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Polymeric organosilicon systems
XXIII. Synthesis and photochemical and thermal properties of (*E*)- and (*Z*)-poly[(disilanylene)ethenylenes]

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Abstract

(*E*)-Poly[(1,2-dimethyl-1,2-diphenyldisilanylene)ethenylene], (*E*)-poly[(1,1,2,2-tetraphenyldisilanylene)ethenylene], (*E*)-poly[(1,1,2,2-tetramethyldisilanylene)ethenylene], (*E*)-poly[(1,2-dimethyl-1,2-diphenyldisilanylene)phenylethenylene], and (*Z*)-poly[(1,2-dimethyl-1,2-diphenyldisilanylene)phenylethenylene] were prepared by the condensation reaction of the respective 1,2-bis(chlorosilyl)ethenes with sodium at 30°C under ultrasonic irradiation. Thermal behavior of the polymers was investigated by thermogravimetric analysis under a nitrogen atmosphere. The weight loss of the polymers at 1000°C was calculated to be 75–88% of the initial weights. Polymers thus obtained are photoactive and irradiation of thin solid films of the polymers in air resulted in the cleavage of the Si–Si bonds in the polymer backbone, leading to the formation of Si–O–Si and Si–O–H bonds. The photolysis of the polymers in benzene gave the degradation products derived from homolytic scission of the Si–Si bonds.

Keywords: Silicon; Polymer; Photolysis; Ceramics

1. Introduction

Polymers with the regular alternating arrangement of an Si–Si bond and π-electron system in a main chain are of considerable interest, because they can be used as functional materials [1,2]. We have demonstrated that poly[(disilanylene)phenylenes] can be used as a top imaging layer for the double-layer photoresist system [3]. Subsequently, we have designed and synthesized various types of alternating polymers, poly[(disilanylene)thienylenes] [4], poly[(disilanylene)butenyne-1,4-diyls] [5], poly[(disilanylene)ethynylenes] [6,7], poly[(disilanylene)dithienylenes] [8], and poly[(disilanylene)phenylenes] [9], and found that these polymers are photoactive.

As a part of our study concerning the synthesis of the alternating polymers composed of a disilanylene unit and π-electron system in the polymer backbone, we carried out the synthesis of the polymers containing an ethenylene unit as the π-system [10]. In this paper, we report the synthesis of (*E*)- and (*Z*)-poly[(disilanylene)ethenylenes] and their photochemical behavior in the solid state and in solution. We also report on the thermogravimetric analysis of the polymers under a nitrogen atmosphere.

2. Results and discussion

2.1. Synthesis of monomers

(*E*)-1,2-Bis(chloromethylphenylsilyl)ethene and (*E*)-1,2-bis(chlorodiphenylsilyl)ethene (**Ia** and **IIa**) were prepared by hydrosilation of chloromethylphenyl- and chlorodiphenylsilane with the respective chlorosilylacetylenes. Thus, the reaction of dichloromethylphenylsilane with 1.2 equiv. of ethynylmagnesium bromide gave a mixture consisting of dichloromethylphenylsilane, chloroethynylmethylphenylsilane, and diethynylmethylphenylsilane in a ratio of 45:33:22. Treatment of the mixture with a slight excess of chloromethylphenylsilane in the presence of a chloroplatinic acid catalyst at 50°C for 20 h afforded a mix-

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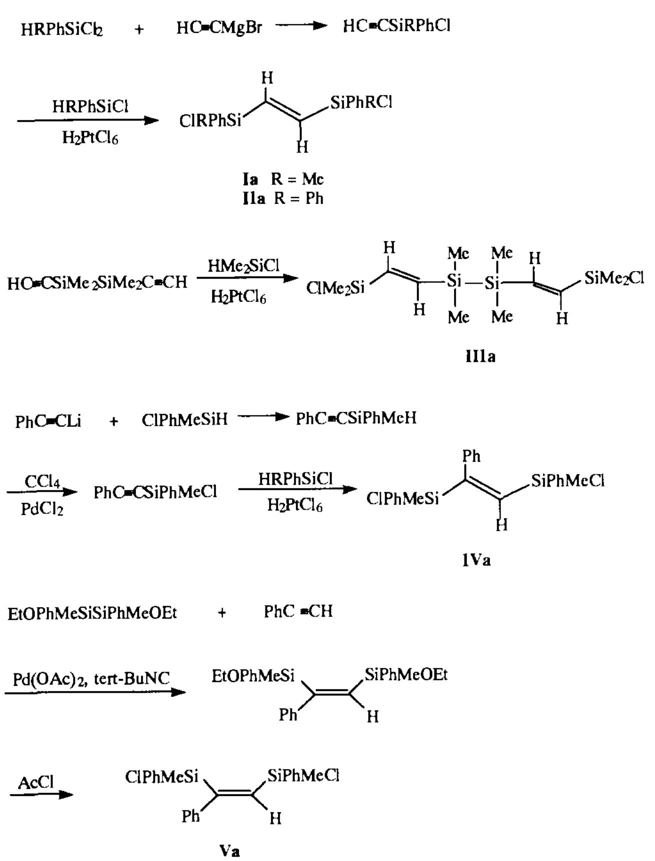
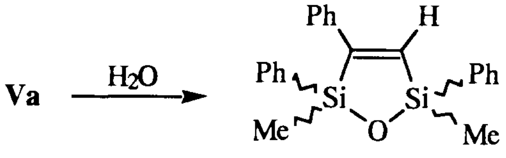


Scheme 1.

ture of **Ia**, dichloromethylphenylsilane, and bis[2-(*E*)-(chloromethylphenylsilyl)ethenyl]methylphenylsilane. Product **Ia** was obtained by fractional distillation of the resulting mixture using a short column under reduced pressure (Scheme 1). The yield was calculated to be 33% from dichloromethylphenylsilane. Similarly, (*E*)-1,2-bis(chlorodimethylsilyl)ethene was prepared by the same method as **Ia** [10], the reaction of ethynylmagnesium bromide with dichlorodimethylsilane, and then the platinum-catalyzed hydrosilation of chloroethynyldimethylsilane with chlorodimethylsilane. However, pure compound is obtained only in low yield by fractional distillation using a short column, because its boiling point is close to those of by-products such as bis[2-(*E*)-chlorodimethylsilyl)ethenyl]dimethylsilane. Therefore, we synthesized 1,2-bis[2-(*E*)-(chlorodimethylsilyl)ethenyl]tetramethyldisilane (**IIIa**) as the starting monomer for the preparation of (*E*)-poly[(1,1,2,2-tetramethyldisilanylene)ethenylene]. Monomer **IIIa** was readily obtained by platinum-catalyzed hydrosilation of 1,2-diethynyltetramethyldisilane with the resulting chlorodimethylsilane in 51% yield.

(*E*)-1,2-Bis(chloromethylphenylsilyl)phenylethene (**IVa**) was obtained by treatment of methylphenyl(phenylethynyl)silane with a catalytic amount of palladium dichloride in carbon tetrachloride, followed by hydrosilation of the resulting chloromethylphenyl(phenylethynyl)silane with chloromethylphenylsilane in the presence of the platinum catalyst, while, (*Z*)-1,2-bis(chloromethylphenyl)phenylethene (**Va**) was prepared by the palladium-catalyzed double-silation of phenylacetylene with 1,2-diethoxy-1,2-dimethyl-diphenyldisilane [11], followed by treatment of the resulting 1,2-di(ethoxymethylphenylsilyl)phenylethene with acetyl chloride in 47% total yield. The structures of the monomers **Ia**–**Va** were verified by spectroscopic analysis as well as by elemental analysis (see Section 3). We also carried out a chemical reaction to confirm the (*Z*)-configuration of compound **Va**. Thus, when **Va** was hydrolyzed in ether, 1,3-dimethyl-1,3,4-triphenyl-2-oxa-1,3-disilacyclopent-4-ene (**VI**) was produced in 81% yield as the sole volatile product.



VI

2.2. Synthesis of poly[(disilanylene)ethenylenes]

In general, the preparation of disilanylene polymers by way of the sodium condensation reaction of bis(chlorosilyl)-substituted derivatives is performed in an aromatic or hydrocarbon solvent at a higher temperature than the melting point of sodium. When we attempted to prepare (*E*)-poly[(1,2-dimethyl-1,2-diphenyldisilanylene)ethenylene] (**Ib**) from the reaction of monomer **Ia** with sodium in refluxing toluene, a polymer whose molecular weight (MW) was determined to be 25 000 by GPC analysis relative to polystyrene standards, was obtained in 40% yield. The ^{1}H NMR spectrum of the polymer, however, shows a broad resonance centered at 1.38 ppm due to ethylene protons along with signals attributed to an olefinic, phenyl, and methylsilyl protons. Moreover, the integral ratio for the ethenylene protons in the ^{1}H NMR spectrum is determined to be lower than the theoretical value for the ideal disilanylene-ethenylene structure. Presumably, reduction of some ethenylene units takes place under the conditions used.

Next, we carried out a similar condensation reaction of **Ia** at low temperature using ultrasonic irradiation to activate the sodium metal surface [12]. Thus, treatment of **Ia** with a slight excess of sodium dispersion in decade at 30°C under ultrasonic irradiation, followed by hydrolysis of the reaction mixture, and then reprecipitation of the resulting products from benzene/ethanol gave **Ib** with molecular weight of 39 800 (MN = 9800) in 60% yield. The structure of polymer **Ib** was verified by spectroscopic analysis as well as by elemental analysis. The ^{1}H NMR spectrum of polymer **Ib** shows two resonances with equal intensities at 0.29 and 0.32 ppm due to diastereomeric methylsilyl protons and signals of olefinic and phenyl protons at 6.69 and 6.85–7.68 ppm, respectively. Its ^{13}C NMR spectrum reveals a signal attributed to olefinic carbons at 149.4 ppm, in addition to signals due to the diastereomeric dimethyldiphenyldisilanylene fragment. No other signals were observed in both ^{1}H and ^{13}C NMR spectra, indicating that polymer **Ib** has the regular alternating arrangement of a disilanylene unit and an ethenylene group.

Monomers **IIa**, **IVa**, and **Va** also undergo polymerization under the same conditions to give (*E*)-poly[(1,1,2,2-tetraphenyldisilanylene)ethenylene] (**IIb**), (*E*)-poly[(1,2-dimethyl-1,2-diphenyldisilanylene)phenylethenylene] (**IVb**), and (*Z*)-poly[(1,2-dimethyl-1,2-diphenyldisilanylene)phenylethenylene] (**Vb**) in 21%, 11%, and 11% yields, respectively. The polymers **Ib**, **IIb**, **IVb**, and **Vb** are white solids and soluble in benzene, toluene, ethers, and chlorocarbons but insoluble in methanol and ethanol. As reported previously, when **IIIa** was treated with sodium under the same conditions, only white solids which are insoluble in benzene and chloroform were formed [10]. However, a soluble polymer, (*E*)-poly[(1,1,2,2-tetramethyldisilanylene) ethenylene] (**IIIb**) could be obtained by the reaction of **IIIa** with 1.95 equiv. of sodium, followed by treatment of the resulting mixture with 0.7 equiv. of methyllithium in 33% yield. The structures of polymers **IIb**–**Vb** were also verified by spectroscopic analysis (see Section 3).

Yields, molecular weights determined by GPC, and melting points of the polymers are summarized in Table 1. The lower yields of polymers **IIb**–**Vb** than that of **Ib** are ascribed to the formation of insoluble substances. For the formation of the insoluble polymers, one might consider the possibility that some cross-linking reactions take place during the polymerization. However, IR spectra of the insoluble polymers are identical with those of the corresponding soluble polymers, indicating that the insoluble polymers also have the regular arrangement of a disilanylene and ethenylene unit.

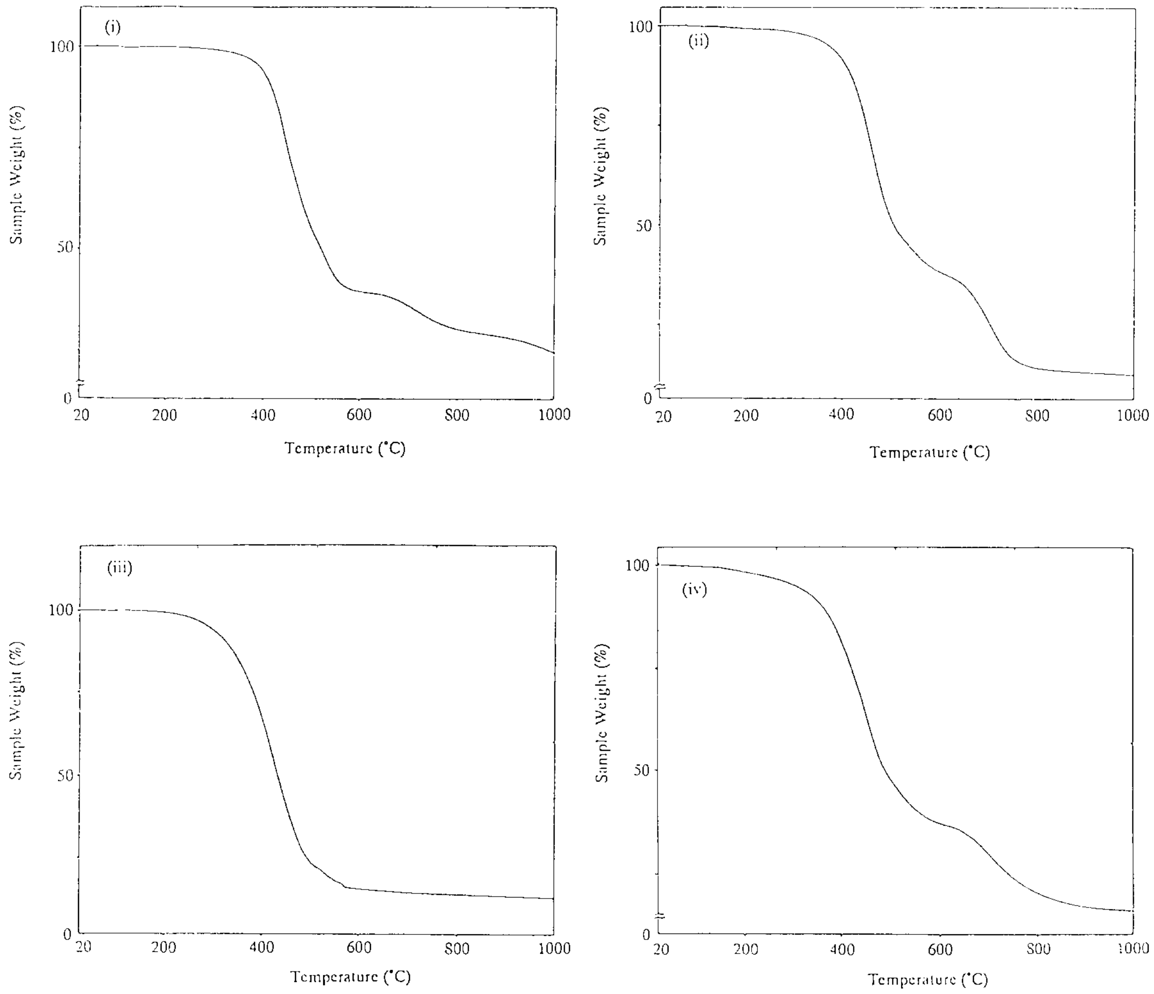
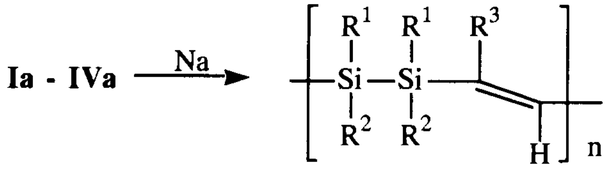
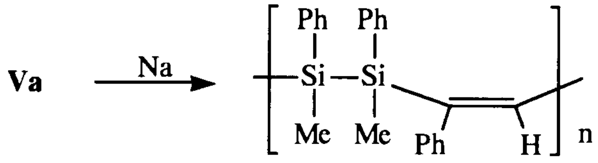


Fig. 1. TGA profile of **Ib** (i), **IIb** (ii), **IIIb** (iii), and **IVb** (iv).



Ib R^1 = Ph, R^2 = Me, R^3 = H
IIb R^1 = Ph, R^2 = Ph, R^3 = H
IIIb R^1 = Me, R^2 = Me, R^3 = H
IVb R^1 = Ph, R^2 = Me, R^3 = Ph



Vb

GPC analysis of the polymers **Ib–IIIb** and **Vb** shows monomodal molecular weight distribution, while **IVb** shows bimodal distribution whose GPC profile shows two separate molecular weight distribution, corresponding to MW = 85 600 (MN = 71 300) and MW = 5 700 (MN = 3 100) in an integral ratio of 1 : 10.

*2.3. Thermal behavior of polymers **Ib–IVb***

The thermal behavior of polymers **Ib–IVb** was examined by thermogravimetric analysis (TGA) in a nitrogen atmosphere and the profiles are shown in Fig. 1. Polymer **IIIb** began to decompose at about 280°C and weight was lost continuously, while polymers **Ib**, **IIb**, and **IVb** decomposed in two steps. The first step was rapid decomposition with weight loss at about 320–570°C and the second was continuous weight loss starting at about 620°C. Total weight loss at 1000°C was calculated to be 75%, 87%, 88%, and 83% of the initial weights for **Ib**, **IIb**, **IIIb**, and **IVb**, respectively.

Table 1
Some properties of polymers **Ib–Vb**

Polymer	Yield (%)	MW	MN	m.p. (°C)
Ib	60	39800	9800	60– 64
IIb	21	3000	2300	108–123
IIIb	33	9900	3900	82– 87
IVb	11	16100	3600	85– 97
Vb	11	7600	2400	110–115

*2.4. Photochemical properties of the polymers **Ib–IVb***

(Disilanylene)ethenylene polymers **Ib–IVb** show characteristic strong UV absorption bands, significantly red shifted relative to those of pentamethylvinyldisilane (λ_{max} = 223 nm) and 1,1,2,2-tetramethyldivinyldisilane (λ_{max} = 225, 227 nm) [13], due to delocalization of the π-electrons through the disilanylene units; they are photoactive, like other alternating polymers composed of an Si–Si bond and π-electron system [3–6,8,9]. When thin solid films of polymers **Ib–IVb** were irradiated with a low-pressure mercury lamp bearing a Vycor filter in air and the progress of the reactions was monitored by UV and IR spectrophotometry, all polymers showed similar photochemical behavior. Irradiation of the films resulted in a rapid decrease of the UV absorption bands with increasing irradiation time, as observed for other alternating disilanylene polymers reported previously [3–6,8,9]. IR spectra of the films after 1-h irradiation revealed strong absorption bands around 3100–3500 and 1100 cm^{-1} due to stretching frequencies of the Si–O–H and Si–O–Si bonds. The formation of the Si–O–H and Si–O–Si bonds can be explained by the reaction of silyl radicals arising from homolytic scission of the Si–Si bonds with oxygen.

In order to learn more about the photochemical properties of the present polymers, we carried out the photolysis of **Ib–IVb** in benzene and followed their molecular weight changes by GPC. As can be seen in Fig. 2, when polymer **Ib** (MW = 39 800) was photolyzed in benzene, the molecular weight of the polymer decreased rapidly with increasing irradiation time and reached a constant value of MW = 10 400 which corresponds to one-fourth of the molecular weight, after 20-h irradiation (curve (i)).

The ^{13}C NMR spectrum of the photodegradation products from the photolysis of polymer **Ib** reveals multiplet signals due to sp^3 carbon atoms at 25–42 ppm, along with methylsilyl carbons and sp^2 carbons. In this spectrum, no resonances attributed to bis(silyl)-substituted ethenylene units are observed. The ^{1}H NMR spectrum shows multiplet signals at 1.0–3.2 due to polysilyl-substituted ethylene and allylic protons and olefinic signals at 5.2–6.7 ppm, along with broad signals at −0.2–0.8 and 6.8–7.7 ppm due to the methylphenylsilylene units.

A possible mechanism for this photodegradation is presented in Scheme 2. The mechanism involves homolytic scission of the Si–Si bonds in the polymer main chain producing silyl radicals. The silyl radicals thus formed may add to ethenylene bonds and phenyl groups leading to the formation of polysilyl-substituted ethylene units and allylic units probably in the cyclohexadienyl ring, respectively. On the basis of the integral ratio of 4.8 : 4.3 : 1 : 7.1 for the signals at −0.2–0.8,

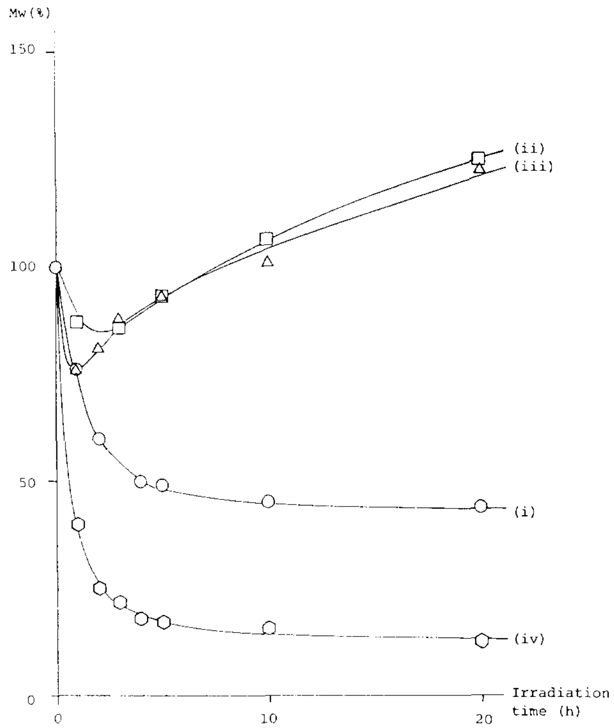
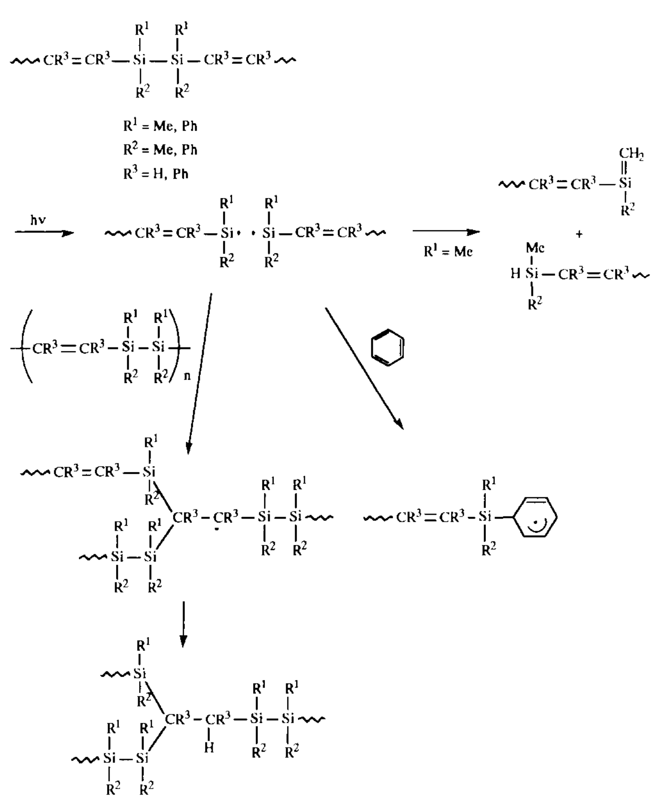


Fig. 2. Plot of the molecular weights (%) based on the starting polymer versus irradiation time for the photolysis of **Ib** (i), **IIb** (ii), **IIIb** (iii), and **IVb** (iv).



Scheme 2.

1.0–3.2, 5.2–6.7, and 6.8–7.7 ppm in the ^{1}H NMR spectrum of the photoproducts of **Ib**, it seems likely that the solvent benzene is incorporated in the products as dihydro- and/or tetrahydrophenylene units to some extent. The formation of Si–H bonds as indicated by weak absorption at 2116 cm^{-1} in the IR spectrum of the photoproducts seems to be responsible for the decrease in the molecular weight of the photoproducts. The formation of the Si–H bonds can be explained by disproportionation of the silyl radicals, giving hydrosilanes and silenes, and also by abstraction of hydrogen atoms from any available source.

The photolysis of polymer **IVb** (MW = 16 100), which has bimodal molecular weight distribution, led to a decrease on the molecular weight (Fig. 2, curve (iv)), similar to that of **Ib**. In this photolysis, the fraction with high molecular weight distribution (MW = 85 600) disappeared completely after 2-h irradiation, and the fraction with low molecular weight distribution (MW = 5700) shifted to a lower region with increasing reaction time. After 20-h irradiation, photodegradation products with molecular weight of MW = 2200 were produced.

The photolysis of polymers **IIb** and **IIIb** proceeded in a different fashion from that of **Ib** and **IVb** (Fig. 2, curves (ii) and (iii)). Thus, when **IIb** (MW = 3000) was photolyzed in benzene, the molecular weight of the photoproducts decreased in the early stages of the photolysis, passed through a minimum value of 2400 after 2 h-irradiation, and then increased with increasing irradiation time. After 20-h irradiation, the photodegradation products with molecular weight of 3700 were obtained. Similarly, when polymer **IIIb** (MW = 9900) was photolyzed, the molecular weight decreased at the early stages of the reaction and reached a minimum value of 7500 after 1-h irradiation, and then increased gradually to form products with molecular weight of 13 200, after 20-h irradiation. A similar profile for the molecular weight change has been reported for the photolysis of poly[(disilanylene)butenyne-1,4-diyls] [5].

The products from the photolysis of the polymers **IIb–IVb** can be explained by assuming the formation of the silyl radicals derived from homolytic scission of the Si–Si bonds, as in the case of the photolysis of polymer **Ib**. IR spectra of the photodegradation products show a weak Si–H absorption band. ^{1}H NMR spectroscopic analysis of the photoproducts indicates the presence of ethylene and allylic units which would be formed from addition of the silyl radicals across the ethenylene units and phenyl rings in the starting polymers. The cyclohexenyl or cyclohexadienyl units would also be produced by the reaction of the silyl radicals with solvent benzene, as shown in Scheme 2. Indeed, when **IIIb** was photolyzed in deuteriobenzene, photoproducts that incorporated with deuteriobenzene were obtained. The

^{2}H NMR spectrum shows broad signals at 1.4–3.0, 5.2–6.2 and 6.3–6.8 ppm, while the ^{1}H NMR spectrum reveals multiplet signals with low intensities at 0.84–1.69 ppm due to ethylene units, along with weak signals, attributed to olefinic protons.

In conclusion, polymers **Ib–IVb** show similar photochemical behavior to other polymers composed of a disilanylene unit and π-system in the solid state. In solution, the photolysis of **Ib** and **IVb** resulted in a rapid decrease in molecular weight, while, **IIb** and **IIIb** in benzene led to a decrease in molecular weight at the early stages of the reactions, but increased with increasing irradiation time. It seems likely that the introduction of a phenyl group on the silicon atom stabilizes the silyl radicals. If the silyl radicals thus formed have a hydrogen atom at the β-position, they would undergo disproportionation, rather than addition to the double bonds, giving silenes and hydrosilanes, which are responsible for the decrease in molecular weight. The absence of a radical-stabilizing moiety such as a phenyl group on the silicon atom as in polymer **IIIb** may facilitate the addition of the silyl radicals across the unsaturated bonds to increase the molecular weight. The silyl radicals generated from polymer **IIb**, which have no β-hydrogen-atom may not undergo disproportionation, but mainly add to the unsaturated bonds.

3. Experimental details

3.1. General

All reactions were carried out under an atmosphere of purified argon. ^{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. Thermogravimetric analysis was carried out using a Seiko SSC5200H thermobalance.

3.2. Materials

Benzene and THF were dried over lithium aluminum hydride and distilled just before use. Decane was dried over sodium and distilled just before use. Carbon tetrachloride was distilled from P_2O_5 and stored over molecular sieves until use. Acetyl chloride was used after simple distillation. 1,2-Diethynyltetramethyldisilane was prepared as reported in the literature [14].

3.3. Preparation of **Ia**

In a 2 three-necked flask fitted with a reflux condenser and dropping funnel was placed a mixture of 191 g (1.0 mol) of dichloromethylphenylsilane and 500 ml of THF, and the flask was cooled to 0°C. To this was added dropwise an ethynyl magnesium bromide/THF solution prepared from 1.2 mol of ethylmagnesium bromide and acetylene in 300 ml of THF. The mixture was allowed to stand at room temperature for 2 h and 300 ml of hexane was added to the mixture to precipitate the magnesium salts. The resulting magnesium salts were filtered off and the solvent was evaporated. The residue was distilled under reduced pressure to give a fraction (180 g) boiling at 98–120°C (40 mmHg), which consists of 45% of dichloromethylphenylsilane, 33% of chloroethynylmethylphenylsilane and 22% of diethynylmethylphenylsilane. A mixture of 8.6 g of this fraction and 7.7 g (49.0 mmol) of chloromethylphenylsilane was placed in a 50-ml flask, and the flask was cooled to 0°C. To this was added 0.05 ml (0.015 mmol) of a 0.3 M solution of H_2PtCl_4/isopropyl alcohol, and the solution was stirred at 50°C for 20 h. The resulting mixture was fractionally distilled under reduced pressure to give 5.3 g (33% yield) of **Ia**: b.p. 160–165°C (1 mmHg). MS *m/z* 321 ($M^+ - Me$). ^{1}H NMR (in CCl_4): δ 0.75 (s, 6H, MeSi); 6.52 (s, 2H, olefinic protons); 6.79–7.46 (m, 10H, Ph). ^{13}C NMR (in $CDCl_3$): δ 0.2, 128.2, 130.7, 133.7, 133.8, 148.9. Anal. Found: C, 55.50; H, 5.25. $C_{16}H_{18}Si_2Cl_2$ Calc.: C, 55.65; H, 5.25%.

3.4. Preparation of **IIa**

To a solution of 253 g (1.0 mol) of dichlorodiphenylsilane in 300 ml of THF was added 1.2 mol of ethynylmagnesium bromide in 200 ml of THF. The resulting mixture was allowed to stand at room temperature for 2 h, and then 300 ml of hexane was added to the mixture. After the resulting magnesium salts were filtered off, the solvent was evaporated. Fractional distillation of the residue under reduced pressure gave 91 g of a mixture consisting of 44% of dichlorodiphenylsilane, 31% of chloroethynyldiphenylsilane, and 12% of diethynyldiphenylsilane (boiling range 80–150°C/17 mmHg). The mixture (36.0 g) was treated with 11.4 g (120 mmol) of chlorodiphenylsilane and 0.05 ml (0.015 mmol) of a 0.3 M solution of H_2PtCl_4/isopropyl alcohol at 50°C for 20 h. Dichlorodiphenylsilane and chlorodiphenylsilane were removed under reduced pressure, the residue was recrystallized from hexane to give 19 g of **IIa** (10% yield): m.p. 86–87°C. MS *m/z* 381 ($M^+ - Ph$). ^{1}H NMR (in CCl_4): δ 7.02–7.05 (m, olefinic and phenyl ring protons). ^{13}C NMR (in $CDCl_3$): δ 128.5, 131.0, 132.6, 135.2, 149.9. Anal. Found: C, 67.52; H, 4.78. $C_{26}H_{22}Cl_2Si_2$ Calc.: C, 67.66; H, 4.80%.

3.5. Preparation of IIIa

A mixture of 3.2 g (19.2 mmol) of 1,2-diethynyltetramethyldisilane, 4.5 g (47.6 mmol) of chlorodimethylsilane, and 0.03 ml (0.009 mmol) of a 0.3 M solution of H_2PtCl_4/isopropyl alcohol was stirred at 50°C for 20 h and the mixture was distilled under reduced pressure to give 3.5 g (51% yield) of **IIIa**: b.p. 155°C (17 mmHg). MS *m/z* 339 ($M^+ -$ Me). ^1H NMR (in CCl_4): δ 1.10 (s, 12H, MeSi); 1.33 (s, 12H, MeSi); 7.18 (d, 2H, $J = 22$ Hz, olefinic protons); 7.63 (d, 2H, $J = 22$ Hz, olefinic protons). ^{13}C NMR (in $CDCl_3$): δ −4.7, 1.7, 146.2, 153.2. Anal. Found: C, 40.40; H, 7.90. $C_{12}H_{28}Si_4Cl_2$ Calc.: C, 40.53; H, 7.94%.

3.6. Preparation of methylphenyl(phenylethynyl)silane

To a solution of 15.6 g (0.10 mol) of chloromethylphenylsilane was added a solution of phenylethynyllithium prepared from 10.2 g (0.10 mol) of phenylacetylene and 63.0 ml (0.10 mol) of a 1.6 M n-butyllithium/hexane solution in 50 ml of THF. The resulting mixture was stirred at room temperature for 2 h, and then hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted twice with 50 ml of ether. The organic layer and extracts were combined and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was distilled under reduced pressure to give 10.1 g (45% yield) of methylphenyl(phenylethynyl)silane: b.p. 110°C (0.1 mmHg). MS *m/z* 222 (M^+). ^1H NMR (in $CDCl_3$): δ 0.67 (d, 3H, $J = 2$ Hz, MeSi); 4.91 (q, 1H, $J = 2$ Hz, HSi); 7.36–7.83 (m, 10H, ring protons). ^{13}C NMR (in $CDCl_3$): δ −3.6, 88.9, 108.1, 122.6, 128.0, 128.2, 128.9, 129.8, 132.1, 133.6, 134.4. IR 2159 cm^{-1} (ν_{Si-H} and $\nu_{C\equiv C}$). Anal. Found: C, 81.08; H, 6.32. $C_{15}H_{14}Si$ Calc.: C, 81.02; H, 6.35%.

3.7. Preparation of chloromethylphenyl(phenylethynyl)silane

A mixture of 7.4 g (33.3 mmol) of methylphenyl(phenylethynyl)silane and 3 mg (0.017 mmol) of palladium dichloride in 50 ml of carbon tetrachloride was stirred at room temperature for 48 h. The solvent and the resulting chloroform were evaporated and the residue was distilled under reduced pressure to give 4.0 g (47% yield) of chloromethylphenyl(phenylethynyl)silane: b.p. 125°C (0.1 mmHg). MS *m/z* 256 (M^+). ^1H NMR (in $CDCl_3$): δ 0.87 (s, 3H, MeSi); 6.93–7.90 (m, 10H, ring protons). ^{13}C NMR (in $CDCl_3$): δ 2.8, 88.2, 108.5, 121.6, 128.2, 128.3, 129.6, 130.9, 132.3, 133.5, 133.8. IR: 2162 cm^{-1} ($\nu_{C\equiv C}$). Anal. Found: C, 69.87; H, 5.10. $C_{15}H_{13}ClSi$ Calcd.: C, 70.16; H, 5.10%.

3.8. Preparation of IVa

A mixture of 4.0 g (15.6 mmol) of chloromethylphenyl(phenylethynyl)silane, 2.4 g (15.6 mmol) of chloromethylphenylsilane, and 0.05 ml (0.015 mmol) of a 0.3 M solution of H_2PtCl_4/isopropyl alcohol was heated at 50°C for 100 h. The resulting mixture was distilled under reduced pressure to give 6.4 g (99% yield) of **IVa**: b.p. 170°C (0.1 mmHg). MS *m/z* 335 ($M^+ -$ Ph). ^1H NMR (in CCl_4): δ 0.15 (s, 3H, MeSi); 0.69 (s, 3H, MeSi); 6.49–7.66 (m, 16H, olefinic and phenyl ring protons). ^{13}C NMR (in $CDCl_3$): δ −0.2, 1.1, 127.1, 127.7, 127.9 (2C), 128.0, 128.3, 130.1, 130.6, 133.3 (2C), 134.0, 135.7, 141.1, 143.7. Anal. Found: C, 63.76; H, 5.36. $C_{22}H_{22}Si_2Cl_2$ Calc.: C, 63.90; H, 5.36%.

3.9. Preparation of (Z)-1,2-bis(ethoxymethylphenylsilyl)-phenylethene

A mixture of 3.5 g (10.6 mmol) of 1,2-diethoxy-1,2-dimethyldiphenyldisilane, 1.62 g (15.9 mmol) of phenylacetylene, 48 mg (0.212 mmol) of palladium diacetate, and 260 mg (3.13 mmol) of tert-butylisonitrile in 30 ml of toluene was heated at 70°C for 5 h. The solvent was evaporated and the residue was distilled under reduced pressure to give 2.6 g (57%) of (*Z*)-1,2-bis(ethoxymethylphenylsilyl)phenylethene as a 1 : 1 diastereomeric mixture: b.p. 170°C (0.1 mmHg). MS *m/z* 432 (M^+). ^1H NMR (in $CDCl_3$): δ 0.37–1.49 (m, 12H, Me); 2.04–2.98 (m, 4H, H_2CO); 6.84 (s, 1H, olefinic proton); 7.00–7.77 (m, 15H, Ph). ^{13}C NMR (in $CDCl_3$): δ −3.0, −2.2, −1.7, −1.5, 17.6, 17.7, 18.3 (2C), 58.4 (2C), 58.5 (2C) 126.3, 126.7, 126.9 (2C), 127.5 (2C), 127.7 (2C), 127.8 (2C), 128.6, 129.1, 129.6 (2C), 134.0, 134.1, 134.4, 134.5, 136.4, 136.8, 138.3 (2C), 146.8, 147.0, 147.6 (2C), 162.4, 162.7. Anal. Found: C, 72.45; H, 7.45. $C_{26}H_{32}Si_2O_2$ Calc.: C, 72.17; H, 7.45%.

3.10. Preparation of Va

A mixture of 2.4 g (5.6 mmol) of *cis*-1,2-di(ethoxymethylphenylsilyl)phenylethene and 50 ml of acetyl chloride was heated at 50°C for 10 h. An excess of acetyl chloride and the resulting ethyl acetate were evaporated and the residue was distilled under reduced pressure to give 1.9 g (82% yield) of **Va** as a 1 : 1 diastereomeric mixture: b.p. 160°C (0.1 mmHg). MS *m/z* 397 ($M^+ -$ Me). ^1H NMR (in CCl_4): δ 0.62 (s, 3H, MeSi); 0.74 (s, 3H, MeSi); 6.80–7.80 (m, 16H, olefinic and phenyl ring protons) ^{13}C NMR (in $CDCl_3$): δ −1.4, −1.2, −1.0, −0.8, 126.7 (2C), 127.9 (2C), 128.1 (2C), 128.6 (2C), 129.2, 130.1 (2C), 133.3, 133.6 (2C), 133.8 (2C), 134.0 (2C), 136.4, 136.6 (2C), 136.8, 140.1 (2C), 143.9 (2C), 163.7, 163.8. Anal. Found: C, 63.83; H, 5.44. $C_{22}H_{22}Cl_2Si_2$ Calc.: C, 63.90; H, 5.36%.

3.11. Hydrolysis of compound Va

A solution of 50 mg (0.121 mmol) of compound **Va** in 10 ml of ether was placed in a 30-ml flask and the flask was cooled to 0°C. To this was added 10 ml of a 1 : 1 mixture of water and THF, and the resulting mixture was stirred for 3 h at room temperature. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and extracts were combined and dried over anhydrous magnesium sulfate. After evaporation of the solvent, flash distillation of the residue under reduced pressure gave 35 mg (81%) of **VI** as a 1 : 1 diastereomeric mixture: MS m/z 358 (M^+). ^{1}H NMR (in $CDCl_3$): δ 0.66 (s, 1.5H, MeSi); 0.68 (s, 1.5H, MeSi); 0.78 (s, 1.5H, MeSi); 0.79 (s, 1.5H, MeSi); 7.20–7.70 (m, 16H, ring protons). ^{13}C NMR (in $CDCl_3$): δ −1.5, −1.3, −1.1, −0.9, 126.5, 127.8 (2C), 127.89, 127.94, 128.0 (2C), 128.5, 130.00, 130.01, 130.05, 130.12, 133.5, 133.66, 133.69, 133.9, 136.2 (2C), 136.4, 136.5, 136.6 (2C), 139.87, 139.91, 143.70, 143.74, 163.5, 163.7. IR: 925 cm^{-1} (ν_{Si-O}). Anal. Found: C, 73.63; H, 6.08. $C_{22}H_{22}OSi_2$ Calc.: C, 73.69; H, 6.18%.

3.12. Preparation of polymer Ib

In a 100-ml three-necked flask fitted with a reflux condenser and dropping funnel was placed 0.74 g (32 mmol) of a sodium dispersion and 20 ml of benzene. To this was added dropwise 4.23 g (12.5 mmol) of **Ia** at room temperature. The resulting mixture was stirred at 30°C under ultrasonic irradiation for 6 h. The resulting mixture was hydrolyzed with ethanol and water. The organic layer was separated and the aqueous layer was extracted with benzene. The organic layer and extracts were combined and dried over anhydrous magnesium sulfate. After the solvent was evaporated, the residue was reprecipitated from benzene/ethanol to give 2.02 g (60% yield) of **Ib**: m.p. 60–64°C. MW = 39 800. MN = 9800. ^{1}H NMR (in CCl_4): δ 0.29 (s, 3H, MeSi); 0.32 (s, 3H, MeSi); 6.69 (s, 2H, olefinic protons); 6.85–7.68 (m, 10H, ring protons). ^{13}C NMR (in $CDCl_3$): δ −5.5, −5.4, 127.7, 127.8, 128.6 (2C), 134.5, 134.8, 136.5, 136.6, 149.4 (2C). UV (THF): λ_{max} 195, 243 (shoulder), 280 nm (shoulder). Anal. Found. C, 72.22; H, 7.05. $(C_{16}H_{18}Si_2)n$ Calc.: C, 72.11; H, 6.81%.

3.13. Preparation of polymer IIb

In a 100-ml flask was placed 0.52 g (22.6 mmol) of sodium dispersion and 20 ml of benzene. To this was added dropwise 5.0 g (10.8 mmol) of **IIa** at room temperature. The resulting solution was stirred at 30°C under ultrasonic irradiation for 10 h. After the usual workup, the products were reprecipitated from chloroform/ethanol to give 0.90 g (21% yield) of **IIb**: m.p. 108–123°C. MW = 3000. MN = 2300. ^{1}H NMR (in $CDCl_3$): δ 7.25 (br. s, olefinic and phenyl ring protons). ^{13}C NMR (in $CDCl_3$): δ 127.9, 129.1, 134.2, 136.1, 150.8. UV (film): λ_{max} 226, 244 (shoulder), 277 nm (shoulder). Anal. Found: C, 79.77; H, 5.78, $(C_{26}H_{22}Si_2)n$ Calc.: C, 79.94; H, 5.68%.

3.14. Preparation of polymer IIIb

In a 100-ml flask was placed 0.25 g (11.0 mmol) of sodium dispersion and 20 ml of benzene. To this was added dropwise 2.0 g (5.63 mmol) of **IIIa** at room temperature. The resulting mixture was stirred at 30°C under ultrasonic irradiation for 10 h. To this was added 0.27 ml (0.41 mmol) of a 1.5 M methyllithium/ether solution at 0°C, and the mixture was heated at 50°C for 30 min. After the usual workup, the products were reprecipitated from chloroform/ethanol to give 0.52 g (33% yield) of **IIIb**: m.p. 82–87°C. MW = 9900. MN = 3900. ^{1}H NMR (in $CDCl_3$): δ 0.10 (s, 12H, MeSi); 6.56 (s, 2H, olefinic protons). ^{13}C NMR (in $CDCl_3$): δ −4.5, 149.7. UV (film): 190, 212 (shoulder), 261 nm. Anal. Found: C, 50.04; H, 9.70. $(C_6H_{14}Si_2)n$ Calc.: C, 50.63; H, 9.91%.

3.15. Preparation of polymer IVb

In a 100-ml flask was placed 0.60 g (26.0 mmol) of sodium dispersion and 20 ml of benzene. To this was added dropwise 3.2 g (7.74 mmol) of **IVa** at room temperature. The resulting mixture was stirred at 30°C under ultrasonic irradiation for 10 h. After the usual workup, the products were reprecipitated from chloroform/ethanol to give 0.28 g (11% yield) of **IVb**: m.p. 85–97°C. MW = 16 100. MN = 3600. ^{1}H NMR (in $CDCl_3$): δ 0.03 (br. s, 6H, MeSi): 6.09–7.74 (m, 16H, olefinic and phenyl ring protons). ^{13}C NMR (in $CDCl_3$): δ −6.9–1.2, 124.7–136.3. UV (film): λ_{max} 194, 223 (shoulder), 267 (shoulder) nm. Anal. Found: C, 74.25; H, 6.46. $(C_{22}H_{22}Si_2)n$ Calc.: C, 77.13; H, 6.47%.

3.16. Preparation of polymer Vb

In a 100-ml flask was placed 0.22 g (9.56 mmol) of sodium dispersion and 20 ml of benzene. To this was added dropwise 1.9 g (4.60 mmol) of **Va** at room temperature. The resulting mixture was stirred at 30°C under ultrasonic irradiation for 10 h. After the usual workup of the resulting mixture, the products were reprecipitated from chloroform/ ethanol to give 0.17 g (11% yield) of **Vb**: m.p. 110–115°C. MW = 7600. MN = 2400. ^{1}H NMR (in $CDCl_3$): δ 0.08 (s, 6H, MeSi); 6.37–7.98 (m, 16H, olefinic and phenyl ring protons). ^{13}C NMR (in $CDCl_3$): δ 1.1, 127.8–130.6, 131.9–135.6. UV (film): λ_{max} 221, 264 nm (shoulder). Anal. Found:

C, 78.38; H, 6.21. $(C_{22}H_{22}Si_2)n$ Calc.: C, 77.13; H, 6.47%.

3.17. Thermogravimetric analysis of polymers ***Ib–IVb***

On a platinum plate was placed 4–5 mg of polymers **Ib–IVb** and the plate was heated from room temperature to 1000°C at a rate of 10°C/min under a nitrogen atmosphere. The results are shown in Fig. 1.

3.18. Photolysis of thin solid films of polymers ***Ib–IVb***

A 10% chloroform solution of polymers **Ib–IVb** 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 1-h irradiation, the UV spectra of the films showed a decrease in the absorption bands, and their IR spectra revealed strong absorption bands at 3500–3100 and 1100 cm^{-1}.

3.19. Photolysis of ***Ib–IVb*** *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 polymers **Ib–IVb** in 25 ml of benzene. The solution was irradiated and the progress of the reaction was monitored by GPC (see Fig. 2). After 20-h irradiation, the solvent was evaporated to give photodegradation products. For the photoproducts from **Ib**: MW = 10400, MN = 2500. ^1H NMR (in $CDCl_3$): δ −0.2–0.8 (m, MeSi, relative integration 67); 1.0–3.2 (m, ethylene and allylic protons, 60); 5.2–6.7 (m, Si–H and olefinic protons, 14); 6.8–7.7 (br. s, Ph, 100). ^{13}C NMR (in $CDCl_3$): δ −5–4, 25–42, 127.8, 128.4, 129.3, 133.4–138. IR 2116 cm^{-1} (ν_{Si-H}). For the photoproducts from **IIb**: MW = 3700. MN = 2600. ^1H NMR (in $CDCl_3$): δ 1.27–2.66 (m, ethylene and allylic protons, 100); 5.20–6.92 (m, Si–H and olefinic protons, 99); 6.75–7.90 (m, Ph, 31). ^{13}C NMR (in $CDCl_3$): δ 35, 118.3, 119.8, 125.1, 127.2–137.2, 140.2. IR 2132 cm^{-1} (ν_{Si-H}). For the photoproducts from **IIIb**: MW = 13200. MN = 8200. ^1H NMR (in $CDCl_3$): δ −0.04 (br. s, MeSi, relative integration 100); 0.4–3.0 (m, ethylene and allylic protons, 58); 5.2–7.2 (m, Si–H and olefinic protons, 20). ^{13}C NMR (in $CDCl_3$): δ −1.9–4.2, 29.9–59.6, 127.2–137.7. IR 2108 cm^{-1} (ν_{Si-H}). For the photoproducts from **IVb**: MW = 2200. MN = 800. ^1H NMR (in $CDCl_3$): δ −0.2–0.9 (m, MeSi, relative integration 52); 1.4–3.2 (m, ethylene and allylic protons, 52); 5.8 (br. s, Si–H or olefinic protons, 23), 6.8–7.6 (br. s, olefinic and phenyl protons, 100). ^{13}C NMR (in $CDCl_3$): δ −5.0–1.0, 30.0, 127.8, 128.4, 129.6, 133.5, 134.5. IR 2122 cm^{-1} (ν_{Si-H}).

3.20. Photolysis of ***IIIb*** *in deuteriobenzene*

A solution of 12.3 mg of **IIIb** (MW = 9800; MN = 3900) in 3 ml of deuteriobenzene was irradiated externally with a low-pressure mercury lamp bearing a Vycor filter for 20 h. After the solvent was evaporated, the residue was analyzed by GPC: MW = 14900. MN = 4400. ^1H NMR (in $CDCl_3$): δ 0.10–0.22 (MeSi, relative integration 100); 0.84, 0.90, 1.25–1.69 (ethylene, 8); 6.59, 6.75, 7.15–7.55 (olefinic protons, 6). ^2H NMR (in $CDCl_3$): δ 1.4–3.0, 5.2–6.2, 6.3–6.8. IR 2122, 2090 cm^{-1} (ν_{Si-H} and ν_{C-D}).

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