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Initial Process of Photoinduced Electron Transfer Reactions of High Molecular Weight Polysilanes to Electron Deficient Sensitizers in Solution

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Fluorescence of 9-cyanoanthracene (CA), 9,10-dicyanoanthracene (DCA) and triphenylpyrylium tetrafluoroborate ($TPP^+BF_4^-$) was quenched by high molecular weight polysilanes in dichloromethane (CH_2Cl_2). The quenching process of fluorescence of sensitizer by polysilanes polymer framework was investigated by measuring quenching rate constant. Small quenching rate constants in the order of 10^8-10^9 mol^{-1} dm^3 s^{-1} were observed for high molecular weight polysilanes, however observation of transient absorption spectrum of pyryl radical (TPP•) was the direct evidence of electron transfer from polysilanes to TPP^+.

Polysilanes are quite unique molecules consisted of silicon chain and chemical properties such as absorption maximum wavelength, ionization potential, electrochemical oxidation potential and so on change with numbers of silicon atoms (n) in a silicon chain. These are explained as σ-conjugation.1)

The fluorescence quenching rate constants of DCA increased with increasing of silicon atoms in silane compounds (n=2 to 6).2) This is explained by changing of the oxidation potentials of oligosilanes with chain length of silicon atoms, and exothermicity of electron transfer process changes with n. The photochemistry of the oligosilanes and electron deficient sensitizers are reviewed very well in a literature.2) In some cases, it is reported that characteristic products are obtained.3) In this paper, we would like to report our investigation of an initial process of photoinduced electron transfer reaction of a polysilane to an electron deficient sensitizer (CA, DCA and TPP^+). The quenching rate constants are very small, however, it is succeeded to obtain direct evidence of electron transfer in the case of TPP^+ sensitization. The small quenching rate constant means the chromophore involved in a quenching process is very long silicon chain unit. The degradation of polysilane by scissions of silicon chain is quite efficient but observation of reaction intermediates by transient absorption was unsuccessful at this moment.

All high molecular weight polysilanes were synthesized by Wurtz type coupling reaction from corresponding dichlorosilane with sodium in toluene as reported.4,5) Dodecamethylcyclohexasilane were used as received (Petrarch). Tetradecamethyl-n-hexasilane was synthesized as reported,6) and purified by GLC (silicone OV-17). Molecular weight (Mw) of polysilanes were characterized by GPC with polystyrene standards. Mw's of polysilanes are 5.2-150×10^4 (Mw/Mn= 1.9-3.8) depending on the substituenets and those correspond to 350-8600 silicon atoms in a polymer chain. Characteristics of polysilanes used in this experiment will be reported elsewhere. Absorption and fluorescence spectra were measured in argon purged CH_2Cl_2

(Dotite) by Hitachi U-3000 and F-4010 spectrometer, respectively. Transient absorption spectra and fluorescence lifetime were measured using the systems at University of Tsukuba based on an excimer laser (XeCl, Lambda Physik LPX-105)-pumped dye laser (FL-3002, Stilbene-3 dye, λ=425 nm), and Horiba NAES-1100 time-resolved fluorometer (single photon counting), respectively.

Fig. 1a depicts absorption spectra of poly[di-n-hexylsilane] (1.4×10^{-4} M) in the presence of DCA (1.2×10^{-4} M) in argon purged CH_2Cl_2. Decreases and shifts of the absorption band at 317 nm to shorter wavelength were observed on prolonged irradiation of DCA at 425 nm. This is interpreted as being due to a decrease in the average length of the silicon atom chain and is similar to the spectral bleaching observed on direct irradiation of poly[di-n-hexylsilane].[1)] Figure 1b and 1c depict similar bleaching curves for solutions of poly[methylphenylsilane] (3.2×10^{-4} M) sensitized DCA (1.4×10^{-4} M) and CA (8.0×10^{-5} M), respectively. In both cases, polymer degradation was observed. If TPP^+ is used as the sensitizer, polymer degradation and efficient bleaching of the yellow color of TPP^+ are both observed. DCA is more stable under these conditions than either CA or TPP^+. The bleaching is likely due to the reaction of sensitizer with radicals as previously reported.[7)]

The intensity and lifetime of fluorescence were measured using the fluorometer and the single-photon counting apparatus in argon purged CH_2Cl_2. The overall reaction sequence is shown in Eqs.1-5 with the Stern-Volmer relationship listed as Eq. 10. Using this equation and plotting either τ_0/τ or I_0/I vs polysilane concentration a line with slope $k_q\tau_0$ is obtained. Using the value of τ_0 measured by single photon counting (12.2, 14.5, and 2.9 ns for DCA, CA, and TPP^+, respectively) k_q can be determined. In the case of TPP^+, TPP^+ is a cation therefore neutral TPP• is generated by an electron transfer reaction (Eq. 5').

The measured k_q's are listed in Table 1. It is important to note that the concentration of the polymer is based on the molecular weight of monomer segment. The exothermicity of the electron transfer process[8a)] is quite high as expected from reduction potentials of the sensitizers (E_{red}, $\Delta E_{0,0}$, and $^*E_{red}$ are -0.89, 2.86, and 1.97 for DCA, -1.70, 3.10, and 1.40 for CA and -0.29, 2.82, and 2.53 for TPP^+, respectively)[8b)] and oxidation potentials of the polymers.[9,10)] Quenching rate constants for series of oligosilanes are also included in Table 1. Note that for disilanes and hexasilanes the quenching rate constants of TPP^+ fluorescence are consistent with diffusion controlled quenching. This is not the case for DCA quenching where disilanes have significantly slower rate constants than the hexasilanes. This is consistent with previous reports of DCA quenching in which a decrease in the quenching rate constant from hexasilane to disilane was correlated with a

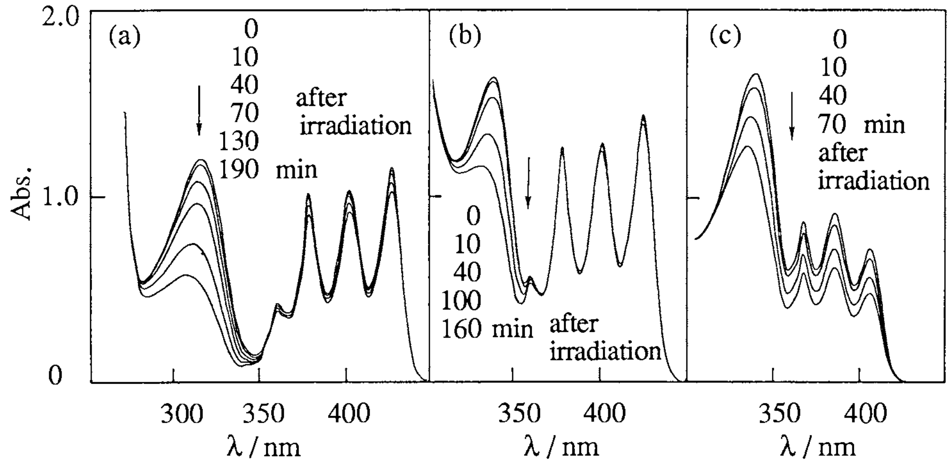

Fig. 1. Change of absorption spectra by irradiation of sensitizer (a and b: DCA; c:CA) in the presence of poly[di-n-hexylsilane] (a) and poly[methylphenylsilane] (b and c) in argon purged CH_2Cl_2.

Table 1. Quenching Rate Constants $(k_q)^{a)}$ of Fluorescence of Sensitizers by Polysilanes

Silanes	DCA		CA		TPP$^+$	
	I_0/I b)	τ_0/τ c)	I_0/I b)	τ_0/τ c)	I_0/I b)	τ_0/τ c)
Poly[4-methoxyphenylmethylsilane] d)	1.0	0.57	1.1	0.47	1.6	1.5
Poly[methylphenylsilane] d)	0.94	0.58	0.80	0.54	0.87	0.73
Poly[methyl-β-phenethylsilane] d)	0.85	0.35	0.29	0.28	0.39	0.30
Poly[propylmethylsilane] d)	0.50	0.33	0.41	0.35	0.58	0.43
dodecamethylcyclohexasilane	21	16	1.4	2.1	29	27
n-tetradecamethylhexasilane	19	22	7.2	8.9	24	25
tetramethyl-1,2-diphenyldisilane	7.3	7.9	5.7	4.8	23	20
hexamethyldisilane e)	2.4					

a) Listed as k_q / 10^9 mol^{-1} dm^3 s^{-1}. b) From Stern-Volmer plot of intensity. c) From Stern-Volmer plot of lifetime. d) Concentration based on molecular weight of monomeric unit. e) From Ref. 2.

$$\mathrm{Sens} \xrightarrow{h\nu} {}^1\mathrm{Sens}^* \tag{1}$$

$$ {}^1\mathrm{Sens}^* \xrightarrow{k_d} \mathrm{Sens} \tag{2}$$

$$ {}^1\mathrm{Sens}^* \xrightarrow{k_f} \mathrm{Sens} + h\nu' \tag{3}$$

$$ {}^1\mathrm{Sens}^* \xrightarrow{k_{isc}} {}^3\mathrm{Sens}^* \tag{4}$$

$$ {}^1\mathrm{Sens}^* + \mathrm{Si} \xrightarrow{k_q[\mathrm{Si}]} \mathrm{Sens}^{\bar{\cdot}} + \mathrm{Si}^{+\cdot} \tag{5}$$

$$ {}^1\mathrm{TPP}^{+*} + \mathrm{Si} \xrightarrow{k_q[\mathrm{Si}]} \mathrm{TPP}\bullet + \mathrm{Si}^{+\cdot} \tag{5'}$$

$$\tau_0 = 1/(k_d + k_f + k_{isc}) \tag{6}$$

$$\tau = 1/(k_d + k_f + k_{isc} + k_q[\mathrm{Si}]) \tag{7}$$

$$I_0 = k_f \tau_0 \tag{8}$$

$$I = k_f \tau \tag{9}$$

$$\tau_0/\tau = I_0/I = 1 + k_q \tau_0 [\mathrm{Si}] \tag{10}$$

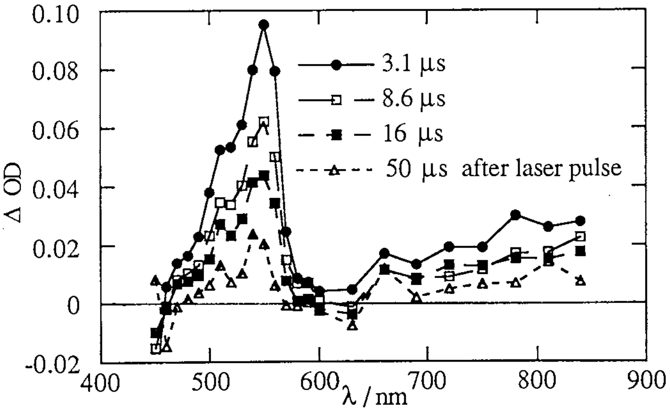

Fig. 2. Transient absorption spectra derived from laser excitation of TPP$^+$ in the presence of poly(methylphenylsilane) (0.12 mol dm^{-3}) in CH_2Cl_2 under argon.

corresponding increase in the oxidation potential (disilane>diphenyldisilane>cyclohexasilane>hexasilane).[9,10] The low oxidation potentials of the high molecular weight polysilanes would be expected to result in very exothermic electron transfer, however the quenching rate constants are still quite low (10^8 mol^{-1} dm^3 s^{-1}). Part of this discrepancy is due to the way in which we have evaluated polymer concentration in terms of monomer units since silicon chains should be the actual quenching chromophore. The trans-gauche model reported[11] for the excited singlet state might not be important in the ground state since very long chain acts as chromophore. The decreased mobility of polysilane polymer will also result in a decrease in the quenching constant. Finally the steric effect of the bulky sidechain substituent should also result in differences in the quenching rate constant. We were unable to observe any evidences of a static quenching component (the Stern-Volmer plots were linear over the concentration range studied) nor was any change in the absorption or fluorescence spectra observed due to complexation. The small difference of the k_q might originate from interference of absorption of light to sensitizer by the weak polysilane absorption during the measurement of the fluorescence intensity.

In addition to the fluorescence quenching measurements described above we also studied the transient absorption spectra of these systems. We were able to observe pyryl radicals (TPP•) following laser excitation

(λ = 425 nm) of TPP^+ (2.5×10^{-4} mol dm^{-3}) in the presence of poly[4-methoxyphenylmethylsilane], poly[methyphenylsilane], poly[methypropylsilane] and dodecamethylcyclohexasilane in argon purged CH_2Cl_2, in all cases we examined. The spectra can be assigned to pyryl radicals (TPP•) by comparison with the spectrum reported.12) Under the conditions employed here dodecamethylcyclohexasilane (0.054 mol dm^{-3}) quenches 80% of excited TPP^+ singlets while poly(methylphenylsilane) (0.12 mol dm^{-3}) quenches only 20%. In the latter case, TPP· is still observed in fairly high optical density as seen in Fig. 2. This suggests the possibility of electron transfer from the excited triplet states ($^3TPP^{+*}$), Eq. 12, as proposed for oxidation of olefins.12b) The excited state reduction potential ($^*E_{red}$) for $^3TPP^{+*}$ is 2.01 ($\Delta E_{0,0}$ and $^*E_{red}$ are 2.30 and 2.01, respectively) comparable to that of $^1DCA^*$. $^3TPP^{+*}$ (at λ = 850 nm, $\tau_T = 1/k_d' = 10\ \mu s$) was quenched with rate constant (k_q') 5×10^8 mol^{-1} dm^3 s^{-1}. This corresponds to that >99% of triplets are quenched.

$$^3TPP^{+*} \xrightarrow{k_d'} TPP^+ \quad (11), \quad ^3TPP^{+*} + Si \xrightarrow{k_q'[Si]} TPP\bullet + Si^{+\bullet} \quad (12)$$

To date we have been unable to detect any other reaction intermediates (i.e. polysilane radicals cation,13) radicals or the radical anions of DCA or CA) in CH_2Cl_2. This may be a consequence of fast back electron transfer since inefficient separation of the cation and the anion radicals comparing to the case of neutral TPP• in these systems. Also charge separation by a migration of a hole along the silicon chain must be slow.

Further studies on the reaction products and detailed reaction mechanisms are in progress.

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References

1) R. D. Miller and J. Michl, *Chem. Rev.*, **89**, 1359 (1989), and references cited therein.
2) Y. Nakadaira, S. Kyushin, and M. Ohashi, *Yuki Gosei Kagaku Kyokaishi*, **48**, 331 (1990).
3) Y. Nakadaira, N. Komatsu, and H. Sakurai, *Chem. Lett.*, **1985**, 1781; Y. Nakadaira, A. Sekiguchi, Y. Funada, and H. Sakurai, *ibid.*, **1991**, 327.
4) J. F. Rabolt, D. Hofer, R. D. Miller, and G. N. Fickes, *Macromolecules*, **19**, 611 (1986).
5) L. A. Harrah and J. M. Zeigler, *Macromolecules*, **20**, 601 (1987).
6) M. Kumada and M. Ishikawa, *J. Organomet. Chem.*, **1**, 153 (1964).
7) S. Kyushin, Y. Nakadaira, and M. Ohashi, *Chem. Lett.*, **1990**, 2191.
8) a) D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 258 (1970). b) M. Chanon and L. Eberson, "Photoinduced Electron Transfer," ed by M. A. Fox and M. Chanon, Elsevier, Amsterdam (1988), Part A, p. 470.
9) H. Watanabe, K. Yoshizumi, T. Muraoka, M. Kato, Y. Nagai, and T. Sato, *Chem. Lett.*, **1985**, 1683; W. G. Boberski and A. L. Allred, *J. Organomet. Chem.*, **88**, 65 (1975).
10) Private communications, R. D. Miller, M. Baier, A. F. Diaz, E. J. Ginsburg, and G. M. Wallraff, submitted to *Pure Appl. Chem.*
11) K. A. Klingensmith, J. W. Downing, R. D. Miller, and J. Michl, *J. Am. Chem. Soc.*, **108**, 7438 (1986).
12) a) F. Pragst, *Electrochim. Acta*, **21**, 497 (1976); b) R. Akaba, H. Sakuragi, and K. Tokumaru, *J. Chem. Soc., Perkin Trans. 2*, **1991**, 291.
13) S. Irie, K. Oka, and M. Irie, Macromolecules, **21**, 110 (1988).

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