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Synthesis of soluble poly(5-hexyloxybenzo[*c*]thiophene-1,3-diylvinylene) via the titanium-induced dicarbonyl-coupling reaction of 5-hexyloxybenzo[*c*]thiophene-1,3-dicarbaldehyde

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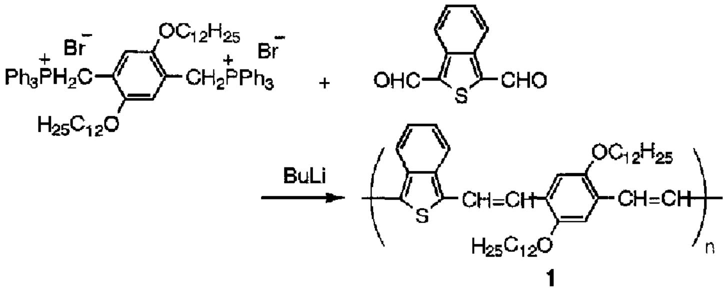
Summary

Titanium-induced dicarbonyl-coupling reaction of 5-hexyloxybenzo[*c*]thiophene-1,3-dicarbaldehyde (**9**) was carried out to obtain poly(5-hexyloxybenzo[c]thiophene-1,3-diylvinylene) (**10**), which was characterized by ^{1}H NMR, IR, UV-vis, and elemental analysis.

Introduction

Poly(arylenevinylene)s are considered to be one of promising candidates for electro or optical materials. Various aromatic or heterocyclic nucleus have been fused onto poly(arylenevinylene) including benzene (1-3), substituted benzene (4-6), naphthalene (7), thiophene (8-10), and furan (11,12). We were interested in benzo[*c*]thiophene as an arylene unit because poly(benzo[*c*]thiophene) has a very small bandgap (~1.1 eV) and whose doped state is transparent in the visible region (13,14). Recently, we reported the synthesis of poly(arylenevinylene) **1** carrying benzo[*c*]thiophene by the Wittig reaction of 2,5-bis(dodecyloxy)-*p*-xylylenebis(triphenylphosphonium bromide) with benzo[*c*] thiophene-1,3-dicarbaldehyde (15). This poly(arylenevinylene), however, contains didodecyloxybenzene unit in addition to benzo[*c*]thiophene unit.



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This work describes the synthesis of poly(5-hexyloxybenzo[*c*]thiophene-1,3-diylvinylene) (**10**) via the titanium-induced dicarbonyl-coupling reaction of 5-hexyloxybenzo[*c*]thiophene-1,3-dicarbaldehyde (**9**).

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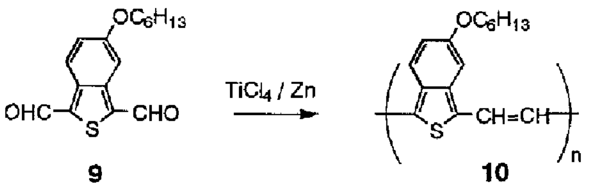
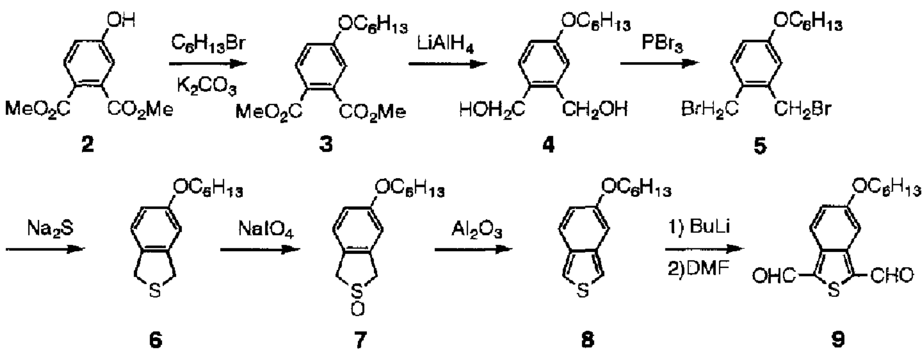


Experimental

materials

The aldehyde, 5-hexyloxybenzo[*c*]thiophene-1,3-dicarbaldehyde (**9**), was prepared from dimethyl 4-hydroxyphthalate (**2**) as a starting material in seven steps as shown in Scheme 1.



Scheme 1. Synthesis of 5-hexyloxybenzo[*c*]thiophene-1,3-dicarbaldehyde (**9**).

dimethyl 4-hexyloxyphthalate (3)

The mixture of dimethyl 4-hydroxyphthalate (**2**) (20.0 g, 95 mmol), potassium carbonate (32.9 g, 240 mmol), and 1-bromohexane (17.3 g, 105 mmol) in 230 ml of DMF was stirred for 5 h at 80 °C. It was poured into water and extracted with ethyl acetate. The organic layer was dried over anhydrous magnesium sulfate and placed under reduced pressure to give **3** (26.6 g, 95%) as yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.80 (d, J = 8.6 Hz, 1H), 7.05 (s, 1H), 7.00 (d, J = 8.6 Hz, 1H), 4.01 (t, J = 6.6 Hz, 2H), 3.92 (s, 3H), 3.87 (s, 3H), 1.8 (m, 2H), 1.5-1.3 (m, 6H), 0.91 (t, J = 6.9 Hz, 3H); IR (KBr, cm^{-1}) 2914, 2826, 1692, 1268. Anal. Calcd for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53. Found. C, 65.45; H, 7.42.

4-hexyloxy-o-xylylenediol (4)

Into a suspension of lithium aluminum hydride(2.9 g, 75 mmol) in 150 ml of ether was added diester **3** (11.1 g, 38 mmol) in 20 ml of ether dropwise and heated under reflux for 1 h. The reaction mixture was cooled to 0 °C and water was added slowly. The mixture was extracted with ether. The extract was dried over anhydrous magnesium sulfate and placed under reduced pressure to give **4** (7.6 g, 84%) as white needles: mp 45-46 °C; ^{1}H NMR ($CDCl_3$) δ 7.24 (d, J = 8.2 Hz, 1H), 6.92 (s, 1H), 6.80 (d, J = 8.2 Hz, 1H), 4.68 (s, 2H), 4.67 (s, 2H), 3.96 (t, J = 6.6 Hz, 2H), 3.13 (brs, 1H), 2.85 (brs, 1H), 1.78 (m, 2H), 1.5-1.2 (m, 6H), 0.90 (t, J = 6.9 Hz, 3H); IR (KBr, cm^{-1}) 3210, 2896. Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found. C, 70.43; H, 9.09.

4-hexyloxy-o-xylylene dibromide (5)

The mixture of **4** (18.6 g, 78 mmol) and phosphorus tribromide (21.2 g, 78 mmol) in 170 ml of benzene was stirred for 5 h at room temperature. The reaction mixture was washed with water, dried over anhydrous magnesium sulfate, and placed under reduced pressure to give **5** (24.1 g, 85%) as white needles: mp 47-48 °C; ^{1}H NMR ($CDCl_3$) δ 7.27 (d, J = 8.2 Hz, 1H), 6.89 (s, 1H), 6.81 (d, J = 8.2 Hz, 1H), 4.66 (s, 2H), 4.62 (s, 2H), 3.95 (t, J = 6.6 Hz, 2H), 1.8 (m, 2H), 1.5-1.2 (m, 6H), 0.91 (t, J = 6.6 Hz, 3H); IR (KBr, cm^{-1}) 2892, 2816, 589. Anal. Calcd for $C_{14}H_{20}Br_2O$: C, 46.18; H, 5.54. Found. C, 46.34; H, 5.42.

*5-hexyloxy-1,3-dihydrobenzo[c]thiophene (**6**)*

The mixture of **5** (9.0 g, 25 mmol) and sodium sulfide nonahydrate (6.3 g, 26 mmol) in 50 ml of DMF was stirred for 4 h at 100 °C. The reaction mixture was poured into water and filtered. The filtrate was extracted with ethyl acetate, dried over anhydrous magnesium sulfate, and placed under reduced pressure to remove the solvent. The residue was passed through a silica gel column using a mixture of hexane and dichloromethane (3:1 by volume) as an eluent to give **6** (2.3 g, 40%) as colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.12 (d, J = 9.2 Hz, 1H), 6.77 (s, 1H), 6.76 (d, J = 6.2 Hz, 1H), 4.22 (s, 2H), 4.20 (s, 2H), 3.93 (t, J = 6.6 Hz, 2H), 1.8 (m, 2H), 1.5-1.3 (m, 6H), 0.90 (t, J = 6.6 Hz, 3H); IR (KBr, cm^{-1}) 2890, 2820, 806. Anal. Calcd for $C_{14}H_{20}OS$: C, 71.14; H, 8.53. Found. C, 71.29; H, 8.49.

*5-hexyloxy-1,3-dihydobenzo[c]thiophene-2-oxide (**7**)*

Into a solution of sodium periodate (1.2 g, 5.7 mmol) in 150 ml of 15% aqueous ethanol was added **6** (1.2 g, 5.2 mmol) and the mixture was heated under reflux for 20 h. The reaction mixture was filtered and the filtrate was placed under reduced pressure to remove the solvents. The residue was passed through a silica gel column using a mixture of dichloromethane and ethyl acetate (3:1 by volume) to give **7** (1.0 g, 80%) as yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.24 (d, J = 8.2 Hz, 1H), 6.87 (s, 1H), 6.85 (d, J = 8.2 Hz, 1H), 4.2 (m, 2H), 4.1 (m, 2H), 3.94 (t, J = 6.6 Hz, 2H), 1.8 (m, 2H), 1.5-1.3 (m, 6H), 0.91 (t, J = 6.9 Hz, 3H); IR (KBr, cm^{-1}) 2892, 1032, 807. Anal. Calcd for $C_{14}H_{20}O_2S$: C, 66.63; H, 7.99. Found. C, 66.39; H, 7.73.

*5-hexyloxybenzo[c]thiophene (**8**)*

The mixture of **7** (1.2 g, 4.8 mmol) and 2.4 g of grade I neutral alumina (Woelm) was heated under 0.1 mmHg pressure at 60 °C in a sublimer to give **8** (0.70 g, 61%) as colorless plates. The compound **8** was unstable and used for the next reaction immediately.

*5-hexyloxybenzo[c]thiophene-1,3-dicarbaldehyde (**9**)*

To the mixture of freshly-prepared **8** (0.46 g, 2.0 mmol) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) (0.54 g, 4.6 mmol) in 16 ml of hexane was added 2.8 ml of 1.6 M butyllithium in hexane dropwise and the mixture was heated under reflux for 30 min into which was added 20 ml of THF. It was cooled to -40 °C, and *N,N*-dimethylformamide (DMF) (0.4 g, 5.4 mmol) was added. The reaction mixture was allowed to warm to room temperature and poured into 40 ml of 0.5 M hydrochloric acid solution. The mixture was neutralized with saturated sodium hydrogen carbonate solution and extracted with dichloromethane. The extract was dried over anhydrous magnesium sulfate and placed under reduced pressure to remove the solvent. The residue was passed through a silica gel column using a mixture of benzene and hexane (1:1 by volume) to give **9** (0.24 g, 42%) as yellow needles: mp 58-59 °C; ^{1}H NMR ($CDCl_3$) δ 10.27 (s, 1H), 10.21 (s, 1H), 8.22 (d, J = 9.2 Hz, 1H), 7.65 (d, J = 2.3 Hz, 1H), 7.2 (m, 1H), 4.02 (t, J = 6.6 Hz, 1H), 1.8 (m, 1H), 1.5-1.2 (m, 1H), 0.85 (t, J = 6.9 Hz, 1H); IR (KBr, cm^{-1}) 2890, 2820, 1615, 793. Anal. Calcd for $C_{16}H_{18}O_3S$: C, 66.18; H, 6.25. Found.

C, 66.05; H, 6.32.

polymerization

The titanium-induced dicarbonyl-coupling reaction of **9** was carried out according to the method of Cook et al (16). Into the suspension of zinc powder (0.78 g, 12 mmol) in 20 ml of solvent (THF, dioxane, glyme, or diglyme) was added titanium tetrachloride (1.14 g, 6.0 mmol) at -10 °C to result a solution into which **9** (0.58 g, 2.0 mmol) was added. The mixture was heated under reflux for 10 h. After cooling it was poured into 10% potassium carbonate solution and the mixture was vigorously stirred for 30 min to deposit a solid material which was removed by filtration, washed with acetone, and dried under reduced pressure. The obtained solid was extracted with THF using Soxhlet extractor for 24 h. The THF extract was placed under reduced pressure to remove the solvent. The residue was dissolved again in a small amount of THF and the resulting solution was poured into an excess of isopropyl ether to precipitate the polymer **10** as dark blue solid.

Results and Discussion

Preliminary experiments in our laboratory showed that the titanium-induced dicarbonyl-coupling reaction of unsubstituted benzo[*c*]thiophene-1,3-dicarbaldehyde was unsuccessful because of the insolubility of the resulting product. It was difficult to separate the product from the reaction mixture. Our idea was to introduce alkyloxy group onto benzo[*c*]thiophene nucleus which allows the resulting polymer soluble in organic solvent. The aldehyde **9** was prepared from dimethyl 4-hydroxyphthalate (**2**) as a starting material in seven steps as shown in Scheme 1.

The results of the polymerizations were summarized in Table 1. In all cases, the obtained polymer was insoluble in acetone, ether, hexane, or methanol but was soluble in chloroform and THF. When the reaction was carried out at high temperature, a large amount of by-products of small molecules were obtained (run 4). THF was found most effective for the polymerization (run 1).

Tale 1. Polymerization of **9** in various solvents

run	solvent	temp., °C	yield, %	10^{-3} M_n (pSt)
1	THF	66	52	22.0
2	glyme	82	36	3.5
3	dioxane	101	45	5.0
4	diglyme	162	20	3.8

Figure 1 shows the IR spectra of **10**. It exhibited absorption band at 910 cm^{-1} due to the C-H out-of-plane bending of trans-vinylene group. The ^1H NMR spectrum of **10** exhibited peaks at 7.8-6.2 (5H), 3.9 (2H), 1.8-1.1 (8H), and 0.9 (3H) ppm as shown in Figure 2. The elemental analysis was in good agreement with the structure **10** (Anal. Found: C, 74.68; H, 6.79. Calcd for $C_{16}H_{18}OS$: C, 74.38; H, 7.02). It was concluded therefore that the titanium-induced dicarbonyl-coupling reaction of **9** afforded **10** free from contaminating inorganic materials.

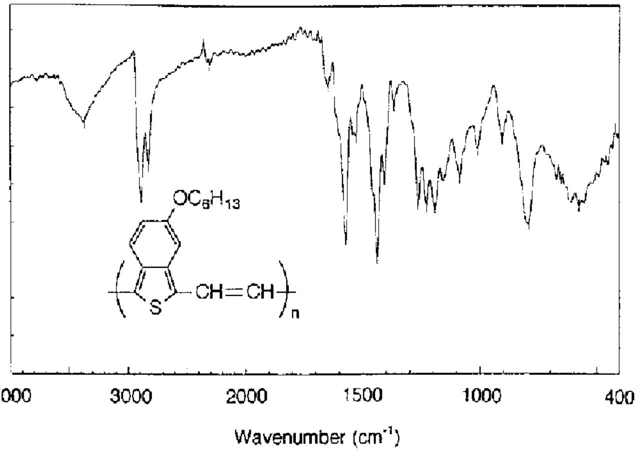


Figure 1. IR spectrum (KBr pellet) of **10** obtained in run 1 of Table 1.

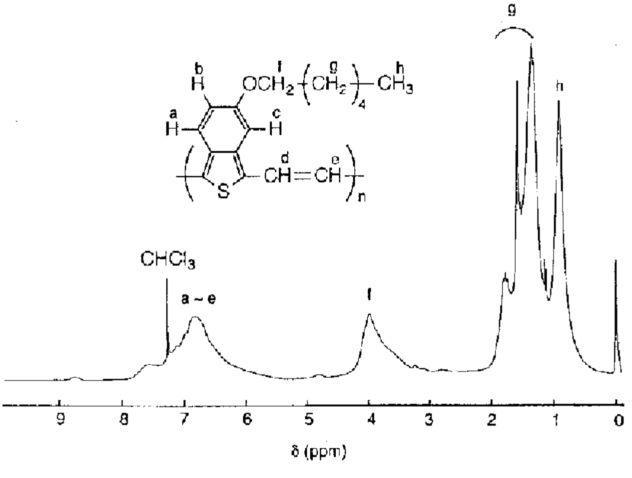
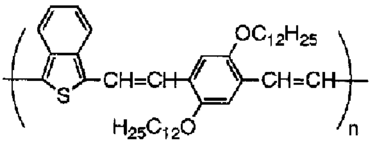


Figure 2. 270-MHz ^{1}H NMR spectrum (in $CDCl_3$) of **10** obtained in run 1 of Table 1.

The UV-vis spectrum of **10** was shown in Figure 3 together with those of **1** and poly(3,4-dibutoxy-2,5-thienylenevinylene) (**11**) (17) for comparison. These polymers display the π-π^* electronic transition around 600 nm for the conjugated structures. It was seen that the absorption edge of **10** was longer in wavelength than those of **1** or **11**. These solution optical spectra confirm that benzo[*c*]thiophene unit is effective in reducing the bandgap of poly(arylenevinylene).



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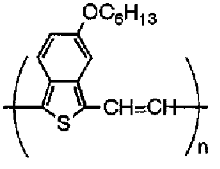

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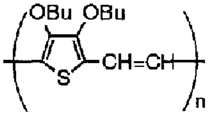

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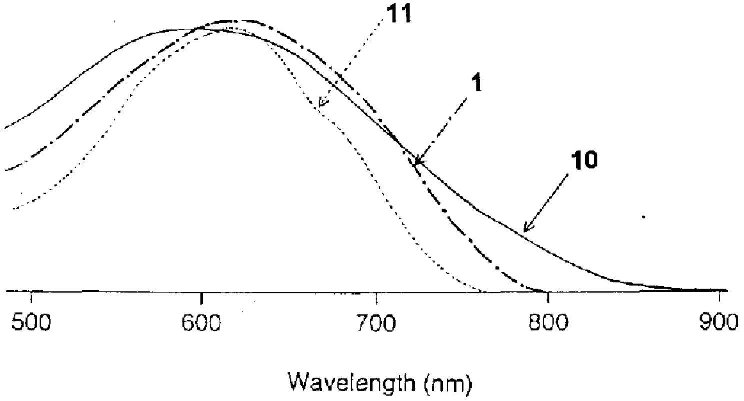

Figure 3. UV-vis spectra of **1**, **10**, and **11** in chloroform.

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