Bull. Chem. Soc. Jpn., **78**, 534–536 (2005)

Synthesis, Structure, and Information about Molecular Weight of Thiophene Homopolymers, Copolymers of 2,5-Thienylene and 2,4-Thienylene, and Their Soluble Nitrates

Masahiro Abe, S. M. Abdul Karim, Isao Yamaguchi, Shin-ichi Kuroda,[1] Kenji Kubota,[1] and Takakazu Yamamoto*

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

[1]Faculty of Engineering, Gunma University,
1-5-1 Tenjincho, Kiryu 376-8515

Received September 3, 2004; E-mail: tyamamot@res.titech.ac.jp

Dehalogenative homopolymerization and copolymerization of 2,5-dibromothiophene and 2,4-dibromothiophene were carried out by using a Ni(II) complex catalyst. Nitration of the polymers gave soluble nitrated polymers which provided information about the degree of polymerization (DP = 58–88) of the original polymers. Chemical properties of the polymers and their nitrates are reported.

Poly(thiophene-2,5-diyl), PTh, is one of the most fundamental heterocyclic π-conjugated polymers. Although PTh shows good physical properties such as high electrical conductivity and thermal stability,[1] its insolubility in organic solvents has prevented its molecular weight and chemical properties from being clarified well.

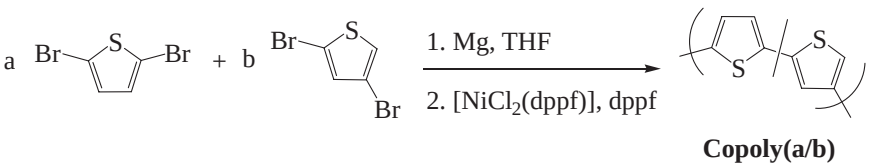
We previously reported that copolymers of *p*-phenylene and *m*-phenylene with a molecular weight of 10^4 showed a good solubility in solvents when the content of the *p*-phenylene unit was in the range of 10–30%.[2] In addition, it was found that insoluble poly(*p*-phenylene), PPP, was solubilized by nitration without cross-linking.[2b,3] Prompted by these findings, we have carried out homopolymerization and copolymerization of 2,5-dibromothiophene and 2,4-dibromothiophene according to Ni-complex-catalyzed Grignard-type polycondensation (cf. Scheme 1) and have obtained basic information about the polymers. Herein we report results of the polymerizations and nitration of the thiophene polymers, focusing on the difference between polyphenylenes and polythiophenes. For the catalyst of the polymerization, [$NiCl_2$(dppf)] (dppf = 1,1′-bis(diphenylphosphino)ferrocene), which gave polyphenylenes with higher molecular weights,[2b] was selected.

The copolymers were obtained in good yields (83–95%) and partially (e.g., about 10% for **Copoly(2/8)**) soluble in $CHCl_3$; however, the solubility was considerably lower than that of the phenylene copolymers. All of PTh, **Copoly(a/b)**, and poly(thiophene-2,4-diyl) (P(2,4-Th)) were insoluble in THF and came out as solids from the polymerization system. IR spectrum of **Copoly(a/b)** showed δ (C–H) peaks of the 2,5-thienylene and 2,4-thienylene units at 795 cm^{-1} and 740 cm^{-1}, respectively. These peak positions were located near those of PTh (790 cm^{-1}) and P(2,4-Th) (740 cm^{-1}). The peak intensity ratio of the two peaks indicated that the composition of the copolymer agreed with the fed monomer ratio (a/b).

Treatment of the polymers with a mixture of HNO_3 and H_2SO_4 gave nitrated polymers: **PTh-NO_2**, **P(2,4-Th)-NO_2**, and **Copoly(a/b)-NO_2** as black powders. Recently, nitration of poly(4-alkylthiophene-2,5-diyl)s was reported, and the nitration was considered to proceed without cross-linking.[4] Table 1 summarizes results of the nitration. The degree of nitration was determined by elemental analysis. As seen from Table 1, about one nitro group was introduced to the thiophene unit. Because the nitro group deactivates the next nitration by decreasing the nucleophilicity of aromatic rings, a second nitration seems to be difficult. However, for **Copoly(8/2)** and **Copoly(2/8)**, the second nitration seems to proceed to some extent to give a degree of nitration higher than 100%. The ^{1}H NMR spectrum of **PTh-NO_2** showed multiplet peaks in a range of δ 8.2–8.8.

After nitration, all polymers became soluble in DMF and DMSO. GPC measurement showed M_n in a range of 8580–11800. The degree of polymerization (DP) estimated from the M_n values was comparable or somewhat larger than that of polyphenylenes.[2] For PTh, data obtained with nitration time of 1 h and 4 h were obtained and are exhibited in Table 1. The degree of nitration increased with time; however, the estimated DP of original PTh was same. Because basic characterization and chemical properties of PTh (e.g., solid structure[5]) have been studied with PTh prepared by the Grignard-type polycondensation, revealing the DP value of PTh prepared by this method is considered to be important. **PTh-NO_2** (nitration time = 4 h), **Copoly(8/2)-NO_2**, and **Copoly(2/8)-NO_2** showed intrinsic viscosity values of 0.15, 0.14, and 0.20 dL g^{-1}, respectively, in DMSO.

Light scattering analysis of **PTh-NO_2** (nitration time = 4 h), **Copoly(5/5)-NO_2**, and **Copoly(2/8)-NO_2** gave M_w values



Copoly(a/b)

Scheme 1.

Published on the web March 11, 2005; DOI 10.1246/bcsj.78.534

Table 1. Results of the Nitration

Copoly(a/b)	Time/h	Degree of nitration/%[a)]	M_n[b)]	M_w[b)]	DP[c)]
Copoly(8/2)	4	111	9.9×10^3	13×10^3	75
Copoly(5/5)	4	99	10×10^3	15×10^3	79
Copoly(3/7)	4	96	9.3×10^3	13×10^3	76
Copoly(2/8)	4	116	12×10^3	20×10^3	88
Copoly(1/9)	4	95	8.6×10^3	11×10^3	69
PTh	1	77	7.9×10^3	10×10^3	67
PTh	4	99	8.5×10^3	11×10^3	67
P(2,4-Th)	4	100	7.4×10^3	15×10^3	58

a) NO_2 groups per the thiophene unit. b) Determined by GPC (vs polystyrene standards; eluent = DMF containing 0.006 mol/L LiBr). M_n = number average molecular weight. M_w = weight average molecular weight. c) Degree of polymerization calculated from M_n.

of 38000, 75000, and 135000 with degrees of depolarization (ρ_v's) of 0.33, 0.31, and 0.27, respectively, in DMF. That the M_w values are larger than those estimated from GPC (cf. Table 1) suggests aggregation of the polymer, and the large ρ_v values indicate that the polymers assume a stiff structure in the solution,[6] similar to the case of nitrated PPP.[3] The ρ_v value gives information about the stiffness of the polymer; an ideally stiff polymer gives a ρ_v value of 1/3.[6] The nitrated copolymer of *p*-phenylene and *m*-phenylene (2:8) showed a small ρ_v value of 0.018 in DMF, revealing that the nitrated phenylene copolymer did not assume a stiff structure due to bending at the *m*-phenylene unit. However, the nitrated thiophene copolymers seem to be able to form a rather linear stiff structure, as discussed below.

Powder X-ray diffraction (XRD) patterns of the *p*-phenylene/*m*-phenylene copolymers were amorphous, showing no distinct peak. On the contrary, XRD patterns of the thiophene copolymers exhibited in Fig. 1 indicate that the copolymers have a certain amount of crystallinity at various a/b ratios. Oli-

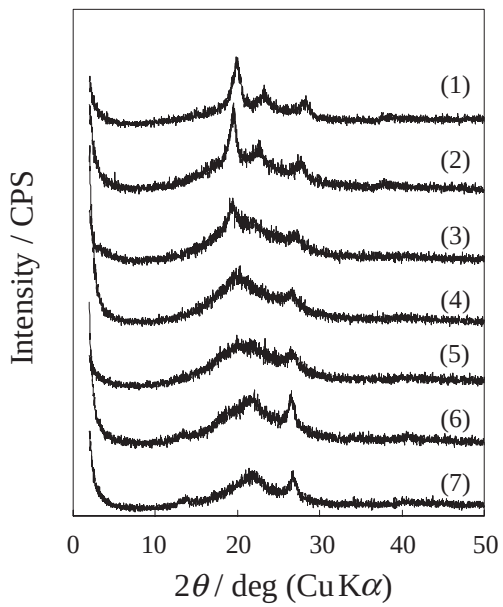


Fig. 1. Powder XRD patterns of (1) **PTh**, **Copoly(a/b)s** ((a:b) = (2) 8:2, (3) 5:5, (4) 3:7, (5) 2:8, (6) 1:9), and (7) **P(2,4-Th)**.

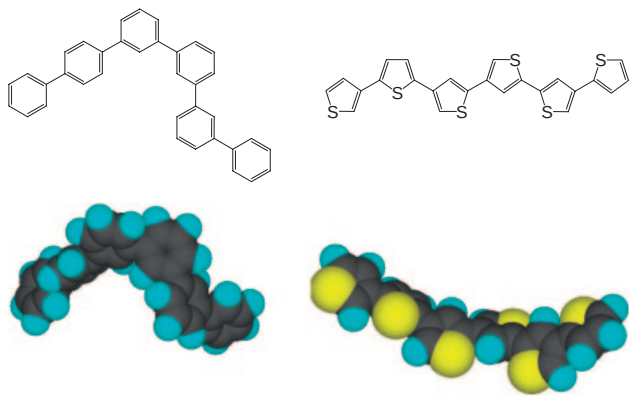


Chart 1. Examples of hexamers of phenylene and thienylene. The molecular structures were calculated by WinMOPAC 3.5.

go-2,5-thienylene and oligo-2,4-thienylene units in the thiophene copolymers seem to have a strong tendency to gather together to form crystalline parts. As exemplified in Chart 1, incorporation of the *m*-phenylene unit causes severe bending of the polymer main chain of the phenylene polymer. However the 2,4-thienylene unit has a structure similar to that of the 2,5-thienylene unit, and the copolymer is considered to have a rather linear structure to allow the polymer molecules to gather together and to form the crystalline part. After nitration, polythiophenes became amorphous, as revealed by their XRD patterns.

For the $CHCl_3$-soluble part of **Copoly(a/b)**, the UV–vis absorption peak reasonably shifted to a shorter wavelength with increase in the 2,4-thienylene unit (e.g., 400, 370, and 280 nm at a/b of 8/2 5/5 2/8). The absorption band of nitrated polythiophenes in DMF became broad and showed a shoulder peak at about 350 nm. **Copoly(5/5)-NO_2** were photoluminescent in DMF with a photoluminescence peak at about 470 nm.

Experimental

Synthesis of Copoly(a/b). A typical procedure: To a THF (9 cm^3) solution of 2,5-dibromothiophene (0.29 g, 1.2 mmol) and 2,4-dibromothiophene (1.2 g, 4.8 mmol) was added a Mg powder (0.15 g, 6.0 mmol) to give a pale brown solution of Grignard compounds. After [$NiCl_2$(dppf)] (41 mg, 0.060 mmol) and dppf (33

mg, 0.060 mmol) were added to the solution, the reaction mixture was refluxed for 8 h under Ar. The reaction mixture was poured into a mixture of MeOH (300 cm^3) and conc. HCl (1 cm^3) to give a precipitate, which was collected by filteration, washed with MeOH (300 cm^3), and dried under vacuum at 80 °C to give **Copoly(2/8)** (0.44 g, 89%).

Nitration of Copoly(a/b). A typical procedure: **Copoly(a/b)** was treated with an excess amount of mixed acid (95% H_2SO_4:61% HNO_3:H_2O = 1:0.17:0.13 vol/vol). The mixture was stirred at 40 °C for 4 h. The nitrated product was poured into cold water, collected by filtration, washed with water, and dried under vacuum. Analytical data of nitrated polythiophenes roughly agreed with a partly hydrated structure. Found for **P(2,4-Th)-NO_2**: C, 34.19; H, 1.64; N, 9.97%. Calcd for $(C_4HNO_2S \cdot 0.65H_2O)_n$: C, 34.61; H, 1.67; N, 10.09%. Found for **Copoly-(5/5)-NO_2**: C, 36.10; H, 1.58; N, 10.43%. Calcd for $\{(C_4HNO_2S)_{0.99}(C_4H_2S)_{0.01} \cdot 0.4H_2O\}_n$: C, 35.89; H, 1.36; N, 10.36%. XPS data of PTh, the copolymer, and nitrated P(2,4-Th) agreed with the chemical structure of the polymers.

References

1 a) R. D. McCullough, *Adv. Mater.*, **10**, 93 (1998). b) T. A. Skotheim, R. L. Elsenbaumer, and J. R. Reynold, "Handbook of Conducting Polymers," 2nd ed, Marcel Dekker, New York (1997). c) T. Yamamoto, *Synlett*, **2003**, 425.

2 a) T. Yamamoto, B. Wu, B.-K. Choi, and K. Kubota, *Chem. Lett.*, **2000**, 720. b) T. Yamamoto, M. Abe, Y. Takahashi, K. Kawata, and K. Kubota, *Polym. J.*, **35**, 603 (2003).

3 T. Yamamoto, B. Choi, and K. Kubota, *Polym. J.*, **32**, 619 (2000).

4 Y. Li, G. Vamvounis, and S. Holdcrft, *Macromolecules*, **35**, 6900 (2002).

5 a) Z. Mo, K.-B. Lee, Y. B. Moon, M. Kobayashi, A. Heeger, and F. Wudl, *Macromolecules*, **18**, 1972 (1985). b) S. Bruckner and W. Porzio, *Makromol. Chem.*, **189**, 961 (1988).

6 a) K. Kubota, H. Urabe, Y. Tominaga, and S. Fujime, *Macromolecules*, **17**, 2096 (1984). b) K. Kubota and B. Chu, *Biopolymers*, **22**, 1461 (1983). c) K. Zero and S. M. Aharoni, *Macromolecules*, **20**, 1957 (1987).