

Dynamics of Charge Carriers on Poly[bis(*p*-alkylphenyl)silane]s by Electron Beam Pulse Radiolysis

Shu Seki,* Yoshinori Matsui, Yoichi Yoshida, and Seiichi Tagawa*

Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

Julian R. Koe

Department of Chemistry, International Christian University, 3-10-2 Osawa, Mitaka, Tokyo 181-8585, Japan

Michiya Fujiki†

NTT Basic Research Laboratories, NTT Coporation, 3-1 Morinosato Wakamiya, Atsugi, Kanagawa 243-0198, Japan

Received: February 11, 2002; In Final Form: May 10, 2002

The degree of electron delocalization along polymer skeletons was discussed for ion radicals of poly[bis(*p*-alkylphenyl)silane]s by electron beam pulse radiolysis. The degree of delocalization of negative charges on the Si chains strongly depended on the substitution position of the alkyl groups (*n*- and *tert*-butyl) on the phenyl rings, though relatively small effects were observed for holes. The empirical relationship between oscillator strength and the degree of delocalization (n_{del}) gave the value of n_{del} as ~ 36 Si units for excess electrons on poly[bis(*p*-*n*-butylphenyl)silane] in contrast to the value of $n_{\text{del}} = 14$ for poly[bis(*p*-*t*-butylphenyl)silane], which was similar to that for poly(methylphenylsilane). The oscillator strength of the cation radicals of poly[bis(*p*-alkylphenyl)silane]s ($f^{+} > 0.65$) was ~ 2 times higher than that of poly(methylphenylsilane) ($f^{+} = 0.35$). Positive charges gave a higher degree of delocalization in poly[bis(*p*-alkylphenyl)silane]s in comparison with that in poly(methylphenylsilane), suggesting that the Si skeleton of poly[bis(*p*-alkylphenyl)silane]s should be good conducting paths for holes.

Introduction

Considerable research effort is being focused on the polysilanes at present because of the electron delocalization along the Si chains (σ -conjugated system¹) and associated interesting characteristics such as near-UV absorption,² photodecomposition,³ and nonlinear optical properties.⁴ On the basis of their ability as positive charge conductors, the dynamics of excess electrons and holes on the Si skeletons have been investigated vigorously in view of their potential application as photoconductors or in electro-luminescent diodes.^{5,6}

A polysilane molecule has a saturated backbone without any π -bonds, consisting of conjugated helical segments joined to each other by a disordered Si conformation. The mean length of the segments is controlled by the steric hindrance of the side chains and/or thermodynamic molecular motions. Several groups reported the synthesis of a series of polysilanes with backbone conformations varying from “random coil”, “stiff” to “rodlike”, by changing the substitution patterns of the polymers.⁷ Recently, optically active polysilanes were developed with tightly locked rodlike helical Si backbones induced by the incorporation of chiral substituents.⁸ The screw sense of the Si backbone was inverted by thermal treatment in diarylpolysilanes with chiro-

tical switching of the main chain chromophores, indicating highly ordered backbone conformations in these polymers.⁹ Diarylpolysilanes with tightly locked Si backbones could be candidates for ideal 1-D structures which would show the 1-D semiconductor and/or quantum wire properties.

Spectroscopic analytical methods have been applied to a variety of radical ions of polysilanes, which correspond precisely to polysilane molecules conducting negative and positive charge carriers on their skeletons.^{10–14} Optical^{10–13} and electron spin resonance^{13,14} spectroscopies were carried out for the radical ions. Localization of the charge carriers was revealed to be suppressed in the polysilanes bearing bulky pendant groups, suggesting not only that the localization in typical dialkyl polysilanes arises from the flexibility of Si catenation, but also that delocalization occurs in polysilanes with “stiff” or “rodlike” Si skeletons. The pulse radiolysis technique is one of the most effective tools to investigate the energy states of reactive intermediates including ionic species. Ion radicals showed transient absorption bands in the near UV and IR regions with very high extinction coefficients ($\sim 10^5 \text{ M}^{-1} \text{ cm}^{-1}$).^{10,15,16} The results also reflected the degree of delocalization of the charge carriers (n_{del}) on the Si skeletons, giving the value of n_{del} as ~ 10 Si units for radical anions of typical alkyl- and aryl-substituted polysilanes.^{15,16}

In the present paper, transient spectroscopy of ion radicals is carried out for diarylpolysilanes by pulse radiolysis. The energy state of the intermediates is discussed in relation to the results in extinction coefficient, oscillator strength, and transition energy

* Corresponding authors. Fax: +81-6-6876-3287. E-mail (S. Seki): seki@sanken.osaka-u.ac.jp. E-mail (S. Tagawa): tagawa@sanken.osaka-u.ac.jp.

† Present address: Nara Institute of Science and Technology (NAIST), Graduate School of Material Science, 8916-5 Takayama, Ikoma, Nara 60-0101, Japan.

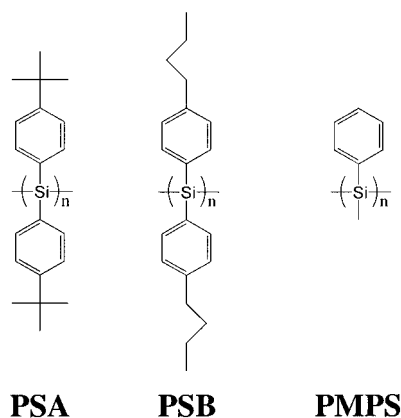


Figure 1. Structures of polysilanes employed.

of the transient absorption. We also present the dependence of the degree of the charge delocalization on the backbone conformation by comparison between diarylpoly-silanes and poly(methylphenylsilane) (**PMPS**), suggesting the greater potentials of the “ordered” Si backbone in the diarylpoly-silanes as charge carrier conductors.

Experimental Section

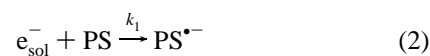
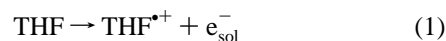
The syntheses of poly[bis(*p*-*t*-butylphenyl)silane] (**PSA**) and poly[bis(*p*-*n*-butylphenyl)silane] (**PSB**) have already been described elsewhere.^{9,17,18} **PSA** and **PSB** were purified by reprecipitation in toluene-2-propanol (IPA) and tetrahydrofuran (THF)-methanol systems. Methylphenyldichlorosilane was purchased from Shin-Etsu Silicon Co. Ltd. and distilled twice prior to use. **PMPS** was prepared by stirring methylphenyldichlorosilane with sodium metal in dry toluene for 5 h at 110 °C. The **PMPS** solution was precipitated in IPA after filtration through a 0.45 μm PTFE filter to eliminate NaCl, and the precipitates were dried under vacuum. **PMPS** was fractionally precipitated again to separate its bimodal distribution. The molecular weight distribution of obtained polymer was measured by gel permeation chromatography using THF as eluent. The values of M_w and M_n of the polymer were 3.2×10^5 and 1.1×10^5 for **PSA**, 6.1×10^5 and 1.5×10^5 for **PSB**, 4.5×10^5 and 2.9×10^5 for **PMPS**, respectively, relative to polystyrene standards. The structures of the polymers are displayed in Figure 1. UV-vis spectra of the polysilanes were recorded on a JASCO V-570 and a Shimadzu UV-3100PC in THF at 1×10^{-4} mol dm^{-3} . The maximum wavelength (λ_{max}) and intensity (ϵ_{ES}) of the lowest excitonic backbone peak of the polysilanes were $\lambda_{\text{max}} = 377$ nm, $\epsilon_{\text{ES}} = 7.6 \times 10^3$ (mol/ dm^3) $^{-1}$ cm^{-1} for **PSA**, $\lambda_{\text{max}} = 393$ nm, $\epsilon_{\text{ES}} = 13.3 \times 10^3$ (mol/ dm^3) $^{-1}$ cm^{-1} for **PSB**, and $\lambda_{\text{max}} = 337$ nm, $\epsilon_{\text{ES}} = 8.7 \times 10^3$ (mol/ dm^3) $^{-1}$ cm^{-1} for **PMPS**, respectively.

Pulse radiolysis measurements were performed at room temperature using an L-band electron linear accelerator at the Institute of Scientific and Industrial Research, Osaka University. All the polysilanes were dissolved in THF or 1-chlorobutane (BuCl) at 0.0050 mol dm^{-3} concentration (base mol unit). The solution was deaerated in a Suprasil quartz cell having a 2 cm optical path, and irradiated with an 8 ns single electron pulse. The details of the apparatus have been described elsewhere.^{11,16} The typical instrument function was ca. 8 ns.

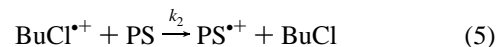
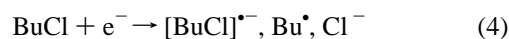
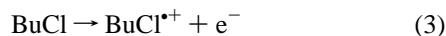
Results and Discussion

The incident electron pulses in the solutions produce anion and cation radicals of the polysilanes in THF and BuCl according to the reaction scheme below,

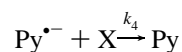
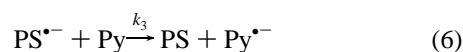
(in THF)



(in BuCl)



where PS denotes the solute polysilane molecule, e_{sol}^- is a solvated electron, k_1 and k_2 are reaction rate constants. The value of k_1 was already reported as $>10^{10}$ M^{-1} s^{-1} at 293 K for a series of polysilanes, suggesting that the formation process of the radical anions occurred within the instrumental function of the present system.¹⁶ The extinction coefficient of $\text{PS}^{\bullet-}$ ($\epsilon^{\bullet-}$) is determined by the electron-transfer reactions between $\text{PS}^{\bullet-}$ and pyrene (Py). The transient absorption of $\text{PS}^{\bullet-}$ can be quenched by the presence of Py, giving $\text{Py}^{\bullet-}$. The reaction scheme can be written as



where X denotes counterion, and k_3 and k_4 are rate constants. The values of k_3 are obtained as 2.8×10^9 M^{-1} s^{-1} for **PSA**, 5.1×10^9 M^{-1} s^{-1} for **PSB**, and 6.5×10^9 M^{-1} s^{-1} for **PMPS**, respectively. The lifetimes of cation and anion radicals are long ($>10^{-6}$ s) enough in the present system to neglect their contribution to the analysis. The concentration unit of the radical ions is defined as moles of added electrons or holes, and the value of $\epsilon^{\bullet-}$ is estimated from the ratio of quenching of the $\text{PS}^{\bullet-}$ transient absorption vs absorbance ascribed to $\text{Py}^{\bullet-}$ at 492 nm based on the known value of the extinction coefficient of $\text{Py}^{\bullet-}$ as 5.0×10^4 M^{-1} cm^{-1} .¹⁹ The extinction coefficient of $\text{PS}^{\bullet+}$ ($\epsilon^{\bullet+}$) was already reported in our previous work as 9.4×10^3 M^{-1} cm^{-1} for **PMPS**,²⁰ and the values of $\epsilon^{\bullet+}$ for **PSA** and **PSB** are determined relative to that of **PMPS** with the assumption of constant yield of radical cations in the present system.

Figure 2 shows the transient absorption spectra of radical anions of the polysilanes. We have already discussed the transient spectra of radical ions of polysilanes including **PMPS**, for which $\text{PS}^{\bullet-}$ or $\text{PS}^{\bullet+}$ shows two absorption bands in the near UV (350 ~ 400 nm: UV band) and IR (>1600 nm: IR band) regions.^{11–13,15,16} The transient spectra of $\text{PS}^{\bullet-}$ or $\text{PS}^{\bullet+}$ strongly suggest the presence of an interband level which is occupied by an excess electron (IBL $^-$) or hole (IBL $^+$). The UV and IR bands in $\text{PS}^{\bullet-}$ are due to the transition from the valence band (VB) to the IBL $^-$ and from the IBL $^-$ to conduction band (CB), respectively (for $\text{PS}^{\bullet+}$, UV: IBL $^+$ -CB, IR: VB-IBL $^+$). The delocalized negative or positive polaron state will give a good interpretation for the IBLs.^{11,15,16,21} In contrast to **PMPS**, **PSA**, or the other polysilanes, the IR band in **PSB** shifts toward the longer wavelength region beyond the detectable range of the present apparatus.

The transient spectra of the cation radicals are displayed in Figure 3. The values of $\epsilon^{\bullet+}$ at the absorption maxima are summarized in the Table together with the values of $\epsilon^{\bullet-}$ for all

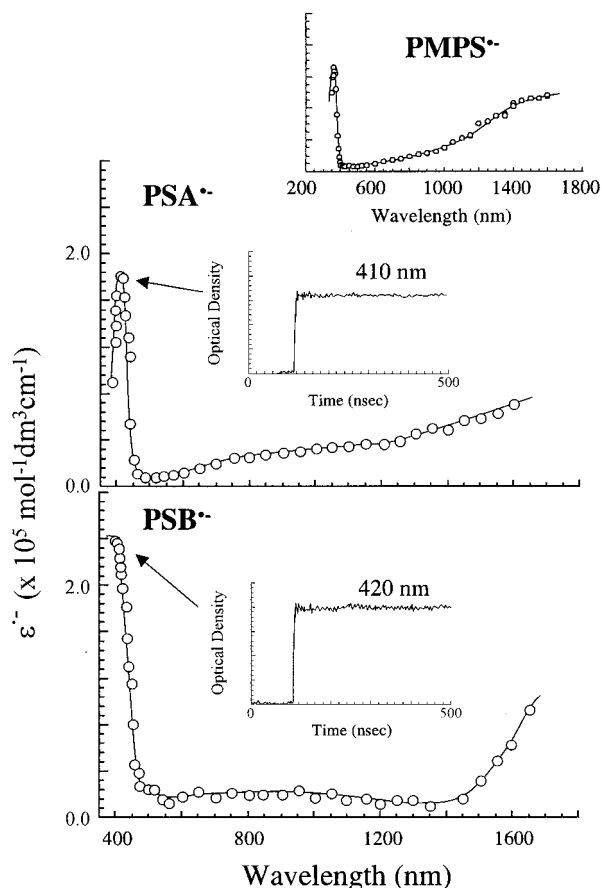


Figure 2. Transient absorption spectra of radical anions of **PMPS**, **PSA**, and **PSB** observed in tetrahydrofuran at 0.0050 M dm⁻³ (base mol unit). All spectra were recorded at 100 ns after electron pulse irradiation. Superimposed figures indicate the kinetic traces of the UV band as indicated by arrows.

the polysilanes. The spectra of diarylpolysilanes (**PSA** and **PSB**) show dramatic differences in comparison with that of **PMPS**. The IR band of both **PSA** and **PSB** is no longer detectable, and shifts to wavelengths >2250 nm (<0.55 eV) which is the absorption maximum of **PMPS**^{•+} observed by the low-temperature matrix isolation technique. This suggests that the energy level of the IBL⁺ locates very close to the edge of the VB in both **PSA** and **PSB**, indicating a smaller energy of positive polaron formation on the Si skeleton of **PSA** and **PSB** (<0.55 eV).

In the quantitative elucidation of the degree of charge delocalization on the Si skeleton, we already reported the determination of the degree of charge delocalization (n_{del}) by the simultaneous observation of the transient bleaching of the lowest excitonic backbone peak ($\Delta_{\text{OD}}^{\text{BI}}$) and the formation of the UV bands ($\Delta_{\text{OD}}^{\text{•-}}$), as the following equation:¹⁵

$$n_{\text{del}} = \frac{\Delta_{\text{OD}}^{\text{BI}} \cdot \epsilon^{\text{•-}}}{\Delta_{\text{OD}}^{\text{•-}} \cdot \epsilon_{\text{ES}}} \quad (7)$$

and we obtained the empirical relationship between the apparent oscillator strength of the UV band ($f^{\text{•-}}$ or $f^{\text{•+}}$) and the value of n_{del} as in eqs 7 and 8:^{15,16}

$$n_{\text{del}} \propto f^{\text{•-}}, f^{\text{•+}} \quad (8)$$

$$f^{\text{•-}} = 4.32 \times 10^{-9} \int \epsilon^{\text{•-}} d\nu, \quad f^{\text{•+}} = 4.32 \times 10^{-9} \int \epsilon^{\text{•+}} d\nu \quad (9)$$

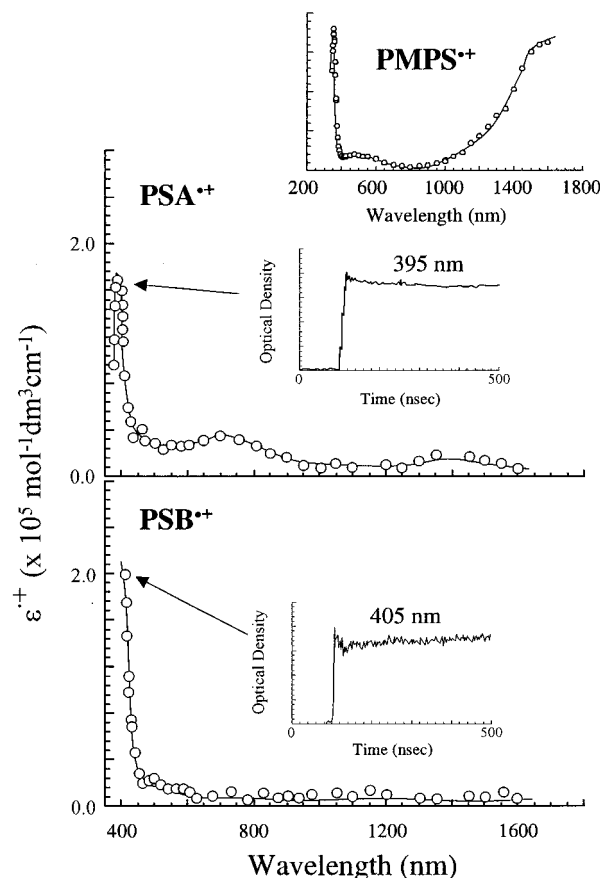


Figure 3. Transient absorption spectra of radical cations of **PMPS**, **PSA**, and **PSB** observed in 1-chlorobutane at 0.0050 M dm⁻³ (base mol unit). All spectra were recorded at 100 ns after electron pulse irradiation. Superimposed figures indicate the kinetic traces of the UV band as indicated by arrows.

TABLE 1: Transient Absorption Maxima, Molar Extinction Coefficients, and Oscillator Strengths of Polysilane Ion Radicals

entry	$\lambda_{\text{max}}^{\text{•-}}$ (nm)	$\epsilon^{\text{•-} a}$ (10 ⁵ M ⁻¹ cm ⁻¹)	$f^{\text{•-} b}$	$\lambda_{\text{max}}^{\text{•+}}$ (nm)	$\epsilon^{\text{•+} a}$ (10 ⁵ M ⁻¹ cm ⁻¹)	$f^{\text{•+} b}$
PMPS	369	1.6	0.68	365	0.94	0.35
PSA	410	1.8	0.73	392	1.7	0.65
PSB	405	2.4	1.9	<405	>2.0	>0.8

^a Molar extinction coefficient per radical anion(−) and cation(+) at the transient absorption maximum, ^b Calculated by Gaussian fitting to transient absorption spectra based on the values of $\epsilon^{\text{•-}}$ of $\epsilon^{\text{•+}}$.

The values of $f^{\text{•-}}$ or $f^{\text{•+}}$ can be obtained by numerical integration of the Gaussian fit to the VB–IBL[−] or the IBL⁺–CB transitions, and the values are also summarized in the table. According to eq 8, the value of n_{del} for **PSB**^{•−} is 2.8 times greater relative to n_{del} for **PMPS**^{•−}, whereas an almost similar value of n_{del} is observed for **PSA**^{•−}. The changes in n_{del} of the radical cations show a different tendency from that of the anions. Both **PSA** and **PSB** exhibit considerably higher values of $f^{\text{•+}}$ than **PMPS**, with magnitudes relative to **PMPS**^{•+} of 1.9 (**PSA**) and >2.3 (**PSB**), respectively. The absolute value of n_{del} estimated previously was obtained as $n_{\text{del}} = 13 \pm 3.4$ Si units for **PMPS**^{•−}. This suggests values of n_{del} as ~14 and ~36 Si units for **PSA** and **PSB**. Viscometric properties were already investigated for **PSB**^{22,23} to elucidate the macroscopic effect of steric bulky substituents on the backbone conformation. Persistence length, q of **PSB** was reported to be $q = 4.5$ – 10 nm, which is anomalously longer than that of conventional polysilanes including **PMPS** ($q = 1.1$ nm²⁴). The empirical relationship

between viscosity index and steady-state optical properties of polysilanes⁷ predicts **PSA** having a similar value of persistence length to **PMPS**. This shows good agreement with the drastic change in n_{del} of **PSA** and **PSB**. Recently, the observation of a photoinduced current transient was reported for **PSB** with not only positive (hole) but negative (electron) charges as conducting carriers.^{25,26} To date, disordered molecular solids including polysilane derivatives have shown almost no electron conduction in the bulk phase due to the presence of impurities and/or disordered Si–Si units which act as deep trapping sites. The present results support the presence of a highly delocalized IBL[−] state along the Si skeleton of **PSB**, suggesting that the Si backbone of **PSB** adopts a tightly locked rigid conformation, and is free from intramolecule trapping sites for not only holes but also electrons. We can also conclude that diarylpolysilanes, especially **PSA**, have intrinsically good conducting paths for holes in comparison to other polysilanes, such as **PMPS**, and should show high isotropic mobility of holes along their Si skeletons.

Conclusion

Transient absorption spectroscopy was carried out for ion radicals of poly[bis(*p*-alkylphenyl)silane]s using the electron beam pulse radiolysis technique. The transient spectra of radical anions strongly depend on the substituents (*t*- or *n*-) of the pendant groups, although relatively small effects were observed for radical cations. The degree of charge delocalization on the Si skeleton is quantitatively discussed on the basis of the empirical relationship between the oscillator strength of the transient absorption and n_{del} . The values of n_{del} for excess electrons show a dramatic increase from ~ 14 to ~ 36 on change of the *p*-alkyl substituents from *tert*-butyl to *n*-butyl, whereas only an small increase (from 1.9 to > 2.3 relative to **PMPS**) is observed in n_{del} for the holes. It is considered that both poly[bis(*p*-*t*-butylphenyl)silane] and poly[bis(*p*-*n*-butylphenyl)silane] have highly delocalized states for holes on their Si skeletons, and that the latter should be a good conductor for not only holes but also electrons after vigorous purification to produce materials free from impurities.

Acknowledgment. We thank Dr. Y. Kunimi and Mr. K. Nishida, and Mr. T. Yamamoto at ISIR, Osaka University for their experimental support. This work is supported in part by grant-in-aid, scientific research from the Ministry of Education, Culture, Sports, Science and Technology in Japan, and from the Japan Society for the Promotion of Science.

References and Notes

- (1) For a review, see Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359.
- (2) West, R. *J. Organomet. Chem.* **1986**, *300*, 327.
- (3) Trefonas, P.; West, R.; Miller, R. D. *J. Am. Chem. Soc.* **1985**, *107*, 2737.
- (4) Kajzar, F.; Messier, J.; Rosilio, C. *J. Appl. Phys.* **1986**, *60*, 3040.
- (5) Kepler, R. G.; Zeigler, J. M.; Harrah, L. A.; Kurtz, S. R. *Phys. Rev.* **1987**, *B35*, 2818.
- (6) Fujii, A.; Yoshimoto, K.; Yoshida, M.; Ohmori, Y.; Yoshino, K. *Jpn. J. Appl. Phys.* **1995**, *34*, L1365.
- (7) Fujiki, M. *J. Am. Chem. Soc.* **1996**, *118*, 7424.
- (8) Fujiki, M. *J. Am. Chem. Soc.* **1994**, *116*, 6017.
- (9) Koe, J. R.; Fujiki, M.; Nakashima, H.; Motonaga, M. *Chem. Commun.* **2000**, 389.
- (10) Ban, H.; Sukegawa, K.; Tagawa, S. *Macromolecules* **1987**, *20*, 1775.
- (11) Seki, S.; Yoshida, Y.; Tagawa, S.; Asai, K. *Macromolecules* **1999**, *32*, 1080.
- (12) Ushida, K.; Kira, A.; Tagawa, S.; Yoshida, Y.; Shibata, H. In *ACS Symposium Series 537*; Thompson, L. F., Ed.; American Chemical Society: Washington, DC, 1994; Chapter 21, p 323.
- (13) Ichikawa, T.; Yamada, Y.; Kumagai, J.; Fujiki, M. *Chem. Phys. Lett.* **1999**, *306*, 275.
- (14) Kumagai, J.; Yoshida, H.; Ichikawa, T. *J. Phys. Chem.* **1995**, *99*, 7965.
- (15) Seki, S.; Yoshida, Y.; Tagawa, S. *Radiat. Phys. Chem.* **2001**, *60*, 411.
- (16) Seki, S.; Kunimi, Y.; Nishida, K.; Yoshida, Y.; Tagawa, S. *J. Phys. Chem.* **2001**, *B105*, 900.
- (17) Koe, J. R.; Fujiki, M.; Nakashima, H. *J. Am. Chem. Soc.* **1999**, *121*, 9734.
- (18) Nakashima, H.; Fujiki, M.; Koe, J. R. *Macromolecules* **1999**, *32*, 7707.
- (19) Gill, D.; Jagur-Grodzinsky, J.; Swarc, M. *Trans. Faraday Soc.* **1964**, *60*, 1424.
- (20) Seki, S.; Grozema, F. C.; Candeias, L. P.; Warman, J. M.; Kawamori, T.; Tagawa, S. *J. Am. Chem. Soc.*, submitted.
- (21) Abkowitz, M. A.; Rice, M. J.; Stolka, M. *Philos. Mag.* **1990**, *B61*, 25.
- (22) Cotts, P.; Miller, R. D.; Sooriyakumaran, R. In *Silicon Based Polymer Science*; Zeigler, J. M., Fearon, F. W. G., Eds.; American Chemical Society: Washington, DC, 1990; Chapter 23, p 397.
- (23) Koe, J. R.; Fujiki, M.; Motonaga, M.; Nakashima, H. *Macromolecules* **2001**, *34*, 1082.
- (24) Estimation of persistence length, q , of **PMPS**. Using values for Si–Si bond length (0.2414 nm) and Si–Si–Si bond angles (114.4°) derived from X-ray diffraction study of poly(dichlorosilane) (see: Koe, J. R.; Powell, D. R.; Buffy, J. J.; Hayase, S.; West, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1441), and viscometric data calculated based on the following empirical relationships: $\epsilon = 1130 \exp(2.90\alpha)$ (see ref 8), where α is the viscoscosity index and ϵ is the lowest excitonic backbone peak intensity per silicon repeating unit ($\epsilon = 8700 \text{ (mol/dm}^3\text{)}^{-1} \text{cm}^{-1}$ for **PMPS**), $R_g = \kappa M^\nu$, where R_g is the chain radius of the gyration, κ is the constant, M is the molecular weight of the polymer, and $\nu = 1/3(\alpha+1)$. The mean-square end-to-end distance $\langle r^2 \rangle$ is derived from the R_g , and the Kuhn segment length of the polymer at the chosen molecular weight is given by $l_k = \langle r^2 \rangle M_L / M$, where M_L is the mass per unit length, and estimated as 590 nm^{-1} for **PMPS**. Since $l_k = 2q$, the persistence, q , therefore approximates to 1.1 nm. For other experimental data of q in conventional polysilanes, see ref 22.
- (25) Hoshino, S.; Furukawa, K.; Ebata, K.; Yuan, C.-H.; Suzuki, H. *J. Appl. Phys.* **2000**, *88*, 2892.
- (26) Hoshino, S.; Furukawa, K.; Ebata, K.; Brely, I.; Suzuki, H. *J. Appl. Phys.* **2000**, *88*, 3408.