Preparation of Oligo(thio-2,5-thienylenes)

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Poly(thio-1,4-phenylene) [poly(*p*-phenylene sulfide)] is a useful high-performance polymer because of its high temperature resistance, dimensional stability, solvent resistance, and high conductivity.[1] In this connection, there have also appeared a large number of patents and papers on syntheses, chemical properties, and industrial use of oligo(thio-1,4-phenylenes). On the other hand, although thiophene has played a very important role in constructing many electronic devices, their thiophene analogs, poly(thio-2,5-thienylene) and oligo(thio-2,5-thienylene), have never attracted keen interest. In 1967, Jones and Moodie synthesized poly(thio-2,5-thienylene) by condensation of thiophene with sulfur dichloride and by self-condensation of 5-chloro-2-thiophenethiol.[2] Thereafter, several reports have appeared on the preparation and properties of poly(thio-2,5-thienylene).[3] As for oligo(thio-2,5-thienylenes), Jones and Moodie reported the preparation of 2,5-bis[(2-thienyl)thio]thiophene (**3**) by reaction of 2,5-dibromothiophene with 2-thiophenethiol.[4] These authors also synthesized the other three constitutional isomers of **3**.[4] We report here the preparation of a higher series of oligo(thio-2,5-thienylenes).

The method reported by Jones and Moodie[4,5] was applied with slight modification to the preparation of oligo(thio-2,5-thienylenes). Thus, oligomers consisting of an odd number of thiophene ring were prepared in the following manner starting from reaction of 2,5-dibromothiophene with 2 equiv of 2-thiophenethiol (**1**) (Scheme 1). The reaction of 2,5-dibromothiophene with 2 equiv of potassium 2-thiophenethiolate in refluxing *N*,*N*-dimethylformamide (DMF) gave 2,5-bis[(2-thienyl)thio]-thiophene (**3**) in a better yield (72%) than previously reported,[4] when copper(I) oxide that was freshly prepared by reduction of copper(II) acetate with hydrazine was used as the catalyst. Bromination of **3** with 2 equiv of *N*-bromosuccinimide (NBS) in a mixture of acetic acid and dichloromethane took place regioselectively to give the dibromide **3′** in 61% yield. The reaction of **3′** with 2 equiv of 2-thiophenethiolate in refluxing DMF in the presence of the foregoing copper(I) oxide gave the expected pentamer **5** in 54% yield. Treatment of **5** with 2 equiv of NBS also brought about regioselective bromination to give the dibromide **5′** in 79% yield. The reaction of **5′** with 2 equiv of 2-thiophenethiolate produced the expected heptamer **7** in 58% yield.

Oligomers containing an even number of thiophene ring were prepared starting from 2,2′-thiobis(thiophene) (**2**)[5] (Scheme 2). Treatment of **2** with 2 equiv of NBS gave the dibromide **2′** in 81% yield. The reaction of **2′** with 2 equiv of 2-thiophenethiolate gave the expected tetramer **4** in 54% yield. Bromination of **4** with 2 equiv of NBS also took place regioselectively to give the dibromide **4′** in 71% yield. The reaction of **4′** with 2 equiv of 2-thiophenethiolate produced the hexamer **6** in 43% yield. Dibromination of **6** with NBS gave a mixture containing several products, from which the desired dibromide was isolated in a low yield after repeated purification by silica gel column chromatography and crystallization. Unfortunatley, however, no expected octamer could be obtained in pure form by reaction of the above dibromide with 2-thiophenethiol.

Structures of new oligomers **4**−**7** and their dibromo derivatives were determined by ^1H and ^{13}C NMR spectrometry, mass spectrometry, and elemental analyses; particularly useful was ^{13}C NMR spectrometry because of their symmetrical structure. Oligomers **4**−**7** are all crystalline compounds, and their melting points tend to rise as the molecules become larger. Figure 1 shows the UV-vis spectra of oligomers **2**−**7** which were determined with chloroform as the solvent in the same concentration (5.0×10^{-5} M). Molar absorption coefficients (ϵ) increase progressively with an increasing number of thiophene ring. The longest absorption maxima (λ_{max}) also increase with an increasing number of thiophene ring, but it is not so much marked as observed with α-thiophene oligomers[6] and (thiophene-2,5-diyl)vinylene oligomers.[7] Apparently, the rate of increase becomes smaller as the number of thiophene ring becomes larger, and finally the λ_{max} value converges around 300 nm. These observations lead to the conclusion that, although the conjugation between thiophene rings takes place through the lone pair electrons on sulfur atom,[4] it attenuates when thiophene rings are separated by several -C_4H_2S−S- units, and therefore the conjugation in the present system is less effective than in the case where thiophene rings are connected by carbon−carbon double bond.[7]

Experimental Section

Melting points are uncorrected. Elemental analyses were performed by the Chemical Analysis Center of Saitama University. Column chromatography was performed with Merck Kieselgel 60 (70−230 mesh).

2-Thiophenethiol was prepared from 2-thienyllithium (purchased from Aldrich) and elemental sulfur.[8] Copper(I) oxide, freshly prepared in the following manner, was used throughout this work. A 20% aqueous solution of hydrazine (55 mL, 0.34 mol) was added to a stirred solution of copper(II) acetate monohydrate (40 g, 0.20 mol) in water (650 mL) over a period of 1 h. The resulting very fine precipitate was subjected to

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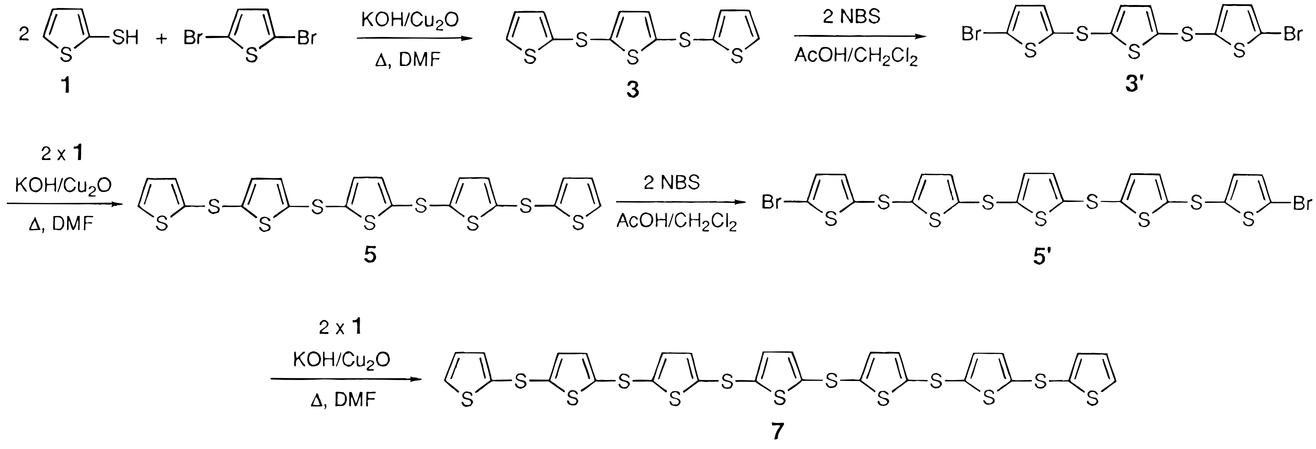
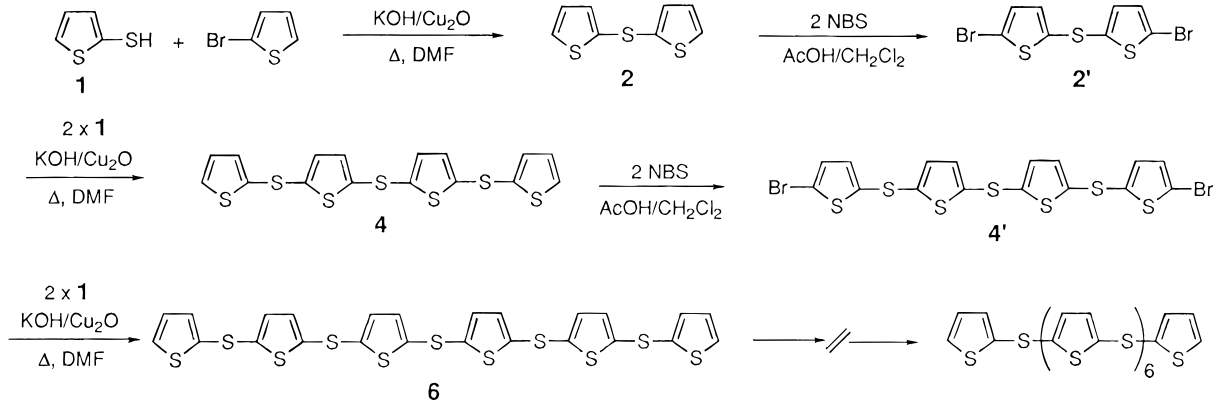
Scheme 1



Scheme 2



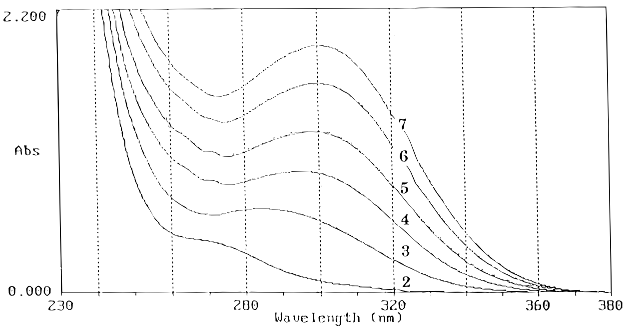


Figure 1. UV/vis spectra of oligomers **2**−**7**.

decantation and then centrifugation, collected by filtration, washed with water, ethanol, and ether successively, and dried in vacuo to give 10.6 g (74%) of copper(I) oxide.

All of the yields reported here are based on analytically pure samples purified by distillation or by recrystallization.

2,2′-Thiobis(thiophene) (2). This sulfide was obtained in a better yield than previously reported[5] by use of the foregoing copper(I) oxide as the catalyst. A solution of 2-thiophenethiol (19.71 g, 0.17 mol) in DMF (20 mL) was added slowly to a stirred mixture of 2-bromothiophene (27.72 g, 0.17 mol), KOH (9.53 g, 0.17 mol), and copper(I) oxide (12.16 g, 0.09 mol) in DMF (100 mL). The mixture was warmed slowly and heated at 130−140 °C for 18 h. The mixture was poured into 6 M HCl (170 mL), and benzene (500 mL) was added to it. The resulting two-phase mixture was stirred for a while and filtered through a pad of Celite. The organic layer was separated, washed with water (100 mL × 10), dried over $MgSO_4$, and evaporated. The residue was distilled to give 28.76 g (70%) of **2**: bp 110−112 °C/0.9 mmHg (bp 75−78 °C/0.06 mmHg[5]); UV-vis ($CHCl_3$) λ_{max} (ϵ) 268 nm (8200).

2,5-Bis[(2-thienyl)thio]thiophene (3). This sulfide was also obtained in a better yield than previously reported[4] by use of the foregoing copper(I) oxide. A solution of 2-thiophenethiol (7.99 g, 69 mmol) in DMF (25 mL) was added to a stirred mixture of 2,5-dibromothiophene (8.43 g, 30 mmol), KOH (3.89 g, 69 mmol), copper oxide(I) (4.94 g, 34 mmol) in DMF (50 mL). The mixture was heated at 130−140 °C for 16 h, cooled to room temperature, and poured into 6 M HCl (120 mL). The resulting two-phase mixture was treated as described above to give 6.73 g (72%) of **3**: bp 171 °C/0.08 mmHg (bp 214−220 °C/0.001 mmHg,[4a] 195−198 °C/0.05 mmHg[4b]); ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.94 (dd, $J = 5.4, 3.8$ Hz, 2H), 6.97 (s, 2H), 7.19 (dd, $J = 3.8, 1.3$ Hz, 2H), 7.34 (dd, $J = 5.4, 1.3$ Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 127.5, 130.2, 131.8, 133.5, 133.8, 139.2; UV-vis ($CHCl_3$) λ_{max} (ϵ) 284 nm (12800).

2,2′-Thiobis[5-(2-thienyl)thio]thiophene (4). NBS (51.16 g, 287 mmol) was added in small portions to an ice-cooled and stirred solution of 28.48 g (144 mmol) of **2** in acetic acid (250 mL) and dichloromethane (360 mL) over a period of 1 h. The mixture was stirred for 3.5 h under ice-cooling. The mixture was poured onto water (500 mL), and the organic layer was separated, washed with water (200 mL × 3), saturated aqueous $NaHCO_3$ solution (200 mL × 2), and water (200 mL × 3), dried over $MgSO_4$, and evaporated. The residue was distilled to give 41.32 g (81%) of the dibromide **2′**, bp 153−155 °C/0.14 mmHg, which solidified on standing: ^{1}H NMR (200 MHz) δ 6.88 (d, $J = 3.8$ Hz, 2H), 6.95 (d, $J = 3.8$ Hz, 2H); ^{13}C NMR (50 MHz) δ 115.7, 130.4, 133.5, 135.6. Anal. Calcd for $C_8H_4Br_2S_2$: C, 26.98; H, 1.13. Found: C, 27.15; H, 1.09. A mixture of the dibromide **2′** (15.34 g, 43 mmol), 2-thiophenethiol (11.78 g, 100 mmol), KOH (5.69 g, 100 mmol), and copper(I) oxide (7.17 g, 50 mmol) in DMF (150 mL) was heated at 130−140 °C for 18 h. The mixture was poured into 6 M HCl (170 mL). After benzene (600 mL) was added, the mixture was stirred for a while and then filtered through a pad of Celite. The organic layer was washed with water, dried, and evaporated. The crystalline residue was purified by crystallization from hexane to give 9.86 g (54%) of **4**: mp 59−60 °C; colorless flakes; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95−7.00 (m, 6H), 7.21 (dd, $J = 3.6, 1.4$ Hz, 2H), 7.37 (dd, $J = 5.4, 1.4$ Hz, 2H); ^{13}C NMR (100 MHz, $CHCl_3$) δ 127.6, 130.4, 131.6, 132.9, 133.6, 133.8, 137.6, 140.3; MS (EI) *m/z* 426 (M^+); UV-vis ($CHCl_3$) λ_{max} (ϵ) 295 nm (18500). Anal. Calcd for $C_{16}H_{10}S_7$: C, 45.04; H, 2.36. Found: C, 45.21; H, 2.28.

2,5-Bis[5-[5-(2-thienyl)thio](2-thienyl)thio]thiophene (5). Compound **3** (4.31 g, 14 mmol) was brominated with NBS (4.91 g, 28 mmol) in a mixture of acetic acid (25 mL) and dichloromethane (50 mL) to give 3.92 g (61%) of the dibromide **3′**: mp 69−70 °C (from hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 6.93 (d, J = 3.6 Hz, 2H), 6.99 (d, J = 3.6 Hz, 2H), 6.99 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 116.0, 130.5, 132.4, 134.2, 135.0, 138.9. Anal. Calcd for $C_{12}H_6Br_2S_5$: C, 30.64; H, 1.28. Found: C, 30.83; H, 1.22. A mixture of the dibromide **3′** (4.01 g, 9 mmol), 2-thiophenethiol (2.28 g, 20 mmol), KOH (1.10 g, 20 mmol), and copper(I) oxide (1.42 g, 10 mmol) in DMF (50 mL) was heated at 130−140 °C for 18 h. The mixture was poured into 6 M HCl (35 mL). After benzene (350 mL) was added, the mixture was stirred for a while and filtered through a pad of Celite. The organic layer was washed with water, dried, and evaporated. The crystalline residue was purified by silica gel column chromatography and then recrystallization from hexane to give 2.50 g (54%) of analytically pure **5**: mp 95−96 °C; colorless flakes; ^1H NMR (400 MHz, $CDCl_3$) δ 6.97−7.01 (m, 8H), 7.22 (dd, J = 3.5, 1.1 Hz, 2H), 7.39 (dd, J = 5.3, 1.1 Hz, 2H); ^{13}C NMR (100 MHz, $CHCl_3$) δ 127.6, 130.5, 131.6, 132.7, 133.2, 133.6, 133.9, 137.3, 138.7, 140.7; MS (EI) *m/z* 540 (M^+); UV-vis ($CHCl_3$) λ_{max} (ϵ) 298 nm (25200). Anal. Calcd for $C_{20}H_{12}S_9$: C, 44.41; H, 2.23. Found: C, 44.48; H, 2.13.

2,2′-Thiobis[5-[5-(2-thienyl)thio](2-thienyl)thio]thiophene (6). A mixture of **4** (15.02 g, 35 mmol) and NBS (14.35 g, 81 mmol) in acetic acid (60 mL) and dichloromethane (120 mL) was stirred at 0 °C for 6 h, and the resulting crystalline precipitate was collected by filtration to give 12.60 g (61%) of the pure dibromide **4′**, mp 100−101 °C. Two recrystallizations of the crude product from the filtrate gave additional **4′** (1.7 g, 10%). ^1H NMR (400 MHz, $CDCl_3$) δ 6.93 (d, J = 3.8 Hz, 2H), 6.97−7.01 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 116.0, 130.6, 132.3, 133.0, 134.2, 135.0, 138.2, 139.2. Anal. Calcd for $C_{16}H_8Br_2S_7$: C, 32.88; H, 1.38. Found: C, 33.15; H, 1.33. A mixture of the dibromide **4′** (12.61 g, 22 mmol), 2-thiophenethiol (6.09 g, 52 mmol), KOH (2.81 g, 50 mmol), and copper(I) oxide (3.61 g, 25 mmol) in DMF (75 mL) was heated at 130−140 °C for 20 h. The mixture was poured into 6 M HCl (85 mL). After benzene (700 mL) was added, the mixture was stirred for a while and filtered through a pad of Celite. The organic layer was washed with water, dried, and evaporated. The crystalline residue was purified by silica gel column chromatography (elution with a 1:1 mixture of hexane and CCl_4) and then recrystallization from cyclohexane to give 6.07 g (43%) of analytically pure **6**: mp 118−119.5 °C; faint yellow crystals; ^1H NMR (400 MHz, $CDCl_3$) δ 6.97−7.01 (m, 10H), 7.22 (dd, J = 3.6, 1.2 Hz, 2H), 7.39 (dd, J = 5.4, 1.1 Hz, 2H); ^{13}C NMR (100 MHz, $CHCl_3$) δ 127.7, 130.6, 131.6, 132.6, 133.0, 133.3, 133.6, 134.0, 137.1, 138.3, 138.9, 140.8; MS (EI) *m/z* 654 (M^+); UV-vis ($CHCl_3$) λ_{max} (ϵ) 300 nm (32300). Anal. Calcd for $C_{24}H_{14}S_{11}$: C, 44.00; H, 2.15. Found: C, 44.26; H, 2.10.

2,5-Bis[5-[5-[5-(2-thienyl)thio](2-thienyl)thio](2-thienyl)-thio]thiophene (7). A mixture of **5** (540 mg, 1 mmol) and NBS (410 mg, 2.3 mmol) in acetic acid (10 mL) and dichloromethane (20 mL) was stirred at 0 °C for 6 h. The resulting precipitate was dissolved by addition of dichloromethane (100 mL), and the mixture was washed with water and $NaHCO_3$ solution, dried, and evaporated. The resulting crystalline residue was chromatographed on a column of silica gel (elution with a 1:1 mixture of hexane and CCl_4) and then recrystallized from cyclohexane to give 560 mg (79%) of analytically pure **5′**: mp 104−105 °C; creamy crystals; ^1H NMR (400 MHz, $CDCl_3$) δ 6.93 (d, J = 3.8 Hz, 2H), 6.98−7.02 (m, 8H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 116.0, 130.6, 132.4, 132.9, 133.0, 134.2, 135.0, 138.2, 138.5, 139.3. Anal. Calcd for $C_{20}H_{10}Br_2S_9$: C, 34.38; H, 1.44. Found: C, 34.82; H, 1.38. A mixture of the dibromide **5′** (500 mg, 0.7 mmol), 2-thiophenethiol (173 mg, 1.5 mmol), KOH (81 mg, 1.5 mmol), and copper(I) oxide (115 mg, 0.8 mmol) in DMF (30 mL) was heated at 130−140 °C for 20 h. The mixture was poured into 6 M HCl (3 mL). After benzene (150 mL) was added, the mixture was stirred for a while and filtered through a pad of Celite. The organic layer was washed with water, dried, and evaporated. The crystalline residue was purified by silica gel column chromatography (elution with a 10:1 mixture of cyclohexane and chloroform) and then recrystallization from cyclohexane to give 292 mg (58%) of analytically pure **7**: mp 129−132 °C; creamy crystals; ^1H NMR (400 MHz, $CDCl_3$) δ 6.96−7.02 (m, 12H), 7.22 (dd, J = 3.6, 1.0 Hz, 2H), 7.39 (dd, J = 5.3, 1.0 Hz, 2H); ^{13}C NMR (100 MHz, $CHCl_3$) δ 127.7, 130.6, 131.6, 132.6, 132.9, 133.0, 133.3, 133.6, 134.0, 137.1, 138.1, 138.5, 139.1, 140.8; UV-vis ($CHCl_3$) λ_{max} (ϵ) 301 nm (38200). Anal. Calcd for $C_{28}H_{16}S_{13}$: C, 43.71; H, 2.09. Found: C, 43.69; H, 2.05.

Attempted Synthesis of the Octamer. Treatment of a solution of the hexamer **6** (662 mg, 1 mmol) with NBS (361 mg, 2 mmol) in dichloromethane (70 mL) and acetic acid (35 mL) at 0 °C for 7 h resulted in the separation of the solid. The solid (830 mg) consisted of several products and was repeatedly purified by silica gel column chromatography and then by crystallization from cyclohexane to give 187 mg (23%) of the dibromide of **6**, mp 132−133 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 6.92 (d, J = 3.8 Hz, 2H), 6.97−7.01 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 116.0, 130.6, 132.4, 132.9, 132.96, 133.03, 134.2, 135.0, 138.2, 138.5, 138.6, 139.3; MS (EI) *m/z* 810, 812, 814 (M^+). A mixture of the above dibromide (163 mg, 0.2 mmol), 2-thiophenethiol (63 mg, 0.54 mmol), copper(I) oxide (33 mg), and KOH (26 mg) in DMF (20 mL) was heated at 130−140 °C for 40 h. Although the mixture was carefully purified by silica gel column chromatography, no expected octamer could be isolated in pure form.

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