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Journal of Organometallic Chemistry 611 (2000) 64–70

Optical properties of pyrrolyl-substituted polysilanes

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Received 26 February 2000; accepted 31 March 2000

Abstract

Pyrrolyl-substituted polysilanes were synthesized in the present study. The pyrrolyl rings directly attached to the Si conjugated main chains with Si–N bonds. Poly(alkylpyrrolylsilane) and poly(phenylpyrrolylsilane) showed a chromophore which is attributed to $\sigma-\sigma^*$ transition in the conjugated system associated with near-UV fluorescence. However, a strong photoluminescence band was observed at 450–500 mn other than the near-UV photoluminescence for the polysilanes. The luminescence is due to the energy relaxation from σ^* to an inter-band level produced by $\sigma-\pi$ mixing between main chain σ-conjugated system and pyrrolyl groups as suggested by theoretical calculations. Transient spectroscopy of the polysilanes was also carried out showing a new chromophore at the vis-IR region (800 nm) other than near-UV (300–400 nm) and IR (~ 2000 nm) absorption bands typically observed for alkyl- and phenyl-substituted polysilanes. It also supports the presence of the mid-gap level in the pyrrolyl-substituted polysilanes. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Polysilane; Pyrrolyl; Pulse radiolysis; Photoluminescence; Inter band level

1. Introduction

Polysilanes (for a review, see Ref. [1]) have attracted considerable attention because of their interesting features such as photovolatilization [2,3], nonlinear optical effects [4], and photoconductivity [5–7]. These properties originate from the delocalization of Si–Si σ-electrons along main chains called σ-conjugated systems [8–12]. A polysilane molecule has been revealed already to have a backbone consisting of conjugated helical segments joined to each other by a disordered Si conformation. Whereas solid state polysilanes have a high electric resistance as insulators, they become p-type semiconductors in the presence of strong electron acceptors, showing their potentials as conducting polymer materials [13]. However the wide band gap (Eg ~ 4 eV) has been a barrier for the effective inter-chain doping that has been able to cause enough delocalization of electrons in the polymer main chain.

Substitution of Si skeleton by the functional groups is an important candidate for the doping techniques. A self-doping to the σ-conjugated Si chain would be realized by some specific side chains which have strong electron donating or accepting properties. Recent studies on the formation and the reactivity of diaminosilylenes implied the possibility of diamino-substituted polysilanes [14], however the intermediates gave only dimmers without the yield of polymerized products. One of the most practical techniques to obtain the polysilane derivatives is the Kipping reaction of dichlorosilane monomers with alkali metal. Reduction of diamino–dichlorosilanes by alkali metals was reported also to give the corresponding silylenes [15]. The intermediates were trapped by aromatic solvents giving diaminosilylaromatics. This suggests that the conventional Kipping method is not appropriate to obtain the diaminosubstituted polysilanes with high molecular weight. The method, however, gave the polysilanes with high molecular weight (~ 10^5) containing an aminoalkyl- or aminophenyl group as their side chains [16,17]. The polymers showed considerable increase in the electric conductivity with the presence of I_2 dopants. This study concluded that the functional groups played a role as a stabilized site for positive charges on Si skeleton because of their electron donating properties.

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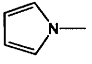
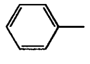
PII: S0022-328X(00)00398-3

Table 1
Pyrrolyl-substituted polysilanes

Entry	R	*Mw* [a]	*Mw/Mn* [a]	λ_{max} (nm)	ε at λ_{max}	Yield (%)
PS1		15000 [b]	6.0	278	5400	15
PS2	n-C_4H_9–	8000	1.7	Shoulder	-	7
PS3		17000	1.9	297	4200	32
PS4	CH_3–	29000	2.5	313	3700	28

[a] Mw and Mn, weight and number average molecular weights relatively determined to polystylene calibration standards; [b] Molecular weight observed at the first run of the GPC measurement. The value gradually decreased at the following runs.

Recent theoretical calculations have shown that the electronic structure of polysilanes contains pyrrole groups [18]. Non-bonding π electrons in the pyrrole groups split the πσ band of σ-conjugated system at the edge of their valence band, suggesting the strong σ–n mixing, leading to new chromophores of the polysilane derivatives. Pyrrole groups also produce localized π states in the band gap because of σ–π mixing. The mixing effect was predicted to cause the localization of negative charges on the Si main chain. These results imply the potential of the functional groups to change the electronic structure of σ-conjugated system by the direct electronic correlation between side and main chains. In the present paper, the synthesis results and optical properties are described for pyrrolyl-substituted polysilanes. We also discuss the degree of electron delocalization on their Si skeleton by the spectroscopic techniques, revealing the potentials of pyrrolyl-substituents as the self-doping materials.

2. Results and discussion

The polymers having pyrrolyl groups were obtained in the present work though the conventional Kipping method has been suggested not to be suitable for the polymerization of diaminopolysilanes [15]. Table 1 summarizes the polymerization results of polysilanes with pyrrolyl substituents. The molecular weight of the polymers were considerably lower than that of alkyl- or aryl-substituted organopolysilanes showing $Mn > 10^4$ at least. Dipyrrolyl-substituted PSI showed less stability in comparison with PS2–PS4 that have one pyrrolyl unit at a Si atom. Degradation of a Si chain in PS1 was observed during a few hours in spite of no change in the molecular weight of PS2–PS4 within the time range. The absorption spectra of the polysilanes are shown in Fig. 1. PS1, PS3, and PS4 have peaks at near-UV region in spite of observed shoulder feature in the spectrum of PS2. The maximum of each spectrum depends strongly on the substitution patterns, and locates at a considerably shorter wavelength region in comparison with that in alkyl or aryl-substituted polysilanes. However the absorption edge of the polymer shows a considerable red shift in comparison with that of alkyl- and phenyl-substituted polysilanes, indicating the splitting of the pσ band in the valence band caused by the σ–n mixing between the Si main chain and lone-pairs in pyrrolyl groups. Based on the theoretical calculations, the degree σ–n mixing depends strongly on the rotation of pyrrolyl groups, and the stacking of pyrrolyl substituents is needed to give the largest degree of mixing effects [18]. The present results indicate that the plane angle of pyrrolyl groups varies by the rotation and/or Si skeleton structures.

Photoluminescence spectra of PS2 are displayed in Fig. 2. PS2 shows two fluorescence bands in near-UV (– 350 nm, S band) and visible (– 490 run, B band) regions, respectively. The S band emission was observed typically for alkyl- and aryl-substituted polysilanes, which had been ascribed to the emission from the 1-D exciton state on the Si conjugated skeletons. The S band disappears in the spectrum recorded for the exci-

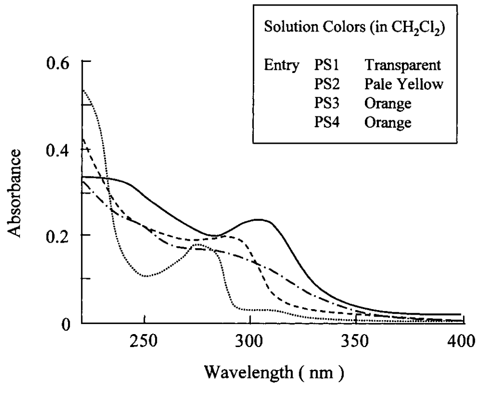


Fig. 1. Absorption spectra of pyrrolyl-substituted polysilanes in THF, 0.05 mM (base mol unit). Dotted, dot-dashed, dashed, and solid lines indicate the spectra of PSI, PS2, PS3, and PS4, respectively.

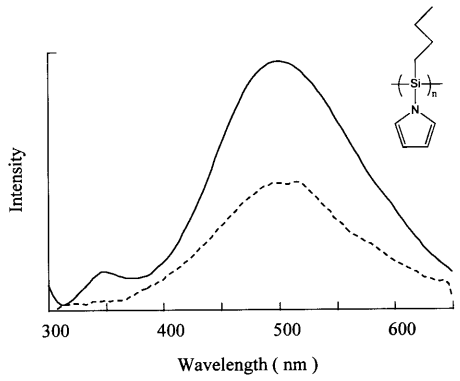


Fig. 2. Photoluminescence spectrum of PS2 in CH_2Cl_2 at 10 mM (base mol unit). Solid and dashed lines denotes the spectra obtained by the excitation at 300 and 260 nm, respectively.

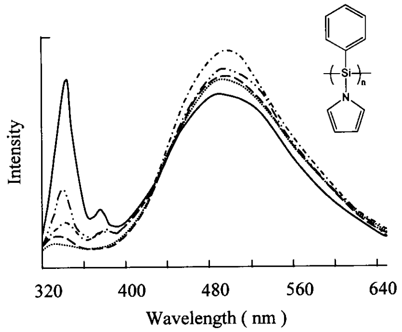


Fig. 3. Photoluminescence spectrum of PS3 in CH_2Cl_2 at 10 mM (base mol unit). Solid, doubledot–dashed, dot–dashed, dashed, and dotted lines denotes the spectra obtained by the excitation at 310, 300, 290, 280, and 270 nm, respectively.

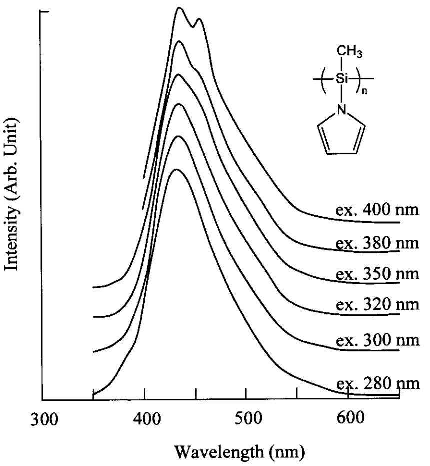


Fig. 4. Photoluminescence spectra of PS4 in THF at 10 mM (base mol unit) recorded by a variety of excitation energy.

tation to lower energy states, despite of the clearly observed B band. The n-levels of the pyrrolyl groups were predicted by the calculation to intrude in the mid-gap, and present at -2 eV lower than the edge of the conduction band: LUCB, -2 eV higher than the highest occupied level of valence band: HOVB [18]. The mid-gap level gives two kinds of photoluminescence at around 2 eV: the transition from LUVB to the mid-gap level, and the excitation from mid-gap level to HOVB. The B band is due to the latter because of dominance of B band for the excitation of the higher energy photons that mainly give the excited states of pyrrolyl groups. The 1-D band structure, hence the conjugated system of Si skeleton is disturbed in PS2 as the observed low extinction coefficients at near-UV in Fig. 1, which leads to higher LUVB levels and lower density of states (DOS) than that of typical polysilanes. This suggests the low yield of photoluminescence due to the transition from LUVB to the mid-gap level in PS2. Fig. 3 illustrates the photoluminescence spectra of PS3. The S band emission is strongly observed for the excitation to the band exciton state in comparison with PS2, suggesting the relatively developed conjugated system along their Si chain. The relative yield of S and B bands changes in the similar manner with an increase in the photon energy of excitation light. The B band in PS2 and PS3 is observed at 500 nm (2.5 eV) indicating higher energy than that calculated [18]. It reflects the disordering of the Si skeleton from a complete all-*trans* conformation, and -0.5 eV lower levels of HOVB. The energy dispersion of B band is also estimated as 0.50 and 0.32 eV for PS2 and PS3, respectively from the full width at half maximum: FWHM of the band. The considerably high dispersion may be due to the low DOS at HOVB and the variation of the mid-gap level given by the rotation of pyrrolyl groups.

PS3, which has the lowest energy of the UV absorption edge in PS1–PS4, indicates the different type of photoluminescence and its dependence on the excitation energy as shown in Fig. 4. The B band seems to be observed at higher energy region (430 mn; 2.8 eV) for the excitation by 4.3 eV photons, however splits into two photoluminescence bands: B_1 at around 440 nm (2.75 eV) and B_2 at 460 nm (2.6 eV) with the increasing excitation energy. The relative photon energy in B_1 and B_2 bands shows a good correspondence to the theoretical models [18], and they are assigned to the transition of mid-gap level-HOVB and LUCB-mid-gap level, respectively. The fitting of the spectra gives the values of 0.30 and 0.16 eV as the FWHM of B_1 and B_2 bands, showing lower values of energy dispersion than that of PS2 and PS3. Because the rotation of pyrrolyl rings is rather enhanced in PS4 by the low steric hindrance of CH_3– groups, it suggests that the relatively long conjugated segments in the Si chain lead to the high DOS especially at LUCB.

Transient spectroscopy of the polysilanes was also carried out in the present study. The transient spectrum of $PS3^{\bullet-}$ is displayed in Fig. 5. The transient spectrum has chromophores at near-UV (380 nm: 3.2 eV) and near-IR (850 nm: 1.4 eV) regions, and the symmetric kinetic traces are observed for both peaks. Fig. 6 shows the transient spectrum of $PS3^{\bullet +}$, which is an analog of the spectrum observed for anion radicals. Another transient chromophore is observed at visible region (480 nm) for both $PS3^{\bullet -}$ and $PS3^{\bullet +}$ with different kinetic traces from ones in near-UV and near-IR bands as shown in the superimposed figure. Silylenes extracted from Si main chains are responsible as the intermediate species because the chromophore is clearly scavenged by addition of methanol. Generally, the near-UV (3–4 eV) and IR (0.5–1 eV) transient chromophores were observed for anion radicals of alkyl- and phenyl substituted polysilanes, and the spectrum of cation radicals was consistent with that of anion radicals [19–22]. The excess electrons or holes on 1-D Si skeleton were found to form the inter-band levels: IBL^- or IBL^+. The UV and IR bands of anion radicals were ascribed to the transition of $HOVB–IBL^-$ ($IBL^+–LUCB$ for cations) and $IBL^-–LUCB$ ($HOVB–IBL^+$), respectively. The similarity in the spectra of radical anions and cations of PS3 suggests the presence of IBL^- (for anions) or IBL^+ (for cations), hence the excess electrons or holes are delocalized in the σ-conjugated system along the main chain. The delocalization of excess charge was discussed already in our previous studies using the polysilanes with structural defects based on the theoretical models of the lattice–electron interaction in a conjugated 1-D chain [8,10,19,23]. According to the Sandrofy C model (for a review, see Ref. [24]), the transition energy of the IR band: $\delta\varepsilon$ reflected the degree of delocalization on a Si skeleton as follows,

$$\delta\varepsilon \approx \left(\frac{\Delta V}{2\alpha}\right)\left(\frac{a}{\zeta_p}\right)^2 \tag{1}$$

where a denotes a lattice unit of a *trans*-chain segment, and ζ_p is the width of lattice–electron interaction. V is the matrix element describing the interaction between two atomic orbitals consisting of a covalent bond, and Δ also denotes the matrix element between two atomic orbitals of a Si atom. α is defined as

$$\alpha \equiv [V(r) - \Delta] \tag{2}$$

$$r = \frac{2}{\sin\theta} \tag{3}$$

where 2θ is the tetrahedral bond angle. Thus, Δ is a parameter which specifies the degree of delocallization of σ electrons on a σ-conjugated segment while V described the localization of a pair electrons in a local bond. The value of $(\Delta V/2\alpha)$ can be estimated as ca. 1 eV using the parameters reported previously in poly(dimethylsilane) [25,26]. The observed $\delta\varepsilon$: ca. 1.4 eV in both $PS3^{\bullet -}$ and $PS3^{\bullet +}$ gives $\zeta_p/a \sim 0.7$. It suggests the highly localized excess of electrons or holes on a Si skeleton as much as a single Si unit.

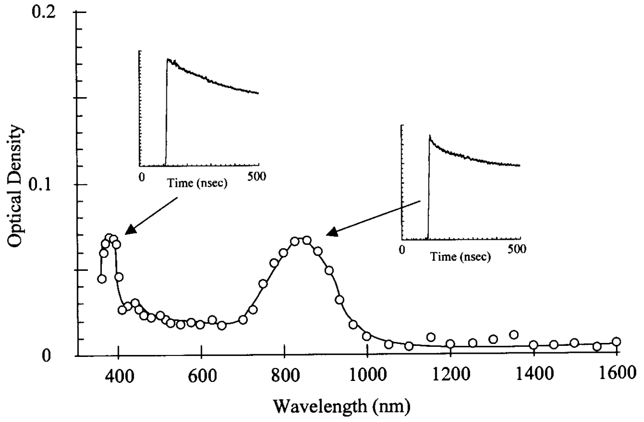


Fig. 5. Transient absorption spectra of $PS3^{\bullet -}$ in THF at 100 mM conc. (base mol unit) at the 15 ns after an electron pulse. Superimposed figures indicate the kinetic traces of the transient absorption bands.

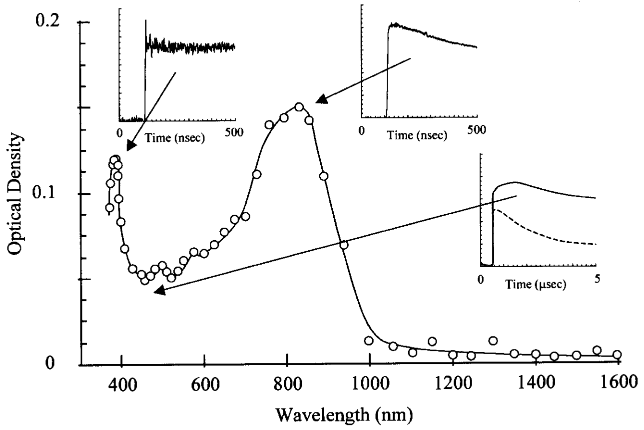


Fig. 6. Transient absorption spectra of $PS3^{\bullet +}$ in CH_2Cl_2 at 100 mM conc. (base mol unit) at the 15 ns after an electron pulse. Superimposed figures indicate the kinetic traces of the transient absorption bands.

Figs. 7 and 8 display the absorption spectra of $PS4^{\bullet -}$ and $PS4^{\bullet +}$ with kinetic traces. $PS4^{\bullet -}$ showed a new chromophore at vis-IR region (800 nm: 1.5 eV) other than near-UV (390 nm: 3.1 eV) and IR (~ 1300 nm: ~ 0.9 eV) absorption bands. An excess electron in the conduction band of PS4 is localized at rather the mid-gap level produced by σ–π mixing between Si main chain and pyrrolyl groups than the IBL^-, and gives the optical absorption at 1.5 eV as the transition between mid-gap level and IBL^-. The total transition energy between mid-gap level and LUCB is estimated as 2.4 eV, showing good correspondence with that discussed in the photoluminescence spectra (in Fig. 4). The spectra observed for $PS4^{\bullet +}$ indicates the similar features as that in the conventional polysilanes. The value of $\delta\varepsilon < 0.6$ eV in $PS4^{\bullet +}$ estimates the degree of hole delocalization as widespread as in poly-

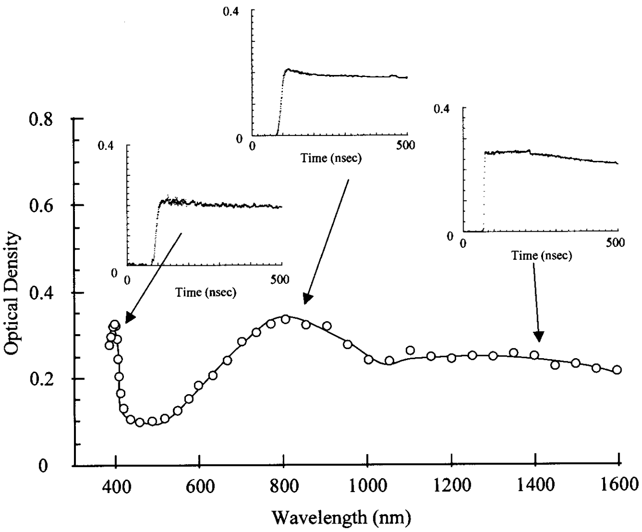


Fig. 7. Transient absorption spectra of PS4$^{\bullet-}$ in THF at 100 mM conc. (base mol unit) at the 15 ns after an electron pulse. Superimposed figures indicate the kinetic traces of the transient absorption bands.

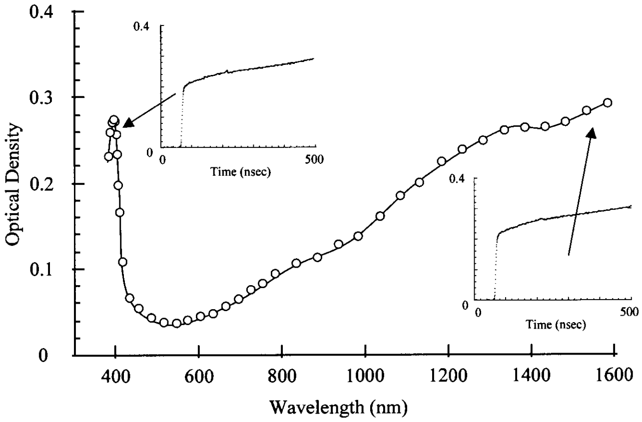


Fig. 8. Transient absorption spectra of PS4$^{\bullet+}$ in CH_2Cl_2 at 100 mM conc. (base mol unit) at the 15 ns after an electron pulse. Superimposed figures indicate the kinetic traces of the transient absorption bands.

(methylphenylsilane). This suggests that the pyrrolyl substitution enables the selective control of the charge delocalization for excess electrons and holes on a Si skeleton by its electron-donating features.

3. Experimental

3.1. Dichlorosilanes

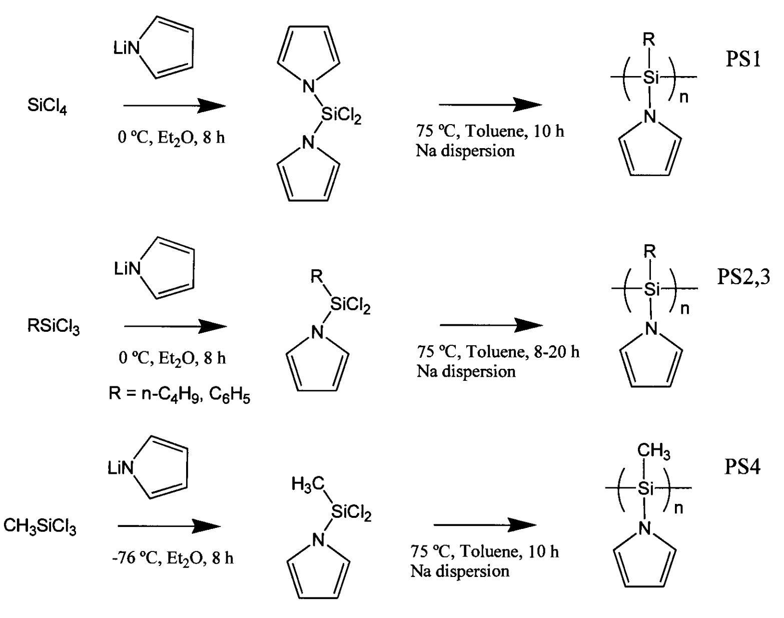
Dichlorosilanes were prepared by the reaction of pyrrolyl–lithium with tri- or tetrachlorosilanes in ether under Ar atmospheres as shown in Scheme 1. Pyrrole, *n*-buthyllithium, and ether were the product of Wako Chemical Co. Ltd. Tri- and tetrachlorosilanes were purchased from Shin-Etsu Chemical Co. Ltd., and distilled prior to use. ^{1}H-NMR spectroscopy was performed by using a JEOL EX-270 NMR spectrometer at 270 MHz, and the results are listed in Table 2 with boiling points and yields of the products.

3.2. Polymerization and characterization

Polymerization was carried out in an Ar atmosphere and in 50 cm^3 dry toluene which was refluxed with sodium during 10 h and distilled before use. The monomer was added into reaction vessel and mixed with sodium dispersion at 75°C during the time shown in Scheme 1. Sodium dispersion in toluene was purchased from Acros Co. Ltd. PS1 and PS2 solutions in toluene were dried under vacuum ($< 10^{-3}$ hPa) at 100°C after passing through a 0.45 μm PTFE filter to eliminate NaCl. PS3 and PS4 solutions were precipitated into methanol after filtration passing through a 0.45 μm PTFE filter, and dried under vacuum. All the procedures were carried out under an Ar atmosphere. The obtained polysilanes showed good solubility for toluene, Tetrahydrofuran (THF), and dichloromethane. The amount of residual Cl atoms were confirmed to be less than 1% in all polysilane derivatives by elemental analysis. Molecular weight distributions of all the polymers were measured by Shimadzu C-R3A gel permeation chromatography (GPC) system with polystylene calibration standards. UV–vis absorption spectra were recorded by Shimadzu UV-3100 PC system. Photoluminescence spectra were measured by Perkin–Elmer LS-5013.

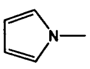
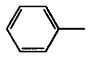
3.3. Pulse radiolysis

The pulse radiolysis measurements were performed with L-band electron linear accelerator at the Radiation Laboratory of the Institute of Scientific and Industrial Research, Osaka University. All the polysilanes were dissolved into THF and CH_2Cl_2 at 0.05 M conc. (base mol unit). The THF solutions were evacuated, and the CH_2Cl_2 solutions were bubbled by Ar gas for 5 min before irradiation. The samples were irradiated with a 2 ns single electron pulse at room temperature. An Xe flash lamp was used as a source of analyzing light with continuous spectrum from 300 to 1600 nm. The analyzing light was monitored with Ritsu MC-10N monochromator, and detected by PIN Si (Hamamatsu S1722) or InGaAs (Hamamatsu G6117-03) photodiodes. The signals were corrected by a Sony/Tektronics SCD 1000 transient digitizer. The typical instrument function was ca. 8 ns.



Scheme 1.

Table 2
Pyrrolyl-substituted dichlorosilane monomers

Entry	R	^{1}H-NMR (270 MHz, CDCl$_3$)	b.p.^{a} (°C / mmHg)	Yield (%)
1		6.44 (t,*J* = 1.98Hz, 4H) 6.91 (t,*J* = 1.98Hz, 4H)	110 / 12	51
2	n-C$_4$H$_9$-	0.92 (t,*J* = 7.25Hz, 3H) 1.28 -1.59 (m, 6H) 6.41 (t,*J* = 1.98Hz, 2H)6.97 (t,*J* = 2.31Hz, 2H)	54 / 8	38
3		6.41 (t,*J* = 1.98Hz, 2H) 6.93 (t,*J* = 2.10Hz, 2H) 7.47 - 7.76 (m, 5H)	90 / 6	50
4	CH$_3$-	6.47 (t,*J* = 1.98Hz, 2H) 7.00 (t,*J* = 2.10Hz, 2H) 1.09 (s, 3H)	45 / 20	32

^{a}, boiling point.

Acknowledgements

The authors acknowledge Professor Y. Yoshida, Professor Y. Yamamoto, Mr K. Maeda, and Mr Y. Matsui at ISIR Osaka University for the experimental supports. We also acknowledge Professor K. Takeda at School of Science and Engineering, Waseda University, and Professor K. Ishigure and Professor K. Asai at Quantum Engineering and System Science, The University of Tokyo for their useful advises. This work was supported by a Grant-in-aid for scientific research from the Ministry of Education, Science and Culture.

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