Radical Ions of Polysilanes with Alkyl and Aryl Side Groups

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ABSTRACT: Absorption spectra of radical ions of polysilanes with alkyl and aryl pendant groups were measured in rigid matrices at 77 K and in solution at room temperature by using γ-irradiation and pulse radiolysis methods. The radical cations and anions of the polysilanes with alkyl pendant groups showed strong and sharp absorption bands in the ultraviolet region ($\sim$360 nm). The absorption maxima shifted to longer wavelengths with increasing bulkiness of the pendant groups. The radical anions of polysilanes with phenyl pendant groups, poly(methylphenylsilane), and copolymers with alkyl-substituted polysilanes had the spectra slightly red-shifted relative to those with sterically unencumbered alkyl substituents. The structural dependence was less significant for the radical cations. The spectra of radical anions of polysilanes with naphthyl groups showed broad bands in the ultraviolet region and a sharp band at 800 nm, which are ascribable to the monomeric radical anion of the pendant naphthyl groups. The radical cations of naphthyl-substituted polysilanes had a band in the infrared region in addition to the visible bands, which indicate the existence of charge resonance interaction between two naphthyl side groups. Pulse radiolysis experiments in solution revealed that the lifetimes of the radical anions, 5–30 μs, are shorter than those of radical cations, 30–100 μs. The radical cations of polysilanes with aryl side groups have longer lifetimes than those of polysilanes with alkyl side groups.

Introduction

Substituted silane polymers have interesting properties.[1] They are readily decomposed by ultraviolet irradiation and have a hole conductive property.[2] The former is applicable for photoresists[3] and the latter for hole transport layers of organic photoconductors.[4] These properties originate from the characteristic electronic structure. The electronic spectra of polysilanes have strong bands in the UV region due to delocalized Si–Si σ bonds. Their ionization potentials are approximately 3 eV lower than those of alkanes of comparable chain length.[5] Because of these electron delocalization characteristics, a number of linear and cyclic polysilanes undergo readily one-electron oxidation and reduction to form radical cations and anions.[6,7]

In our previous papers,[8] the absorption spectra of radical ions of polysilastyrene and cyclic polysilanes have been measured in rigid matrices at 77 K as well as in solution at room temperature by using γ-irradiation and pulse radiolysis methods. The absorption band of the radical anion of polysilastyrene was observed at 365 nm, while the radical cation had two bands at 358 and 2000 nm at 77 K. The latter band was ascribed to the charge resonance interaction between pendant phenyl groups. Radical ions of cyclic polysilanes, $(Me_2Si)_n$, where $n = 5$–7, also had the absorption bands in the visible and near-infrared region. A pulse radiolysis study of the radical ions of polysilanes has also been carried out by Tagawa et al.[9]

In the present paper, we have extended the study to the polysilanes with various alkyl and aryl side groups and explored the relation between the polymer structures and the absorption spectra of the radical ions.

Experimental Section

Polysilanes were synthesized according to the conventional method.[10] The polymers and copolymers synthesized and the molecular weights are summarized in Tables I and II. The molecular weights of the polysilanes were determined by gel permeation chromatography based on polystyrene standards. The compositions of these copolymers were determined by ^{1}H NMR signal intensities and are also shown in Table II.

2-Methyltetrahydrofuran (MTHF) and n-butyl chloride (n-BuCl) were purified by repeated distillation. The solution in a Suprasil cell (optical path length, 2 mm) was degassed, and the frozen solution was γ-irradiated at a dose rate of 1.2×10^{19} eV/g·h at 77 K. The optical absorption changes induced by irradiation and by subsequent warming were measured with a Shimadzu UV-3100 spectrophotometer.

Details of the present pulse radiolysis system were reported previously.[11] The energy of the electron pulse was 10 MeV, and the duration was 0.5 μs.

Results and Discussion

Absorption Spectra of Radical Ions of Alkyl-Substituted Polysilanes. It is well established that a solute radical anion is produced in irradiated 2-methyltetrahydrofuran (MTHF) by the reaction of an electron with a solute molecule.[12] Figure 1 shows the absorption spectra of MTHF solutions containing 1×10^{-2} M poly(methyl-n-propylsilane) and poly(methyl-n-hexylsilane) at 77 K irradiated with a dose of 3×10^{19} eV/g. These spectra with absorption maxima at 363 and 365 nm are ascribable to radical anions of poly(methyl-n-propylsilane) and poly(methyl-n-hexylsilane), respectively. By addition of an electron scavenger, n-BuCl, these bands disappeared. This result confirms that these bands are due to the radical anions.

These radical anions were unstable and disappeared at room temperature. It needs a pulse radiolysis technique to detect them at room temperature. Figure 2 shows the transient absorption spectra of 1×10^{-2} M poly(methyl-n-propylsilane), poly(methyl-n-hexylsilane), and poly(di-n-hexylsilane) in MTHF solutions, observed immediately after the pulse at room temperature. From the similarity with the spectra observed at 77 K, these transient absorption spectra at room temperature are assigned to the spectra of radical anions of the polysilanes. The

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Table I
Absorption Bands of Radical Ions for Polysilanes, $-(R_1R_2Si)_n(R'_1R'_2Si)_m-$

					λ_{max}, nm			
					anion		cation	
R_1	R_2	R'_1	R'_2	$M_w \times 10^{-3}$ [a]	77 K	rt	77 K	rt
Me	*n*-Pr			85, 13	363	360	355	350
Me	*n*-Hex			65, 13	365	365	361	355
n-Hex	*n*-Hex			150	*b*	370	374	360
Me	Ph			220	*b*	370[c]	*b*	*b*
Me	Ph	Me	Me	67[d]	365	365	358, 2000	360
Me	Ph	Me	*n*-Hex	260, 13[e]	368	370	358, 2000	360
Me	1-Naph	Me	Me	16[f]	480, 800	390, 480	480, 1450	390, 480
Me	2-Naph	Me	Me	17[g]	470, 800	420, 470	470, 1450	420, 470

[a] Molecular weights were determined by GPC analysis and are relative to polystyrene calibration standards. [b] Not measured. [c] Reference 9a. [d] $(MePhSi)_{1.0}(Me_2Si)_{1.0}$. [e] $(MePhSi)_{1.0}\{Me(n\text{-}Hex)Si\}_{1.0}$. [f] $\{Me(1\text{-}Naph)Si\}_{1.0}(Me_2Si)_{2.6}$. [g] $\{Me(2\text{-}Naph)Si\}_{1.0}(Me_2Si)_{2.6}$.

Table II
Absorption Bands of Radical Cations of Copolymers in the Infrared Region

				λ_{max} at 77 K, nm	
polymer	composition	m[a]	M_w	charge resonance bands	charge resonance bands after annealing
1-PSN	$\{Me(1\text{-}Naph)Si\}_{1.0}(Me_2Si)_{2.6}$	0.4	16 000	1450	1300
2-PSN$_1$	$\{Me(2\text{-}Naph)Si\}_{1.0}(Me_2Si)_{2.6}$	0.4	17 000	1450	1300
2-PSN$_2$	$\{Me(2\text{-}Naph)Si\}_{1.0}(Me_2Si)_{1.0}$	1.0	17 000	1700	1400
2-PSN$_3$	$\{Me(2\text{-}Naph)Si\}_{1.0}(Me_2Si)_{0.5}$	2.0	17 000	2000	1700

[a] *m* is the Me(1-Naph)Si or Me(2-Naph)Si to Me_2Si ratio for copolymers.

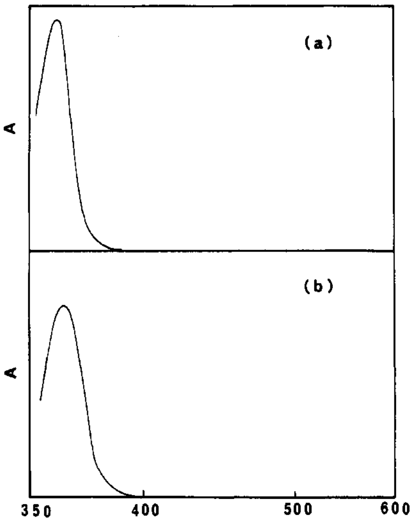

Figure 1. Absorption spectra of MTHF solutions containing 1×10^{-2} M alkyl-substituted polysilanes irradiated with a dose of 3×10^{19} eV/g at 77 K: (a) poly(methyl-*n*-propylsilane); (b) poly(methyl-*n*-hexylsilane).

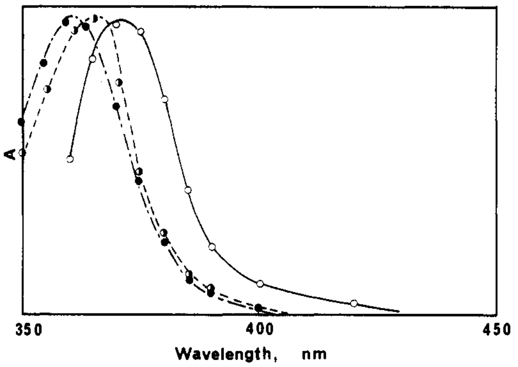

Figure 2. Transient absorption spectra of MTHF solutions containing 1×10^{-2} M (●) poly(methyl-*n*-propylsilane), (◑) poly(methyl-*n*-hexylsilane), and (○) poly(di-*n*-hexylsilane) at room temperature immediately after the pulse.

absorption maxima of poly(methyl-*n*-propylsilane), poly(methyl-*n*-hexylsilane), and poly(di-*n*-hexylsilane) radical anions are observed at 360, 365, and 370 nm, respectively. This indicates that absorption maxima of the radical anions shift to longer wavelengths with an increase in the size of the alkyl side chains. The size dependence coincides with the behavior of the absorption spectra of neutral alkyl-substituted polysilanes reported by Harrah et al.[13] They suggested that the shift comes from the steric hindrance of the substituents, which causes straining of the Si–Si backbone bonds and/or a backbone conformational change. A similar discussion is applicable to the radical anions of polysilanes having alkyl side groups. The steric effect of the substituents still remains in the radical-anion states.

A solute radical cation is produced in irradiated *n*-butyl chloride (*n*-BuCl) by the reaction of a positive hole with a solute molecule.[12] Absorption spectra of 2×10^{-2} M poly(methyl-*n*-propylsilane), poly(methyl-*n*-hexylsilane), and poly(di-*n*-hexylsilane) in BuCl matrices irradiated with a dose of 3×10^{19} eV/g at 77 K are shown by the solid curves of Figure 3. These absorption bands at 355, 361, and 374 nm are ascribable to the radical cations of poly(methyl-*n*-propylsilane), poly(methyl-*n*-hexylsilane), and poly(di-*n*-hexylsilane), respectively. These absorption bands disappeared by the addition of MTHF, which acts as a positive hole scavenger. This result confirms our assignment that these bands are due to the radical cations.

It is reported that thermal annealing causes the radical cation to change the spectrum owing to the relaxation to the stable conformation.[14] The broken curves in Figure 3 are the absorption spectra after thermal annealing at the temperature slightly higher than 77 K. The thermal annealing resolved the vibrational structures by conformational relaxation about silicon–silicon backbone bonds. The radical-cation spectra have clear vibrational structures in contrast to the spectra of neutral and radical-anion polymers.

The radical cations are also detected in *n*-BuCl solution at room temperature by a pulse radiolysis method. The absorption maxima of the radical cations of poly(methyl-*n*-propylsilane), poly(methyl-*n*-hexylsilane), and poly(di-*n*-hexylsilane) are observed at 350, 355, and 360 nm, respectively. The spectral shift with an increase in the size of the alkyl side groups is analogous to the behavior

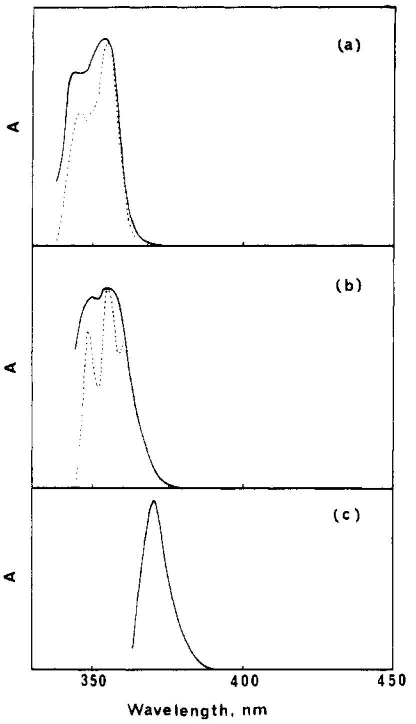

Figure 3. Absorption spectra of *n*-BuCl solutions containing 2 × 10^{-2} M (a) poly(methyl-*n*-propylsilane), (b) poly(methyl-*n*-hexylsilane), and (c) poly(di-*n*-hexylsilane) irradiated with a dose of 3 × 10^{19} eV/g at 77 K: (—) immediately after irradiation; (- - -) after annealing.

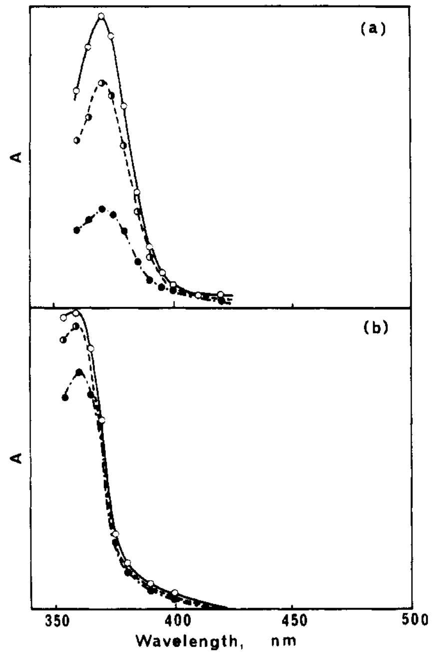

Figure 4. Transient absorption spectra of a MTHF solution (a) and BuCl solution (b) containing 2 × 10^{-2} M poly(methylphenylsilane-*co*-methyl-*n*-hexylsilane) at room temperature immediately (○) and 10 (◑) and 50 μs (●) after the pulse.

of the radical anions. The absorption bands of the radical ions reflect the size of the pendant substituents, similar to the spectra of neutral polysilanes. It is worthwhile to note that the absorption bands of radical cations at room temperature showed blue shifts in comparison with the bands at 77 K.

Absorption Spectra of Radical Ions of Phenyl-Substituted Polysilanes. Figure 4a shows the transient absorption spectra of a MTHF solution of poly(methylphenylsilane-*co*-methyl-*n*-hexylsilane) irradiated with an electron pulse at room temperature. The absorption band at 370 nm is ascribable to the radical anion of the polysilane on the basis of the spectral data in the γ-irradiated rigid matrix at 77 K. Figure 4b exhibits the transient absorption spectra of a *n*-BuCl solution containing 2 × 10^{-2} M poly(methylphenylsilane-*co*-methyl-*n*-hexylsilane), observed immediately and 10 and 50 μs after the pulse. The absorption band at 360 nm is assigned to the radical cation of poly(methylphenylsilane-*co*-methyl-*n*-hexylsilane) on the basis of the spectral data in the γ-irradiated rigid matrix at 77 K. It is noted that the absorption maximum of the radical cation showed a blue shift compared with that of the radical anion. The decay rate of the radical cation was slower than that of the radical anion.

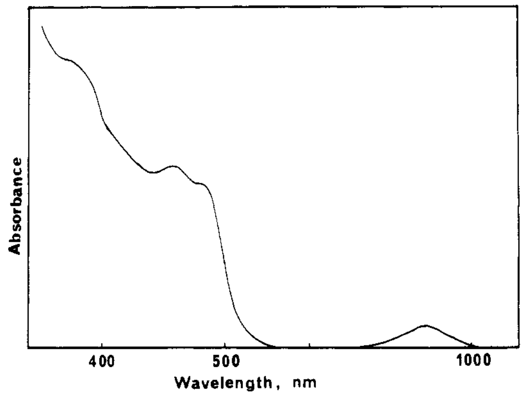

Figure 5. Absorption spectrum of a MTHF solution containing 4 × 10^{-2} M poly(methyl-1-naphthylsilane-*co*-dimethylsilane) irradiated with a dose of 3 × 10^{19} eV/g at 77 K.

Table I summarized absorption spectral data of the radical anions in a MTHF solution and the radical cations in a *n*-BuCl solution studied for several alkyl- and aryl-substituted polysilanes at 77 K and at room temperature. The radical anions of polysilanes having phenyl chromophores, poly(methylphenylsilane), and poly(methylphenylsilane-*co*-methyl-*n*-hexylsilane) show the absorption maxima around 370 nm, which are slightly red-shifted relative to the maxima of polysilanes with sterically unencumbered alkyl substituents. The absorption bands of radical cations of poly(methylphenylsilane-*co*-methyl-*n*-hexylsilane) and poly(methylphenylsilane-*co*-dimethylsilane) lie around 360 nm, which are 5–10 nm shorter than the maxima of the radical anions.

Although the absorption maxima of the radical ions, especially the radical cations of alkyl-substituted polysilanes, showed red shifts upon cooling to 77 K, the maxima of the aryl-substituted polysilanes remained constant. This behavior is similar to the observation of the absorption spectra of the corresponding neutral polysilanes.[13]

The radical cations of polysilanes having phenyl side groups exhibited additional bands in the infrared region beside the ultraviolet bands. The infrared bands are due to a charge resonance interaction between two phenyl chromophores.[8] The appearance of the bands clearly indicates that the radical-ion state delocalizes to the pendant phenyl groups and two phenyl groups interact with each other in the radical-cation state of the polysilanes. The interaction is similar to that observed in the case of the vinyl polymers having aromatic side groups, such as polystyrene as previously reported.[8,15]

Absorption Spectra of Radical Ions of Naphthyl-Substituted Polysilanes. Figure 5 shows the absorption spectrum of a MTHF solution containing 4 × 10^{-2} M poly(methyl-1-naphthylsilane-*co*-dimethylsilane) at 77 K irradiated with a dose of 3 × 10^{19} eV/g. The spectrum is ascribable to the radical anion of poly(methyl-1-naphthylsilane-*co*-dimethylsilane).[12] This was confirmed by

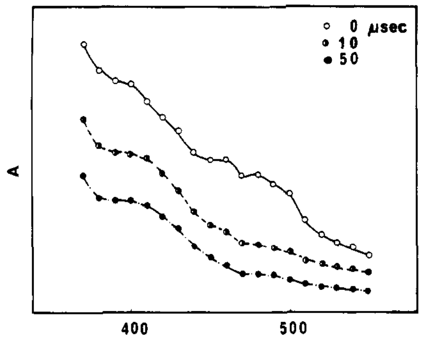

Figure 6. Transient absorption spectra of a MTHF solution containing 2×10^{-2} M poly(methyl-1-naphthylsilane-*co*-dimethylsilane) at room temperature immediately (○) and 10 (◑) and 50 μs (●) after the pulse.

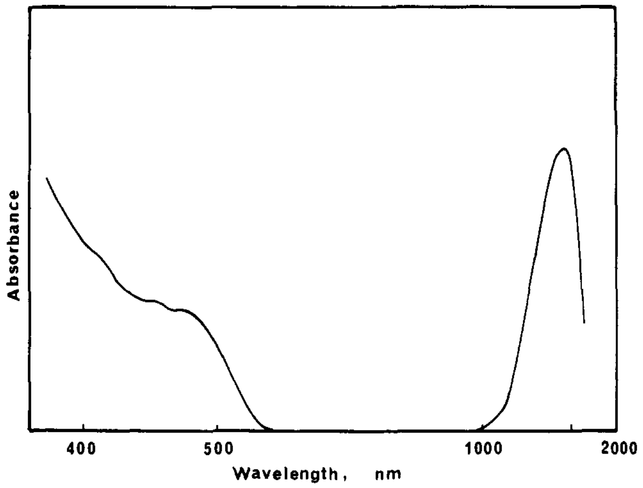

Figure 7. Absorption spectrum of a *n*-BuCl solution containing 8×10^{-2} M poly(methyl-1-naphthylsilane-*co*-dimethylsilane), $\{\text{Me(1-Naph)Si}\}_{1.0}(\text{Me}_2\text{Si})_{2.6}$ ($m = 0.4$), irradiated with a dose of 3×10^{19} eV/g at 77 K.

the addition of an electron scavenger. The radical anion has absorption peaks at 390, 460, 480, and around 800 nm. These bands disappeared gradually when the sample was photoirradiated with light longer than 450 nm. The spectrum also disappeared by thermal annealing.

The absorption band at around 800 nm is similar to the monomeric radical anion of 2-ethylnaphthalene.[15] The appearance of the band in the polymer spectrum indicates that each electron is localized in a naphthyl pendant group in the polymer at 77 K. Delocalization along the polymer backbone is negligible in the radical-anion state of the naphthyl-substituted polysilanes.

Figure 6 shows the transient absorption spectra of a MTHF solution containing 2×10^{-2} M poly(methyl-1-naphthylsilane-*co*-dimethylsilane), observed immediately after the pulse and at 10 and 50 μs after the pulse at room temperature. The absorption spectra are ascribable to the radical anion of poly(methyl-1-naphthylsilane-*co*-dimethylsilane). By the addition of an electron scavenger, *n*-BuCl, these bands at 390, 460, and 480 nm disappeared. The radical anion decayed in 20 μs at room temperature.

Figure 7 shows the absorption spectrum of *n*-BuCl containing 8×10^{-2} M poly(methyl-1-naphthylsilane-*co*-dimethylsilane) at 77 K irradiated with a dose of 3×10^{19} eV/g. This spectrum is assigned to the radical cation of poly(methyl-1-naphthylsilane-*co*-dimethylsilane).[12] The radical cation has the absorption bands at around 480 and 1450 nm. The monomeric radical cation of ethylnaphthalene was reported to have the band at around 690 nm.[15-17] The monomer band is not observed in the radical-cation spectrum. The absence of the monomer band indicates that the radical-cation state is not localized to each naphthyl pendant group. As observed for the phenyl-substituted polysilane systems, the radical cation also exhibited an additional strong band in the infrared region, around 1450 nm. The band is assigned to the charge resonance band between more than two naphthyl chromophores. The appearance of the band indicates the localization of the radical-cation state in the two naphthyl side groups.

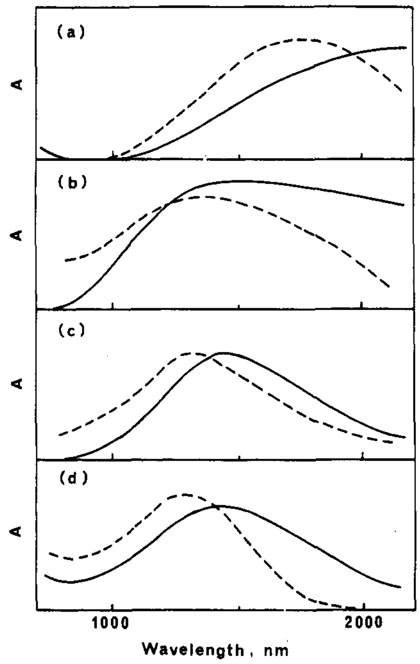

Figure 8. Absorption spectra of BuCl solutions containing 5×10^{-2} M (a) $2\text{-PSN}_3\{\text{Me(2-Naph)Si}\}_1(\text{Me}_2\text{Si})_{0.5}$ ($m = 2.0$), (b) $2\text{-PSN}_2\{\text{Me(2-Naph)Si}\}_1(\text{Me}_2\text{Si})_{1.0}$ ($m = 1.0$), (c) $2\text{-PSN}_1\{\text{Me(2-Naph)Si}\}_1(\text{Me}_2\text{Si})_{2.6}$ ($m = 0.4$), and (d) $1\text{-PSN}\{\text{Me(1-Naph)Si}\}_1(\text{Me}_2\text{Si})_{2.6}$ ($m = 0.4$) irradiated with a dose of 3×10^{19} eV/g: (—) immediately after irradiation; (- - -) after thermal annealing at 100 K.

The charge resonance band is known to change the position depending on the conformation of the pendant naphthyl groups.[14,15] We carefully examined the spectral changes induced by thermal annealing. A dramatic spectral shift was observed. The band shifted from 1450 to 1300 nm as shown in Figure 8d. The shift indicates the geometrical reorientation of the pendant naphthyl groups to the more stable conformation by thermal annealing.

The transient absorption spectrum of a *n*-BuCl solution containing 2×10^{-2} M poly(methyl-1-naphthylsilane-*co*-dimethylsilane) was also measured at room temperature immediately after the pulse. The transient spectrum in the solution was identical to the spectrum observed in rigid matrices at 77 K.

As observed for poly(methyl-1-naphthylsilane-*co*-dimethylsilane), *n*-BuCl solutions of poly(methyl-2-naphthylsilane-*co*-dimethylsilane) with different naphthyl group contents, 2-PSN$_1$ (m = Me(2-naphthyl)Si/Me$_2$Si = 0.4), 2-PSN$_2$ (m = Me(2-naphthyl)Si/Me$_2$Si = 1.0), and 2-PSN$_3$ (m = Me(2-naphthyl)Si/Me$_2$Si = 2.0) also exhibited absorption bands ascribable to the radical cations in the infrared region in addition to the ultraviolet bands. Absorption spectra in the infrared region immediately after irradiation of 2-PSN$_1$, 2-PSN$_2$, and 2-PSN$_3$ in *n*-BuCl matrices at 77 K are shown by solid curves in Figure 8. The peak positions shift to lower wavelengths with an increase in the naphthyl content. Thermal annealing causes the spectra to shift to shorter wavelengths as shown by the broken curves in Figure 8.

Table III
Half-Lives of Radical Ions for Polysilane Homo- and Copolymers, $-(R_1R_2Si)_n(R'_1R'_2Si)_m-$, at Room Temperature

substituents				half-life, μs	
R_1	R_2	R'_1	R'_2	anion	cation
Me	*n*-Pr			20	30
Me	*n*-Hex			5	30
n-Hex	*n*-Hex			30	*a*
Me	Ph	Me	Me	30	85
Me	Ph	Me	*n*-Hex	30	100
Me	1-Naph	Me	Me	20	40
Me	2-Naph	Me	Me	15	90

[a] Not measured.

Table II summarizes the absorption bands of the radical cations of the copolymers with different naphthyl group contents. The peak position of the charge resonance band of 2-PSN_3 at around 2000 nm is similar to that observed for poly(2-vinylnaphthalene).[15] Upon thermal annealing, the infrared band shows a blue shift to 1700 nm. In 2-PSN_1, the absorption maximum is observed at 1450 nm and shifts to 1300 nm by thermal annealing. The peak position of the charge resonance band and the blue shift owing to conformational relaxation are similar to those of dinaphthylpropane.[15]

Decay Behavior of the Radical Ions. Half-lives of the radical anions and cations of polysilanes having alkyl and aryl side groups are summarized in Table III. The lifetimes of the radical anions lie in the range of 5–30 μs. The lifetimes are shorter than those of the radical cations. The radical cations of polysilanes with aryl side groups have longer lifetimes than those of polysilanes with alkyl side groups.

Spectral Interpretation. The nature of the transitions in polysilanes has been assigned as follows:[13,18] (1) The first transition in alkyl-substituted polysilanes arises from a delocalized σ–σ^* transition. (2) The long wavelength band of the mononuclear aryl-substituted polysilanes, such as a polysilane having a phenyl side group, is composed of two transitions, σ–σ^* and π–π^*. (3) In the polynuclear aryl substituents, such as polysilanes having naphthyl side groups, the transition is best characterized as a localized π–π^* naphthalene-like excitation.

The absorption spectra of the radical anions and cations of polysilanes having alkyl side groups showed strong and sharp absorption bands in the ultraviolet region and the peak positions shifted to longer wavelengths with an increase in the bulkiness of the side groups. This indicates that the electrons in the radical-anion state and holes in the radical-cation state are delocalized over the silicon main chain.

The radical anions of polysilanes with phenyl pendant groups have spectra analogous to those of the radical anions of alkyl-substituted polysilanes. The absorption spectra of the radical cations of phenyl-substituted polysilane in the ultraviolet region are different from that of the radical cation of polystyrene[15] and are analogous to those of the radical cations of alkyl-substituted polysilanes. The results indicate that the electronic states of the radical ions of the phenyl-substituted polysilanes are similar to those of the alkyl-substituted polysilanes. Both the radical-anion and -cation states are delocalized along the main chain. The appearance of the charge resonance band for the spectrum of the radical cation of phenyl-substituted polysilane suggests that delocalization of the radical-cation state from the main chain to the pendant phenyl groups is not ignored.

The absorption spectra of the radical anions of polysilanes with naphthyl substituents showed broad bands in the ultraviolet region and a sharp band at 800 nm. The added electron is considered to be localized on the pendant naphthyl π-rings, because the spectral shape of the absorption at 800 nm is similar to that of the radical anion of monomeric ethylnaphthalene.[15]

The radical cations of naphthyl-substituted polysilanes had strong bands in the near-infrared region due to charge resonance interaction in addition to the bands shorter than 600 nm. The band due to the monomeric radical cation of the naphthyl group was not observed. These results suggest that the radical-cation state is localized in the two naphthyl side groups.

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Registry No. $Cl_2SiMePr$ (homopolymer), 88002-81-7; $Cl_2SiMePr$ (SRU), 88003-13-8; $Cl_2SiMe(n\text{-}Hex)$ (homopolymer), 88002-83-9; $Cl_2SiMe(n\text{-}Hex)$ (SRU), 88003-15-0; $Cl_2Si(n\text{-}Hex)_2$ (homopolymer), 97036-67-4; $Cl_2Si(n\text{-}Hex)_2$ (SRU), 94904-85-5; $Cl_2SiMePh$ (homopolymer), 31324-77-3; $Cl_2SiMePh$ (SRU), 76188-55-1; $(Cl_2SiPhMe)(Cl_2SiMe_2)$ (copolymer), 70158-17-7; $(Cl_2SiPhMe)(Cl_2SiMe(n\text{-}Hex))$ (copolymer), 106043-87-2; $(Cl_2SiMe(1\text{-}Naph))(Cl_2SiMe_2)$ (copolymer), 99560-01-7; $(Cl_2SiMe(2\text{-}Naph))(Cl_2SiMe_2)$ (copolymer), 115341-65-6.