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Description	

**Syntheses and enantioselective recognition of  
chiral poly(phenyleneethynylene)s bearing  
bulky optically active menthyl groups**

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**Running heads:**

Enantioselective recognition by chiral poly(phenyleneethynylene)s

## **Abstract**

Two optically active poly(menthoxy carbonyl phenylene ethynylene)s were synthesized by polycondensation using a palladium-copper catalyst system. All polymers showed Cotton effects in the absorption region of the main chain, meaning that chirality is induced to the main chain. Moreover, these chiral polymers showed the enantioselective recognition ability for chiral menthol in CD spectra.

## **Keywords:**

Poly(phenylene ethynylene) / Menthyl Group / Enantioselective Recognition

## **Introduction**

Enantioselective recognition by chiral main chain of polymers is a very interesting subject in polymer science. Some researchers including us reported that various chiral polymers show good enantioselective recognition ability in high-performance liquid chromatography [1-8], in membrane permeation and in adsorption [9-19]. In addition, we synthesized several optically active  $\pi$ -conjugated polymers that have chiral

main chains in anticipation of producing functional materials with high enantioselective recognition ability [12,16,19].

In this study, we synthesized new  $\pi$ -conjugated polymers bearing bulky chiral groups, i.e., two (+)-menthyl groups-containing poly(phenyleneethynylene)s in an attempt to prepare a polymer having a chiral main chain which shows enantioselective recognition ability.

## **Experimental Section**

### **Materials**

Toluene and triethylamine were distilled over calcium hydride. 3,5-Dibromobenzoic acid (Tokyo Kasei), 1,3-dibromobenzene (Tokyo Kasei), 1,4-diiodobenzene (*p*-PI, Tokyo Kasei), 2-methyl-3-butyn-2-ol (Janssen Chimica), (+)- and (-)-menthol (Tokyo Kasei) were used as obtained.

### **Synthesis of Monomers [Scheme 1]**

All the following reaction procedures were conducted under dry nitrogen according to the reaction conditions of ref. 20.

#### **(+)-Menthyl 3,5-dibromobenzoate [(+)-*m*-MtPBr]**

Thionyl chloride (42.8 g, 360 mmol) was added to 3,5-dibromobenzoic acid (10 g, 35.7 mmol), and stirring was continued at the reflux temperature for 3 h. The remaining thionyl chloride was evaporated to give a brown liquid which was added to a toluene (50 ml) solution of (+)-menthol (8.00 g, 51.2 mmol). This solution was stirred for 14 h at the reflux temperature. The solvent was evaporated, and the resulting crude product was purified by silica-gel chromatography using hexane as an eluent ( $R_f=0.21$ ). The product was yellow viscous liquid. Yield: 98.4%;  $[\alpha]_D^{20}=+45^\circ$  (c 0.51, chloroform);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS)  $\delta$  0.78 and 0.93 (2d, 6H,  $(\text{CH}_3)_2\text{CH-}$ ), 0.92 (d, 3H,  $\text{CH}_3\text{CH-}$ ), 1.00-2.36 (m, 9H,  $\text{CH}$  and  $\text{CH}_2$  of menthoxy group), 4.94 (ddd, 1H,  $\text{COO-CH}$ ), 7.84 (s, 1H,  $\text{CH}$  of phenyl ring), 8.10 (s, 2H, 2( $\text{CH}$ ) of phenyl ring); IR ( $\text{cm}^{-1}$ , NaCl) 2960 (C-H), 1724 (C=O), 1222 (C-O).

### **(+)-Menthyl 3,5-bis(3-hydroxy-3-methyl-1-butyryl)benzoate**

In triethylamine (200 ml) were dissolved (+)-*m*-MtPBr (6.35 g, 14.6 mmol), 2-methyl-3-butyryl-2-ol (7.40 g, 88.1 mmol), bis(triphenylphosphine)-palladium(II) chloride (3.9 mg,  $5.56 \times 10^{-3}$  mmol), cuprous iodide (3.65 mg,  $1.92 \times 10^{-2}$  mmol), and triphenylphosphine (7.3 mg,  $2.79 \times 10^{-2}$  mmol). The solution was stirred for 16 h at the reflux

temperature. The resulting salt was removed by filtration, and the filtrate was condensed to yield a crude product which was purified by silica-gel chromatography using hexane as an eluent ( $R_f=0.28$ ). The product was red-brown viscous liquid. Yield; 95.6%;  $[\alpha]_D^{20}=+37^\circ$  (c 0.47, chloroform);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS)  $\delta$  0.78 and 0.93 (2d, 6H,  $(\text{CH}_3)_2\text{CH-}$ ), 0.92 (d, 3H,  $\text{CH}_3\text{CH-}$ ), 1.62 (s, 12H,  $(\text{HOC}(\text{CH}_3)_2)_2$ ), 1.00-2.36 (m, 9H,  $\text{CH}$  and  $\text{CH}_2$  of menthoxy group), 2.57 (s, 2H, 2(-OH)), 4.94 (ddd, 1H,  $\text{COO-CH}$ ), 7.63 (s, 1H,  $\text{CH}$  of phenyl ring), 7.99 (s, 2H, 2( $\text{CH}$ ) of phenyl ring); IR ( $\text{cm}^{-1}$ , NaCl) 3368 (-OH), 2964 (C-H), 1724 (C=O), 1222 (C-O).

### **(+)-Menthyl 3,5-diethynylbenzoate [(+)-*m*-MtPE]**

Sodium hydride (80wt%, 5.94 g, 35 mmol) was added to a toluene solution (200 ml) of (+)-menthyl 3,5-bis(3-hydroxy-3-methyl-1-butynyl)benzoate (5.94 g, 14.0 mmol), and the mixture was heated at 100 °C with stirring for 1 h. After the usual work up, the product was purified with silica-gel chromatography using hexane as an eluent ( $R_f=0.45$ ). Yellow viscous liquid was obtained in 85.2% yield.  $[\alpha]_D^{20}=+55^\circ$  (c 0.25, chloroform);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS)  $\delta$  0.78 and 0.93 (2d, 6H,  $(\text{CH}_3)_2\text{CH-}$ ), 0.92 (d, 3H,  $\text{CH}_3\text{CH-}$ ), 1.00-2.36 (m, 9H,  $\text{CH}$  and  $\text{CH}_2$  of menthoxy group), 3.14 (s, 2H,  $\text{HC}\equiv\text{C}$ ), 4.95 (ddd, 1H,  $\text{COO-CH}$ ),

7.76 (s, 1H,  $\underline{\text{CH}}$  of phenyl ring), 8.10 (s, 2H, 2( $\underline{\text{CH}}$ ) of phenyl ring); IR ( $\text{cm}^{-1}$ , NaCl) 3312 (H-C $\equiv$ ), 2960 (C-H), 2120 (C $\equiv$ C), 1724 (C=O), 1222 (C-O).

### **1,3-Bis(3-hydroxy-3-methyl-1-butynyl)benzene**

The reaction similar to that for (+)-menthyl 3,5-bis(3-hydroxy-3-methyl-1-butynyl)benzene was run with 1,3-dibromobenzene (6.67 g, 28.2 mmol) instead of (+)-*m*-MtPBr. The product was purified by silica-gel chromatography using chloroform as an eluent ( $R_f=0.28$ ) to give red-brown viscous liquid. Yield; 86.1%;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  1.61 (s, 12H, 2( $\text{HOC}(\underline{\text{CH}}_3)_2$ ), 2.11 (b, 2H, 2( $-\underline{\text{OH}}$ )), 7.17-7.57(m, 4H,  $\underline{\text{CH}}$  of benzene ring); IR ( $\text{cm}^{-1}$ , NaCl) 3368 ( $-\text{OH}$ ), 2992 (C-H).

### **1,3-Diethynylbenzene [*m*-PE]**

The reaction similar to that for (+)-*m*-MtPE was run with (+)-1,3-bis(3-hydroxy-3-methyl-1-butynyl)benzene (3.49 g, 27.7 mmol). The crude product was distilled (bp 60 °C/100 mmHg), and the resulting product was yellow liquid. Yield; 85.2%;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS)  $\delta$  2.35 (s, 2H,  $\underline{\text{HC}}\equiv\text{C}$ ), 7.14-7.26 (m, 4H,  $\underline{\text{CH}}$  of phenyl ring); IR ( $\text{cm}^{-1}$ , NaCl)

3312 (H-C≡), 2960 (C-H), 2120 (C≡C).

## **Polycondensation (Scheme 2) [20,21]**

### **Polycondensation of polymer from *p*-PI and (+)-*m*-MtPE (1)**

(+)-*m*-MtPE (1.42 g, 4.61 mmol) and *p*-PI (1.52 g, 4.61 mmol) were dissolved in triethylamine (200 ml) and tetrahydrofuran (20 ml), and triphenylphosphine (550 mg, 2.10 mmol), cuprous iodide (275 mg, 1.45 mmol), and bis(triphenylphosphine)palladium (II) chloride (298 mg, 0.425 mmol) were added to this solution. After stirring for 24 h at the reflux temperature, the precipitated salt, triethylammonium iodide, was filtered at room temperature, and was rinsed with ethyl ether. The filtrates and the ether were combined, and the solvent was evaporated to dryness. The residue was dissolved in a minimum amount of chloroform, and the solution was poured into methanol (200 ml) to form a precipitate that was separated by centrifugation. Reprecipitation from chloroform solution to methanol was carried out twice. The resulting polymer was dried under vacuum to give **1** as a brown solid. Yield: 97.7%;  $[\alpha]_D^{20} = +24^\circ$  (c 0.067, chloroform). Anal. Calcd for H-(C<sub>27</sub>H<sub>26</sub>O<sub>2</sub>)<sub>2</sub>-I: C, 72.65; H, 5.94. Found: C, 72.4; H, 5.66. GPC data were listed in Table 1.



## **Polycondensation of polymer from (+)-*m*-MtPBr and *m*-PE (2)**

The reaction similar to that for *p*-PI with **1** was run with *m*-PE (1.07 g, 8.49 mmol) instead of (+)-*m*-MtPE. The resulting polymer was dried under vacuum to give **2** as a green solid. Yield: 100%;  $[\alpha]_D^{20} = +28^\circ$  (c 0.75, chloroform). GPC data were listed in Table 1.

## **Measurements**

Specific rotation was measured using a HORIBA SEPA-200 polarimeter at 589 nm. Circular dichroism (CD) spectra were taken on a JASCO J-720WI spectropolarimeter. NMR spectra were obtained with a Varian UNITY plus-500 (500 MHz). GPC was analyzed using SHODEX GPC KF-806L columns and a 655A UV detector (254 nm). IR spectra were measured on a HITACHI 270-30 spectrophotometer. Emission spectra were obtained with a Shimadzu RF-5000 spectrofluorophotometer. Differential scanning calorimetry (DSC) and thermogravimetry (TG) were measured with Shimadzu DSC-50 and TGA-50, respectively.

## **Circular Dichroism (CD) Spectra Measurements of Chiral Poly(phenyleneethynylene)s in the Presence of Optically Active Menthol**

A typical measurement is described as follows. **1** (10.0 mg,  $2.62 \times 10^{-2}$  mmol) and (+)- or (-)-menthol (409 mg, 2.62 mmol) were dissolved in chloroform (37.5 ml), and CD of this solution was measured at  $-15^{\circ}\text{C}$ . Other CD spectra were also measured under similar conditions.

## Results and Discussion

The monomers, (+)-*m*-MtPBr, (+)-*m*-MtPE, and *m*-PE, were synthesized in good yields (Scheme 1). Under the catalyst system, i.e., bis(triphenylphosphine)palladium dichloride, cuprous iodide, and triphenylphosphine, the polycondensation between the diethynylbenzenes and the dihalobenzenes (Scheme 2) proceeded to give solids which were soluble in common organic solvents such as tetrahydrofuran, chloroform, triethylamine, and toluene but insoluble in methanol. These results of the polycondensation are shown in Table 1.

Table 2 shows the results of characterization of the polymers, and the lower spectra of Figure 1 show UV-vis ones for the polymers. Since **1** has longer cutoff wavelength than **2**, **1** has a longer  $\pi$ -conjugation main chain than **2**. And these polymers emitted the blue fluorescence. The  $T_g$  and  $T_d$  values for **1** were higher than those for **2** (Table 2). This result demonstrates that the main chain of **1** is more rigid than that of **2**.

All the polymers were optically active ( $[\alpha]_D^{20}=+24 \sim +28$ , Table 2) and showed the CD signals at the absorption bands of the main chains. Therefore, they had chirality in the main chains (the upper spectra in Figure 1). Since (+)-*m*-MtPE has no CD signal in this region, this result also indicates that the Cotton effect of the polymers are attributable to the polymer chains. The peaks of the CD curves at the absorption bands of the main chain of **1** ( $[\theta]: -2220$ ) were higher than that of **2** ( $[\theta]: +987$ ).

Figure 2 shows the CD spectra of two chiral poly(phenyleneethynylene)s in the presence of (+)- or (-)-menthol in chloroform at  $-15^\circ\text{C}$ . Since the magnitudes of the CD bands in the presence of (-)-menthol are different from those in the presence of (+)-menthol, these polymers were found to have an ability of the enantioselective recognition.

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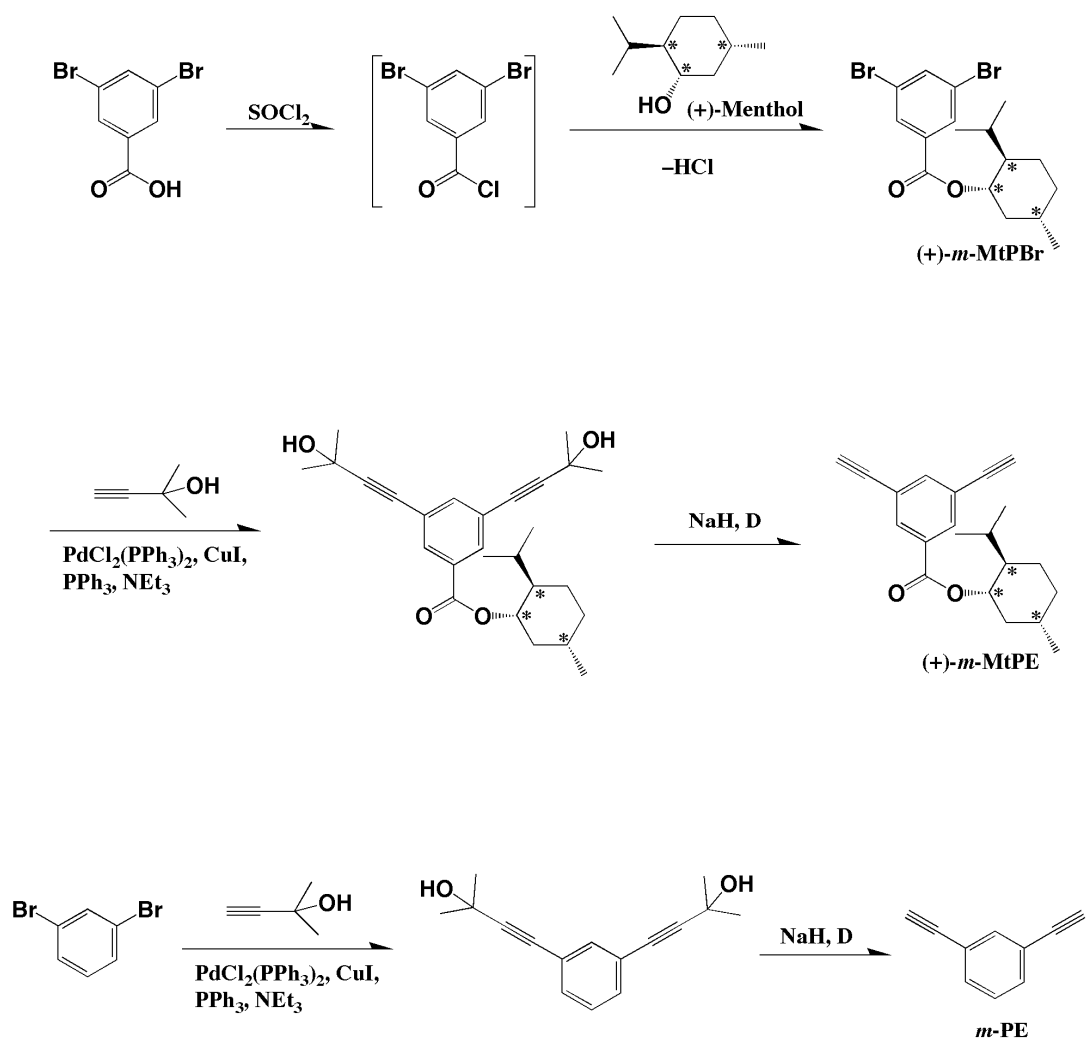
## CAPTIONS FOR SCHEMES AND FIGURES

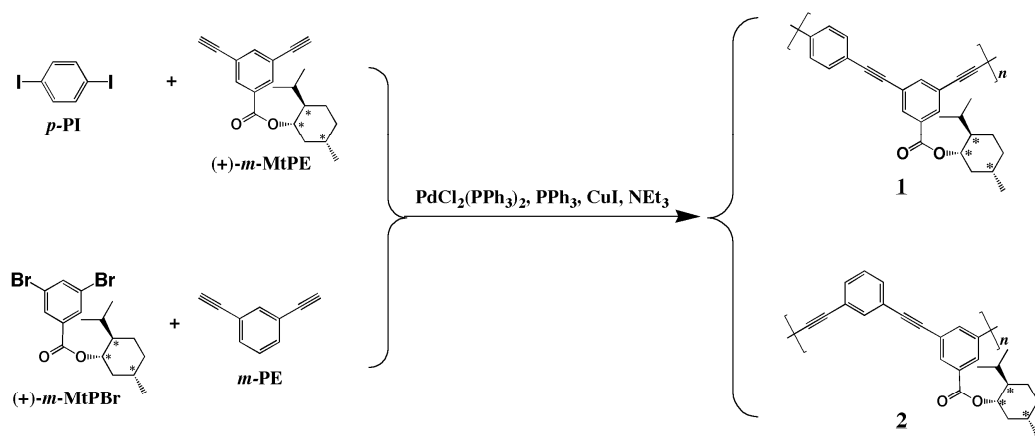
**Scheme 1.** Synthetic routes to the monomers.

**Scheme 2.** Synthesis of poly(phenyleneethynylene)s by polycondensation.

**Figure 1.** CD and UV-vis spectra of (+)-MtPE, 1 and 2 at  $-15^{\circ}\text{C}$  in chloroform.

**Figure 2.** CD spectra of optically active poly(phenyleneethynylene)s in the presence of (+)- or (-)-menthol at  $-15^{\circ}\text{C}$  in chloroform.  
(a) 1, (b) 2.





**Scheme 2.**



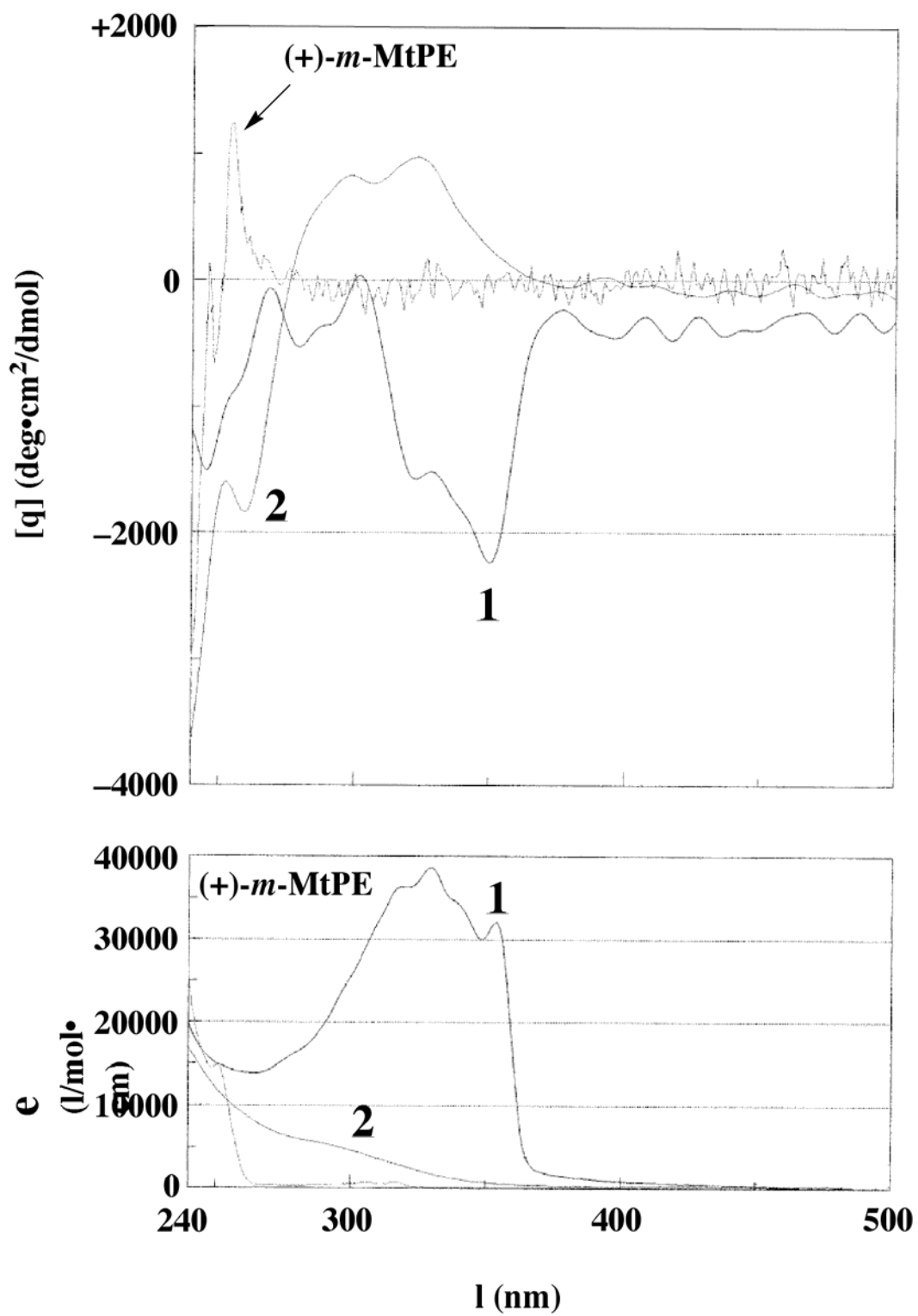
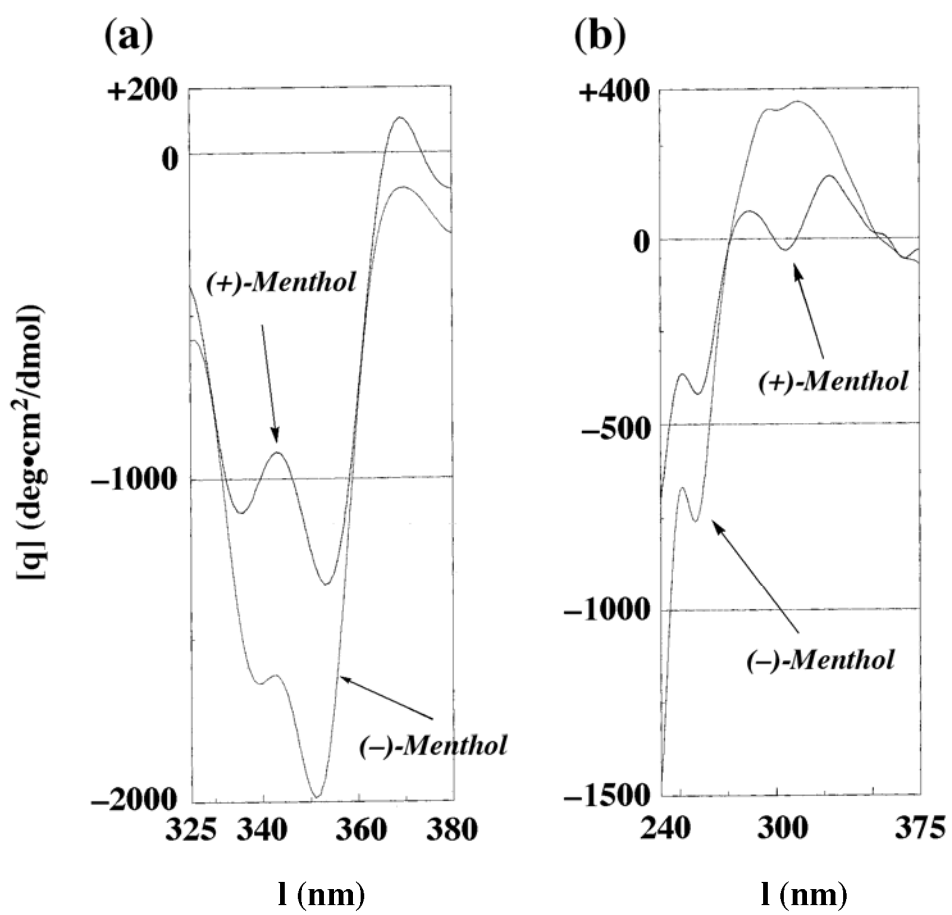


Figure 1.



**Figure 2.**

**Table 1. Polycondensation of optically active poly(phenyleneethynylene)s.**

<b>Poly(phenylene-ethynylene)<sup>a)</sup></b>	<b>Yield (%)</b>	<b><math>\overline{M}_w</math><sup>b)</sup></b>	<b><math>\overline{P}_w</math><sup>b)</sup></b>	<b><math>\overline{M}_n</math><sup>b)</sup></b>	<b><math>\overline{P}_n</math><sup>b)</sup></b>	<b><math>\overline{M}_w/\overline{M}_n</math><sup>b)</sup></b>
<b>1</b>	<b>97.7</b>	<b>8390</b>	<b>22.0</b>	<b>5310</b>	<b>13.9</b>	<b>1.58</b>
<b>2</b>	<b>100</b>	<b>2910</b>	<b>7.62</b>	<b>1560</b>	<b>4.08</b>	<b>1.87</b>

a) See Scheme 2 for the codes.

b) Determined by GPC correlated to standard polystyrene,

$\overline{P}_w$ : weight-average degree of polymerization,

$\overline{P}_n$ : number-average degree of polymerization.

**Table 2. Characterization of optically active poly(phenyleneethynylene)s.**

Poly(phenylene-ethynylene) <sup>a)</sup>	Color	$\lambda_{\max}^b$ (nm)	$\lambda_{\text{em}}^c$ (nm)	$T_g^d$ (°C)	$T_d^e$ (°C)	$[\alpha]_D^{20\text{ f)}$ deg	$[\eta]_{\max}(\lambda(\text{nm}))^g$ (deg•cm <sup>2</sup> /dmol)
1	Brown	354	444	>140	305	+24	-2220 (350)
2	Green	No peaks	470	75	248	+28	+987 (323)

a) See Scheme 2 for the codes.

b) Wavelength of the absorption maximum. See Figure 1.

c) Wavelength of the emission maximum (excited at 370nm).

d) Determined by DSC under N<sub>2</sub>. Heating rate was 10°C/min.

e) Temperature of decomposition determined by TGA under N<sub>2</sub>. Heating rate was 10°C/min.

f) Specific rotation in chloroform (conc.=0.011-0.075 g/dl).

g) Molar ellipticity ([ $\eta$ ]) of peaks of CD spectrum at the  $\lambda$ .