Polymeric Organosilicon Systems. 22. Synthesis and Photochemical Properties of Poly[(disilanylene)oligophenylylenes] and Poly[(silylene)biphenylylenes]

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Poly[4,4′-(tetramethyldisilanylene)biphenylylene] (**1a**), poly[4,4′-(tetraethyldisilanylene)biphenylylene] (**1b**), and poly[4,4′-(1,2-dimethyl-1,2-diphenyldisilanylene)biphenylylene] (**1c**) were prepared by the condensation reaction of the respective 4,4′-bis(chlorosilyl)biphenyls with sodium. Poly[4,4′-(dimethylsilylene)biphenylylene] (**1d**), poly[4,4′-(methylphenylsilylene)biphenylylene] (**1e**), and poly[3,3′-(dimethylsilylene)biphenylylene] (**1f**) were obtained from the nickel-catalyzed dehalogenative coupling of the products formed from the reaction of the respective bis(bromophenyl)-substituted silanes with magnesium. Poly[(disilanylene)terphenylylenes] **2a–c** and poly[(disilanylene)quaterphenylylenes] **3a–c** were also synthesized by the similar nickel-catalyzed dehalogenative coupling reactions of di-Grignard reagents prepared from the respective bis(4-bromophenyl)-substituted disilanes, with *p*-dibromobenzene and 4,4′-dibromobiphenyl, respectively. The disilanylene-substituted polymers **1a–c**, **2a–c**, and **3a–c** were found to be photoactive. Irradiation of the thin solid films prepared from these polymers in air resulted in scission of the Si–Si bonds, leading to the formation of degradation products including silanol and siloxy units. Poly[(silylene)biphenylylenes] **1d–f** were found to be inert toward UV irradiation. Photochemical behavior of the disilanylene-substituted polymers was also investigated in solution, and photoactivities of these polymers were found to decrease with increasing the degree of an extension of the π-electron system. The results of crystal orbital calculations for poly[(disilanylene)oligophenylylenes] have also been reported.

Introduction

Considerable interest has been focused on the chemistry of organosilicon polymers, because they can be used as functionality materials such as photoresists, precursors of ceramics, and conducting and photoconducting materials.[1] Recently, we have reported that poly[*p*-(disilanylene)phenylenes] which can be used as the top imaging layer for the double layer photoresist system can be readily prepared from the sodium condensation reaction of *p*-bis(chlorosilyl)benzenes. Since this original finding, many papers concerning the synthesis and usage of the polymers in which a regular alternating arrangement of an organosilicon unit and π-electron system such as phenylene,[2] ethynylene,[3] butenyne-1,4-diyl,[4] diethynylene,[5] naphthylene,[6] and thienylene[7] is found in the polymer backbone have been published to date.

In general, the polymers that have a disilanylene unit and π-electron system in the polymer chain are photoactive in the solid state as well as in solution. Irradiation of these polymers in solution causes a rapid change of their molecular weights, which can be explained by homolytic scission of an Si–Si bond, generating silyl radicals. Silyl radicals thus formed undergo further

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reactions with two different pathways. One involves disproportionation of the silyl radicals leading to the formation of a silene and hydrosilane, and the other comprises addition of the silyl radicals across the π-electron system leading to the cross-linking. The former reaction results in a decrease of the molecular weights, while the latter leads to an increase of the molecular weights. Introduction of an alkyl substituent, such as a methyl group, onto the silyl radical center enhances the cross-linking reaction, whereas replacement of the alkyl substituent by an aryl group on the silicon atom facilitates recombination and also disproportionation because of the increased stabilization of the silenes due to the presence of the aryl group.

Very recently, we reported the synthesis and photochemical properties of poly[(disilanylene)thienylenes][7e] and poly[(disilanylene)bithienylenes].[7f] In the photochemical properties of these polymers, the bithienylene-substituted disilanylene polymers were found to be less photoactive than the thienylenedisilanylene-substituted polymers, regardless of the substituents on the silicon atom. It is of interest to us to learn the relationship between photoactivity of the alternating polymers composed of a disilanylene unit and π-electron system and the number of the π-electron unit in the polymer backbone.

In this paper, we report the synthesis and photochemical properties of poly[(disilanylene)oligophenylylenes] with a different number of phenylene groups and poly[(silylene)biphenylylenes], in comparison with the photochemical behavior of poly[p-(disilanylene)phenylenes] reported previously.[2b] We also report the results of crystal orbital calculations for poly[(disilanylene)oligophenylylenes].

Results and Discussion

Synthesis of Poly[(disilanylene)biphenylylenes]. Poly[4,4′-(tetramethyldisilanylene)biphenylylene] (**1a**), poly[4,4′-(tetraethyldisilanylene)biphenylylene] (**1b**), and poly[4,4′-(1,2-dimethyl-1,2-diphenyldisilanylene)biphenylylene] (**1c**) were synthesized by the sodium condensation reaction of the respective bis(chlorosilyl)-substituted biphenyls in 45, 77, and 49% yields, respectively (Scheme 1). The structures of the polymers **1a**–**c** were verified by spectroscopic analysis. IR spectra of the polymers show no absorptions at around 1100 cm^{-1}, indicating the absence of Si–O bonds in the polymer chain. ^{1}H and ^{13}C NMR spectra were wholly consistent with the structures proposed for **1a**–**c** (see Experimental Section). Furthermore, chemical shifts of dimethylsilyl protons and biphenyl ring protons, and also dimethylsilyl and biphenyl ring carbons, were consistent with those observed for a model compound, 4,4′-bis(pentamethyldisilanyl)biphenyl, which was prepared from the reaction of a di-Grignard reagent of 4,4′-biphenylylene dibromide with 2 equiv of chloropentamethyldisilane. These results clearly indicate that polymers **1a**–**c** must have a regular alternating arrangement of a disilanylene group and a biphenylylene group. Polymers **1a**–**c** are white solids and are soluble in benzene, toluene, ethers, and chlorocarbons but are insoluble in saturated hydrocarbons and alcohols. Some properties of polymers **1a**–**c** are summarized in Table 1. Polymers **1a**–**c** melt at 120–200 °C without decomposition. The molecular weights of the polymers were determined to be M_w = 14 000–27 000 (M_w/M_n = 2.46–2.86) by GPC, relative to polystyrene standards.

Scheme 1

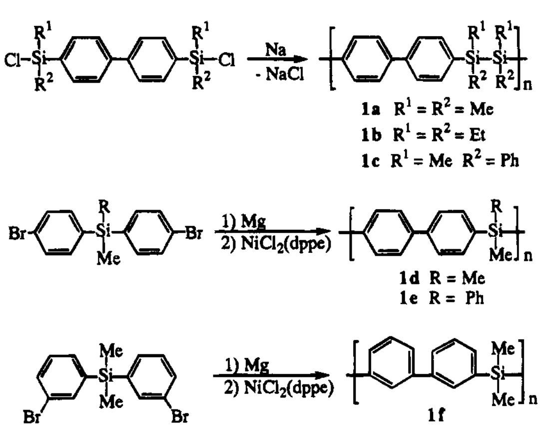

Table 1. Properties of Polymers

polymer	yield (%)	mp (°C)	M_w	M_n
1a	45	192–202	17000	6000
1b	77	122–134	27000	10000
1c	49	169–183	14000	5800
1d	31	180–183	10000	2800
1e	63	172–193	31000	7300
1f	60	49–62	4600	2100
2a	39	113–126	9500	4900
2b	62	99–110	8500	4000
2c	63	143–161	7000	3600
3a	32	120–138	5800	4000
3b	30	104–127	7000	4500
3c	49	180–199	6900	3400
4b	75	192–216	11000	5800

Synthesis of Poly(silylenebiphenylylenes). Recently, we reported that the dehalogenative coupling reaction of bis(bromothienyl)silane with magnesium offers a convenient route for the preparation of poly(silylenebithienylenes) and poly[(disilanylene)bithienylenes].[7f] Using this method, we prepared poly[4,4′-(dimethylsilylene)biphenylylene] (**1d**), poly[4,4′-(methylphenylsilylene)biphenylylene] (**1e**), and poly[3,3′-(dimethylsilylene)biphenylylene] (**1f**). Thus, when bis(4-bromophenyl)dimethylsilane was treated with 1 equiv of magnesium in THF, a mixture of starting bis(bromophenyl)dimethylsilane, mono-Grignard reagent, and di-Grignard reagent was found to be formed in the ratio of 1:2:1 by GLC analysis of the hydrolysis products. Heating this mixture at 230 °C for 100 h in a sealed glass tube in the presence of a catalytic amount of dichloro(bis(diphenylphosphino)ethane)nickel(II), followed by hydrolysis of the mixture and reprecipitation of the products from ethanol–chloroform, gave **1d** in 31% yield. The reactions of bis(4-bromophenyl)methylphenylsilane and bis(3-bromophenyl)dimethylsilane with 1 equiv of magnesium, followed by treatment of the resulting solutions with the nickel catalyst under

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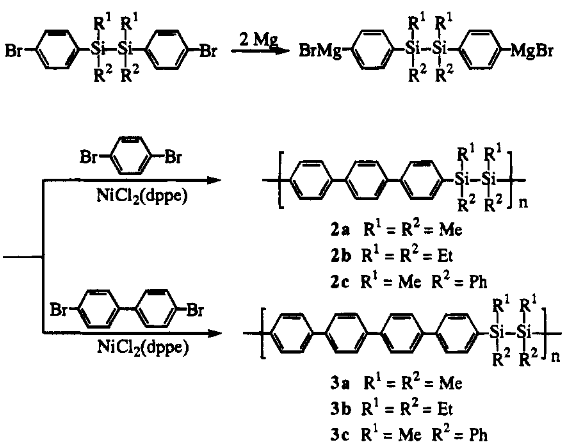
the same conditions, also proceeded smoothly to give **1e** and **1f** in 63% and 60% yields, respectively. The structures of polymers **1d**−**f** were verified by spectroscopic analysis. All spectral data obtained for polymers **1d**−**f** are wholly consistent with those of the proposed structures (see Experimental Section). The combustion elemental analyses for polymers **1d**−**f** are not in accord with their theoretical values. Carbon contents for these polymers are always found to be lower than their calculated ones, as often observed for organosilicon polymers.[2f,g] The formation of ceramics such as silicon carbide seems to be the reason for the lower values of the carbon contents. Indeed, the IR spectrum of the ash obtained from the combustion of polymer **1d** under the same conditions as elemental analysis reveals absorption bands at 1260 and 800 cm^{-1} due to the vibration of the Si−C bonds, along with a strong absorption band at 1090 cm^{-1} attributed to the stretching frequencies of Si−O bonds. The polymers thus obtained are white solids and soluble in common organic solvents. Some properties of polymers **1d**−**f** are summarized in Table 1. Polymer **1f**, whose molecular weight was determined to be lower than those of **1d** and **1e**, melts at lower temperature than **1d** and **1e**. The lower molecular weight of polymer **1f** relative to those of **1d** and **1e** may be ascribed to the steric hindrance due to meta substitution.

Recently, Corriu and his co-workers reported that polymers **1d** and **1e** can be obtained by the reaction of 4,4′-biphenylylenedilithium with the corresponding dichlorosilanes in 90% and 70% yields, although the molecular weights of the polymers are low.[2f]

We attempted to prepare poly[(disilanylene)biphenylylenes] by the similar nickel-catalyzed dehalogenative coupling reaction. Thus, the reaction of 1,2-bis(4-bromophenyl)tetramethyldisilane with 1 equiv of magnesium, followed by treatment with the nickel catalyst, afforded a polymer whose molecular weight was determined to be M_w = 19 000 in 19% yield as white solids. ^{1}H and ^{13}C NMR spectra of this polymer reveal signals whose chemical shifts are consistent with those of **1a** prepared from the sodium condensation reaction. However, in addition to these signals, many signals with low intensities in both aromatic and silyl methyl regions are observed (see Experimental Section). Furthermore, this polymer melts at 135−144 °C, a lower temperature than the melting point of **1a** prepared from the sodium condensation reaction. These results suggest the loss of regularity in the polymer backbone. Presumably, some redistribution reactions involving scission of an Si−Si bond by a nickel catalyst take place during the polymerization.[8]

Synthesis of Poly[(disilanylene)terphenylylenes] and Poly[(disilanylene)quaterphenylylenes]. In the nickel-catalyzed homo-coupling reaction of bis(bromophenyl)silanes and bis(bromophenyl)tetramethyldisilane as described above, heating the reaction mixture at 230 °C is necessary for obtaining the polymers. In contrast to this coupling, the cross-coupling reactions of 1,4-dibromobenzene with di-Grignard reagents prepared from bis(bromophenyl)disilanes in the presence of a catalytic amount of dichloro(diphenylphosphinoethane)nickel(II) in THF proceeded smoothly at 150 °C to give the respective poly[(disilanylene)terphenylylenes] (Scheme 2). Usual workup and reprecipitation of the resulting polymers from ethanol−chloroform afforded poly[4,4′-(disilanylene)terphenylylenes] **2a**−**c** in moderate yields. Poly[4,4′-(disilanylene)quaterphenylylenes] **3a**−**c** were also obtained by similar cross-coupling reactions using 4,4′-dibromobiphenyl instead of 1,4-dibromobenzene as the starting compound. The structures of polymers **2a**−**c** and **3a**−**c** were verified by spectrometric analysis. ^{1}H and ^{13}C NMR spectra of these polymers are wholly consistent with the expected structures with only one exception of polymer **3a**. The ^{13}C NMR spectrum of **3a** shows three CH signals with low intensities at 120−140 ppm, presumably due to a terminal phenyl and bromophenyl group in the polymer chain, along with signals due to the quaterphenylylene and tetramethyldisilanylene unit (see Experimental Section). In ^{1}H and ^{13}C NMR spectra, no signals other than those originated from **3a** are observed in the silyl methyl region, indicating that cleavage of the Si−Si bond observed in the dehalogenative coupling of bis(4-bromophenyl)tetramethyldisilane at 230 °C does not occur in this reaction. Elemental analyses for the terphenylylene- and quaterphenylylene-substituted polymers again are not in accord with their theoretical values, as in the case of poly(silylenebiphenylylenes). The carbon contents were always determined to be lower than the calculated values. IR spectra of the ash obtained by combustion of polymers **2c** and **3a** under the same conditions as the elemental analyses show absorptions due to the vibration of the Si−C bonds at 1260 and 800 cm^{-1} for **2c** and 1220 and 800 cm^{-1} for **3a**, along with strong absorption bands at 1070 cm^{-1} attributed to Si−O bonds.

Scheme 2



Yields and some properties of polymers **2a**−**c** and **3a**−**c** are also summarized in Table 1. These polymers are soluble in halocarbons, and slightly soluble in aromatic solvents, but insoluble in alcohols and saturated hydrocarbons. The low yields of polymers **2a**−**c** and **3a**−**c** may be ascribed to the formation of oligomers which are soluble in ethanol and also the formation of insoluble polymers. IR spectra of both oligomers and insoluble polymers are very similar to those of the respective soluble polymers. Therefore, it seems likely that they have the structure consisting of the alternating arrangement, similar to that of soluble polymers.

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[8] The activation of an Si−Si bond by a nickel-catalyst has been reported. For example, see: Ishikawa, M.; Naka, A.; Ohshita, J. *Organometallics* **1992**, *11*, 3004 and references therein.

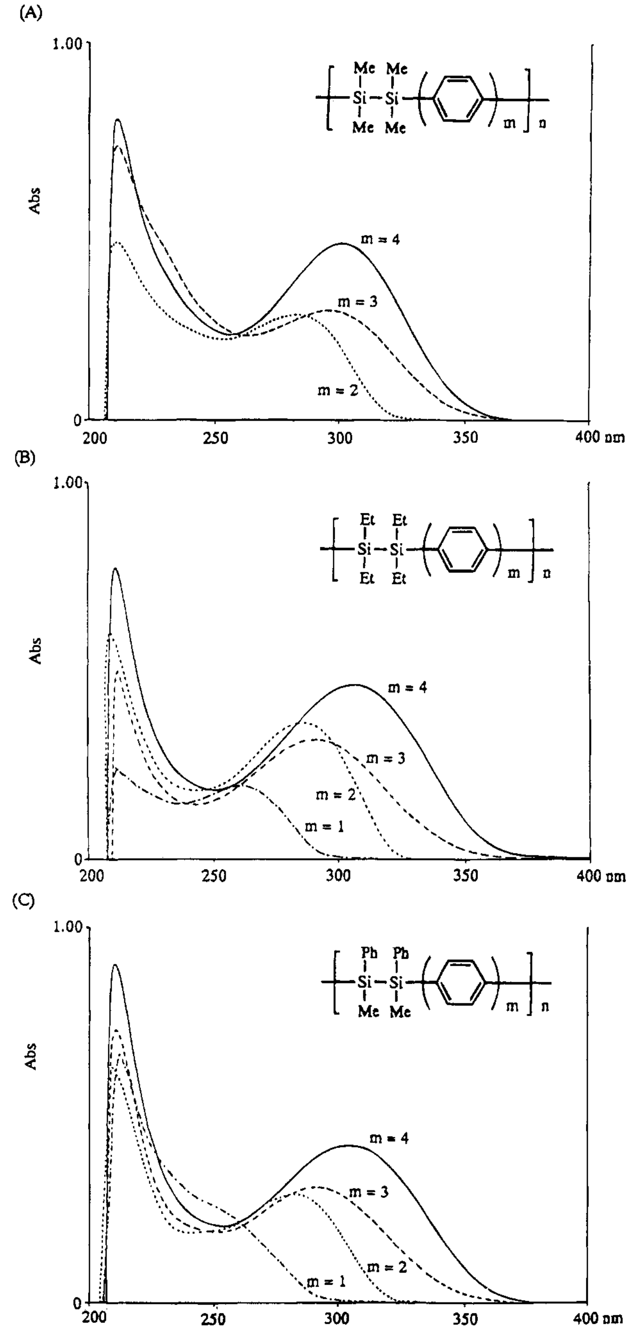

Figure 1. UV spectra of (A) polymers **1a**, **2a**, and **3a**, (B) polymers **1b**, **2b**, **3b**, and **4b**, and (C) polymers **1c**, **2c**, **3c**, and **4c** in THF (1.00×10^{-5} unit mol/L).

Photochemical Properties. UV spectral data obtained for the present polymers are shown in Figure 1, together with those of poly[*p*-(tetraethyldisilanylene)-phenylene] (**4b**) and poly[*p*-(1,2-dimethyl-1,2-diphenyldisilanylene)phenylene] (**4c**).[2b] The absorption maxima of disilanylenebiphenylylene polymers **1a**–**c** are red-shifted about 10 nm relative to the corresponding silylenebiphenylylene polymers, due to the delocalization of π-electrons through the disilanylene unit (see Experimental Section). Comparing a series of disilanylene polymers with the same substituents on the silicon atom, the absorption maximum is found to move to longer wave length as the number of phenylenes located between disilanylene units is increased in the solid state and also in solution.

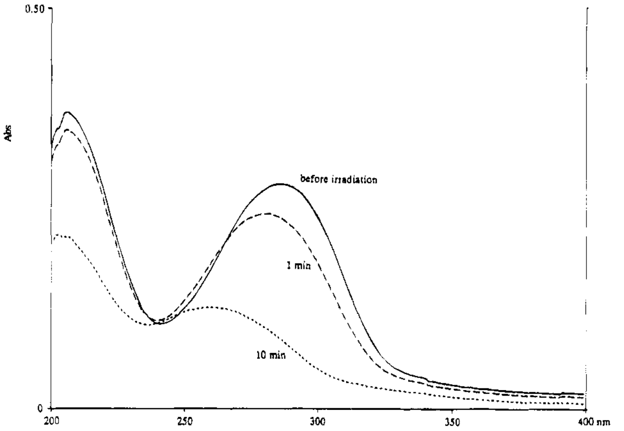

Figure 2. UV spectra of polymer **1a** (—) before irradiation, (— — —) after 1 min irradiation, and (- - -) after 10 min irradiation.

Like other disilanylene polymers reported previously,[2a−d,3a,4,6,7a,e,f] polymers **1a**–**c** are photoactive in solid films as well as in solution. Irradiation of the thin solid films prepared from **1a**–**c** with a low-pressure mercury lamp in air led to a rapid decrease of the absorption bands in the UV region, indicating that cleavage of the Si–Si bonds occurred during the photolysis, as shown in Figure 2. After 1 h irradiation, IR spectra of the resulting films show the presence of an Si–OH and Si–O–Si bond, which would be formed from the reaction of silyl radicals arising from homolytic scission of the Si–Si bonds with oxygen, as shown in Figure 3.

Irradiation of a benzene solution of **1a**–**c** led to decrease in the molecular weight as shown in Figure 4. For example, the molecular weight of the photoproducts obtained from **1a** after 10 h irradiation was determined to be $M_w = 6600$ ($M_w/M_n = 2.62$), which corresponds to about 1/2.5 of the molecular weight of the starting polymer (Figure 4a). IR and ^{1}H and ^{13}C NMR spectra obtained for the photoproducts from **1a** are almost the same as those of the starting polymer **1a**, with the exception of the presence of an Si–H bond which is observed by the IR spectrum as a weak absorption at 2120 cm^{-1} and by the ^{1}H NMR spectrum as a weak signal at 4.36 ppm. The UV spectrum reveals a 6 nm blue-shifted absorption maximum relative to that of the starting polymer **1a**. These facts indicate that homolytic scission of the Si–Si bonds, followed by disproportionation of the resulting silyl radicals leading to the formation of silenes and hydrosilanes, occurs during the photolysis. Indeed, irradiation of a benzene solution of **1a** in the presence of methanol resulted in a rapid decrease of the molecular weight (Figure 4b), which can be understood in terms of addition of methanol to the silenes arising from the disproportionation of the silyl radicals. It seems likely that the direct reaction of methanol with the Si–Si bonds in the photochemically excited molecule is also involved in this photolysis. A similar profile for the photodegradation of other disilanylene-containing polymers has been reported previously.[2a−d,3a,4,6,7a,e,f]

As can be seen in Figure 4c, polymer **1b** is less photoactive than polymers **1a** and **1c**. Presumably, introduction of ethyl groups on the silicon atom stabilizes the silyl radicals sterically to facilitate the recombination of the radicals.

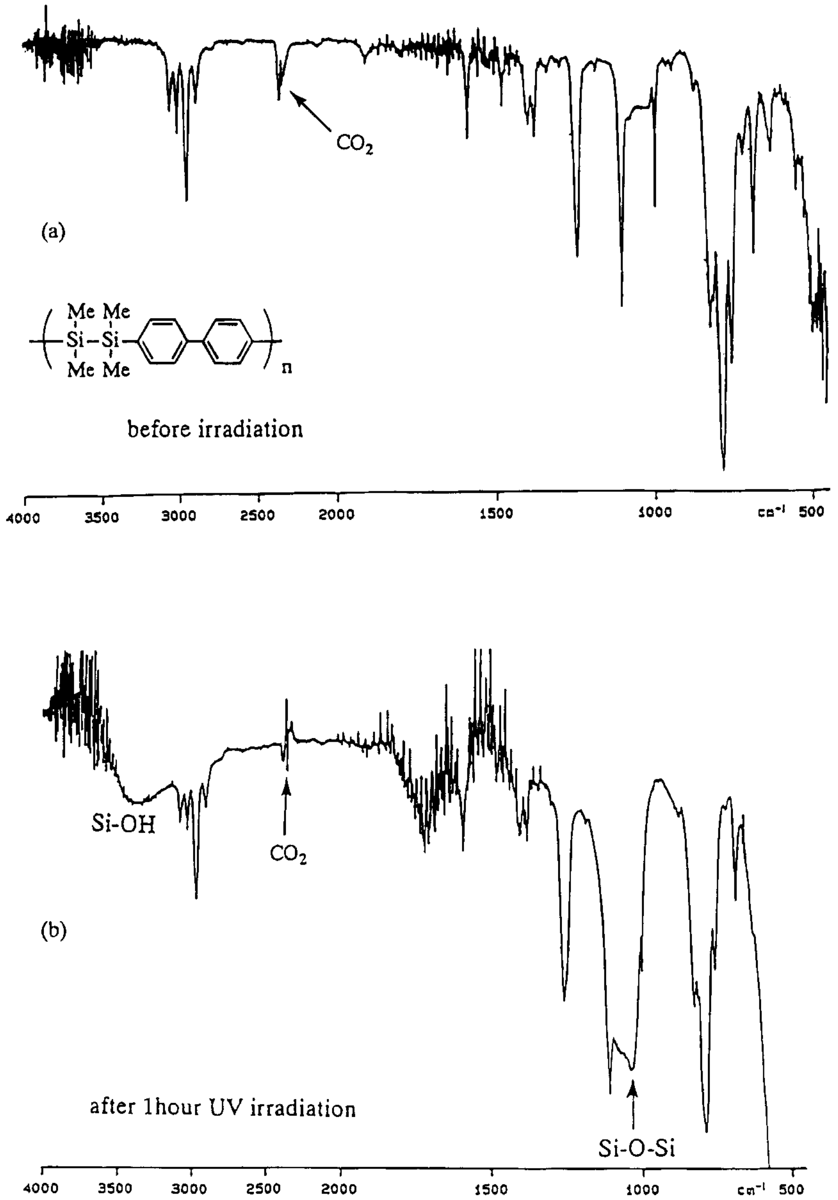

Figure 3. IR spectra of polymer **1a** (a) before irradiation and (b) after 1 h irradiation.

On the basis of the reaction mechanism proposed for **1a**, silylenebiphenylylene polymers **1d–f** that have no Si–Si bonds in the polymer backbone seem to be stable toward UV irradiation. In fact, no changes were observed in IR and UV spectra of their thin solid films, after 1 h irradiation in air. In the photolysis of polymers **1d–f** in a benzene solution for 10 h, again no changes for their molecular weights were observed. These facts clearly indicate that the presence of the Si–Si bond in the polymer main chain is essential for photoactivity.

Although the present (disilanylene)biphenylylene polymers **1a–c** are photoactive, the rate of photodegradation is much slower than that of poly[*p*-(tetraethyldisilanylene)phenylene] (**4b**) and poly[*p*-(1,2-dimethyl-1,2-diphenyldisilanylene)phenylene] (**4c**)[2b] as shown in Figures 5a,d and 6a,d. IR, UV, and ^{1}H and ^{13}C NMR spectra for the photodegradation products obtained from **4b** and **4c** are quite different from those of the starting polymers. Relatively large amounts of the Si–H bond and dihydrophenylene units can be detected by IR and ^{1}H NMR spectrometric analyses. UV absorption bands observed at about 250 nm for **4b** and **4c** completely disappear after 10 h irradiation, as reported previously.[2b] The low photoactivities of polymers **1a–c** may be ascribed to the disilanylenebiphenylylene structure. Indeed, in sharp contrast to the photochemical behavior of pentamethylphenyldisilane, which readily produces a silene via a 1,3-trimethylsilyl shift,[9] the model compound, 4,4′-bis(pentamethyldisilanyl)biphenyl was found to be inert toward UV irradiation.

Photochemical properties of polymers **2a–c** and **3a–c** were also investigated. Polymers **2a–c** and **3a–c** show similar photoactive properties to those of **1a–c** in the solid state in air. However, the rate of degradation leading to the formation of an Si–O and Si–OH group which can be determined by IR spectroscopic technique is slower than those of **1a–c**. The rate of the decrease of an absorption band in UV spectra during irradiation is also slower than those of **1a–c**. The photoactivities in the solid state decrease in the order of **1a–c** ≫ **2a,b** > **3a,b** > **2c**, **3c**. Photochemical behaviors of polymers

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(9) Ishikawa, M.; Fuchikami, T.; Sugaya, T.; Kumada, M. *J. Am. Chem. Soc.* **1975**, *97*, 5923.

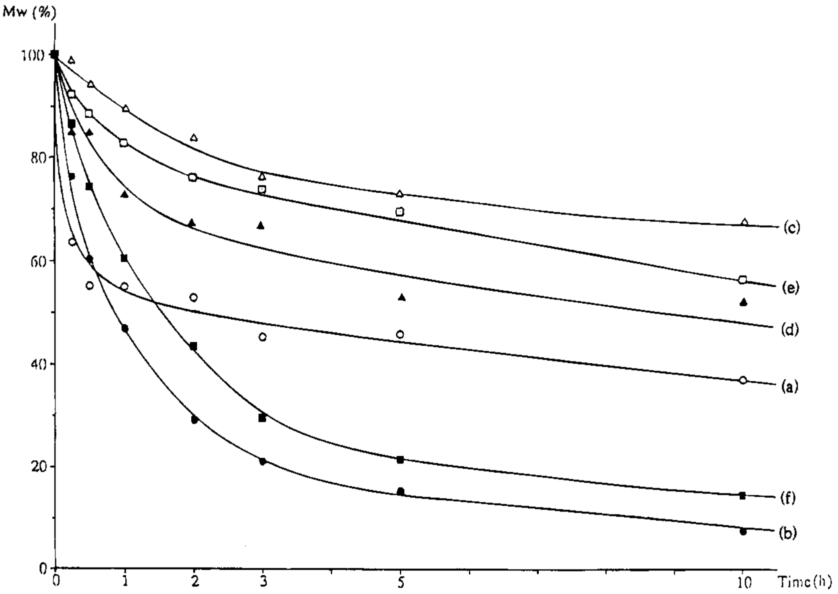


Figure 4. Plot of the molecular weights (%) based on the starting polymer vs irradiation time for the photolysis of **1a**−**c**: (a) irradiation of **1a** in benzene; (b) irradiation of **1a** in the presence of methanol; (c) irradiation of **1b** in benzene; (d) irradiation of **1b** in the presence of methanol; (e) irradiation of **1c** in benzene; (f) irradiation of **1c** in the presence of methanol.

2b,c and **3b,c** were also examined in solution. In contrast to the photolysis of polymers **1a**−**c** and **4b,c**, changes of the molecular weight in the photolysis of **2b** and **2c** were always small, as shown in Figures 5b and 6b. Since polymers **2a** and **3a** are almost insoluble in benzene and in other solvents, the photochemical behavior of these polymers could not be investigated.

The molecular weight changes on the photolysis of quaterphenylylene-substituted polymers **3b** and **3c** in benzene are shown in Figures 5c and 6c, indicating that these quaterphenylylene polymers are almost inert toward UV irradiation. All spectral data obtained for the photoproducts from **2b,c** and **3b,c** are consistent with the respective starting polymers, although absorption maxima in UV spectra for the photoproducts obtained from **2c** and **3c** shifted slightly to the shorter wavelength. Even though the photolysis of polymers **2b,c** and **3b,c** in benzene was carried out in the presence of methanol, no changes were observed in IR and ^{1}H and ^{13}C NMR spectra of the photoproducts, after 10 h irradiation.

In order to learn more about the relationship between wavelength of the incident light used in the photolysis and photoactivity of the disilanylene polymers, we carried out the photolysis of polymer **2b** in benzene with a high-pressure mercury lamp bearing a Pyrex filter (300−350 nm). No changes were observed in its molecular weight and in ^{1}H and ^{13}C NMR spectra for the polymer recovered after 10 h irradiation.

As can be seen in Figures 5 and 6, the photochemical behavior of terphenylylene- and quaterphenylylene-substituted polymers (m = 3 and 4) is very different from that of phenylene- and biphenylylene-substituted polymers (m = 1 and 2). In order to elucidate the origin of this difference, we carried out crystal orbital calculations using poly[(disilanylene)oligophenylylenes] as model polymers.

Analysis of the Electronic Properties. Crystal orbital (CO) calculations based on the semiempirical approximation were carried out to clarify the change in the electronic properties depending on the number of phenylenes of poly[(disilanylene)oligophenylylenes]. The following four kinds of polymers simplified by the use of hydrogen as substituent were employed.

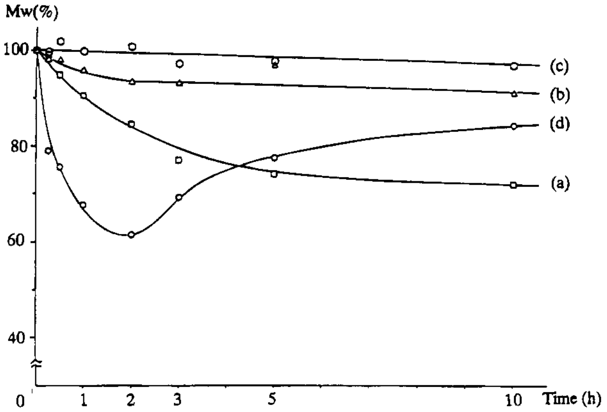


Figure 5. Plot of molecular weights (%) based on the starting polymer vs irradiation time for the photolysis of (a) **1b**, (b) **2b**, (c) **3b**, and (d) **4b** in benzene.

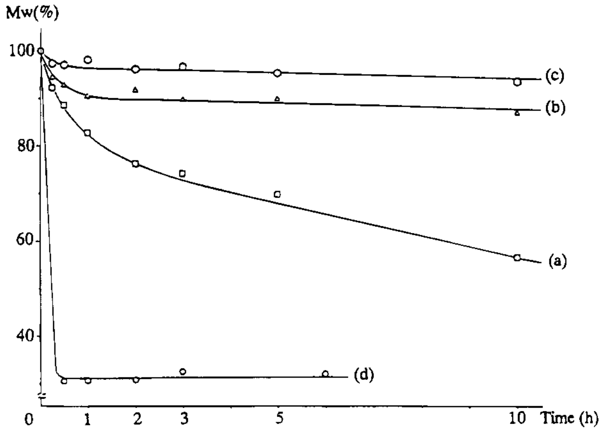
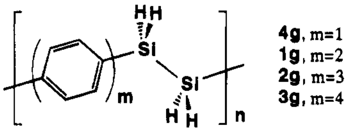


Figure 6. Plot of molecular weights (%) based on the starting polymer vs irradiation time for the photolysis of (a) **1c**, (b) **2c**, (c) **3c**, and (d) **4c**[2b] in benzene.



4g, m=1
1g, m=2
2g, m=3
3g, m=4

It has been suggested from the X-ray diffraction data that in *p*-phenylene oligomer the adjacent phenyl rings are slightly rotated by 22.7° to avoid the steric repulsion of the ortho hydrogens.[10] However, since the band structure of the 22.7°-rotated poly(*p*-phenylene) (PPP) has been reported to be quite similar to that of the planar PPP,[11] the latter geometry for the phenyl unit was employed for the sake of simplicity. From the energetical analysis of the configuration of poly(disilanylenethienylene),[12] the disilanylene unit can also be considered to form the coplanar structure with the π-conjugated part.

The calculated band structures are shown in Figure 7. Since all the polymers possess considerably wide gaps and narrow bandwidths, these are expected to be electrically insulating or semiconducting in the intrinsic state. Both the highest occupied crystal orbital (HOCO) and the lowest unoccupied crystal orbital (LUCO) patterns are of σ-nature for $m = 1$, 2, and 3. For $m = 4$, however, the HOCO pattern changes into π-nature. An energy shift to higher level of the HO band is also seen with the increase in m.

In Figure 8 the π–π^* and σ–σ^* gaps, which were scaled with the factors that fit the calculated data to the experimental ones with respect to PPP[13,14] and PS (polysilane),[15,16] respectively, are plotted vs m. The experimental values obtained from the UV absorption of ethyl-substituited polymers (Figure 1b; **4c**–**1c**) are also shown for the sake of comparison. The experimental data show good agreement with the calculated π–π^* transition energies. The magnitudes of π-type and σ-type gaps interchange between $m = 1$ and 2.

The LUCO patterns for $m = 1$ and 2 are of σ-type, mostly consisting of antibonding combination of 3s AO of Si atoms.[12,15] Therefore, the HO → LU (σ–σ^*) transition is expected to cause the cleavage of the Si–Si bond. The photoactivity of the polymers with $m = 1$ and 2 can thus be stronger than the others, as seen in Figure 6.

It is worth noting that the extension of the π-electron system results in the decrease of the photoactivity of the present disilanylene polymers. Investigation on the photochemistry of the other disilanylene polymers that have various oligo π-electron systems is in progress.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL Model JNM-EX-270 spectrometer, a JEOL Model JNM-FX-90A spectrometer, and a JEOL Model JNM-PMX-60 spectrometer, using a deuteriochloroform or carbon tetrachloride solution containing tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-infrared spectrometer. Mass spectra were measured on a Shimadzu Model GCMS-QP 1000 spectrometer. UV spectra were measured on a Hitachi U-3210 spectrophotometer.

Materials. Benzene and THF were dried over sodium–potassium alloy and distilled just before use. Carbon tetrachloride was distilled from P_2O_5 and stored over molecular sieves until use.

Preparation of 4,4′-Bis(dimethylsilyl)biphenyl. To a solution of 64.1 mmol of 4,4′-biphenylylenedimagnesium dibromide prepared from 1.56 g of magnesium and 20.0 g of 4,4′-dibromobiphenyl in 50 mL of THF was added dropweise 13 mL of chlorodimethylsilane at 0 °C. 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 extracts were combined, washed with water, and then dried over anhydrous magnesium sulfate. After the solvent was evaporated, the residue was distilled under reduced pressure to give 8.0 g (46% yield) of 4,4′-bis(dimethylsilyl)biphenyl: bp 106 °C (1 mmHg); MS *m/z* 270 (M$^+$); ^{1}H NMR (δ in $CDCl_3$) 0.42 (d, 12H, J = 3.6 Hz, MeSi), 4.52 (sept, 2H, J = 3.6 Hz, HSi), 7.64 (d, 4H, J = 8.6 Hz, ring protons), 7.67 (d, 4H, J = 8.6 Hz, ring protons); ^{13}C NMR (δ in $CDCl_3$) −3.7, 126.6, 134.5, 136.4, 141.8. Anal. Calcd for $C_{16}H_{22}Si_2$: C, 71.04; H, 8.20. Found: C, 70.98; H, 8.00.

Preparation of 4,4′-Bis(chlorodimethylsilyl)biphenyl. A mixture of 7.4 g (27.4 mmol) of 4,4′-bis(dimethylsilyl)biphenyl and 5 mg (0.03 mmol) of palladium dichloride in 30 mL of carbon tetrachloride was heated to reflux for 5 h. After the palladium salts were filtered off, carbon tetrachloride and the resulting chloroform were evaporated. The residue was distilled under reduced pressure to give 7.2 g (78% yield) of 4,4′-bis(chlorodimethylsilyl)biphenyl: bp 164–168 °C (1 mmHg); mp 92.0–95.0 °C; MS *m/z* 338 (M$^+$); ^{1}H NMR (δ in $CDCl_3$) 0.37 (s, 12H, MeSi), 7.29 (d, 4H, J = 7.6 Hz, ring protons), 7.37 (d, 4H, J = 7.9 Hz, ring protons); ^{13}C NMR (δ in $CDCl_3$) 2.1, 126.9, 133.7, 135.4, 142.6. Anal. Calcd for $C_{16}H_{20}Cl_2Si_2$: C, 56.62; H, 5.94. Found: C, 56.90; H, 5.93.

4,4′-Bis(diethylsilyl)biphenyl. This compound was prepared using the same procedure as that of 4,4′-bis(dimethylsilyl)biphenyl (55% yield): bp 116–117° C (0.3 mmHg); MS

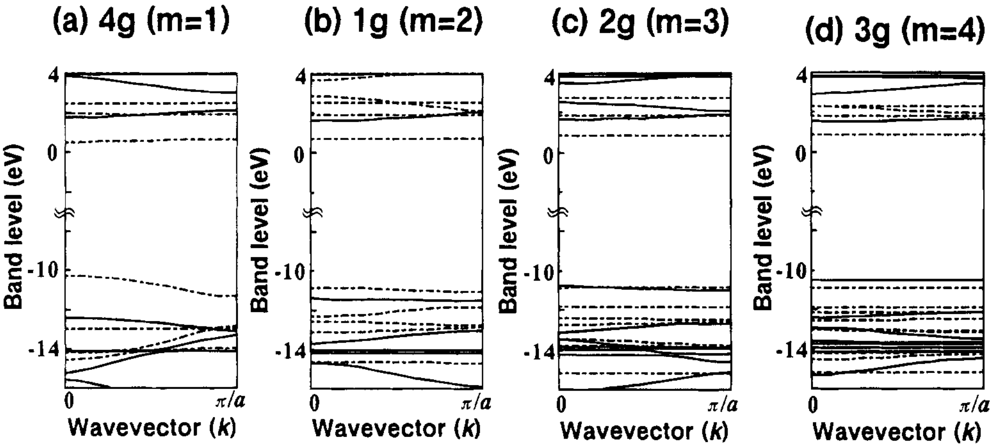


Figure 7. Band structures of (a) **4g** (m = 1), (b) **1g** (m = 2), (c) **2g** (m = 3), and (d) **3g** (m = 4). Solid and dashed lines indicate π- and σ-bands, respectively.

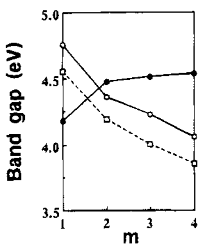


Figure 8. Changes of the $\sigma-\sigma^*$ (black circles) and the $\pi-\pi^*$ (white circles) band gaps (scaled values; see text) of poly[(disilanylene)(phenylene)$_m$]. The squares indicate the experimental values of λ_{max} in Figure 1b. The lines are guides for the eye.

m/z 326 (M$^+$); ^{1}H NMR (δ in CDCl$_3$) 0.56–0.63 (m, 8H, CH$_2$-Si), 0.75 (br t, 12H, J = 7.8 Hz, Me), 3.96 (quintet, 2H, J = 3.3 Hz, HSi), 7.31 (br s, 8H, ring protons); ^{13}C NMR (δ in CDCl$_3$) 3.5, 8.1, 126.5, 134.5, 135.2, 141.2. Anal. Calcd for $C_{20}H_{30}Si_2$: C, 73.55; H, 9.26. Found: C, 73.50; H, 9.02.

4,4′-Bis(chlorodiethylsilyl)biphenyl. This compound was prepared by using the same procedure as that of 4,4′-bis(chlorodimethylsilyl)biphenyl (86% yield after recrystallization from hexane): mp 48.0–50.5 °C; MS *m/z* 394 (M$^+$); ^{1}H NMR (δ in CDCl$_3$) 0.75 (br s, 20H, EtSi), 7.31 (d, 4H, J = 7.9 Hz, ring protons), 7.36 (d, 4H, J = 7.6 Hz, ring protons); ^{13}C NMR (δ in CDCl$_3$) 6.7, 8.1, 126.8, 133.4, 134.2, 142.4. Anal. Calcd for $C_{20}H_{28}Cl_2Si_2$: C, 60.74; H, 7.14. Found: C, 60.71; H, 7.03.

4,4′-Bis(methylphenylsilyl)biphenyl. This compound was obtained in 30% yield using the same procedure as that of 4,4′-bis(dimethylsilyl)biphenyl: mp 35.5–37.0 °C; MS *m/z* 394 (M$^+$); ^{1}H NMR (δ in CDCl$_3$) 0.65 (d, 6H, J = 3.63 Hz, MeSi), 4.96 (q, 2H, J = 3.96 Hz, HSi), 7.25–7.65 (m, 18H, ring protons); ^{13}C NMR (δ in CDCl$_3$) −5.0, 126.7, 128.0, 129.6, 134.4, 134.8, 135.2, 135.3, 142.0. Anal. Calcd for $C_{26}H_{26}Si_2$: C, 79.13; H, 6.64. Found: C, 79.11; H, 6.53.

Preparation of 4,4′-Bis(chloromethylphenylsilyl)biphenyl. The same procedure as that of 4,4′-bis(chlorodimethylsilyl)biphenyl was used for the preparation of this compound. After removal of the solvent, the residue was flashly distilled, and the fraction boiling at 180–200 °C (0.5 mmHg) was collected (55% yield): MS *m/z* 447 (M$^+$ − Me); ^{1}H NMR (δ in CDCl$_3$) 0.83 (s, 6H, MeSi), 7.26–7.61 (m, 18H, ring protons); ^{13}C NMR (δ in CDCl$_3$) 0.9, 126.9, 128.2, 130.6, 133.8, 134.1, 134.57, 134.63, 142.7. Anal. Calcd for $C_{26}H_{24}Cl_2Si_2$: C, 67.37; H, 5.22. Found: C, 67.37; H, 5.15.

Preparation of Poly[4,4′-(tetramethyldisilanylene)-biphenylylene] (1a). In a 200 mL three-necked flask fitted with a reflux condenser and dropping funnel were placed 0.7 g (30.5 mmol) of sodium dispersion and 85 mL of toluene. To this was dropwise added a solution of 4.26 g (12.6 mmol) of 4,4′-bis(chlorodimethylsilyl)biphenyl in 20 mL of toluene at room temperature. The resulting mixture was heated to reflux for 6 h and hydrolyzed with ethanol and water. The organic layer was separated, and the aqueous layer was extracted with chloroform. The organic layer and extracts were combined, washed with water, and then dried over anhydrous magnesium sulfate. After the solvent was evaporated off, the residue was reprecipitated from ethanol–chloroform and then from isopropyl alcohol–chloroform to give 2.40 g (45% yield) of **1a**: mp 192–202 °C; M_w = 17 000; M_n = 6000; ^{1}H NMR (δ in CDCl$_3$) 0.38 (s, 12H, MeSi), 7.48 (d, 4H, J = 8.0 Hz, ring protons), 7.57 (d, 4H, J = 8.0 Hz, ring protons); ^{13}C NMR (δ in CDCl$_3$) −3.8, 126.3, 134.4, 137.9, 141.0; UV (film) λ_{max} 282, 222 nm; UV (THF) λ_{max} 284 (ϵ 27 300), 209 nm (ϵ 41 300). Anal. Calcd for $(C_{16}H_{20}Si_2)_n$: C, 71.57; H, 7.51. Found: C, 71.41; H, 7.34.

The same procedure as that of **1a** was used for the preparation of **1b** and **1c**.

Poly[4,4′-(tetraethyldisilanylene)biphenylylene] (1b) (77% yield after reprecipitation from isopropyl alcohol–chloroform): mp 122–134 °C; M_w = 27 000; M_n = 10 000; ^{1}H NMR (δ in CDCl$_3$) 0.99 (br s, 20H, EtSi), 7.45 (d, 4H, J = 7.6 Hz, ring protons), 7.58 (d, 4H, J = 7.6 Hz, ring protons); ^{13}C NMR (δ in CDCl$_3$) 3.7, 8.2, 126.1, 135.0, 136.2, 140.7; UV (film) λ_{max} 284, 204 nm; UV (THF) λ_{max} 288 (ϵ 36 300), 210 nm (ϵ 59 400). Anal. Calcd for $(C_{20}H_{28}Si_2)_n$: C, 74.00; H, 8.69. Found: C, 73.70; H, 9.46.

Poly[4,4′-(1,2-dimethyl-1,2-diphenyldisilanylene)biphenylylene] (1c) (49% yield after reprecipitation from hexane–chloroform): mp 169–183 °C; M_w = 14 000; M_n = 5800; ^{1}H NMR (δ in CDCl$_3$) 0.71 (s, 6H, MeSi), 7.29–7.62 (m, 18H, ring protons); ^{13}C NMR (δ in CDCl$_3$) −4.0, 126.4, 127.9, 129.0, 135.2, 135.5, 135.7, 136.4, 141.2; UV (film) λ_{max} 283 nm; UV (THF) λ_{max} 282 (ϵ 28 900), 210 nm (ϵ 62 300). Anal. Calcd for $(C_{26}H_{24}Si_2)_n$: C, 79.53; H, 6.16. Found: C, 79.50; H, 6.07.

Preparation of 4,4′-Bis(pentamethyldisilanyl)biphenyl. To a solution of 16.1 mmol of the di-Grignard reagent prepared from 5.03 g of 4,4′-dibromobiphenyl and 0.94 g of magnesium in 80 mL of THF was added 6.7 g (40.2 mmol) of chloropentamethyldisilane. The resulting solution was heated to reflux for 10 h and then hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and ether extracts were combined and dried over anhydrous magnesium sulfate. The solvent was evaporated off, and the residue was crystallized from ethanol to give 1.4 g (21% yield) of 4,4′-bis(pentamethyldisilanyl)biphenyl: mp 64.5–65.5 °C (after recrystallization from ethanol); MS *m/z* 414 (M$^+$); ^{1}H NMR (δ in CDCl$_3$) 0.08 (s, 18H, Me$_3$Si), 0.37 (s, 12H, Me$_2$Si), 7.39 (br s, 8H, ring protons); ^{13}C NMR (δ in CDCl$_3$) −3.8, −2.0, 126.5, 134.3, 138.3, 141.2. Anal. Calcd for $C_{22}H_{38}Si_4$: C, 63.69; H, 9.23. Found: C, 63.72; H, 9.06.

Preparation of Bis(4-bromophenyl)dimethylsilane. In a 50 mL two-necked flask fitted with a reflux condenser and dropping funnel was placed 5.1 g (21.6 mmol) of 1,4-dibromobenzene in 20 mL of diethyl ether, and the flask was cooled down to −80 °C. To this was added 14.0 mL (21.7 mmol) of a 1.55 M *n*-butyllithium–hexane solution through a dropping funnel over a period of 1 h. The resulting solution was allowed to stand for 12 h at room temperature. To this was added 1.4 g (10.8 mmol) of dichlorodimethylsilane at room temperature. After the mixture was heated to reflux for 3 h, the resulting solution was hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with hexane. The organic layer and hexane extracts were combined and washed with water, and then dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was chromatographed on a silica gel column eluting with hexane to give 3.0 g (76% yield) of bis(4-bromophenyl)dimethylsilane: mp 74 °C; MS *m/z* 368 (M$^+$); ^{1}H NMR (δ in CCl$_4$) 0.49 (s, 6H, Me$_2$Si), 7.09 (d, 4H, J = 7 Hz, ring protons), 7.29 (d, 4H, J = 7 Hz, ring protons); ^{13}C NMR (δ in CDCl$_3$) −2.6, 124.2, 131.1, 135.7, 136.4. Anal. Calcd for $C_{14}H_{14}Br_2Si$: C, 45.43; H, 3.81. Found C, 45.42; H, 3.81.

Bis(4-bromophenyl)methylphenylsilane, bis(3-bromophenyl)dimethylsilane, 1,2-bis(4-bromophenyl)tetramethyldisilane, 1,2-bis(4-bromophenyl)tetraethyldisilane, and 1,2-bis(4-bromophenyl)-1,2-dimethyldiphenyldisilane were prepared in a similar manner to that of bis(4-bromophenyl)dimethylsilane.

Bis(4-bromophenyl)methylphenylsilane (69% yield): mp 64 °C; MS *m/z* 430 (M$^+$); ^{1}H NMR (δ in CCl$_4$) 0.75 (s, 3H, MeSi),

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6.95–7.45 (m, 13H, ring protons); ^{13}C NMR (δ in $CDCl_3$) −3.4, 124.7, 128.1, 129.9, 131.2, 134.5, 134.9, 135.2, 136.8. Anal. Calcd for $C_{19}H_{16}Br_2Si$: C, 52.80; H, 3.37. Found: C, 52.81; H, 3.68.

Bis(3-bromophenyl)dimethylsilane (42% yield): MS *m/z* 368 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.56 (s, 6H, MeSi), 7.25 (d, 2H, J = 7.92 Hz, ring protons), 7.40 (br d, 2H, J = 7.26 Hz, ring protons), 7.49–7.53 (m, 2H, ring protons), 7.60 (br s, 2H, ring protons); ^{13}C NMR (δ in $CDCl_3$) −2.7, 123.0, 129.7, 132.4, 132.5, 136.6, 140.6. Anal. Calcd for $C_{14}H_{14}Br_2Si$: C, 45.43; H, 3.81. Found: C, 45.42; H, 3.81.

1,2-Bis(4-bromophenyl)tetramethyldisilane (83% yield): mp 75.5–77.0 °C; MS *m/z* 426 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.31 (s, 12H, Me_2Si), 7.18 (d, 4H, J = 8.3 Hz, ring protons), 7.43 (d, 4H, J = 8.3 Hz, ring protons); ^{13}C NMR (δ in $CDCl_3$) −4.1, 123.4, 130.9, 135.3, 137.5. Anal. Calcd for $C_{16}H_{20}Br_2Si_2$: C, 44.87; H, 4.71. Found: C, 44.87; H, 4.56.

1,2-Bis(4-bromophenyl)tetraethyldisilane. After workup as usual, the product was flashly distilled under reduced pressure to give 1,2-bis(4-bromophenyl)tetraethyldisilane (79% yield): bp 180–200 °C; MS *m/z* 482 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.76–0.89 (m, 20H, EtSi), 7.06 (d, 4H, J = 8.3 Hz, ring protons), 7.32 (d, 4H, J = 8.3 Hz, ring protons); ^{13}C NMR (δ in $CDCl_3$) 3.4, 8.0, 123.2, 130.9, 135.8, 135.9. Anal. Calcd for $C_{20}H_{28}Br_2Si_2$: C, 49.59; H, 5.83. Found: C, 49.53; H, 5.60.

1,2-Bis(4-bromophenyl)-1,2-dimethyldiphenyldisilane (20% yield): mp 188.5–191.0 °C; MS *m/z* 550 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.62 (s, 6H, MeSi), 7.18 (br d, 4H, J = 7.9 Hz, ring protons), 7.28–7.34 (m, 10H, ring protons), 7.40 (br d, 4H, J = 7.9 Hz, ring protons); ^{13}C NMR (δ in $CDCl_3$) −4.2, 124.0, 128.0, 129.3, 131.1, 135.1, 135.2, 135.5, 136.6. Anal. Calcd for $C_{26}H_{24}Br_2Si_2$: C, 56.53; H, 4.38. Found: C, 56.53; H, 4.24.

Preparation of Poly[4,4′-(dimethylsilylene)biphenylylene] (1d). In a Pyrex tube (10 mm × 150 mm) was placed 24.3 mg (1.00 mmol) of magnesium, and the tube was carefully dried in vacuo. Purified argon was introduced into the Pyrex tube, and then a solution of 366 mg (1.00 mmol) of bis(4-bromophenyl)dimethylsilane in 2 mL of THF was added. The mixture was warmed at 50 °C with stirring until all magnesium was consumed (2–3 h). To this was added 6.9 mg (1.3 mol%) of dichlorobis((diphenylphosphino)ethane)nickel(II), and then the tube was degassed under reduced pressure (0.1 mmHg) and sealed. The sealed glass tube was heated at 230 °C for 100 h, and the resulting mixture was hydrolyzed. The organic layer was separated, and the aqueous layer was extracted with chloroform. The organic layer and extracts were combined and dried over anhydrous magnesium sulfate. After the solvent was evaporated, the residue was reprecipitated from ethanol–chloroform to give 63 mg (31% yield) of **1d**: mp 180–183 °C; M_w = 10 000; M_n = 2800; ^{1}H NMR (δ in CCl_4) 0.62 (s, 6H, MeSi), 7.42 (br s, 8H, ring protons); ^{13}C NMR (δ in $CDCl_3$) −2.3, 126.5, 134.6, 137.1, 141.7; UV (film) λ_{max} 275, 205 nm. Anal. Calcd for $(C_{14}H_{14}Si)_n$: C, 79.94; H, 6.71. Found: C, 69.22; H, 6.63.[19a]

Polymers **1e** and **1f** were obtained by the same procedure as that of **1d**.

Poly[4,4′-(methylphenylsilylene)biphenylylene] (1e) (63% yield): mp 172–193 °C; M_w = 31 000; M_n = 7300; ^{1}H NMR (δ in $CDCl_3$) 0.91 (br s, 3H, MeSi), 7.41 (br s, 4H, ring protons), 7.63 (br s, 9H, ring protons); ^{13}C NMR (δ in $CDCl_3$) −3.3, 126.6, 127.9, 129.5, 135.1, 135.8, 136.0, 141.2; UV (film) λ_{max} 273, 221 nm. Anal. Calcd for $(C_{19}H_{16}Si)_n$: C, 83.77; H, 5.92. Found: C, 80.36; H, 6.34.

Poly[3,3′-(dimethylsilylene)biphenylylene] (1f) (60% yield): mp 49–62 °C; M_w = 4600; M_n = 2100; ^{1}H NMR (δ in $CDCl_3$) 0.58 (s, 6H, MeSi), 7.35–7.72 (m, 8H, ring protons); ^{13}C NMR (δ in $CDCl_3$) −2.4, 128.2, 133.0, 133.1, 134.1, 138.6, 140.8; UV (film) λ_{max} 257, 224 nm. Anal. Calcd for $(C_{14}H_{14}Si)_n$: C, 79.94; H, 6.71. Found: C, 76.32; H, 6.92.

Preparation of 1a from Dehalogenative Coupling Reaction. Dehalogenative coupling of 1,2-bis(4-bromophenyl)tetramethyldisilane which was carried out by the same procedure as that of **1d** gave **1a** (19% yield): mp 135–144 °C; M_w = 19 200; M_n = 7300; ^{1}H NMR (δ in $CDCl_3$) 0.38, 0.41, 0.60 (MeSi), 7.21–7.57 (m, ring protons); ^{13}C NMR (δ in $CDCl_3$) −3.8, −2.4, 126.3, 126.4, 126.5, 126.7, 133.3, 133.4, 133.9, 134.4, 134.6, 134.7, 134.9, 141.0, 143.8; UV (film) λ_{max} 276, 220 nm.

Poly[4,4′-(tetramethyldisilanylene)terphenylylene] (2a). A mixture of 428.3 mg (1.00 mmol) of 1,2-bis(4-bromophenyl)tetramethyldisilane and 48.1 mg (2.00 mmol) of magnesium in 2.4 mL of THF in a 10 mm i.d. Pyrex tube was stirred at 50 °C for 3 h untill all the magnesium was consumed. To this were added 5.3 mg (0.001 mmol) of dichloro(bis(diphenylphosphino)ethane)nickel(II) and 235.9 mg (1.0 mmol) of 1,4-dibromobenzene. The tube was degassed and sealed, and then the tube was heated at 150 °C for 100 h. The resulting mixture was hydrolyzed with water. After usual workup as above, the product was reprecipitated from ethanol–chloroform to give 134.4 mg (39% yield) of **2a:** mp 113–126 °C; M_w = 9500; M_n = 4900; ^{1}H NMR (δ in $CDCl_3$) 0.39 (s, 12H, MeSi), 7.48–7.71 (m, 12H, ring protons); ^{13}C NMR (δ in $CDCl_3$) −3.8, 126.3, 127.4, 134.4, 138.0, 140.0, 140.6; UV (film) λ_{max} 294, 204 nm; UV (THF) λ_{max} 295 (ϵ 29 300), 210 nm (ϵ 72 900). Anal. Calcd for $(C_{22}H_{24}Si_2)_n$: C, 76.68; H, 7.02. Found: C, 75.10; H, 7.47.

The same procedure as that of **2a** was used for the preparation of polymers **2b** and **2c**.

Poly[4,4′-(tetraethyldisilanylene)terphenylylene] (2b) (62% yield): mp 98.5–110.0 °C; M_w = 8500; M_n = 4000; ^{1}H NMR (δ in $CDCl_3$) 1.00 (br s, 20H, EtSi), 7.30–7.72 (m, 12H, ring protons); ^{13}C NMR (δ in $CDCl_3$) 3.8, 8.2, 126.1, 127.3, 135.0, 136.2, 140.3, 140.7; UV (film) λ_{max} 294, 205 nm; UV (THF) λ_{max} 293 (ϵ 31 500), 211 nm (ϵ 49 700). Anal. Calcd for $(C_{26}H_{32}Si_2)_n$: C, 77.93; H, 8.05. Found: C, 73.26; H, 7.88.

Poly[4,4′-(1,2-dimethyl-1,2-diphenyldisilanylene)terphenylylene] (2c) (63% yield): mp 143–161 °C; M_w = 7000; M_n = 3600; ^{1}H NMR (δ in $CDCl_3$) 0.70 (s, 6H, MeSi), 7.30–7.66 (m, 22H, ring protons); ^{13}C NMR (δ in $CDCl_3$) −4.0, 126.4, 127.4, 127.9, 129.0, 135.2, 135.7, 136.4, 139.9, 141.0, 141.2; UV (film) λ_{max} 292 nm; UV (THF) λ_{max} 291 (ϵ 30 800), 210 nm (ϵ 73 100). Anal. Calcd for $(C_{32}H_{28}Si_2)_n$: C, 82.00; H, 6.02. Found: C, 78.78; H, 5.72.[19b]

Polymers **3a–c** were obtained in a similar manner to that of polymer **2a**, using 4,4′-dibromobiphenyl instead of 1,4-dibromobenzene as the starting compound.

Poly[4,4′-(tetramethyldisilanylene)quaterphenylylene] (3a) (32% yield): mp 120–138 °C; M_w = 5800; M_n = 4000; ^{1}H NMR (δ in $CDCl_3$) 0.38 (s, 12H, MeSi), 7.50–7.71 (m, 16H, ring protons); ^{13}C NMR (δ in $CDCl_3$) −3.8 (relative intensity 100, MeSi), 126.3 (76, CH), 127.3 (73, CH), 127.5 (79, CH), 128.6 (11, CH), 133.4 (9, CH), 134.4 (74, CH), 134.8 (19, CH), 139.6 (16, ipso-C), 140.1 (14, ipso-C), 140.6 (13, ipso-C), 141.0 (14, ipso-C); UV (film) λ_{max} 304, 208 nm; UV (THF) λ_{max} 301 (ϵ 46 400), 211 nm (ϵ 77 300). Anal. Calcd for $(C_{28}H_{28}Si_2)_n$: C, 79.94; H, 6.71. Found: C, 72.30; H, 6.89.[19c]

Poly[4,4′-(tetraethyldisilanylene)quaterphenylylene] (3b) (30% yield): mp 104–127 °C; M_w = 7000; M_n = 4500; ^{1}H NMR (δ in $CDCl_3$) 1.00 (br s, 20H, EtSi), 7.29–7.72 (m, 16H, ring protons); ^{13}C NMR (δ in $CDCl_3$) 3.7, 8.2, 126.1, 127.3, 127.4, 135.0, 136.3, 139.5, 140.0, 140.6; UV (film) λ_{max} 305, 204 nm; UV (THF) λ_{max} 306 (ϵ 46 200), 211 nm (ϵ 77 400). Anal. Calcd for $(C_{32}H_{36}Si_2)_n$: C, 80.61; H, 7.61. Found: C, 76.52; H, 7.45.

Poly[4,4′-(1,2-dimethyl-1,2-diphenyldisilanylene)quaterphenylylene] (3c) (49% yield): mp 180–199 °C; M_w = 6900; M_n = 3400; ^{1}H NMR (δ in $CDCl_3$) 0.70 (s, 6H, MeSi), 7.30–7.69 (m, 26H, ring protons); ^{13}C NMR (δ in $CDCl_3$) −4.0, 126.3, 127.3, 127.4, 127.9, 129.0, 135.2, 135.7, 136.4, 139.6, 139.9, 141.0, 141.2; UV (film) λ_{max} 305 nm; UV (THF) λ_{max} 304 (ϵ 41,000), 211 nm (ϵ 89,700). Anal. Calcd for $(C_{38}H_{32}Si_2)_n$: C, 83.77; H, 5.92. Found: C, 80.04; H, 6.12.

Preparation of 1,4-Bis(diethylsilyl)benzene. To a solution of 0.145 mmol of 1,4-phenylenedimagnesium dibromide in 200 mL of THF was added 36.0 g (0.294 mmol) of chlorodiethylsilane at 0 °C. The resulting mixture was allowed to stand overnight at room temperature. After hydrolysis of the mixture with water and usual workup as above, the product was distilled under reduced pressure to give 14.9 g (41% yield) of 1,4-bis(diethylsilyl)benzene: bp 60–61 °C (0.4 mmHg); MS *m/z* 250 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.80–0.91 (m, 8H, CH_2-Si), 1.03 (br t, 12H, J = 7.6 Hz, Me), 4.21 (quintet, 2H, J = 3.3 Hz, HSi), 7.52 (s, 4H, ring protons); ^{13}C NMR (δ in $CDCl_3$) 3.3, 8.1, 133.9, 136.6; IR ν_{Si-H} 2110 cm^{-1}. Anal. Calcd for $C_{14}H_{26}Si_2$: C, 67.12; H, 10.46. Found: C, 66.96; H, 10.30.

Preparation of 1,4-Bis(chlorodiethylsilyl)benzene. A mixture of 10.0 g (39.9 mmol) of 1,4-bis(diethylsilyl)benzene and 10 mg (0.056 mmol) of $PdCl_2$ in 45 mL of carbon tetrachloride was heated to reflux for 3 h. The solvent and the resulting $CHCl_3$ were evaporated, and the residue was distilled under reduced pressure to give 10.1 g (79% yield) of 1,4-bis(chlorodiethylsilyl)benzene: bp 139–142 °C (0.3 mmHg); MS *m/z* 289 (M^+ – Et); ^{1}H NMR (δ in $CDCl_3$) 0.70 (br s, 20H, Et), 7.28 (s, 4H, ring protons); ^{13}C NMR (δ in $CDCl_3$) 6.6, 8.0, 133.1, 136.5. Anal. Calcd for $C_{14}H_{24}Cl_2Si_2$: C, 52.64; H, 7.57. Found: C, 52.44; H, 7.55.

Preparation of Poly[*p*-(tetraethyldisilanylene)phenylene] (4b). To a vigorously stirred mixture of 0.9 g (39.1 mmol) of sodium dispersion in 20 mL of toluene was added 5.0 g (15.7 mmol)of 1,4-bis(chlorodiethylsily)benzene at room temperature. The resulting mixture was heated to reflux for 5 h and then hydrolyzed with water. Usual workup as above followed by reprecipitation from ethanol–chloroform gave 2.93 g (75% yield) of polymer **4b** as white solids: mp 192–216 °C; M_w = 11 000; M_n = 5800; ^{1}H NMR (δ in $CDCl_3$) 0.95 (br s, 20H, Et), 7.27 (s, 4H, ring protons); ^{13}C NMR (δ in $CDCl_3$) 3.5, 8.1, 133.6, 137.2; UV (film) λ_{max} 260 nm; UV (THF) λ_{max} 260 (ϵ 24 900), 212 (ϵ 19 400) nm. Anal. Calcd for $(C_{14}H_{24}Si_2)_n$: C, 67.66; H, 9.73. Found: C, 68.44; H, 9.71.

Photolysis of Thin Solid Films of Polymers. A 10% chloroform solution of polymers **1a–c**, **2a–c**, and **3a–c** was coated on a quartz plate or an NaCl plate and dried under reduced pressure to give solid films with a thickness of 0.05–0.1 mm. The films were irradiated with a low-pressure mercury lamp (254 nm) bearing a Vycor filter in air. After a 1 h irradiation, UV spectra of the resulting films showed disappearance of the absorption bands at 280–300 nm, and their IR spectra revealed strong absorptions at 3500–3000 and 1040 cm^{-1} for **1a**, 3600–3200 and 1080 cm^{-1}for **1b**, 3500–3000 and 1090 cm^{-1} for **1c**, 3500–3200, 1080, and 1040 cm^{-1} for **2a**, 3600–3200 and 1070 cm^{-1} for **2b**, 3500–3200 and 1080 cm^{-1} for **2c**, 3500–3200 and 1080 cm^{-1} for **3a**, 3500–3200 and 1070 cm^{-1} for **3b**, and 3500–3200 and 1080 cm^{-1} for **3c**. No changes were observed for the films prepared from **1d–f** in IR and UV spectra after a 1 h irradiation.

Photolysis of Polymers 1a–f, 2b,c, 3b,c, and 4b in Benzene. In a 25 mL reaction vessel fitted with a low-pressure mercury lamp bearing a Vycor filter was placed 50–60 mg of a polymer in 25 mL of benzene. The solution was irradiated, and the progress of the reaction was monitored by GPC whose results are shown in Figures 4a,c,e and Figures 5 and 6. After a 10 h irradiation, the solvent was evaporated to give photodegradation products. IR and ^{1}H NMR spectra obtained for the photoproducts showed stretching vibrations of an Si–H bond and a signal due to an Si–H proton, respectively. For the photoproducts obtained from **1a**: M_w = 6600; M_n = 2500; IR ν_{Si-H} 2120 cm^{-1}; ^{1}H NMR (δ in $CDCl_3$) 4.36 (Si–H); UV (film) λ_{max} 203, 276 nm. For the photoproducts obtained from **1b**: M_w = 19 500; M_n = 7900; IR ν_{Si-H} 2110 cm^{-1}; ^{1}H NMR (δ in $CDCl_3$) 4.25 (Si–H); UV (film) λ_{max} 283, 204 nm. For the photoproducts obtained from **1c**: M_w = 8000; M_n = 2600; IR ν_{Si-H} 2110 cm^{-1}; ^{1}H NMR (δ in $CDCl_3$) 5.01 (Si–H); UV (film) λ_{max} 279 nm. For the photoproducts obtained from **2b:** M_w = 7800; M_n = 3300; UV (THF) λ_{max} 294, 220 nm. For the photoproducts obtained from **2c:** M_w = 6100; M_n = 2900; UV (film) λ_{max} 291 nm. For the photoproducts obtained from **3b:** M_w = 5600; M_n = 3400; UV (film) λ_{max} 307 nm. For the photoproducts obtained from **3c:** M_w = 6200; M_n = 2800; UV (film) λ_{max} 300 nm. For the photoproducts obtained from **4b:** M_w = 9000; M_n = 4400; IR ν_{Si-H} 2110 cm^{-1}; ^{1}H NMR (δ in $CDCl_3$) 0.30–1.05 (m, EtSi), 4.19 (HSi), 5.40–6.60 (m, olefinic protons), 7.20–7.85 (m, ring protons); ^{13}C NMR (δ in $CDCl_3$) 3.3, 3.8, 6.5, 6.8, 6.9, 7.1, 7.2, 7.4, 7.5, 7.6, 7.9, 8.0, 8.1, 8.5 (EtSi), 125–129, 133.3–134.9 (sp^2 carbons); UV (film) λ_{max} 232 nm (shoulder).

No changes were observed for the molecular weights of polymers **1d–f** after a 10 h irradiation in benzene solution. IR and ^{1}H and ^{13}C NMR spectra of the photoproducts from **1d–f**, **2b,c**, and **3b,c** are identical with those of the starting polymers.

Photolysis of Polymers in the Presence of MeOH. A solution of 50–60 mg of a polymer and 1 mL of methanol in 25 mL of benzene was irradiated internally with a low-pressure mercury lamp, and the progress of the reaction was monitored by GPC (the results obtained from the photolysis of **1a–c** are shown in Figures 4b,d,f). After a 10 h irradiation, the solvent was evaporated to give photodegradation products. For the photoproducts obtained from **1a**: M_w = 2400; M_n = 1000; IR ν_{Si-H} 2120 cm^{-1}; ^{1}H NMR (δ in $CDCl_3$) 0.41, 0.44 (MeSi), 3.50 (MeO), 4.50 (HSi), 7.38–7.67 (m, ring protons); ^{13}C NMR (δ in $CDCl_3$) –3.84, –3.75, –3.5, –2.4, –2.3, –1.7, –1.3, –1.1, 0.1 (MeSi), 50.7 (MeO), 126.3, 126.4, 126.5, 126.6, 127.8, 128.7, 133.5, 134.0, 134.2, 134.4, 134.5, 134.7, 137.9, 141.0, 141.9, 142.2 (ring carbons); UV (film) λ_{max} 203, 271 nm. For the photoproducts obtained from **1b**: M_w = 14 700; M_n = 4600; IR ν_{Si-H} 2110 cm^{-1}; ^{1}H NMR (δ in $CDCl_3$) 0.89 (EtSi), 3.40 (weak, MeO), 4.15 (weak, HSi), 7.34 (br d, J = 7.3 Hz, ring protons), 7.46 (br d, J = 7.3 Hz, ring protons); ^{13}C NMR spectrum is identical with that of the starting polymer; UV (film) λ_{max} 276 nm. For the photoproducts obtained from **1c**: M_w = 1400; M_n = 360; IR ν_{Si-H} 2110 cm^{-1}; ^{1}H NMR (δ in $CDCl_3$) 0.63–0.75 (MeSi), 3.61 (MeO), 5.03 (HSi), 7.39–7.63 (m, ring protons); ^{13}C NMR (δ in $CDCl_3$) –5.0, –4.1 –3.5 (MeSi), 51.3 (MeO), 126.4–141.2 (ring carbons); UV (film) λ_{max} 272 nm. For the photoproducts obtained from **2b**: M_w = 7600; M_n = 3700. For the photoproducts obtained from **2c**: M_w = 5400; M_n = 2200.

No changes were observed in the molecular weights for polymer **3b** and **3c** after a 10 h irradiation. IR and ^{1}H and ^{13}C NMR spectra of the photoproducts from **2b,c** and **3b,c** are identical with those of the starting polymers.

Photolysis of Polymer 2b with a High-Pressure Mercury Lamp. A solution of 50.4 mg of polymer **2b** (M_w = 6200; M_n = 3100) in 100 mL of benzene was irradiated with a high-pressure mercury lamp bearing a Pyrex filter for 10 h. The solvent was evaporated and the residue was analyzed by GPC: M_w = 5500; M_n = 2800. ^{1}H and ^{13}C NMR spectra of the photoproducts are identical with those of **2b**.

Photolysis of 1,4-Bis(chlorodiethylsilyl)benzene. A solution of 210 mg of 1,4-bis(chlorodiethylsilyl)benzene in 25 mL of hexane was irradiated with a low-pressure mercury lamp for 4 h. After the solvent was evaporated, the residue was analyzed by ^{1}H NMR spectroscopy, showing that the starting compound was recovered unchanged.

Method of the Crystal-Orbital Calculation. The one-dimensional crystal orbital (CO) calculation was performed at the semiempirical (CNDO/2) approximations for the model polymers. The geometries of poly[(disilanylene)phenylene] (**4g**, m = 1) and poly[(disilanylene)biphenylylene] (**1g**, m = 2) were energetically optimized by the energy gradient method[17] under the assumption that the phenylene and the disilanylene units are coplanar. For poly[(disilanylene)terphenylylene] (**2g**, m = 3) and poly[(disilanylene)quaterphenylylene] (**3g**, m = 4), the geometries were constructed utilizing those of **4g** and **1g**. The overlap and the electron repulsion integrals were consid-

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(17) See, for instance, Tanaka, K.; Shichiri, T.; Kobashi, M.; Yamabe, T. *Synth. Met.* **1988**, *24*, 167.

ered as far as the fourth nearest neighboring cell at maximum (ca. 20–30 Å from the central cell in average). Polarization functions such as silicon 3d atomic orbitals (AOs) were suppressed, since it has been pointed out that these do not give an appreciable contribution to the electronic structure of silicon atoms in silane oligomers.[18]

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(18) Nelson, J. T.; Pietro, W. J. *J. Phys. Chem.* **1988**, *92*, 1365.

(19) (a) IR spectrum of the ash obtained from combustion of polymer **1d** under the same conditions as the elemental analysis shows strong absorption bands at 1260, 800 (ν_{Si-C}), and 1090 cm^{-1} (ν_{Si-O}). (b) For polymer **2c**: IR 1260, 800 (ν_{Si-C}), 1070 cm^{-1} (ν_{Si-O}). (c) For polymer **3a**: IR 1220, 800 (ν_{Si-C}), 1070 cm^{-1} (ν_{Si-O}).