

Original Paper

## Synthesis of Poly(arylenevinylene)s Carrying Benzo[c]thiophene as Arylene Unit

Masataka KUBO, Takahito ITOH and Shouji IWATSUKI  
(Department of Chemistry for Materials)

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### Abstract

The Wittig reactions between benzo[c]thiophene-1,3-dicarbaldehyde (**2**) and 2,5-dialkyloxy-p-xylylenebis(triphenylphosphonium bromide)s (**7**) were carried out to obtain poly(1,3-benzo[c]thiophenediylvinylene-*alt*-2,5-dialkyloxy-1,4-phenylenevinylene)s (**8**), where alkyloxy is hexyloxy (**8a**), octyloxy (**8b**), or dodecyloxy (**8c**). The longer the alkyloxy group, the higher the degree of polymerization of the product. The optical band gap of poly(1,3-benzo[c]thiophenediylvinylene-*alt*-2,5-didodecyloxy-1,4-phenylenevinylene) (**8c**) was found to be 1.7 eV. This value was much lower than that of poly(1,4-phenylenevinylene-*alt*-2,5-didodecyloxy-1,4-phenylenevinylene) (2.5 eV).

### Key words

Poly(arylenevinylene), Benzo[c]thiophene, Wittig reaction, Optical bandgap

### 1. Introduction

Poly(arylenevinylene)s are considered to be one of promising candidates for electro or optical materials. Many attempts have been made to prepare various poly(arylenevinylene)s including poly(1,4-phenylene,<sup>1-3</sup> 2,6-disubstituted-1,4-phenylene,<sup>4-6</sup> 1,4-naphthalene,<sup>7</sup> 2,5-thienylene,<sup>8-10</sup> 2,5-furylene,<sup>11,12</sup> 2,5-selenophenediyl<sup>13</sup>, 4,7-benzo[b]thiophenediyl,<sup>14</sup> and 4,7-benzo[b]furandiyl-vinylene<sup>14</sup>)s. They were successfully prepared by so-called sulfonium salt method. (Arylene dimethylene)bis(dialkylsulfonium halide) was reacted with base in aqueous solution to obtain a soluble precursor polymer which was cast into film. It was heated under inert gas to yield poly(arylenevinylene) film.

Recently, poly(benzo[c]thiophene) has attracted particular attention because it has a small bandgap (1.1 eV) and whose conducting doped state is transparent in the visible region.<sup>15,16</sup> It is expected that poly(arylenevinylene) which contains benzo[c]thiophene as an arylene unit

exhibits a small band gap. The third-order nonlinear susceptibility,  $\chi^{(3)}$ , of  $\pi$ -conjugated polymer is enhanced through lengthening of the delocalization distance. Agrawal et al. proposed that  $\chi^{(3)}$  is proportional to the 6th power of the delocalization length which is exhibited as  $W/Eg$ , where  $W$  is the bandwidth and  $Eg$  is the band gap of the polymer.<sup>17</sup>

This work described the preparation of poly(arylenevinylene)s carrying benzo[c]thiophene as an arylene unit.

## 2. Experiments

2-1. General Procedures. <sup>1</sup>H NMR were measured with a JEOL EX-270 (270-MHz) nuclear magnetic resonance spectrometer using tetramethylsilane as an internal standard. IR spectra were measured with Jasco IR-700 infrared spectrophotometer. UV-Vis spectra were measured with Jasco UVIDEc-403B spectrophotometer. Melting points were measured with a Büchi 510 capillary melting point apparatus. Gel permeation chromatography (GPC) was carried out with a set of Tosoh TSK-gel G3000H and G2500H using tetrahydrofuran (THF) and standard polystyrenes as an eluent and references, respectively. Elemental analysis was performed on Yanaco MT-2 CHN CORDER.

2-2. Benzo[c]thiophene-1,3-dicarbaldehyde (**2**). Into the mixture of freshly-prepared benzo[c]thiophene<sup>18</sup> (**1**) (2.1 g, 15 mmol), *N,N,N',N'*-tetramethylethylenediamine (TMEDA) (4.2 g, 36 mmol), and 20 mL of hexane, 22 mL of 1.6 M butyllithium in hexane was added dropwise below 40 °C and the reaction mixture was heated under reflux for 30 min. It was cooled to -40 °C and *N,N*-dimethylformamide (DMF) (3.0 g, 42 mmol) was added via air-tight syringe. The reaction mixture was allowed to warm to room temperature and poured into 300 mL of 10% hydrochloric acid solution. The mixture was neutralized with saturated sodium bicarbonate solution to separate the organic layer. The aqueous layer was extracted with chloroform and the combined organic layer was dried over anhydrous magnesium sulfate and placed under reduced pressure to remove the solvents. The residue was recrystallized from hexane to give 2.28 g (78%) of **2** as yellow needles: mp 157-158 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ) 10.40 (s, 2H), 8.4-8.3 (m, 2H), 7.6-7.5 (m, 2H); IR (KBr, cm<sup>-1</sup>)  $\nu_{C=O}$  1607; Anal. Calcd for C<sub>10</sub>H<sub>6</sub>O<sub>2</sub>S: C, 63.14; H, 3.18. Found: C, 63.00; H, 3.15.

2-3. Diethyl 2,5-Dialkyloxyterephthalate (**4**). The mixture of diethyl 2,5-dihydroxyterephthalate<sup>19</sup> (**3**) (2.0 g, 8.0 mmol), potassium carbonate (5.5 g, 40 mmol), 100 mL of DMF, and 1-bromohexane (3.0 g, 18 mmol), 1-bromooctane (3.5 g, 18 mmol), or 1-bromododecane (4.5 g, 18 mmol) 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. The residue was recrystallized from ethanol to give diethyl 2,5-dihexyloxyterephthalate (**4a**), diethyl 2,5-dioctyloxyterephthalate (**4b**), or diethyl 2,5-didodecyloxyterephthalate (**4c**).

**4a**: yellow needles; yield 83%; mp 33-34 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ) 7.34 (s, 2H), 4.37 (q,  $J = 7.2$  Hz, 4H), 4.00 (t,  $J = 6.6$  Hz, 4H), 1.9-1.3 (m, 22H), 0.90 (t,  $J = 6.6$  Hz, 6H); IR (KBr, cm<sup>-1</sup>)  $\nu_{C=O}$  1697. Anal. Calcd for C<sub>24</sub>H<sub>38</sub>O<sub>6</sub>: C, 68.22; H, 9.06. Found: C, 68.42; H, 9.15.

**4b**: yellow needles; yield 89%; mp 38-40 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ) 7.33 (s, 2H), 4.37 (q,  $J = 7.2$  Hz, 4H), 4.00 (t,  $J = 6.6$  Hz, 4H), 1.9-1.3 (m, 30H), 0.88 (t,  $J = 6.6$  Hz, 6H); IR (KBr,  $\text{cm}^{-1}$ )  $\nu_{\text{C=O}}$  1698. Anal. Calcd for  $\text{C}_{28}\text{H}_{46}\text{O}_6$ : C, 70.26; H, 9.69. Found: C, 70.18; H, 9.60.

**4c**: white needles; yield 55%; mp 58-59 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ) 7.34 (s, 2H), 4.37 (q,  $J = 7.2$  Hz, 4H), 4.00 (t,  $J = 6.6$  Hz, 4H), 1.9-1.3 (m, 46H), 0.88 (t,  $J = 6.6$  Hz, 6H); IR (KBr,  $\text{cm}^{-1}$ )  $\nu_{\text{C=O}}$  1659. Anal. Calcd for  $\text{C}_{36}\text{H}_{62}\text{O}_6$ : C, 73.18; H, 10.58. Found: C, 73.32; H, 10.49.

2-4. 2,5-Dialkyloxy-p-xylylene Alcohol (**5**). Into the suspension of lithium aluminum hydride (0.47 g, 12 mmol) in 10 mL of ether **4a** (2.5 g, 6.0 mmol), **4b** (2.9 g, 6.0 mmol), or **4c** (3.5 g, 6.0 mmol) in 60 mL of ether was added dropwise and heated under reflux for 30 min. The reaction mixture was cooled to 0 °C and water was added slowly. The mixture was repeatedly extracted with ether and the extract was dried over anhydrous magnesium sulfate and placed under reduced pressure to give 2,5-dihexyloxy- (**5a**), 2,5-dioctyloxy- (**5b**), or 2,5-didodecyloxy-p-xylylene alcohol (**5c**).

**5a**: white needles; yield 90%; mp 97 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ) 6.84 (s, 2H), 4.67 (s, 4H), 3.98 (t,  $J = 6.6$  Hz, 4H), 1.9-1.3 (m, 16H), 0.90 (t,  $J = 6.6$  Hz, 6H); IR (KBr,  $\text{cm}^{-1}$ )  $\nu_{\text{O-H}}$  3260. Anal. Calcd for  $\text{C}_{20}\text{H}_{34}\text{O}_4$ : C, 70.97; H, 10.12. Found: C, 71.06; H, 10.27.

**5b**: white needles; yield 86%; mp 99-100 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ) 6.84 (s, 2H), 4.67 (s, 4H), 3.98 (t,  $J = 6.6$  Hz, 4H), 1.9-1.3 (m, 24H), 0.89 (t,  $J = 6.6$  Hz, 6H); IR (KBr,  $\text{cm}^{-1}$ )  $\nu_{\text{O-H}}$  3258. Anal. Calcd for  $\text{C}_{24}\text{H}_{42}\text{O}_4$ : C, 73.05; H, 10.73. Found: C, 73.23; H, 10.81.

**5c**: white needles; yield 94%; mp 109-110 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ) 6.84 (s, 2H), 4.67 (d,  $J = 8.4$  Hz, 4H), 3.98 (t,  $J = 6.6$  Hz, 4H), 1.9-1.3 (m, 40H), 0.88 (t,  $J = 6.6$  Hz, 6H); IR (KBr,  $\text{cm}^{-1}$ )  $\nu_{\text{O-H}}$  3320. Anal. Calcd for  $\text{C}_{32}\text{H}_{58}\text{O}_4$ : C, 75.84; H, 11.53. Found: C, 75.77; H, 11.45.

2-5. 2,5-Dialkyloxy-p-xylylene Bromide (**6**). Into the suspension of **5a** (1.7 g, 5.0 mmol), **5b** (2.0 g, 5.0 mmol), or **5c** (2.5 g, 5.0 mmol) in 200 mL of benzene was added phosphorous tribromide (0.95 g, 3.5 mmol) in 10 mL of benzene and stirred for 5 h. The reaction mixture was washed with water, dried over magnesium sulfate, and placed under reduced pressure to remove the solvent. The residue was recrystallized from hexane to give 2,5-dihexyloxy- (**6a**), 2,5-dioctyloxy- (**6b**), or 2,5-didodecyloxy-p-xylylene bromide (**6c**).

**6a**: white needles; yield 88%; mp 88-86 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ) 6.85 (s, 2H), 4.53 (s, 4H), 3.98 (t,  $J = 6.6$  Hz, 4H), 1.9-1.3 (m, 24H), 0.88 (t,  $J = 6.6$  Hz, 6H); Anal. Calcd for  $\text{C}_{20}\text{H}_{32}\text{Br}_2\text{O}_2$ : C, 51.74; H, 6.95. Found: C, 51.78; H, 7.02.

**6b**: white needles; yield 76%; mp 85-89 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ) 6.85 (s, 2H), 4.53 (s, 4H), 3.98 (t,  $J = 6.6$  Hz, 4H), 1.9-1.3 (m, 16H), 0.91 (t,  $J = 6.6$  Hz, 6H); Anal. Calcd for  $\text{C}_{24}\text{H}_{40}\text{Br}_2\text{O}_2$ : C, 55.39; H, 7.75. Found: C, 55.53; H, 7.85.

**6c**: white needles; yield 92%; mp 93-94 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ) 6.85 (s, 2H), 4.53 (s, 4H), 3.98 (t,  $J = 6.6$  Hz, 4H), 1.9-1.3 (m, 40H), 0.88 (t,  $J = 6.6$  Hz, 6H); Anal. Calcd for  $\text{C}_{32}\text{H}_{56}\text{Br}_2\text{O}_2$ : C, 60.76; H, 8.92. Found: C, 60.88; H, 8.98.

2-6. 2,5-Dialkyloxy-p-xylylenebis(triphenylphosphonium bromide) (**7**). The mixture of triphenylphosphine (2.4 g, 9.2 mmol), 70 mL of ethanol, and **6a** (1.9 g, 4.0 mmol), **6b** (2.1

g, 4.0 mmol), or **6c** (2.5 g, 4.0 mmol) was stirred at room temperature for 15 h. It was placed under reduced pressure to remove the solvent and the residue was recrystallized from a mixture of ethanol and ether to give 2,5-dihexyloxy- (**7a**), 2,5-dioctyloxy- (**7b**), or 2,5-didodecyloxy-p-xylylenebis(triphenylphosphonium bromide) (**7c**).

**7a**: white plates; yield 86%;  $^1\text{H NMR}$  (DMSO- $d_6$ ,  $\delta$ ) 7.9-7.6 (m, 30H), 6.50 (s, 2H), 4.87 (d,  $J = 13.9$  Hz, 4H), 2.97 (t,  $J = 6.6$  Hz, 4H), 1.3-1.0 (m, 16H), 0.84 (t,  $J = 6.6$  Hz, 6H); Anal. Calcd for  $\text{C}_{24}\text{H}_{38}\text{Br}_2\text{O}_2\text{P}_2$ : C, 68.02; H, 6.32. Found: C, 68.23; H, 6.25.

**7b**: white powders; yield 78%;  $^1\text{H NMR}$  (DMSO- $d_6$ ,  $\delta$ ) 7.9-7.6 (m, 30H), 6.52 (s, 2H), 4.88 (d,  $J = 13.9$  Hz, 4H), 3.00 (t,  $J = 6.6$  Hz, 4H), 1.3-1.0 (m, 24H), 0.88 (t,  $J = 6.6$  Hz, 6H); Anal. Calcd for  $\text{C}_{60}\text{H}_{70}\text{Br}_2\text{O}_2\text{P}_2$ : C, 68.96; H, 6.75. Found: C, 68.88; H, 6.79.

**7c**: white powders; yield 76%;  $^1\text{H NMR}$  (DMSO- $d_6$ ,  $\delta$ ) 7.9-7.6 (m, 30H), 6.51 (s, 2H), 4.88 (d,  $J = 13.9$  Hz, 4H), 2.99 (t,  $J = 6.6$  Hz, 4H), 1.3-1.0 (m, 40H), 0.86 (t,  $J = 6.6$  Hz, 6H); Anal. Calcd for  $\text{C}_{68}\text{H}_{86}\text{Br}_2\text{O}_2\text{P}_2$ : C, 70.58; H, 7.49. Found: C, 70.54; H, 7.33.

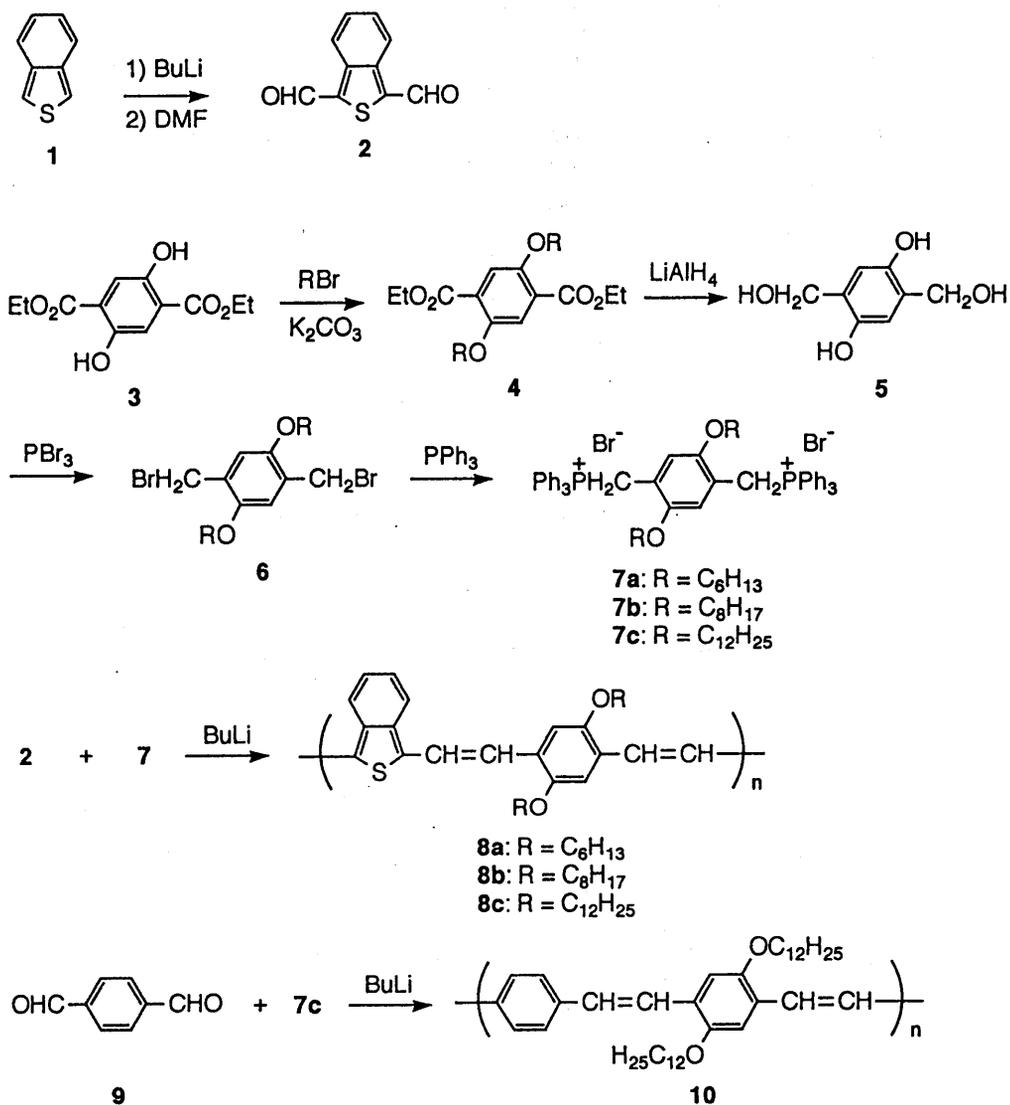
2-7. Poly(1,3-benzo[*c*]thiophenediylvinylene-alt-2,5-dialkyloxy-1,4-phenylenevinylene) (**8**). Into the mixture of **2**, solvent, and **7a**, **7b**, or **7c** a given amount of 1.6 M butyllithium in hexane was added dropwise by air-tight syringe and the reaction mixture was stirred for 5 h at room temperature. The mixture was poured into excess ethanol to precipitate the polymer. It was washed with ethanol and dried under reduced pressure to constant weight.

2-8. Poly(1,4-phenylenevinylene-alt-2,5-didodecyloxy-1,4-phenylenevinylene) (**10**). Into the solution of **7c** (324 mg, 0.28 mmol) and telephthalaldehyde (**9**) (37.6 mg, 0.28 mmol) in 5 mL of THF, 0.43 mL of 1.6 M butyllithium in hexane was added using air-tight syringe with stirring at room temperature. After stirring for 24 h, the reaction mixture was poured into excess ethanol to precipitate the polymer. It was washed with ethanol to give 91 mg (57%) of **10** as orange solid:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ) 7.2-6.6 (m), 4.2-3.8 (br), 2.0-1.2 (m), 0.8 (br). GPC measurement with polystyrenes as a reference showed a relative molecular weight of 8000.

### 3. Results and Discussion

3-1. Wittig Reaction of **2** with **7**. Preliminary experiments showed that it was difficult to prepare unsubstituted poly(4,7-benzo[*c*]thiophenediylvinylene) via sulfonium salt method because of the instability of benzo[*c*]thiophene. The attempt to synthesize 1,3-bis(halomethyl)benzo[*c*]thiophene was unsuccessful. It was found that benzo[*c*]thiophene-1,3-dicarbaldehyde (**2**) can be obtained as stable crystals. Our idea was to prepare poly(arylenevinylene) carrying benzo[*c*]thiophene unit by using dialdehyde **2** as a starting material (Scheme I). The Wittig reaction between **2** and 2,5-dialkyloxy-p-xylylenebis(triphenylphosphonium bromide)s (**7**) were carried out. Compound **7** is carrying alkyloxy groups to make the resulting polymer soluble in organic solvent. The polymerization results are summarized in Table I. Compound **7a** was not soluble in THF but soluble in polar solvents such as ethanol and DMSO. On the other hand, the product **8a** was not soluble in ethanol or DMSO but soluble in THF. The reaction proceeded heterogeneously (run 1-5). Compound **7b** was more soluble in THF than **7a** and the degree of polymerization (DP) of the product **8b** was higher than that of **8a** (run 7). However, DP of **8b** was still low and the product obtained from run 7 gave brittle film. Compound **7c** with dodecyloxy group was

Scheme I  
Synthesis of Poly(arylenevinylene)s **8a**, **8b**, **8c** and **10**



easily soluble in THF and the reaction proceeded homogeneously (run 9). The DP of the polymer **8c** was much higher than that of **8a** or **8b**. Polymer **8c** gave tough dark purple film with metallic luster by a conventional casting method. It was concluded that longer alkyloxy group enhanced the solubility of the phosphonium salt in THF, leading a high molecular weight product.

Table I. The Wittig Reaction of **2** with **7a**, **7b**, or **7c**

run	<b>2</b> , mmol	<b>7</b> , mmol	BuLi., mmol	solv., mL	temp., °C	yield, %	DP <sup>a</sup>
<b>7a</b>							
1	0.27	0.27	0.68	EtOH, 14	25	79	23
2	0.27	0.27	0.68	THF, 18	25	69	3
3	0.27	0.27	0.68	THF, 18	50	69	3
4	0.27	0.27	0.68	DMSO, 15	25	75	23
5	0.27	0.27	0.68	DMSO, 15	60	74	23
<b>7b</b>							
6	0.20	0.20	0.48	EtOH, 10	25	91	23
7	0.20	0.20	0.48	THF, 10	25	67	29
8	0.20	0.20	0.48	DMSO, 10	25	93	22
<b>7c</b>							
9	0.23	0.23	0.56	THF, 15	25	78	920

<sup>a</sup> Determined by GPC.

Fig. 1 shows the IR spectrum of poly(1,3-benzo[*c*]thiophenediylvinylene-*alt*-2,5-didodecyloxy-1,4-phenylenevinylene) (**8c**). It exhibits absorption peak at 946  $\text{cm}^{-1}$  due to the C-H out-of-plane bending of the *trans* vinylene. Its  $^1\text{H}$  NMR shows absorption peak at 8.2-6.8, 4.2-3.7, 2.0-1.0, and 0.9 ppm due to aromatic and vinylene protons, methylene protons (1-position of dodecyloxy group), methylene protons (2-11-positions of dodecyl group), and methyl protons as shown in Fig. 2.

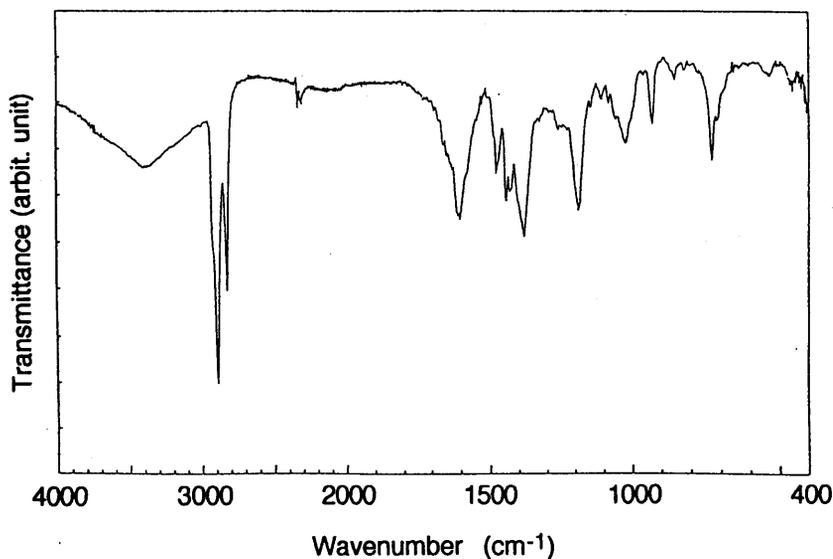


Fig 1 IR spectrum of poly(arylenevinylene) **8c** (KBr).

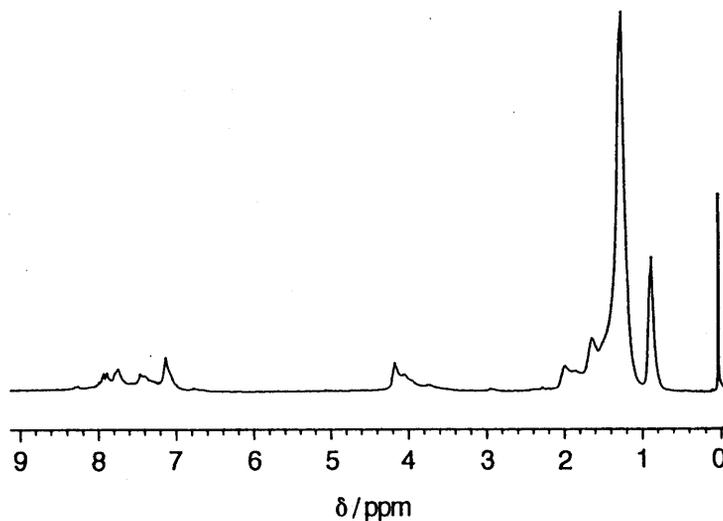


Fig.2  $^1\text{H}$  NMR spectrum of poly(arylenevinylene) **8c** in  $\text{CDCl}_3$ .

3-2. Effect of Benzo[c]thiophene Unit in Poly(arylenevinylene). To investigate the effect of benzo[c]thiophene unit in poly(arylenevinylene), the Wittig reaction of **7c** with telephthalaldehyde (**9**) was carried out to obtain poly(1,4-phenylenevinylene-*alt*-2,5-didodecyloxy-1,4-phenylenevinylene) (**10**). Polymer **10** has phenylene group instead of benzo[c]thiophene moiety. Fig. 3 shows the UV-Vis spectra of **8c** and **10** in THF. The optical bandgap ( $E_g$ ) of **8c** was 1.7 eV which is much lower than that of **10** ( $E_g = 2.5$  eV), indicating that benzo[c]thiophene unit in poly(arylenevinylene) is effective in reducing the bandgap of poly(arylenevinylene).

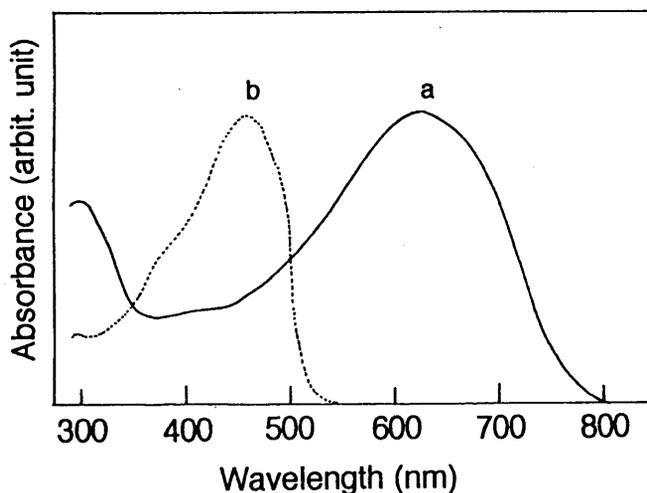


Fig.3 UV-Vis spectra of (a) **8c** and (b) **10** in THF.

#### 4. Concluding remarks

- i) Benzo[c]thiophene unit was successfully fused onto poly(arylenevinylene) backbone by the Wittig reaction between benzo[c]thiophene-1,3-dicarbaldehyde and 2,5-dialkyloxy-p-xylylenebis(triphenylphosphonium bromide)s.
- ii) It was found that benzo[c]thiophene unit reduced the band gap of the resulting poly(arylenevinylene).
- iii) This synthetic approach to soluble poly(arylenevinylene) has the advantage of being able to introduce various aromatic unit into poly(arylenevinylene) by using aromatic dialdehyde compound as a starting material.

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