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Pulse Radiolysis Study on Organopolysilane Radical Anions

Hiroshi Ban* and Ken Sukegawa

NTT Electrical Communications Laboratories, Tokai Ibaraki 319-11, Japan

Seiichi Tagawa

Research Center for Nuclear Science and Technology, University of Tokyo, Tokai Ibaraki 319-11, Japan.

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ABSTRACT: Poly(methylpropylsilane) (PMPrS) and poly(methylphenylsilane) (PMPS) were investigated by pulse radiolysis with 2-ns time resolution. PMPrS and PMPS solutions in tetrahydrofuran (THF) exhibit strong single absorption bands at 363 and 372 nm, respectively, in the transient spectra. These transient species react with pyrene to produce pyrene radical anions. They also decay in reaction with added $CHCl_3$. Chloromethylated PMPS does not exhibit such a transient absorption, indicating that electron dissociative attachment occurs. These facts indicate that the observed transient species are radical anions. The polymer radical anions have a long lifetime and do not decay within 150 ns. The extinction coefficients of PMPrS and PMPS radical anions are both $(1.6 \pm 0.2) \times 10^5\ M^{-1}\ cm^{-1}$. The electron-transfer rate from polymer radical anions to pyrene is $(1.2 \pm 0.1) \times 10^{10}\ M^{-1}\ s^{-1}$ for PMPrS and $(1.4 \pm 0.2) \times 10^{10}\ M^{-1}\ s^{-1}$ for PMPS. The reaction rate of PMPrS with the solvated electron in THF is $(3.4 \pm 0.5) \times 10^9\ M^{-1}\ s^{-1}$.

Introduction

Organopolysilanes have unique optical properties. They have strong UV absorption bands in the 300–360-nm region,[1] which has been attributed to σ–σ^* or σ–3π transitions.[2-4] As the chain length increases, they show a bathochromic shift which is thought to arise from delocalization of the σ electrons.[5] Although organopolysilanes consist of Si–Si single bonds, they resemble carbon conjugative compounds. Extended Hückel MO calculation has shown that cyclic organopolysilanes have similar energy levels to benzene.[6] Recently, poly(methylphenylsilane) has been found to exhibit nonlinear optical properties.[7]

Si–Si bonds of organosilanes are broken by UV irradiation to produce radical fragments or silylene.[8] This photoreaction and the photoinduced radical species have been thoroughly investigated in terms of their application to photoresists.[9-11] Concerning their ionic states, cyclic organopolysilanes, such as $(Si(CH_3)_2)_n$ (n = 4–6) and $(Si(C_6H_5)_2)_m$ (m = 4, 5), form radical anions by reduction with alkali metal[6,12-14] and radical cations by oxidation with $AlCl_3$.[15] ESCA studies have shown that unpaired electrons of these ions are delocalized over the ring skeleton. Properties of ionic states of linear organopolysilanes have not yet been reported. If they are ionized, the unpaired electron is expected to be delocalized along the polymer chain. The electric properties of linear organopolysilanes seem interesting from the viewpoint of their potential semiconductivity.[16]

This report deals with radical anions of high molecular weight linear organopolysilanes, poly(methylpropylsilane) (PMPrS) and poly(methylphenylsilane) (PMPS). Their optical properties and kinetics were determined by means of pulse radiolysis.

Experimental Section

PMPrS and PMPS were prepared according to the method previously reported.[17] Molecular weight was measured by gel permeation chromatography (GPC) on the basis of the standard polystyrene. Weight average molecular weight (M_w) and polydispersity (M_w/M_n) of PMPrS were 2.1×10^4 and 2.1 and those of PMPS were 22.4×10^4 and 5.7. Chloromethylated PMPS (CMPMPS) was also prepared according to the method used for the chloromethylation of polystyrene[18] and poly(diphenylsiloxane).[19] Two grams of PMPS was dissolved in a mixture of 20 mL of chloromethyl methyl ether and 20 mL of chloroform. Two grams of $SnCl_4$ was slowly dropped into the solution at 0 °C. After stirring for 15 h at 5 °C, the solution was poured into methanol to obtain CMPMPS. CMPMPS was refined by sedimentation twice with tetrahydrofuran (THF)–methanol. The yield was 90%. M_w and M_w/M_n of CMPMPS were 2.7×10^4 and 2.4, respectively. Chloromethyl groups are thought to attach on para or ortho positions of phenyl groups by the Friedel–Crafts reaction.

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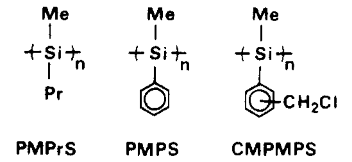

Figure 1. Molecular structures of poly(methylpropylsilane) (PMPrS), poly(methylphenylsilane) (PMPS), and chloromethylated PMPS (CMPMPS).

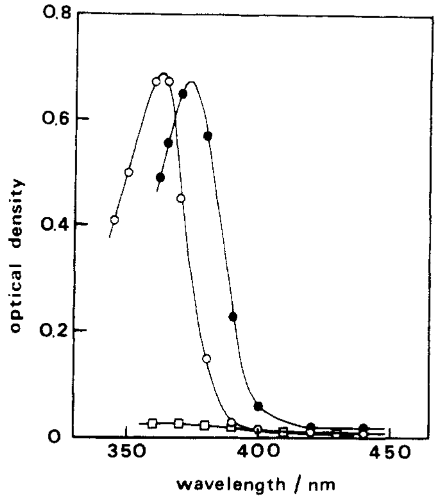

Figure 2. Transient UV absorption spectra of PMPrS, PMPS, and CMPMPS in THF solutions at 40 ns after an electron pulse: (○) 93 mM PMPrS, (●) 123 mM PMPS, (□) 2 mM CMPMPS.

The existence of the chloromethyl group and Si-Si bond in CMPMPS was confirmed by the IR spectrum. The ratio of chloromethylation of phenyl groups was found to be over 95 mol % from the ^{1}H NMR spectrum. The UV absorption peak (λ_{max}) of CMPMPS in THF solution appeared at 340 nm, and its molar extinction coefficient was 8.2×10^3 per Si–Si unit. Molecular structures of PMPrS, PMPS, and CMPMPS are drawn in Figure 1. Insoluble materials produced during polymerization were eliminated with a micropore filter.

All solutions for pulse radiolysis measurements, were prepared on the vacuum line. THF was dehydrated with sodium metal and distilled into the cell on the line. The samples were degassed 3 times under 2×10^{-4} Torr.

The pulse radiolysis measurement was performed with the linear accelerator instruments at the University of Tokyo.[20,21] The samples were irradiated with a 2-ns single pulse electron beam at room temperature, and their electronic absorption spectra were measured. Acquisition time was 200 ns.

Results and Discussion

The absorption spectra of transient species were observed by 2-ns electron pulse irradiation for both PMPrS and PMPS solutions in THF. Their UV spectra at 40 ns after the pulse revealed single absorption bands as shown in Figure 2. λ_{max} appeared at 363 nm for PMPrS and at 372 nm for PMPS. This 363-nm band is 57 nm longer than λ_{max} of PMPrS in THF, 306 nm, and the 372-nm band is 32 nm longer than λ_{max} of PMPS, 340 nm. The transient absorption change at 365 nm for 93 mM PMPrS solution was shown in Figure 3. No decay was observed at 365 nm, and the shape of the absorption spectrum did not change within the acquisition time. When the polymer concentration was low, growth of the transient absorption band was easily observed. Its λ_{max} and shape did not changed during this growth period. No other preceding transient absorption bands were observed.

These bands were not likely to be due to benzyl-type radicals, which usually appear at 300–320 nm.[22] They are believed to correspond to anionic species since they are generally much more stable than cation species in THF.

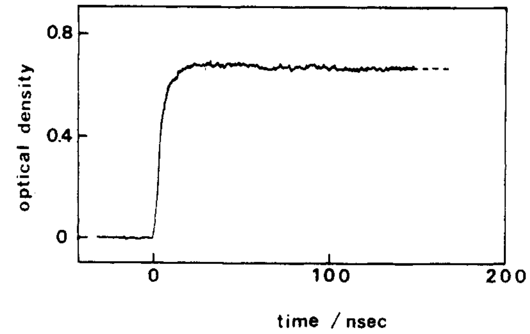

Figure 3. Optical density change of 93 mM PMPrS solution in THF after the pulse, which was monitored at 365 nm.

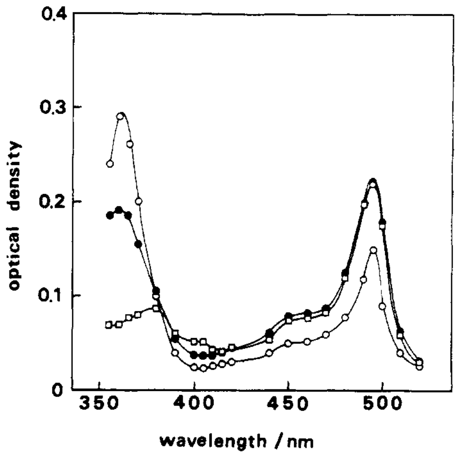

Figure 4. Transient UV–vis absorption spectra of 69 mM PMPrS solution with 2.2 mM pyrene immediately (○), 20 ns (●), and 60 ns (□) after an electron pulse.

λ_{max} values of $(SiMe_2)_5^{\bullet -}$ and $(SiMe_2)_6^{\bullet -}$, 645 and 425 nm,[12] are relatively longer than the λ_{max}s in Figure 2. However, λ_{max}s of cyclic organopolysilane radical anions shift to the shorter wavelength side as the ring size becomes large. A linear polymer with a large degree of polymerization can be regarded as the infinite state of increasing ring size of cyclic compounds. Therefore, λ_{max}s in Figure 2 seemed to be appropriate for radical anions. Then anion scavengers were used to confirm this assignment. When a small amount of pyrene was added into PMPrS solution, the transient absorption band with λ_{max} at 363 nm rapidly decayed as shown in Figure 4. And the absorption band with λ_{max} at 493 nm, assigned to pyrene radical anion, increased as the 363-nm peak decreased. Absorption bands for pyrene radical cations were not observed. Figure 4 shows that the electron-transfer reaction took place from the transient species to pyrene. The same behavior was observed for PMPS. When a small amount of $CHCl_3$ was added, the transient absorption bands also decayed rapidly and completely with a single exponential curve. No other absorption band appeared during the decay. These results confirm that the transient species should be assigned to radical anions. Furthermore, CMPMPS solution in THF did not exhibit such a transient absorption band as shown in Figure 1. The chloromethyl group in CMPMPS is thought to unstabilize anions as halides usually scavenge them. In the case of chloromethylated polystyrene, the solvated electron reacts with chloromethyl groups, and Cl^- and radical fragments are produced.[22] Such electron dissociative attachment is thought to occur similarly in the case of CMPMPS. This supports the assignment discussed above that radical anions of PMPrS and PMPS were produced by the reaction with the solvated electron which was generated by the electron pulse irradiation to THF.

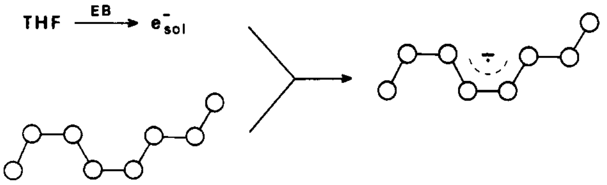

Figure 5. Scheme of the reaction and the resulting polymer radical anion. EB denotes electron beam. Polymer molecule is simply represented by the skeleton of catenating Si atoms. Solvated electron is generated by the electron beam irradiation to THF and then reacts on polymer molecule.

This reaction is schematically drawn in Figure 5. Added electrons in the polymer radical anions are expected to delocalize along the catenated silicon atoms since added electrons in cyclic polysilane radical anions are delocalized over the silicon atoms.[12,23]

The absorption bands of PMPrS and PMPS in the THF solution appear at 306 and 340 nm, respectively. Electronic interaction between the main chain and the phenyl groups in PMPS, which is σ–π mixing between Si_{3p} and C_{2p} orbitals,[24,25] causes a lowering of the transition energy. The λ_{max} of PMPS radical anion appeared 9 nm longer than that of PMPrS radical anion. This shift is probably attributed to the delocalization of the added electron over the phenyl groups as well as the main chain.

A cyclic polysilane and a disilane were also investigated. $(SiMe_2)_6$ solution in THF did not exhibit any distinct transient absorption bands in 300–600-nm region, whereas λ_{max} of electrolytically reduced $(SiMe_2)_6{}^{\bullet -}$ appears at 425 nm. When 5.7 mM pyrene was added into 137 mM $(SiMe_2)_6$ solution, pyrene radical anion was produced quite similarly to the pyrene solution after the pulse. The solvated electron was completely captured by added pyrene and did not react with $(SiMe_2)_6$. $(SiMe_3)_2$ solution in THF exhibited a similar behavior, and its radical anion was not observed.

Electron-transfer reaction rates and extinction coefficients of polymer radical anions, ϵ, were determined at room temperature. The extinction coefficients were obtained on the basis of ϵ for pyrene radical anion.[26] Reaction equations can be written as

$$P^{\bullet -} + Py \xrightarrow{k_1} P + Py^{\bullet -} \qquad (1)$$

$$Py^{\bullet -} + X \xrightarrow{k_2} Py \qquad (2)$$

where P, Py, and X denote polymer, pyrene, and counterion, respectively, and k_1 and k_2 are rate constants. Concentration units of polymer and polymer radical anion were defined as mole of Si–Si unit per liter and mole of added electron per liter, respectively. The decay rate of pyrene radical anion, k_2, was determined to be 3.4×10^6 s^{-1} for a 2.9 mM pyrene solution in THF. $k_1 = (1.2 \pm 0.1) \times 10^{10}$ M^{-1} s^{-1}, $k_2 = (3.8 \pm 0.3) \times 10^6$ s^{-1}, and $\epsilon = (1.6 \pm 0.2) \times 10^5$ M^{-1} cm^{-1} were obtained for PMPrS solution with pyrene. k_1 values independently calculated from the decay curve of $P^{\bullet -}$ and the growth curve of $Py^{\bullet -}$ were coincided closely. This k_2 value agreed with that for the pyrene solution. These agreements in k_1 and k_2 assure accuracy of these values. $k_1 = (1.4 \pm 0.2) \times 10^{10}$ M^{-1} s^{-1}, $k_2 = (3.6 \pm 0.3) \times 10^6$ s^{-1}, and $\epsilon = (1.6 \pm 0.2) \times 10^5$ M^{-1} cm^{-1} were also obtained for PMPS solution with pyrene. λ_{max}, ϵ, and k_1 are summarized in Table I. Both PMPrS and PMPS revealed similar ϵ, k_1, and k_2 values. The observed ϵ values of polymer radical anions were quite large compared with those of PMPrS and PMPS solutions in THF, which were 5.9×10^3 and 1.1×10^4 per Si–Si unit, respectively. The reason for these strong absorptions of polymer radical anions is thought to be that the excess electron density is more polarizable and the increased polarizability leads to greatly enhanced oscillator strengths for the absorption.

Table I
Summary of λ_{max}, ϵ, k_1, and k_3

	λ_{max}, nm	ϵ,[a] M^{-1} cm^{-1}	k_1, M^{-1} s^{-1}	k_3, M^{-1} s^{-1}
PMPrS	306	5.9×10^3		
PMPS	340	1.1×10^4		
$PMPrS^{\bullet -}$	363	$(1.6 \pm 0.2) \times 10^5$	$(1.2 \pm 0.1) \times 10^{10}$	$(3.4 \pm 0.5) \times 10^9$
$PMPS^{\bullet -}$	372	$(1.6 \pm 0.2) \times 10^5$	$(1.4 \pm 0.2) \times 10^{10}$	

[a] Extinction coefficient is defined as Si–Si unit for polymers and added electron unit for polymer radical anions.

The solvated electron was captured by polymers before reactions of eq 1 and 2.

$$P + e_{sol}{}^{-} \xrightarrow{k_3} P^{\bullet -} \qquad (3)$$

Rate constant k_3 can be obtained from the slope of the logarithm of the apparent reaction rate vs. polymer concentration. By the use of five different concentration samples, k_3 was determined to be $(3.4 \pm 0.5) \times 10^9$ M^{-1} s^{-1} for PMPrS, which is also summarized in Table I. k_3 for PMPS was not determined accurately; however, it appeared to be near the k_3 value for PMPrS, judged from its apparent reaction rate.

Conclusion

Radical anions of organopolysilanes were studied by pulse radiolysis. Single transient absorption bands were observed at 363 and 372 nm for PMPrS and PMPS solutions in THF. When pyrene was added, these bands decayed and pyrene radical anion was formed. When $CHCl_3$ was added, they also decayed. CMPMPS did not exhibit such a transient absorption band. From these facts, the observed transient absorption bands were assigned to radical anions. Polysilane radical anions did not decay within 150 ns. λ_{max}s of the PMPS radical anion were 9 nm longer than λ_{max}s of the PMPrS radical anion. This shift is probably attributed to the delocalization of added electrons over the phenyl groups as well as the main chain. No distinct peaks corresponding to radical anions were observed for $(SiMe_2)_6$ and $(SiMe_3)_2$ solutions in THF.

Kinetics and extinction coefficients of PMPrS and PMPS radical anions were determined. Electron-transfer rate from polymer anions to pyrene were $(1.2 \pm 0.1) \times 10^{10}$ and $(1.4 \pm 0.2) \times 10^{10}$ M^{-1} s^{-1} for PMPrS and PMPS, respectively. Extinction coefficients of PMPrS and PMPS radical anions were both $(1.6 \pm 0.2) \times 10^5$ M^{-1} cm^{-1}. The reaction rate of PMPrS with the solvated electron was determined to be $(3.4 \pm 0.5) \times 10^9$ M^{-1} s^{-1}.

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Registry No. PMPrS, 88003-13-8; PMPS, 76188-55-1; $(SiMe_2)_6$, 4098-30-0; $(SiMe_3)_2$, 1450-14-2; pyrene, 129-00-0.

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Ionic Conductivity in Branched Polyethylenimine–Sodium Trifluoromethanesulfonate Complexes. Comparisons to Analogous Complexes Made with Linear Polyethylenimine

Caroline S. Harris, Mark A. Ratner,* and Duward F. Shriver*

Department of Chemistry and Materials Research Center, Northwestern University, Evanston, Illinois 60201.

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ABSTRACT: Complexes between branched polyethylenimine and $NaSO_3CF_3$ were formed with a polymer repeat unit to salt ratio of 6:1, 12:1, and 20:1. All three complexes are amorphous in contrast to linear polyethylenimine which forms partially crystalline complexes at ratios above 6:1 (lower salt concentrations). The 6:1 complex of branched polyethylenimine has a higher T_g (12 °C) and a lower conductivity (10^{-8} S/cm at 40 °C) than the corresponding complex of linear polyethylenimine (−5 °C and 10^{-7} S/cm). The glass transition temperature of the polymer–salt complex decreases by 43 deg upon decreasing the salt concentration from that of the 6:1 complex to that of the 20:1 complex. Correspondingly, the conductivity of the 20:1 complex at 40 °C is 2 orders of magnitude higher than that of the 6:1 complex. N–H stretching frequencies of linear and branched polyethylenimines and their polymer–salt complexes were studied by infrared spectroscopy. An increase in frequency of the N–H stretching mode of both polymers is seen upon complex formation.

Introduction

Solid polymer electrolytes have attracted considerable attention due to their potential application in high energy density batteries.[1,2] These solvent-free systems consist of a solid polymer host in which a salt, usually an alkali metal salt, has been dissolved. Polymer–salt complexes can either be fully amorphous or partially crystalline depending on the polymer and salt employed. Crystalline polymer–salt complexes have the disadvantage of multiphase behavior which greatly complicates the study of their ion-transport and decreases conductivity.[3,4]

Polymer characteristics which should favor polymer–salt complex formation include a low glass transition temperature, T_g, and a high concentration of polar groups.[5] The majority of studies in the past have focused on polymers with ether oxygens as the polar groups. These polymers include linear polymers such as poly(ethylene oxide), PEO, and poly(propylene oxide), PPO, with which the initial studies of polymer electrolytes were made.[2] Other polymer hosts with ether oxygens as the polar group include comblike polymers[6,7] and cross-linked polymer networks.[8,9]

Recently polymers with polar groups other than oxygen have been investigated. One such study from our laboratory utilized poly(alkylene sulfides) to form complexes with the silver salts, silver nitrate and silver trifluoromethanesulfonate.[10] Linear polyethylenimine, LPEI, with secondary nitrogens as the polar groups has been shown by us[11] and others[12] to form conductive polymer–salt complexes with alkali-metal salts. There is also a branched form of polyethyleneimine, BPEI, which has a ratio of primary-to-secondary-to-tertiary nitrogens of 1:2:1.[13,14] BPEI is fully amorphous and has a T_g of 226 K, 27 deg lower than that of LPEI. In the present research, we investigated complex formation between BPEI and sodium trifluoromethanesulfonate, $NaSO_3CF_3$. We determined the conductivity of the BPEI–$NaSO_3CF_3$ complexes and compare our results to our previous study with LPEI.

Experimental Section

BPEI was obtained as a 50% solution in water, average molecular weight 50 000–60 000 (Aldrich Chemical Co.). The polymer was dialyzed under a constant N_2 purge against distilled deionized water which was deaerated by boiling. Cellulose membrane (Union Carbide) was used for the dialysis tubing. After removing the water under reduced pressure, the polymer was further dried under high vacuum (10^{-5} Torr) for 60 h at 58 °C.

Recent grade methanol (MCB) was dried by reflux over iodine-activated magnesium, followed by distillation under a dry nitrogen atmosphere. $NaSO_3CF_3$ was commercial reagent grade material recrystallized from methanol and dried under vacuum at 150 °C. All dried materials were handled in a dry nitrogen or argon atmosphere by using standard Schlenk techniques or in an argon-filled drybox. The polymer–salt complexes were prepared by dissolving stoichiometric quantities of polymer and salt in dried MeOH. After a homogeneous solution was obtained, the methanol was removed under vacuum. The resulting com-

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