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Photochemical Properties of Network and Branched Polysilanes

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ABSTRACT: Linear, branched, and network polysilanes were synthesized by the copolymerization of dichloromethylphenylsilane and trichlorophenylsilane. The influence of the Si-skeleton on absorption and emission spectra was investigated. The sharp σ–σ^* absorption band (λ_{max} 334 nm) of linear poly(methylphenylsilylene) changed into a broad one with branching. The shift of the absorption edge to a longer wavelength (410 nm) suggests that the increase of σ-conjugation is due to the silicon network structure. The sharp emission (λ_{max} 355 nm) of linear poly(methylphenylsilylene) also shifted to the broad emission (λ_{max} 471 nm) for network poly(phenylsilyne). The intermediates formed during the photodegradation of polysilanes with various Si-skeletons were investigated by flash photolysis. The time-resolved absorption spectra exhibited the absorption bands of a silyl radical and silylenes. The significant influence of the excitation wavelength was observed. Silylene was produced effectively by the excitation at shorter wavelength (π–π^* excitation). The transient absorption spectrum for network poly(phenylsilyne) suggested the formation of a silylsilylene in the silicon network structure. The absorption of the silylsilylene appeared at longer wavelength (λ_{max} 550 nm) compared to that of low molecular weight silylene (λ_{max} 480 nm).

Introduction

Polysilane is an organosilicon polymer that has an Si–Si backbone and an organic side chain. Since the synthesis of soluble polysilanes with high molecular weight was reported about 10 years ago,[1-3] polysilanes have attracted considerable attention as a new functional class of polymer. The photoresist in microlithography has been investigated as one field of application for polysilanes because the σ-bond of the Si–Si backbone is easily decomposed by irradiation with UV light.[4-6] The mechanism of photodegradation of polysilanes is quite complicated. During the photodegradation of polysilanes, various kinds of intermediates are produced, for example, a silyl radical, silylene, and silene.[7,8] The photodegradation shows an excitation-wavelength dependence.[9] The kind of organic substituent influences the mechanism of the photodegradation.[10] As another field of application for polysilanes, the semiconducting properties have been investigated.[2] Polysilanes with a linear main chain have a so-called one-dimensional silicon structure. The absorption spectrum of the linear polysilanes shows an intense absorption band in the UV region due to σ-conjugation along the Si–Si backbone.[11] Recently new polysilanes with various Si-skeletons have been investigated.[12-16] Bianconi et al. first reported poly(n-hexylsilyne) as a silicon network polymer in 1988. The network polysilane was recognized as a polymer that has a two-dimensional Si-skeleton and a two-dimensional σ-conjugation along the Si-skeletons. Organic polysilanes can be regarded as a low-dimensional silicon compound compared with crystalline silicon or amorphous silicon that have three-dimensional Si–Si bonds. Matsumoto et al. reported the concept of classification of polysilanes on the basis of Si-skeleton dimensionality.[17]

In a previous paper we investigated the photodegradation of aryl- and alkyl-substituted polysilanes by flash photolysis.[18] The transient absorption spectra obtained by flash photolysis revealed the formation of a silyl radical and silylene as transient intermediates, and the influence of an organic side chain was observed. In this paper we will report the influence of the Si-skeleton on the photochemical properties of polysilanes. We synthesized a poly(phenylsilyne) that has a silicon network structure and branched polysilanes by copolymerization using methylphenyldichlorosilane and phenyltrichlorosilane as monomers. Their photochemical behavior was compared with poly(methylphenylsilylene) having a linear structure. The polysilanes used in microlithography as positive resists require the photodissociative properties. On the other hand, the semiconducting polysilanes need the light resistance. We expect that the photochemical behavior of polysilanes can be controlled by the molecular design of these Si-skeletons. Recently, Wilson et al. reported the excited-state dynamics of one- and two-dimensional alkyl-substituted polysilanes and the branched poly(n-hexylmethylsilylene) copolymers.[16] They note the dramatic effects of branching structure on the photochemical behavior of polysilanes. In this paper we will report the photochemical properties of aryl-substituted polysilanes with various Si-skeletons. The transient intermediates during the photodegradation of them were investigated by flash photolysis.

Experimental Section

Materials. Poly(methylphenylsilylene) having a linear Si–Si main chain was prepared by the Kipping reaction of dichloromethylphenylsilane with sodium metal and 18-crown-6 in toluene at 110 °C with rapid stirring. The molecular weight distribution of linear poly(methylphenylsilylene) becomes narrow by the addition of crown ether.[19] Poly(phenylsilyne) having a silicon network structure was prepared by similar procedures using trichlorophenylsilane as a monomer. Branched polysilanes were prepared by copolymerization of dichloromethylphenylsilane and trichlorophenylsilane. Methanol was used as a work-up solvent. The clear THF (tetrahydrofuran)–MeOH mixed solution containing polysilane was prepared by the addition of a proper amount of MeOH before precipitation. The mixed solution was stirred for 12 h to replace an unreacted chlorine group by a methoxy group. All polymers were purified by reprecipitation using MeOH as a precipitant. The molecular weight distributions were measured by gel permeation chromatography using monodispersed polystyrenes as standards. Absorption and emission spectra of the polysilanes were measured using THF (spectrozole, Nakarai Tesque Inc.). Transient absorption spectra were measured using THF which was dehydrated by sodium and degassed up to 10^{-5} Torr to avoid the quenching of silylene by moisture. Cyclohexane (Dotite spectrozole) was dehydrated by calcium hydride and degassed up to 10^{-5} Torr. These solvents were transferred to a cylindrical quartz cell (10-cm length and 1-cm diameter) on a vacuum line.

Measurements. Absorption and emission spectra were measured by a Hitachi U-3500 and a Shimadzu RF-502A,

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Table I
Characterization of Poly(methylphenylsilylene-*co*-phenylsilyne)s

abbrevn	monomer feed composn (mole fraction) $MePhSiCl_2/PhSiCl_3$	M_w (M_w/M_n)	polym composn (mole fraction) MePhSi/PhSi	methoxy end group (mole fraction) -OMe/Si
PMePhSi 10/0	1.0/0	3120 (1.73)	1.00/0	
PMePhSi 9/1	0.9/0.1	6580 (2.62)	0.94/0.06	0.20/0.80
PMePhSi 8/2	0.8/0.2	2320 (1.67)	0.80/0.20	0.22/0.78
PMePhSi 7/3	0.7/0.3	2700 (1.62)	0.76/0.24	0.24/0.76
PPhMeSi 6/4	0.6/0.4	1390 (1.65)	0.57/0.43	0.33/0.67
PPhMeSi 5/5	0.5/0.5	1341 (1.44)	0.42/0.58	0.33/0.67
PPhMeSi 4/6	0.4/0.6	1034 (1.28)	0.37/0.63	0.34/0.66
PMePhSi 3/7	0.3/0.7	970 (1.20)	0.26/0.74	0.16/0.84
PMePhSi 2/8	0.2/0.8	940 (1.23)	0.24/0.76	0.11/0.89
PMePhSi 1/9	0.1/0.9	1245 (1.54)	0.09/0.91	0.15/0.85
PMePhSi 0/10	0/1.0	913 (1.73)	0/1.00	0.14/0.86

respectively. ^1H NMR spectra were recorded on a Bruker AC-250 instrument. Xenon-flash photolysis experiments were carried out using a 100-J lamp with a half-duration of about 10 μs. The decay curves of transient absorption were measured using a digital storage scope. The time-resolved absorption spectra were measured by a double-flash system using a stroboflash (half-duration of about 3 μs) as a monitor light and a multichannel photodetector (MCPD). Band-pass filters, UV-D33S (240–410 nm), and a long-pass filter, UV-33 (300 nm), were used to select the excitation wavelength during the photolysis of the polysilanes. All experiments were carried out at 22 °C. The molecular modeling and optimization of the structure were carried out by Chem3D Plus (Cambridge Scientific Computing Inc.).[20,21]

Results

Absorption and Emission Spectra. Table I shows the abbreviations and characteristics of the polysilanes. The polysilanes are represented by PMePhSi D/T using the monomer feed composition ratio of dichloromethylphenylsilane to trichlorophenylsilane (D/T). The polymer composition was determined by ^1H NMR on the basis of the signals of the methyl proton and phenyl proton. The ratios of the methylphenylsilylene unit to the phenylsilyne unit correspond well to those of the monomer feed composition. The increase of the phenylsilyne unit indicates the increase of a branched structure. The ratios of the methoxy end group to the Si unit were determined by ^1H NMR on the basis of the signals of methoxy protons and phenyl protons. The ^1H NMR spectrum of poly(methylphenylsilylene) showed the sharp lines of methoxy protons near 3.5 ppm. The spectrum showed the fine splitting due to the free rotation of the methoxy group at the polymer end. On the other hand, poly(methylphenylsilylene-*co*-phenylsilyne) showed two kinds of spectral lines for the methoxy protons, sharp lines near 3.5 ppm and a broad line near 2.8 ppm. The latter may be assigned to the methoxy group bonded to the silicon atom at a branching point. If trichlorophenylsilane reacts at two chlorine groups and one unreacted chlorine group remains, a linear structure must be formed regardless of the monomer feed composition, and the methoxy/Si ratio is nearly 1. A methoxy group/Si ratio that deviates from unity suggests the existence of a branched structure of polysilane. The molecular weight of polysilane decreased with the branching structure as shown in Table I.

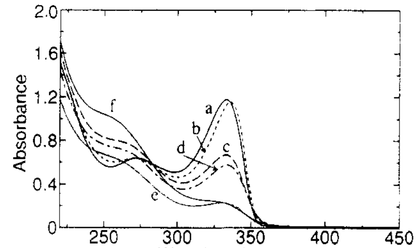

Figure 1. Absorption spectra of poly(methylphenylsilylene-*co*-phenylsilyne)s in THF: (a) PMePhSi 10/0, (b) PMePhSi 9/1, (c) PMePhSi 8/2, (d) PMePhSi 7/3, (e) PMePhSi 6/4, (f) PMePhSi 5/5. Concentration: 8 × 10^{-4} M (Si unit).

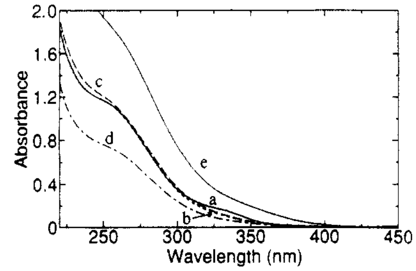

Figure 2. Absorption spectra of poly(methylphenylsilylene-*co*-phenylsilyne)s in THF: (a) PMePhSi 4/6, (b) PMePhSi 3/7, (c) PMePhSi 2/8, (d) PMePhSi 1/9, (e) PMePhSi 0/10. Concentration: 8 × 10^{-4} M (Si unit).

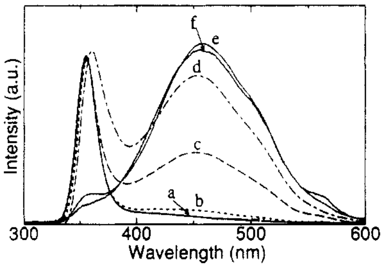

Figure 3. Emission spectra of poly(methylphenylsilylene-*co*-phenylsilyne)s in THF: (a) PMePhSi 10/0, (b) PMePhSi 9/1, (c) PMePhSi 8/2, (d) PMePhSi 7/3, (e) PMePhSi 6/4, (f) PMePhSi 5/5. Concentration: 5 × 10^{-4} M (Si unit). Excitation wavelength: 280 nm.

The absorption spectra of polysilane changed dramatically with the branching structure. Linear poly(methylphenylsilylene) (PMePhSi 10/0) shows a sharp σ–σ* absorption band at 334 nm (Figure 1). The absorption at 273 nm is attributable to the π–π* band of the phenyl group. The absorbance of the σ–σ* band decreases and the absorption at 250 nm increases with increasing the feed composition of trichlorophenylsilane. Such a tendency becomes more clear for PMePhSi D/T with high trichlorophenylsilane composition as shown in Figure 2. The absorption at 330 nm almost disappears and the absorption edge shifts to longer wavelength. Poly(phenylsilyne) (PMePhSi 0/10) shows an absorption edge at 410 nm.

The emission spectra of polysilanes were also influenced dramatically by the branching structure. In Figure 3, the emission spectrum of poly(methylphenylsilylene) (PMePhSi 10/0) shows a sharp emission peak, exhibiting a mirror image with the σ–σ* absorption band. Such an emission spectrum is assigned to a linear Si–Si chain of polysilane.

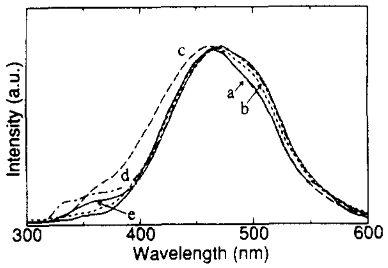

Figure 4. Emission spectra of poly(methylphenylsilylene-*co*-phenylsilyne)s in THF: (a) PMePhSi 4/6, (b) PMePhSi 3/7, (c) PMePhSi 2/8, (d) PMePhSi 1/9, (e) PMePhSi 0/10. Concentration: 5 × 10^{-4} M (Si unit). Excitation wavelength: 280 nm.

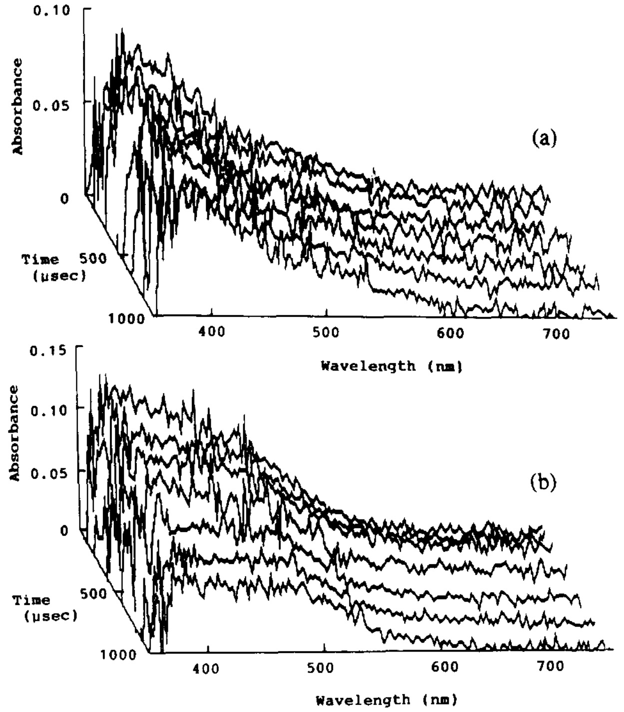

Figure 5. Time-resolved absorption spectra obtained by flash photolysis for a 1 mM THF solution of PMePhSi 8/2: (a) spectra obtained by the excitation using UVD-33S and UV-33 filters; (b) spectra obtained by the excitation using UVD-33S filter only.

With increasing the trichlorophenylsilane component in the monomer feed composition, a broad emission appears at 450 nm. Such a broad emission is quite similar to that of the silicon network polymer, poly(*n*-hexylsilyne). Polysilanes with a high trichlorophenylsilane feed composition show only a broad emission (Figure 4). The emission spectra were obtained by the excitation at 280 nm. The shapes of the emission spectra were independent of excitation wavelength. Another noticeable feature appears in Figures 3 and 4. The emission maximum of the broad emission gradually shifted to a longer wavelength with increasing trichlorosilane feed composition. Poly(phenylsilyne) (PMePhSi 0/10) shows the emission maximum at 471 nm while the poly(methylphenylsilylene-*co*-phenylsilyne) copolymer (PMePhSi 8/2) shows one at 452 nm. In addition, poly(phenylsilyne) shows an emission shoulder at 500 nm (Figure 4).

Transient Absorption Spectra by Flash Photolysis. The appearance of transient intermediates during the photodecomposition of polysilanes was investigated by flash photolysis. The time-resolved absorption spectra obtained by flash photolysis for a 1 mM THF solution of PMePhSi 8/2 are shown in Figure 5. In the flash photolysis measurements, two kinds of optical filters, UV-D33S and UV-33, were used to select the excitation wavelength.[18] Using both filters, the σ–σ* absorption band of the Si–Si chain can be excited. Using only the UV-D33S filter, σ–σ* and π–π* absorption bands of the phenyl group are excited. Parts a and b of Figure 5 were obtained using both the UV-D33S and UV-33 filters and using only the UV-D33S filter, respectively. The former spectra show absorption maxima at 380 nm. In the latter absorption spectra, a broad absorption appears at 480 nm in addition to the 380-nm peak. Similar wavelength dependence was also observed for PMePhSi 5/5 and poly(phenylsilyne) (PMePhSi 0/10) as shown in Figures 6 and 7, respectively. The broad absorption band shifts to longer wavelength with increasing trichlorophenylsilane components in the monomer feed. The shift of the broad band is clear by the difference spectrum between the transient absorption spectrum obtained by π–π* excitation (spectrum b) and that by σ–σ* excitation (spectrum a). The difference transient absorption spectra at 50 μs are depicted in Figure 8. The absorption maxima for PMePhSi 8/2 and PMePhSi 0/10 (poly(phenylsilyne)) are 480 and 550 nm, respectively.

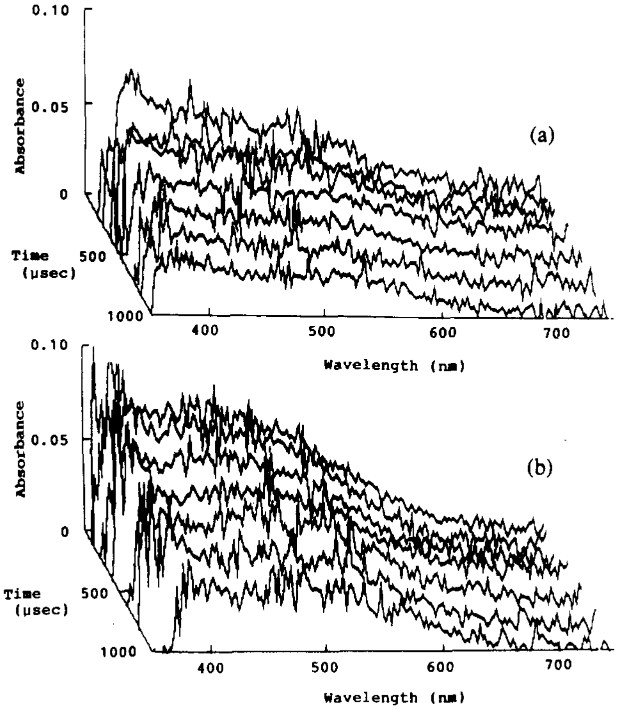

Figure 6. Time-resolved absorption spectra obtained by flash photolysis for a 1 mM THF solution of PMePhSi 5/5: (a) spectra obtained by the excitation using UVD-33S and UV-33 filters; (b) spectra obtained by the excitation using a UVD-33S filter only.

The effect of the addition of triethylsilane on the braod absorption was investigated. Triethylsilane is an effective silylene quencher.[10] Figure 9 shows the time-resolved absorption spectra of poly(phenylsilyne) obtained by flash photolysis of a 1 mM cyclohexane solution. The broad absorption band decreased by the addition of triethysilane. The decrease of the absorption at 550 nm is larger than that at 400 nm.

Discussion

Absorption and Emission Spectra. The structure of silicon network polymers such as poly(*n*-hexylsilyne) is presumed to be a semirigid quasi-two-dimensional, puckered, sheetlike structure on the basis of ^{29}Si NMR.[13,16] A network structure consisting of various kinds of silane rings is postulated.[13,16] However, the network structure remains unclear because of the amorphous state. The absorption spectrum of a network polysilane is characterized by the

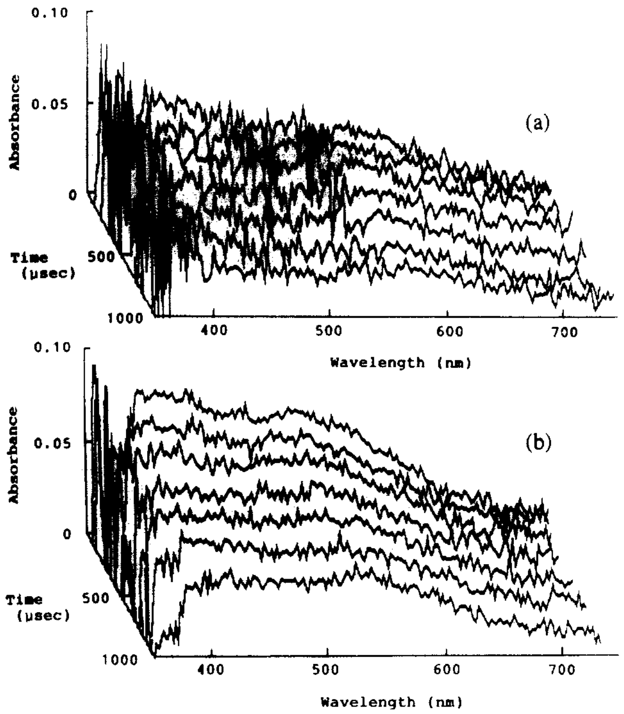

Figure 7. Time-resolved absorption spectra obtained by flash photolysis for a 1 mM THF solution of poly(phenylsilyne) (PMePh 0/10): (a) spectra obtained by the excitation using UVD-33S and UV-33 filters; (b) spectra obtained by the excitation using a UVD-33S filter only.

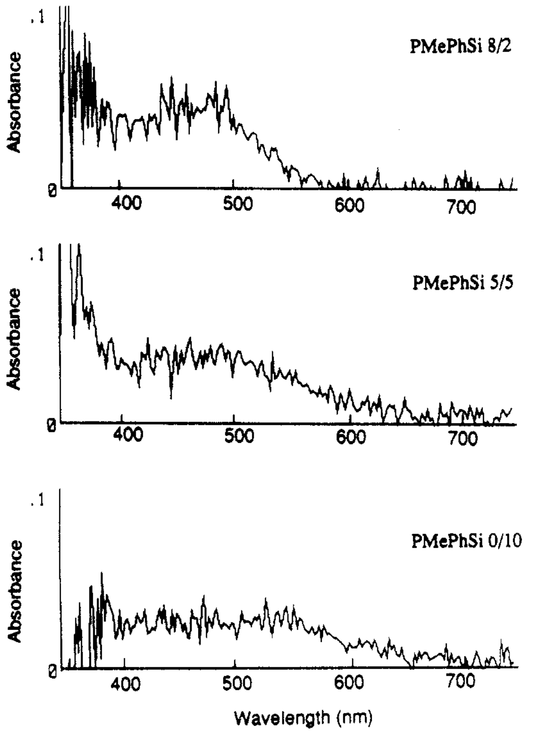

Figure 8. Difference transient spectra obtained by flash photolysis for a 1 mM THF solution of polysilanes. Delay time: 50 μs. These spectra were obtained by subtracting the transient absorption using UVD-33S and UV-33 filters from that using a UVD-33S filter.

broad absorption band tailing to 400 nm as shown in Figure 4. Nagai et al. have reported the synthesis and absorption spectra of peralkyl- and persilylcyclotrisilanes and peralkyl- and persilylcyclotetrasilanes.[22,23] Such cyclic silanes show broad absorption spectra similar to those of network polysilanes. The persilyl compounds show a longer absorption edge than peralkyl compounds because of the increase of σ-conjugation. Persilylcyclostrisilane shows a spectrum quite similar to that of network polysilanes. Persilycyclotrisilane has an absorption edge at 400 nm and an absorption shoulder at 320 nm. Such three- and four-membered Si-rings must be included in the network structures of poly(alkylsilyne) and poly(arylsilyne). In Table I, the ratio of methoxy groups to Si units decreased with increasing the trichlorophenylsilane unit in the monomer feed composition. For example, the –OMe/Si ratio is 0.14/0.86 (mol ratio) for poly(phenylsilyne) (PMePhSi 0/10) while that for PMePhSi 5/5 is 0.33/0.67. This result also suggests the existence of a network structure for poly(phenylsilyne). If trichlorophenylsilane reacts at two chlorine groups and one unreacted chlorine group remains, a linear structure must be formed regardless of the monomer feed composition, and the methoxy/Si ratio is nearly unity.

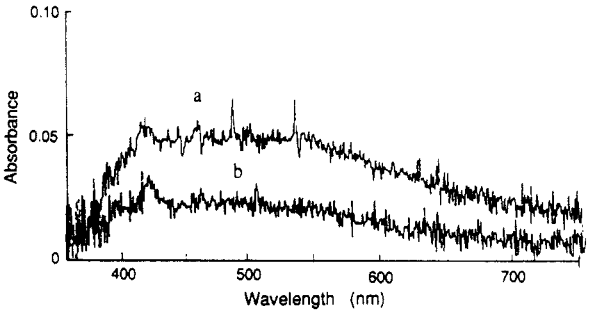

Figure 9. Time-resolved absorption spectra obtained by flash photolysis for a 1 mM cyclohexane solution of poly(phenylsilyne) (PMePhSi 0/10): (a) transient absorption spectra at 100 μs after flash photolysis; (b) transient absorption spectra at 100 μs after flash photolysis with 2×10^{-3} M of triethylsilane as a silylene quencher.

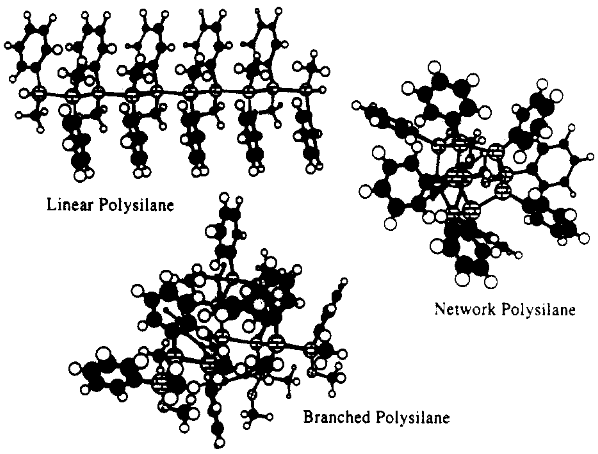

Figure 10. Postulated structures of linear, branched, and network polysilanes.

The molecular weight of network poly(arylsilyne) shown in Table I is quite lower than that of network poly(alkylsilyne) that is higher than 10 000. The molecular weight of poly(methylphenylsilylene-*co*-phenylsilyne) decreases with increasing trichlorophenylsilane composition in the monomer feed. The reactivity of the chlorine group may decrease with the formation of a cyclic Si-ring and the bulkiness of the Ph group. In addition, the molecular weight of copolymers produced by incorporating trichlorophenylsilane may be reduced by backbiting reactions of the growing anionic chain. Illustrations of linear, branched, and network polysilanes are depicted in Figure 10. For the branched and network polysilanes, certain Si-skeletons of 10 Si units were postulated, and the molecular models were depicted after optimization of the structure. The molecular model for network poly(phenylsilyne) gives the appearance of a quite bulky Si-skeleton. The core formed by a Si-network frame is surrounded by bulky phenyl groups. It is reasonably expected that the σ-conjugation of network poly(phenylsilyne) is enhanced by the Si-skeleton in the core. Absorption spectra in Figures 1 and 2 suggest an increase in the σ-conjugation with increasing branching structure.

The emission spectra also changed drastically by branching as shown in Figures 3 and 4. Poly(methylphenylsilylene) (PMePhSi 10/0) shows a sharp emission peak at 355 nm that is assigned to the emission from a linear Si–Si skeleton. Branched polysilanes show a broad emission peak at 450 nm. Such a broad emission is assigned to that from the branching or cyclic structure of the silicon backbone.[15,16] The spectral change from the 350-nm band of linear polysilane to the 450-nm band of network polysilane is not continuous. The branching or cyclic structure must be considered as an excitation energy trapping site. The energy migration in polysilane is well-known.[24] The broad emission must originate from the trapping site following an extreme energy migration. In Figures 3 and 4, the emission maximum of the broad band shifts gradually to longer wavelength with increasing branched structure. Such a change was also reported for poly(*n*-hexylsilyne).[16] This may be due to the lowering of the energy level of the trapping site. The broad emission band of network poly(phenylsilyne) is not simple. The emission shoulder at 500 nm was observed for PMePhSi 0/10 in Figure 4.

There is somewhat a difference on the change of the emission spectrum by branching between poly(*n*-hexylmethylsilylene-*co*-*n*-hexylsilyne) and poly(methylphenylsilylene-*co*-phenylsilyne). In the case of the former, the incorporation of only a 5% branching structure completely changes the emission spectrum into a broad one. On the other hand, the poly(methylphenylsilylene-*co*-phenylsilyne) needs about a 40% branching structure to change into a braod band. This must result from the difference of molecular weight and the extension of the silicon network structure. Poly(*n*-hexylsilyne) has the higher molecular weight and the growth of silicon network structure compared with poly(phenylsilyne).

Transient Absorption Spectra. In our previous paper, we reported the photodegradation of poly(cyclohexylmethylsilylene) and poly(phenylmethylsilylene) by flash photolysis and quenching experiments.[18] The time-resolved absorption spectra of poly(cyclohexylmethylsilyne) showed a sharp transient absorption peak at 370 nm, and the transient absorption bands were assigned to a silyl radical by quenching experiments using methylene chloride as a radical quencher. The wavelength dependence of the intermediate during photodegradation was observed for poly(phenylmethylsilylene).[18] The transient absorption spectrum obtained by the σ–σ^* band excitation showed broad transient absorption near 400 nm. This was assigned to the silyl radical by quenching experiments using methylene chloride as a quencher. When poly(phenylmethylsilylene) was excited at shorter wavelength (π–π^* band region), an additional transient absorption appeared near 480 nm, which was assigned to be silylene using triethylsilane as a silylene trap agent. Similar excitation wavelength dependence was observed for poly(methylphenylsilylene-*co*-phenylsilyne) as shown in Figures 5–7. By the σ–σ^* excitation, the absorption peak at 380 nm appears in Figure 5a. This absorption band can be assigned to the silyl radical on the basis of the results on the flash photolysis of poly(methylphenylsilylene).[18] The absorption band at longer wavelength increased by the excitation at a shorter wavelength band (π–π^* band).

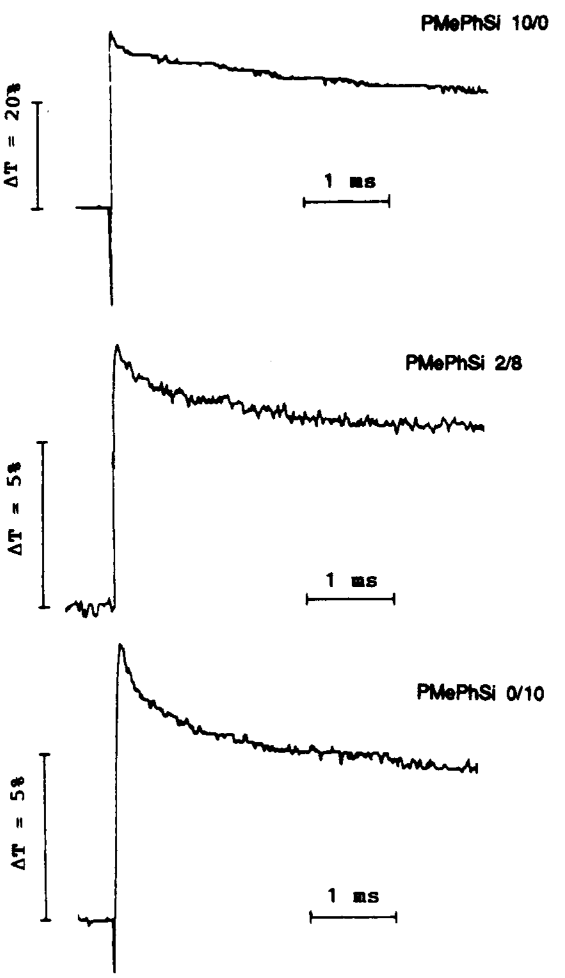

Figure 11. Decay curves of transient absorption obtained by flash photolysis. Monitor wavelength: 400 nm.

The difference absorption spectrum for poly(phenylsilyne) exhibits the new absorption band at 550 nm (Figure 8). This absorption is different from those of the silyl radical (380 nm) and the low molecular weight silylene (480 nm). One possibility for the assignment of this species is a silylsilylene that is attached the Si–Si chain. Recently, McKinley et al. reported the reaction path for the formation of disilylsilylene by UV irradiation of poly(di-*n*-alkylsilylene)s, which are produced by reductive elimination.[25] Poly(phenylsilyne) has a high possibility of the formation of silylsilylene because it has a Si atom that connects with three Si atoms in the silicon network. The absorption band at 550 nm is decreased by the addition of the silylene quencher triethylsilane as shown in Figure 9. The absorption band at 550 nm is reasonably assigned to silylsilylene formed in the silicon network structure of poly(phenylsilyne).

Figure 10 illustrated the image that the bulkiness of branched and network polysilanes influences the decay of intermediates during the photodegradation. Decay curves monitored at 400 nm in vacuo are compared for the linear (PMePhSi 10/0), branched (PMePhSi 2/8), and network (PMePhSi 0/10) polysilanes (Figure 11). This absorption at 400 nm is assigned to the silyl radical. The slope of the decay curves increases with branching. The back-reaction, that is, radical coupling, must be enhanced by the rigid Si-skeleton of the silicon network structure because of the low diffusibility of the radical site. It is like a radical pair in the silicon skeleton. The decay curves were analyzed assuming second-order reaction of the radical coupling reaction. The apparent second-order constants determined by the decay analysis are plotted against trichlo-

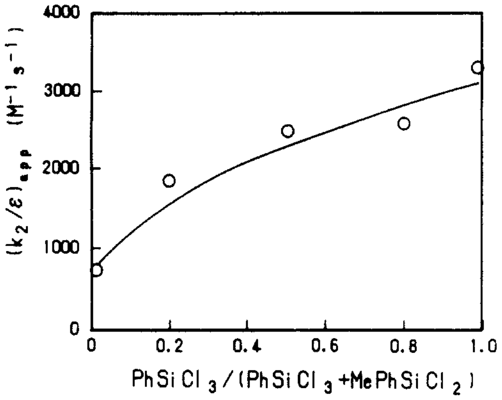

Figure 12. Apparent second-order rate constants of a silyl radical coupling reaction.

rophenylsilane composition in Figure 12. The apparent decay constant increased with increasing trichlorophenylsilane composition. Bianconi et al. reported the light resistance of silicon network polymer.[12] As one reason for the light resistance, rapid back-reaction of the transient intermediates due to the bulkiness of network polysilane can be considered.

Conclusions

The branching structure of the Si-skeleton of polysilane could be controlled by the copolymerization of dichloromethylphenylsilane and trichlorophenylsilane. The sharp σ–σ^* absorption band of linear poly(methylphenylsilylene) changed into a broad absorption band of a silicon network structure with branching. Branched and network polysilanes showed broad emission spectra that are characteristic of a silicon network structure. The Si-skeleton of branched and network polysilanes influenced the transient absorption spectra obtained by flash photolysis. The transient absorption band for silylene shifted to longer wavelength with branching. The absorption peak at 550 nm was observed for network poly(phenylsilyne). The formation of silylsilylene in the silicon network structure was suggested.

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