June, 1993] © *1993 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***66***, *1795—1798(1993)* 1795

Polymeric Organosilicon Systems. 16.
Synthesis and Photochemical Properties of Poly[(1,2-dimethyl-1,2-diphenyl-1,2-disilanylene)naphthylenes]

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(Received February 8, 1993)

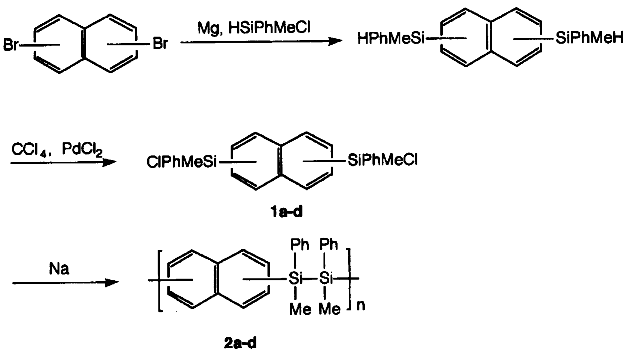
Poly[(1,2-dimethyl-1,2-diphenyl-1,2-disilanylene)-1,4-naphthylene], poly[(1,2-dimethyl-1,2-diphenyl-1,2-disilanylene)-1,5-naphthylene], poly[(1,2-dimethyl-1,2-diphenyl-1,2-disilanylene)-2,6-naphthylene], and poly[(1,2-dimethyl-1,2-diphenyl-1,2-disilanylene)-2,7-naphthylene] were synthesized by the condensation reaction of the corresponding bis(chloromethylphenylsilyl)naphthalenes with sodium. Photochemical properties of these polymers have been reported.

We have demonstrated that the polymers which have an alternating arrangement of a disilanylene unit and a π-electron system such as vinylene,[1] ethynylene,[2,3] 1,3-butadiyne-1,4-diyl,[4] 1-buten-3-yne-1,4-diyl,[5,6] and phenylene,[7,8] in the polymer main chain, are highly photoactive, and one of these polymers, poly[(1,2-dimethyl-1,2-diphenyl-1,2-disilanylene)-*p*-phenylene] can be used as a top imaging layer of the double layer photoresist system.[8] As a part of continuing effort to obtain the polymer with high photosensitivity, we have synthesized copolymers composed of an alternating 1,2-dimethyl-1,2-diphenyl-1,2-disilanylene group and 1,4-, 1,5-, 2,6-, and 2,7-naphthylene unit by the sodium condensation reaction of the corresponding bis(chloromethylphenylsilyl)naphthalenes and investigated their photochemical properties in the solid state as well as in solution.

The synthesis and photochemical behavior of only one disilanylenenaphthylene polymer, poly[(1,1,2,2-tetramethyl-1,2-disilanylene)-1,4-naphthylene] have been reported so far by Lee and Weber.[9]

Results and Discussion

Synthesis of Poly[(1,2-dimethyl-1,2-diphenyl-1,2-disilanylene)naphthylenes]. The starting monomers, 1,4-, 1,5-, 2,6-, and 2,7-bis(chloromethylphenylsilyl)naphthalene (**1a**—**d**) were prepared by two-step synthesis, that is, the reaction of chloromethylphenylsilane with naphthylenedimagnesium dibromides gave bis(methylphenylsilyl)naphthalenes in 36—52% yields, and treatment of the resulting hydrosilanes with carbon tetrachloride in the presence of a catalytic amount of palladium dichloride yielded **1a**—**d** in 64—83% yields, as expected (Scheme 1).



Scheme 1.

Treatment of monomer **1a** with a slight excess of sodium dispersion in refluxing toluene for 8 h, and then hydrolysis, and reprecipitation of the resulting hydrocarbon solution from chloroform-ethanol gave poly[(1,2-dimethyl-1,2-diphenyl-1,2-disilanylene)-1,4-naphthylene] (**2a**) in 40% yield. In this reaction, a 53% yield of an insoluble polymer in chloroform which was separated before reprecipitation, was also formed. Similar reaction of **1b**, **1c**, and **1d** gave poly[(1,2-dimethyl-1,2-diphenyl-1,2-disilanylene)-1,5-naphthylene] (**2b**), poly[(1,2-dimethyl-1,2-diphenyl-1,2-disilanylene)-2,6-naphthylene] (**2c**), and poly[(1,2-dimethyl-1,2-diphenyl-1,2-disilanylene)-2,7-naphthylene] (**2d**) in 44, 12, and 12% yields, respectively, together with 43—60% yields of chloroform-insoluble polymers. The relatively low yields of polymers **2c** and **2d** as compared with those of **2a** and **2b** may be ascribed to the formation of oligomers which are soluble in ethanol.

These polymers thus obtained are white solids and soluble in chlorocarbons, ethers, and aromatic solvents. They are slightly soluble in saturated hydrocarbons but insoluble in alcohols. Polymers **2a** and **2b** melt at about 200 °C, while polymers **2c** and **2d** melt at 120—150 °C. The molecular weights of these polymers were determined to be $M_w=16300$ ($M_w/M_n=6.8$), 19900 (12), 13700 (5.5), and 9600 (6.0) for **2a**, **2b**, **2c**, and **2d**, respectively by GPC, relative to polystyrene standards.

The structures of the polymers **2a**—**d** were verified by spectroscopic analysis (see Experimental Section). ^{1}H and ^{13}C NMR spectra and IR spectra of **2a** and **2b** are wholly consistent with the (1,2-dimethyl-1,2-diphenyl-1,2-disilanylene)-1,4- and -1,5-naphthylene structure. ^{1}H and ^{13}C NMR spectra of polymers **2a** and **2b** reveal only two signals with equal intensities in the methylsilyl region due to the presence of two kinds of a diastereotopic group. IR spectra show no absorptions at about 1050 cm^{-1}, indicating that no siloxane units are included in the polymer main chain. In contrast, IR spectra of disilanylene-2,6- and -2,7-naphthylene polymers **2c** and **2d** show absorptions at 1050 cm^{-1}, indicating the presence of siloxane unit, which would be formed from hydrolysis of the chlorosilyl group remaining in the resulting polymer during work-up. The ^{13}C NMR spectrum of the polymer **2c** shows signals at −5.0 and −4.0 ppm with an intensity ratio of 5 : 2. Upon UV-irradiation of a benzene solution of **2c**, the signal at −5.0 ppm remained unchanged, while that at −4.0 ppm disappeared completely, indicating that the former is assignable to the signal of a disilaxane group and the latter is ascribed to the disilanylene methyl carbon (vide infra). Similarly, the ^{13}C NMR spectrum of **2d** shows a signal at −4.0 ppm due to the disilanylene methyl carbon and two signals at −0.5 and −5.0 ppm, attributed to methyl carbons of the siloxy groups. The intensity ratio of 3 : 6 : 2 for the signals at −0.5, −4.0, and −5.0 ppm observed in the ^{13}C NMR spectrum of **2d** clearly indicates that a large amount of siloxy unit is included in the polymer chain.

It seems likely that the presence of the siloxy group in the polymer main chain of **2c** and **2d** interrupts the delocalization of the π-electron system through the polymer chain. In fact, UV spectra of 1,4- and 1,5-naphthylene polymers **2a** and **2b** show two strong absorption maxima at about 240 and 310 nm which are remarkably red-shifted as compared to those of trimethyl(1-naphthyl)silane (λ_{max} in $CHCl_3$ 237 (ε=6600) and 284 nm (ε=6300)), but, those of 2,6- and 2,7-naphthylene polymers **2c** and **2d**, however, reveal only a strong absorption band at about 220 and 240 nm, respectively, although a small shoulder at about 300 nm in both cases is observed.

Photolysis of Polymers 2a—d. First we studied the photolysis of polymers **2a**—**d** in the solid state. Thus, the thin solid film of the polymer was irradiated in air with low-pressure mercury lamp and the progress of the reaction was monitored by UV and IR spectra. All four polymers show similar photochemical behavior in the film. UV spectra show the decrease of the absorption band with increasing reaction time. IR spectra of the photoproducts obtained from the photolysis of **2a**—**d** show the presence of Si–OH and Si–O–Si groups. As a typical example, IR and UV spectra of polymer **2a** before and after irradiation are shown in Figs. 1 and 2. The formation of the Si–OH and Si–O–Si groups can be explained by the reaction of silyl radicals arising from photochemical scission of an excited Si–Si bond with oxygen in air, as observed in the case of other disilanylene polymers reported previously.[1—8)]

In order to obtain more information about the photochemical behavior of the polymers **2a**—**d**, we carried out the photolysis of **2a**—**d** in benzene, and the progress of the reaction was monitored by GPC. As can be seen in Fig. 3, the molecular weights of the photoproducts rapidly decreased with increasing irradiation time. ^{1}H and ^{13}C NMR spectra of the resulting photoproducts show only broad and unsolved signals in the silyl methyl and naphthyl regions, similar to those of poly[(1,1,2,2-tetramethyl-1,2-disilanylene)-1,4-naphthylene] reported by Lee and Weber,[9)] while their IR spectra show absorptions due to the stretching frequencies of an Si–H at about 2100 cm^{-1}. These results can be reasonably

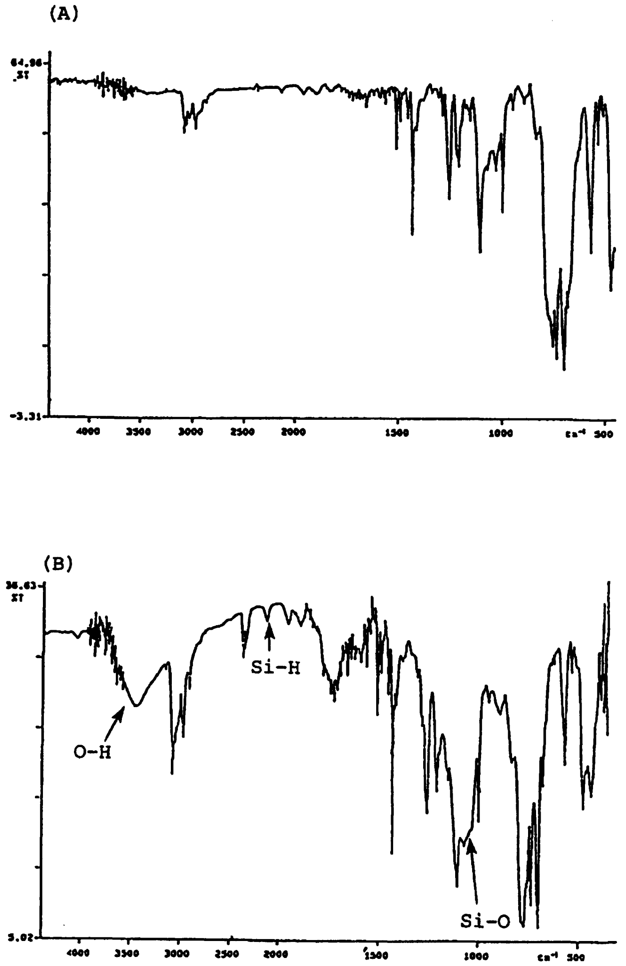


Fig. 1. IR spectra of polymer **2a**: (A) before irradiation; (B) after 17 h irradiation.

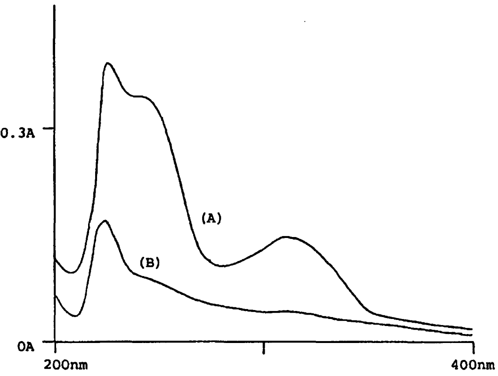


Fig. 2. UV spectra of polymer **2a**: (A) before irradiation; (B) after 1 h irradiation.

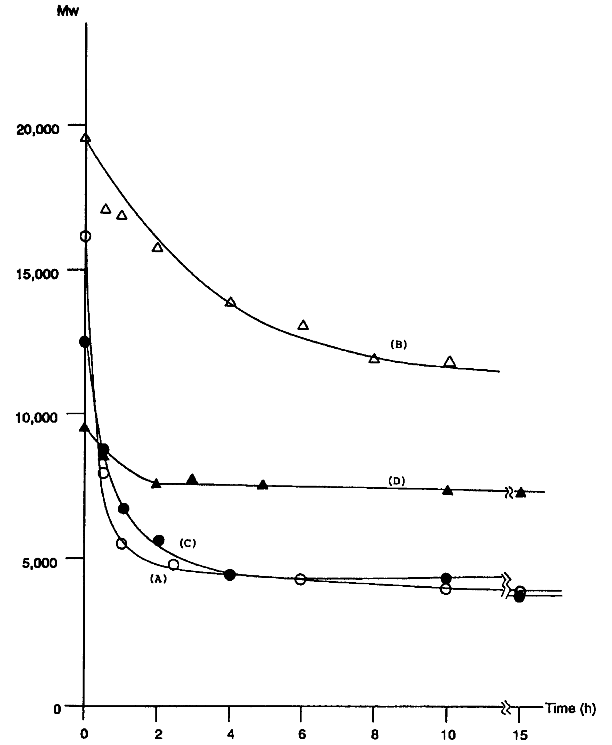


Fig. 3. Plots of molecular weights of photoproducts vs irradiation time for (A) polymer **2a**, (B) polymer **2b**, (C) polymer **2c**, and (D) polymer **2d** in benzene.

explained in terms of homolytic scission of a silicon–silicon bond, followed by disproportionation reaction of the resulting silyl radicals leading to the formation of silene and hydrosilane, as described for the photodegradation mechanism of poly[(disilanylene)phenylene].(7)

The polymer **2d** is found to be less active than the others. This low activity of polymer **2d** is probably due to the presence of siloxy units in the polymer chain. ^{13}C NMR spectra of the photodegradation product from **2d** showed the absence of the signal at −4.0 ppm due to the disilanylene methyl carbon, but the signals of siloxy methyl carbons at −0.5 and −5.0 ppm remained unchanged after irradiation.

Experimental

General. All reactions were carried out under an atmosphere of purified argon. Toluene and THF were dried over sodium and distilled just before use. CCl_4 was dried over anhydrous calcium chloride and distilled just before use. NMR spectra were measured on a JEOL model PLX-60, FX-90A, and EX-270 spectrometer. IR spectra were recorded on a Perkin–Elmer 1600 FT-infrared spectrophotometer. UV spectra were recorded on a Hitachi U-3210 spectrometer. 1,4-, 1,5-, 2,6-, and 2,7-Dibromonaphthalene were prepared as described in the literatures.(10)

Preparation of 1,4-Bis(methylphenylsilyl)naphthalene: In a 200 mL two necked flask fitted with a dropping funnel and reflux condenser was placed 7.1 g (0.29 mol) of magnesium and 50 mL of THF. To this was added a mixture of 31.2 g (0.11 mol) of 1,4-dibromonaphthalene and 46 g (0.29 mmol) of chloromethylphenylsilane through the dropping funnel over a period of 20 min. The resulting mixture was stirred over night at room temperature, and then hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was distilled under reduced pressure to give 14.5 g (36% yield) of the title compound: Bp 205—207 °C (0.2 mmHg, 1 mmHg=133.322 Pa); MS *m/z* 368 (M^+); IR ν_{Si-H} 2124 cm^{-1}, ^{1}H NMR (in C_6D_6) δ=0.73 (d, 6H, J=3.6 Hz, MeSi), 5.25 (q, 2H, J=3.6 Hz, HSi), 7.1—7.9 (m, 16H, ring protons); ^{13}C NMR (in C_6D_6) δ=−4.5, 125.8, 128.0, 128.9, 129.5, 134.4, 134.9, 135.2, 136.2, 136.8. Anal. Calcd for $C_{24}H_{24}Si_2$: C, 78.20; H, 6.56%. Found: C, 77.90; H, 6.49%.

For the preparation of 1,5-, 2,6-, and 2,7-bis(methylphenylsilyl)naphthalene, the same procedure was used as above.

1,5-Bis(methylphenylsilyl)naphthalene: 63% yield; bp 220—235 °C (0.1 mmHg); mp 69—72 °C; MS *m/z* 368 (M^+); IR ν_{Si-H} 2098 cm^{-1}, ^{1}H NMR (in C_6D_6) δ=0.66 (d, 6H, J=4.2 Hz, MeSi), 5.59 (q, 2H, J=4.2 Hz, HSi), 7.02—7.83 (m, 14H, ring protons), 8.33 (d, 2H, J=8.0 Hz, ring protons); ^{13}C NMR (in C_6D_6) δ=−4.4, 125.4, 128.0, 129.5, 130.4, 134.5, 134.9, 135.0, 135.4, 137.0. Anal. Calcd for $C_{24}H_{24}Si_2$: C, 78.20; H, 6.56%. Found: C, 78.16; H, 6.43%.

2,6-Bis(methylphenylsilyl)naphthalene: 52% yield; bp 218 °C (0.1 mmHg); mp 52 °C; MS *m/z* 368 (M^+); IR ν_{Si-H} 2121 cm^{-1}, ^{1}H NMR (in C_6D_6) δ=0.58 (d, 6H, J=3.6 Hz, MeSi), 5.20 (q, 2H, J=3.6 Hz, HSi), 6.93—7.98 (m, 16H, ring protons); ^{13}C NMR (in $CDCl_3$) δ=−5.0, 127.4, 128.0, 129.6, 131.0, 133.4, 133.8, 134.9, 135.2, 135.7. Anal. Calcd for $C_{24}H_{24}Si_2$: C, 78.20; H, 6.56%. Found: C, 78.22; H, 6.62%.

2,7-Bis(methylphenylsilyl)naphthalene: 39% yield; bp 215—217 °C (0.1 mmHg); MS *m/z* 368 (M^+); IR ν_{Si-H} 2120 cm^{-1}, ^{1}H NMR (in C_6D_6) δ=0.56 (d, 6H, J=3.6 Hz, MeSi), 5.20 (q, 2H, J=3.6 Hz, HSi), 6.93—7.98 (m, 16H, ring protons); ^{13}C NMR (in $CDCl_3$) δ=−4.9, 127.1, 128.0, 129.6, 131.6, 132.5, 133.1, 134.5, 134.9, 135.3, 136.1. Anal. Calcd for $C_{24}H_{24}Si_2$: C, 78.20; H, 6.56%. Found: C, 78.18; H, 6.54%.

1,4-Bis(chloromethylphenylsilyl)naphthalene (1a). A mixture of 14.5 g (39.3 mmol) of 1,4-bis(methylphenylsilyl)naphthalene and 86 mg (0.48 mmol) of palladium dichloride in 200 mL of CCl_4 was heated to reflux for 3 h. The mixture was cooled down to room temperature and filtered to remove the palladium catalyst. After the solvent was removed off, the residue was distilled under reduced pressure to give 11.0 g of **1a** (64% yield): Bp 215—220 °C (0.1 mmHg); mp 150—153 °C; MS *m/z* 436 (M^+); ^{1}H NMR (in CCl_4) δ=1.06 (s, 6H, MeSi), 7.09—8.01 (m, 16H, ring protons); ^{13}C NMR (in $CDCl_3$) δ=2.4, 126.0, 128.2, 129.3, 130.6, 134.0, 134.3, 134.9, 135.8, 136.0. Anal. Calcd for $C_{24}H_{22}Si_2Cl_2$: C, 65.89; H, 5.07%. Found: C, 65.78; H, 4.91%.

For the preparation of **1b**—**d**, the same procedure was used.

1,5-Bis(chloromethylphenylsilyl)naphthalene (1b): Compound **1b** was isolated by recrystallization from CCl_4: 64% yield; mp 205—207 °C; MS *m/z* 436 (M^+); ^{1}H NMR (in CCl_4) δ=1.05 (s, 6H, MeSi), 7.17—8.17 (m, 16H, ring protons); ^{13}C NMR (in $CDCl_3$) δ=2.6, 125.2, 128.2, 130.5, 131.9, 132.9, 134.0, 135.3 (two carbons), 136.4. Anal. Calcd for $C_{24}H_{22}Si_2Cl_2$: C, 65.89; H, 5.07%. Found: C, 65.72; H, 5.03%.

2,6-Bis(chloromethylphenylsilyl)naphthalene (1c): 80% yield; bp 251—253 °C (0.1 mmHg); MS m/z 436 (M^+); ^{1}H NMR (in CCl_4) $\delta=1.02$ (s, 6H, MeSi), 7.11—8.21 (m, 16H, ring protons); ^{13}C NMR (in $CDCl_3$) $\delta=0.9$, 128.0, 128.9, 130.0, 130.6, 133.5, 133.7, 134.1, 134.9, 135.3. Anal. Calcd for $C_{24}H_{22}Si_2Cl_2$: C, 65.89; H, 5.07%. Found: C, 66.12; H, 5.15%.

2,7-Bis(chloromethylphenylsilyl)naphthalene (1d): 83% yield; bp 243—247 °C (0.1 mmHg); MS m/z 436 (M^+); ^{1}H NMR (in CCl_4) $\delta=0.97$ (s, 6H, MeSi), 7.13—8.16 (m, 16H, ring protons); ^{13}C NMR (in $CDCl_3$) $\delta=1.0$, 127.5, 128.2, 130.6, 130.9, 132.0, 132.7, 134.1, 134.4, 135.2, 136.0. Anal. Calcd for $C_{24}H_{22}Si_2Cl_2$: C, 65.89; H, 5.07%. Found: C, 65.82; H, 5.08%.

Synthesis of Poly[(1,2-dimethyl-1,2-diphenyl-1,2-disilanylene)-1,4-naphthylene] (2a). In a 50 mL flask fitted with a reflux condenser was placed 3.0 g (25.2 mmol) of sodium dispersion and 15 mL of toluene. To this was added 2.0 g (4.5 mmol) of **1a**, and the mixture was heated to reflux for 8 h. The mixture was cooled down to 0 °C and hydrolyzed with ethanol and water. The insoluble materials (1.1 g; 53% yield) were filtered off, and the organic layer of the filtrate was separated. 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 to give 0.79 g of **2a** (40% yield): Mp 183—201 °C; UV (film) λ_{max} 223, 241, 308; ^{1}H NMR (in CCl_4) $\delta=0.80$ (br. s, 6H, MeSi), 6.30—8.10 (m, 16H, ring protons); ^{13}C NMR (in $CDCl_3$) $\delta=-2.3$, -1.7, 124.7, 127.8, 129.1, 130.0, 132.4, 132.7, 135.2, 136.8, 137.2; $M_w=16300$; $M_n=2400$. Anal. Calcd for $[C_{24}H_{22}Si_2]_n$: C, 78.63; H, 6.05%. Found: C, 78.14; H, 6.03%. IR spectrum of the insoluble materials is consistent with that of **2a**.

For the preparation of polymers **2b**—**d**, the same procedure was used.

Poly[(1,2-dimethyl-1,2-diphenyl-1,2-disilanylene)-1,5-naphthylene] (2b): 44% yield: mp 195—206 °C; UV (film) λ_{max} 237, 303; ^{1}H NMR (in CCl_4) $\delta=0.80$ (br. s, 6H, MeSi), 6.60—8.10 (m, 16H, ring protons); ^{13}C NMR (in $CDCl_3$) $\delta=-2.8$, -2.1, 124.5, 127.6, 128.6, 131.4, 135.0, 135.2, 135.6, 135.9, 138.1; $M_w=19900$; $M_n=1600$. Anal. Calcd for $[C_{24}H_{22}Si_2]_n$: C, 78.63; H, 6.05%. Found: C, 78.49; H, 6.24%. IR spectrum of the insoluble polymer (54% yield) is consistent with that of **2b**.

Poly[(1,2-dimethyl-1,2-diphenyl-1,2-disilanylene)-2,6-naphthylene] (2c): 12% yield: mp 133—151 °C; UV (film) λ_{max} 217, 243 (shoulder), 301 (shoulder); ^{1}H NMR (in $CDCl_3$) $\delta=0.73$ (br. s, 6H, MeSi), 7.25—8.02 (m, 16H, ring protons); ^{13}C NMR (in $CDCl_3$) $\delta=-5.0$, -4.0, 127.1, 127.8, 127.9, 128.0, 129.0, 131.4, 133.1, 134.9, 135.2, 135.8; $M_w=13700$; $M_n=2500$. IR spectrum of the insoluble polymer (60% yield) is consistent with that of **2c**.

Poly[(1,2-dimethyl-1,2-diphenyl-1,2-disilanylene)-2,7-naphthylene] (2d): 12% yield: mp 122—129 °C; UV (film) λ_{max} 243, 294 (shoulder); ^{1}H NMR (in $CDCl_3$) $\delta=0.72$ (br. s, 6H, MeSi), 7.25—7.88 (m, 16H, ring protons); ^{13}C NMR (in $CDCl_3$) $\delta=-5.0$, -4.0, -0.5, 126.8, 127.8, 127.9, 129.7, 131.0, 134.1, 138.9, 135.2, 136.2, 136.4; $M_w=9600$; $M_n=1900$. IR spectrum of the insoluble polymer (43% yield) is consistent with that of **2d**.

Photolysis of the Polymers 2a—d in Solid Films. A ca. 20% chloroform solution of the polymer was coated on a quartz or NaCl plate and dried under reduced pressure to give a solid film with a thickness of ca. 0.1 mm. The film was irradiated with low-pressure mercury lamp bearing Vycor filter and the progress of the reaction was monitored by UV and IR spectra.

Photolysis of the Polymers 2a—d in Benzene. In a 25 mL reaction vessel fitted internally with a low-pressure mercury lamp was placed ca. 50 mg of the polymer in 20 mL of benzene. The solution was irradiated at room temperature and the progress of the reaction was monitored by GPC.

This research was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas, New Functionality Materials, Design, Preparation, and Control, from the Ministry of Education, Science and Culture to which our thanks are due. We thank Shin-Etsu Chemical Co., Ltd., Nitto Electric Co., Ltd., Dow Corning Japan Ltd., Toshiba Silicone Co., Ltd., Kaneka Corporation, and Sumitomo Electric Industry for financial support.

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