

Electronic absorption spectra of radical ions of alkyl silicon network polymers

Setsuko Irie ^{a,*}, Yoshihiko Shono ^a, Masahiro Irie ^b, Masaaki Suzuki ^c, Takeshi Okutani ^c

^a *Research Institute for advanced Science and Technology, Osaka Prefecture University, Gakuencho 1-2, Sakai, Osaka, 593, Japan*

^b *Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka, 812, Japan*

^c *Hokkaido National Industrial Research Institute, Tsukisamu-higashi 2-17, Sapporo, Hokkaido, 062, Japan*

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Abstract

Absorption spectra of radical ions of silicon network polymers formed by γ -irradiation have been measured in rigid matrices at 77 K. Both the radical anion and cation showed very broad absorption bands in visible and near-infrared wavelength regions. The radical anion spectrum was sensitive to photoillumination and changed the band shape by selective photobleaching. Thermal annealing of the radical cation caused a blue shift of the absorption spectrum. The broad band shape and the selective band bleaching indicated the coexistence of various cyclic structures in the network polysilane radical ion spectra. © 1998 Elsevier Science S.A. All rights reserved.

1. Introduction

Silicon backbone polymers have attracted much attention because of their unusual photochemical and photophysical properties [1]. While the polymers are structurally analogous to saturated hydrocarbons, these polymers exhibit intense near-UV absorption bands due to transitions between σ -delocalized silicon–silicon bonding and antibonding orbitals.

The polysilanes have either linear or network structure depending on the number of substituents on the silicon atoms. When the silicon monomer unit contains only one alkyl or aryl substituent, the polymer constructs network structures [2–6]. The silicon network polymers have structural and electronic properties between those of linear silicon backbone polymers and amorphous silicon. The polymers have strong near-UV to visible absorption bands, moderate quantum yields of visible fluorescence and large radiative rates. Although the polymers are potentially applicable to

various optoelectronic devices [7], little is known about their electronic properties. In previous papers, we have studied electronic properties of radical ions of linear polysilanes [8,9] and cyclic polysilanes [10]. Here, we report on the electronic absorption spectra of radical ions of alkyl silicon network polymers.

2. Experimental

Silicon network polymers with *n*-hexyl, *n*-butyl, and *n*-propyl were synthesized according to the method developed by Furukawa et al. [4]. ¹³C solution NMR and solid state ²⁹Si-NMR spectra were measured on a JEOL spectrometer (JNM-GSX270). IR spectra were obtained by a Perkin Elmer 1760X spectrometer. Absorption spectra of radical ions were measured by rigid matrices method using γ -irradiation, as previously reported [8]. 2-Methyltetrahydrofuran (MTHF) and *n*-butylchloride (BuCl) were purified by repeated distillation. All samples were prepared using the freeze thaw cycle method. Electronic absorption and emission

* Corresponding author. Fax: +81 722 549935.

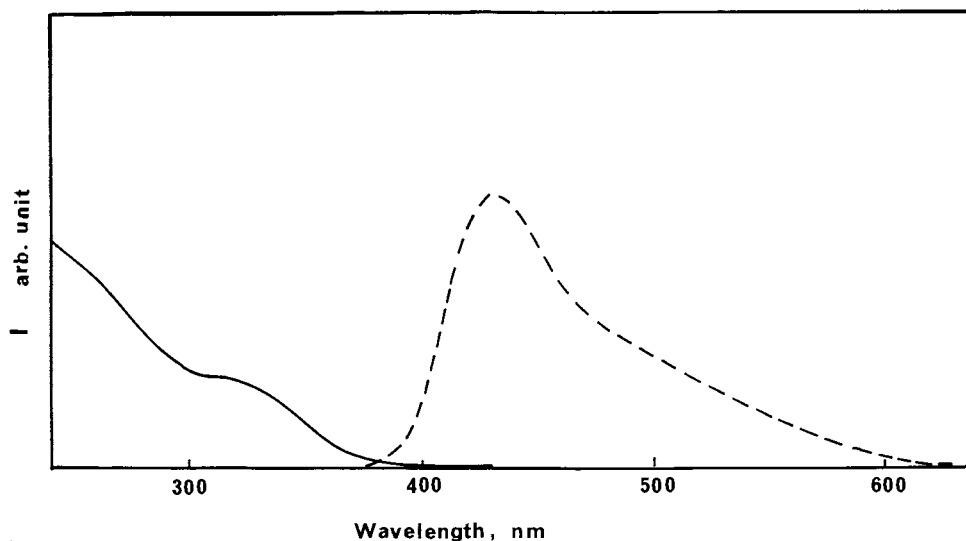


Fig. 1. Absorption (—) and emission (---) spectra of a *n*-hexyl silicon network polymer at room temperature.

spectra were measured with a Shimadzu absorption spectrometer (UV-3100) and a Hitachi fluorescence spectrometer (F-4010), respectively. ESR measurement was carried out at 77 K with a JEOL spectrometer (3BX).

3. Results and discussion

Wurtz coupling reactions of alkyltrichlorosilanes in the presence of sodium and crown ether yielded polysilane polymers. The polymers were analyzed with ^{13}C solution NMR, solid state ^{29}Si -NMR and IR spectroscopies. Both NMR and IR spectra agreed to those of network polysilanes reported by Bianconi et al. [3] and Furukawa et al. [4]. The molecular weight distributions measured by a gel permeation chromatography ($M_w = 80000$) were also similar to those reported as network polysilanes [4]. These results indicated that the synthesized polymers have a network structure and silicon atoms with three silyl substituents. As an example, absorption and emission spectra of a *n*-hexyl network polymer are shown in Fig. 1. The large Stokes shift indicates that the photoexcited energy migrates in the polymer network and is trapped in a stable emitting site as suggested by Weidman et al. [5].

The absorption spectra of radical anions of the polymers were measured in MTHF by γ -irradiation. It is well established that a solute radical anion is produced in irradiated MTHF by the reaction of an electron with a solute molecule [11]. The solid curve in Fig. 2 shows the absorption spectra of a MTHF solution containing 1×10^{-2} M of a *n*-hexyl silicon network polymer at 77 K irradiated with a dose of 3×10^{19} eV g^{-1} after photobleaching the trapped electrons. This spectrum is assigned to the radical anion of a *n*-hexyl silicon net-

work polymer. The absorption spectrum is very broad in visible and near infrared regions and has a peak at about 1400 nm. Watanabe et al. [12] reported a similar absorption spectrum in the 500–1500 nm region for the radical anion of a phenyl substituted silicon network polymer produced by pulse radiolysis. The broadness of the spectra is characteristic of the radical anions of network polysilanes.

In order to know the electronic transition characteristics of the radical anions, the sample was photoilluminated with visible light ($\lambda > 650$ nm and $\lambda > 450$ nm). Photoillumination electronically excites the radical anion species into higher excited states and induces bleaching of the absorption band by electron release from the radical anion. The broken curve in Fig. 2 shows the absorption spectrum of the radical anion of the *n*-hexyl silicon network polymer after photoillumination with $\lambda > 650$ nm light at 77 K, and the dotted curve is the spectrum after photoillumination with $\lambda > 450$ nm light. Photoillumination with $\lambda > 450$ nm light has a more pronounced effect on the bleaching than the illumination with $\lambda > 650$ nm light. The photobleaching behavior depends on the photoillumination wavelength.

To obtain more detailed information concerning the photobleaching behavior, the sample was irradiated with monochromatic light using interference glass filters ($\lambda = 700, 600, 520, 400$ nm). Although the absorption band was effectively photobleached by irradiation with 520 and 400 nm lights, 700 nm light scarcely photobleached the absorption spectrum even after prolonged irradiation. Fig. 3(A) shows the absorption spectra before photobleaching (a), after bleaching with 400 nm light (b) and after bleaching with 520 nm light (c). The difference spectra (a–b) and (b–c), are shown by dotted and broken lines in Fig. 3(B), respectively. The photobleaching was continued long enough (~ 30 min) for the spectrum to reach a stationary state. The 400

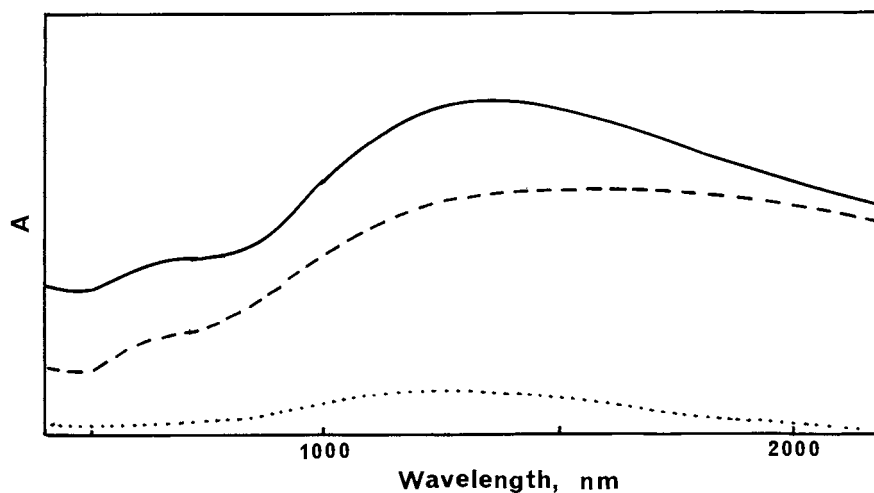


Fig. 2. Absorption spectra of a *n*-hexyl silicon network polymer in MTHF solution (1×10^{-2} M) irradiated with a dose of 3×10^{19} eV g^{-1} at 77 K (—) after photobleaching the trapped electron; (---) after photoillumination with $\lambda > 650$ nm light; (· · ·) after photoillumination with $\lambda > 450$ nm light.

nm light mainly bleached the infrared absorption band around 2000 nm, while the 520 nm light photobleached the band around 1200 nm. These results suggest that there exist more than two different species, which respond to special wavelength light.

The wavelength dependence of the photobleaching behavior indicates that photoinduced thermal annealing is not the main cause of the bleaching but electronic

excitation to higher excited states induces the spectral bleaching. The energy of 520 nm light is high enough to release an electron from the radical anion, while the energy of 700 nm light is below the ionization potential of the anion in MTHF at 77 K. The 400 nm light can release an electron from the radical anion having an electronic transition around 2000 nm, which has a longer σ -conjugation than the radical anion bleached with 520 nm light.

We examined the effect of the addition of BuCl into MTHF. BuCl is known to capture free electrons. By the addition of a small amount of BuCl (2 volume %), the far infrared band extending 2000 nm disappeared and only the near infrared band around 1200 nm remained. The spectrum around 1200 nm disappeared by irradiation with 520 nm light for 10 min. When the amount of the added BuCl was increased to 30 volume %, both 2000 and 1200 nm bands disappeared. This result confirms that these infrared absorption bands are due to the radical anions.

It is reported that silicon network polymers have several cyclic structures [3,5,6]. Since standard reductive condensation synthesis of linear poly(dialkylsilane) typically converts half or more of the monomers into cyclic oligomers, it is reasonable to assume similar cyclization reactions take place in the network polysilanes. The rather high solubility of network polysilanes is attributed to the cyclic structures, most likely consisting of five- and six-member rings [5,6]. In a previous paper [10], we have reported the absorption spectra of radical ions of cyclic polysilanes, $(\text{SiMe}_2)_5$, $(\text{SiMe}_2)_6$, and $(\text{SiMe}_2)_7$ in rigid matrices at 77 K by using γ -irradiation. The absorption maxima of radical anions showed a red shift from 670 to 900 nm and broadening of the spectral shape with increasing ring size from five- to seven-member rings. The radical anion spectrum of the

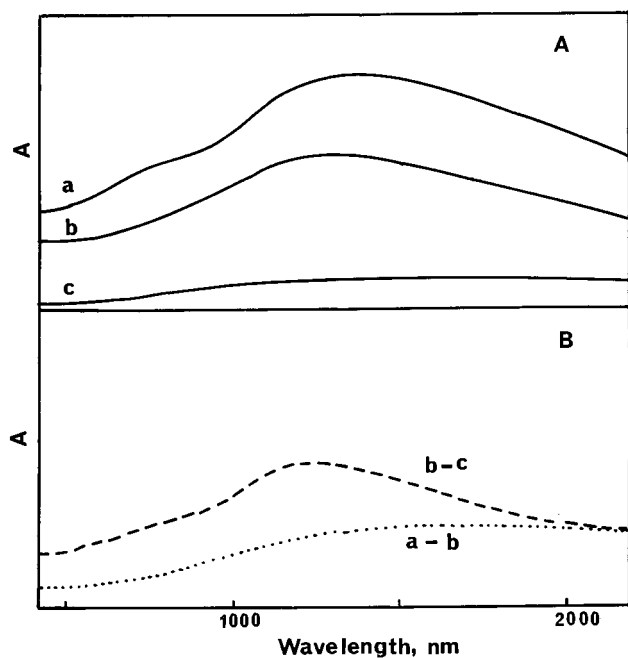


Fig. 3. (A) Absorption spectra of a *n*-hexyl silicon network polymer in MTHF solution (1×10^{-2} M) irradiated with a dose of 3×10^{19} eV g^{-1} at 77 K: (a) after photobleaching the trapped electron; (b) after photoillumination with 400 nm light; (c) after photoillumination with 520 nm light. (B) (---) The difference spectrum (a-b), and (· · ·) the difference spectrum (b-c).

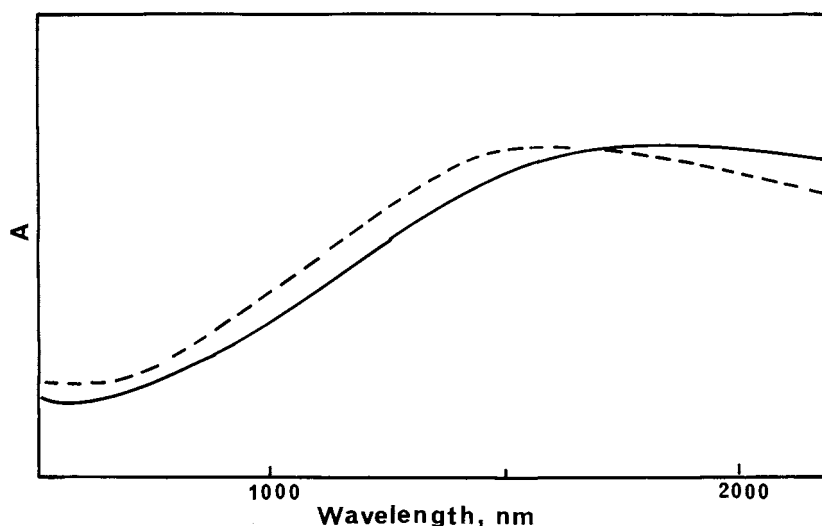


Fig. 4. Absorption spectra of a *n*-hexyl silicon network polymer in BuCl solution (5×10^{-2} M) irradiated with a dose of 3×10^{19} eV g^{-1} at 77 K: (—) immediately after irradiation; (---) after thermal annealing at 100 K.

n-hexyl silicon network polymer shown in Fig. 2 has a shoulder at around 650 nm. The absorption band is similar to that of cyclic polysilane (SiMe_2)₅, which lies around 670 nm [10]. The absorption maxima about 1200 nm are ascribable to larger cyclic polysilanes. These results indicate that the broad absorption spectrum is the superposition of several radical anion bands of various cyclic polysilanes. Radical anions of network polysilanes with *n*-butyl and *n*-propyl side groups gave similar absorption spectra.

The radical anion was also detected by ESR measurement. MTHF solutions containing 5×10^{-2} M of a *n*-hexyl silicon network polymer and oligomeric silanes, (SiMe_2)₅ and (SiMe_2)₆, were irradiated at 77 K with a dose at 3×10^{19} eV g^{-1} and measured with an ESR spectrometer. A singlet spectrum with *g* value of 2.0037 and the line width (ΔH_{msl}) of 1.1 mT was observed for the *n*-hexyl silicon network polymer. The *g* value of the spectrum is consistent with that observed in the case of NaK alloy reduction [3]. Similar radical anion spectra were also observed for cyclic oligomeric silanes, (SiMe_2)₅, (SiMe_2)₆ [13]. The ESR line width of the cyclic oligosilanes ($\Delta H_{\text{msl}} = 0.5$ mT) was narrower than that of the network polysilanes. To know the correlation with the absorption spectra, we have carried out the photoillumination experiment. When the sample was photoilluminated with $\lambda > 650$ nm light, the ESR spectrum was bleached to 1/4 of the initial intensity. The signal intensity remained constant even after prolonged irradiation. Upon additional photoillumination with $\lambda > 450$ nm light, the ESR spectrum almost completely bleached. This result agrees to the result obtained in the electronic absorption measurement as shown in Fig. 2. The good correlation between ESR and electronic absorption spectra confirmed that the infrared absorption bands are due to the network polysilane radical anions.

A solute radical cation is produced in irradiated BuCl by the reaction of a positive hole with a solute molecule [11]. The solid curve in Fig. 4 is the absorption spectrum of a BuCl solution containing 5×10^{-2} M of a *n*-hexyl silicon network polymer at 77 K irradiated with a dose of 3×10^{19} eV g^{-1} . A broad absorption spectrum was observed in the visible and near-infrared regions. In comparison with the radical anion, the absorption spectrum has no clear band in the 500–800 nm region. All spectra of radical cations of polysilanes with *n*-hexyl, *n*-butyl, and *n*-propyl alkyl substituents gave similar spectra. Side chain effect on the absorption spectrum of the radical cation was not observed. We tried to measure the ESR spectrum in BuCl matrix, but could not detect any sharp ESR spectrum.

The broken curve in Fig. 4 is the absorption spectrum of a *n*-hexyl silicon network polymer cation after thermal annealing at a temperature slightly higher than 77 K. After thermal annealing, the absorption band showed a blue shift. This result is similar to the result observed for linear polysilanes but in contrast with the spectra of cyclic polysilanes. In the case of cyclic polysilanes, thermal annealing did not affect the spectrum.

In the case of linear poly(methyl-*n*-hexylsilane), both radical anions and cations gave strong sharp bands in UV region ($\lambda_{\text{max}} = 361$ nm: radical cation, 370 nm: radical anion) and weak bands in near infrared region ($\lambda_{\text{max}} \sim 2000$ nm) [9]. The anions and cations of the linear polysilanes had no absorption in visible region ($400 < \lambda < 750$ nm). On the other hand, the absorption spectra of the radical anions and cations of network polysilanes showed a very broad band in visible and near infrared regions. The broad absorption band shape is characteristic of the spectra of the radical anion and cation.

Superposition of several cyclic structures in the network polymers is considered to result in the broad radical ion spectra irrespective of the side chain substituents.

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