One-Pot Synthesis of Perfluorobutyl-Substituted Polysilyne

Akira Watanabe,* Osamu Ito, and Takao Miwa†
Institute for Chemical Reaction Science, Tohoku University, Katahira, Aoba-ku, Sendai 980-77
†*Hitachi Research Laboratory, Hitachi, Ltd., Hitachi, Ibaraki 319-12*

(Received May 1, 1995)

One-pot synthesis of perfluorobutyl-substituted polysilynes from perfluorobutyl iodide and tetrachlorosilane was achieved by electrochemical reduction using a magnesium working electrode. Absorption and emission spectra of those polymers showed characteristics of a silicon network polymer.

Polysilanes which have a silicon network structure and organic side chains are called polysilynes, based on the Si-repeating unit. The silicon network structure enhances the thermal stability of polysilynes compared with polysilylenes with a linear Si-Si main chain. One of the promising applications is a precursor for inorganic films, for example, SiC, SiO_2 and so on.[1,2] The organic side chains remain in the films prepared by heat treatment of polysilynes at lower than 400°C, and the softness of the organic side chain prevents the cracking formation of the heat-treated films.[2] The most suitable application of polysilynes must be a precursor for a thin insulating film having Si-O-Si structure, which are usually prepared by sol-gel processes. The micropatterning of an insulating film is possible using photochemical oxidation of polysilyne film.[1,2] The organic side chain of polysilyne also provides a possibility for the modification of the electrical properties such as dielectric properties. Our purpose is focused on the formation of an inorganic film having a low dielectric constant by introducing fluorine-containing group as an organic side chain to polysilynes. However, there are some serious problems in preparing fluorine-containing polysilynes. First, fluorine groups are reactive under the condition of a Wurtz-type reaction using sodium metal in a hot toluene. (3,3,3-trifluoropropyl)methylpolysilane reported by Fujino and co-workers is the first example as a fluorine-containing polysilane.[3] However, the yield is less than 4% due to the side reaction of fluorinated substituents during Wurtz-type reaction, and there is no report on polysilyne having perfluoro-alkyl group. Second, it is usually difficult to obtain trichlorosilane monomers having a perfluorinated organic substituent commercially. By these reasons, we investigated one-pot synthesis of perfluorobutyl-substituted polysilynes from perfluorobutyl halide and tetrachlorosilane by electrochemical polymerization. Electrochemical polymerization has been reported as one of the promising methods,[4-7] where the polysilanes can be prepared under a mild condition.

Perfluorobutyltrichlorosilane, the monomer of perfluorobutyl-substituted polysilyne, was prepared by Grignard reaction of perfluorobutyl iodide and tetrachlorosilane, and perfluorobutyl-substituted polysilyne was obtained by the electrochemical polymerization using a magnesium working electrode. The procedures are as follows: A magnesium working electrode and a nickel counter electrode which were separated by a teflon net were put on the bottom of a separable flask containing tetrahydrofuran (THF) solution (20 ml) of $LiClO_4$ (0.016 mol) as an electrolyte. A reflux condenser and a pressure-equalized dropping funnel containing tetrachlorosilane (0.016 mol) and perfluorobutyl iodide in THF (20 ml) were fitted with the separable flask. The system was purged with N_2. The THF solution was dropped on the magnesium electrode cooling with an ice bath. A Grignard reaction between tetrachlorosilane and perfluorobutyl iodide proceeded on the magnesium electrode for 1 hr. The Grignard reaction product, perfluorobutyltrichlorosilane, was electrochemically reduced by the potential sweep method between 0 and -3.0 V (cell voltage, sweep rate; 50 mV/s) under an ultrasonic field at 0 °C for 3 hr. The reaction mixtures were poured into methanol (100 ml) to remove magnesium fragment, and then dropped into distilled water (400 ml) to remove inorganic salts and to obtain polymer as precipitate. The yield and the characteristics of perfluorobutyl-substituted polysilynes are summarized in Table 1. The abbreviation of PFBuSi1/1 corresponds to the polymer obtained from perfluorobutyl iodide and tetrachlorosilane substrates in the ratio 1 to 1, and PFBuSi2/1 and PFBuSi3/1 are polymers for a 2 to 1 and a 3 to 1 ratio, respectively.

Table 1. Yields and characteristics of polymers

	Yield /%	M_w $(M_w/M_n)^a$	F/Si ratio[b]
PFBuSi1/1	3.8[c]	9,700 (1.89)	
	7.2[d]		1.4
PFBuSi2/1	17.8	4,900 (1.43)	19.8
PFBuSi3/1	20.4	4,400 (1.36)	24.7

[a] The molecular weight and the molecular weight distribution were measured by GPC using monodispersed polystyrene as standards. [b] The elemental ratio was determined by XPS spectra. [c] Yield for soluble part. [d] Yield for insoluble part.

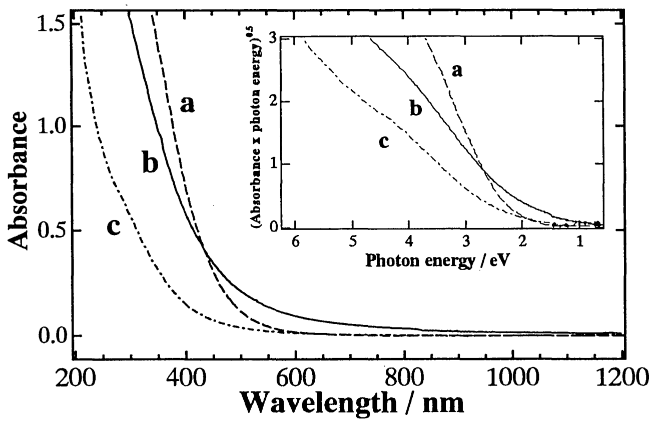

Figure 1. Absorption spectra of perfluorobutyl-substituted polysilynes; (a) diffuse reflectance spectrum of PFBuSi1/1 (1.0 wt% dispersed in KBr), (b) 5 mM PFBuSi2/1 in THF (2 mm optical path length), and (c) 5 mM PFBuSi3/1 in THF (2 mm optical path length).

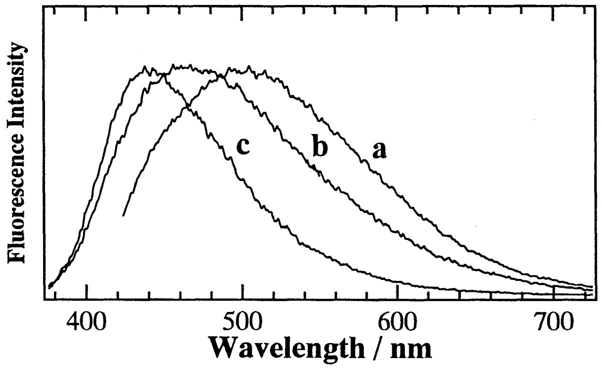

Figure 2. Emission spectra of perfluorobutyl-substituted polysilynes; (a) PFBuSi1/1 powder, (b) 1 mM PFBuSi2/1 in THF, and (c) 5 mM PFBuSi3/1 in THF. Excitation; 375 nm.

The yield increases with increasing the ratio of perfluorobutyl iodide to tetrachlorosilane in Table 1. This suggests that the substitution of chlorine group of silane by perfluorobutyl group and the coupling of the perfluorobutyl-substituted silanes proceeded simultaneously during the electrolysis. The F/Si ratio from XPS spectra is not so accurate to quantify the elemental ratio, but the increase of the F/Si ratio of product with the perfluorobutyl iodide/tetrachlorosilane substrate ratio is seen evidently in Table 1. XPS spectra also showed the existence of oxygen atoms which was incorporated by the substitution of remaining chlorine group of polymer with methoxy group of methanol after electrochemical polymerization. During the electrochemical polymerization, the quantity of electricity passed was ca. 34 C, which is lower than the value expected from the polymer yield. This suggests that the polymerization is not simple electrochemical process but rather complicated reaction where electrochemically activated magnesium electrode and lithium deposited on the cathode surface are concerning.

The absorption and emission spectra of perfluorobutyl-substituted polysilynes (PFBuSi) are structureless and broad as shown in Figures 1 and 2, which show the features of polysilyne having a silicon network structure.[8, 9] The absorption tail extending lower energy region is characteristic of amorphous semiconductors. From the Tauc plot inserted in Figure1, the optical band gap $E_{g,opt}$ of PFBuSi are determined to be 2.26, 1.90, and 2.30 eV for PFBuSi1/1, PFBuSi2/1, and PFBuSi3/1, respectively. The $E_{g,opt}$ values are extremely low in comparison with the values of usual polysilyne without fluorine group (ca. 3 eV).[8-10] Emission spectra of PFBuSi also show the spectral shift to lower energy region compared with polyalkylsilynes. XPS spectra of PFBuSi show the existence of iodine atom. The ratios of iodine to silicon determined by XPS spectra are 0.006, 0.120, and 0.148 for PFBuSi1/1, PFBUSi2/1, and PFBuSi3/1, respectively. The anomalous low $E_{g,opt}$ of PFBuSi as shown in Figure 1 may be cased by the existence of iodine in PFBuSi.

Polysilanes shows characteristic signals of Si-Si bond stretching in the range from 500 to 200 cm^{-1} in the Raman and far-IR spectra and they give the information on the Si-skeleton of polysilanes.[10, 11] In Figure 3, Raman spectra of PFBuSi are compared with poly(di-*n*-hexylsilylene) with a linear Si-Si main chain and poly(perfluorobutylsilyne) obtained by electrochemical polymerization of perfluorobutyltrichlorosilane which was prepared by Grignard reaction of perfluorobutyl iodide and tetrachlorosilane in a different vessel prior to the electrochemical polymerization. PFBuSi1/1 prepared by one-pot synthesis shows quite similar Raman spectrum to that of poly(perfluorobutylsilyne). The Raman bands in the 450-500 cm^{-1} range are characteristic of the asymmetric Si-Si stretching, and the band at 370 cm^{-1} is assigned to the symmetric Si-Si stretching. Both polymers show broad Raman spectra compared with poly(di-*n*-hexylsilylene), which are characteristic of silicon network structure. PFBuSi shows overlapping of sharp Raman bands to broad bands, which suggests the existence of a linear Si-Si chain.

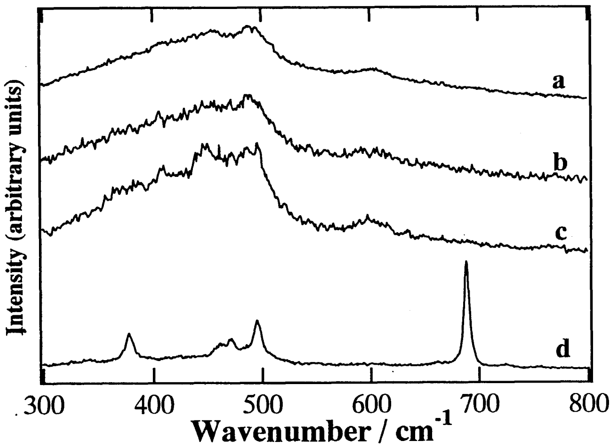

Figure 3. Raman spectra of polysilanes; (a) poly(perfluorobutylsilyne) from perfluorobutyltrichlorosilane prepared by Grignard reaction, (b) PFBuSi1/1, (c) PFBuSi1/2, (d) poly(di-*n*-hexylsilylene).

References and Notes

1 A. Watanabe, T, Komatsubara, O. Ito and M. Matsuda, J. Appl. Phys., **77**, 2796 (1995).

2 A. Watanabe, Y. Nagai and M. Matsuda, *Jpn. J. Appl. Phys.*, **34**, L452 (1995)

3 M. Fujino, T. Hisaki, M. Fujiki and N. Matsumoto, *Macromolecules*, **25**, 1079 (1992).

4 T. Shono, S. Kashimura, M. Ishifune and R. Nishida, *J. Chem. Soc., Chem. Commun.*, **1990**, 1160.

5 A. Kunai, T. Kawakami, E. Toyoda, Ishikawa, *Organometallics*, **10**, 2001 (1991).

6 Ch. Jammegg, S. Graschy, E. Hengge, *Organometallics*, **13**, 2397 (1994).

7 A. Watanabe, T. Komatsubara, M. Matsuda, Y. Yoshida and S. Tagawa, *Macromol. Chem. Phys.*, **196**, 1229 (1995).

8 K. Furukawa, M. Fujino and N. Matsumoto, *Macromolecules*, **23**, 3423 (1990).

9 A. Watanabe, H. Miike, Y. Tsutsumi and M. Matsuda, *Macromolecules*, **26**, 2111 (1993).

10 H. Kuzmany, J. F. Rabolt, B. L. Farmer and R. D. Miller, *J. Chem. Phys.*, **85**, 7413 (1986).

11 A. Watanabe, M. Matsuda, Y. Yoshida and S. Tagawa, *ACS Symp. Series*, **579**, 408 (1994).