a π-electron system has been reported, although a few papers concerning the synthesis and properties of functional group-substituted polycarbosilanes[6,7] have been published so far.

Recently, Tilley and his co-workers reported the zirconocene complex-catalyzed dehydrogenative coupling of bis(silyl)benzenes, which gives polymers composed of a phenylene and hydrosilylene unit.[8] However, they always obtain only insoluble cross-linked polymers or oligomers with low molecular weights, depending on the reaction conditions and the substituent on the silicon atom.

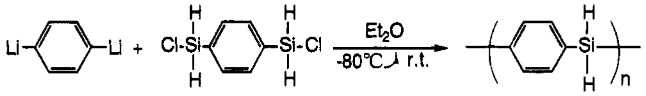
In this paper, we report the synthesis of four types of the polymers containing silicon—hydrogen bonds, poly[*m*- and *p*-(methylsilylene)phenylenes], poly[*p*-(phenylsilylene)phenylene], and poly[*p*-(silylene)phenylene]. We also report some reactions of these polymers with olefins and acetylenes in the presence of a platinum catalyst and results of thermogravimetric analysis of these polymers, compared with poly[*p*-(dimethylsilylene)phenylene].

Results and Discussion

Preparation of Poly[(silylene)phenylenes]. Treatment of dichloromethylsilane with 1 equiv of *p*-dilithiobenzene in ether, followed by hydrolysis with water, gave poly[*p*-(methylsilylene)phenylene] (**1a**) in 11% yield, after twice reprecipitation from chloroform–ethanol. The structure of **1a** was verified by spectroscopic and elemental analysis. The IR spectrum of polymer **1a** shows an absorption band at 2121 cm^{-1} due to stretching frequencies of an Si—H bond. Its ^{1}H NMR spectrum reveals a doublet, quartet, and singlet signal at 0.60, 4.91, and 7.53 ppm, due to MeSi, HSi, and phenylene protons, in addition to signals with low intensities attributed to an ethoxy group, which is probably produced from ethanolysis of the unreacted chlorosilyl group. The ^{13}C NMR spectrum shows a silyl methyl signal at −5.3 ppm and phenylene signals at 134.3 and 136.6 ppm. Its ^{29}Si NMR spectrum displays only one signal at −17.6 ppm. These results clearly indicate that polymer **1a** must have a regular alternating arrangement of a methylsilylene group and *p*-phenylene unit. The reaction of dichloromethylsilane with *m*-dilithiobenzene afforded poly[*m*-(methylsilylene)phenylene] (**2a**) in 31% yield. A similar reaction of phenyldichlorosilane with *p*-dilithiobenzene produced poly[*p*-(phenylsilylene)phenylene] (**3a**) in 58% yield. Poly[*p*-(silylene)phenylene] (**4a**) was also obtained from the reaction of *p*-bis(chlorosilyl)benzene and *p*-dilithiobenzene in 15% yield. All spectral data obtained for polymers **2a**–**4a** are consistent with the proposed structures (see Experimental Section). The combustion elemental analysis for polymers **3a** and **4a** is not in accord with their theoretical values. Carbon contents for **3a** and **4a** are always determined as values lower than their calculated ones. The formation of ceramics such as silicon carbide seems to be the reason for the lower values of carbon content. Indeed, the IR spectrum of the ash obtained from the combustion of polymer **4a** under the same conditions as elemental analysis



1a: *p*-, R=Me
2a: *m*-, R=Me
3a: *p*-, R=Ph



4a

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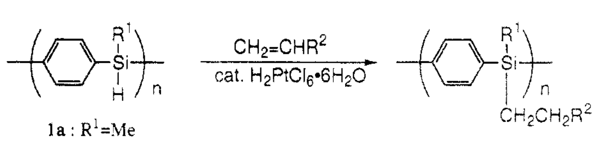
Table 1. Properties of Polymers 1a–4a

polymer	yield (%)	mp (°C)	M_w	M_n	Si—H ^{1}H NMR (ppm)	Si—H IR (cm^{-1})
1a	11	53–58	14 000	4400	4.91	2121
2a	31	viscous liquid	5 700	1600	4.88	2123
3a	58	102–105	11 000	4100	5.46	2125
4a	15	92–102	13 000	3000	4.88	2138

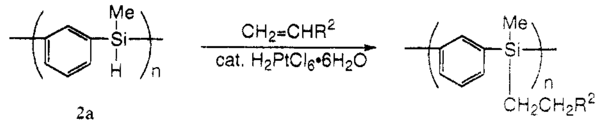
reveals absorption bands at 1209 and 798 cm^{-1} due to the vibration of the Si—C bonds, along with a strong absorption band at 1110 cm^{-1} attributed to the stretching frequencies of Si—O bonds. Some properties of polymers **1a**–**4a** are summarized in Table 1. Polymer **2a** is a viscous liquid, while polymers **1a**, **3a**, and **4a** are white solids which melt without decomposition. Polymers **1a**–**4a** are soluble in common organic solvents, such as chlorocarbons and aromatic hydrocarbons, and are slightly soluble in saturated hydrocarbons, but insoluble in alcohols. The molecular weights of these polymers were determined to be M_w = 11 000–14 000 (M_w/M_n = 2.7–4.3) for **1a**, **3a**, and **4a**, and M_w = 5700 (M_w/M_n = 3.6) for **2a** by GPC, relative to polystyrene standards. The lower yields of polymers **1a** and **4a** relative to those of **2a** and **3a** may be ascribed to the formation of insoluble polymers. IR spectra of the insoluble polymers obtained for the synthesis of **1a** and **4a** are the same as those of soluble polymers. Therefore, it seems likely that the insoluble polymer would have the alternating arrangement of a silylene group and a π-electron system in the polymer backbone.

Reactions of Polymers 1a–3a with Olefins. The Si—H bond in polymer **1a** can be readily transformed into an Si—alkyl bond by treatment with an olefin in the presence of a platinum catalyst. When the reaction of **1a** (M_w = 14 000; M_n = 4400) with a slight excess of trimethylvinylsilane in the presence of a catalytic amount of H_2PtCl_6 in benzene at room temperature was monitored by an IR spectrophotometer, an Si—H absorption band at 2121 cm^{-1} of the starting polymer **1a** decreased with increasing reaction time and disappeared after 12 h. After removal of any platinum salts by complexation with EDTA·2Na or treatment of the reaction mixture with silica gel column chromatography under an inert atmosphere, the concentrated mixture was reprecipitated from chloroform–ethanol to give poly{*p*-[methyl(2-(trimethylsilyl)ethyl]silylene]phenylene} (**1b**) in 67% yield, whose molecular weight was determined to be M_w = 31 000 (M_n = 8700) by GPC analysis, relative to polystyrene standards. Removal of the platinum salts is necessary for isolation of the polymer. The presence of the platinum salts in the mixture always leads to a cross-linking reaction of the resulting polymer in the course of isolation steps, giving an insoluble polymer, although the mechanism for the cross-linking reaction leading to the insoluble materials is still unknown. The structure of **1b** was verified by spectrometric analysis. IR and ^{1}H NMR spectra for **1b** did not show the presence of any Si—H bonds, indicating that all Si—H bonds were replaced by 2-(trimethylsilyl)ethyl groups. Furthermore, addition of an Si—H bond in polymer **1a** to trimethylvinylsilane proceeded with high regiospecificity. In fact, no signals due to the [1-(trimethylsilyl)ethyl]silylene unit were detected in its ^{1}H NMR spectrum. Similar reactions of **1a** with styrene and 1-hexene in the presence of the platinum catalyst also proceeded regiospecifically, yielding poly{*p*-[methyl(2-phenethyl)silylene]phenylene} (**1c**) and poly[*p*-(*n*-hexylmethylsilylene)phenylene] (**1d**) in 52% and 45% yields, respectively (Table 2).



1a : R^1=Me
3a : R^1=Ph

1b : R^1=Me, R^2=SiMe$_3$
1c : R^1=Me, R^2=Ph
1d : R^1=Me, R^2=$(CH_2)_3CH_3$
3b : R^1=Ph, R^2=SiMe$_3$



2a

2b : R^2=SiMe$_3$
2c : R^2=Ph

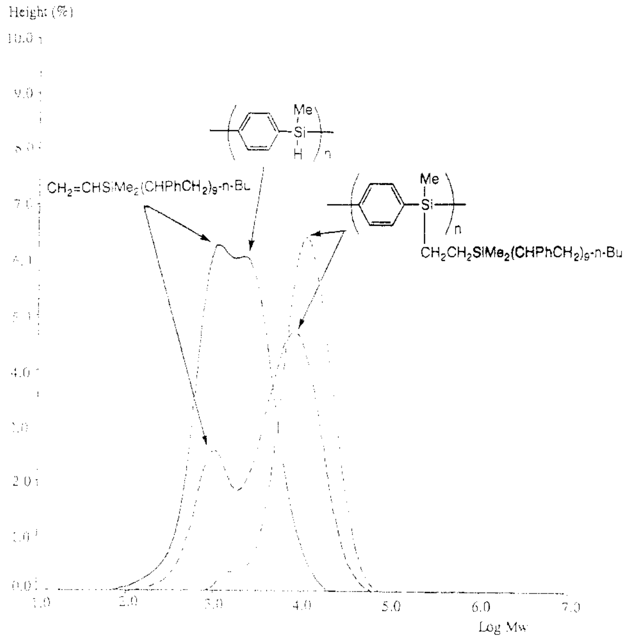
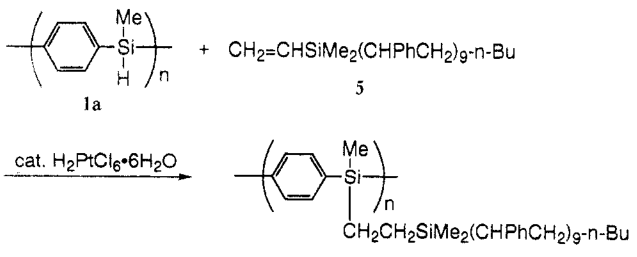


Figure 1. GPC profile of molecular weight changes for the reaction of polymer **1a** and **5** (—) before reaction, (- - -) after 23 h of reaction, and (– · –) after reprecipitation from chloroform–isopropyl alcohol.

The reaction of polymer **1a** (M_w = 5300; M_n = 2500; n = 20) with a slight excess of dimethyl(polystyryl)vinylsilane (**5**) (M_w = 1800; M_n = 1300; n = 9) in the presence of the platinum catalyst at room temperature for 23 h afforded a graft polymer (**1e**) in 67% yield. As can be seen in Figure 1, starting polymer **1a** is completely consumed after 23 h of reaction, but some polymer **5** is recovered unchanged. The molecular weight of **1e** was determined to be M_w = 19 000 (M_n = 12 000), after reprecipitation from chloroform–isopropyl alcohol. IR, ^{1}H, and ^{13}C NMR spectral data obtained for **1e** are wholly consistent with the graft structure (see Experimental Section).



1e

The reactions of polymers **2a** and **3a** with trimethylvinylsilane under the same conditions also proceeded with

Table 2. Hydrosilation of Polymers 1a–3a with Olefins

starting polymer (M_w/M_n)	olefin	yield (%)	product mp (°C)	product M_w	product M_n
1a (14 000/4400)	$CH_2{=}CHSiMe_3$	67	76–93	31 000	8700
1a (4600/1100)	$CH_2{=}CHPh$	52	66–72	25 000	5000
1a (15 000/5000)	$CH_2{=}CH(CH_2)_3CH_3$	45	35–46	30 000	8400
1a (5300/2500)	$CH_2{=}CHSiMe_2(CHPhCH_2)_9Bu$	67	59–64	20 000	12000
2a (5700/1600)	$CH_2{=}CHSiMe_3$	53	40–50	11 000	1800
2a (5700/1600)	$CH_2{=}CHPh$	85	oil	11 000	2400
3a (11 000/4100)	$CH_2{=}CHSiMe_3$	78	137–140	21 000	8800
3a (11 000/4100)	$CH_2{=}CHPh$	51[a]		390 000	12000

[a] weight %.

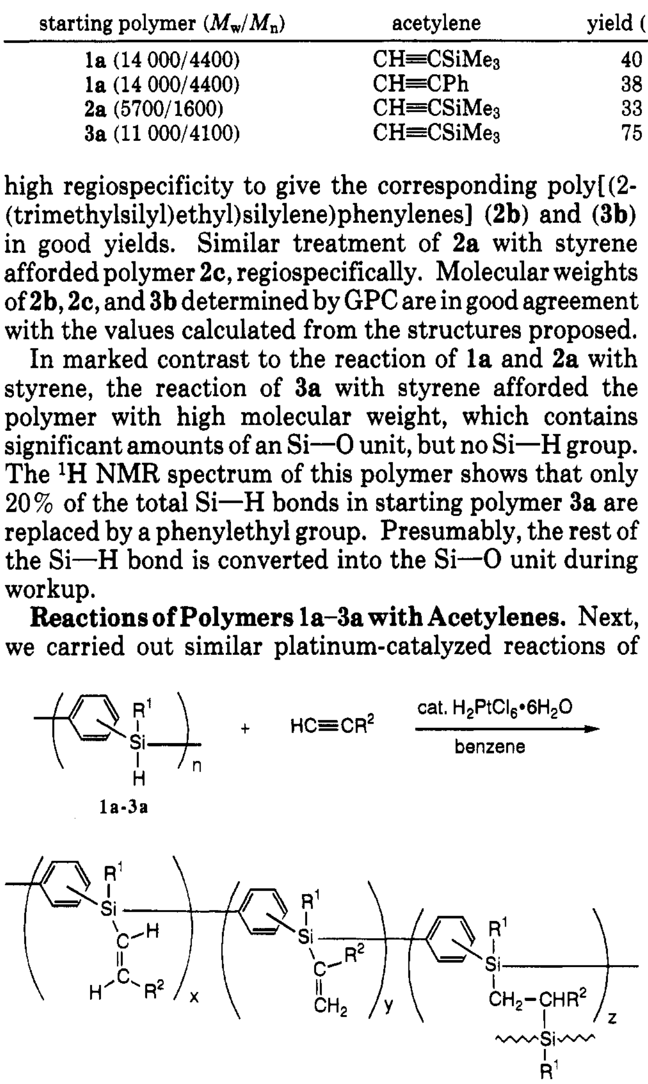
Table 3. Hydrosilylation of Polymers 1a–3a with Acetylenes

starting polymer (M_w/M_n)	acetylene	yield (%)	product mp	product M_w	product M_n	x:y:z
1a (14 000/4400)	$CH{\equiv}CSiMe_3$	40	137–143	45 000	10 000	76:19:5
1a (14 000/4400)	$CH{\equiv}CPh$	38	137–141	195 000	12 000	73:18:9
2a (5700/1600)	$CH{\equiv}CSiMe_3$	33	52–57	7 000	2 500	74:26:0
3a (11 000/4100)	$CH{\equiv}CSiMe_3$	75	178–183	19 000	8 000	92:8:0

high regiospecificity to give the corresponding poly[(2-(trimethylsilyl)ethyl)silylene)phenylenes] (**2b**) and (**3b**) in good yields. Similar treatment of **2a** with styrene afforded polymer **2c**, regiospecifically. Molecular weights of **2b**, **2c**, and **3b** determined by GPC are in good agreement with the values calculated from the structures proposed.

In marked contrast to the reaction of **1a** and **2a** with styrene, the reaction of **3a** with styrene afforded the polymer with high molecular weight, which contains significant amounts of an Si—O unit, but no Si—H group. The ^1H NMR spectrum of this polymer shows that only 20% of the total Si—H bonds in starting polymer **3a** are replaced by a phenylethyl group. Presumably, the rest of the Si—H bond is converted into the Si—O unit during workup.

Reactions of Polymers 1a–3a with Acetylenes. Next, we carried out similar platinum-catalyzed reactions of polymers **1a**–**3a** with acetylenes. Thus, treatment of **1a** (M_w = 14 000; M_n = 4400) with a slight excess of (trimethylsilyl)acetylene in the presence of a catalytic amount of H_2PtCl_6 in benzene at room temperature for 14 h gave poly{*p*-[methyl((trimethylsilyl)ethenyl)silylene]-phenylene} (**1f**) in 40% yield as white solids after reprecipitation from chloroform–ethanol. No absorption bands due to an Si—H bond in polymer **1f** thus obtained were observed in its IR spectrum. The ^1H NMR spectrum of **1f** shows two sets of a doublet with coupling constants of 25.9 and 6.2 Hz in the olefin region, which correspond to a trans and geminal coupling, respectively. ^{13}C NMR spectroscopic analysis of **1f** with the use of DEPT experiments indicates the presence of α,β- and α,α-disubstituted olefin carbons, at 145.0, 155.5 and 144.9, 165.1 ppm, respectively. These results clearly indicate that the platinum-catalyzed reaction of **1a** with (trimethylsilyl)acetylene proceeded with less regioselectivity relative to that with olefins, to give the polymer bearing both a methyl(1-(trimethylsilyl)ethenyl)silylene and methyl(2-(trimethylsilyl)ethenyl)silylene group in the polymer backbone.



1a-**3a**

1f: *p*-, R^1=Me, R^2=$SiMe_3$
1g: *p*-, R^1=Me, R^2=Ph
2f: *m*-, R^1=Me, R^2=$SiMe_3$
3f: *p*-, R^1=Ph, R^2=$SiMe_3$

That the cross-linking reaction took place in this reaction was confirmed by the fact that the ^1H NMR spectrum of polymer **1f** reveals multiplet signals at 0.77–1.98 ppm, and its ^{13}C DEPT NMR experiments show signals with low intensities at −1.92 and −2.69 ppm, due to methylene and methine carbons. These signals can be attributable to an α,α,β-trisilyl-substituted ethyl group. Presumably, the methyl((trimethylsilyl)ethenyl)silylene moieties formed from the hydrosilation of (trimethylsilyl)acetylene with polymer **1a** undergo further hydrosilation, leading to the formation of the cross-linked α,α,β-trisilyl-substituted ethyl unit. The molecular weight of polymer **1f** was determined to be M_w = 45 000 (M_n = 10 000), which is much higher than the value expected from the simple 1:1 hydrosilation product, reflecting the cross-linking reaction. Similar reaction of **1a** with phenylacetylene gave polymer **1g**, which involves methyl(1-phenethyl)silylene, methyl-(2-phenethyl)silylene, and cross-linked units. Although ^1H and ^{13}C NMR spectra for polymers **1f** and **1g** show rather complex patterns due to the presence of three kinds of units in the polymer chain, all signals observed are assignable (see Experimental Section). The ratio of three units involved in the polymer chain was determined to be approximately 15:4:1 for **1f** and 8:2:1 for **1g**, by ^1H NMR spectroscopic analysis. In Figure 2, the ^1H—^1H COSY spectrum of **1g** is presented as a typical example.

Results on the reactions of polymers **1a**–**3a** with acetylenes are summarized in Table 3. The reaction of polymers **2a** and **3a** with (trimethylsilyl)acetylene proceeded in a way different from that of **1a**. No cross-linked units were observed in the polymers. This fact may be ascribed to the steric requirement due to meta substitution for polymer **2a** and introduction of a phenyl group onto the silicon atom for polymer **3a**.

Unfortunately, all attempts to obtain soluble polymers from the platinum-catalyzed hydrosilation reactions of

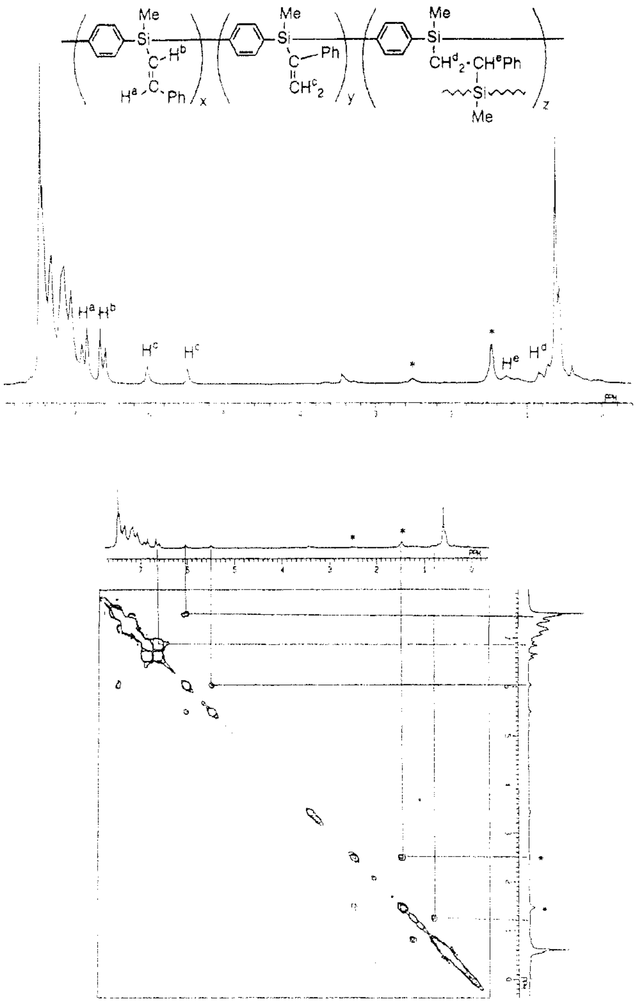
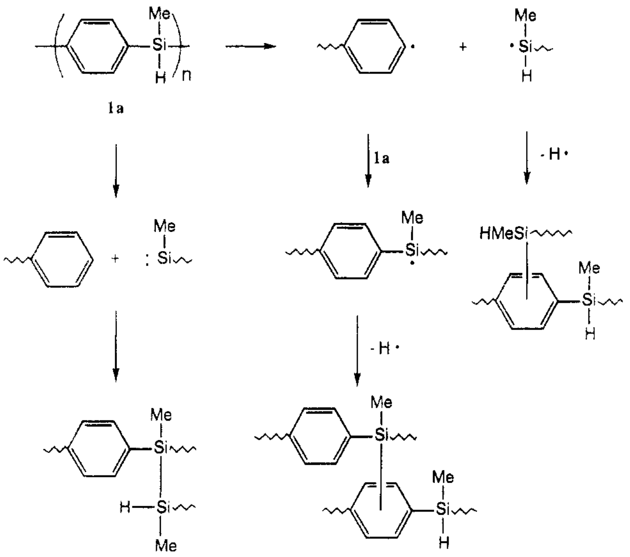


Figure 2. ^{1}H–^{1}H COSY spectrum of polymer **1g**. Asterisks indicate signals due to the terminal ethoxy group.

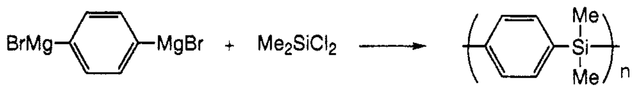
4a with olefins and acetylenes were unsuccessful. In all cases, only insoluble materials were obtained. Although IR spectra of these insoluble materials show the absence of an Si—H bond, no apparent evidence for the formation of an alkyl— or alkenyl—silicon bond in the products was obtained.

Thermogravimetric Analysis of Polymers 1a and 4a, and Poly[*p*-(dimethylsilylene)phenylene] (6). Thermogravimetric analysis (TGA) for polymers **1a** and **4a** was examined in air, as well as in a nitrogen atmosphere. The results are shown in Figure 3 A–D. Interestingly, polymer **1a** decomposed in air in a manner different from that in nitrogen. Thus, in air, the weight of polymer **1a** remains almost unchanged up to about 500 °C and then decreases continuously to reach a constant value of 55% loss of the initial weight at 800 °C. Under nitrogen, the weight of the polymer continuously decreases in a range of 330–1000 °C, and the total weight loss at 1000 °C is calculated to be 25% of the initial weight. TGA for polymer **4a** shows its weight loss with two distinguishable steps both in air and in nitrogen. One is a rapid decrease at about 320 °C and the other is continuous weight loss starting at about 600 °C. Total weight loss at 1000 °C is found to be 55% and 50% of the initial weight in air and in nitrogen, respectively.

Scheme 1



Recently, Corriu et al. reported the thermal properties of poly[(silylene)ethylenes].[7] They found that the pyrolysis of the polymer having an Si—H bond leads to higher ceramic yield than that of the polymer bearing no Si—H bonds. In order to compare the thermal behavior of the present polymers having the Si—H bonds with that of the polymer containing no Si—H bonds, we prepared poly[*p*-(dimethylsilylene)phenylene] (**6**) from the reaction of



6

p-phenylenedimagnesium dibromide and dichlorodimethylsilane and examined the thermogravimetric analysis. As shown in Figures 3E and 3F, polymer **6** shows continuous weight loss starting at 400 °C both in air and in nitrogen. The total weight loss of polymer **6** at 1000 °C is found to be 75% and 87% of the initial weight in air and in nitrogen, respectively, higher than that of polymers **1a** and **4a**, in accord with the results reported by Corriu et al.

Corriu and his co-workers have reported that the crosslinking process involving the formation of silylene species, followed by addition of the resulting silylenes to the Si—H bonds in the polymer chain, is responsible for the high ceramic yields in the pyrolysis of the polymers bearing the Si—H bonds. In order to learn more about the role of the Si—H bonds in the polymer backbone, we carried out the pyrolysis of polymers **1a** and **6** at 480 °C and analyzed the resulting volatile products by mass spectrometry. The results are shown in Figure 4 with tentative assignments of the peaks. The mass spectrum of the volatile products from the pyrolysis of **1a** reveals the presence of the peaks corresponding to oligomers with low intensities, which would be formed from cleavage of the Si—phenylene bonds in the polymer main chain (Scheme 1). On the other hand, the IR spectrum of the residual substances from the pyrolysis shows the decrease of the absorption at 2121 cm^{-1} due to the Si—H bonds. The decrease of this absorption can be understood by two independent pathways. One involves a 1,2-hydrogen shift from the silicon atom to ipso-carbon of the phenylene ring, leading to the formation of silylene intermediates, and the other comprises abstraction of hydrogen from the Si—H bonds by carbon radicals such as the phenyl radical produced from homolytic scission of the Si—phenylene bonds, giving the silyl radicals. The resulting silylenes may insert into the Si—H bonds of the polymer, leading to cross-linking, while the silyl radicals would undergo homolytic aromatic substitution onto the phenyl rings or couple with other radicals (Scheme 1). Elimination of methane from methylsilylene units might be considered for the decrease of

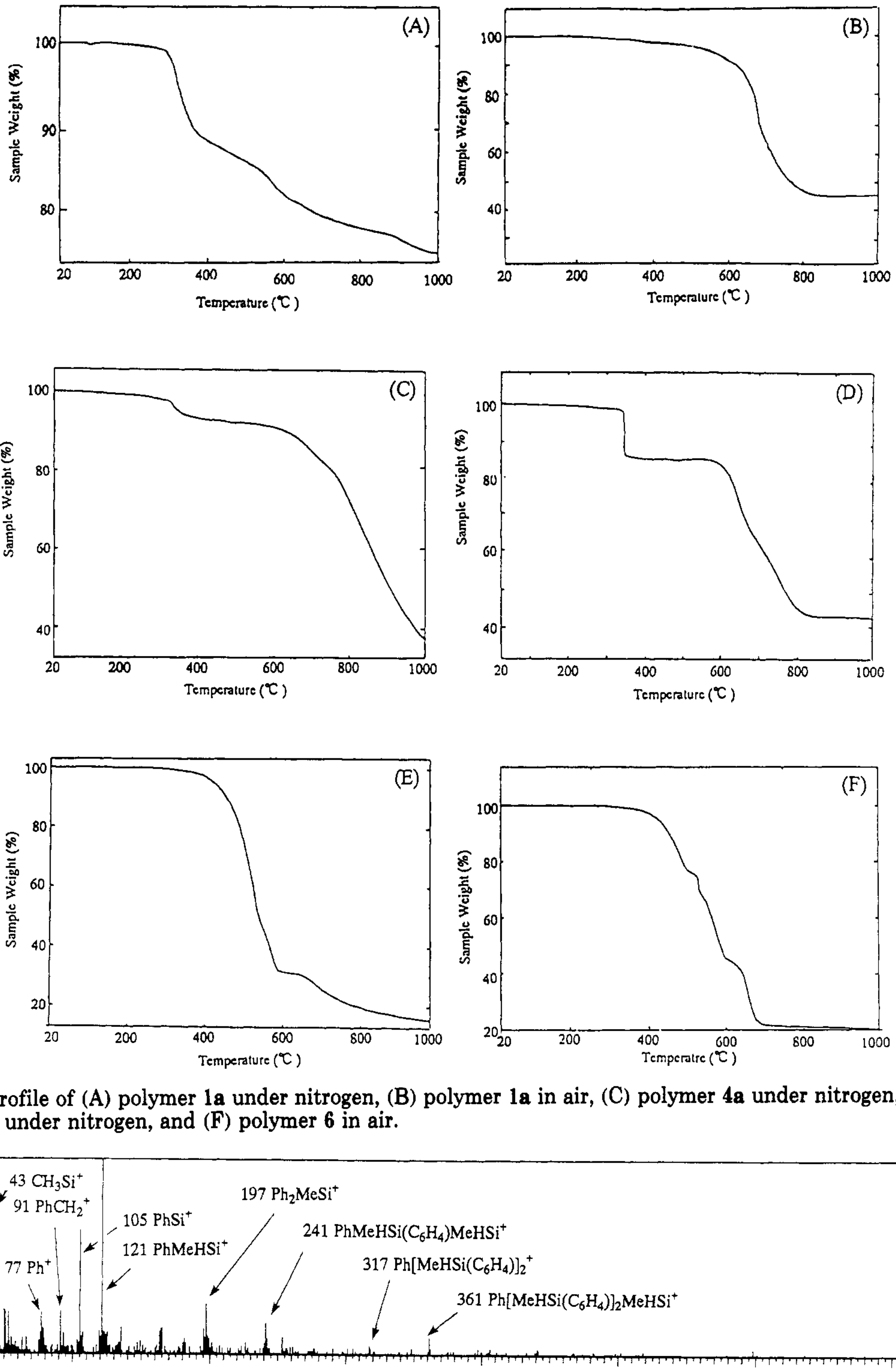


Figure 3. TGA profile of (A) polymer **1a** under nitrogen, (B) polymer **1a** in air, (C) polymer **4a** under nitrogen, (D) polymer **4a** in air, (E) polymer **6** under nitrogen, and (F) polymer **6** in air.

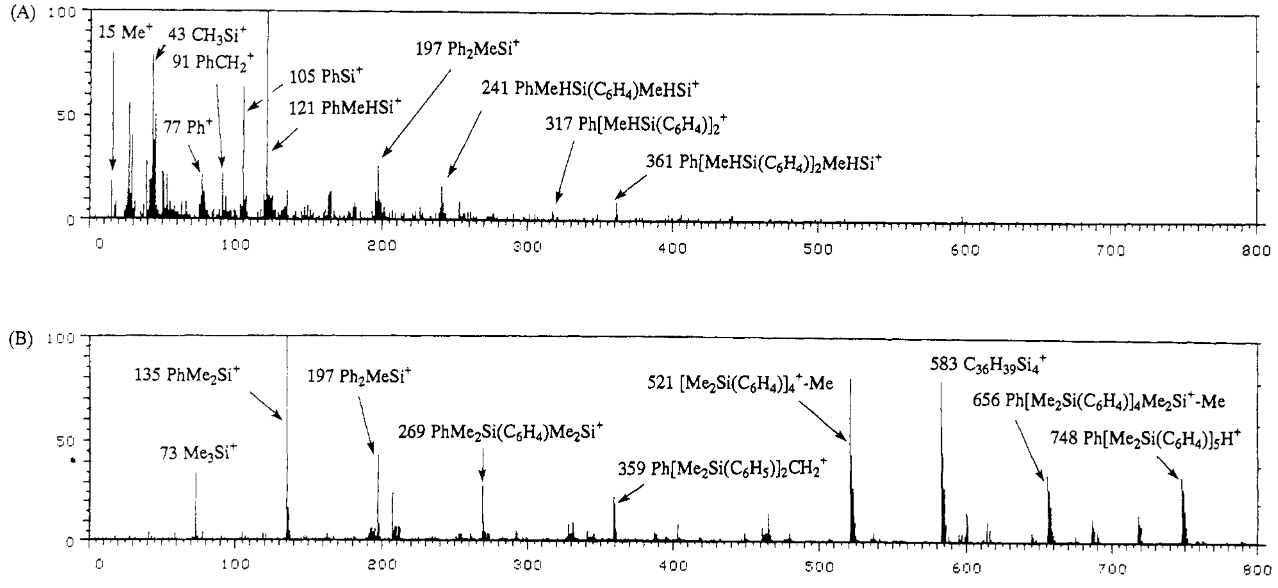


Figure 4. Mass spectra of volatile products from the pyrolysis of (A) polymer **1a** and (B) polymer **6** at 480 °C, showing tentative assignments of the main peaks.

the Si—H bonds; however, no molecular ion of methane was detected by mass spectrometric analysis of the gaseous products. The presence of a peak at *m/z* 91 assignable to $PhCH_2^+$ suggests the formation of a benzylsilyl unit.

Similar pyrolysis of **4a** under the same conditions produced only a small amount of volatile products. IR spectroscopic analysis of the residual products produced from the pyrolysis indicates again the decrease of the absorption band due to the Si—H bonds, as in the case of polymer **1a**.

The mass spectrum of the volatile products formed from the pyrolysis of **6** at 480 °C shows peaks attributed to (dimethylsilylene)phenylene oligomers with 1–5 silicon atoms with high intensities. The IR spectrum of the residual products shows almost the same as that of **6**, indicating that cleavage of the Si—phenylene takes place mainly in the pyrolysis. On the basis of the results obtained from the present pyrolysis, it seems likely that the Si—H bonds in the polymer chain play an important role for the cross-linking reaction of the polymers, presumably via the formation of silylene species and silyl radicals.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of purified argon. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a JEOL Model JNM-EX-270 spectrometer using a deuteriochloroform solution containing tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-infrared spectrometer. UV spectra were measured on a Hitachi U-3210 spectrophotometer. Thermogravimetric analysis was carried out using a SEIKO SSC5200H thermobalance.

Materials. Benzene, hexane, ether, cyclohexane, pentane, and THF were dried over sodium–potassium alloy and distilled just before use. 1,4-Bis(chlorosilyl)benzene was prepared as described in the literature.[9]

Preparation of Poly[*p*-(methylsilylene)phenylene] (1a). A mixture of 3.11 g (13.2 mmol) of *p*-dibromobenzene and 10 mL of hexane was placed in a 100 mL two-necked flask fitted with a reflux condenser and dropping funnel. To this was added 20 mL (32.2 mmol) of a 1.61 M *n*-butyllithium–hexane solution through the dropping funnel at room temperature, and the mixture was heated to reflux for 1 h. The resulting white precipitates were filtered out, washed with two portions of 10 mL of hexane, and then dried under reduced pressure to give 0.726 g (8.07 mmol, 61% yield) of *p*-dilithiobenzene.

In a 50 mL two-nicked flask was placed 5 mL of an ether solution of 0.926 g (8.05 mmol) of dichloromethylsilane, and the flask was cooled at −80 °C. To this was added a suspension of 0.726 g (8.07 mmol) of *p*-dilithiobenzene in 25 mL of ether, over a period of 15 min. The resulting mixture was allowed to warm to room temperature and stirred for 39 h. After hydrolysis of the mixture 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 solvent, the residue was reprecipitated from chloroform–ethanol to give 0.168 g (11% yield) of poly[*p*-(methylsilylene)phenylene] as white solids: mp 53–58 °C; M_w = 14 000; M_n = 4400; ^{1}H NMR (δ in CDCl$_3$) 0.60 (br d, 3H, J = 3.3 Hz, MeSi), 4.91 (br q, 1H, J = 3.6 Hz, HSi), 7.53 (br s, 4H, ring protons); ^{13}C NMR (δ in CDCl$_3$) −5.25 (MeSi), 134.3, 136.6 (ring carbons); ^{29}Si NMR (δ in CDCl$_3$) −17.6; IR $\nu_{\text{Si-H}}$ 2121 cm^{-1}; UV (THF) $\lambda_{\max}$ 208 (ϵ 28 000), 237 (ϵ 22 000) nm. Anal. Calcd for $(C_7H_8Si)_n$: C, 69.93; H, 6.71. Found: C, 70.12; H, 6.96.

Preparation of Poly[*m*-(methylsilylene)phenylene] (2a). In a 200 mL two-necked flask was placed 20 mL of an ether solution of 0.970 g (8.43 mmol) of dichloromethylsilane, and the flask was cooled at −80 °C. To this was added a suspension of 8.43 mmol of *m*-dilithiobenzene prepared by treatment of *m*-dibromobenzene with 2 equiv of *n*-butyllithium in 70 mL of ether at room temperature over a period of 35 min. The resulting mixture was allowed to warm to room temperature, stirred for 19 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 solvent, the residue was dissolved in 10 mL of chloroform and poured into 200 mL of methanol. A pale yellow viscous oil was separated from the methanol solution which was collected by decantation and washed with two portions of 50 mL of methanol. Vacuum drying of the oily substance gave 845 mg (31% yield) of poly[*m*-(methylsilylene)phenylene]: M_w = 5700; M_n = 1600; ^{1}H NMR (δ in CDCl$_3$) 0.55 (br d, 3H, J = 3.6 Hz, MeSi), 4.88 (br q, 1H, J = 3.6 Hz, HSi), 7.14–7.83 (m, 4H, ring protons); ^{13}C NMR (δ in CDCl$_3$) −4.96 (MeSi), 134.7, 135.8, 136.0, 141.2 (ring carbons); IR $\nu_{\text{Si-H}}$ 2123 cm^{-1}; UV (film) $\lambda_{\max}$ 256 nm. Anal. Calcd for $(C_7H_8Si)_n$: C, 69.93; H, 6.71. Found: C, 69.75; H, 6.74.

Preparation of Poly[*p*-(phenylsilylene)phenylene] (3a). In a 50 mL two-necked flask was placed 2.30 g (13.0 mmol) of phenyldichlorosilane, and the flask was cooled at −80 °C. To this was added a suspension of 13.0 mmol of *p*-dilithiobenzene in 30 mL of ether prepared as above over a period of 25 min. The resulting mixture was allowed to warm to room temperature, stirred for 25 h, and then hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with benzene. The organic layer and the extracts were combined and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was reprecipitated from chloroform–ethanol, then from chloroform–hexane, and finally from chloroform–isopropyl alcohol to give 1.45 g (58% yield) of poly[*p*-(phenylsilylene)phenylene] as white solids: mp 102–105 °C; M_w = 11 000; M_n = 4100; ^{1}H NMR (δ in CDCl$_3$) 5.46 (br s, 1H, HSi), 7.38 (br s, 4H, phenylene ring protons), 7.58 (br s, 6H, phenyl ring protons); ^{13}C NMR (δ in CDCl$_3$) 128.1, 130.0, 132.7, 135.0, 135.1, 135.3, 135.9 (ring carbons); IR $\nu_{\text{Si-H}}$ 2125 cm^{-1}; UV (THF) $\lambda_{\max}$ 209 (ϵ 65 000), 233 (ϵ 47 000) nm. Anal. Calcd for $(C_{12}H_{10}Si)_n$: C, 79.06; H, 5.53. Found: C, 77.53; H, 5.58.

Preparation of Poly(*p*-silylenephenylene) (4a). In a 100 mL two-necked flask was placed 20 mL of an ether solution of 2.405 g (11.6 mmol) of *p*-bis(chlorosilyl)benzene, and the flask was cooled at −80 °C. To this was added a suspension of 11.6 mmol of *p*-dilithiobenzene in 40 mL of ether over a period of 30 min. The resulting mixture was allowed to warm to room temperature, stirred for 20 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 solvent, the residue was reprecipitated twice from chloroform–hexane to give 0.348 g (15% yield) of poly[*p*-(silylene)phenylene] as white solids: mp 92–102 °C; M_w = 13 000; M_n = 3000; ^{1}H NMR (δ in CDCl$_3$) 4.88 (br s, 2H, HSi), 7.57 (br s, 4H, ring protons); ^{13}C NMR (δ in CDCl$_3$) 133.3, 135.2 (ring carbons); IR $\nu_{\text{Si-H}}$ 2138 cm^{-1}; UV (film) $\lambda_{\max}$ 207, 243, 279 nm. Anal. Calcd for $(C_6H_6Si)_n$: C, 67.86; H, 5.69. Found: C, 32.67;[10] H, 5.36.

Reaction of Polymer 1a with Trimethylvinylsilane. A mixture of 70.8 mg of **1a** (M_w = 14 000; M_n = 4400), 83.1 mg (0.829 mmol) of trimethylvinylsilane, and 7.1 mg (0.014 mmol) of $H_2PtCl_6 \cdot 6H_2O$ in 1.0 mL of benzene was stirred at room temperature for 12 h. The solvent was evaporated, the residue was chromatographed on a silica gel column eluting with ethyl acetate to remove any platinum complexes, and then the products were reprecipitated from chloroform–methanol to give 96.9 mg (67% yield) of polymer **1b**: mp 76–93 °C; M_w = 31 000; M_n = 8700; ^{1}H NMR (δ in CDCl$_3$) 0.06 (br s, 9H, Me$_3$Si), 0.48–0.59 (m, 2H, CH$_2$), 0.62 (br s, 3H, MeSi), 1.00–1.10 (m, 2H, CH$_2$), 7.58 (br s, 4H, ring protons); ^{13}C NMR (δ in CDCl$_3$) −5.2 (MeSi), −2.2 (Me$_3$Si), 6.2, 8.8 (CH$_2$), 133.8, 138.1 (ring carbons); UV (film) $\lambda_{\max}$ 236 nm. Anal. Calcd for $(C_{12}H_{10}Si_2)_n$: C, 65.38; H, 9.14. Found: C, 63.42; H, 9.37.

Reaction of Polymer 1a with Styrene. A mixture of 86.4 mg of **1a** (M_w = 4600; M_n = 1100), 0.137 g (1.317 mmol) of styrene, and 18.4 mg (0.036 mmol) of $H_2PtCl_6 \cdot 6H_2O$ in 0.5 mL of benzene was stirred at room temperature for 3 h. The resulting mixture was poured into 100 mL of methanol, and the product was reprecipitated from benzene–methanol to give 88.3 mg (52% yield) of polymer **1c**: mp 66–72 °C; M_w = 25 000; M_n = 5000; ^{1}H NMR (δ in CDCl$_3$) 0.45 (br s, 3H, MeSi), 1.28–1.31 (m, 2H, CH$_2$SiMe), 2.55–2.58 (m, 2H, CH$_2$Ph), 6.85–7.16 (m, 5H, phenyl ring protons), 7.42 (br s, 4H, phenylene ring protons); ^{13}C NMR (δ in CDCl$_3$) −4.67 (MeSi), 16.0 (CH$_2$SiMe), 29.8 (CH$_2$Ph), 125.6, 127.7 (2C), 128.3 (2C), 133.8 (2C), 137.8, 144.7 (ring carbons); UV (film) $\lambda_{\max}$ 239 nm. Anal. Calcd for $(C_{15}H_{16}Si)_n$: C, 80.30; H, 7.19. Found: C, 78.99; H, 7.03.

Reaction of Polymer 1a with 1-Hexene. A mixture of 71.6 mg of **1a** (M_w = 15 000; M_n = 5000), 72.8 mg (0.865 mmol) of

1-hexene, and 12.4 mg (0.024 mmol) of $H_2PtCl_6\cdot 6H_2O$ in 2.0 mL of pentane was stirred at 0 °C for 2 h, and then the temperature of the mixture was kept at 10 °C for 65 h. To this was added 100 mg of EDTA·2Na, and the mixture was stirred for 3 h at 10 °C. The EDTA salts were filtered off, and the solvent was evaporated under reduced pressure to give 61.0 mg (45% yield) of polymer **1d**: mp 35–46 °C; $M_w = 30\,000$; $M_n = 8400$; ^{1}H NMR (δ in $CDCl_3$) 0.54 (br s, 3H, MeSi), 0.78–1.46 (m, 12H, *n*-hexyl), 7.50 (br s, 4H, ring protons); ^{13}C NMR (δ in $CDCl_3$) −4.62 (MeSi), 14.1, 22.6, 23.8, 31.4, 33.3 (*n*-hexyl), 133.7, 138.2 (ring carbons); UV (film) λ_{max} 237, 266 nm. Anal. Calcd for $(C_{13}H_{20}Si)_n$: C, 76.40; H, 9.86. Found: C, 72.48; H, 10.09.

Preparation of Dimethyl(polystyryl)vinylsilane (nBu-$(CH_2CHPh)_9SiMe_2CH{=}CH_2$) (5). To a solution of 2.0 mL (17.5 mmol) of styrene in 10 mL of cyclohexane was added 1.29 mL (2.1 mmol) of a 1.63 M *n*-butyllithium–hexane solution at 0 °C. The resulting mixture was stirred at room temperature for 30 min. To this was added 1 mL of THF and 0.34 mL (2.49 mmol) of chlorodimethylvinylsilane, and the resulting mixture was stirred for additional 2 h at room temperature. The 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 anhydrous magnesium sulfate. The solvent was evaporated, and the residue was reprecipitated from chloroform–hexane. The white precipitates were filtered off, and the filtrate was concentrated and reprecipitated from chloroform–methanol to give 1.24 g (59% yield) of compound **5**: mp 36–46 °C; $M_w = 1800$; $M_n = 1300$; ^{1}H NMR (δ in $CDCl_3$) −0.22 to +0.05 (m, 6H, Me_2Si), 0.72–2.48 (m, 42H, CH_2CHPh and Bu), 5.41–5.64 (m, 1H, olefin protons), 5.83–6.08 (m, 2H, olefin protons), 6.31–7.37 (m, 46H, ring protons); ^{13}C NMR (δ in $CDCl_3$) −5.5, −5.4, −5.3, −4.6, −4.4 (Me_2Si), 14.0, 22.5, 26.9, 31.8 (Bu), 33.0–47.0 (m, CH_2CHPh), 124.2, 125.6, 127.6, 127.9, 128.0 (ring CH), 132.4, 137.4 (olefin carbons), 142.8 (Ph–CSi ipso-carbon), 145.6–147.1 (m, phenyl ipso-carbons); UV (film) λ_{max} 262, 269 nm. Anal. Calcd for $C_{80}H_{90}Si$: C, 89.00; H, 8.40. Found: C, 88.61; H, 8.55.

Reaction of Polymer 1a with 5. A mixture of 60.0 mg of **1a** ($M_w = 5300$; $M_n = 2500$), 0.773 g (0.716 mmol) of dimethyl(polystyryl)vinylsilane, and 5.2 mg (0.010 mmol) of $H_2PtCl_6\cdot 6H_2O$ in 3.0 mL of toluene was stirred at room temperature for 23 h. The resulting mixture was poured into 200 mL of methanol, and the resulting solids were reprecipitated from chloroform–isopropyl alcohol to give 447 mg (67% yield) of polymer **1e**: mp 59–64 °C; $M_w = 18\,000$; $M_n = 12\,000$; ^{1}H NMR (δ in $CDCl_3$) −0.40 to +0.12 (m, 6H, Me_2Si), 0.12–0.49 (m, 4H, CH_2Si), 0.61 (br s, 3H, MeSi), 0.66–2.40 (m, 37H, CH_2CHPh and Bu), 6.29–7.66 (m, 43H, ring protons); ^{13}C NMR (δ in $CDCl_3$) −5.95 to −4.50 (m, Me_2Si and MeSi), 6.0 (CH_2Si), 14.0, 22.4, 26.9, 31.8 (Bu), 35.0–47.0 (m, polystyryl), 124.1, 125.6, 127.7, 128.0 (phenyl ring CH), 133.5, 133.7, 133.8 (phenylene ring CH), 144.5–146.6 (m, phenyl and phenylene ipso-carbons); UV (film) λ_{max} 262, 269 nm. Anal. Calcd for $(C_{87}H_{98}Si_2)_n$: C, 87.09; H, 8.23. Found: C, 85.93; H, 8.18.

Reaction of Polymer 2a with Trimethylvinylsilane. A mixture of 145 mg of **2a** ($M_w = 5700$; $M_n = 1600$), 173 mg (1.73 mmol) of trimethylvinylsilane, and 3.1 mg (0.006 mmol) of $H_2PtCl_6\cdot 6H_2O$ in 1.0 mL of benzene was stirred at room temperature for 23 h. The resulting mixture was poured into 100 mL of ethanol, and the precipitates were collected to give 156.7 mg (53% yield) of polymer **2b**: mp 42–44 °C; $M_w = 11\,000$; $M_n = 1800$; ^{1}H NMR (δ in $CDCl_3$) 0.05 (s, 9H, Me_3Si), 0.18 (br m, 2H, CH_2SiMe_3), 0.61 (br s, 3H, MeSi), 1.01 (br m, 2H, CH_2SiMe), 7.39–7.84 (m, 4H, ring protons); ^{13}C NMR (δ in $CDCl_3$) −4.9 (MeSi), −2.2 (Me_3Si), 6.4, 8.9 (CH_2), 127.1, 135.3, 136.4, 140.4 (ring carbons); UV (film) λ_{max} 238, 260 nm. Anal. Calcd for $(C_{12}H_{20}Si_2)_n$: C, 65.38; H, 9.14. Found: C, 65.36; H, 8.92.

Reaction of Polymer 2a with Styrene. A mixture of 98.5 mg of **2a** ($M_w = 5700$; $M_n = 1600$), 0.208 g (2.00 mmol) or styrene, and 4.3 mg (0.0083 mmol) of $H_2PtCl_6\cdot 6H_2O$ in 0.6 mL of benzene was stirred at room temperature for 17 h. To this was added about 100 mg of EDTA·2Na, and the resulting mixture was stirred for 4 h. The EDTA salts were filtered off, and the solvent was evaporated under reduced pressure to give 164 mg (85% yield) of polymer **2c**: mp 74–77 °C; $M_w = 11\,000$; $M_n = 2400$; ^{1}H NMR (δ in $CDCl_3$) 0.14–1.01 (m, 3H, MeSi), 1.17–1.51 (m, 2H, CH_2SiMe), 2.39–2.77 (m, 2H, CH_2Ph), 6.77–7.93 (m, 9H, ring protons), ^{13}C NMR (δ in $CDCl_3$) −4.4 (MeSi), 16.5 (CH_2SiMe), 30.0 (CH_2Ph), 125.6, 127.3, 127.7, 128.3, 135.0, 135.5, 136.0, 144.9 (ring carbons); UV (film) λ_{max} 216, 256 nm. Anal. Calcd for $(C_{15}H_{16}Si)_n$: C, 80.30; H, 7.19. Found: C, 74.30; H, 6.50.

Reaction of Polymer 3a with Trimethylvinylsilane. A mixture of 76.1 mg of **3a** ($M_w = 11\,000$; $M_n = 4100$), 60.9 mg (0.608 mmol) of trimethylvinylsilane, and 6.7 mg (0.013 mmol) of $H_2PtCl_6\cdot 6H_2O$ in 1.0 mL of benzene was stirred at room temperature for 83 h. The resulting mixture was poured into 100 mL of ethanol, and the precipitates were collected to give 89.2 mg (78% yield) of polymer **3b**: mp 137–140 °C; $M_w = 21\,000$; $M_n = 8800$; ^{1}H NMR (δ in $CDCl_3$) −0.05 (s, 9H, Me_3Si), 0.49–0.61 (m, 2H, CH_2SiMe_3), 1.17–1.30 (m, 2H, CH_2SiPh), 7.35 (br s, 4H, phenylene ring protons), 7.50 (br s, 5H, phenyl ring protons); ^{13}C NMR (δ in $CDCl_3$) −2.21 (Me_3Si), 5.27, 9.01 (CH_2), 127.8, 129.3, 135.0, 135.7, 136.3 (ring carbons); UV (film) λ_{max} 266 nm. Anal. Calcd for $(C_{17}H_{22}Si_2)_n$: C, 72.27; H, 7.85. Found: C, 70.67; H, 7.52.

Reaction of Polymer 3a with Styrene. A mixture of 74.8 mg of **3a** ($M_w = 11\,000$; $M_n = 4100$), 80.1 mg (0.769 mmol) of styrene, and 2.2 mg (0.0043 mmol) of $H_2PtCl_6\cdot 6H_2O$ in 1.0 mL of benzene was stirred at room temperature for 11 h. The resulting mixture was poured into 100 mL of ethanol to give 78.6 mg of polymer as dark gray solids: $M_w = 390\,000$; $M_n = 12\,000$; ^{1}H NMR (δ in $CDCl_3$) 1.18 (br s), 1.29–1.73 (m), 1.62 (m), 2.72 (br s), 3.81 (br s), 7.33–7.55 (m); ^{13}C NMR (δ in $CDCl_3$) 18.4, 29.9, 126.7–128.5, 134.0–136.4. Anal. Calcd for $(C_{20}H_{18}Si)_n$: C, 83.86; H, 6.33. Found: C, 72.91; H, 5.83.

Reaction of Polymer 1a with Trimethylsilylacetylene. A mixture of 70.0 mg of **1a** ($M_w = 14\,000$; $M_n = 4400$), 72.3 mg (0.736 mmol) of trimethylsilylacetylene, and 7.9 mg (0.015 mmol) of $H_2PtCl_6\cdot 6H_2O$ in 0.7 mL of benzene was stirred at room temperature for 14 h. To this was added about 100 mg of EDTA·2Na, and the mixture was stirred for 3 h. The EDTA salts were filtered off, and the solvent was evaporated under reduced pressure. Then the residue was reprecipitated from chloroform–methanol to give 55.9 mg (40% yield) of polymer **1f**: mp 137–143 °C; $M_w = 45\,000$; $M_n = 10\,000$; ^{1}H NMR (δ in $CDCl_3$) −0.05 (s, 0.6H, Me_3SiCH_2), −0.04 (s, 1.8H, $Me_3SiC{=}$), 0.08 (s, 7.2H, $Me_3SiCH{=}C$), 0.60 (s, 3H, $MeSiCH{=}$ and $MeSiC{=}$), 0.67 (s, 0.2H, $MeSiCH_2$), 0.77–0.96 (m, 0.16H, CH_2), 1.22–1.41 (m, 0.08H, CH), 6.24 (d, 0.20H, $J = 6.2$ Hz, $H_2C{=}$), 6.52 (d, 0.20H, $J = 6.2$ Hz, $H_2C{=}$), 6.78 (d, 0.80H, $J = 25.9$ Hz, $HC{=}CH$), 6.89 (d, 0.80H, $J = 25.9$ Hz, $HC{=}CH$), 7.50 (m, 4.6H, ring protons); ^{13}C NMR (δ in $CDCl_3$) −4.33, −4.27 (MeSi), −2.69 (CH), −1.92 (CH_2), −1.60, −0.23 (Me_3Si), 144.9 ($H_2C{=}CSiMe_3$), 145.3 ($HC{=}CHSiMe_3$), 155.5 ($CH{=}CHSiMe_3$), 165.1 ($C(SiMe_3){=}CH_2$), 134.0, 134.1, 134.4, 134.5, 137.6 (ring carbons); UV (film) λ_{max} 228 nm. Anal. Calcd for $(C_{17}H_{20}Si_2)_n$: C, 72.79; H, 7.19. Found: C, 71.58; H, 7.34.

Reaction of Polymer 1a with Phenylacetylene. A mixture of 73.1 mg of **1a** ($M_w = 14\,000$; $M_n = 4400$), 67.2 mg (0.658 mmol) of phenylacetylene, and 7.4 mg (0.014 mmol) of $H_2PtCl_6\cdot 6H_2O$ in 0.7 mL of benzene was stirred at room temperature for 20 h. To this was added about 100 mg of EDTA·2Na, and the resulting mixture was stirred for 3 h. The EDTA salts were filtered off, and the solvent was evaporated under reduced pressure. The residue was reprecipitated from chloroform–methanol and then from chloroform–ethanol to give 56.7 mg (38% yield) of polymer **1g**: mp 137–141 °C; $M_w = 195\,000$; $M_n = 12\,000$; ^{1}H NMR (δ in $CDCl_3$) 0.34 (br s, 0.3H, MeSiCH), 0.52 (br s, 0.6H, $MeSiC{=}CH_2$), 0.58 (br s, 2.4H, $MeSiCH{=}CH$), 0.84–0.96 (m, 0.2H, CH_2), 1.16–1.31 (m, 0.1H, CH), 5.47, 6.00 (br s, 0.4H, $CH_2{=}$), 6.61, 6.86 (d, 1.6H, $J = 19$ Hz, $CH{=}CH$), 7.04–7.46 (m, 10.5H, ring protons); ^{13}C NMR (δ in $CDCl_3$) −3.9, −3.5 (MeSi), 14.5 (CH), 22.6 (CH_2), 124.6 ($CH{=}CHPh$), 132.0 ($CH_2{=}CPh$), 126.6, 127.1, 127.5, 127.7, 127.9, 128.1, 128.3, 128.5, 133.6, 133.9, 134.2, 134.5, 134.6, 134.9, 137.0, 137.1, 137.5, 138.0 (ring carbons), 143.8 ($CPh{=}CH_2$), 147.2 ($CHPh{=}CH$); UV (film) λ_{max} 242, 262 nm. Anal. Calcd for $(C_{15}H_{14}Si)_n$: C, 81.02; H, 6.35. Found: C, 80.29; H, 6.42.

Reaction of Polymer 2a with Trimethylsilylacetylene. A mixture of 73.0 mg of **2a** ($M_w = 5700$; $M_n = 1600$), 52.9 mg (0.713 mmol) of trimethylsilylacetylene, and 7.9 mg (0.015 mmol) of $H_2PtCl_6\cdot 6H_2O$ in 0.7 mL of benzene was stirred at room temperature for 14 h. To this was added about 100 mg of EDTA·2Na, and the mixture was stirred for 9 h. The EDTA salts were filtered off and the solvent was evaporated under reduced pressure. The residue was reprecipitated from chloroform–methanol to give 41.2 mg (33% yield) of polymer **3f**: mp 52–57 °C; M_w = 7000; M_n = 2500; ^{1}H NMR (δ in $\mathrm{CDCl_3}$) –0.13, –0.09 (br s, 2.2H, $\mathrm{Me_3SiC{=}CH_2}$), 0.03 (br s, 6.8H, $\mathrm{Me_3SiCH{=}CH}$), 0.54, 0.59 (br s, 3H, MeSi), 6.20, 6.45 (br, 0.5H, $\mathrm{H_2C{=}C}$), 6.84, 6.72 (br d, 1.5H, J = 22 Hz, HC═CH), 7.01–7.86 (m, 4H, ring protons); ^{13}C NMR (δ in $\mathrm{CDCl_3}$) –4.08 ($\mathrm{Me_3SiC{=}CH_2}$), –1.60 ($\mathrm{Me_3SiCH{=}CH}$), –0.20 ($\mathrm{MeSiCH_2}$), 1.03 (MeSiC═), 127.0 127.1, 127.2, 135.2, 135.3, 135.4, 135.6, 135.8, 135.9, 136.0, 141.1, 141.6 (ring carbons), 145.6, 155.3 ($\mathrm{CH{=}CHSiMe_3}$), 145.7, 150.7 ($\mathrm{H_2C{=}CSiMe_3}$); UV (film) λ_{max} 202, 278 nm. Anal. Calcd for $\mathrm{(C_{12}H_{18}Si_2)}_n$: C, 65.98; H, 8.31. Found: C, 65.90; H, 8.21.

Reaction of Polymer 3a with Trimethylsilylacetylene. A mixture of 75.3 mg of **3a** (M_w = 11 000; M_n = 4100), 55.8 mg (0.568 mmol) of trimethylsilylacetylene, and 3.3 mg (0.0064 mmol) of $\mathrm{H_2PtCl_6{\cdot}6H_2O}$ in 1.0 mL of benzene was stirred at room temperature for 23 h. The resulting mixture was poured into 100 mL of ethanol and gave 87.0 mg (75% yield) of polymer **3f**: mp 168–176 °C; M_w = 19 000; M_n = 8000; ^{1}H NMR (δ in $\mathrm{CDCl_3}$ –0.10 (s, 0.7H, $\mathrm{MeSiC{=}CH_2}$), 0.11 (s, 8.3H, $\mathrm{Me_3SiCH{=}C}$), 6.41 (d, 0.08H, J = 6.9 Hz, $\mathrm{H_2C{=}}$), 6.73 (d, 0.08H, J = 6.9 Hz, $\mathrm{H_2C{=}}$), 6.83 (d, 0.92H, J = 22.4 Hz, olefin proton), 7.09 (d, 0.92H, J = 22.4 Hz, olefin proton), 7.39 (br s, 4H, phenylene ring protons), 7.53 (m, 5H, phenyl ring protons); ^{13}C NMR (δ in $\mathrm{CDCl_3}$) –1.58 ($\mathrm{Me_3Si}$), 114.7 ($\mathrm{CH_2{=}CSiMe_3}$), 117.8 ($\mathrm{C(SiMe_3){=}CH_2}$), 127.7, 127.8, 129.5, 134.16, 134.21, 134.6, 135.0, 135.2, 135.4, 135.6, 135.7, 136.1 (ring carbons), 143.1, 158.1 (olefin carbons); UV (THF) λ_{max} 208 (ε 91 000) nm. Anal. Calcd for $\mathrm{(C_{17}H_{20}Si_2)}_n$: C, 72.79; H, 7.19. Found: C, 71.58; H, 7.34.

Preparation of Poly[*p*-(dimethylsilylene)phenylene] (6). To a solution of 8.69 mmol of *p*-phenylenedimagnesium dibromide prepared from *p*-dibromobenzene and magnesium in 6 mL of THF was added dropwise a solution of 1.01 g (7.8 mmol) of dichlorodimethylsilane in 3 mL of THF at room temperature. The resulting mixture was heated to reflux for 16 h. The mixture was cooled to room temperature, and 0.6 mL (0.9 mmol) of a 1.5 M methyllithium–ether solution was added to the mixture to translate the Si—Cl bonds remaining unchanged to methyl groups. After refluxing for 1 h, the 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 anhydrous magnesium sulfate. The solvent was evaporated and the residue was reprecipitated from chloroform–ethanol to give 0.361 g (31% yield) of polymer **6**: mp 194–200 °C;, M_w = 2800; M_n = 1800; ^{1}H NMR (δ in $\mathrm{CDCl_3}$) 0.53 (br s, 6H, MeSi), 7.50 (br s, 4H, ring protons); ^{13}C NMR (δ in $\mathrm{CDCl_3}$) –2.6 (MeSi), 133.4, 138.9 (ring carbons). Anal. Calcd for $\mathrm{(C_8H_{10}Si)}_n$: C, 71.57; H, 7.51. Found: C, 71.42; H, 7.49.

Thermogravimetric Analysis of Polymers 1a, 4a, and 6. On a platinum plate was placed 8–10 mg of a polymer, and the plate was heated from room temperature to 1000 °C at a rate of 10 °C/min.

Pyrolysis of Polymers 1a, 4a, and 6 at 480 °C. In a quartz sample tube was placed 10 mg of a polymer, and the tube was heated 480 °C under reduced pressure (2×10^{-7} mmHg). The gas evolved was directly introduced into the mass spectrometer. After heating at 480 °C for 15 min, the residue was analyzed by IR spectroscopy.

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(10) The IR spectrum for the ash obtained from combustion of polymer **4a** under the same conditions as used for elemental analysis shows absorption bands at 1209 and 798 cm^{-1} and 1110 cm^{-1} due to $\nu_{\mathrm{Si{-}C}}$ and $\nu_{\mathrm{Si{-}O}}$.