

## NOTE

# Preparation of New $\pi$ -Conjugated Thiophene-Pyrrole Copolymers Having Ethynyl Substituents at the *N*-Position of Pyrrole

By Takakazu YAMAMOTO\* and Risako YAMASHITA

KEY WORDS: Copolymers / Thiophene / Pyrrole / UV-visible Spectra / Electrochemical Response /

$\pi$ -Conjugated polymers are the subject of many papers.<sup>1</sup> Polythiophenes and polypyrroles are centrally important  $\pi$ -conjugated polymers, and some of them have been adopted in industry.<sup>2,3</sup>

Copolymers of thiophene and pyrrole have also been reported.<sup>4,5</sup> The copolymers have usually been prepared by oxidative polymerization of the monomers. However, characterization of the copolymers prepared by the oxidative polymerization and revealing their chemical properties have not been explored much. We now report synthesis of three alternating copolymers of thiophene and pyrrole *via* organometallic polycondensation and chemical properties of the synthesized copolymers.

As the pyrrole unit, we are recently concerned with that having an acetylenic  $-C\equiv CR$  side chain at the *N*-position,<sup>5</sup> and the copolymers reported in this paper also have acetylenic  $-C\equiv CR$  side chains at the *N*-position. The  $-C\equiv CR$  side chain has a  $\pi$ -electron system which is expected to have an electronic interaction with the  $\pi$ -conjugated system of the polypyrrole main chain, and  $\pi$ -conjugated polymers having such electronic interaction between the main chain and the side chain has attracted interaction of polymer chemists.<sup>6</sup>

Non-substituted pyrrole has high chemical reactivity,<sup>7</sup> and non-substituted polypyrrole undergoes various oxidation and reduction reactions participated by hydrogen(s) in the pyrrole unit.<sup>7d</sup> Consequently enough characterization of  $\pi$ -conjugated polymers constituted of the non-substituted pyrrole unit is sometimes difficult.<sup>7d</sup> However, the pyrrole unit with the  $-C\equiv CR$  side chain at the *N*-position is chemically stable even when it is in a  $\pi$ -conjugated polymer system.<sup>5</sup>  $\pi$ -Conjugated polymers with acetylenic  $-C\equiv CR$  side chains are the subject of recent interest.<sup>8</sup>

## RESULTS AND DISCUSSION

The following alternating copolymers, **P1**, **P2**, and **P3**, were synthesized according to Pd-catalyzed Stille type polycondensation between the bis(trimethylstannyl) monomer and dibromo monomer, as shown in Scheme 1. **P1** and **P2** were partly (about 1/3) soluble in DMF, and **P3** was soluble in organic solvents such as chloroform, DMF, and THF. GPC (gel

permeation chromatography) of the DMF-soluble parts of **P1** and **P2** showed number average molecular weight ( $M_n$ 's) of 4800 and 4000 with  $M_w/M_n$  values ( $M_w$  = weight average molecular weight) of 2.0 and 2.4, respectively. **P3** showed  $M_n$  and  $M_w$  of 2600 and 4160, respectively. Although the  $M_n$  and  $M_w$  values of **P1-P3** were not large, the polymers are considered to show basic chemical properties of such thiophene-pyrrole copolymers. **P3** has a large  $\pi$ -conjugated side chain which is expected to communicate electronically with the main chain.<sup>6</sup> However, synthesis of  $\pi$ -conjugated polymers with such a large  $\pi$ -conjugated side chain has no precedent to our knowledge. Revealing electronic and optical properties of polymers with such a large  $\pi$ -conjugated side chain might expand chemistry of  $\pi$ -conjugated polymers.

The IR spectra of **P1-P3** were reasonable for the molecular structure, and showed a  $\nu(C\equiv C)$  peak at about  $2250\text{ cm}^{-1}$ . Figure 1 shows  $^1\text{H}$  NMR spectrum of **P2**. The  $-\text{CH}_3$  signal of the tolyl group and the pyrrole-H signal appear at  $\delta$  2.40 and 6.82, respectively.

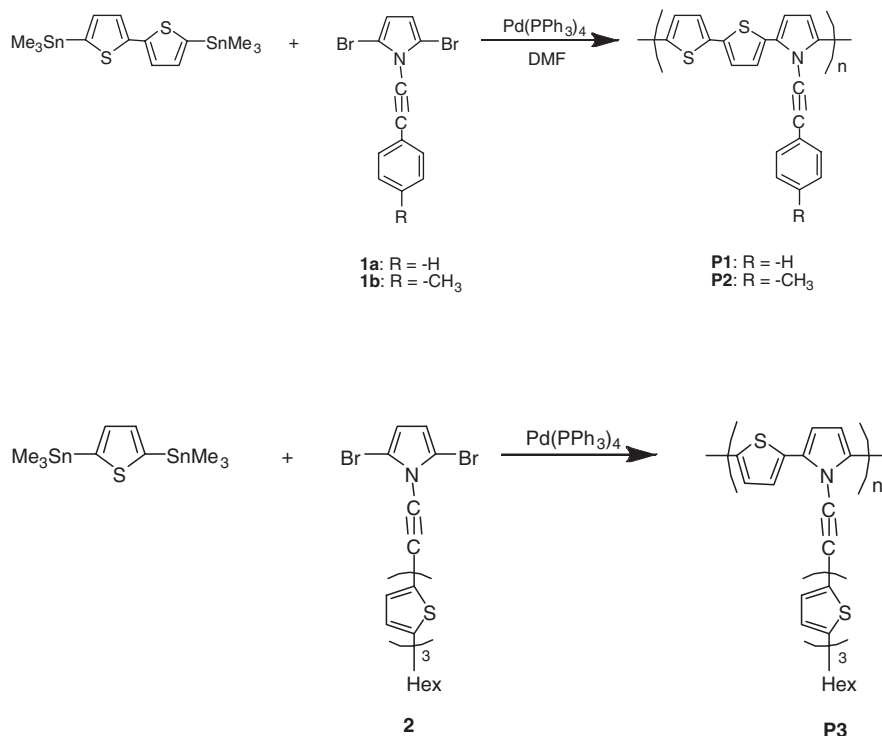
The peak area ratio between the  $\text{CH}_3$  signal and the aromatic signals agrees with the molecular structure of **P2**. The peak area ratio between the aliphatic signals and aromatic signals in the  $^1\text{H}$  NMR spectrum of **P3** also agrees with the molecular structure of **P3**. **P1** gave rise to only the aromatic-H signals in the  $^1\text{H}$  NMR spectrum, and its characterization was made mainly based on data from elemental analysis, IR, and GPC. CP/MAS solid- $^{13}\text{C}$  NMR spectra of the polymers showed acetylenic C signals at about  $\delta$  83 and 74. Powder X-ray diffraction (XRD) patterns of **P1** and **P2** showed some peaks (*e.g.*, at  $d = 4.8$  and  $3.8\text{ \AA}$  for **P1** and  $d = 13.3, 4.5,$  and  $3.9\text{ \AA}$  for **P2**, respectively). An assumption of a laterally face-centered type packing of **P2**, similar to that of poly(3-methylthiophene),<sup>9</sup> gave a calculated density of  $1.33\text{ g cm}^{-3}$ , which agreed with an observed density of  $1.34\text{ g cm}^{-3}$  in the experimental error. The XRD pattern of **P3** showed only a broad peak at  $d = 4.2\text{ \AA}$  which is considered to correspond to loose packing<sup>10</sup> of the hexyl groups in the side chain.

Figure 2 shows UV-vis spectrum of **P1** in DMF and cast film.

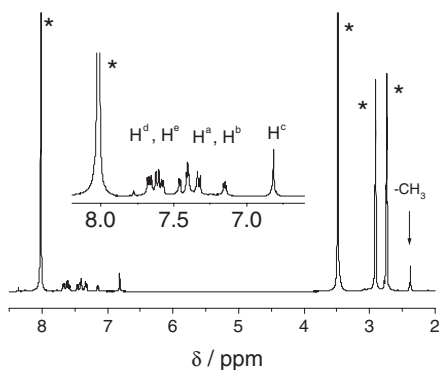
As shown in Figure 2, the UV-vis peak of **P1** appears at 469 nm in DMF. **P2** and **P3** show the UV-vis peaks at 435 nm

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

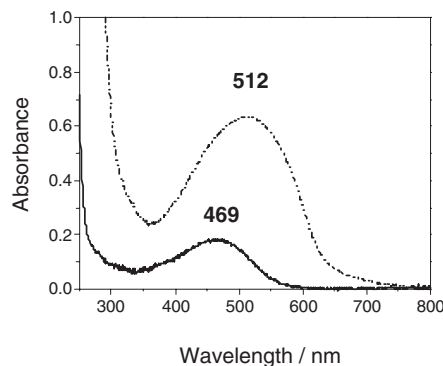
\*To whom correspondence should be addressed (Tel: +81-45-924-5220, Fax: +81-45-924-5976, E-mail: tyamamot@res.titech.ac.jp).



**Scheme 1.** Synthesis of the thiophene-pyrrole copolymers.



**Figure 1.** <sup>1</sup>H NMR spectrum of **P2** in DMF-*d*<sub>7</sub>. Peaks with \* are due to solvent impurities (DMF-*d*<sub>6</sub>'s and H<sub>2</sub>O). The signal at  $\delta$  6.82 (H<sup>f</sup>) is assigned to pyrrole-H. Other aromatic signals (H<sup>a</sup>, H<sup>b</sup>, H<sup>d</sup>, and H<sup>e</sup>) appear in the range of  $\delta$  7.15–7.8.



**Figure 2.** UV-vis spectra of **P1** in DMF (solid line) and cast film on a non-fluorescent glass plate (broken line). The numbers in the figure indicate the wavelength of the peak in nm.

and 410 nm, respectively, in DMF. The  $\lambda_{\text{max}}$  values of **P1-P3** are comparable to those (*ca.* 400–440 nm) of reported copolymers of pyrrole, thiophene, and 3-dodecylthiophene,<sup>4b</sup> which have been prepared by oxidative polymerization of the mixed monomers and reduced (or neutralized) by treatment with hydrazine. The  $\lambda_{\text{max}}$  values are also comparable to those of polythiophene ( $\lambda_{\text{max}} = \text{ca.}$  440 nm) and head-to-tail type poly(3-alkylthiophene) ( $\lambda_{\text{max}} = \text{ca.}$  450 nm),<sup>1</sup> revealing that various  $\pi$ -conjugated polymers constituted of similar five-member rings give the UV-vis peak at near positions. The UV-vis peaks of **P1-P3** show only small shifts between the solution and the cast film (from 469, 435, 410 nm in solutions to 512, 452, and 425 nm in films for **P1**, **P2**, and **P3**, respectively),

which suggest the absence of a strong electronic interaction between the polymer molecules in the solid. Diffuse reflectance spectra of DMF-insoluble parts of **P1** and **P2** showed their absorption peaks at 462 and 461 nm, respectively.

Electrochemical properties of **P1-P3** have been investigated by cyclic voltammetry (CV) using cast films of the polymers. The CV charts showed oxidation (or p-doping) peaks at 0.30, 0.28, and 0.29 V vs. Ag<sup>+</sup>/Ag for **P1**, **P2**, and **P3**, respectively. The oxidation peaks located between those of polythiophene (about 0.6 V vs. Ag<sup>+</sup>/Ag) and polypyrrole (about -0.2 V vs. Ag<sup>+</sup>/Ag).<sup>1</sup> Coupled reduction (or p-undoping) peaks of the polymers were broadened, and broad reduction peaks of **P2** and **P3** appeared at about 0.15 and -0.05 V vs. Ag<sup>+</sup>/Ag, respectively.

As described above, new thiophene-pyrrole copolymers have been synthesized. The obtained results give additional information about such a type of copolymers constituted of thiophene and pyrrole rings.

## EXPERIMENTAL

Commercially available 5,5'-bis(trimethylstannyl)-2,2'-bithiophene ( $\text{Me}_3\text{Sn-Th}_2\text{-SnMe}_3$ ) and 2,5-bis(trimethylstannyl)-thiophene ( $\text{Me}_3\text{Sn-Th-SnMe}_3$ ) were used as purchased. The monomer **1a** were prepared according to the literature.<sup>5</sup>

IR and UV-vis spectra were recorded on a JASCO FT/IR-460plus and a Shimadzu UV-3100PC spectrometers, respectively. UV-vis diffuse reflectance spectra<sup>11</sup> were measured on a Shimadzu UV-3100PC spectrometer equipped with an integrating sphere assembly and transformed to the UV-vis absorption spectra using Kubelka-Munk theory;  $\text{BaSO}_4$  was the reference standard.  $^1\text{H}$  NMR spectra were obtained with JEOL JNM-LA300 and JEOL JNM-EX400 spectrometers. Cyclic voltammetry was carried out using a Hokuto Denko HSV-100 system. The cast film on a glassy carbon electrode, a Pt plate ( $1 \times 2$  cm), and  $\text{Ag}^+/\text{Ag}$  were used as the working, counter, and reference electrodes, respectively. The measurement was carried out in a DMF solution of  $[\text{NBu}_4]\text{BF}_4$  (0.10 M) under  $\text{N}_2$  at room temperature. Powder and film XRD data were obtained with a RINT 2100Ultima<sup>+</sup>/PC diffractometer. GPC was carried out with a TOSOH HLC-8120 liquid chromatograph using DMF containing LiBr (0.01 M) as the eluent.

The monomers **1b** and **2** were prepared according to the methods described below.

Pyrrole (2.46 g, 36.3 mmol) and NaH (0.88 g, 36.6 mmol) were added to 50 mL of dry THF, and the mixture was stirred for 2 h at 60 °C. After cooled to room temperature, 2-*p*-tolyl-1-chloroethyne<sup>12</sup> (5.00 g, 33.3 mmol) was added, and the reaction mixture was stirred for 24 h at 60 °C. After addition of water, the product was extracted with hexane and dried with  $\text{Na}_2\text{SO}_4$ . Purification by column chromatography on  $\text{SiO}_2$  (eluent = hexane) gave 1-(2-*p*-tolylethynyl)pyrrole as a white solid (3.68 g, 61% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.36 (d, 8.4 Hz, 2H), 7.13 (d, 8.4 Hz, 2H), 6.92 (t, 2.2 Hz, 2H), 6.20 (t, 2.2 Hz, 2H), 2.35 (s, 3H). Anal: Calcd. for  $\text{C}_{13}\text{H}_{11}\text{N}$ : C, 86.15%; H, 6.12%; N, 7.73%; Found: C, 86.39%; H, 6.23%; N, 7.57%.

*N*-Bromosuccinimide (NBS, 1.65 g, 9.28) was added to a DMF (80 mL) solution of 1-(2-*p*-tolylethynyl)pyrrole (0.80 g, 4.42 mmol), and the mixture was stirred at 0 °C (ice bath). After warmed to room temperature, the reaction mixture was stirred for 16 h. After addition of water, the product was extracted with hexane and dried over  $\text{Na}_2\text{SO}_4$ . Purification by column chromatography on  $\text{SiO}_2$  (eluent = hexane) gave the monomer **1b** as a colorless liquid (1.00 g, 66% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.45 (d, 7.9 Hz, 2H), 7.16 (d, 7.9 Hz, 2H), 6.21 (s, 2H), 2.37 (s, 3H). Anal: Calcd. for  $\text{C}_{13}\text{H}_9\text{Br}_2\text{N}$ : C, 46.06%; H, 2.68%; Br, 47.14%; N, 4.13%; Found: C, 46.29%; H, 2.46%; Br, 47.30%; N, 4.20%.

Reaction of 1-(5''-hexyl)-2'',2';5',2-terthiophene,<sup>13</sup> Hex- $\text{Th}_3\text{H}$  (2.10 g, 5.10 mmol), and  $\text{H-C}\equiv\text{C-SiMe}_3$  (0.75 g, 7.65

mmol) by Sonogashira coupling in the presence of tetrakis-(triphenylphosphine)palladium,  $\text{Pd}(\text{PPh}_3)_4$ , and CuI at 65 °C gave a yellow powder of Hex- $\text{Th}_3\text{-C}\equiv\text{C-SiMe}_3$  (1.95 g, 4.56 mmol, 90% yield). Treatment of the product with KOH gave a yellow powder of Hex- $\text{Th}_3\text{-C}\equiv\text{CH}$  in 92% yield. Reaction of the product with *N*-chlorosuccinimide gave a yellow powder of Hex- $\text{Th}_3\text{-C}\equiv\text{C-Cl}$  in 58% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.10 (d, 3.9 Hz, 1H), 7.03 (d, 3.9 Hz, 1H), 6.96 (dd, 3.9 and 2.2 Hz, 3H), 6.67 (d, 3.9 Hz, 1H), 2.78 (t, 7.6 Hz, 2H), 1.65 (t, 7.6 Hz, 2H), 1.31–1.23 (m, 6H), 0.88 (t, 6.8 Hz, 3H). Anal: Calcd. for  $\text{C}_{20}\text{H}_{19}\text{ClS}_3$ : C, 61.43%; H, 4.90%; Cl, 9.07%; S, 24.60%; Found: C, 61.43%; H, 4.97%; Cl, 8.96%; S, 24.82%.

The product (0.66 g, 1.69 mmol) was added to the reaction mixture obtained by reaction of pyrrole (0.13 g, 1.86 mmol) and sodium hydride (45 mg, 1.86 mmol) in THF (30 mL), and the mixture was stirred for 24 h at 60 °C. The obtained product was worked-up to obtain a pyrrole derivative having a Hex- $\text{Th}_3\text{-C}\equiv\text{C-}$  substituent at the *N*-position. The product (0.24 g, 0.57 mmol) was treated with NBS (0.21 g, 1.20 mmol) in DMF (30 mL) at room temperature for 16 h. After addition of water, the product was extracted with chloroform and worked-up by column chromatography on  $\text{SiO}_2$  (eluent = hexane) to obtain an orange powder of monomer **2** (0.32 g, 0.55 mmol, 82% yield). Details of the synthesis of **2** and **P3** will be reported elsewhere.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  6.93 (d, 3.9 Hz, 2H), 6.72 (d, 3.9 Hz, 1H), 6.64 (m, 3H), 6.24 (s, 2H), 2.76 (t, 7.6 Hz, 2H), 1.65 (t, 7.6 Hz, 2H), 1.36–1.21 (m, 6H), 0.87 (t, 6.7 Hz, 3H). Anal: Calcd. for  $\text{C}_{24}\text{H}_{21}\text{Br}_2\text{NS}_3$ : C, 49.75%; H, 3.65%; Br, 27.58%; N, 2.42%; S, 16.60%; Found: C, 49.42%; H, 3.50%; Br, 27.36%; N, 2.65%; S, 16.31%.

Preparation of **P1-P3** was carried out as described below.

A mixture of the monomer **1a** (0.91 g, 2.80 mmol),  $\text{Me}_3\text{Sn-Th}_2\text{-SnMe}_3$  (1.38 g, 2.80 mmol), and  $\text{Pd}(\text{PPh}_3)_4$  (0.162 g, 0.14 mmol) in 30 mL of dry DMF was stirred for 48 h at 70 °C. The reaction mixture was poured into an aqueous solution of potassium fluoride and the mixture was stirred for 24 h at room temperature. The precipitate was collected by filtration, washed with diluted hydrochloric acid, aqueous ammonia, water, and methanol, and dried under vacuum to obtain a brown solid of **P1** (0.62 g, 1.88 mmol based on the repeating unit, 67% yield).  $^1\text{H}$  NMR ( $\text{DMF-}d_6$ ):  $\delta$  7.72 (2H), 7.59 (3H), 7.57 (2H), 7.42 (2H), 6.83 (2H). CP/MAS solid- $^{13}\text{C}$  NMR (100 MHz):  $\delta$  131.9, 127.8, 123.4, 112.5, 85.32, 72.87. Anal: Calcd. for  $(\text{C}_{20}\text{H}_{11}\text{NS}_2)_n$ : C, 72.92%; H, 3.37%; N, 4.25%; S, 19.47%; Found: C, 70.44%; H, 3.55%; N, 3.70%; S, 18.93%. The discrepancy between the calculated and found values is considered to be, at least partly, due to high thermal stability of the polymer.

**P2** was prepared analogously using the monomer **1b** (0.36 g, 1.06 mmol) and  $\text{Me}_3\text{Sn-Th}_2\text{-SnMe}_3$  (0.52 g, 1.06 mmol), and **P3** was prepared from the monomer **2** (0.31 g, 0.54 mmol) and  $\text{Me}_3\text{Sn-Th-SnMe}_3$  (0.22 g, 0.54 mmol). They were obtained in 35% and 46% yields. The low yields of **P2** and **P3** are considered to be due to loss of the polymer during work-up including repeated washing the polymers.  $^1\text{H}$  NMR spectrum of **P2** is shown in Figure 1, and CP/MAS solid- $^{13}\text{C}$  NMR

(100 MHz) showed peaks at  $d = 135.7, 132.5, 129.0, 125.0, 111.6, 81.2, 76.1,$  and  $21.2$ . **P3** gave the following  $^1\text{H}$  NMR data in  $\text{CDCl}_3$ :  $\delta$  7.50–6.20 (br, 8H, Th-H), 6.13 (2H, pyrrole-H), 2.70 (2H), 1.63 (2H), 1.25 (6H), 0.81 (3H).

**Acknowledgment.** We are grateful to Professor T. Koizumi and Mr. Y. Yamagata of Tokyo Institute of Technology and Professor T. Shiono of Hiroshima University for helpful discussion and experimental supports. This work was partly supported by a Grant-in-Aid for Science Research in Priority Area “Super-Hierarchical Structures” from Ministry of Education, Culture, Sports, Science, and Technology, Japan.

Received: January 4, 2008

Accepted: April 16, 2008

Published: June 11, 2008

## REFERENCES

- T. A. Skotheim and J. R. Reynolds, “Handbook of Conducting Polymers,” 3rd ed., Boca Raton, Florida, 2007.
  - D. Fichou, “Handbook of Oligo- and Polythiophenes,” Wiley-VCH, Weinheim, 1999.
  - H. S. Nalwa, “Handbook of Organic Conductive Molecules and Polymers,” Wiley, Chichester, 1997.
  - T. Yamamoto and H. Kokubo, *Electrochim. Acta*, **50**, 1453 (2005).
- F. Jonas and G. Heywang, *Electrochim. Acta*, **39**, 1345 (1994).
  - H. Tomozawa, Y. Saida, Y. Ikenoue, F. Murai, Y. Suzuki, T. Tawa, and Y. Ohta, *J. Photopolym. Sci. Technol.*, **4**, 707 (1996).
  - F. Wudl, M. Kobayashi, and A. J. Heeger, *J. Org. Chem.*, **49**, 3382 (1984).
- Y. Kudoh, K. Akami, and M. Yasue, *Synth. Met.*, **102**, 973 (1999).
- H. Röckel, J. Huber, R. Gleiter, and W. Schuhmann, *Adv. Mater.*, **6**, 568 (1994).
  - W. Czerwinski, G. Wrzeszcz, K. Kania, J. F. Rabek, and L. A. Linden, *J. Mater. Sci.*, **35**, 2305 (2000).
  - G. Zotti, S. Zecchin, G. Schiavon, A. Berlin, G. Pagani, M. Borgonovo, and R. Lazzaroni, *Chem. Mater.*, **9**, 2876 (1997).
- T. Yamamoto, M. Yoshizawa, A. Mahmut, M. Abe, S.-I. Kuroda, and S. Sasaki, *J. Polym. Sci., Part A: Polym. Chem.*, **43**, 6223 (2005).
  - R. Yamashita, T. Koizumi, S. Sasaki, and T. Yamamoto, *Polym. J.*, **39**, 1202 (2007).
- W. A. Little, *Phys. Rev.*, **135**, 1416 (1964).
- H. A. Potts and G. F. Smith, *J. Chem. Soc.*, 4018 (1957).
  - B. Sakurai, *Bull. Chem. Soc. Jpn.*, **11**, 374 (1936).
  - A. Sonn, *Chem. Ber.*, **72B**, 2150 (1039).
  - T. Yamamoto, Z.-H. Zhou, I. Ando, and M. Kikuchi, *Makromol. Chem., Rapid Commun.*, **14**, 833 (1993).
- Y. Li, G. Vamvounis, and S. Holdcroft, *Macromolecules*, **35**, 6900 (2002).
  - H. Hayashi and T. Yamamoto, *Kobunshi Ronbunshu*, **58**, 221 (2001).
  - T. Sato, Z. Cai, T. Shiono, and T. Yamamoto, *Polymer*, **47**, 37 (2006).
- T. Yamamoto, D. Komarudin, M. Arai, B.-L. Lee, H. Sugauma, N. Asakawa, Y. Inoue, K. Kubota, S. Sasaki, T. Fukuda, and H. Matsuda, *J. Am. Chem. Soc.*, **120**, 2047 (1998).
- E. F. Jordan, Jr., D. W. Feldeisen, and A. N. Wrigley, *J. Polym. Sci. Part A-1*, **9**, 1835 (1971).
  - H. W. Hsieh, B. Post, and H. Morawetz, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 1241 (1976).
- V. N. Kuznetsov and N. Serpone, *J. Phys. Chem. C*, **111**, 15277 (2007).
  - P. Kubelka and F. Munk, *Z. Tech. Phys.*, **12**, 593 (1931).
- W. Verboom, H. Westmijze, L. De Noten, P. Vermeer, and H. J. T. Bos, *Synthesis*, 296 (1979).
- A. Cravino, S. Roquet, O. Aleveque, P. Leriche, P. Frere, and J. Roncali, *Chem. Mater.*, **18**, 2584 (2006).