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Short communication

Carbon–Silicon coupling between fluorenyl Grignard reagents and dichlorosilanes for synthesis of novel copolymers and chemical properties of the copolymers

Naoyuki Kitamura[1,2] **and Takakazu Yamamoto**[2]*

[1]JFE Chemical, 9-2, Kokancho, Kasaoka, Okayama 714-0063, Japan
[2]Chemical Resources Laboratory, Tokyo Institute of Technology, 4259, Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

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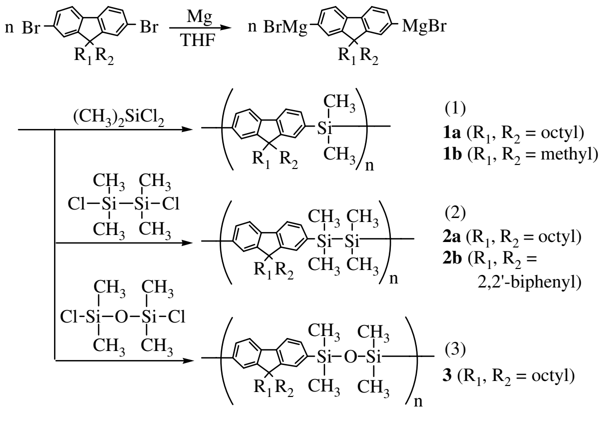
A series of novel silicon-containing fluorene polymers has been prepared by carbon–silicon (C–Si) coupling between fluorenyl Grignard reagents and dichlorosilanes, and their optical and thermal properties have been studied. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: polysilanes; fluorene; C–Si coupling; UV–vis; photoluminescence

Fluorene, as a building unit of polymeric materials, has attracted attention owing to its high stability, planarity and possibility for functionalization at the 9-position. Polyester, polyamide and polyurethane polymers consisting of fluorene units are known. Recently, polydialkylfluorenes (PFs)[1–4] with π-conjugated main chains have been found to be important candidates for organic light-emitting diodes (OLEDs), because of their excellent luminescent efficiencies and chemical stability.

In contrast, polysilanes (PSs) are known as σ-conjugated materials and have been used as hole transporting materials.[5–11] The usefulness of PS as light emitting layers has also been reported;[12–18] however, polymers containing both fluorene-2,7-diyl and silylene units have not been reported. Herein, we report the synthesis of a series of novel polymers containing both units using the C–Si coupling reaction.

The synthesis routes for the polymers are shown in Scheme 1. Reactions of Grignard reagents of dibromofluorenes with commercially available dichlorodimethylsilane (for **1a** and **1b**), 1,2-dichlorotetramethyldisilane (for **2a** and **2b**) and 1,3-dichloro-1,1,3,3-tetramethyldisiloxane (for **3**) gave the polymers in good yields except for **1b**. For **1b**, the low yield is considered to be due to the low solubility of the starting monomer. Data from elemental analyses and ^{1}H NMR data of the polymers were consistent with the structures of the polymers. All polymers had good solubility in organic solvents such as chloroform.



Scheme 1. Synthetic routes for the polymers.

Table 1 shows the synthesis results of the polymers. Polymers **1a, 2a** and **3** were obtained as oily products, whereas **1b** and **2b** were powdery polymers. GPC analysis of the polymers gave a number-average molecular weight M_n of 2.3×10^3 to 4.7×10^3 and weight-average molecular weight M_w of 4.0×10^3 to 9.0×10^3. **1b** and **2b** had intrinsic viscosities η of 12 $cm^3 g^{-1}$ and 7 $cm^3 g^{-1}$ in chloroform respectively. Dichlorodiphenylsilane had a lower reactivity than dichlorodimethylsilane, presumably due to its bulky structure, and gave a lower yield of about 10% in a reaction carried out separately.

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*Correspondence to: Takakazu Yamamoto, Chemical Resources Laboratory, Tokyo Institute of Technology, 4259, Nagatsuta, Midori-ku, Yokohama 226-8503, Japan.
E-mail: tyamamot@res.titech.ac.jp

Table 1. Yield and molecular weight data of polymers

			Molecular weight[a]		
Polymer	Yield (%)	Appearance	M_n	M_w	M_w/M_n
1a	99	Oil	4700	9000	1.9
1b	35	Powder	4200	6700	1.6
2a	84	Oil	3100	4300	1.4
2b	71	Powder	2300	4000	1.8
3	82	Oil	3900	5900	1.5

[a] Gel permeation chromatography (GPC) data (polystyrene standard; eluent: chloroform).

Table 2. UV–vis and photoluminescence (PL) data of the polymers

		PL[a]		
Polymer	UV[a] λ_{max} (nm)	λ_{ex} (nm)	λ_{em} (nm)	ϕ_{PL} (%)
1a	287,316	314	376,396	54
1b	287,312	310	396	89
2a	293,324	320	381	43
2b	269,311,323	270	401	>99
3	285,312	285	375,395	60

[a] Measured in chloroform.

Table 2 summarizes the optical data of the polymers in chloroform. The UV–vis peak of the corresponding monomeric fluorene at 305 ± 4 nm is shifted to a longer wavelength, supporting an assumption of the presence of conjugation along the polymer chain. However, the degree of conjugation is considerably smaller than that observed with fully π-conjugated fluorene homopolymers, which usually show a UV–vis peak at about 385 nm. One of the intriguing properties of the polymers is that they show medium or strong blue photoluminescence. In particular, **1b** and **2b** give very high quantum yields.

All polymers were thermally stable, and **1a, 1b, 2a, 2b** and **3** showed 5 wt% loss temperatures at 402 °C, 455 °C, 404 °C, 435 °C and 415 °C respectively in thermogravimetric analysis. Differential scanning calorimetry analysis of **2b** gave T_g of 135 °C and T_m of 146 °C.

In summary, a series of novel silicon-containing fluorene polymers has been prepared by C–Si coupling. They showed high solubility, good thermal stability, and excellent photoluminescent properties.

EXPERIMENTAL

The purities of the dichlorodimethylsilane, 1,2-dichlorotetramethyldisilane and 1,3-dichloro-1,1,3,3-tetramethyldisiloxane used were higher than 98%, 95% and 97% respectively.

Polymer 1a

To a solution of 2,7-dibromo-9,9-dioctyl fluorene (5.40 g, 9.84 mmol) in 43 cm^3 of dry tetrahydrofuran was added magnesium (0.625 g, 25.7 mmol). After stirring the reaction mixture under reflux for 8 h to form the Grignard reagent, a portion of the solution (15 cm^3, 3.0 mmol) was separated, and to this solution was added dichlorodimethylsilane (0.36 cm^3, 3.0 mmol). The mixture was allowed to react for 48 h at 60 °C. After cooling to room temperature, the reaction mixture was poured into a mixture of methanol (260 cm^3) and concentrated hydrochloric acid (30 cm^3) and stirred overnight. After removal of the supernatant, the residual slurry was dissolved in chloroform (150 cm^3). The resulting solution was washed with diluted hydrochloric acid, followed by water, and then the solvent was removed by evaporation. The residue obtained was dissolved in 10 cm^3 of chloroform, and the solution was added dropwise to 300 cm^3 of methanol with stirring. After overnight stirring and removal of the solution, the product was dried under vacuum for 11 h at 60 °C to obtain **1a** (1.59 g, 99% yield). Anal. Found: C, 80.99; H, 10.14; Br, 0. Calc. for $H-(C_{31}H_{46}Si)_{10}-OH$: C, 83.00; H, 10.38%. $M_n = 4700$. It is known that silicon-containing compounds sometimes give a lower carbon content than the actual amount.[19–21] ^1H NMR data agreed with the structure of the polymer. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.62 (m, 2H, ArH), 7.20–7.53 (m, 4H, ArH), 1.88 (b, 4H, $-CH_2-$), 0.88–1.20 (b, 20H, $-CH_2-$), 0.73 (m, 6H, $C-CH_3$), 0.60 (b, 4H, $-CH_2-$), 0.56 and 0.29 (s, 6H, $Si-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.1, 142.1, 141.9, 138.7, 137.2, 132.8, 131.5, 128.6, 127.4, 126.7, 122.9, 119.2, 54.9, 40.2, 40.0, 31.8, 30.0, 29.2, 23.8, 22.6, 14.1, 0.98, −1.71.

Other polymers were prepared analogously.

Polymer 1b

Anal. Found: C, 78.30; H, 7.24; Cl, 0. Calc. for $H-(C_{17}H_{18}Si)_{17}-OH$: C, 81.19; H, 7.26%. $M_n = 4200$. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.40–7.81 (m, 6H, ArH), 1.44–1.64 (m, 6H, $C-CH_3$), 0.63 and 0.38–0.42 (m, 6H, $Si-CH_3$).

Polymer 2a

Anal. Found: C 74.52; H 9.63; Br, 0. Calc. for $HOC_4H_{12}Si_2-(C_{33}H_{52}Si_2)_6-OH$: C, 76.68; H, 10.39%. $M_n = 3100$. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.61–7.65 (m, 2H, ArH), 7.27–7.40 (m, 4H, ArH), 1.95 (b, 4H, $-CH_2-$), 0.95–1.23 (m, 20H, $-CH_2-$), 0.79 (t, 6H, $C-CH_3$), 0.62 (b, 4H, $-CH_2-$), 0.10–0.45 (m, 12H, $Si-CH_3$).

Polymer 2b

Anal. Found: C, 78.05; H, 6.45; Cl, 0. Calc. for $H-(C_{29}H_{26}Si_2)_5-OH$: C, 80.20; H, 6.13%. $M_n = 2300$. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.20–7.90 (m, 14H, ArH), −0.67–0.36 (m, 12H, $Si-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.0, 148.8, 142.1, 141.7, 133.1, 129.3, 127.7, 127.6, 127.4, 127.0, 124.1, 122.4, 120.0, 119.3, 66.0, 1.78, −0.01, −4.14, −4.42.

Polymer 3

Anal. Found: C, 73.55; H, 9.54. Calc. for H–$(C_{33}H_{52}OSi_2)_7$–OH: C, 75.71; H, 10.07%. $M_n = 3900$. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60–7.80 (m, 2H, ArH), 7.28–7.60 (m, 4H, ArH), 1.95 (b, 4H, $-CH_2-$), 0.95–1.25 (b, 20H, $-CH_2-$), 0.77 (t, 6H, $C-CH_3$), 0.64 (b, 4H, $-CH_2-$), 0.28–0.45 and 0.00–0.08 (m, 12H, $Si-CH_3$).

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