Synthesis and Light-Emitting Behavior of Silicon-Bridged Fluorene Copolymers Bearing Oligoarylenevinylene Chromophore

By Koji TAKAGI,* Ai TAHARA, and Hiroki KAKIUCHI

Silicon-bridged fluorene copolymers bearing oligoarylenevinylene chromophore with longer effective conjugation length than terfluorene were prepared by the Suzuki coupling copolymerization, where the polymer structure was designed so that the absorption spectrum of energy-accepting oligoarylenevinylene chromophore can overlap with the emission spectrum of energy-donating terfluorene chromophore. The content of oligoarylenevinylene segment in **2a5**, **2a10**, **2a20**, **2a48**, and **2a100** could be well controlled by the monomer feed ratio as evidenced by the UV spectra of copolymers in solution. Since the fluorescence from oligoarylenevinylene segment was observed in copolymers and the polymer blend system did not afford longer wavelength emission in dilute solution, the importance of intra-polymer chain energy transfer between chromophores was demonstrated. The fluorescence peaks of **2b13**, **2c11**, and **2d3** ascribed to the emission from oligoarylenevinylene segment were observed in thin film through the intra- and inter-polymer chain energy transfer.

KEY WORDS: Silicon / Fluorene / Copolymer / Energy Transfer / Light-Emission /

Conjugated polymers are applicable to many optoelectronic devices such as light-emitting diode, photovoltaic cell, field-effect transistor, fluorescent sensor, and so on. Polymer materials have merit over low molecular weight counterparts in that thin film with superior mechanical flexibility can be obtained by cost-effective printing processes, which enable the realization of ubiquitous products. On the other hand, polymers are the mixture of many chains having various length, namely, the concentration of terminal group differs one by one. The chain length and terminal group of conjugated polymer significantly influence optoelectronic properties of material, however, their fine control is still the matter of argument.¹ In addition, the structure defects contaminated in polymer backbone are difficult to be removed by the purification technique to decrease the quality of material. These problems often result in the poor color purity and/or the short lifetime of the light-emitting device. Since the excited energy and charge carrier can transfer along the conjugated polymer chain, even trace amount of irregular structure is responsible for the low device reliability. One simple technique to improve device performance is the introduction of insulating segment into the conjugated main chain, which can nicely define the effective conjugation length irrespective of the chain length, terminal group, and sometimes structure defect. For the past decades, we and other groups have utilized organosilicon units as the insulating segment.^{2,3} Some polymers showed high fluorescence quantum yields owing to the enhancement of radiation from the singlet excited state as observed in low molecular weight materials.⁴ We also reported that fluorene-based polymers including the tetrahedral organosilicon unit have zigzag conformation and therefore amorphous character, which contributed to the thermally stable blue-light emission in thin film.²ⁱ

Figure 1. Non-conjugated polymer having terfluorene-dimethylsilylene sequence as repeating unit.

Recently, intramolecular energy transfer along a non-conjugated supramolecular system or a polymer chain has been extensively investigated because it may serve as a useful model to mimic the natural light harvesting process.⁵ It is known that the photoinduced through-space interaction occurs in 4-donor-4'-acceptor substituted diphenyldimethylsilanes.⁶ The polymer **1** (Figure 1) having terfluorene-dimethylsilylene sequence as the repeating unit emits fluorescence ($\lambda_{\text{max}} = 404$ nm) in high quantum yield (0.92) in solution, which is one of the most basic and important factor to furnish the effective energy transfer.⁷ Taking these facts into account, silicon-bridged fluorene copolymers incorporating second chromophore (minor component) having longer effective conjugation length than terfluorene are envisaged to bring about the energy transfer⁸ to obtain a longer wavelength emission. The copolymers should be designed so that the absorption spectrum of energy-accepting oligoarylenevinylene chromophore can overlap with the emission spectrum of energy-donating terfluorene chromophore. Accordingly, four types of copolymers **2** (Figure 2) with various combinations of energy donor/acceptor segments were prepared and optical properties in solution and film states were investigated in order to confirm the fluorescence energy transfer.

Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso, Showa, Nagoya 466-8555 Japan

*To whom correspondence should be addressed (Tel/Fax: +81-52-735-5264, E-mail: takagi.koji@nitech.ac.jp).

Figure 2. General chemical formula of four types of copolymers with various combinations of energy donor/acceptor segments.

EXPERIMENTAL

Materials

All reactions were performed under nitrogen. Dry tetrahydrofuran (THF) was purchased from Kanto Chemical Co. Tetrakis(triphenylphosphine)palladium(0) [Pd(PPh₃)₄] was purchased from TCI Co. 9,9-Dihexylfluorene-2,7-bis(trimethylene borate) **3** was purchased from Aldrich Chemical Co. Ethanol (EtOH) was distilled from Mg(OEt)₂. 2,5-Bis(tributylstannyl)thiophene **4**,⁹ bis(7,7'-dibromo-9,9',9'-tetrahexyl)fluorenyldimethylsilane **5**,²¹ and 2,5-bis(triphenylphosphoniummethyl)-4-(2'-ethylhexyloxy)anisole dibromide **6**¹⁰ were prepared according to the literature. Other reagents were used as received.

Instrumentation

¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 200 FT NMR spectrometer using tetramethylsilane (¹H NMR, δ 0.00) or CDCl₃ (¹³C NMR, δ 77.0) as internal reference peaks. Infrared (IR) spectra were recorded on a Nicolet Impact 400D FT-IR spectrophotometer. Elemental analyses (EA) were performed on a Perkin Elmer PE2400II by CHN mode. Gel permeation chromatographic (GPC) analyses were carried out on a Tosoh DP-8020 using tandem TSK Multipore H_{XL}-M columns (THF as an eluent, flow rate = 1.0 mL/min, 40 °C) equipped with the refractive index detector (RI-8010) on the basis of standard polystyrene samples. Ultraviolet (UV) spectra were recorded on a Shimadzu UV-1650PC spectrophotometer. Photoluminescence (PL) and excitation spectra were recorded on a Shimadzu RF-5300PC spectrofluorometer. The measurements were carried out using 1 cm quartz cell or 1 cm $\times$ 5 cm quartz plate. Fluorescence quantum yields (QYs) in solution were determined relative to quinine sulfate in 0.1 N H₂SO₄ with a QY of 0.55.

Monomer Synthesis

2,5-Bis[(*E*)-4'-bromo- β -styryl]-4-(2''-ethylhexyloxy)anisole **7**. To **6** (3.2 g, 3.2 mmol) and 4-bromobenzaldehyde (1.2 g,

6.7 mmol) dissolved in EtOH (100 mL) was added *t*-BuOK (1.9 g, 17 mmol) in EtOH (70 mL) and the mixture was stirred for 65 h at room temperature. After filtering inorganic salts, the filtrate was concentrated to dryness, which was washed with cold MeOH and dried *in vacuo* to give pale yellow solid in 1.2 g (62% yield). ¹H NMR (200 MHz, CDCl₃) δ (ppm) 7.58–7.33 (10H), 7.20–6.97 (4H), 4.04–3.88 (5H), 1.82 (m, 1H), 1.69–1.21 (8H), 1.11–0.81 (6H). ¹³C NMR (200 MHz, CDCl₃) δ (ppm) 151.4, 151.3, 136.9, 136.8, 131.7, 128.0, 127.9, 127.7, 127.6, 126.6, 126.4, 124.1, 123.9, 121.1, 121.0, 110.7, 109.6, 71.8, 56.2, 39.7, 30.9, 29.2, 24.2, 23.1, 14.1, 11.3. IR (ATR, cm⁻¹) 2960, 2930, 2870, 1500, 1480, 1460, 1420, 1340, 1260, 1210, 1070, 1040, 1010, 964, 852, 808. Anal. Calcd. for: C₃₁H₃₄Br₂O₂: C, 62.22; H, 5.73. Found: C, 61.89; H, 5.58.

2,5-Bis[(*E*)-5'-bromo-2'- β -thienylenevinyl]-4-(2''-ethylhexyloxy)anisole **8**. To **6** (1.2 g, 1.3 mmol) and 2-bromo-5-formylthiophene (0.48 g, 2.5 mmol) dissolved in EtOH (40 mL) was added *t*-BuOK (0.67 g, 6.0 mmol) in EtOH (25 mL) and the mixture was stirred for 23 h at room temperature. After filtering inorganic salts, the filtrate was concentrated to dryness, which was passed through SiO₂ chromatography (CH₂Cl₂ as an eluent). Thus obtained product was dissolved in toluene (30 mL) containing I₂ (11 mg) and heated to reflux for 3 h. The solution was washed with aq. Na₂S₂O₃ and evaporated to dryness. The product was purified by SiO₂ chromatography (hexane:EtOAc = 10:2 in volume as an eluent) (R_f = 0.46) to give brown solid in 0.35 g (46% yield). ¹H NMR (200 MHz, CDCl₃) δ (ppm) 7.24–6.65 (10H), 4.13–3.66 (5H), 1.78 (m, 1H), 1.69–1.18 (8H), 1.11–0.79 (6H). ¹³C NMR (200 MHz, CDCl₃) δ (ppm) 151.3, 151.2, 130.4, 125.9, 125.8, 123.7, 123.5, 121.7, 121.6, 111.0, 110.2, 108.9, 71.7, 56.1, 39.7, 30.9, 29.2, 24.2, 23.1, 14.1, 11.3. IR (ATR, cm⁻¹) 2954, 2929, 2871, 1733, 1524, 1496, 1463, 1432, 1415, 1400, 1348, 1267, 1205, 1037, 951, 862, 833, 781. Anal. Calcd. for: C₂₇H₃₀Br₂O₂S₂: C, 53.12; H, 4.95. Found: C, 52.93; H, 4.78.

Polymerization

2a20 (Typical Procedure). To a two-necked flask equipped with a reflux condenser containing **3** (0.11 g, 0.22 mmol), **5**

Scheme 1. Suzuki coupling copolymerization using **3**, **5**, and **7** as monomers.

(0.14 g, 0.16 mmol), and **7** (36 mg, 60 μmol) dissolved in THF (8 mL) were added 2M aq. K_2CO_3 (1.3 mL, 2.6 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (7.2 mg, 6.2 μmol). The mixture was heated to reflux for 24 h, washed with 1M aq. HCl, and extracted with CH_2Cl_2 . The organic phase was dried over MgSO_4 and concentrated to precipitate in methanol. The obtained polymer was subjected to Soxhlet extraction with acetone and dried *in vacuo* at 60 $^\circ\text{C}$ to give a yellow powder in 0.21 g (51% yield). ^1H NMR (200 MHz, CDCl_3) δ (ppm) 8.02–7.31, 7.22–6.88 (103H), 4.07–3.94 (5H), 2.23–1.81 (58H), 1.26–0.43 (360H). IR (ATR, cm^{-1}) 2952, 2927, 2852, 1490, 1460, 1411, 1263, 1212, 1037, 966, 812. Other polymerizations were likewise performed using **3**, **4**, **5**, **7**, and **8** in combination and their structure were confirmed by ^1H NMR and IR spectra.

2b13 (brown powder). ^1H NMR (200 MHz, CDCl_3) δ (ppm) 7.82–7.30, 7.24–6.88 (158H), 4.02–3.90 (5H), 2.22–1.83 (94H), 1.29–0.53 (592H). IR (ATR, cm^{-1}) 2963, 2929, 2857, 2364, 2345, 1458, 1418, 1260, 1020, 798.

2c11 (yellow powder). ^1H NMR (200 MHz, CDCl_3) δ (ppm) 7.79–7.28, 7.24–7.07 (127H), 4.03–3.93 (5H), 2.12–1.83 (54H), 1.28–0.48 (382H). IR (ATR, cm^{-1}) 2956, 2928, 2857, 1605, 1464, 1263, 1092, 1038, 819, 797, 694.

2d3 (reddish orange powder). ^1H NMR (200 MHz, CDCl_3) δ (ppm) 7.80–7.28, 7.21–6.03 (239H), 3.99–3.83 (5H), 2.19–1.81 (133H), 1.28–0.51 (808H). IR (ATR, cm^{-1}) 2957, 2928, 2857, 1607, 1463, 1262, 1216, 1092, 1023, 797, 689.

RESULTS AND DISCUSSION

Preparation

Dibromo monomers **7** and **8** were synthesized by the Wittig reaction. Since the NMR and IR spectra of initial product obtained by the reaction of **6** with 2-bromo-5-formylthiophene suggested a mixture of *E/Z* isomer, the transformation from *Z* to *E* isomer was carried out by catalytic amount of I_2 in refluxed toluene. Polymers (**2a5**, **2a10**, **2a20**, **2a48**, and **2a100**) with various concentration of oligoarylenevinylene segment were subsequently obtained by the Suzuki coupling copolymerization using **3**, **5**, and **7** as monomers (Scheme 1). The *x* value was calculated by comparing the integral ratio of methyl and methylene proton signals adjacent to the oxygen of alkoxy substituents observed at approximately 4 ppm with those of

Table 1. Characterization of copolymers with various oligoarylenevinylene segments

Code	Yield (%) ^a	M_n^b	M_w/M_n^b	Theoretical <i>x</i>	Calculated <i>x</i> ^c
2a5	47	9700	2.0	0.05	0.05
2a10	39	11800	1.7	0.10	0.10
2a20	51	12100	2.2	0.20	0.20
2a48	50	16900	2.3	0.50	0.48
2a100	38	16100	2.7	1.0	(1.0)
2b13	32	8800	1.6	0.10	0.13
2c11	38	8300	2.0	0.15	0.11
2d3	31	6700	1.7	0.05	0.03

^aIsolated yield after precipitation into MeOH and Soxhlet extraction with acetone. ^bEstimated by GPC (THF, PSt standard). ^cCalculated from ^1H NMR spectrum.

aromatic proton signals or methylene proton signals adjacent to the carbon at 9-position of fluorine observed at around 2 ppm in the ^1H NMR spectrum (Table I). If **5** has much higher reactivity than **7** (or *vice versa*) in the coupling reaction with **3**, two bromo functionalities may react with **3** to give new bis(trimethylene borate) species which slowly reacts with remaining **7** (or **5**) to force terfluorene and oligoarylenevinylene segments to be alternatively arranged, especially for **2a48** having these two segments in the equivalent ratio. Judging from the ^{13}C chemical shift of carbon substituted by the bromine, however, **5** (121.6 ppm) and **7** (121.1 ppm) are supposed to have comparable reactivity toward the oxidative addition of zero valent palladium species. Accordingly, the coupling reaction of **5** and **7** with **3** equally takes place at the initial stage of polymerization to give a chance for these two segments to consecutively connect to afford so-called segment block copolymer though the accurate sequence cannot be determined. The number averaged molecular weight ranged from 9700 to 17000 and the polydispersity indices were around 2. All polymers were readily soluble in organic solvents such as toluene, CHCl_3 , and THF thanks to the zigzag main chain arisen from the tetrahedral organosilicon unit. Likewise, **2b13**, **2c11**, and **2d3** were prepared by the Suzuki and Stille coupling copolymerization using **3**, **4**, **5**, **7**, and **8** in combination and the molar ratio *x* could be nearly controlled by the monomer feed ratio (Figure 3).

Figure 3. Chemical formula of **2b13**, **2c11**, and **2d3**.

Optical Properties

The UV and PL spectra of polymers were collected in CHCl_3 under the concentration of 10^{-6} M per average molecular weight of two kinds of repeating unit. By the increment of oligoarylenevinylene segment, the absorption maximum peak of terfluorene at 358 nm decreased and that of oligoarylenevinylene at 420 nm increased (Figure 4a). The observation of an isosbestic point at 387 nm indicates that the oligoarylenevinylene chromophore could be introduced in the polymer chain as intended. The emission maximum peak was observed at 401 nm with the vibronic fine structure at 422 nm in **1**, which gradually decreased as the total amount of terfluorene that absorb the excitation light at 358 nm in the polymer chain diminished (Figure 4b). Meanwhile, the fluorescence at 477 nm became prominent with concomitant decrease of quantum yield which dropped from 0.92 (**1**) to 0.54 (**2a48**). The fluorescence color varied from blue (**1**) to green (**2a48**) in naked eye. It is a matter of importance that the intensities of fluorescence at 401 nm and 477 nm are comparable in **2a10**, however, only the fluorescence at 401 nm is detected when **1** and **2a100** are blended in the molar ratio of 9:1 to keep the content of oligoarylenevinylene segment as same as that in **2a10** (polymer blend system) (Figure 5a). These results strongly support that the energy transfer from the energy-donating terfluorene to the energy-accepting oligoarylenevinylene occurs “within a single polymer chain” in dilute solution. Furthermore, the energy transfer behavior of **2a10** and the polymer blend system was different in thin film obtained by spin-coating a toluene solution of polymer under the condition of 500 rpm for 5 s and then 2000 rpm for 60 s. The fluorescence of oligoarylenevinylene chromophore at 481 nm with the vibronic fine structure at 510 nm was solely observed in **2a10**. On the contrary, the non-negligible shoulder peak at 414 nm arisen from terfluorene chromophore was detected in the polymer blend system

Figure 4. UV (a) and PL (b) spectra of polymers (**1**, **2a5**, **2a10**, **2a20**, and **2a48**) in CHCl_3 .

(Figure 5b), although polymer chains were present in close proximity each other to enable through space energy transfer in thin film. Accordingly, not only the inter-polymer chain but also the intra-polymer chain interaction of chromophores is

Figure 5. PL spectra of **2a10** and polymer blend (1:2a100 = 9:1) in (a) CHCl_3 and (b) thin film.

indispensable for the effective energy transfer, which may occur incompletely in the polymer blend system. According to the method by Luh *et al.*,^{8b} the absorption spectrum of **2a48** was compared with the excitation spectrum monitored at 477 nm, where two spectra are normalized at the maximum wavelength of the energy-donating terfluorene (420 nm). The efficiency of energy transfer was estimated to be 66%. This value is much lower than materials having alternatively arranged sequence of energy-donor and energy-acceptor separated by the dimethylsilylene unit (87%). Since **2a48** may have a segment block character as mentioned above, the excited energy of terfluorene cannot be efficiently transferred to the oligoarylenevinylene chromophore.

Finally, the UV and PL spectra of **2b13**, **2c11**, and **2d3** were measured in thin film. The absorption maxima were observed at 363 nm for **2b13** bearing terfluorene and at 393 nm for **2c11** and **2d3** bearing bifluorenylthiophene as the major component, as found in CHCl_3 solution. The fluorescence peak was detected at 535 nm, 517 nm, and 570 nm for **2b13**, **2c11**, and **2d3**, respectively, which ascribed to the emission from oligoarylenevinylene chromophore included in the polymer chain as the minor component (Figure 6). It is conceivable that the intra- and inter-polymer chain energy transfers bring about to harvest the excited energy of terfluorene or bifluorenylthiophene toward oligoarylenevinylene chromophore having the longer effective conjugation length.

Figure 6. PL spectra of **2a10**, **2b13**, **2c11**, and **2d3** in thin film.

Received: April 15, 2009

Accepted: May 26, 2009

Published: July 9, 2009

REFERENCES

- a) A. Yokoyama, R. Miyakoshi, and T. Yokozawa, *Macromolecules*, **37**, 1169 (2004).
 - b) R. Miyakoshi, A. Yokoyama, and T. Yokozawa, *Macromol. Rapid Commun.*, **25**, 1663 (2004).
 - c) R. Miyakoshi, A. Yokoyama, and T. Yokozawa, *J. Am. Chem. Soc.*, **127**, 17542 (2005).
 - d) E. E. Sheina, J. Liu, M. C. Iovu, D. W. Laird, and R. D. McCullough, *Macromolecules*, **37**, 3526 (2004).
 - e) M. C. Iovu, E. E. Sheina, R. R. Gil, and R. D. McCullough, *Macromolecules*, **38**, 8649 (2005).
 - f) M. Jeffries-El, G. Sauvé, and R. D. McCullough, *Macromolecules*, **38**, 10346 (2005).
- a) R.-M. Chen, K.-M. Chien, K.-T. Wong, B.-Y. Jin, and T.-Y. Luh, *J. Am. Chem. Soc.*, **119**, 11321 (1997).
 - b) Y.-J. Miao and G. C. Bazan, *Macromolecules*, **30**, 7414 (1997).
 - c) H. Li and R. West, *Macromolecules*, **31**, 2866 (1998).
 - d) D. S. Kim and S. C. Shim, *J. Polym. Sci., Part A: Polym. Chem.*, **37**, 2263 (1999).
 - e) S. H. Jung, H. K. Kim, S. H. Kim, Y. H. Kim, S. C. Jeoung, and D. Kim, *Macromolecules*, **33**, 9277 (2000).
 - f) A. Mori, E. Takehisa, H. Kajiro, Y. Nishihara, and T. Hiyama, *Macromolecules*, **33**, 1115 (2000).
 - g) J. Ohshita, A. Takata, H. Kai, A. Kunai, K. Komaguchi, M. Shiotani, A. Adachi, K. Sakamaki, K. Okita, Y. Harima, Y. Kunugi, K. Yamashita, and M. Ishikawa, *Organometallics*, **19**, 4492 (2000).
 - h) X. Jiang, Y. Harima, K. Yamashita, A. Naka, K. K. Lee, and M. Ishikawa, *J. Mater. Chem.*, **13**, 785 (2003).
 - i) K. Takagi, H. Kakiuchi, and M. Suzuki, *Kobunshi Ronbunshu*, **63**, 663 (2006).
 - j) K. Takagi, H. Kakiuchi, Y. Yuki, and M. Suzuki, *J. Polym. Sci., Part A: Polym. Chem.*, **45**, 4786 (2007).
 - k) X.-H. Zhou, Y.-H. Niu, F. Huang, M. S. Liu, and A. K.-Y. Jen, *Macromolecules*, **40**, 3015 (2007).
- For a polymer containing silole segment, see: K. L. Chan, M. J. McKiernan, C. R. Towns, and A. B. Holmes, *J. Am. Chem. Soc.*, **127**, 7662 (2005).
- a) S. Kyushin, M. Ikarugi, M. Goto, H. Hiratsuka, and H. Matsumoto, *Organometallics*, **15**, 1067 (1996).
 - b) H. Maeda, Y. Inoue, H. Ishida, and K. Mizuno, *Chem. Lett.*, **30**, 1224 (2001).
 - c) S. Yamaguchi and K. Tamao, *J. Chem. Soc., Dalton Trans.*, 3693, (2001).

- 1998.
- d) S. Yamaguchi and K. Tamao, *J. Organomet. Chem.*, **653**, 223 (2002).
5. a) S. E. Webber, *Chem. Rev.*, **90**, 1469 (1990).
- b) A. Adronov, S. L. Gilat, J. M. J. Fréchet, K. Ohta, F. V. R. Neuwahl, and G. R. Fleming, *J. Am. Chem. Soc.*, **122**, 1175 (2000).
- c) M. A. Fox, *Acc. Chem. Res.*, **32**, 201 (1999).
- d) C. Devadoss, P. Bharathi, and J. S. Moore, *J. Am. Chem. Soc.*, **118**, 9635 (1996).
- e) J. M. Serin, D. W. Brousmiche, and J. M. J. Fréchet, *Chem. Commun.*, **2002**, 2605.
- f) C. Hippus, F. Schlosser, M. O. Vysotsky, V. Böhmer, and F. Würthner, *J. Am. Chem. Soc.*, **128**, 3870 (2006).
6. a) C. A. van Walree, M. R. P. Roest, W. Schuddeboom, L. W. Jenneskens, J. W. Verhoeven, J. M. Warman, H. Kooijman, and A. L. Spek, *J. Am. Chem. Soc.*, **118**, 8395 (1996).
- b) A. Zehnacker, F. Lahmani, C. A. Van Walree, and L. W. Jenneskens, *J. Phys. Chem. A*, **104**, 1377 (2000).
7. T. Förster, *Ann. Phys.*, **437**, 55 (1948).
8. a) Y.-J. Cheng, T.-Y. Hwu, J.-H. Hsu, and T.-Y. Luh, *Chem. Commun.*, 1978, (2002).
- b) Y.-J. Cheng and T.-Y. Luh, *Chem.-Eur. J.*, **10**, 5361 (2004).
- c) Y.-J. Cheng, S. Basu, S.-J. Luo, and T.-Y. Luh, *Macromolecules*, **38**, 1442 (2005).
9. W. You, S. Cao, Z. Hou, and L. Yu, *Macromolecules*, **36**, 7014 (2003).
10. T. Ahn, S.-Y. Song, and H.-K. Shim, *Macromolecules*, **33**, 6764 (2000).