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Polymer 42 (2001) 351–355

polymer

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Polymer Communication

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

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Received 23 March 2000; received in revised form 19 May 2000; accepted 19 May 2000

Abstract

Two optically active poly(menthoxycarbonylphenyleneethynylene)s were synthesized by polycondensation using a palladium–copper catalyst system. All polymers showed Cotton effects in the absorption region of the main chain, implying that chirality is induced to the main chain. Moreover, these chiral polymers showed the enantioselective recognition ability for chiral menthol in the circular dichroism (CD) spectra. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(phenyleneethynylene); Menthyl group; Enantioselectivite recognition

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1. 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 π-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 π-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 that shows enantioselective recognition ability.

2. Experimental section

2.1. 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.

2.2. Synthesis of monomers

The synthetic routes to the monomers are given in Scheme 1. All the following reaction procedures were conducted under dry nitrogen, according to the reaction conditions of Ref. [20].

2.2.1. (+)-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 that 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%; $[\alpha]_D^{20} = +45°$ (c 0.51, chloroform); ^{1}H NMR (CDCl$_3$, TMS) δ 0.78 and 0.93 (2d, 6H, $(CH_3)_2CH$–), 0.92 (d, 3H, CH_3CH–), 1.00–2.36 (m, 9H, C*H* and C*H*$_2$ of menthoxy group), 4.94 (ddd, 1H, COO–C*H*), 7.84 (s, 1H, C*H* of phenyl ring), 8.10 (s, 2H,

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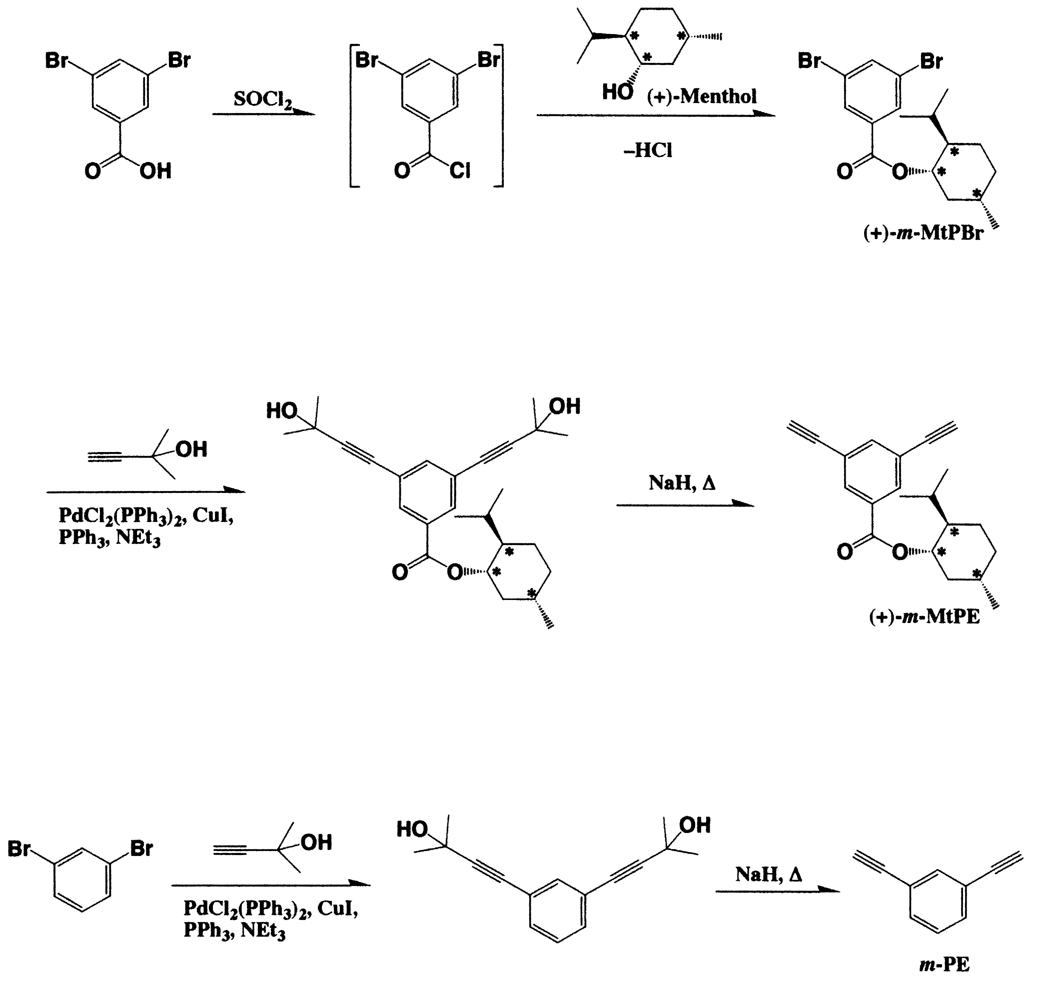
PII: S0032-3861(00)00391-8



Scheme 1.

2(C*H*) of phenyl ring); IR (cm^{-1}, NaCl) 2960 (C–H), 1724 (CyO), 1222 (C–O).

2.2.2. (+)-Menthyl 3,5-bis(3-hydroxy-3-methyl-1-butynyl)benzoate

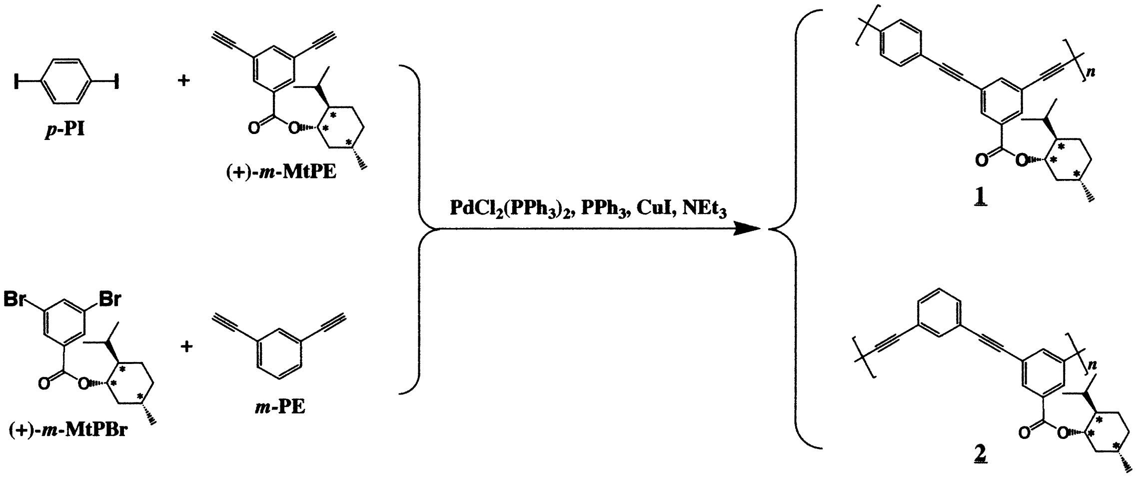
In triethylamine (200 ml) were dissolved (+)-*m*-MtPBr (6.35 g, 14.6 mmol), 2-methyl-3-butyn-2-ol (7.40 g, 88.1 mmol), bis(triphenylphosphine)-palladium(II) chloride (3.9 mg, 5.56×10^{-3} mmol), cuprous iodide (3.65 mg, 1.92×10^{-2} mmol), and triphenylphosphine (7.3 mg, 2.79×10^{-2} mmol). The solution 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 that was purified by silica-gel chromatography using hexane as an eluent ($R_f = 0.28$). The product was a red–brown viscous liquid. Yield: 95.6%; $[\alpha]_D^{20} = +37°$ (c 0.47, chloroform); ^{1}H NMR (CDCl$_3$, TMS) δ 0.78 and 0.93 (2d, 6H, (CH_3)$_2$CH–), 0.92 (d, 3H, CH_3CH–), 1.62 (s, 12H, (HOC(CH_3)$_2$–)$_2$), 1.00–2.36 (m, 9H, C*H* and CH_2 of menthoxy group), 2.57 (s, 2H, 2(–O*H*)), 4.94 (ddd, ^{1}H, COO–C*H*), 7.63 (s, 1H, C*H* of phenyl ring), 7.99 (s, 2H, 2(C*H*) of phenyl ring); IR (cm^{-1}, NaCl) 3368 (–OH), 2964 (C–H), 1724 (CyO), 1222 (C–O).

2.2.3. (+)-Menthyl 3,5-diethynylbenzoate [(+)-m-MtPE]

Sodium hydride (80 wt%, 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 procedures, the product was purified with silica-gel chromatography using hexane as an eluent ($R_f = 0.45$). A yellow viscous liquid was obtained in 85.2% yield. $[\alpha]_D^{20} = +55°$ (c 0.25, chloroform); ^{1}H NMR (CDCl$_3$, TMS) δ 0.78 and 0.93 (2d, 6H, (CH_3)$_2$CH–), 0.92 (d, 3H, CH_3CH–), 1.00–2.36 (m, 9H, C*H* and CH_2 of menthoxy group), 3.14 (s, 2H, *H*CxC), 4.95 (ddd, 1H, COO–C*H*), 7.76 (s, 1H, C*H* of phenyl ring), 8.10 (s, 2H, 2(C*H*) of phenyl ring); IR (cm^{-1}, NaCl) 3312 (H–Cx), 2960 (C–H), 2120 (CxC), 1724 (CyO), 1222 (C–O).

2.2.4. 1,3-Bis(3-hydroxy-3-methyl-1-butynyl)benzene

A reaction similar to that for (+)-menthyl 3,5-bis(3-hydroxy-3-methyl-1-butynyl)benzene was run with



Scheme 2.

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 a red–brown viscous liquid. Yield: 86.1%; ^{1}H NMR ($CDCl_3$, TMS) δ 1.61(s, 12H, 2(HOC(CH_3)$_2$–), 2.11 (b, 2H, 2(–O*H*)), 7.17–7.57(m, 4H, C*H* of benzene ring); IR (cm^{-1}, NaCl) 3368 (–OH), 2992 (C–H).

2.2.5. 1,3-Diethynylbenzene [m-PE]

A 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). The resulting product was a yellow liquid. Yield: 85.2%; ^{1}H NMR ($CDCl_3$, TMS) δ 2.35 (s, 2H, *H*CxC), 7.14–7.26 (m, 4H, C*H* of phenyl ring); IR (cm^{-1}, NaCl) 3312 (H–Cx), 2960 (C–H), 2120 (CxC).

2.3. Polycondensation

Synthesis of poly(phenyleneethynylene)s by polycondensation is given in Scheme 2 [20,21].

2.3.1. 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); 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%; $[\alpha]_D^{20} = +24°$ (c 0.067, chloroform). Anal. Calcd for H–($C_{27}H_{26}O_2$)$_2$–I: C, 72.65; H, 5.94. Found: C, 72.4; H, 5.66. The GPC data are listed in Table 1.

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

A 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%; $[\alpha]_D^{20} = +28°$ (c 0.75, chloroform). The GPC data are listed in Table 1.

2.4. 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

Table 1
Polycondensation of optically active poly(phenyleneethynylene)s

Poly(phenyleneethynylene)[a]	Yield (%)	$\bar{M}_w$[b]	$\bar{P}_w$[b]	$\bar{M}_n$[b]	$\bar{P}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]
1	97.7	8390	22.0	5310	13.9	1.58
2	100	2910	7.62	1560	4.08	1.87

[a] See Scheme 2 for the codes.

[b] Determined by GPC correlated to standard polystyrene: $\bar{P}_w$, weight-average degree of polymerization; $\bar{P}_n$, number-average degree of polymerization.

Table 2
Characterization of optically active poly(phenyleneethynylene)s

Poly(phenyleneethynylene)[a]	Color	λ_{max}[b] (nm)	λ_{em}[c] (nm)	T_g[d] (°C)	T_d[e] (°C)	$[\alpha]_D^{20}$[f] (°)	$[\theta]_{max}(\lambda\,(nm))$[g](° cm^2/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 Fig. 1.
[c] Wavelength of the emission maximum (excited at 370 nm).
[d] Determined by DSC under N_2. The heating rate was 10°C/min.
[e] Temperature of decomposition determined by TGA under N_2. The heating rate was 10°C/min.
[f] Specific rotation in chloroform (concentration = 0.011–0.075 g/dl).
[g] Molar ellipticity ($[\theta]$) of peaks of CD spectrum at the λ.

(500 MHz).The GPC was analyzed using SHODEX GPC KF-806L columns and a 655A UV detector (254 nm). The IR spectra were measured on a HITACHI 270-30 spectrophotometer. The emission spectra were obtained with a Shimadzu RF-5000 spectrofluorophotometer. Differential scanning calorimetory (DSC) and thermogravimetry (TG) were measured with Shimadzu DSC-50 and TGA-50, respectively.

2.5. Circular dichroism 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, 2.62×10^{-2} mmol) and (+)- or (−)-menthol (409 mg, 2.62 mmol) were dissolved in chloroform (37.5 ml), and the CD of this solution was measured at −15°C. Other CD spectra were also measured under similar conditions.

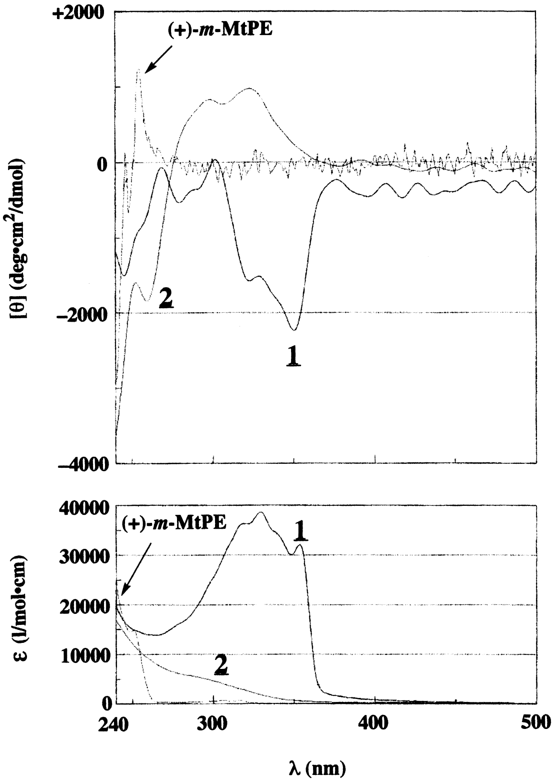


Fig. 1. CD and UV-vis spectra of (+)-MtPE, **1** and **2** at −15°C in chloroform.

3. 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 that were soluble in common organic solvents such as tetrahydrofuran, chloroform, triethylamine and toluene, but insoluble in methanol. The results of this polycondensation are given in Table 1.

Table 2 shows the results of the characterization of the polymers; the lower spectra of Fig. 1shows the results of the

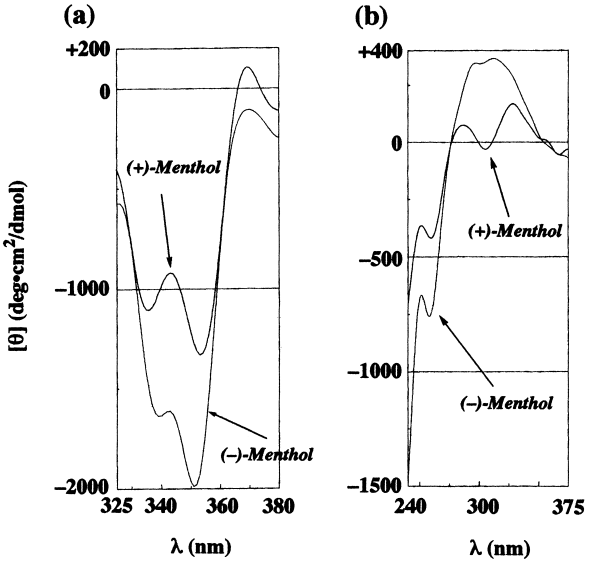


Fig. 2. CD spectra of optically active poly(phenyleneethynylene)s in the presence of (+)- or (−)-menthol at −15°C in chloroform: (a) **1**, (b) **2**.

UV-vis for the polymers. Since **1** has a longer cutoff wavelength than **2**, **1** has a longer π-conjugation main chain than **2**. Further, 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 $\{[\alpha]_D^{20} = +24–+28$, 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 Fig. 1). Since (+)-*m*-MtPE has no CD signal in this region, this result also indicate 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).

Fig. 2 shows the CD spectra of two chiral poly(phenyleneethynylene)s, in the presence of (+)- or (−)-menthol in chloroform at −15°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 the ability of enantioselective recognition.

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