Radiation-Induced Degradation of Alkyl-Substituted Polysilanes in Solution

Setsuko Irie*

Research Institute for Advanced Science and Technology, University of Osaka Prefecture, Gakuencho 1-2, Sakai, Osaka 593, Japan

Masahiro Irie

Institute of Advanced Material Study, Kyushu University, Kasuga-koen 6-1, Kasuga, Fukuoka 816, Japan

Received May 9, 1994®

ABSTRACT: Radiation-induced degradation of two alkyl-substituted polysilanes, poly(methyl-*n*-propylsilane) and poly(di-*n*-hexylsilane), has been studied in mixed solvents of *n*-butyl chloride (BuCl) and tetrahydrofuran (THF). The polysilanes readily degraded in BuCl, while the degradation was strongly suppressed by the addition of a small amount of THF. Mechanistic as well as spectroscopic studies revealed that radical cations of the polysilanes play a more important role than the radical anions as intermediates in the radiation-induced degradation.

Introduction

Substituted silane polymers, which contain only silicon atoms in the backbone, represent a new class of radiation-sensitive materials.[1] The polysilanes readily undergo main-chain scission upon irradiation with both UV light and high-energy radiation (γ-rays, X-rays, or electron beams). Although many studies have been carried out concerning photodegradation, little is known about the radiation-induced degradation of polysilanes. Radiation-induced degradation is the key step of electron beam or X-ray lithography.[1]

Polysilanes have an intense electronic absorption band in the near-UV region arising from delocalization of the σ-orbitals of the Si atoms in the backbone. The spectrum depends not only on the nature of the side groups but also on the length and conformation of the backbone. The high fluorescence quantum yield and lack of vibrational coupling in the spectrum suggested that the singlet state is highly delocalized and is not responsible for the main-chain scission.[2] The low quantum yield of phosphorescence and strong vibrational coupling in the triplet spectrum support that the triplet state is the precursor to the homolytic photoinduced bond cleavage. In previous papers,[3] we have studied the absorption spectra of radical anions and cations of polysilanes and their behavior in solution by pulse radiolysis and rigid matrix methods. In this paper, we examine the radiation-induced molecular weight decrease of alkyl-substituted polysilanes in various solvents with the aim of revealing the role of radical ions in the radiation-induced degradation process. The radical ions are considered to play important roles not only in the radiation-induced degradation but also in photoinduced fragmentation and/or subsequent reaction of polysilanes and oligosilanes in the presence of electron donor or acceptor sensitizers.[4]

Experimental Section

Alkyl-substituted polysilanes were synthesized by the Wurtz coupling method, i.e., by reacting dichloroorganosilanes dissolved in toluene with metallic sodium.[5] Tetrahydrofuran (THF), 2-methyltetrahydrofuran (MTHF), *n*-butyl chloride (BuCl), and benzene were purified by repeated distillation. All samples for irradiation were prepared under a reduced pressure of less than 10^{-5} mmHg. Irradiation was carried out with ^{60}Co γ-rays. The molecular weights of the polysilanes were determined by gel permeation chromatography with μ-Styragel (Waters; 10^5, 10^4, 10^3, and 5×10^2 Å) based on polystyrene standards. Electronic absorption spectral measurement was carried out with a Shimadzu UV-3100 spectrophotometer. Absorption spectra of the radical anions and cations of the polysilanes were measured in the frozen glassy solution at 77 K as previously reported.[3]

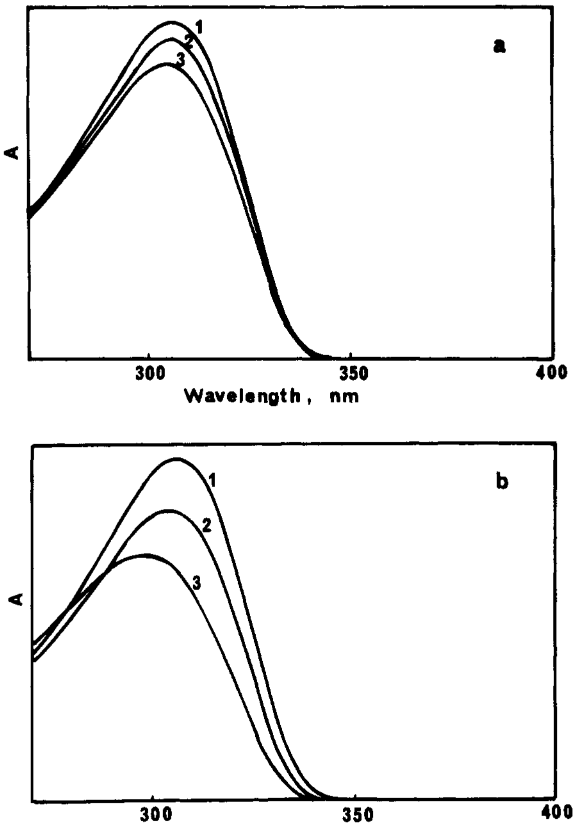

Figure 1. Absorption spectral change of poly(methyl-*n*-propylsilane) in THF (a) and BuCl (b) upon γ-irradiation. Dose rate: 1.5×10^{19} eV/g·h. Curve 1, 0 h; curve 2, 2 h; curve 3, 6 h. [Polysilane] = 1×10^{-2} M.

® Abstract published in *Advance ACS Abstracts,* January 15, 1995.

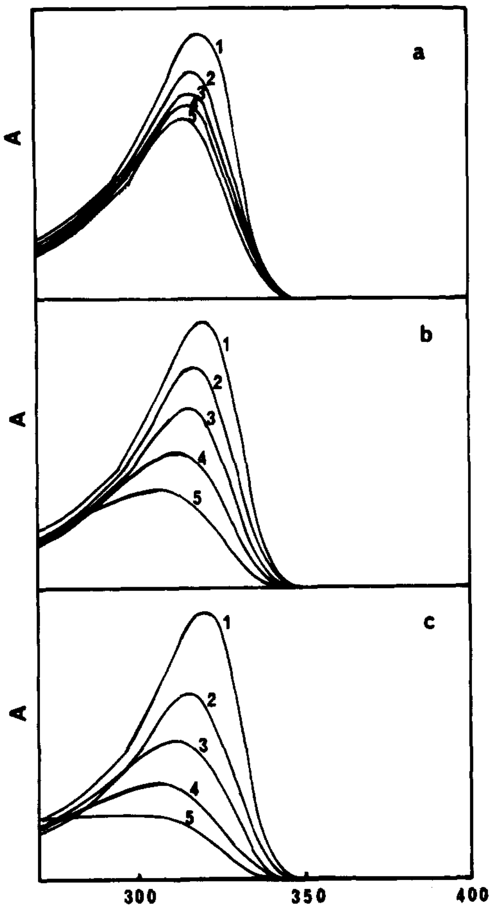

Figure 2. Absorption spectral change of poly(di-*n*-hexylsilane) in THF (a), BuCl (b), and benzene (c) upon γ-irradiation. Dose rate: 1.5 × 10^{19} eV/g·h. Curve 1, 0 h; curve 2, 1 h; curve 3, 2 h; curve 4, 4 h; curve 5, 6 h. [Polysilane] = 1 × 10^{-2} M.

Results and Discussion

1. Radiation-Induced Degradation of Polysilanes in Solution. Alkyl-substituted polysilanes exhibit an intense absorption band at 300–330 nm which is assigned to the delocalized σ–σ^* transition.[6] The absorption maximum and the molar extinction coefficient depend on the molecular weight. Both increase rapidly initially with increasing catenation and approach limiting values beyond a degree of polymerization of 40–50.[7] These quantities can be used as a measure of the molecular weight of polysilanes. Panels a and b of Figure 1 show the absorption spectral changes of poly(methyl-*n*-propylsilane) in THF and BuCl upon γ-irradiation, respectively. Before irradiation in the dark, the absorption maxima are observed at 308 nm in both solvents. When the solutions are exposed to γ-rays, the absorption maxima shift to shorter wavelengths and the intensities decrease. These spectral changes indicate that the polymer chains are cleaved by γ-irradiation in both solvents. Similar spectral changes were observed for poly(di-*n*-hexylsilane), which has long alkyl side chains, in THF, BuCl, and benzene, as shown in Figure 2. The progressive blue shift in the absorption maxima suggests that the molecular weight is being continuously reduced upon exposure to γ-rays by a chain scission process. Such spectral bleaching is also reported for alkyl-substituted polysilanes upon exposure to UV light[1,8] and ultrasonic waves.[9]

The molecular weight decreases were confirmed by GPC measurement as demonstrated in parts a and b of Figure 3, which show the decreases in the molecular weight of poly(di-*n*-hexylsilane) in THF and BuCl solution upon γ-irradiation, respectively. Poly(di-*n*-hexylsilane) is degraded to lower molecular weight fragments upon exposure to γ-irradiation. Radiation-induced molecular weight decrease of poly(methyl-*n*-propylsilane) was also confirmed by GPC measurement.

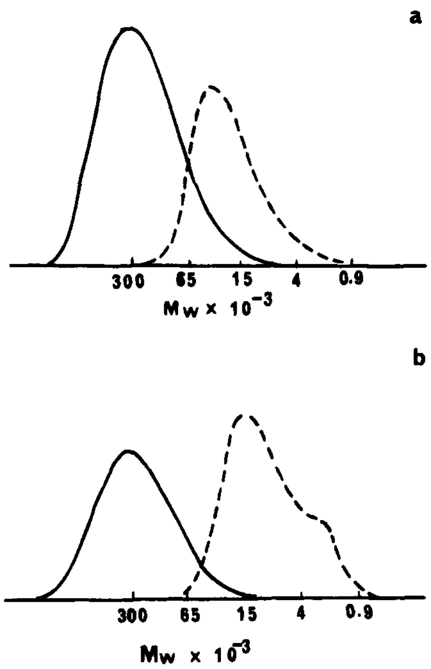

Figure 3. Change in molecular weight distribution of poly(di-*n*-hexylsilane) in THF (a) and BuCl (b) upon γ-irradiation. Molecular weights are the values of polystyrene standards. (—) Original polymer; (- - -) after γ-irradiation, Dose: 6 × 10^{19} eV/g.

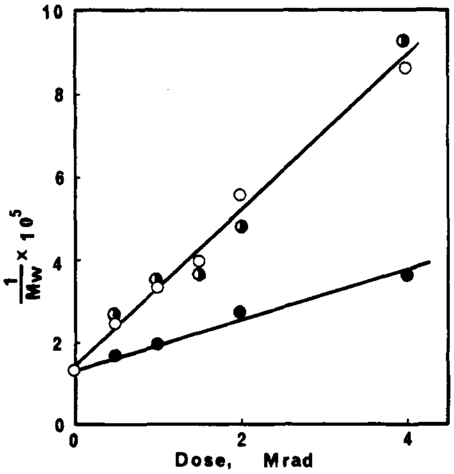

Figure 4. Plot of M_w^{-1} versus absorbed dose for a solution of poly(methyl-*n*-propylsilane) in THF (●), BuCl (◐), and benzene (○). [Polysilane] = 1 × 10^{-2} M.

The IR spectrum of the polysilanes after degradation did not exhibit any absorption at 1030 cm^{-1}. The absence of the IR band at 1030 cm^{-1}, which is characteristic of Si–O–Si bonds, indicates that no oxidation of the silicon backbone occurred under high vacuum in solution. This is in contrast to the result of photodegradation in the presence of air.[8]

High-energy radiation produces various kinds of reactive intermediates, such as radicals, cations, anions, and excited molecules, in polysilane solutions.[10] It is well established[11] that a radical anion is produced in irradiated THF or MTHF by the reaction of an electron

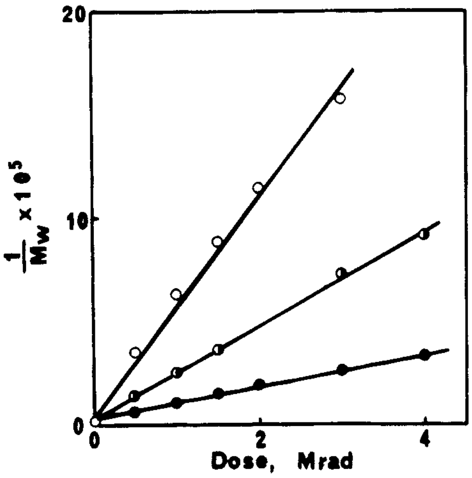

Figure 5. Plot of M_w^{-1} versus absorbed dose for a solution of poly(di-*n*-hexylsilane) in THF (●), BuCl (◑), and benzene (○). [Polysilane] = 1 × 10^{-2} M.

with a solute molecule. On the other hand, a solute radical cation is produced in irradiated BuCl by the reaction of a positive hole with a solute molecule. To reveal the contribution of the radical ion intermediates in the degradation process of polysilanes, poly(methyl-*n*-propylsilane) was irradiated in THF, BuCl, and benzene in the absence of air, and the weight-average molar mass M_w was plotted as a function of irradiated dose, as shown in Figure 4. As can be seen from Figure 4, $1/M_w$ increases linearly with the irradiation dose in the three solvents. The linear plot indicates that the number of backbone scissions of poly(methyl-*n*-propylsilane) is proportional to the incident dose. The molecular weight decrease was much larger in benzene and BuCl than in THF. A similar solvent dependence of the γ-ray-induced degradation was observed for poly(di-*n*-hexylsilane), as shown in Figure 5. More efficient degradation was observed in benzene than in THF and BuCl.

It is generally agreed that the radiolysis of benzene solution leads to the formation of excited states of solute molecules rather than ions and radicals by energy transfer from the solvent to solute molecules.[10] Both excited singlet and triplet states are formed. The results shown in Figures 4 and 5 indicate that excited state formation by energy transfer from benzene to polysilanes caused efficient degradation of the polymers. This is a similar process to that observed for photodegradation. Michl et al. reported that the triplet state is a potential candidate for precursors to the homolytic bond cleavage in the case of photodegradation of alkyl-substituted polysilanes.[2] A similar discussion can be applied to the γ-ray-induced degradation in benzene, because the yield of triplet state solute molecules is relatively high in benzene solution.

The difference in the degradation efficiency between poly(methyl-*n*-propylsilane) and poly(di-*n*-hexylsilane) is attributed to the difference in the energy transfer efficiency. The excited energy of solvent benzene is considered to be readily transferred to poly(di-*n*-hexylsilane) in comparison to poly(methyl-*n*-propylsilane), because both excited singlet and triplet energies of the former polysilanes are lower than those of the latter.

2. Degradation Mechanism via Radical and Radical Ion Intermediates. Besides the excited states, radical ions are also considered to take part in the degradation process. With the aim of revealing the contribution of radical ions in the degradation process,

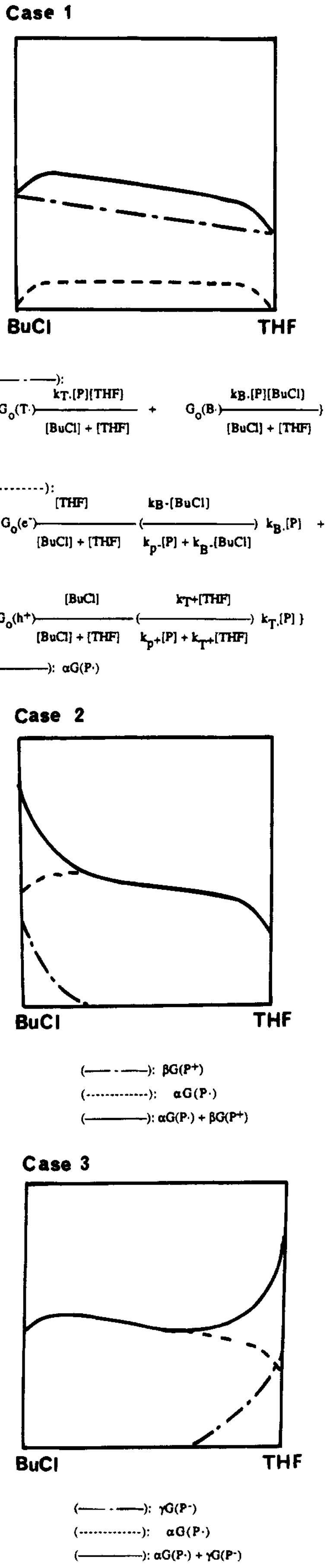

Figure 6. Solvent composition dependences of G(S): case 1, radical mechanism; case 2, radical cation and radical mechanism; case 3, radical anion and radical mechanism.

we examined the solvent effects on the degradation of the alkyl-substituted polysilanes in THF–BuCl mixture systems. In the radiolysis of the mixture of THF and BuCl, the general reaction mechanism is as follows:

$$\mathrm{THF} \rightsquigarrow \mathrm{T}^{\bullet},\ \mathrm{e}$$

$$\mathrm{BuCl} \rightsquigarrow \mathrm{B}^{\bullet},\ \mathrm{h}^{+}$$

$$\mathrm{e} + \mathrm{P} \xrightarrow{k_{\mathrm{P}^-}} \mathrm{P}^{-}$$

$$\mathrm{T}^{\bullet} + \mathrm{P} \xrightarrow{k_{\mathrm{T}^\bullet}} \mathrm{P}^{\bullet}$$

$$\mathrm{h}^{+} + \mathrm{P} \xrightarrow{k_{\mathrm{P}^+}} \mathrm{P}^{+}$$

$$\mathrm{B}^{\bullet} + \mathrm{P} \xrightarrow{k_{\mathrm{B}^\bullet}} \mathrm{P}^{\bullet}$$

$$\mathrm{h}^{+} + \mathrm{THF} \xrightarrow{k_{\mathrm{T}^+}} \mathrm{T}^{\bullet}$$

$$\mathrm{e} + \mathrm{BuCl} \xrightarrow{k_{\mathrm{B}^-}} \mathrm{B}^{\bullet}$$

where P = polymer, e and h^+ represent an electron and a hole, respectively, and the superscripts "+" and "−" indicate radical ions of the relevant molecules. The yield of radical ($P^{\bullet}$), radical cation (P^+), and radical anion (P^-) polysilanes in the mixed solvents are expressed as follows, under the assumption that the energy transfer between THF and BuCl is negligible. Radical and charge recombinations are not taken into account to avoid extreme complexity.

$$G(\mathrm{P}^{\bullet}) = G_0(\mathrm{T}^{\bullet})\frac{k_{\mathrm{T}^\bullet}[\mathrm{P}][\mathrm{THF}]}{[\mathrm{BuCl}] + [\mathrm{THF}]} + G_0(\mathrm{B}^{\bullet})\frac{k_{\mathrm{B}^\bullet}[\mathrm{P}][\mathrm{BuCl}]}{[\mathrm{BuCl}] + [\mathrm{THF}]} + G_0(\mathrm{e})\frac{[\mathrm{THF}]}{[\mathrm{BuCl}] + [\mathrm{THF}]}\left(\frac{k_{\mathrm{B}^-}[\mathrm{BuCl}]}{k_{\mathrm{P}^-}[\mathrm{P}] + k_{\mathrm{B}^-}[\mathrm{BuCl}]}\right)k_{\mathrm{B}^\bullet}[\mathrm{P}] + G_0(\mathrm{h}^{+})\frac{[\mathrm{BuCl}]}{[\mathrm{BuCl}] + [\mathrm{THF}]}\left(\frac{k_{\mathrm{T}^+}[\mathrm{THF}]}{k_{\mathrm{P}^+}[\mathrm{P}] + k_{\mathrm{T}^+}[\mathrm{THF}]}\right)k_{\mathrm{T}^\bullet}[\mathrm{P}] \quad (1)$$

$$G(\mathrm{P}^{+}) = G_0(\mathrm{h}^{+})\frac{[\mathrm{BuCl}]}{[\mathrm{BuCl}] + [\mathrm{THF}]}\left(\frac{k_{\mathrm{P}^+}[\mathrm{P}]}{k_{\mathrm{P}^+}[\mathrm{P}] + k_{\mathrm{T}^+}[\mathrm{THF}]}\right) \quad (2)$$

$$G(\mathrm{P}^{-}) = G_0(\mathrm{e})\frac{[\mathrm{THF}]}{[\mathrm{BuCl}] + [\mathrm{THF}]}\left(\frac{k_{\mathrm{P}^-}[\mathrm{P}]}{k_{\mathrm{P}^-}[\mathrm{P}] + k_{\mathrm{B}^-}[\mathrm{BuCl}]}\right) \quad (3)$$

where $G_0(\mathrm{T}^{\bullet})$ and $G_0(\mathrm{e})$ are the *G*-values of radicals and electrons in THF, respectively. $G_0(\mathrm{B}^{\bullet})$ and $G_0(\mathrm{h}^{+})$ are, on the other hand, the *G*-values of radicals and holes in BuCl, respectively. Then the yield of chain scission *G*(S) can be expressed by eq 4.

$$G(\mathrm{S}) \sim \alpha G(\mathrm{P}^{\bullet}) + \beta G(\mathrm{P}^{+}) + \gamma G(\mathrm{P}^{-}) \quad (4)$$

In Figure 6, we illustrate the solvent composition dependences of *G*(S) in the following typical cases.

Case 1: Radical mechanism, in which the contribution of radical ions is negligible ($\beta = \gamma = 0$)

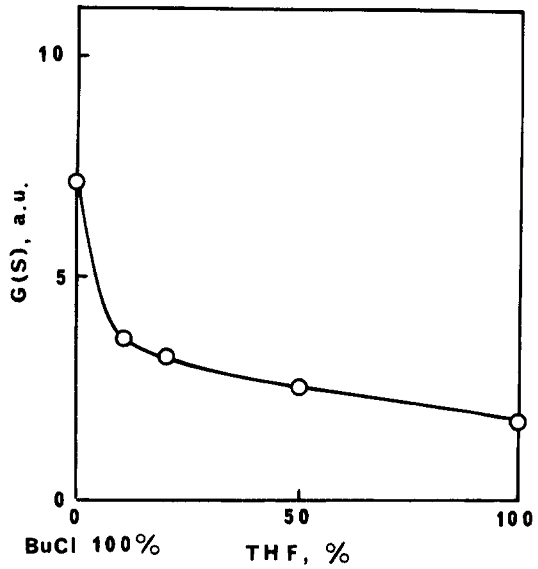

Figure 7. Solvent dependence of the molecular weight decrease of poly(methyl-*n*-propylsilane) in mixed solvents of BuCl and THF.

$$G(\mathrm{S}) \sim \alpha\left(G_0(\mathrm{T}^{\bullet})\frac{k_{\mathrm{T}^\bullet}[\mathrm{P}][\mathrm{THF}]}{[\mathrm{BuCl}] + [\mathrm{THF}]} + G_0(\mathrm{B}^{\bullet})\frac{k_{\mathrm{B}^\bullet}[\mathrm{P}][\mathrm{BuCl}]}{[\mathrm{BuCl}] + [\mathrm{THF}]}\right) + G_0(\mathrm{e})\frac{[\mathrm{THF}]}{[\mathrm{BuCl}] + [\mathrm{THF}]}\left(\frac{k_{\mathrm{B}^-}[\mathrm{BuCl}]}{k_{\mathrm{P}^-}[\mathrm{P}] + k_{\mathrm{B}^-}[\mathrm{BuCl}]}\right)k_{\mathrm{B}^\bullet}[\mathrm{P}] + G_0(\mathrm{h}^{+})\frac{[\mathrm{BuCl}]}{[\mathrm{BuCl}] + [\mathrm{THF}]}\left(\frac{k_{\mathrm{T}^+}[\mathrm{THF}]}{k_{\mathrm{P}^+}[\mathrm{P}] + k_{\mathrm{T}^+}[\mathrm{THF}]}\right)k_{\mathrm{T}^\bullet}[\mathrm{P}]$$

Case 2: Radical and radical cation mechanism, in which the contribution of radical anions is negligible ($\gamma = 0$)

$$G(\mathrm{S}) \sim \alpha G(\mathrm{P}^{\bullet}) + \beta G_0(\mathrm{h}^{+})\frac{[\mathrm{BuCl}]}{[\mathrm{BuCl}] + [\mathrm{THF}]}\left(\frac{k_{\mathrm{P}^+}[\mathrm{P}]}{k_{\mathrm{P}^+}[\mathrm{P}] + k_{\mathrm{T}^+}[\mathrm{THF}]}\right)$$

Case 3: Radical and radical anion mechanism, in which the contribution of radical cations is negligible ($\beta = 0$)

$$G(\mathrm{S}) \sim \alpha G(\mathrm{P}^{\bullet}) + \gamma G_0(\mathrm{e})\frac{[\mathrm{THF}]}{[\mathrm{BuCl}] + [\mathrm{THF}]}\left(\frac{k_{\mathrm{P}^-}[\mathrm{P}]}{k_{\mathrm{P}^-}[\mathrm{P}] + k_{\mathrm{B}^-}[\mathrm{BuCl}]}\right)$$

According to the analysis described above, it is possible to estimate which kind of intermediates, radicals, radical cations, or radical anions, contribute more to the degradation process from the solvent composition dependence of *G*(S). We measured the relative degradation yields, *G*(S), of poly(methyl-*n*-propylsilane) in THF–BuCl. Figure 7 shows the results. The poly(methyl-*n*-propylsilane) was effectively degraded in BuCl, while the degradation was strongly suppressed by the addition of a small amount of THF. According to the analysis, this behavior agrees with case 2. In case 2, the radical cations play a more important role than the radical anions in addition to the radicals. A similar result was observed for poly(di-*n*-hexylsilane), as shown in Figure 8. These results suggest that radical cations play an

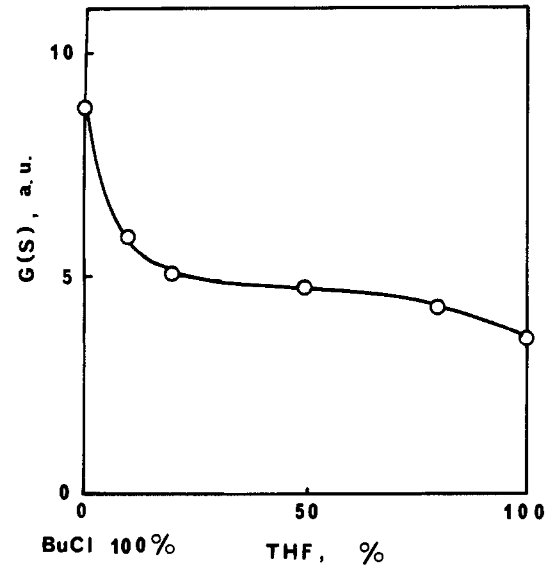

Figure 8. Solvent dependence of the molecular weight decrease of poly(di-*n*-hexylsilane) in mixed solvents of BuCl and THF.

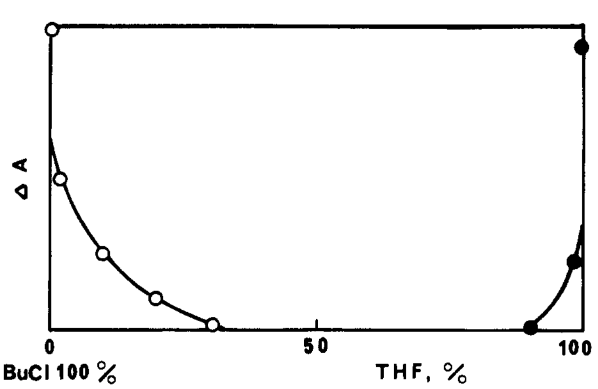

Figure 9. Solvent dependence of the change in the relative yield of radical cations (○) and anions (●) of poly(methyl-*n*-propylsilane) in mixed solvents of BuCl and MTHF at 77 K.

important role in the degradation of alkyl-substituted polysilanes in solution.

To confirm the radical cation mechanism further, we also measured the solvent composition dependence of the yield of the radical cations and anions by using a rigid matrix method at 77 K. Figure 9 shows the solvent composition dependence of the relative yield of poly(methyl-*n*-propylsilane) radical ions in the MTHF−BuCl system. The radical cation yield decreases by the addition of a small amount of MTHF and agrees with the behavior of G(S) in solution, as shown in Figures 7 and 8. The radical anion yield also showed a strong solvent composition dependence. It decreases at low BuCl content. However, no such strong composition dependence of G(S) at low BuCl content was observed in the degradation experiment, as shown in Figures 7 and 8. These results clearly indicate that the reaction path through the radical anions is negligible in the degradation process. The radical cation and the neutral radical intermediates almost equally contribute to the degradation in BuCl solution by γ-irradiation

References and Notes

(1) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359. West, R. *J. Organomet. Chem.* **1986**, *300*, 327.

(2) Harrah, L. A.; Zeigler, J. M. *Macromolecules* **1987**, *20*, 601. Michl, J.; Downing, J. W.; Karatsu, T.; Mckinley, A. J.; Poggi, G.; Wallraff, G. M.; Sooriyakumaran, R.; Miller, R. D. *Pure Appl. Chem.* **1988**, *60*, 959.

(3) Irie, S.; Oka, K.; Irie, M. *Macromolecules* **1988**, *21*, 110. Irie, S.; Oka, K.; Nakao, R.; Irie, M. *J. Organomet. Chem.* **1990**, *388*, 253. Irie, S.; Irie, M. *Macromolecules* **1992**, *25*, 1776.

(4) Wallraff, G. M.; Miller, R. D.; Baier, M.; Ginsburg, E. J.; Kunz, R. R. *J. Photopolym. Sci. Technol.* **1992**, *5*, 111. Wallraff, G. M.; Miller, R. D.; Clecak, N.; Baier, M. *Proc. SPIE* **1991**, *1466*, 211. Nakadaira, Y.; Kyushin, S.; Ohashi, M. *Yuki Gosei Kagaku Kyokaishi* **1990**, *48*, 331.

(5) Miller, R. D. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 813. Zhang, X.-H.; West, R. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 159. Trefonas, P., III; Djurovich, I.; Zhang, X.-H.; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Soc., Polym. Lett. Ed.* **1983**, *21*, 819.

(6) Michl, J.; Downing, J. W.; Karatsu, T.; Klingensmith, K. A.; Wallraff, G. M.; Miller, R. D. In *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K., Alloock, H., Eds.; ACS Symposium Series 360; American Chemistry Society: Washington, DC, 1988; p 61. McCrary, V. R.; Sette, F.; Chen, C. T.; Lovinger, A. J.; Robin, M. B.; Stohr, J.; Zeigler, J. M. *J. Chem. Phys.* **1988**, *88*, 5925.

(7) Trefonas, P.; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 823.

(8) Miller, R. D. In *Silicon-Based Polymer Science*; Zeigler, J. M., Fearon, F. W. G., Eds.; Advances in Chemistry Series 224; American Chemical Society: Washington, DC, 1990; p 413.

(9) Irie, S.; Irie, M. *Radiat. Phys. Chem.* **1992**, *40*, 107.

(10) Mezyk, S. P.; Yamamura, S.; Thomas, J. K. In *Radiation Effects on Polymers*; Clough, R. L., Shalaby, S. W., Eds.; American Chemical Society: Washington, DC, 1991.

(11) Shida, T.; Haselbach, E.; Bally, T. *Acc. Chem. Res.* **1984**, *17*, 180. Shida, T. *Annu. Rev. Phys. Chem.* **1991**, *42*, 55. Shida, T. In *Electronic Absorption Spectra of Radical Ions*; Elsevier: Amsterdam, 1988.

MA941144Z