Polymeric Organosilicon Systems. 11. Synthesis and Some Properties of Poly(disilanylenebutenyne-1,4-diyls) and Poly[(methylphenylsilylene)butenyne-1,4-diyl][1]

Joji Ohshita, Akira Matsuguchi, Kenji Furumori, Reng-Fang Hong,[2] and Mitsuo Ishikawa*

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 724, Japan

Toru Yamanaka and Tsuneaki Koike

Mitsui Petrochemical Industry Company, Ltd., Nagaura Sodegaura, Chiba 299, Japan

Jun Shioya

Sumitomo Electric Industries, Ltd., Shimaya, Konohana-ku, Osaka 554, Japan

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ABSTRACT: Three types of poly(disilanylenebutenyne-1,4-diyls) were synthesized by rhodium(I)-catalyzed head-to-head coupling of diethynyldisilanes. Poly[(methylphenylsilylene)butenyne-1,4-diyl] was also prepared by the rhodium(I)-catalyzed reaction of diethynylmethylphenylsilane. Copolymerization of 1,2-diethynyltetraphenyldisilane and 1,2-diethynyltetramethyldisilane in a ratio of 1:1 afforded an alternating polymer. Molecular weights of the polymers obtained were determined to be M_w = 10 000–100 000 by GPC relative to polystyrene standards. The poly(disilanylenebutenyne-1,4-diyls) were found to be highly photoactive. Irradiation of these polymers with UV light caused scission of Si–Si bonds in the polymer backbone in solid state and also in solution. In contrast to these polymers, poly[(methylphenylsilylene)butenyne-1,4-diyl] was found to be photochemically stable. The polymers can be cast to thin solid films by spin-coating. When the thin solid films prepared from the poly(disilanylenebutenyne-1,4-diyls) were doped with SbF_5 vapor, highly conducting films whose conductivities were measured by the four-probe method to be 10^{-3}–10^{0} S·cm^{-1} in air and 10^{-4}–10^{-3} S·cm^{-1} in vacuo were obtained.

Introduction

The polymers that have silicon–silicon bonds in a main chain are of considerable interest, because they might be used as functional materials such as photoresists, semiconducting materials, and precursors of silicon carbide.[3] In 1984, we reported the first synthesis of poly(disilanylenephenylenes) and demonstrated that these polymers can be used as the top imaging layer in the double-layer resist system.[4] Since that time, many papers concerning the synthesis and properties of the polymers that have a regular alternating arrangement of an Si–Si bond and a π-electron system such as ethenylene,[5] ethynylene,[6,7] diethynylene,[8,9] furylene,[10,11] and thienylene[12,13] in the polymer backbone have been published. We have found that these polymers are highly photoactive and become conducting, when thin solid films of the polymers are treated with SbF_5 vapor. The method used for the synthesis of these polymers is limited to either the sodium condensation reactions of bis(chlorosilyl)-substituted compounds[4,5,10-13] or the reaction of dilithio compounds bearing π-electron systems[7,9] with 1,2-dichlorodisilanes, with the exception of the ring-opening polymerization of 1,2,5,6-tetrasilacycloocta-3,7-diynes catalyzed by alkyllithium.[6] Although the sodium condensation reaction of bis(chlorosilyl)-substituted compounds offers a convenient route to the polymer synthesis, there are some limitations for reproducibility of the yields and molecular weights of the polymers. Moreover, this method cannot be used for synthesis of the polymers bearing functional groups which are sensitive to alkali metals.

Recently, we have reported that the rhodium(I)-catalyzed dimerization reaction of ethynylsilanes afforded enynes in high yields[14] and that this reaction can be applicable to the synthesis of poly(disilanylenebutenyne-1,4-diyls), which involve an enyne unit as the π-electron system.[1] In this paper we report the synthesis of poly(disilanylenebutenyne-1,4-diyls) and poly(silylenebutenyne-1,4-diyl) by the rhodium(I)-catalyzed reaction of 1,2-diethynyldisilanes and diethynylsilane in detail. We also report the photochemical and conducting properties of the resulting polymers.

Results and Discussion

Synthesis of Poly(disilanylenebutenyne-1,4-diyls) and Poly[(methylphenylsilylene)butenyne-1,4-diyl]. The reactions of 1,2-diethynyldisilanes with a catalytic amount of a rhodium(I) complex readily proceed to give poly(disilanylenebutenyne-1,4-diyls) in good yields. Thus, when 1,2-diethynyl-1,2-dimethyldiphenyldisilane (**1a**) was treated with 1 mol % of chlorotris(triphenylphosphine)-rhodium(I) in toluene at room temperature for 2 days, poly[(1,2-dimethyldiphenyldisilanylene)butenyne-1,4-diyl] (**2a**) was obtained as a light yellow solid in 73% yield (Scheme I). Monitoring the progress of this reaction by an IR spectrometer, the absorption bands at 3280 and 2040 cm^{-1} due to the stretching frequencies of an acetylenic C–H bond and a monosubstituted carbon–carbon triple bond of the starting monomer decrease with increasing reaction time. A new absorption band at 2146 cm^{-1} attributable to the stretching frequency of a disubstituted carbon–carbon triple bond appears during the reaction, and this band increases with increasing reaction time. After 2 days, the IR spectrum of the reaction mixture showed that almost all starting **1a** was consumed as indicated by the disappearance of the absorption bands at 3280 and 2040 cm^{-1}. Only one absorption band at 2146 cm^{-1} was observed in the region of the stretching vibration of the acetylenic bonds.

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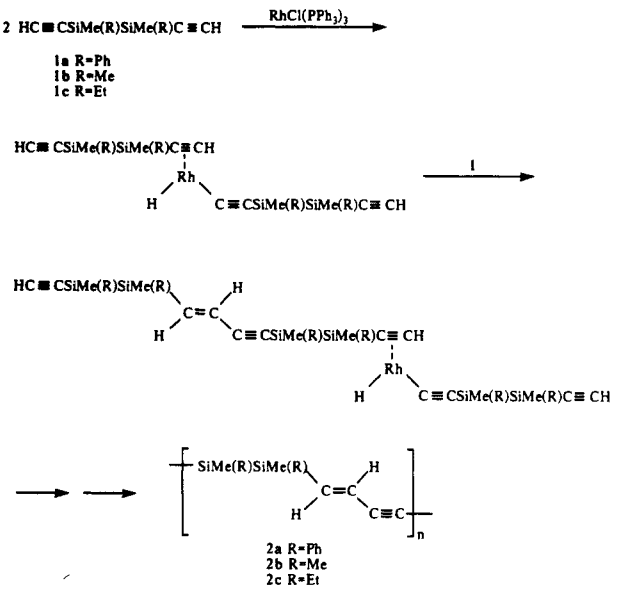
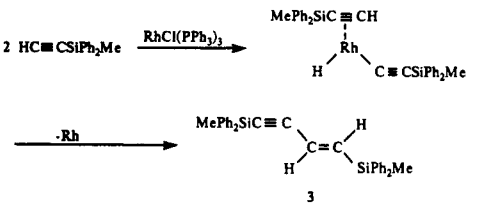
Scheme I



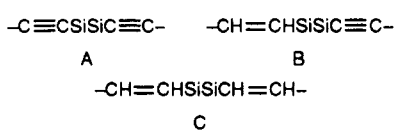
The structure of **2a** was verified by spectrometric analysis. The ^1H NMR spectrum of **2a** shows a singlet at 0.47 ppm and doublets at 5.93 and 6.66 ppm attributed to methylsilyl protons and olefinic protons, respectively. The coupling constant of the olefinic protons (19 Hz) clearly indicates that the polymer should have an (*E*)-configuration. Furthermore, IR and ^1H and ^{13}C NMR spectra of **2a** are similar to those of 1,4-bis(methyldiphenylsilyl)butenyne (**3**) prepared from the rhodium(I)-



catalyzed reaction of ethynylmethyldiphenylsilane, as shown in Figure 1. These results clearly indicate that the polymer backbone consists of the repeating unit of -SiCH=CHC≡CSi-.

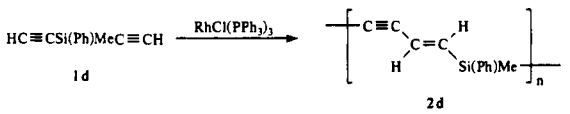
In the ^{13}C NMR spectrum of **2a**, which is similar to that of **3**, each of the two singlets due to two kinds of methylsilyl carbons observed for **3**, however, splits into two signals, with an intensity ratio of 1:1 in the spectrum of **2a**. Each of the two acetylenic carbons at about 91 and 110 ppm for **2a** also splits into four signals in the ratio of approximately 1:1:1:1. A similar splitting is also found for the olefinic carbons of **2a**. Thus, each of the two signals of the olefinic carbons observed in the spectrum of **3** splits into two signals with equal intensities. These splittings can be best explained by the existence of three kinds of microstructures in the polymer backbone. The reaction presumably proceeds with activation of an acetylenic C–H bond, followed by addition of this bond across a triple bond of the molecule coordinating on the rhodium atom as shown in Scheme I. The C–H bond activation probably occurs both in the monomer and in the polymer with equal probability, and therefore the polymer having three kinds of microstructures, A–C, with a statistical ratio of 1:2:1 in the main chain would be produced.

A similar reaction of 1,2-diethynyltetramethyldisilane (**1b**) and 1,2-diethyl-1,2-diethynyldimethyldisilane (**1c**) in the presence of the rhodium(I) catalyst readily proceeded to give poly[(tetramethyldisilanylene)butenyne-1,4-diyl]



(**2b**) and poly[(1,2-diethyldimethyldisilanylene)butenyne-1,4-diyl] (**2c**) in 52% and 58% yield, respectively.

The present rhodium-catalyzed reaction can also be used for the synthesis of a poly(silylenebutenyne-1,4-diyl). Thus, when diethynylmethylphenylsilane (**1d**) was treated with the rhodium(I) catalyst in toluene under the same conditions, poly[(methylphenylsilylene)butenyne-1,4-diyl] (**2d**) was obtained in 60% yield.



The structures of polymers **2b–d** were confirmed by spectrometric analysis (see the Experimental Section). Analysis of ^{13}C NMR spectra of polymers **2b** and **2c** indicates the presence of three different microstructures, A–C, in the ratio of 1:2:1. Similar analysis for polymer **2d** again shows the presence of microstructures analogous to A–C in the ratio of 1:2:1.

Polymers **2a–d** thus obtained are light yellow solids and soluble in common organic solvents, such as benzene, toluene, ethers, and chlorocarbons, but slightly soluble in hydrocarbons and insoluble in alcohols. Polymers **2a** and **2d** melt at 90–95 and 114–122 °C, respectively, without decomposition, while **2b** and **2c** do not melt even above 300 °C. The molecular weights of the polymers were determined by GPC, relative to polystyrene standards, to be M_w = 117 000 (M_w/M_n = 6.1), 28 000 (13.0), 22 000 (2.7), and 24 000 (3.5) for **2a–d**, respectively.

Although monomers **1a–d** could be transformed into polymers **2a–d** with high molecular weights, 1,2-diethynyltetraphenyldisilane (**1e**) and 1,3-diethynylhexamethyltrisilane did not afford the corresponding polymers under the same conditions. The starting compounds were recovered unchanged.

When 1,4-diethynylbenzene was used as a starting monomer, insoluble substances were produced. No soluble polymers were obtained in this system. The presence of silylene or disilanylene units in the polymer chain seems to be necessary for obtaining soluble polymers in the present reaction.

Synthesis of Copolymer from Diethynyltetraphenyldisilane (1e) and 1b. As mentioned above, diethynyltetraphenyldisilane (**1e**) afforded no polymer in the presence of the rhodium(I) catalyst even at 50 °C. However, when a 1:1 mixture of **1e** and **1b** was treated with the rhodium(I) catalyst at room temperature, the reaction proceeded successfully to give alternating copolymer **2e** in 55% yield. Polymer **2e** thus obtained is a light yellow solid and melts at 84–98 °C without decomposition. The molecular weight was measured to be 16 000 (M_w/M_n = 2.6) by GPC relative to polystyrene standards. The IR spectrum shows an absorption band at 2146 cm^{-1} due to the stretching frequency of a disubstituted carbon–carbon triple bond. The ^1H NMR spectrum of **2e** reveals two doublets at 6.00 and 6.54 ppm (J = 19 Hz) due to trans olefinic protons. The ^{13}C NMR spectrum of **2e** shows four signals at 89.1, 111.7 and 123.8, 146.3 ppm attributed to olefinic and acetylenic carbons, respectively. In contrast to ^{13}C NMR spectra of **2a–d** in which each of the four resonances due to the olefinic and acetylenic carbons splits into two, the spectrum for **2e**, however, shows no such

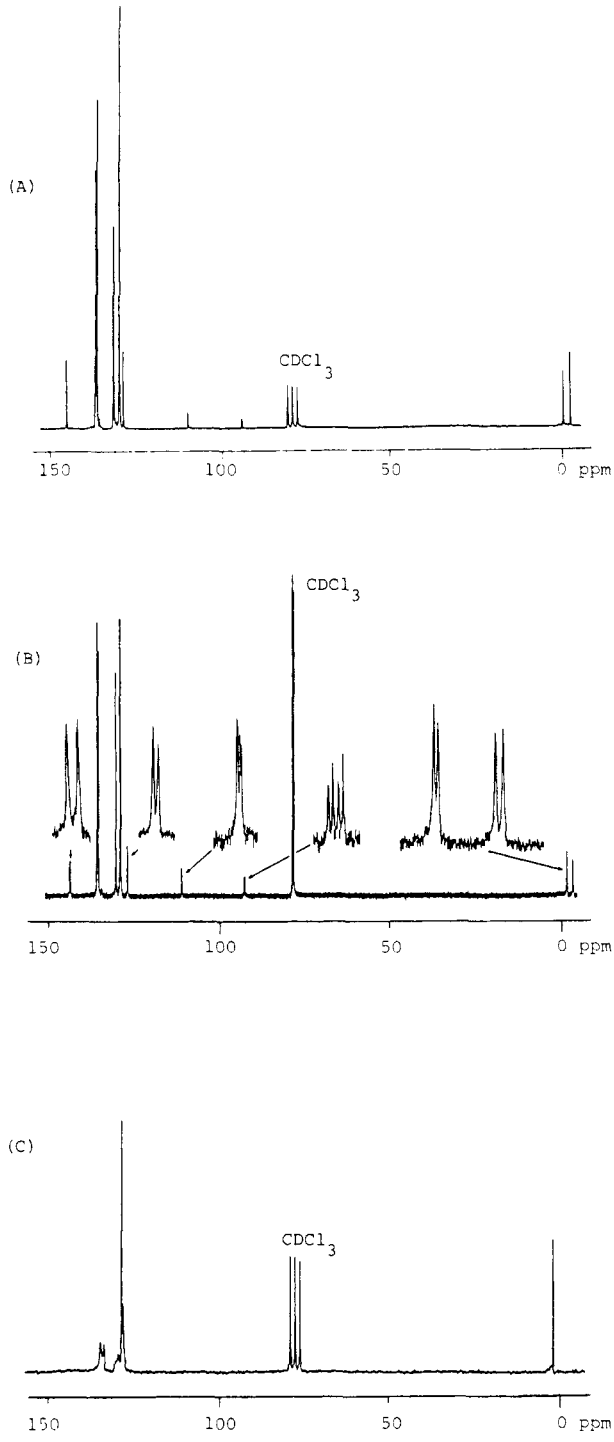


Figure 1. Decoupled ^{13}C NMR spectra: (A) (*E*)-1,4-bis(methyldiphenylsilyl)-1-buten-3-yne; (B) poly[(1,2-dimethyldiphenyldisilanylene)butenyne-1,4-diyl] (**2a**); (C) soluble products from the photolysis of **2a** in benzene.

splitting, indicating the presence of only one microstructure in the polymer backbone.

In order to get more information about the structure of **2e**, we carried out the copolymerization of 1,2-bis(deuterioethynyl)tetraphenyldisilane (**1f**) with **1b** under the same conditions. As expected, copolymer **2f** was obtained in 49% yield. The ^1H NMR spectrum of copolymer **2f** thus obtained shows no signals at 6.54 ppm, due to the olefinic protons, and the signal at 6.00 ppm observed as a doublet in the ^1H NMR spectrum of **2e** changes to a broad singlet, indicating that only the proton at the C_2 position in the enyne unit was replaced by a deuterium atom (Figure 2). These results can be best understood by

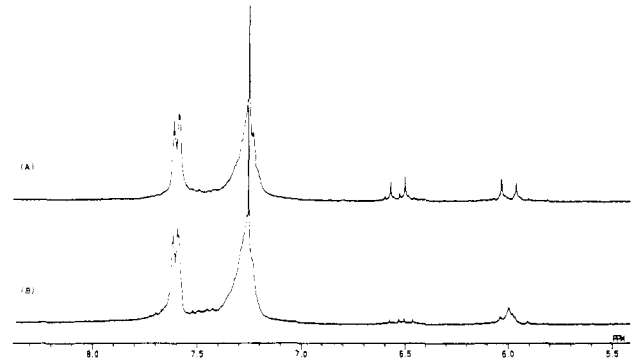
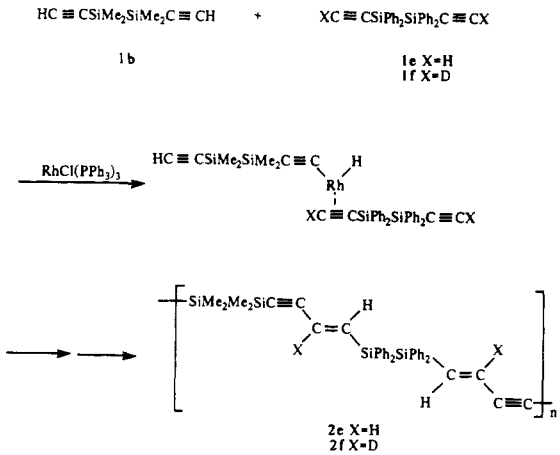


Figure 2. ^1H NMR spectra of **2e** (A) and **2f** (B).

Scheme II



assuming that the C–H bond activation by the rhodium(I) catalyst occurs only in the acetylenic C–H bond of **1b** but not in the acetylenic C–H bond of **1e** and **1f**. The triple bonds of **1e** and **1f**, however, can coordinate more easily to the rhodium species than that of **1b**. Addition of the activated C–H bond across the coordinated triple bond would produce the respective copolymers **2e** and **2f** as shown in Scheme II.

Photochemical Properties of Polymers 2a–e. UV spectra of disilanylene polymers **2a–c** and **2e** show absorption bands at about 290 nm which are remarkably red-shifted relative to that of **2d** (λ_{max} 220 nm), due to the delocalization of π-electrons through the Si–Si bonds and enyne units. Such red shifts are always observed in the polymers which involve a regular alternating arrangement of a disilanylene unit and a π-electron system.[3-14]

We investigated the photochemical behavior of the disilanylene polymers **2a–c** and **2e** by irradiating their thin solid films with a low-pressure mercury lamp in air. The progress of the reactions was followed by UV and IR spectroscopic methods. Irradiation of the films of **2a–c** and **2e** resulted in a rapid decrease of the absorption at about 290 nm in their UV spectra as shown in Figure 3, and IR spectra of the resulting films revealed strong absorption bands at 3100 and 1050 cm^{-1} due to O–H and Si–O groups, respectively, as shown in Figure 4. These results can be understood in terms of the homolytic scission of an Si–Si bond, followed by the reaction of the resulting silyl radicals with oxygen in air, analogous to the similar photolysis of poly(*p*-disilanylenephenylene) reported previously.[4]

In order to learn much more about the photochemical properties of these polymers, we carried out the photolysis of polymers **2a–c** and **2e** in a benzene solution and followed the molecular weight changes of photodegrada-

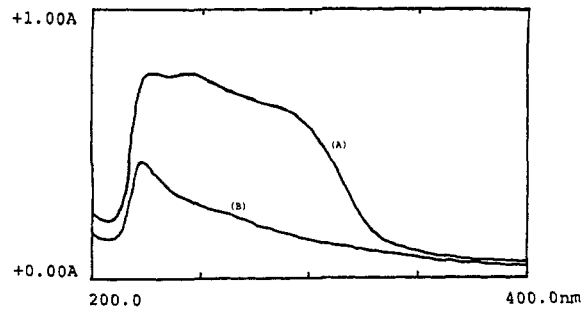


Figure 3. UV spectra of a thin solid film of **2a**: (A) before irradiation; (B) after irradiation.

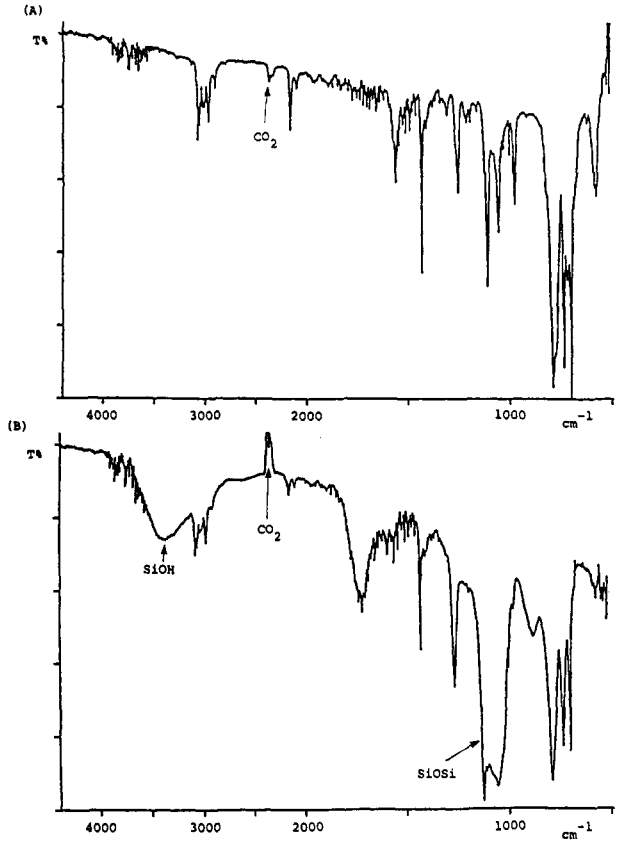
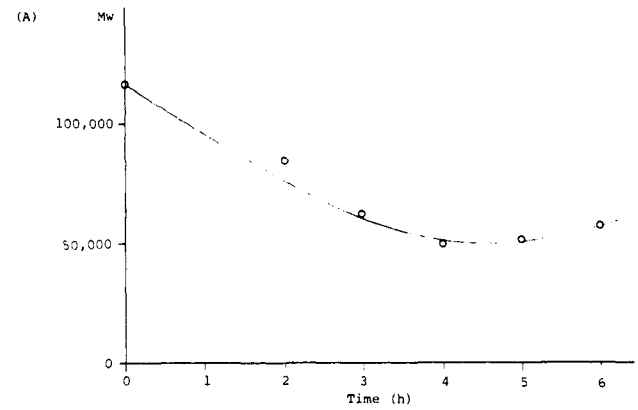


Figure 4. IR spectra of a thin solid film of **2a**: (A) before irradiation; (B) after irradiation.

tion products by GPC. As can be seen in Figure 5, the molecular weights of the photoproducts in the photolysis of **2a** and **2e** decreased in the early stages of the reaction but increased gradually with increasing irradiation time. Finally, insoluble products were produced in the reaction mixture. After 40 h of irradiation, the soluble products separated from the insoluble substances in the resulting mixture were analyzed by ^1H and ^{13}C NMR spectrometric methods. ^1H NMR spectra of soluble products obtained from the photolysis of **2a** and **2e** show no signals in the region of olefinic protons. ^{13}C NMR spectra also reveal no resonances attributed to the olefinic carbons and acetylenic carbons (see Figure 1C).

A possible mechanism for this photodegradation is shown in Scheme III. The mechanism involves homolytic scission of Si–Si bonds in the polymer backbone to produce silyl radicals, which can add across the unsaturated bonds. At the early stages of the photolysis, cleavage of the Si–Si bonds would result mainly in a decrease of the molecular weights of the photoproducts, but with increasing reaction time, the reaction of carbon radicals arising from addition of the initially formed silyl radicals to unsaturated bonds



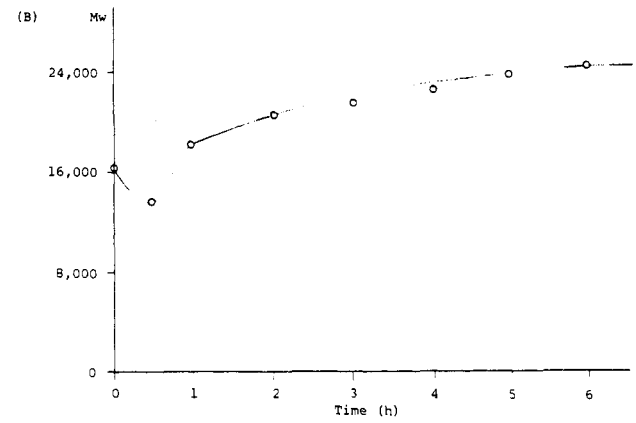
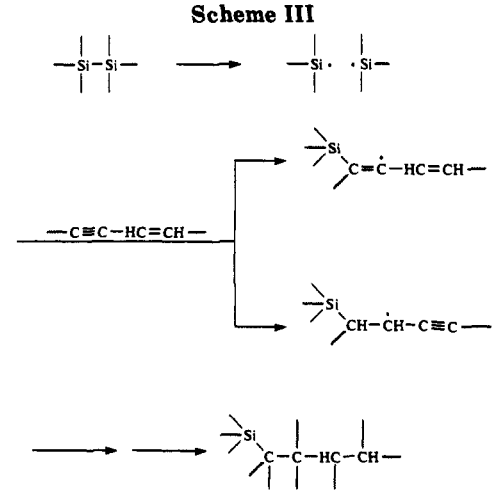


Figure 5. Plot of molecular weights of products vs irradiation time for **2a** (A) and **2e** (B).

Scheme III



would be responsible for the increase of the molecular weights of the photoproducts, although the fate of the carbon radicals is still unknown. A similar profile for the molecular weight changes has been observed in the photolysis of poly[*p*-(1,2-diethyldimethyldisilanylene)phenylene].[4] The presence of the Si–Si bonds in the polymer backbone seems to be absolutely necessary for photoactive properties of these polymers. In fact, silylene polymer **2d** did not show such photochemical behavior. Irradiation of the thin solid film prepared from **2d** showed no changes in both the IR and UV spectra. In the photolysis of **2d**

Table I
Conductivities of the Thin Solid Films of Polymers 2a–e after Doping with SbF_5

	conductivity, S·cm^{-1}		
polymer	in air (μm)[a]	in vacuo (μm)[a]	after 6 days in vacuo
2a	1×10^{0} (92)	5×10^{-4} (1.0)	5×10^{-5}
2b	2×10^{-2} (46)		
2c	1×10^{-3} (44)		
2d	1×10^{-1} (40)	2×10^{-4} (1.0)	7×10^{-6}
2e	4×10^{-2} (34)[b]	1×10^{-3} (1.5)	8×10^{-5}

[a] Thickness of a film. [b] In a nitrogen atmosphere.

in a benzene solution, again no change was observed for the molecular weight of the product.

Photolysis of polymers **2b** and **2c**, which have less hindered substituents on the silicon atom, led to the formation of large amounts of insoluble substances even in the early stages of the photolysis. Presumably the rate of addition of the silyl radical across the unsaturated bonds is sufficiently fast. The lack of a radical stabilizing group on the silicon atom such as a phenyl group may also accelerate such an addition reaction.

Conducting Properties of 2a–e. Polymers **2a–e** can be cast to thin solid films by spin-coating. Polymers **2a–e** are insulators but become semiconducting upon treatment with an oxidizing agent. Thus, when the films prepared by spin-coating on a quartz plate were treated with a stream of SbF_5 vapor diluted with nitrogen gas at atmospheric pressure, the transparent films changed to dark green or blue after 2 h of doping. The excess of SbF_5 vapor was removed by pumping (1 mmHg) for 30 min. The films were allowed to stand in air for 2 h, and then conductivities were measured by the four-probe method as shown in Table I.

The conductivities for polymers **2a**, **2d**, and **2e** were also measured under reduced pressure. Thus, the films were placed in a glass vessel connected to a conductivity measuring instrument. After the glass vessel was evacuated with a pump (10^{-2} mmHg), the films were doped with SbF_5 vapor evaporating from liquid SbF_5 at room temperature. The conductivities of the films were measured simultaneously with doping by the four-probe method. The conductivities rapidly increased at the beginning of doping and were 10^{-4}–10^{-3} S·cm^{-1} during doping for 5 h. When the doped films were allowed to stand in an atmosphere of SbF_5 vapor, the conductivities gradually decreased and finally reached constant values (10^{-6}–10^{-5} S·cm^{-1}) after 5–6 days. The maximum conductivity (σ_{max}) during doping and the value observed after 6 days are shown in Table I.

Interestingly, when the doped films which reached the constant value are exposed to air, the conductivities suddenly increase more than 2 or 3 orders of magnitude.[15] For example, when the doped film **2e**, whose conductivity was 8×10^{-5} S·cm^{-1} after 6 days of standing in an atmosphere of SbF_5 vapor, was exposed to air, its conductivity increased rapidly and reached 7×10^{-2} S·cm^{-1}. It seems likely that a trace of moisture in the air plays an important role for increasing conductivity, although no evidence is obtained at the present stage.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of purified argon. ^{1}H and ^{13}C NMR spectra were recorded on JEOL Model JNM-GX-500, JNM-GX-400, JNM-EX-270, JNM-FX-90A, and JNM-PMX-60 spectrometers, using deuteriochloroform or carbon tetrachloride containing tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. Mass spectra were measured on a Shimadzu Model GCMS QP-1000 spectrometer.

Materials. 1,2-Dimethyldiphenyldisilane,[16] 1,2-diethynyltetramethyldisilane,[17] 1,1,2,2-tetraphenyldisilane,[16] 1,3-dichlorohexamethyltrisilane,[18] 1,4-diethynylbenzene,[19] and chlorotris(triphenylphosphine)rhodium(I)[20] were prepared as reported in the literature. Ether, benzene, THF, and hexane used as solvents were dried over lithium aluminum hydride and distilled just before use.

Preparation of 1,2-Dichloro-1,2-dimethyldiphenyldisilane. A solution of 71.7 g (0.296 mol) of 1,2-dimethyldiphenyldisilane and ca. 10 mg (0.0564 mmol) of palladium dichloride in 500 mL of carbon tetrachloride was refluxed for 2 days. The solvent was evaporated, and the residue was distilled under reduced pressure to give 48.7 g of 1,2-dichloro-1,2-dimethyldiphenyldisilane[21] [117 °C (0.4 mmHg), 65% yield].

Preparation of 1,2-Diethynyl-1,2-dimethyldiphenyldisilane (1a). To a solution of ethynylmagnesium bromide prepared from 0.5 mol of ethylmagnesium bromide and acetylene in 300 mL of THF in a 1-L three-necked flask was added 48.7 g (0.19 mol) of 1,2-dichloro-1,2-dimethyldiphenyldisilane through a dropping funnel over a period of 30 min. The resulting solution was allowed to stand at room temperature for 2 h 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, washed with water, and dried over potassium carbonate. After the solvent was evaporated, the residue was distilled under reduced pressure to give **1a** as a 1:1 mixture of a diastereomer. Recrystallization of the mixture from ethanol gave one isomer as a pure form (19% yield). Further reaction was carried out using this diastereomer: bp 138–140 °C (1.0 mmHg); mp 34–36 °C; IR $\nu_{\equiv CH}$ 3280, $\nu_{C\equiv C}$ 2040 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.48 (s, 3 H, MeSi), 0.54 (s, 3 H, MeSi), 2.56 (s, 2 H, acetylenic protons), 7.2–7.8 (m, 10 H, Ph). Anal. Calcd for $C_{18}H_{18}Si_2$: C, 74.42; H, 6.24. Found: C, 74.35; H, 6.10.

Preparation of 1,2-Diethyl-1,2-dimethyldiphenyldisilane. To a solution of 0.59 mol of (ethylmethylphenylsilyl)lithium prepared from 112 g (0.59 mol) of chloroethylmethylphenylsilane and 37 g (4.5 equiv) of lithium in 500 mL of THF was added an equimolar amount of chloroethylmethylphenylsilane (0.59 mol) with ice-cooling. The resulting mixture was allowed to stand at room temperature for 2 h 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, washed with water, and dried over potassium carbonate. After evaporation of the solvents, the residue was distilled under reduced pressure to give 114.9 g of 1,2-diethyl-1,2-dimethyldiphenyldisilane (66% yield): bp 110 °C (0.06 mmHg); MS *m/e* 298 (M^+); ^{1}H NMR (60 MHz, CCl_4) δ 0.34 (s, 6 H, MeSi), 0.91 (br s, 10 H, Et), 6.73–6.99 (m, 10 H, Ph); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ –6.37, –6.26 (MeSi), 5.44, 5.55, 7.93 (Et), 127.7, 128.3, 134.2 (Ph). Anal. Calcd for $C_{18}H_{26}Si_2$: C, 72.41; H, 8.78. Found: C, 72.31; H, 8.65.

Preparation of 1,2-Dichloro-1,2-diethyldimethyldisilane. A mixture of 111.3 g (0.37 mol) of 1,2-diethyl-1,2-dimethyldiphenyldisilane and a catalytic amount of aluminum trichloride was dissolved in 100 mL of benzene. Dry hydrogen chloride gas was passed through the solution (ca. 1 mL/min) with stirring for 20 h at room temperature. After 5 mL of acetone was added to the solution, the solvent and hydrogen chloride were removed. The residue was distilled under reduced pressure to give 57.2 g of 1,2-dichloro-1,2-diethyldimethyldisilane (73% yield): bp 90–93 °C (23 mmHg); MS *m/e* 214 (M^+); ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.57 (s, 6 H, MeSi), 1.00–1.14 (m, 10 H, Et); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ –0.6, –0.4 (MeSi), 6.6, 10.0 (Et). Anal. Calcd for $C_6H_{16}Cl_2Si_2$: C, 33.48; H, 7.49. Found: C, 33.53; H, 7.39.

Preparation of 1,2-Diethyl-1,2-diethynyldimethyldisilane (1c). Ethynylmagnesium bromide was prepared from the reaction of 0.225 mol of ethylmagnesium bromide and acetylene in 300 mL of THF in a 1-L three-necked flask. To this was added 15.47 g (0.072 mol) of 1,2-dichloro-1,2-diethyldimethyldisilane through a dropping funnel over a period of 30 min. The resulting solution was allowed to stand at room temperature for 2 h 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 washed with water.

After the solvent was evaporated, the residue was distilled under reduced pressure to give 11.85 g of **1c** (84% yield): bp 77–79 °C (15 mmHg); MS *m/e* 194 (M^+); IR $\nu_{\equiv CH}$ 3287, $\nu_{C\equiv C}$ 2028 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.47 (s, 6 H, MeSi), 0.6–1.47 (m, 10 H, EtSi), 2.57 (s, 2 H, acetylenic protons); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ −5.1 (MeSi), 6.1, 8.0 (EtSi), 87.1, 96.1 (acetylenic carbons). Anal. Calcd for $C_{14}H_{18}Si_2$: C, 61.78; H, 9.33. Found: C, 61.59; H, 9.23.

Preparation of Diethynylmethylphenylsilane (1d). Ethynylmagnesium bromide was prepared from the reaction of 0.17 mol of ethylmagnesium bromide and acetylene in 300 mL of THF in a 1-L three-necked flask. To this was added 10.0 g (0.052 mol) if dichloromethylphenylsilane through a dropping funnel over a period of 30 min. The resulting solution was allowed to stand at room temperature for 2 h 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 washed with water. After the solvent was evaporated, the residue was distilled under reduced pressure to give 3.8 g of **1d** (42% yield): bp 120 °C (30 mmHg); MS *m/e* 170 (M^+); IR $\nu_{\equiv CH}$ 3276, $\nu_{C\equiv C}$ 2040 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) 0.45 (s, 3 H, MeSi), 2.42 (s, 2 H, acetylenic protons), 7.19–7.61 (m, 5 H, Ph); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ −0.7 (MeSi), 84.5, 96.0 (acetylenic carbons), 128.1, 130.3, 132.3, 133.9 (Ph). Exact ms calcd for $C_{11}H_{10}Si$: 170.0552. Found: 170.0560.

Preparation of 1,2-Dichlorotetraphenyldisilane. A solution of 18.33 g (0.05 mol) of 1,1,2,2-tetraphenyldisilane in 80 mL of CCl_4 was heated to reflux with a catalytic amount of palladium dichloride (ca. 5 mg, 0.0282 mmol) for 20 h. After the solvent was removed under reduced pressure, the residue was recrystallized from hexane to give 20.7 g of 1,2-dichlorotetraphenyldisilane[22] (95% yield) as a white crystal: mp 99.5–100.5 °C; MS *m/e* 434 (M^+); ^1H NMR (60 MHz, CCl_4) 7.25–7.93 (m, Ph).

Preparation of 1,2-Diethynyltetraphenyldisilane (1e). Ethynylmagnesium bromide was prepared from the reaction of 0.08 mol of ethylmagnesium bromide and acetylene in 300 mL of THF in a 1-L three-necked flask. To this solution was added 8.71 g (0.02 mol) of 1,2-dichlorotetraphenyldisilane through a dropping funnel over a period of 30 min. The resulting solution was allowed to stand at room temperature for 2 h 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 washed with water. After the solvent was evaporated, the residue was recrystallized from ethanol to give 8.29 g of **1e** (64% yield): mp 151–151.5 °C; MS *m/e* 414 (M^+); IR $\nu_{\equiv CH}$ 3277, $\nu_{C\equiv C}$ 2030 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 2.19 (s, 2 H, acetylenic protons), 6.83–7.75 (m, 20 H, Ph); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 84.4, 99.7 (acetylenic carbons), 128.0, 129.8, 131.8, 134.5, 135.5. Anal. Calcd for $C_{28}H_{22}Si_2$: C, 81.11; H, 5.35. Found: C, 80.96; H, 5.35.

Preparation of 1,2-Bis(deuterioethynyl)tetraphenyldisilane (1f). To a solution of 2.0734 g (5.01 mmol) of **1e** in 12 mL of ether was added 8 mL (12.0 mmol) of a 1.5 M hexane solution of *n*-BuLi at room temperature. The resulting mixture was heated to reflux for 2 h, and then 0.22 mL (11.0 mmol) of D_2O was added dropwise with ice-cooling. The resulting mixture was allowed to stand at room temperature for 10 h. The solvent was removed under reduced pressure, and the residue was extracted three times with 10 mL of benzene. The extracts were combined, and benzene was removed under reduced pressure to give crude **1f**. The crude product was recrystallized from ethanol to give 1.1847 g of pure **1f** (56% yield): mp 150.5–151.5 °C; MS *m/e* 416 (M^+); IR $\nu_{C\equiv C}$ 2030 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 6.83–7.75 (m, 20 H, Ph).

Preparation of 1,3-Diethynylhexamethyltrisilane. Ethynylmagnesium bromide was prepared from the reaction of 0.112 mol of ethylmagnesium bromide and acetylene in 350 mL of THF in a 1-L three-necked flask. To this was added 6.9 g (0.028 mol) of 1,3-dichlorohexamethyltrisilane through a dropping funnel over a period of 30 min. The resulting solution was allowed to stand at room temperature for 2 h 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 washed with water. After the solvent was evaporated, the residue was treated with a silica gel column chromatography using hexane as an eluent to give 1.98 g of 1,3-diethynylhexamethyltrisilane (32% yield): MS *m/e* 224 (M^+); ^1H NMR (in CCl_4) δ 0.22 (s, 6 H, Me_2Si), 0.28 (s, 12 H, Me_2Si), 2.31 (s, 2 H, acetylenic protons). Anal. Calcd for $C_{10}H_{20}Si_3$: C, 53.49; H, 8.98. Found: C, 53.33; H, 8.95.

Preparation of Poly[(1,2-dimethyldiphenyldisilanylene)butenyne-1,4-diyl] (2a). A solution of 2.05 g (7.1 mmol) of **1a** and 2 mol % of chlorotris(triphenylphosphine)rhodium(I) in 2 mL of toluene was stirred for 2 days at room temperature. After removal of the solvent under reduced pressure at room temperature, the residue was reprecipitated twice from isopropyl alcohol–chloroform to give 1.50 g (73% yield) of **2a**: mp 90–95 °C; IR $\nu_{C\equiv C}$ 2146 cm^{-1}; M_w = 117 000; M_n = 19 200; ^1H NMR (60 MHz, CCl_4) δ 0.47 (br s, 6 H, MeSi), 5.93 (d, 1 H, J = 19 Hz, olefinic proton), 6.66 (d, 1 H, J = 19 Hz, olefinic proton), 6.87–7.91 (m, 10 H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ −5.7, −5.4, −3.9, −3.8 (MeSi), 91.2, 91.3, 91.5, 91.6, 109.81, 109.84, 109.9 (acetylenic carbons), 125.8, 125.9, 142.5, 142.8 (olefinic carbons), 127.86, 127.93, 127.97, 128.1, 129.3, 134.4, 134.5, 134.6, 134.7, 134.8, 134.9 (Ph); UV (film) λ_{max} 294 nm.

Preparation of Poly[(tetramethyldisilanylene)butenyne-1,4-diyl] (2b). A solution of 0.9853 g (5.92 mmol) of **1b** and 0.102 g (2 mol %) of chlorotris(triphenylphosphine)rhodium(I) in 2 mL of toluene was stirred for 2 days at room temperature. The solvent was removed under reduced pressure at room temperature. Then the residue was reprecipitated twice from isopropyl alcohol–benzene to give 0.516 g (52% yield) of **2b**: mp >300 °C; M_w 28 000; M_n 2200; IR $\nu_{C\equiv C}$ 2149 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 0.13–0.29 (br, 12 H, MeSi), 5.91 (d, 1 H, J = 19 Hz, olefinic proton), 6.54, 6.56 (2d, 1 H, J = 19 Hz, olefinic proton); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ −4.58, −4.47, −2.96, −2.85 (MeSi), 92.80, 93.04, 107.99 (acetylenic carbons), 123.92, 124.13, 144.72, 145.05 (olefinic carbons); UV (film) λ_{max} 293 nm.

Preparation of Poly[(1,2-diethyldimethyldisilanylene)butenyne-1,4-diyl] (2c). A solution of 2.1225 g (10.9 mmol) of **1c** and 0.1028 mg (1 mol %) of chlorotris(triphenylphosphine)rhodium(I) in 10 mL of toluene was stirred at room temperature for 21 h. After evaporation of the solvent, the residue was reprecipitated twice from isopropyl alcohol–chloroform to give 1.2264 g (58% yield) of **2c**: mp >300 °C; M_w = 22 000, M_n = 8300; IR $\nu_{C\equiv C}$ 2146 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.12, 0.19, 0.26, 0.27 (s, 6 H, MeSi), 0.61–1.23 (m, 10 H, EtSi), 5.91, 5.97 (2d, 1 H, J = 19 Hz, olefinic proton), 6.46, 6.50 (2d, 1 H, J = 19 Hz, olefinic proton); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ −6.59, −4.69 (MeSi), 5.38, 6.47, 8.04 (EtSi), 92.28, 103.98 (acetylenic carbons), 124.29, 124.51, 143.74, 143.96 (olefinic carbons); UV (film) λ_{max} 300 nm.

Preparation of Poly[(methylphenylsilylene)butenyne-1,4-diyl] (2d). A solution of 1.23 g (7.22 mmol) of **1d** and 42.9 mg (6.4 mol %) of chlorotris(triphenylphosphine)rhodium(I) in 2 mL of toluene was stirred at room temperature for 14 days. After removal of the solvent, the residue was reprecipitated from ethanol–chloroform to give 0.732 g (60% yield) of **2d**: M_w = 24 000; M_n = 6700; IR $\nu_{C\equiv C}$ 2155 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 0.47, 0.52, 0.58 (3s with an intensity ratio of 1:2:1, 3 H, MeSi), 6.11, 6.21 (2d, 1 H, J = 18.9 Hz, olefinic proton), 6.66, 6.70 (2d, 1 H, J = 18.9 Hz, olefinic proton), 7.41–7.65 (Ph); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ −4.8, −2.7, −0.3 (MeSi), 91.1, 91.2, 106.9, 108.0 (acetylenic carbons), 126.4, 126.7, 142.1, 142.2 (olefinic carbons), 128.0, 129.9, 133.7, 134.2, 134.5 (Ph); UV (film) λ_{max} 220 nm.

Rhodium(I)-Catalyzed Reaction of 1,3-Diethynylhexamethyltrisilane. A mixture of 0.449 g (2.0 mmol) of 1,3-diethynylhexamethyltrisilane and 37.0 mg (2 mol %) of chlorotris(triphenylphosphine)rhodium(I) in 2 mL of toluene was stirred at room temperature for 2 days. The GLC analysis and IR and ^1H NMR spectrometric analyses of the reaction mixture showed that all starting 1,3-diethynylhexamethyltrisilane remained unchanged.

Rhodium(I)-Catalyzed Reaction of 1,4-Diethynylbenzene. A solution of 383 mg (3.04 mmol) of 1,4-diethynylbenzene and 0.5 mol % of chlorotris(triphenylphosphine)rhodium(I) in 5 mL of toluene was stirred at room temperature. After 24 h of reaction, a large amount of insoluble gel was formed. The solvent was removed to give yellow solids (ca. 100% yield), which were insoluble in alcohol, benzene, chlorocarbons, ethers, and hydrocarbons.

Rhodium(I)-Catalyzed Reaction of 1e. A mixture of 2.0733 g (5.0 mmol) of **1e** and 92.5 mg (2 mol %) of chlorotris(tri-

phenylphosphine)rhodium(I) in 2 mL of toluene was stirred at 50 °C for 2 days. The solvent was evaporated under reduced pressure. The GLC analysis and IR and ^1H NMR spectrometric analyses of the resulting mixture showed that all starting **1e** remained unchanged.

Preparation of Copolymer 2e. A mixture of 1.0367 g (25 mmol) of **1e**, 0.4159 g (25 mmol) of **1b**, and 92.5 mg (2 mol %) of chlorotris(triphenylphosphine)rhodium(I) in 2 mL of toluene was stirred at room temperature for 60 h. The solvent was evaporated under reduced pressure, and the residue was reprecipitated twice from isopropyl alcohol–chloroform to give 0.80 g of **2e** (55% yield): M_w = 16 000; M_n = 6200; mp 84–98 °C; IR $\nu_{C\equiv C}$ 2146 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.19 (s, 12 H, Me_2Si), 6.00 (d, 2 H, J = 19 Hz, olefinic protons), 6.54 (d, 2 H, J = 19 Hz, olefinic protons), 7.19–7.62 (m, 20 H, Ph); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ −4.4 (MeSi), 89.1, 111.7 (C≡C), 123.8, 146.3 (olefinic carbons), 127.9, 129.5, 132.9, 135.6 (Ph); UV (film) λ_{max} 293 nm.

Preparation of Copolymer 2f. A mixture of 0.6251 g (1.5 mmol) of **1f**, 0.2496 g (1.5 mmol) of **1b**, and 55.5 mg (2 mol %) of chlorotris(triphenylphosphine)rhodium(I) in 0.8 mL of toluene was stirred at room temperature for 60 h. The solvent was evaporated under reduced pressure, and the residue was reprecipitated twice from isopropyl alcohol–chloroform to give 0.424 g of **2f** (49% yield): mp 84–95 °C; M_w = 16 000, M_n = 1900; IR $\nu_{C\equiv C}$ 2146 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.19 (s, 12 H, Me_2Si), 6.00 (br s, 2 H, olefinic protons), 7.19–7.62 (m, 20 H, Ph).

Photolysis of the Polymers in Solid Films. A 10% chloroform solution of polymers **2a–e** was coated on a quartz plate or NaCl plate and dried under reduced pressure to give a solid film with a thickness of ca. 0.05–0.1 mm. The film was irradiated with a low-pressure mercury lamp bearing a Vicor filter in air. The UV spectrum of the films after 1 h of irradiation revealed the disappearance of the absorption at about 290 nm, and its IR spectrum indicated strong absorptions at 3100 and 1050 cm^{-1}. The UV and IR spectra obtained from irradiation of the film of **2a** are presented in Figures 3 and 4 as typical examples.

Photolysis of Polymers 2a–e in Benzene. In a 25-mL reaction vessel bearing a Vicor filter fitted internally with a low-pressure mercury lamp was placed a benzene solution of ca. 100 mg of polymers **2a–e**. The solution was irradiated, and the progress of the reaction was monitored by GPC. The results are shown in Figure 5.

Measurement of the Conductivity of Thin Solid Films of 2a–e in Air. A 10% methylene dichloride solution of the polymer was spin-coated on a quartz plate by spiner (2000 rpm) and baked at 70 °C for 2 h under reduced pressure. The thickness of the resulting film was measured by the mechanical probe method (Dektak 3030). The film was treated with a stream of SbF_5 vapor diluted by dry nitrogen (0.2 mL of SbF_5 in 0.9 L of N_2 per minute) for 2 h. At this point, the transparent films changed to dark green or blue. Then, excess of SbF_5 vapor was evacuated under reduced pressure at 1 mmHg for 30 min. After the resulting films were allowed to stand in air for 2 h, the conductivities of the films were measured by the four-probe method.

Measurement of the Conductivity of Thin Films of 2a, 2d, and 2e in Vacuo. A 10% THF solution of **2a**, **2d**, and **2e** was spin-coated on a silicone wafer by spiner (2000 rpm). The thickness of the resulting films was measured by an Okazaki Mfg. Co., Ltd., Model D-10SS. The films were placed in a glass vessel connected to a conductivity measuring instrument. The glass vessel was also connected with a container containing liquid SbF_5, which was degassed prior to use. After the vessel was evacuated with a pump (1 mmHg), the SbF_5 vapor was introduced from liquid SbF_5 at room temperature. The conductivities of the films were measured simultaneously with doping by the four-probe method. The maximum conductivity (σ_{max}) observed during doping for 5 h was shown in Table I. The films were allowed to stand in an atmosphere of SbF_5 vapor for 6 days to obtain constant values. Then, a supply of SbF_5 vapor was stopped, the excess of SbF_5 vapor was removed by pump, and the doped films were exposed to air.

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