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Synthesis and Characterization of Poly(*p*-phenylene[3-(alkylthio)-2,5-thienylene]-*p*-phenylene)

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ABSTRACT: Alternating copolymers, poly(*p*-phenylene[3-(alkylthio)-2,5-thienylene]-*p*-phenylene)s (**4**) were prepared by the nickel-catalyzed polymerization of 3-(alkylthio)-2,5-bis(4-chlorophenyl)thiophenes (**3**). Polymerizations were conducted in *N*-methyl-2-pyrrolidinone (NMP) in the presence of nickel chloride, zinc, triphenylphosphine, and 2,2′-bipyridine under mild conditions. The resulting polymers **4** had a weight-average molecular weight up to 47 000. The microstructure of polymers was investigated by ^{13}C-NMR spectroscopy, and it has been found that the obtained polymers had the expected regiorandom structures. The polymers were readily soluble in chloroform, dichloromethane, and THF and can be processed into uniform films from their solutions. Degenerate four-wave mixing measurements on polymer **4b** yielded a third-order susceptibility as high as 5.5×10^{-11} esu.

Introduction

The third-order nonlinear optical response of conjugated polymers has recently received much attention and poly(thiophene)s and poly(*p*-phenylene)s have attracted particular interest owing to their highly conjugated structure.[1] For practical applications, these polymers must satisfy the following requirements: high nonlinear optical susceptibilities, a high laser damage threshold, high transparency, and good processability. The processability of aromatic polymers is improved by the introduction of long side chains onto the aromatic rings. However, these substituents induce the structural asymmetry in the monomers and the resulting polymers contain both head−tail and head−head linkages. This configurational disorder prevents a long-range π electron delocalization. To remedy this problem, the synthesis of alternating copolymers that contain arylene and bithiophene repeat units has been reported.[2]

We were interested in an alternating copolymer containing an alkylthio-substituted phenylene−thienylene−phenylene moiety conjugated along the backbone because of the synthetic flexibility for substitution in the thiophene rings and the promising optical and electronic properties of both poly(*p*-phenylene) and polythiophene.

In the previous papers, we showed the nickel-catalyzed coupling polymerization of aryl dichlorides is a very useful method for the syntheses of poly(ether ketone)s,[3] poly(ether sulfone)s,[4] poly(3-phenyl-2,5-thiophene)s,[5] poly(4-substituted *m*-phenylene)s[6] and poly(*p*-phenylene).[7] Therefore, this method must be applicable to the synthesis of the alternating copolymers.

This article describes a successful synthesis of poly(*p*-phenylene[3-(alkylthio)-2,5-thienylene]-*p*-phenylene)s (**4**) by the nickel-catalyzed polymerization of 3-(alkylthio)-2,5-bis(4-chlorophenyl)thiophene and their optical and electrochemical properties. In this monomer, as the alkylthio-substituted thienylene unit is placed between phenyl rings, the polymerization is not affected by the steric effect of the alkylthio groups, and the configurational disorder of the obtained polymer does not prevent the long-range π electron delocalization.

Experimental Section

Materials. Reagent grade anhydrous $NiCl_2$ was dried at 220 °C under vacuum. Triphenylphosphine (PPh_3) and 2,2′-bipyridine (bpy) were purified by recrystallization from *n*-hexane. Powdered (400-mesh) zinc was purified by stirring with acetic acid, filtering, washing thoroughly with ethyl ether, and drying under vacuum. *N*-Methyl-2-pyrrolidinone (NMP) was stirred over powdered calcium hydride overnight, then distilled under reduced pressure, and stored over molecular sieves 4-A.

1,4-Bis(4-chlorophenyl)-2-butene-1,4-dione (1). In a 500 mL three-necked round-bottomed flask fitted with a reflux condenser connected to a calcium chloride drying tube, a nitrogen inlet, and a mechanical stirrer were placed fumaryl chloride (10 mL, 92 mmol), chlorobenzene (30 mL, 0.31 mol), and carbon disulfide (67 mL). To this stirred solution was added slowly anhydrous aluminum chloride (35 g, 0.26 mol) in small portions. The mixture was heated at 45−50 °C for 3 h. A condenser was attached to one of the side necks, and the carbon disulfide was distilled. The reaction mixture was cooled and poured over cracked ice containing hydrochloric acid. The mixture was extracted with dichloromethane. The combined organic layer was washed with diluted aqueous HCl solution, water, and aqueous 10% Na_2CO_3 solution, dried over anhydrous magnesium sulfate, and filtered. After evaporation of the solvent, the residue was crystallized from acetone to give red needles. Yield: 13 g (47%). Mp: 172−173 °C. IR (KBr): υ (cm^{-1}) 1650 (C═O), 1600, 1500 (arom. C−H). ^{1}H-NMR ($CDCl_3$): δ (ppm) 7.51 (d, $J = 8.6$ Hz, benzene, 4H), 8.01 (d, $J = 8.6$ Hz, benzene, 4H), 7.98 (s, CH═CH, 2H). ^{13}C-NMR ($CDCl_3$): δ (ppm) 129.3, 130.2, 135.1, 140.6, 134.8, 188.3. Anal. Calcd for $C_{16}H_{10}O_2Cl_2$: C, 62.97; H, 3.30. Found: C, 63.16; H, 3.41.

2-(Butylthio)-1,4-bis(4-chlorophenyl)butane-1,4-dione (2a). A few drops of triethylamine (TEA) were added to a solution of compound **1** (5.19 g, 17.0 mmol) and 1-butanethiol (4.87 g, 17.0 mmol) in THF (150 mL). The solution was stirred

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at room temperature for 2 h. The solvent was removed under reduced pressure and the residue was crystallized from ethanol to yield white needles. Yield: 5.24 g (78%). Mp: 88−90 °C. IR (KBr): υ (cm^{-1}) 2960 (C−H), 1680 (C=O), 1600, 1500 (arom. C−H). ^{1}H-NMR ($CDCl_3$): δ (ppm) 0.85 ppm (t, J = 6.9 Hz, CH_3, 3H), 1.32 (sext, J = 6.9 Hz, CH_2, 2H), 1.46 (quint, J = 6.9 Hz, CH_2, 2H), 2.39 (dt, ^3J = 7.6 Hz, ^2J = 11.9 Hz, SCH_2, 1H), 2.56 (dt, ^3J = 7.6 Hz, ^2J = 11.9 Hz, SCH_2, 1H), 3.39 (dd, ^2J = 3.6 Hz, ^3J = 17.8 Hz, CH_2, 1H), 4.06 (dd, ^3J = 10.2, 17.8 Hz, CH, 1H), 4.77 (dd, ^2J = 3.6 Hz, ^3J = 10.2 Hz, CH_2, 1H), 7.43 (d, J = 8.6 Hz, benzene, 2H), 7.45 (s, thiophene, 1H), 7.46 (d, J = 8.6 Hz, benzene, 2H), 7.91 (d, J = 8.6 Hz, benzene, 2H), 8.02 (d, J = 8.6 Hz, benzene, 2H). ^{13}C-NMR ($CDCl_3$): δ (ppm) 13.5, 22.0, 29.1, 31.2, 41.1, 41.5, 128.9, 129.0, 129.5, 130.1, 134.1, 134.4, 139.4, 140.0, 193.6, 196.4. Anal. Calcd for $C_{20}H_{20}O_2SCl_2$: C, 60.76; H, 5.09. Found: C, 60.97; H, 5.18.

2-(Decylthio)-1,4-bis(4-chlorophenyl)butane-1,4-dione (2b). Compound (**2b**) was prepared by the reaction of **1** with 1-decanethiol. The procedure is the same as that used for the synthesis of compound **2a**. Recrystallization from ethanol yielded white needles. Yield: 6.77 g (83%). Mp: 31−32 °C. IR (KBr): υ (cm^{-1}) 2960 (C−H), 1680 (C=O), 1600, 1500 (arom. C−H). ^{1}H-NMR ($CDCl_3$): δ (ppm) 0.85 ppm (t, J = 6.9 Hz, CH_3, 3H), 1.25 (m, CH_2, 14H), 1.46 (m, CH_2, 2H), 2.39 (dt, ^3J = 7.6 Hz, ^2J = 11.9 Hz, SCH_2, 1H), 2.56 (dt, ^3J = 7.6 Hz, ^2J = 11.9 Hz, SCH_2, 1H), 3.39 (dd, ^2J = 3.6 Hz, ^3J = 17.8 Hz, CH_2, 1H), 4.06 (dd, ^3J = 10.2, 17.8 Hz, CH, 1H), 4.77 (dd, ^2J = 3.6 Hz, ^3J = 10.2 Hz, CH_2, 1H), 7.43 (d, J = 8.6 Hz, benzene, 2H), 7.45 (s, thiophene, 1H), 7.46 (d, J = 8.6 Hz, benzene, 2H), 7.91 (d, J = 8.6 Hz, benzene, 2H), 8.02 (d, J = 8.6 Hz, benzene, 2H). ^{13}C-NMR ($CDCl_3$): δ (ppm) 14.1, 22.6, 28.8, 29.1, 29.2, 29.4, 29.5, 31.8, 41.1, 41.4, 128.9, 129.0, 129.5, 130.1, 134.0, 134.4, 139.4, 139.9, 193.6, 196.4. Anal. Calcd for $C_{26}H_{32}O_2SCl_2$: C, 65.13; H, 6.73. Found: C, 65.17; H, 6.75.

2-(Octadecylthio)-1,4-bis(4-chlorophenyl)butane-1,4-dione (2c). Compound **2c** was prepared by the reaction of **1** with 1-octadecanethiol. The procedure is the same as that used for the synthesis of compound **2a**. Recrystallization from ethanol yielded white needles. Yield: 7.24 g (72%). Mp: 46−47 °C. IR (KBr): υ (cm^{-1}) 2960 (C−H), 1680 (C=O), 1600, 1500 (arom. C−H). ^{1}H-NMR ($CDCl_3$): δ (ppm) 0.85 ppm (t, J = 6.9 Hz, CH_3, 3H), 1.25 (m, CH_2, 30H), 1.46 (m, CH_2, 2H), 2.39 (dt, ^3J = 7.6 Hz, ^2J = 11.9 Hz, SCH_2, 1H), 2.56 (dt, ^3J = 7.6 Hz, ^2J = 11.9 Hz, SCH_2, 1H), 3.39 (dd, ^2J = 3.6 Hz, ^3J = 17.8 Hz, CH_2, 1H), 4.06 (dd, ^3J = 10.2 Hz, 17.8 Hz, CH, 1H), 4.77 (dd, ^2J = 3.6 Hz, ^3J = 10.2 Hz, CH_2, 1H), 7.43 (d, J = 8.6 Hz, benzene, 2H), 7.45 (s, thiophene, 1H), 7.46 (d, J = 8.6 Hz, benzene, 2H), 7.91 (d, J = 8.6 Hz, benzene, 2H), 8.02 (d, J = 8.6 Hz, benzene, 2H). ^{13}C-NMR ($CDCl_3$): δ (ppm) 14.1, 22.7, 28.8, 29.1 29.1, 29.3, 29.4, 29.5, 29.5, 29.7, 31.9, 41.1, 41.5, 128.9, 129.0, 129.5, 130.1, 134.1, 134.4, 139.5, 140.0, 193.7, 196.4. Anal. Calcd for $C_{34}H_{48}O_2SCl_2$: C, 69.01; H, 8.18. Found: C, 69.17; H, 8.25.

3-(Butylthio)-2,5-bis(4-chlorophenyl)thiophene (3a). A mixture of **2a** (4.74 g, 12.0 mmol) and Lawesson's reagent (4.98 g, 12.3 mmol) in dry toluene (100 mL) was refluxed with stirring for 2 h. After evaporation of toluene, petroleum ether (bp 35−60 °C) was added to the residue. The mixture was refluxed for 1 h, and the insoluble materials were filtered off. The filtrate was concentrated under vacuum to give a faint yellow solid. Recrystallization from methanol produced white needles. Yield: 3.07 g (65%). Mp: 114−116 °C. IR (KBr): υ (cm^{-1}) 2960 (C−H), 1520 (arom. C−H), 1490, 1410 (thiophene C−H), 1090 (C−Cl), and 810 (thiphene ring). ^{1}H-NMR ($CDCl_3$): δ (ppm) 0.85 (t, J = 6.9 Hz, CH_3, 3H), 1.33 (sext, J = 6.9 Hz, CH_2, 2H), 1.51 (quint, J = 6.9 Hz, CH_2, 2H), 2.79 (t, J = 6.9 Hz, SCH_2, 2H), 7.33 (d, J = 8.6 Hz, benzene, 2H), 7.36 (s, thiophene, 1H), 7.37 (d, J = 8.6 Hz, benzene, 2H), 7.49 (d, J = 8.6 Hz, benzene, 2H), 7.60 (d, J = 8.6 Hz, benzene, 2H). ^{13}C-NMR ($CDCl_3$): δ (ppm) 13.5, 22.0, 31.2, 35.8, 126.7, 128.6, 129.1, 130.2, 127.6, 129.5, 132.0, 132.0, 133.7, 133.8, 139.5, 141.1. Anal. Calcd for $C_{20}H_{18}S_2Cl_2$: C, 61.08; H, 4.58. Found: C, 60.99; H, 4.62.

3-(Decylthio)-2,5-bis(4-chlorophenyl)thiophene (3b). Compound (**3b**) was prepared from (**2b**) and Lawesson's reagent. The procedure is the same as that used for the synthesis of compound **3a**. Recrystallization from methanol yielded white needles. Yield: 4.12 g (72%). Mp: 81−82 °C. IR (KBr): υ (cm^{-1}) 2960 (C−H), 1520 (arom. C−H), 1490, 1410 (arom. thiophene, C−H), 1090 (C−Cl), 810 (thiophene ring). ^{1}H-NMR ($CDCl_3$): δ (ppm) 0.85 (t, J = 6.9 Hz, CH_3, 3H), 1.22 (m, CH_2, 14H), 1.52 (m, CH_2, 2H), 2.79 (t, J = 6.9 Hz, SCH_2, 2H), 7.33 (d, J = 8.6 Hz, benzene, 2H), 7.36 (s, thiophene, 1H), 7.37 (d, J = 8.6 Hz, benzene, 2H), 7.49 (d, J = 8.6 Hz, benzene, 2H), 7.60 (d, J = 8.6 Hz, benzene, 2H). ^{13}C-NMR ($CDCl_3$): δ (ppm) 14.1, 22.6, 28.8, 29.1, 29.2, 29.4, 29.5, 31.8, 35.8, 126.7, 127.6, 128.6, 129.1, 129.5, 130.2, 132.0, 132.0, 133.7, 133.8, 139.5, 141.1. Anal. Calcd for $C_{26}H_{30}S_2Cl_2$: C, 65.39; H, 6.33. Found: C, 65.55; H, 6.29.

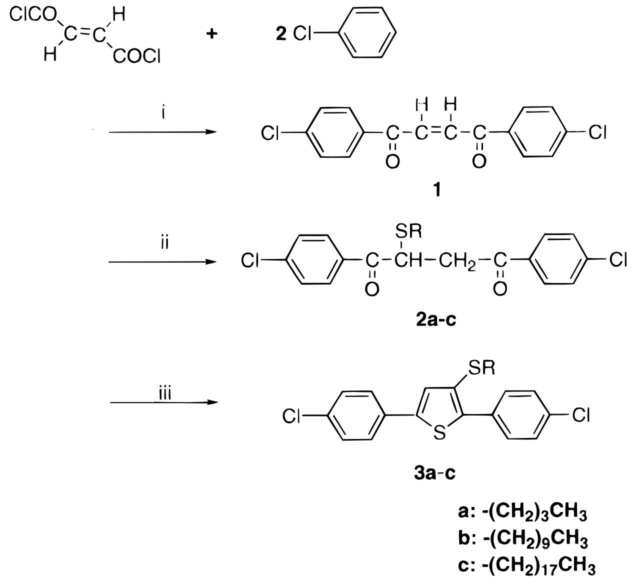
3-(Octadecylthio)-2,5-bis(4-chlorophenyl)thiophene (3c). Compound (**3c**) was prepared from (**2c**) and Lawesson's reagent. The procedure is the same as that used for the synthesis of compound **3a**. Recrystallization from methanol yielded white needles. Yield: 5.17 g (73%). Mp 92−93 °C. IR (KBr): υ (cm^{-1}) 2960 (C−H), 1520 (arom. C−H), 1490, 1410 (arom. thiophene, C−H), 1090 (C−Cl), 810 (thiophene ring). ^{1}H-NMR ($CDCl_3$): δ (ppm) 0.87 (t, J = 6.9 Hz, CH_3, 3H), 1.22 (m, CH_2, 30H), 1.52 (m, CH_2, 2H), 2.79 (t, J = 6.9 Hz, SCH_2, 2H), 7.33 (d, J = 8.6 Hz, benzene, 2H), 7.36 (s, thiophene, 1H), 7.37 (d, J = 8.6 Hz, benzene, 2H), 7.49 (d, J = 8.6 Hz, benzene, 2H), 7.60 (d, J = 8.6 Hz, benzene, 2H). ^{13}C-NMR ($CDCl_3$): δ (ppm) 14.1, 22.7, 28.8, 29.1, 29.1, 29.3, 29.4, 29.5, 29.5, 29.7, 31.9, 35.8, 126.7, 127.6, 128.6, 129.1, 129.5, 130.2, 132.0, 132.0, 133.7, 133.8, 139.5, 141.1. Anal. Calcd for $C_{34}H_{46}S_2Cl_2$: C, 69.24; H, 7.86. Found: C, 69.53; H, 7.75.

Polymer Synthesis. A typical example of the polymerization follows.

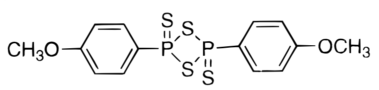
Polymer 4b from 3b. In a 25-mL two-necked round-bottomed flask were placed $NiCl_2$(4.5 mg, 0.035 mmol), PPh_3 (78 mg, 0.30 mmol), 2,2′-bipyridine (5.4 mg, 0.035 mmol), zinc (100 mg, 1.5 mmol), and monomer **3b** (240 mg, 0.50 mmol). The flask was evacuated and filled with nitrogen three times. Then NMP (0.5 mL) was added via syringe through a septum cap. The mixture was stirred at 90 °C for 24 h. The mixture was diluted with NMP (1 mL) and poured into a large amount of HCl/methanol = 1/9. The polymer was collected, washed with methanol, and dried in *vacuo* at 50 °C for 24 h. Yield: 0.20 g (100%). IR (film): υ (cm^{-1}) 2930, 2850 (C−H), 1600, 1530, 1480, 1470 (thiophene, benzene ring), 820 (*p*-substituted benzene ring). ^{1}H-NMR ($CDCl_3$): δ (ppm) 0.86 (br, CH_3, 3H), 1.22 (br, CH_2, 30H), 1.56 (br, CH_2, 2H), 2.83 (br, SCH_2, 2H), 7.2−7.8 (br, benzene, 8H, thiophene, 1H). ^{13}C-NMR ($CDCl_3$): δ (ppm) 14.0, 22.6, 28.7, 29.1 29.1, 29.3, 29.5, 31.9, 35.9, 125.6, 126.0, 126.7, 126.8, 127.3, 127.4, 128.3, 129.3, 130.2, 133.0, 133.8, 139.6, 140.3, 141.8. Anal. Calcd for $C_{26}H_{30}S_2$: C, 76.80; H, 7.44. Found: C, 76.54; H, 7.41.

Measurements. The infrared spectra were recorded on a HORIBA FT-210 spectrometer. The UV−visible spectra were obtained on a SHIMADZU UV-2200 spectrophotometer. The NMR spectra were measured on JEOL EX 270 (^{1}H, 270 MHz; ^{13}C, 68.5 MHz) spectrometer as a $CDCl_3$ solution using TMS as an internal standard. Thermogravimetric analyses (TGA) were performed on a Seiko SSC/5200 (TG/DTA 220) thermal analyzer at a heating rate 10 °C·min^{-1}. The glass transition temperature (T_g) was measured on a Seiko SSC/5200 (DSC 220) instrument at a heating rate 20 °C·min^{-1} in nitrogen. Molecular weights were determined by a gel permeation chromatography (GPC) using polystyrene as a standard on a JASCO TRIROTAR-III HPLC equipped with a Shodex KF-80M column at 40 °C in THF. The cyclic voltammograms were measured in acetonitrile solution containing 0.1 M tetrabutylammonium perchlorate (TBAPC) and 10 mM monomer with the aid of a Hokuto Denko HA-501 potentiostat/galvanostat. The scanning rate was 100 mV·s^{-1}. A Pt disk with a diameter of 2 mm was used as a working electrode, and an aqueous SCE was used as the reference electrode. The third-order nonlinear optical susceptibility $\chi(3)$ of polymer **4b** was measured by using a degenerated four-wave mixing (DFWM) with short optical pulses to reduce thermal effects. A mode-locked Ti:sapphire laser was used as a pump source. The pulse duration and the repetition rate of the laser system were 120 fs and 80 MHz, respectively, and the central wavelength was turned to 775

Scheme 1



Conditions: i) AlCl3, CS2, reflux, 3 h. ii) R-SH, TEA, THF, 2 h. iii) Lawesson's reagent, Toluene, reflux, 2 h.



Lawesson's reagent

nm. The optical pulses are split and overlapped spatially and temporally on the sample with a cross angle of 2.3°. The diffracted single of DFWM was detected by a Ge photodiode with a pinhole, to reduce scattering of the pump beam.

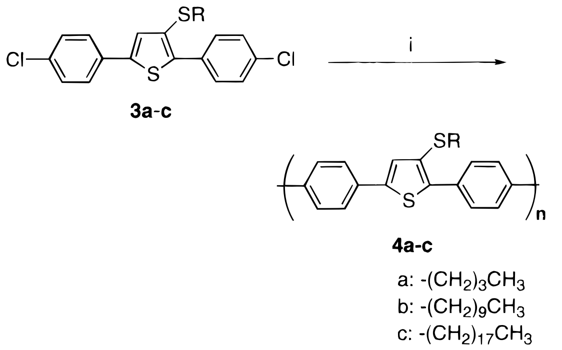
Results and Discussion

Monomer Synthesis. The most widely used method at present for the synthesis of alternating monomers containing arylene and thienylene repeating units in the literature is the nickel-catalyzed Kumada coupling of diiodobenzenes with halomagnesium thiophenes.[8] This method, however, is not straightforward nor is it easily performed on a large scale. Therefore, an alternative easier synthesis should be developed. The thiophene ring is easily formed by the treatment of 1,4-diketones with Lawesson's reagent.[9] Furthermore, the butene-1,4-dione structure is easily converted to 1,4-diketone compounds by the Michael addition, which may enable us to introduce solubilizing groups onto the thiophene rings. Therefore, we decided to prepare the following monomers consisting of a phenylene–thienylene–phenylene unit through this route.

As polymer-forming monomers, 3-(alkylthio)-2,5-bis-(4-chlorophenyl)thiophenes (**3**) were prepared by the reactions outlined in Scheme 1. In the first step, the Friedel–Crafts reaction of chlorobenzene with fumaryl chloride provided 1,4-bis(4-chlorophenyl)-2-butene-1,4-dione (**1**). Then the Michael addition of alkylthiols to compound **1** yielded 2-(alkylthio)-1,4-bis(4-chlorophenyl)butane-1,4-diones (**2**), which were converted to monomers **3** in good yields by treatment with Lawesson's reagent.

Polymerization. On the basis of previous results on the syntheses of poly(3-substituted thiophene)s by the nickel-catalyzed coupling polymerization of 3-substituted 2,5-dichlorothiophenes,[5] the polymerization of **3** was performed with 0.50 mmol of monomer in NMP in the presence of $NiCl_2$, zinc, triphenylphosphine (PPh_3), and 2,2′-bipyridine (bpy) at 90 °C for 24 h (Scheme 2).

Scheme 2



Condition: i) $NiCl_2$(0.035mmol), bpy(0.035mmol), TPP(0.30mmol), Zn(1.55mmol), NMP, N_2.

Table 1. Synthesis of Polymers 4[a]

monomer	polymer	yield, %	M_n[b]	M_w[b]	M_w/M_n[b]
3a	**4a**	100	1000	2300	2.3
3b	**4b**	100	11000	47000	4.3
3c	**4c**	100	4500	10000	2.3

[a] Reaction condition: monomer 0.50 mmol, $NiCl_2$ 0.035 mmol, bpy 0.035 mmol, TPP 0.30 mmol, Zn 1.55 mmol, NMP 0.5 mL, temperature 90 °C, and time 24 h. [b] Determined by GPC with polystyrene as standard.

Polymerizations proceeded homogeneously and then heterogeneously to give poly(*p*-phenylene[3-(alkylthio)-2,5-thienylene]-*p*-phenylene)s (**4**) in a quantitative yield. The polymerizations of **3a** rapidly produced a polymer precipitation that limited the molecular weight. On the other hand, monomer **3b** and **3c** polymerized in a homogeneous state for 12 h, giving relatively high molecular weight polymers. These results are summarized in Table 1.

Polymer Characterization. Polymers **4b** and **4c** were yellow solids and were soluble in chloroform, THF and dichloromethane at room temperature (Table 2). Yellow and transparent films could be cast from the chloroform solutions of polymers **4b** and **4c**. Polymers **4** were confirmed to be the corresponding poly(*p*-phenylene[3-(alkylthio)-2,5-thienylene]-*p*-phenylene)s **4** by infrared, UV–visible, ^{1}H-NMR, and ^{13}C-NMR spectroscopies and elemental analyses.

Infrared Spectroscopy. The IR spectra of the polymers exhibited characteristic absorptions at 2930 and 2850 cm^{-1} due to the aliphatic C–H stretching and two strong absorptions at 1470 and 1490 cm^{-1} that are assigned to the 2,3,5-trisubstituted thiophene ring vibration. The para-disubstituted benzene ring bending mode was observed at 820 cm^{-1}. Furthermore, no absorption ascribed to the C–Cl stretching was detected.

Elemental Analyses. Elemental analyses showed very good agreement between experimental and theoretical results for the proposed polymer structures.

NMR Spectroscopy. The ^{1}H-NMR spectra of polymers **4** showed four signals at 0.86, 1.22, 1.56, and 2.83 ppm for the methyl, two methylenes, and methylene next to the sulfur atom, respectively, and two broad signals at 7.2 and 7.8 ppm due to the phenyl and thienyl H resonances. The most conclusive spectroscopic evidence for the proposed polymers was provided by ^{13}C-NMR spectroscopy. A typical ^{13}C-NMR spectrum of polymer **4b** is shown in Figure 1 together with the assignments of observed resonances. The calculated chemical shifts are all within ±2 ppm of observed

Table 2. Solubility of Polymers 4[a]

	solvent								
polymer	NMP	DMAc	DMF	DMSO	THF	$CHCl_3$	CH_2Cl_2	toluene	H_2SO_4
4a	±	±	±	±	±	+	±	±	−
4b	±	±	±	±	+	+	+	±	−
4c	±	±	±	±	+	+	+	±	−

[a] Key: (+) soluble at room temperature; (±) partially soluble or swelling; (−) insoluble.

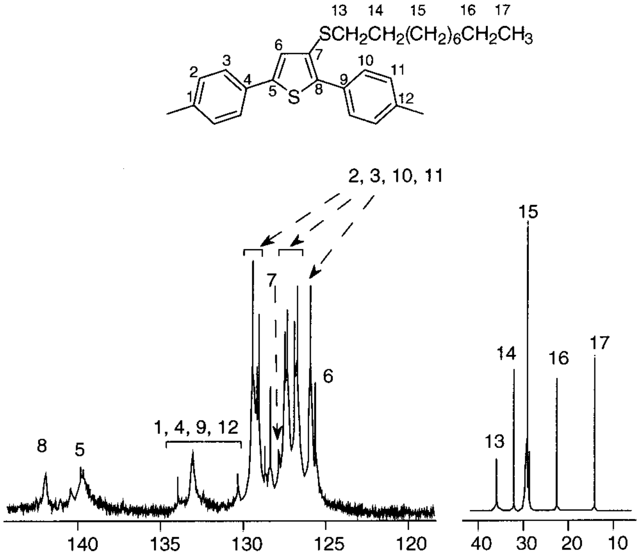


Figure 1. ^{13}C-NMR spectrum of polymer **4b** in $CDCl_3$.

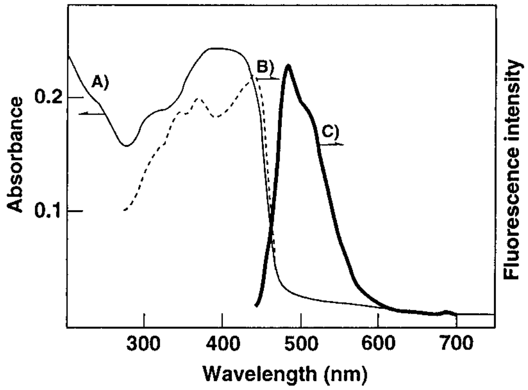


Figure 2. UV–vis spectrum of polymer **4b** (film) (A), fluorescence excitation spectrum of polymer **4b** (film) (B), and fluorescence emission spectrum of polymer **4b** (film) (C).

values. Several splittings of resonances due to benzene and thiophene ring carbons at around 125–143 ppm were observed. They should be derived from regiorandom structures because nonsymmetric monomer, **3a** will be expected to give the four regioselective polymers, that is, head-to-head, head-to-tail, tail-to-head, and tail-to-tail linkages, considering triads of monomer units. These findings clearly indicate the formation of the expected polymer **4b**.

UV–Visible and Fluorescence Spectroscopies. Since the relation between electronic structure and the backbone conformation is a general and interesting feature of conjugated polymers. Figure 2 shows the UV–vis absorption spectrum obtained from polymer **4b** film. The wavelength of the $\pi-\pi^*$ transition of the polymer determined from this spectrum is 400 nm, which is longer wavelength by about 60 nm than that of monomer **3b**, indicating the presence of a better extended π-conjugation system along the polymer backbone. The λ_{max} data also shows that the polymer film had a middle $\pi-\pi^*$ transition energy between those of the poly(dialkoxyphenylene)[10] (λ_{max} = 330 nm) and the random poly(alkylthiophene)[11] (λ_{max} = 430 nm) (Table 3).

Table 3. UV–Vis and Fluorescence Data for Polymers

	maximum absorption wavelength (nm)	
compound	UV–vis	fluorescence emission
monomer **3b**	340	420
polymer **4b**	400	485
poly(2,5-dibutoxy-1,4-phenylene)[a]	330	410
poly(3-hexylthiophene)[b]	430	550

[a] Reference 10. [b] Reference 11.

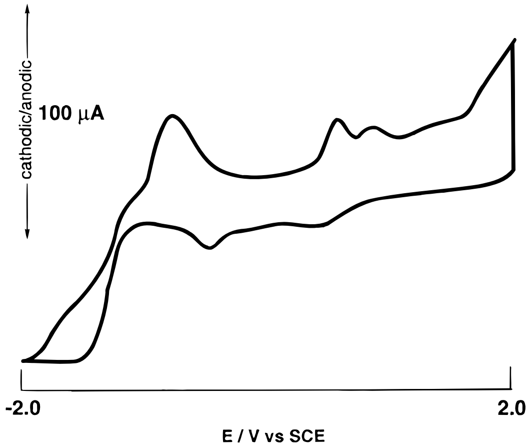


Figure 3. Cyclic voltammogram of polymer **4b**.

Figure 2 includes the fluorescence and excitation spectra of polymer **4b** that gives a bright greenish-yellow fluorescence with the maximum emission wavelength of 485 nm with the excitation wavelength at 435 nm in solid state. This emission is corresponding to the onset of $\pi-\pi^*$ transition of the electronic absorption spectra. The band gap of the polymer (2.57 eV) estimated from the onset position of the absorption (481 nm) essentially agrees with the λ_{max} value (485 nm, 2.55 eV) of the main fluorescence peak, indicating that the fluorescence takes places by migration of electrons in the conducting band to the valence band. Furthermore, this polymer with a very intense fluorescence will be applied to excellent electroluminescence materials.

Cyclic Voltammogram. The cyclic voltammogram of polymer **4b** coated on a Pt wire from chloroform solution was measured in a one-compartment three-electrode cell with a Pt wire counter electrode and an SCE reference. The electrolyte was 1 M TBAPC in acetonitrile, and the cell was purged with argon. The cyclic voltammogram (Figure 3) between −2.0 and +2.0 V vs SCE shows a clear oxidation peak at about −0.75 V vs SCE and two weak peaks at 0.53 and 0.80 V vs SCE. On the other hand, two weak peaks and a large peak were observed at +0.41 and −0.46 V vs SCE and at −1.65 V vs SCE on the return scan due to reduction of the oxidized polymer. Poly(phenylene)s exhibit a doping and undoping redox cycle at −1.9 and −0.7 V vs Ag/Ag$^+$,[12] whereas poly(thiophene)s show a doping and

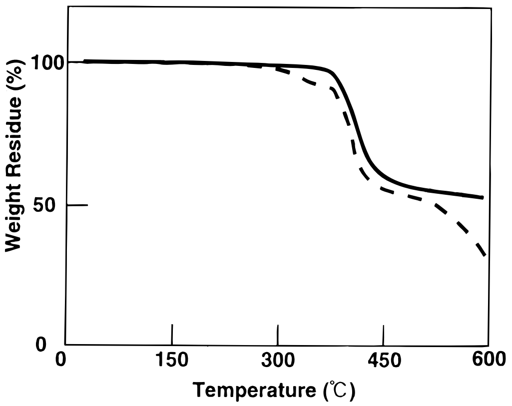


Figure 4. TG traces of polymer **4b** in air (---) and in nitrogen (—).

Table 4. Thermal Behavior of Polymers 4

polymer	decomposition temp,[a] °C	
	in air	in nitrogen
4a	380	380
4b	380	380
4c	380	400

[a] Temperature at which a 10% weight loss was recorded by TG at a heating rate of 10 °C·min^{-1}.

undoping redox cycle at 0.4 and 0.6 V vs Ag/Ag^{+}.[13] For poly(di-2-thienyl-2,5-dimethoxyphenylene), a broad oxidation process was observed between 0.6 and 1.2 V while two reduction processes were observed at 0.9 and 0.5 V, respectively. These two cathodic peaks had been attributed to the sequential reduction of bipolarons and polarons on the conjugated chain. Therefore, the peaks at −1.65 and −0.75 V and 0.53 and 0.80 V may be attributed to the redox cycles of poly(phenylene) and poly(thiophene) units, respectively.

During this oxidation−reduction cycle, the color of polymer changed from yellow at +0.4 V to brown at around +0.6 V and to purple at around −1.6 V.

Molecular Weight Chromatography. The molecular weight of the polymers was estimated (relative polystyrene standard) by GPC in THF. The chromatograms of polymer **4b** should unimodal distribution and indicated that M_n and M_w values were 11 000 and 47 000, respectively. The ratio of M_w/M_n was 4.3. As poly(thienylene−biphenylene)s are considerably more rigid than polystyrene, the molecular weights obtained by GPC are only rough estimations.

Thermal Properties. The thermal stability of the polymer was examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Typical traces of TGA for polymer **4b** are shown in Figure 4. The weight loss due to alkylthio side chains started at 350 °C and continued until around 450 °C in nitrogen and air. The chair yield above 450 °C in nitrogen is 68%, which is in good agreement with the expected values (67%) for a side chain degradation. The second stage of weight loss in air appears at about 530 °C for polymer **4b**. This feature can be attributed to degradation of the main chain. All polymers showed 10% weight loss at around 380 °C in nitrogen (Table 4). The T_g and T_m values of polymers **4a** and **4b** were not observed. On the other hand, polymer **4c** showed the clear endothermic peak at 46 °C, which is attributed to the melting point of the side chains.

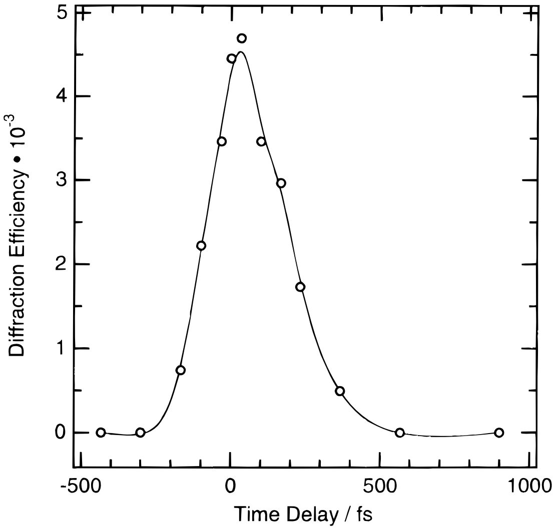


Figure 5. Time-dependent DFWN signal for polymer **4b**. The pump and probe intensities are 14.7 and 7.4 MW·cm^{-2}, respectively.

NLO Property. The third-order nonlinear optical susceptibility $\chi^{(3)}$ of polymer **4b** was measured by using a transient, degenerate four-wave mixing (DFWM) experiment. A mode-locked Ti:sapphire laser was used as a pump source. The pulse duration and the repetition rate of the laser system were 120 fs and 80 MHz, respectively, and the central wavelength was tuned to 775 nm. The pulses are split and overlapped spatially and temporally on the sample. The diffracted signal of DFWM was detected by a Ge photodiode with a pinhole, in order to reduce a scattering of the pump beam.

Figure 5 shows the time-resolved DFWM signal on polymer **4b**. Opened circles are experimental results. The vertical axis shows the diffraction efficiency R. The diffraction efficiency means the DFWM-signal intensity normalized by the intensity of the probe beam. The horizontal axis shows the time interval between the pump and the probe pulses. The pump intensity I_1 and the probe intensity I_2 are 14.7 and 7.4 MW/cm^2, respectively. The central excitation wavelength λ of 775 nm was tuned to the nonresonant region of polymer **4b**. In the experimental result as shown in Figure 5, the signal decay time of 200 fs was very fast and close to the pump pulse duration. In a nonresonant excitation, the real carrier transition is absent and the nonlinear optical effect takes place only while the excitation pulse pumps a sample. The third-order nonlinear optical susceptibility $|\chi^{(3)}|$ is given by

$$|\chi^{(3)}| = \frac{\lambda n^2 \epsilon_0 c}{12\pi}\sqrt{\frac{R}{I_1 I_2}}\left(\frac{\Delta k}{\sin(\Delta k L)}\right) \qquad (1)$$

where ϵ_0 and c are the dielectric constant of vacuum and the light velocity in vacuum, respectively.[14,15] R is the diffraction efficiency at the time delay of 0 ps. n=1.5 is the refractive index confirmed experimentally. $\Delta k = 2k_{\text{probe}} - k_{\text{pump}} - k_{\text{signal}}$ and L=100 μm are the phase mismatch and the optical path in the sample, respectively. The third-order nonlinear optical susceptibility $|\chi^{(3)}|$ of 5.5 × 10^{-11} esu was estimated from eq 1. This $\chi^{(3)}$ value is comparable to that of poly(aryleneethynylene)s at a resonance region.[16]

Conclusions

In summary, our studies indicate that poly(*p*-phenylene[3-(alkylthio)-2,5-thienylene]-*p*-phenylene)s (**4**) with relatively high molecular weights can be readily prepared by the nickel-catalyzed polymerization of 3-(alkylthio)-2,5-bis(4-chlorophenyl)thiophenes (**3**). Polymers **4b** and **4c** with long alkylthio side chains showed good solubility, film forming property, and thermal stability. Furthermore, polymer **4b** exhibited the large third-order susceptibility as high as 5.5×10^{-11} esu and will be used to make interesting optical devices.

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