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Stability of Radicals in Aryl-Substituted Polysilanes with Linear and Planar Silicon Skeleton Structures[†]Shu Seki,^{*,‡,§} Keith R. Cromack,[§] Alexander D. Trifunac,[§] Yoichi Yoshida,^{||} Seiichi Tagawa,^{||} Keisuke Asai,[⊥] and Kenkichi Ishigure[⊥]

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This paper discusses the stability of radicals produced under γ -irradiation for phenyl-substituted polysilanes with different backbone structures. Poly(methylphenylsilane) and structural defect-containing phenyl-substituted polysilanes were irradiated by ^{60}Co γ -rays in the solid state. Temperature dependence of the EPR signal intensity from the radicals induced by radiolysis was measured. The radicals appeared to be more stable as the induced defect density in the backbone structure was increased, indicating that the structure defects on the polymer backbone may play a role in stabilizing silyl radicals. The migration of unpaired electrons was also observed from chain ends to chain center leading to stable radical species. The estimated-branched structures were less than 3.5% in the linear polysilane obtained by conventional Wurtz coupling condensation.

Introduction

Polysilane derivatives have attracted considerable attention because of their interesting physical properties. Experimental results and modeling of polysilanes and related materials suggest that the conjugated σ -bonding in the silicon skeleton is responsible for their unique physical properties, such as photo-sensitivity, and photoconductivity, nonlinear optical properties.

A Wurtz coupling reaction of dichlorosilane is often the choice method for synthesizing polysilane derivatives. However, when this method is used it is impossible to avoid the creation of structural defects, such as branching and oxidized sites, in the silicon skeleton. While the occurrence of structural defects may be widespread, the relationship between the defect structure and various physical properties of polysilanes has not been elucidated. Fujiki reported the synthesis of structural defect-containing poly(methylphenylsilane), as well as the relationship between the fraction of the induced defects and the intensity of broad emission band observed around 2.9 eV.¹ Fujiki reported that the branching structure in the silicon skeleton could be influenced by changing the $\text{SiRCl}_3/\text{SiRR}'\text{Cl}_2$ monomer ratio in the coupling reaction, and observed broad emission bands in addition to the 3.4–3.6 eV emission band of the linear polysilane. The intensity of the new emission band increased with

the structural defect density in the silicon skeleton, and this band was ascribed to the photoluminescence from the defect structure. It was suggested that the defect density in linear polysilane was <1%, considering the relative emission intensities.¹

There is another point of view that considers the polysilane derivatives as silicon materials of low dimensionality. Matsumoto et al. considered the polysilanes as one-dimensional silicon materials, amorphous and crystalline silicon as the three-dimensional silicon materials; polysilanes with a network silicon skeleton were considered to be two-dimensional silicon materials.² Their modeling calculations showed the band gap energy of 1D-Si and 2D-Si to be 3.4 and 2.5 eV, respectively. For the 3D-Si it was 1.7 eV for amorphous silicon and 1.1 eV for crystalline silicon. The reduction of the band gap energies was ascribed to the extension of the σ -conjugated system in the silicon skeleton. Their experimental results on photoluminescence of these silicon materials supported these calculations. They also suggested that the increasing defect (branching) structure density in the silicon skeleton could develop into a silicon network, i.e., conversion from 1D-Si to 2D-Si with an extended σ -conjugated system. Brus also discussed silicon optical and electronic properties as a function of dimensionality.³ Brus focused on the luminescence spectra of these silicon materials and suggested a model of structural change from direct to indirect gap materials with increasing dimensionality of the silicon skeleton.

Many polysilanes have a strong UV absorption band which originates from the σ -to- σ^* transition. Photochemistry of polysilanes has been considered to involve chain scission on exposure to UV light, and several groups^{4–9} have reported the potential use of polysilanes as UV photoresist materials. There

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are reports on the characteristics of the UV light-induced reactive intermediates of polysilanes using EPR spectroscopy. McKinly et al. observed radicals of di-*n*-pentyl- and methylpentyl-substituted polysilanes in *n*-octane and *n*-pentane solutions at 200–350 K induced by 248–330 nm light.⁹ Their data showed EPR spectra consisting of a doublet of doublets, which were assigned to two unpaired electrons on silicon atoms in the low-temperature region, giving rise to a triplet state at higher temperatures. Thus a silicon-centered radical pair was formed as a result of UV light exposure. They proposed three primary reaction routes: silylene extraction, homolytic cleavage, and alkyl side chain elimination followed by polymer skeleton scission. Todesco et al. also reported UV light-induced radical formation in poly[dimethylsilane-*co*-methyl(1-naphthylsilane)] in methyltetrahydrofuran;¹⁰ however, the corresponding EPR spectra turned out to be those of solvent radicals. As the above-mentioned studies illustrate, the reactive intermediates and the stability of these polymer materials in photo- and radiation-induced reactions have not been adequately elucidated. In contrast, many investigations have been reported for small silane and oligosilane molecules. Silyl radical formation in alkyl-substituted silicon-centered molecules was observed by many groups in the 1970s. Benett et al.¹¹ and Krusic et al.¹² reported trimethylsilyl radical formation on exposure to UV light. Benett et al.¹³ and Cooper et al.¹⁴ also presented the EPR spectra of dimethyl(trimethylsilyl)silyl radicals generated by UV light exposure. The observed coupling constant of β -hydrogen in this radical was considerably larger than that of Me₃Si and was ascribed to the conjugative interaction of the neighboring silicon atom.

The present paper describes the observation of silyl radicals in solid-state poly(methylphenylsilane) (PMPS), PMPS containing structural defects, and poly(phenylsilane) (PPS) with a silicon skeleton network. PMPS is one of the most popular polysilanes because of its stability in the solid state, ease of handling, and good film-forming properties. Furthermore, PMPS has σ -conjugated substituents, and the phenyl group itself is bulky in comparison to alkyl side chains, so that PMPS has a more rigid silicon skeleton than the other alkyl-substituted polysilanes. PMPS is one of the most suitable polysilanes for use as an optical and photoconductive material. This paper discusses the stability of reactive intermediates in these polymers and the effect of defect structures in the main chains.

Experimental Section

Linear PMPS was synthesized by the conventional sodium condensation (Wurtz coupling) method from the methylphenyldichlorosilane monomer. Defect-containing PMPS was synthesized by the same procedure with the monomer mixture of methylphenyldichlorosilane and *p*-tolyltrichlorosilane. The ratio of the mixture was changed from 0.27 wt % to 20 wt %. For poly(phenylsilane) (PPS) with a network silicon skeleton, phenyltrichlorosilane was taken as a monomer. All chlorosilanes were doubly distilled products from Shinetsu Chemical Co. Ltd. Polymerization reactions were carried out in an Ar atmosphere, in 100 mL of toluene, with 20 mL of diethylene glycol–dimethyl ether as reflux solvent, except for the polymerization of PPS. PPS was prepared using decane as a reflux solvent in order to obtain a relatively high-molecular-weight polymer. The monomer was added into the reaction vessel and mixed with molten sodium metal over a 4-h period. PMPS and defects-containing PMPS solutions were precipitated using isopropyl alcohol after filtration to remove NaCl, and the precipitates were dried under vacuum. To eliminate the remaining NaCl, toluene solutions of these polymers were

TABLE 1: Polymerization Results and Characteristics of Polysilane Samples

entry	Si-based defect density per total Si units	weight average molecular weight	glass transition temperature
1	0.0	3.2×10^4	379 K
2	0.045	1.6×10^4	385 K
3	0.090	1.2×10^4	392 K
4	0.18	1.1×10^4	399 K
5	1.0	2.4×10^4	

transferred into separatory funnels, washed with water, and precipitated twice with toluene–isopropyl alcohol and tetrahydrofuran(THF)–methanol mixtures. PPS was first precipitated by direct addition of isopropyl alcohol into the reaction vessel, and then washed with water after filtration. The purification was carried out using the same procedure as for PMPS. PMPS and defects-containing PMPS showed good solubility in toluene, THF, methyl THF (MTHF), chloroform, and dichloromethane. PPS was partially soluble in toluene, and the insoluble component was removed by filtration. The amounts of residual Cl atoms were confirmed to be less than 0.1% in solid PPS by elemental analysis. For defect-containing polysilanes, the ratio of branching structure for each polymer was confirmed by NMR using a JEOL EX-270 1H NMR spectrometer in the Institute of Scientific and Industrial Research, Osaka on a Shimadzu C-R3A gel permeation chromatography (GPC) system. Phase-transition temperatures were measured on the Perkin–Elmer DSC-7 system.

Electron spin resonance measurements were carried out using a Varian X-band EPR spectrometer. The microwave power used was typically 0.2 mW that was increased to 5 mW for measurements above 250 K. Polymer samples in suprasil quartz cells were evacuated to 10^{-4} Pa, and irradiated by a ⁶⁰Co γ -ray source in the Chemistry Division at Argonne National Laboratory to the dose of 1.9–3.8 kGy. After the irradiation at 77 K, samples were transferred to a liquid helium cryostat, and EPR measurements were carried out at temperatures from 4 to 270 K.

For optical measurements, samples in 1 cm quartz cells were dissolved in MTHF and evacuated. Frozen solutions were irradiated with ⁶⁰Co γ -rays at 77 K with a dose of 1.9 kGy, and the absorption spectra were measured by a Varian Cary UV–Vis–NIR spectrometer after bleaching the solvated electron absorption band in MTHF.

Results and Discussion

Table 1 shows the polymerization results for PMPS, defect-containing PMPS, and PPS. The ratio of tolyl and methyl protons measured by 1H NMR spectra establishes that the concentration of defect structures was proportional to the ratio of trichlorosilane/dichlorosilane monomers. The changes in phase transition temperatures as shown in Table 1 support the presence of the defect structures in the silicon skeleton. The molecular weights of these polymers decrease slightly with increase in defect densities.

In our previous work we described the γ -radiolysis-induced silyl radicals in poly(dimethylsilane).¹⁵ The silyl radicals were quite stable and were probably created via the main chain scission of the silicon skeleton. Several other studies suggested the creation of silyl radicals induced by photolysis and by other types of ionizing radiation.^{4,9} There has been little discussion on the relative stability of radical species in polysilanes. Figure 1 shows the EPR spectrum of γ -irradiated defect-containing PMPS at 6 K. The spectrum exhibits weak hyperfine satellites owing to the presence of ²⁹Si (relative abundance 4.7%; spin = 1/2). A simulated EPR spectrum, calculated using values of coupling constants previously observed in γ -irradiated poly-

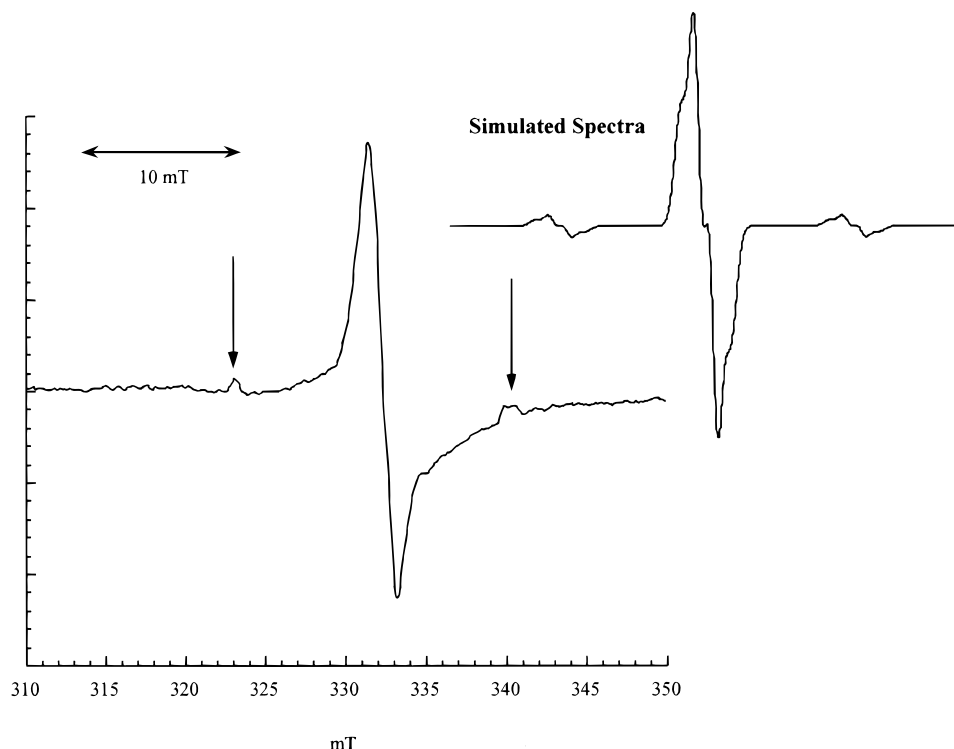


Figure 1. EPR spectrum of defect-containing γ -irradiated PMPS at 6 K with simulated spectrum of $-\text{MePhSi}-\text{MePhSi}\cdot$ using coupling constants in refs 13 and 15.

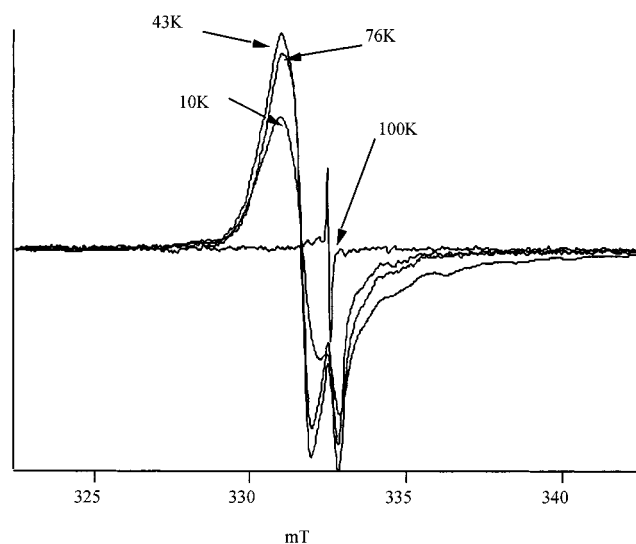


Figure 2. Temperature dependence on EPR signals of linear PMPS.

(dimethylsilane)¹⁵ and diphenylsilyl radicals¹⁶ is also shown in Figure 1. The spectrum was simulated using a Gaussian approximation line shape with 0.28 mT linear, typical for EPR spectra in amorphous polymer solids. The observed spectrum exhibits the same features as the simulated spectrum of silyl radicals with small differences in the peak width; i.e., 1.41 mT for the observed spectrum and 1.38 mT for the simulated spectrum, respectively. The coupling constant of ^{29}Si is 18.2 mT, in good agreement with previously reported values for coupling constants in silyl radicals.¹⁶ Thus the EPR spectrum is assigned to the silicon-centered neutral radical. Because of the asymmetry of the amorphous polymer, the spectrum was broadened due to small coupling constants of hydrogen atoms of phenyl groups (reported as 0.097, 0.092, and 0.045 mT for *p*-, *o*-, and *m*-hydrogen, respectively).¹⁷ In Figure 2 we illustrate the temperature dependence of the EPR signal intensity of

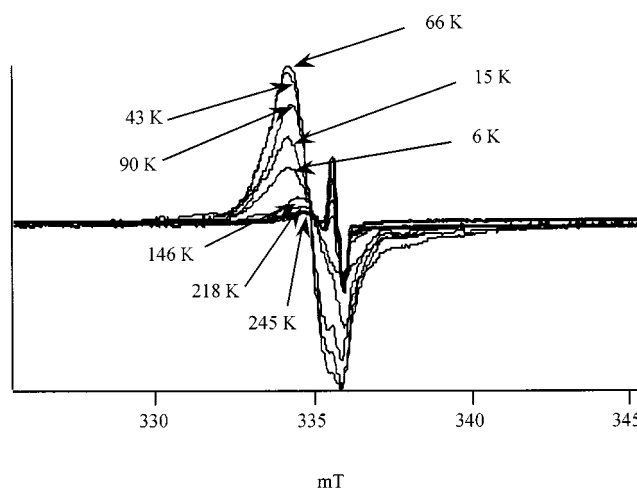


Figure 3. Temperature dependence on EPR signals of defect-containing PMPS with the defect density at 0.090.

γ -irradiated linear PMPS. The EPR signals could not be resolved because the coupling constants of phenyl protons of silicon-centered radicals are small. In the aryl-substituted linear PMPS, a broad signal was observed below 90 K. The signal was ascribed to silicon-centered neutral silyl radicals as described before. The *g*-factor of the radical is estimated to be 2.0066 at all temperatures. The signal intensity decreased rapidly at higher temperature, and the signal completely disappeared at 100 K, suggesting recombination of silyl radicals with increasing temperature. Figures 3 and 4 show similar temperature dependence for defect-containing PMPS and PPS with a network silicon skeleton, respectively. The defect density of the PMPS, which represents the ratio of the branched Si units to the total Si units, is 0.09. It is evident that the EPR peak intensity decreases with an increasing number of branched Si structures on the silicon skeleton. The shapes of these EPR signals are nearly the same for PPS, and the *g*-factor is 2.0036.

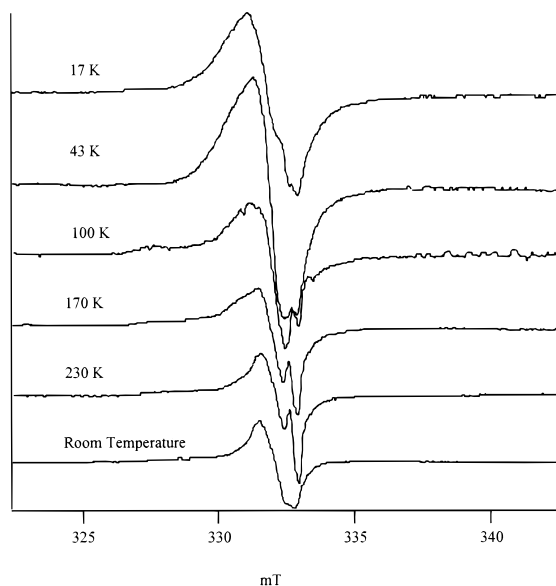


Figure 4. Temperature dependence of EPR signal of the polysilane with a network-like silicon skeleton.

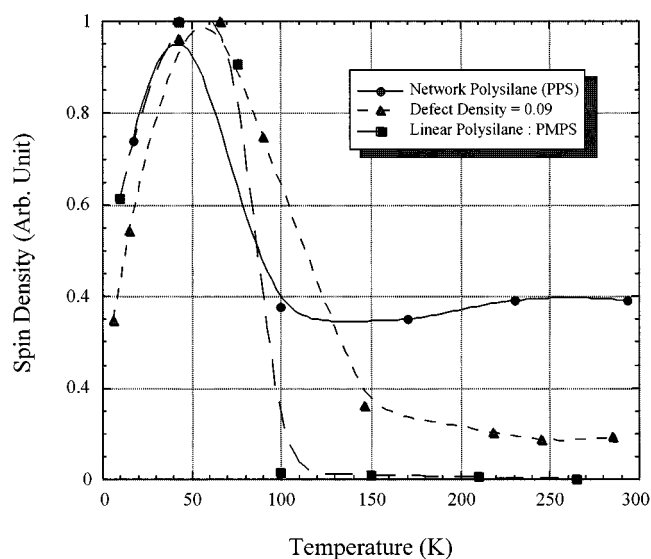


Figure 5. Temperature dependence of EPR signal intensity of PMPS, defect-containing PMPS (defect density of 0.090), and PPS.

Therefore it appears that once silicon-centered neutral silyl radicals are formed in these polysilanes, they are trapped and stabilized at branching sites of the silicon skeleton. However, the spectra are shifted to higher magnetic field in γ -irradiated defect-containing PMPS. The g -factors of the observed radicals are also changed from 2.0064 at 15 K to 2.0038 at 245 K. This indicates the overlap of two radical species that are assigned to $-\text{MePhSi}\cdot$ radicals produced by main chain scission, and to $-\text{PhSi}\cdot$ radicals by side chain scission reactions. Figure 5 shows the temperature dependence of the EPR signal intensity for γ -irradiated polysilanes. The signal intensity does not change above 200 K for PPS and defects-containing PMPS. This allows one to estimate total spin density of $-\text{PhSi}\cdot$ type radicals, as a function of defect density, as shown in Figure 6. The spin density is not proportional to the defect density but appears to be approximately proportional to the logarithm of defect density. This may be due to migration of unpaired electrons from chain end to the branched sites with rising temperature. The radical at the branched site shows greater stability compared to the chain end radicals. Therefore the presence of branched structures enhances the chain scission reaction. One can use this to

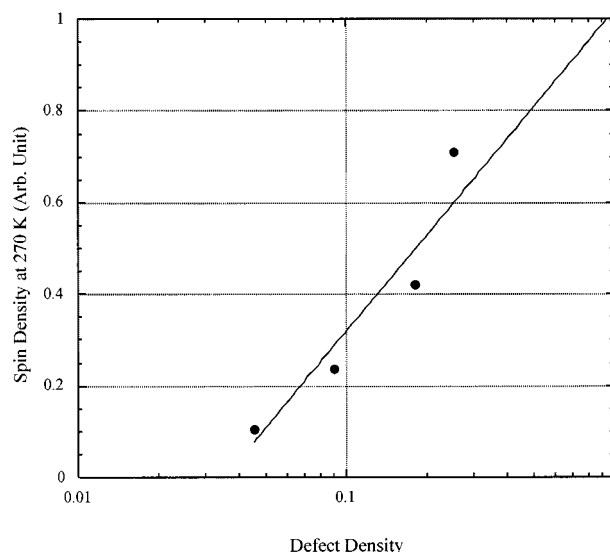


Figure 6. Dependence of spin density on defect density as calculated from EPR spectra observed at 270 K.

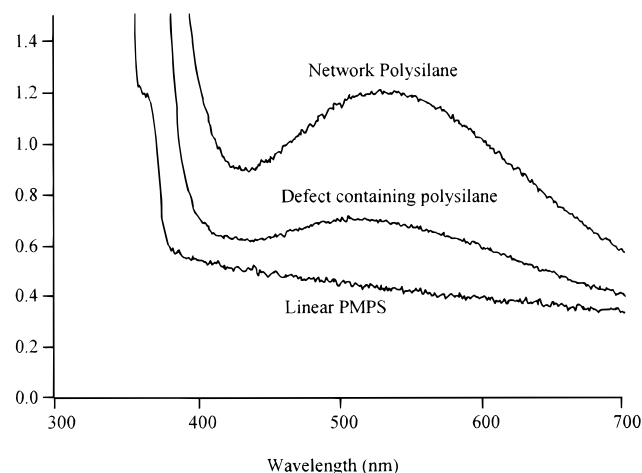


Figure 7. UV-vis absorption spectra of polysilane MTHF solutions (77 K) irradiated by γ -rays to a dose of 1.9 kGy. Solute concentration was 30 mmol/L in all solutions used.

estimate the defect density in linear polysilanes and to compare it with the NMR-based estimates mentioned in the Experimental Section. No EPR signal is observed for γ -irradiated linear PMPS at 270 K, suggesting that the amount of branched sites is less than 3.5% in the polymer.

Figure 7 shows the results of optical spectroscopy of these polysilanes after γ -radiolysis in the MTHF matrix at 77 K. Electrons created by the ionizing radiation in the MTHF matrix are transferred to the solute polysilane molecules producing radical anions of the polysilane. We have reported electron beam pulse radiolysis studies, where anion and cation radicals on linear and branched polysilane molecules were found to exhibit simultaneously a sharp UV absorption band around 370 nm and a broad IR band.^{18,19} Extinction coefficients of the radical anions decrease with the increase in defect density, while the absorption maxima occurred in the same wavelength range. In the case of linear PMPS, a weak absorption band was observed at 375 nm that can be ascribed to the anion radicals of PMPS. However, the anionic species were not observed in defect-containing PMPS and PPS. Figure 6 also illustrates a new, broad absorption band observed at 520 and 540 nm for defect-containing PMPS and network PPS, respectively. The intensity of this band was seen to increase and shift to a longer

wavelength upon increasing the density of defect structures in the silicon skeleton. This absorption was also observed in the presence of 50 mM CCl₄, a typical scavenger of anionic species, indicating that absorption was due to neutral species. This new absorption band must be due to the neutral silyl radicals generated as a result of direct or indirect excitation of the solute polysilane molecules. This implies that relatively stable silyl radical species occur at the branching site of highly branched PMPS and PPS at 77 K, while the silyl radicals in the predominantly linear PMPS are less stable and recombine more readily.

Conclusion

Neutral silyl radicals in solid aryl-substituted polysilanes were less stable than radicals derived from dimethyl-substituted polysilanes. The defect (branch) structure in the silicon skeleton appears to be able to stabilize silyl radicals, and highly branched silyl radicals exhibited remarkable stability, even close to room temperature. Conjugation effects of the silicon skeleton on these radical species may be small, and the unpaired electrons were concentrated on the highly branched silicon atoms. These branched silyl radicals exhibited optical absorption around 540 nm in MTHF matrix at 77 K. The unpaired electrons migrated from the chain ends to the chain center leading to stable radical species. Therefore EPR spectroscopy can be used to assess the presence of branched structure in the silicon skeleton. The estimated-branched structures were less than 3.5% in the linear polysilane obtained by conventional Wurtz coupling condensation.

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