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Preparation of Poly(3,4-dibutoxy-2,5-thienylene-vinylene) via Titanium-Induced Dicarbonyl-Coupling Reaction of 3,4-Dibutoxythiophene-2,5-dicarbaldehyde

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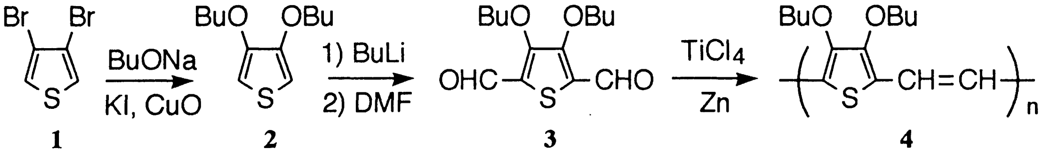
3,4-Dibutoxythiophene-2,5-dicarbaldehyde was found to be readily subject to the titanium-induced dicarbonyl-coupling reaction to give poly(3,4-dibutoxy-2,5-thienylene-vinylene) with molecular weight of 35000 and high solubility in organic solvent like chloroform. In addition electroconductivity and third-order nonlinear optical susceptibility for its polymer film were measured.

In general fully π-conjugated polymers are incapable of being processed to desired forms due to lack of fusibility and solubility. Kossmehl *et al.* prepared poly(2,5-thienylene-vinylene) (PTV) as intractable powder in the Wittig reaction of thiophene-2,5-dicarbaldehyde with (2,5-thiophenediyldimethylene)bis(triphenylphosphonium chloride).1) Cook *et al.* carried out the titanium-induced dicarbonyl-coupling reaction2) of terephthalaldehyde to obtain poly(1,4-phenylene-vinylene) (PPV) which was, however, unable to be isolated as a pure compound from the reaction mixture.3)

Recently, quite a few efforts were made to improve processability of fully π-conjugated polymers by introducing long alkyl or alkyloxy groups to their arylene nucleus. For example, poly(3-alkylthiophene), where alkyl was longer than butyl, was found to be soluble in conventional organic solvents such as chloroform and toluene.4,5) Blohm *et al.* performed the nickel-catalyzed coupling reaction of 3,4-dibutoxy-2,5-dilithiothiophene with 1,2-dichloroethylene to obtain poly(3,4-dibutoxy-2,5-thienylene-vinylene) soluble in chloroform.6)

This letter describes a novel preparation route for poly(3,4-dibutoxy-2,5-thienylene-vinylene) (**4**) soluble in a conventional organic solvent, as shown in Scheme 1, including the titanium-induced dicarbonyl-coupling reaction of 3,4-dibutoxythiophene-2,5-dicarbaldehyde (**3**).

Sodium (13.1 g, 57 mmol) was dissolved in 240 mL of butanol and then into it were added 3,4-dibromothiophene7) (**1**) (23.0 g, 95 mmol), potassium iodide (0.2 g, 1.2 mmol), and copper(II) oxide (8.0



Scheme 1.

g,100 mmol). After heated under reflux for 100 h, the reaction mixture was cooled and the remaining solid material was filtered out. The filtrate was poured into 200 mL of water and the resulting mixture was extracted with three 50-mL portions of ethyl ether. Combined extract was dried over anhydrous magnesium sulfate and placed first under moderately reduced pressure to remove the solvent. Then, the remaining material was distilled under reduced pressure to give 3,4-dibutoxythiophene (**2**) (10.5 g, 48%) as pale yellow oil; bp 110-112 °C / 3 mmHg; IR (neat) 1187, 870 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.15 (s, 2H), 3.98 (t, *J*=6.6 Hz,4H), 1.8-1.7 (m, 4H), 1.5-1.4 (m, 4H), 0.96 (t, *J*=7.4 Hz,6H); Anal. Found: C, 63.35; H, 8.95%. Calcd for $C_{12}H_{20}O_2S$: C, 63.12; H, 8.83%.

The formylation at 2- and 5-positions of **2** was carried out according to the method of Feringa *et al.*[8] Into **2** (10.3 g, 45 mmol) and tetramethylenediamine (TMEDA) (12.6 g, 108 mmol) in 14 mL of hexane was dropwise added 68 mL of 1.6 M (1M=1 mol dm^{-3}) butyllithium hexane solution. The resulting mixture was heated under reflux for 30 min to obtain the suspension of 3,4-dibutoxy-2,5-dilithiothiophene into which was added 54 mL of tetrahydrofuran (THF). After it was cooled to -40 °C, *N,N*-dimethylformamide (8.9 g, 120 mmol) was dropwise added. Then, the reaction mixture was allowed to warm to room temperature and poured into 800 mL of 0.5 M hydrochloric acid solution and then was added a sufficient amount of a saturated sodium hydrogen carbonate solution for letting the aqueous layer part of the mixture be neutral. The organic layer part was separated and the aqueous layer part was extracted with three 100-mL portions of chloroform. The organic layer part and the extract were combined, dried over anhydrous magnesium sulfate, and placed under reduced pressure to remove solvent to remain a dark orange oily material which was passed through a silica gel column using carbon tetrachloride as an eluent. The yellow band was collected to give 3,4-dibutoxythiophene-2,5-dicarbaldehyde (**3**) (6.2 g, 50%) as yellow viscous oil; IR (neat) 1636, 870 cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.10 (s, 2H), 4.27 (t, *J*=6.4 Hz,4H), 1.8-1.7 (m, 4H), 1.5-1.4 (m, 4H), 0.91 (t, *J*=7.4 Hz,6H); Anal. Found: C, 59.30; H, 6.96%. Calcd for $C_{14}H_{20}O_4S$: C, 59.13; H, 7.09%.

The titanium-induced dicarbonyl-coupling reaction of **3** was carried out according to the method of Cook *et al.*[3] Into the suspension of zinc powder (2.36 g, 36 mmol) in 25 mL of THF was added titanium tetrachloride

(3.41 g, 18 mmol) at -10 °C to result a green-yellow solution into which **3** (0.85 g, 3 mmol) in 5 mL of THF was added. The mixture was heated under reflux for 10 h. After cooled it was poured to 50 mL of 10% potassium carbonate solution and the resulting mixture was vigorously stirred for 30 min to deposit a solid material which was separated by filtration, washed with acetone using Soxhlet extractor for 24 h, and then extracted with chloroform for 24 h. The chloroform extract was placed under reduced pressure to obtain 1.1 g of **4** as a dark blue solid material capable of being cast from its THF solution into a dark blue film with golden luster. ^1H NMR spectrum of **4** in $CDCl_3$ showed peaks at 6.9 (2H), 4.0 (4H), and 1.7-0.8 (14 H) ppm, assignable to vinylene proton, 1-methylene proton of butoxy group, and 2- and 3-methylene and 4-methyl protons of butoxy group, respectively (Fig. 1.). IR spectrum of the neat film of **4** showed absorption bands at 935 and 787 cm^{-1} due to trans-vinylene and thiophene ring, respectively (Fig. 2.). The number-average molecular weight ($\bar{M}_n$) of **4** was measured to be 35000 by gel permeation chromatography (GPC) using THF and standard polystyrenes as an eluent and reference, respectively (Fig. 3.). Anal. Found: C, 66.33; H, 8.12%. Calcd for $C_{14}H_{20}O_2S$: C, 66.63; H, 7.99%. Found values were in good agreement with the calculated ones for poly(3,4-dibutoxy-2,5-thienylene-vinylene), indicating that **4** was free from contaminating inorganic material. UV-vis spectrum of the neat film of **4** exhibited a broad absorption at 605 nm (Fig. 4.) which was close to the value of **4** obtained by Blohm *et al.*[6] (λ_{max} = 607 nm). It was concluded therefore that the titanium-induced dicarbonyl-coupling reaction of 3,4-dibutoxythiophene-2,5-dicarbaldehyde (**3**) afforded poly(3,4-dibutoxy-2,5-thienylene-vinylene) (**4**) in as high as 73% yield with high molecular weight and high solubility in chloroform and THF similarly to the nickel-catalyzed coupling reaction of 3,4-dibutoxy-2,5-dilithiothiophene with 1,2-dichloroethylene.[6]

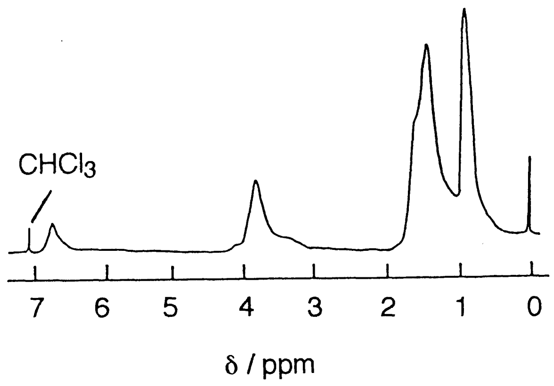


Fig. 1. ^1H NMR spectrum of **4** in chloroform-d.

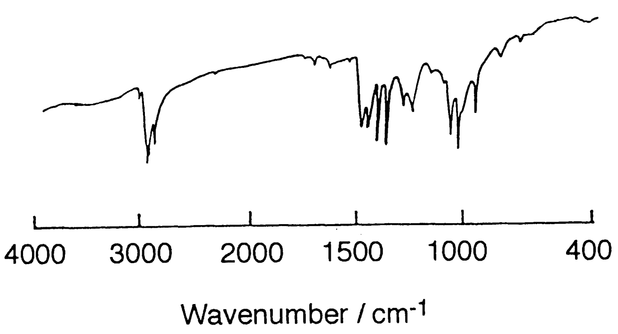


Fig. 2. IR spectrum of the neat film of **4**.

The electroconductivity of the neat film of **4** was measured to be below 10^{-9} S cm^{-1} at room temperature without dopant, and when doped by I_2 it increased to 0.2 S cm^{-1}. This value is much lower than that for PTV

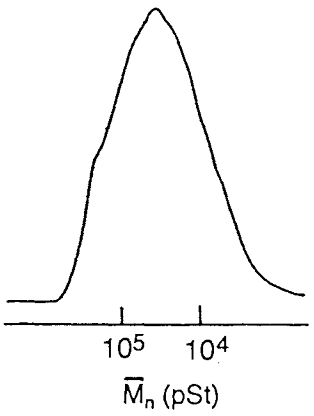


Fig.3. GPC curve of **4**.

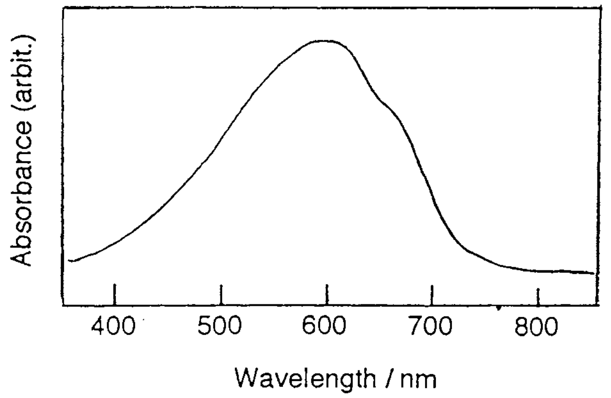


Fig.4. UV-vis spectrum of the neat film of **4**.

film doped by I_2 (230[9], 62[10], and 60[11] S cm^{-1}). Thus, it was conceivable that butoxy groups at 3- and 4-positions make PTV soluble in organic solvents such as chloroform and THF whereas they could prevent PTV molecules from adopting an extensively planar conformation. Nonlinear third-order optical susceptibility ($\chi^{(3)}$) for **4** was evaluated by the Maker fringe method[12] to be as high as 8×10^{-11} esu at wavelength of 1.90 μm, indicating that **4** is one of possible nonlinear third-order optical materials.

This process was considered to allow poly(3,4-dibutoxy-2,5-thienylene-vinylene) to be prepared in high yield as well as in high state of purity.

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