www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 611 (2000) 78–84

Journal of Organo metallic Chemistry

Photochemical bis-silylation of C_{60}: synthesis of a novel C_{60} main chain polysilane

Takatsugu Wakahara [a], Takuya Kondo [a], Mutsuo Okamura [a], Takeshi Akasaka [a,b,*], Yoshitaka Hamada [c], Toshiyasu Suzuki [b], Masahiro Kako [d], Yasuhiro Nakadaira [d]

[a] *Graduate School of Science and Technology, Niigata University, Niigata 950-2181, Japan*
[b] *Institute for Molecular Science, Okazaki 444-8585, Japan*
[c] *Shin-Etsu Chemical Co. Ltd., Matsuida, Gunma 379-0224, Japan*
[d] *Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182-8585, Japan*

Received 8 March 2000; accepted 26 March 2000

Abstract

The photoreaction of polysilanes and cyclic oligosilanes with C_{60} has been investigated. Photoirradiation of a solution of C_{60} and polysilanes in benzene in a degassed quartz tube at 20°C with a low-pressure mercury-arc lamp has afforded the C_{60}–polysilane adduct in moderate yield, in which C_{60} is incorporated into the polysilane chain. A unique electronic property of the C_{60} main chain polysilane has also been elucidated. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Polysilane; Oligosilane; C_{60}; Fullerene; Bis-silylation; Dopant; Redox

1. Introduction

Polysilanes, in which extensive delocalization of σ-electrons takes place along the silicon chain, have many interesting electronic properties and represent a unique feature of materials [1,2]. Meanwhile, C_{60}, the third allotropic form of carbon, has attracted many attentions by its novel structure and property [3–5]. A combination of fullerene and polysilane may form a new type of organic compounds and can open a new field in material science.

In the course of our study on the chemical functionalization of C_{60} with organosilicon compounds, we already reported the photochemical mono- and bis-silylation of fullerenes. In the silylene addition, we obtained the silirane derivatives which have three membered ring formed to the double bond between six- and six-membered ring of C_{60} (1,2-adducts) [6]. Meanwhile, photochemical addition of disiliranes onto C_{60} gives 1,2- [7] and 1,4-adducts [8], in which five- and seven-membered units can be formed, respectively. It was also found that the photochemical reaction of C_{60} with disilane affords the corresponding bis-silylated adducts [9,10]. Based on the spectral and theoretical investigation, we concluded that this adduct has the so-called 1,6-addition pattern [9,11]. Several control experiments show this photochemical reaction proceeds via the formation of silyl radical by homolysis of a Si–Si bond and its addition to C_{60}. It has been well known that upon photolysis of polysilane with a UV lamp, a facile bond cleavage of the Si–Si bond takes place to afford the corresponding silyl radical [1]. To extend this silylation reaction onto C_{60}, we have carried out the photoreaction of polysilane with C_{60} to afford a novel silicon polymer, which incorporates C_{60} in the polysilane chain. Several attempts to synthesize C_{60} main chain polymers have been reported according to the multi-step synthesis concepts [12]. In order to control the polysilane chain-length in C_{60}–polysilane adduct, we also carried out the photoreaction of cyclic oligosilanes with C_{60}.

---

* Corresponding author. Fax: +81-25-2627390.
E-mail address: akasaka@gs.niigata-u.ac.jp (T. Akasaka).

PII: S0022-328X(00)00293-X

2. Results and discussion

2.1. Photoreaction of polysilane with C_{60}

The mixture of C_{60} and polysilanes **1**–**3** in benzene in a degassed quartz tube was photo-irradiated with a low-pressure mercury-arc lamp. The reaction mixture was separated by gel permeation column chromatography to collect the high molecular unit. The obtained polymer exhibits absorption over 400 nm (Fig. 1a, 1b, Scheme 1).

This result suggests the incorporation of C_{60} in the polysilane chain, because the original polysilanes **1**–**3** have no absorption in this wavelength region. The mass spectra of C_{60}–polysilane adducts analyzed by fast atom bombardment mass spectroscopy (FABMS) shows the C_{60} signal, which also confirms that C_{60} is incorporated in the polysilane chain. Elemental analysis of C_{60}–polysilane **1** adduct reveals that about 14 wt% of C_{60} is incorporated into the polysilane chain (Fig. 2). The definitive evidence for direct connection of C_{60} with polysilane chain was gained by ^{13}C-NMR measurement of the adduct obtained from the ^{13}C-enriched C_{60} and polysilane (Fig. 3). The broad signal between 130 and 150 ppm originated from the sp^2 carbon on C_{60} skeleton reveals that C_{60} actually attaches to the polysilane chain. The ^{29}Si-NMR of C_{60}–polysilane **1** adduct and original polysilane **1** are shown in Fig. 4. The signals around −40 ppm indicate the existence of polysilane units in the C_{60}–polysilane **1** adduct.

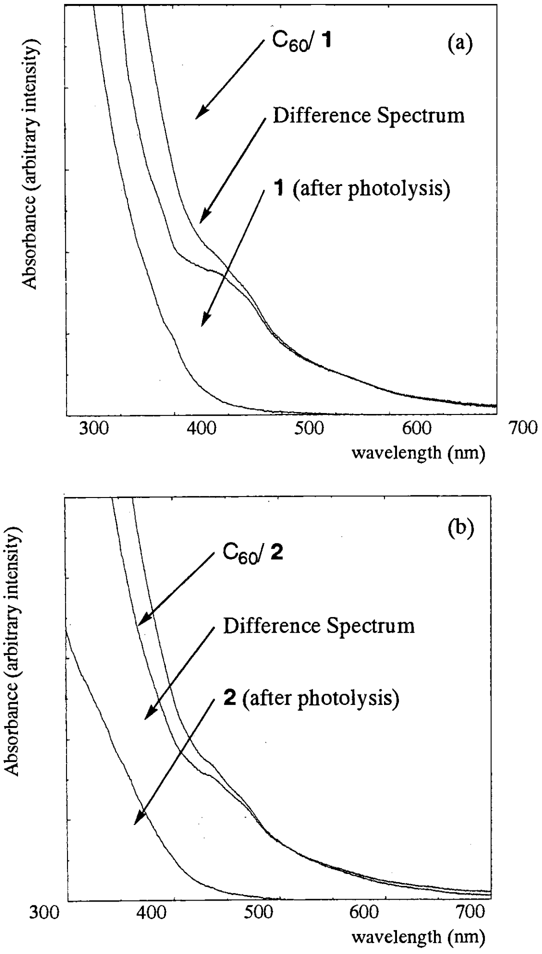
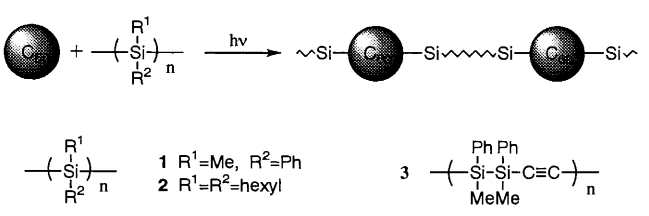


Fig. 1. UV–Vis spectra of (a) C_{60}–**1**, (b) C_{60}–**2**.



Scheme 1.

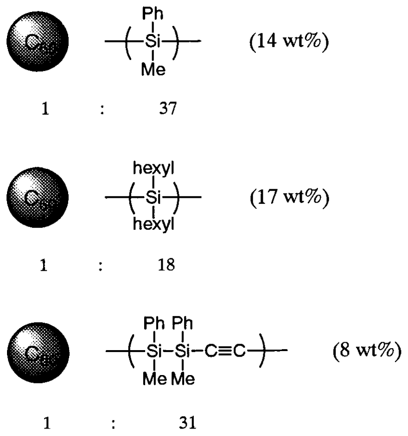


Fig. 2. Incorporation of C_{60} into polysilane measured by elemental analysis.

The molecular weight distribution and weight average molecular weight of C_{60}–polysilane adducts and polysilanes, which was irradiated by the same conditions described above, are shown in Fig. 5. The molecular weights given are relative to polystyrene standard. The molecular weight of the adducts are higher than those of irradiated polysilanes, indicating that C_{60} might act as a linker.

The incorporation of C_{60} into polysilane was not observed upon irradiation at > 300 nm where the cleavage of Si–Si bond does not take place. Formation of C_{60}–polysilane adduct was also suppressed by addition of CCl_4, which is known as a good silyl-radical scavenger [13]. These results indicate that the formation of C_{60}–polysilane adduct, rationalized in terms of the intermediacy of a silyl radical generated by photochemical Si–Si cleavage of polysilane.

2.2. Photoreaction of cyclic oligosilane with C_{60}

A mixture of C_{60} and cyclopentasilane **4** in benzene in a degassed quartz tube was photolyzed by a low-pressure mercury-arc lamp (Scheme 2). The reaction mixture was then injected into gel permeation column chromatography to separate and collect the high molecular unit. The obtained polymer exhibits absorption over 400 nm indicating the incorporation of C_{60}, in the polysilane chain, because the polymer which was synthesized by the similar procedure in the absence of C_{60}, have no absorption in this wavelength region (Fig. 6).

FABMS spectrum of C_{60}–polysilane adducts shows tile C_{60} signal, which also suggests that C_{60} is incorporated in the polysilane chain. ^{13}C- and ^{13}C DEPT-NMR spectra are shown in Fig. 7. The broad signal between 130 and 150 ppm in the ^{13}C-NMR, which disappeared in the ^{13}C DEPT-NMR spectrum, is certainly originated from the sp^2 carbon on C_{60} skeleton. This result reveals that C_{60} actually attaches to the polysilane chain. The ^{29}Si-NMR of the adduct is shown in Fig. 8. The signals around −30 to −40 ppm indicates the existence of polysilane units in the adduct. By elemental analysis, it is suggested that about 38 wt% of C_{60} is incorporated into the polysilane chain. We have also carried out the photoreaction cyclopentasilane **5**

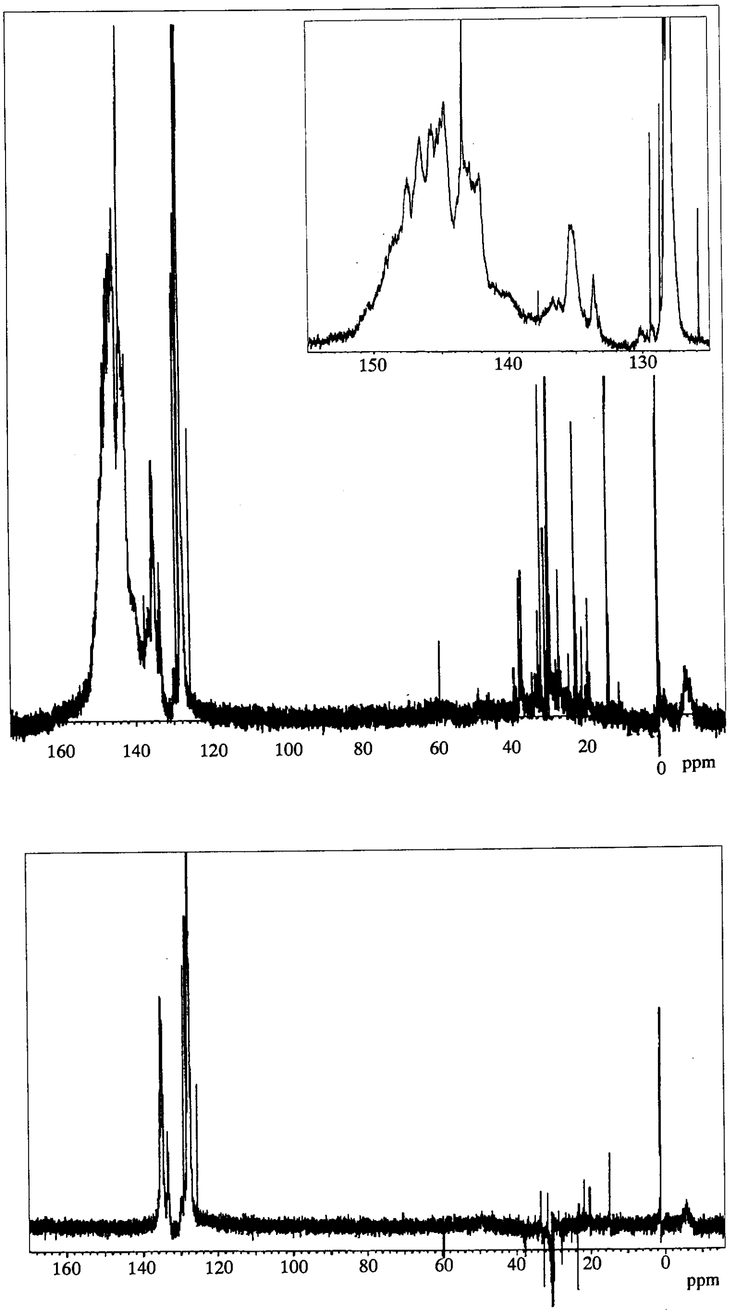


Fig. 3. ^{13}C-NMR (top) and ^{13}C DEPT-NMR(bottom) of ^{13}C enriched C_{60}–**1**.

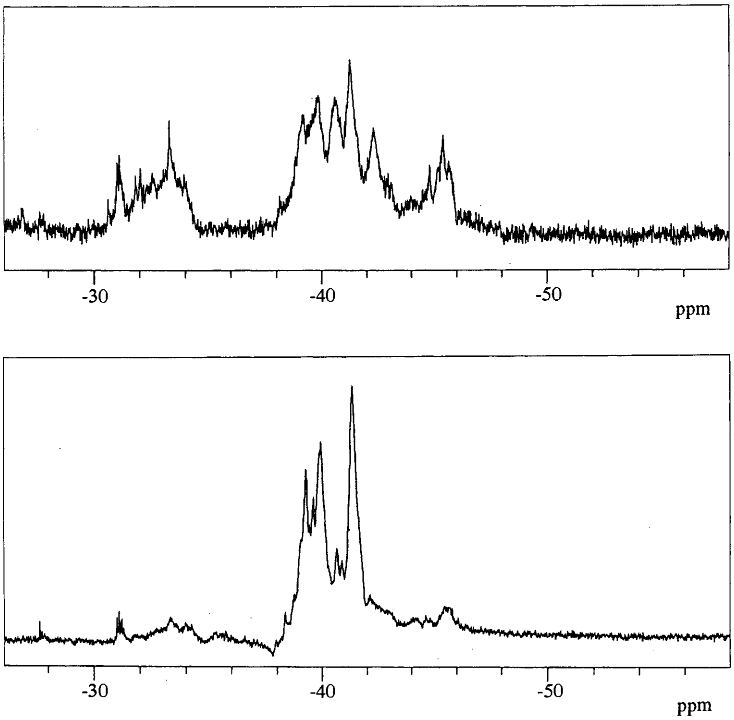


Fig. 4. ^{29}Si-NMR of C_{60}–**1** (top) and **1** (bottom).

and cyclohexasilane **6** with C_{60}. In these cases, the high molecular unit could not be collected, but $C_{60}(SiR_2)_4$ (R = Me, Et) were obtained after HPLC separation [14]. From the ^{1}H-, ^{13}C-NMR and UV–Vis spectrum, $C_{60}(SiR_2)_4$ have Cs symmetry and would be 1,4-addition products with fast ring inversion (Fig. 9). It was reported that cyclohexasilane **6** formed $(SiMe_2)_4$ with elimination of two silylene (R_2Si:) by UV irradiation, followed by ring opening reaction resulted in formation of 1,4-diradical (Scheme 3) [15]. The 1,4-diradicals reacted with C_{60} to give the adducts. These adducts may be good precursors for new silicon–C_{60} polymer by the ring opening polymerization.

2.3. Electronicproperty of C_{60}–polysilane adduct

In order to investigate the electronic property of C_{60}–polysilane adduct, its redox potentials were measured and compared to those of C_{60} and polysilane itself (Table 1). The C_{60}–**1** adduct has a lower oxidation potential than C_{60} and a lower reduction potential than polysilane. These data indicate that a C_{60}–polysilane adduct has unique electronic property.

It has been reported that C_{60} acts as a good dopant for photoconductive polymers [16]. Wang et al., reported that C_{60}-doped polysilane is a good photoconductor [17]. Although photoconductivity of C_{60}–**1** polysilane adduct has not been measured yet, thermal conductivity of iodine-doped C_{60}–**1** (5×10^{-6} S cm^{-1}) is similar to that of the mixture of C_{60} and **1** (6×10^{-6} S cm^{-1}). The thermal conductivity of original polysilane itself is 1×10^{-6} S cm^{-1}. These data reveal that C_{60} main chain polysilane has a higher thermal conductivity than original polysilane.

In conclusion, we carried out the photochemical reaction of polysilanes and cyclic oligosilanes with C_{60} and obtained the C_{60}–polysilane adducts in which C_{60} was incorporated into a polysilane chain. The incorporation of C_{60} into polysilane could promise to open the further extension of its application for a new type of material.

3. Experimental

3.1. General procedure

^{1}H-, ^{13}C- and ^{29}Si-NMR spectra were measured on a Varian Unity Plus 500 or Bruker AVANCE 300 spectrometers. FABMS spectra were obtained with JEOL SX-102. The UV–Vis spectra were measured on Shimadzu UV-2400PC spectrometer. Gel permeation chromatographic separation was performed on a model LC-918 recycling preparative HPLC (Japan Analytical Industry Co. Ltd.) with a series of Jaigel 1H and 2H columns using toluene as eluent. Cyclic voltammetry experiments were performed at 1 mM analyte concentration in 1,2-dichlorobenzene with 0.1 M Bu_4NPF_6, Ag–$AgNO_3$ (CH_3CN) reference electrode, and Pt disc working electrode. Ferrocene (0.5 mM) was added as an internal reference. The scan rate was 20 mV s^{-1}.

Difference pulse voltammetry experiments were carried out under the same conditions used for CV measurement. Pulse amplitude, pulse width and pulse period were 50 mV, 50 ms and 200 ms, respectively. The scan rate was 20 mV s^{-1}.

All experiments were carried out under argon atmosphere. Benzene was distilled from sodium benzophenone ketyle immediately prior to use. 1,2-Dichlorobenzene was freshly distilled over sodium under reduced pressure. Bu_4NPF_6 was recrystallized from absolute ethanol and dried in a vacuum prior to use.

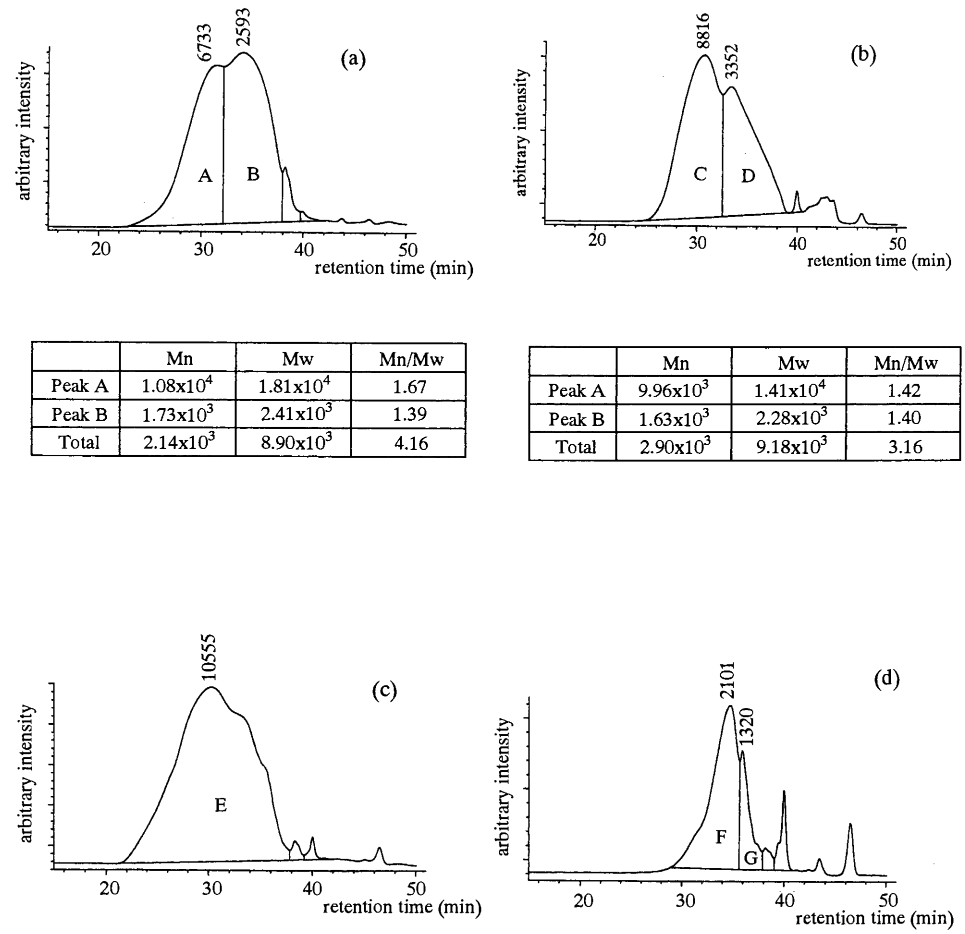
3.2. Synthesis of C_{60} adducts of polysilane

A solution of C_{60} (36 mg, 0.05 mmol) and polysilanes **1**–**3** (18 mg) in deaerated benzene (40 ml) was photo-irradiated with a low pressure mercury lamp for 3 h. C_{60}–polysilane **1**–**3** adducts (12 mg, 10 mg and 9 mg) were obtained after HPLC separation.

3.3. Synthesis of C_{60} adducts of cyclic oligosilane

Typically, a solution of C_{60} (36 mg, 0.05 mmol) and cyclic oligosilane $(Me_2Si)_6$ (17 mg, 0. 05 mmol) in deaerated benzene (40 ml) was photo-irradiated with a low pressure mercury lamp for 4.5 h. $C_{60}(SiMe_2)_4$ was isolated in 18% yield after HPLC separation.

^1H-NMR (500 MHz, CS_2–C_6D_6 = 3:1): δ 0.44(s, 3H), 0.48(s, 3H), 0.57(s, 3H), 0. 90(s, 3H); ^{13}C-NMR (125 MHz, CS_2–C_6D_6 = 3:1): δ 165.47, 150.97, 149.26, 148.69, 148.38, 148.26,147.70, 147.14, 146.70, 145.56, 145.40, 145.26, 145.19, 145.18, 145.04, 144.99, 144.70, 144.67, 144.00, 143.58, 143.33, 143.17, 143.11, 143.02,



(a)

	Mn	Mw	Mn/Mw
Peak A	1.08x10^4	1.81x10^4	1.67
Peak B	1.73x10^3	2.41x10^3	1.39
Total	2.14x10^3	8.90x10^3	4.16

(b)

	Mn	Mw	Mn/Mw
Peak A	9.96x10^3	1.41x10^4	1.42
Peak B	1.63x10^3	2.28x10^3	1.40
Total	2.90x10^3	9.18x10^3	3.16

(c)

	M_n	M_w	M_n/M_w
Peak E	5.08x10^3	2.56x10^4	5.04
Total	4.11x10^3	2.53x10^3	6.16

(d)

	M_n	M_w	M_n/M_w
Peak F	2.67x10^3	3.42x10^3	1.28
Peak G	1.05x10^3	1.11x10^3	1.05
Total	1.27x10^3	2.72x10^3	2.13

Fig. 5. Molecular weight distribution and weight avarage molecular weight of (a) C_{60}–**1**, (b) **1** (after photolysis), (c) C_{60}–**2** and (d) **2** (after photolysis).

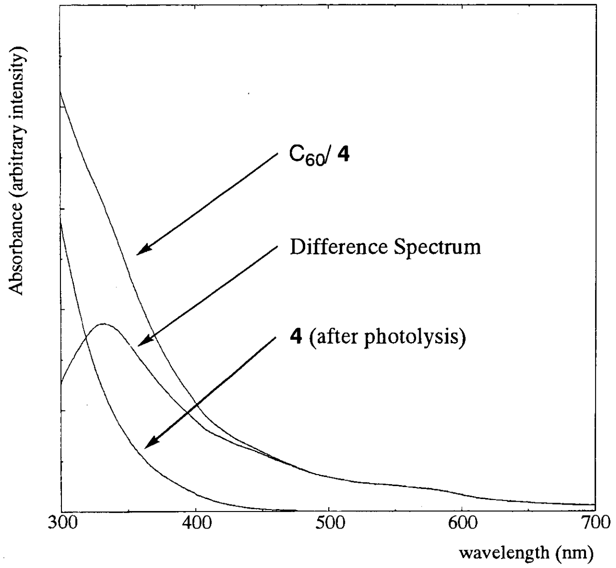
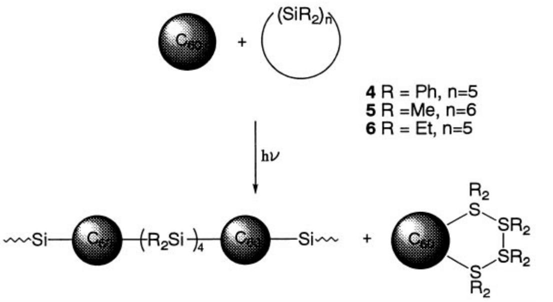


Fig. 6. UV–Vis spectra of C_{60}–**4**.



Scheme 2.

142.23, 142.07, 141.53, 140.92, 140.04, 138.93, 136.95, 61.80, −4.19, −5.59, −5.65, −5.70; 29 Si−INEPT (60 MHz, CS_2–C_6D_6 = 3:1); δ −1.38, −41.39; FABMS (toluene–NBA) *m*/*z*: $952(M)^+$, $720(C_{60})^+$. $C_{60}(SiEt_2)_4$, ^{1}H-NMR (300 MHz, CS_2–C_6D_6 = 3:l): δ 1.79(m, 1H), 1.63(m, 1H), 1.42 ∼ 1.13 (m, 18H); ^{13}C-NMR (75 MHz CS_2–C_6D_6 = 3:1): δ 166.13, 150.86, 149.76, 148.61, 148.23 (overlapped), 147.61, 147.11, 146.57, 145.31 (overlapped), 145.22, 145.16, 144.99, 144.89, 144.68, 144.58, 143.86, 143.60, 143.30, 143.10, 142.98, 142.87, 142.16, 142.05, 140.74, 140.05, 139.31, 137.24, 136.68, 62.37, 10.81, 10.78, 9.33, 9.21, 6.10, 5.57, 5.42, 4.80; ^{29}Si-INEPT (60 MHz, CS_2–C_6D_6 = 3:1): δ 1.74, −30.23 FABMS (toluene–NBA) *m*/*z*: $1064(M)^+$, $720(C_{60})^+$

Acknowledgements

This work was supported in part by a grant from the Asahi Glass Foundation and the Uchida Energy Science Promotion Foundation and by a Grant-in-Aid for Scientific Research on Priority Area (A) on 'The Chemistry of Inter-element Linkage' (No. 09239217, 10133217, 11120218) from the Ministry of Education, Science, Sports, and Culture of Japan.

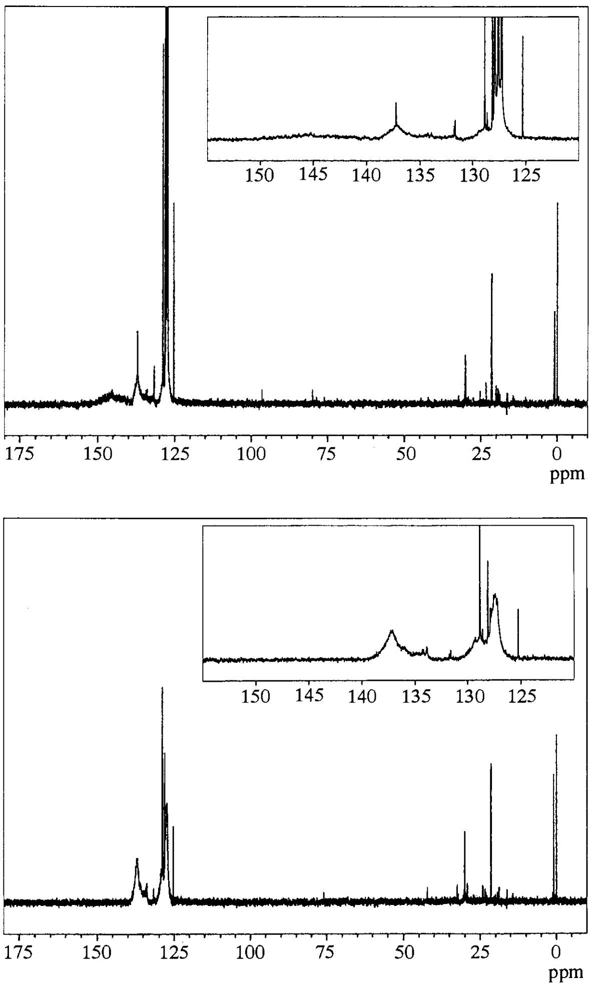


Fig. 7. ^{13}C-NMR (top) and ^{13}C DEPT-NMR(bottom) of C_{60}–**4**.

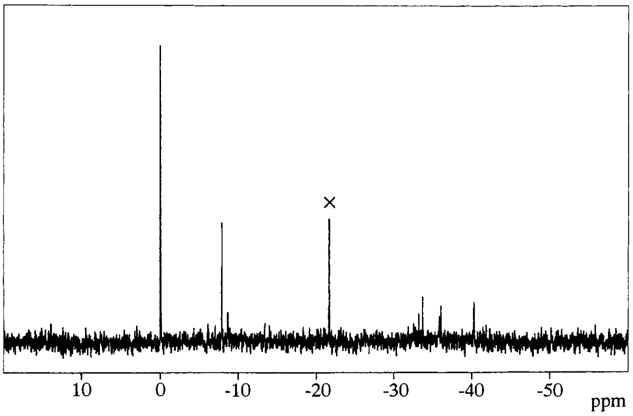
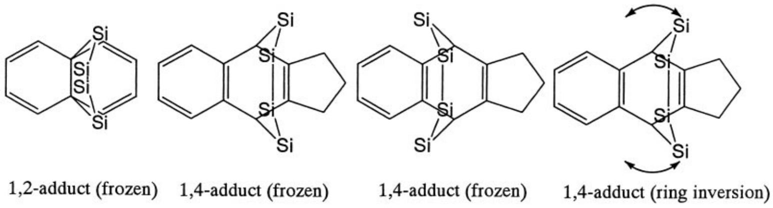
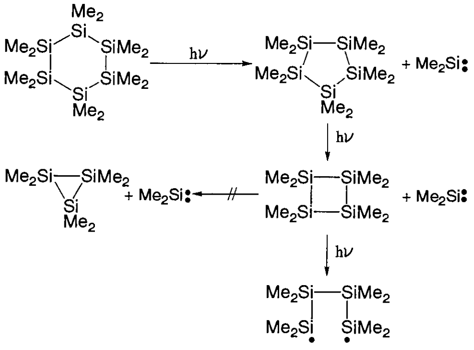


Fig. 8. ^{29}Si-NMR of C_{60}–**4**.



1,2-adduct (frozen) 1,4-adduct (frozen) 1,4-adduct (frozen) 1,4-adduct (ring inversion)

Fig. 9. Possible structure of $C_{60}(SiR_2)_4$ with Cs symmetry.



Scheme 3.

Table 1
The redox potentials of C_{60}–polysilane **1** adduct, polysilane **1** and C_{60}

Compounds	$_{ox}E_1^{a,b}$	$_{red}E_1^c$	$_{red}E_2^c$	$_{red}E_3^c$
C_{60}–**1**	+0.77	−1.24	−1.63	−2.15
1	+0.75	−2<		
C_{60}	+1.21	−1.12	−1.50	−1.95

References

[1] R. West, in: S. Patai, Z Rappoport (Eds.), The Chemistry of Organic Silicon Compounds, Part 2, Wiley, Chichester, England, 1989 chapter 19.

[2] R.D. Miller, J. Michl, Chem. Rev. 89 (1989) 1359.

[3] A. Hirsch, The Chemistry of the Fullerenes, Thime Verlag, Stuttgart, 1994.

[4] R. Taylor, The Chemistry of Fullerenes, World Scientific, Singapore, 1995.

[5] A. Hirsch, Fullerenes and Related Structures, Springer, Berlin, 1998.

[6] T. Akasaka, W. Ando, K. Kobayashi, S. Nagase, J. Am. Chem. Soc. 115 (1993) 1605.

[7] T. Akasaka, W. Ando, K. Kobayashi, S. Nagase, J. Am. Chem. Soc. 115 (1993) 10366.

[8] T. Akasaka, K. Kobayashi, S. Nagase, T. Suzuki, in: K.M. Kadish, R.S. Ruoff (Eds.), Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials, vol. 4, The Electrochemical Society, Pennington, NJ, 1997, p. 265.

[9] T. Akasaka, T. Suzuki, Y. Maeda, M Ara, T. Wakahara, K. Kobayashi, S. Nagase, M. Kako, Y. Nakadaira, M Fujitsuka, O. Ito, J. Org. Chem. 64 (1999) 566.

[10] (a) T. Kusukawa, A Shike, W. Ando, Tetrahedron 52 (1996) 4995. (b) T. Kusukawa, W. Ando, Organometallics 16 (1997) 4027. (c) T. Kusukawa, W. Ando, J. Organomet. Chem. 559 (1998) 11.

[11] Recently, it has been reported that the reaction of tris(trimethylsilyl)silyllithium with C_{60} provided the 1, 6-adduct. T. Kusukawa, W. Ando, Angew. Chem. Int. Ed. Engl. 35 (1996) 1315.

[12] (a) A.M. Rao, P. Zhou, K.A. Wang, G.T. Hager, J.M. Holden, Y. Wang, W.T. Lee, X.X. Bi, P.C. Eklund, D.S. Cornett, M.A Duncan, I. Arnster, Science 259 (1993) 955. (b) A. Gügel, P. Belik, M. Walter, A. Kraus, H. Harth. M. Wagner, J. Spickermann, K. Müllen, Tetrahedron 52 (1996) 5007. (c) M. Taki, S. Takigami, Y. Watanabe, Y. Nakarnura, J. Nishimura, Polym. J. 292 (1996) 1020. (d) H. Okamura, T. Terauchi, M. Minoda, T. Fukuda, K. Komatsu, Macromolecules 30 (1997) 5279; (e) M. Ozawa, J. Li, K. Nakahara, L. Xiao, H. Sugawara, K. Kitazawa, K. Kinbara, K. Saigo, J. Polym. Sci. Sect. A Polym. Chem. 36 (1998) 3139.

[13] Y. Nakadaira, N. Komatsu, H. Sakurai, Chem. Lett. (1985) 1781.

[14] $C_{60}(SiAr_2)_4$ was reported recently. T. Kusukawa, Y. Kabe, W. Ando, Organometallics 14 (1995) 2142.

[15] M. Ishikawa, M. Kumada, Adv. Organomet. Chem. 19 (1981) 51.

[16] (a) Y. Wang, Nature 356 (1992) 585. (b) N.S. Sariciftci, L. Smilowitz, A.J. Heeger, F. Wudl, Science 258 (1992) 1474.

[17] Y. Wang, R. West, C.H. Yuan, J. Am. Chem. Soc. 115 (1993) 3844.