

# Synthesis of an optically active poly(aryleneethynylene) bearing galvinoxyl residues and its chiroptical and magnetic properties

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## ABSTRACT

We synthesized an optically active poly(binaphthyl-6,6'-diylethynylene-1,3-phenyleneethynylene) with pendant galvinoxyl residues. The hydrogalvinoxyl precursor polymer was given by polymerization of (1,3-diiodophenyl)hydrogalvinoxyl and 6,6'-diethynyl-2,2'-dihexyloxybinaphthyl using Pd(PPh<sub>3</sub>)<sub>4</sub> catalyst ( $M_w = 4.6 \times 10^4$ ,  $M_w/M_n = 3.0$ ). The polymer yielded the corresponding polyradical with high spin concentration by treatment of the polymer solution with PbO<sub>2</sub>. In the CD spectra of the polymer and polyradical taken in various solutions, clear Cotton effects were observed in the absorption region of the binaphthyl chromophore, while no Cotton effect was observed in that of the galvinoxyl chromophore. On the other hand, in the MCD, Faraday effects were observed in the absorption region of the backbone and galvinoxyl chromophore. The static magnetic susceptibility of the chiral polyradical was measured using a SQUID magnetometer, and showed weak antiferromagnetic interaction.

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## 1. Introduction

Optically active polymers promise interesting technological applications in optical resolution, chiral sensors, chiroptics, micro-electronics and chiral magnets due to the disymmetric nature [1]. It is well known that some poly(1,3-phenyleneethynylene)s can form helical foldamer conformation depending on their side groups and/or solvent [2–4], while poly(aryleneethynylene)s [5–12] including poly(1,3-phenyleneethynylene)s [13–15] have been investigated as a backbone structure of polyradical for magnetic materials. We have already synthesized an optically active poly(1,3-phenyleneethynylene) bearing galvinoxyl units and dimethyl(10-(1S)-pinanyl)silyl groups, and the CD spectra exhibited solvatochromism in the solution [16]. In this study, we aimed construction of stable asymmetric backbone structure, and synthesized an optically active poly(binaphthyl-6,6'-diylethynylene-1,3-phenyleneethynylene) **1b** bearing galvinoxyl units via synthesis of the hydrogalvinoxyl precursor polymer **1a** by condensation polymerization of (1,3-diiodophenyl)hydrogalvinoxyl (**2a**) and 6,6'-diethynyl-2,2'-dihexyloxybinaphthyl (**3**) using Pd(PPh<sub>3</sub>)<sub>4</sub> catalyst

(Scheme 1). The natural optical activity, magnetic optical activity and magnetic interaction of the polymers were discussed in terms of the circular dichroism (CD) spectra, the magnetic circular dichroism (MCD) spectra and SQUID measurements, respectively.

## 2. Experiment

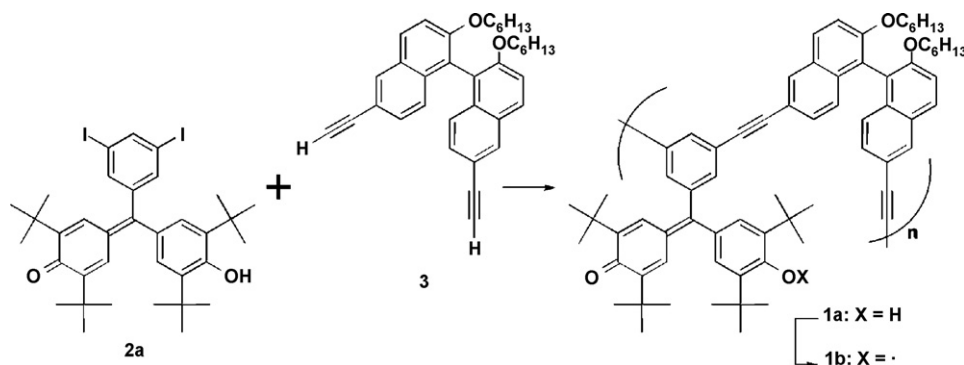
### 2.1. Materials

The monomer **2a** [16] and **3** [17] were synthesized according to the literature procedures. Tetrakis(triphenylphosphine)palladium (0) (Pd(PPh<sub>3</sub>)<sub>4</sub>) (Aldrich Co.) was used without further purification. Other conventional reagents were used as-received or purified by conventional methods.

### 2.2. Polymerization

The monomer **2a** (0.38 g, 0.51 mmol), **3** (0.26 g, 0.51 mmol), tetrakis(triphenylphosphine)palladium (0) (30 mg, 0.025 mmol), and copper iodide (20 mg, 0.10 mmol) were placed in a Schlenk tube equipped with a three-way stopcock, a reflux condenser, a rubber septum, and a Teflon-coated magnetic stirring bar. The tube was placed under vacuum, followed by a nitrogen backflush. THF (0.5 ml) and triethylamine (0.5 ml) were transferred to the tube, and

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Scheme 1.

the solution was stirred at room temperature for 24 h. The solution was treated with aqueous 3 N HCl, extracted with chloroform, washed with saturated saline, and dried over anhydrous sodium sulfate. The solvent was evaporated, and the crude product was purified by precipitation from chloroform into methanol to yield the polymer as yellow powder. The yield and the molecular weight are given in Table 1. IR (KBr,  $\text{cm}^{-1}$ ): 3630 ( $\nu_{\text{O-H}}$ ), 2964–2880 ( $\nu_{\text{C-H}}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz; ppm)  $\delta$  0.72 (t, 6H,  $\text{CH}_3$  in hexyloxy), 0.82–1.12 (m, 12H,  $\text{CH}_2$  in hexyloxy), 1.25 (s, 9H, *tert*-butyl), 1.28 (s, 9H, *tert*-butyl), 1.42 (m, 22H, *tert*-butyl and  $\text{CH}_2$  in hexyloxy), 3.85–4.02 (m, 4H,  $\text{CH}_2$  in hexyloxy), 5.54 (s, 1H, OH), 7.05 (s, 2H, ArH in **2a**), 7.09 (br, 1H, ArH in **2a**), 7.11 (d, 2H,  $J=8.8$  Hz, ArH in **3**), 7.27 (br, 2H, ArH in **3**), 7.29 (br, 1H, ArH in **2a**), 7.39 (d, 2H,  $J=1.2$  Hz, ArH in **2a**), 7.41 (d, 2H,  $J=9.1$  Hz, ArH in **3**), 7.79 (t, 1H,  $J=1.2$  Hz, ArH in **2a**), 7.89 (d, 1H,  $J=9.1$  Hz, ArH in **3**), 8.05 (br, 2H, ArH in **3**).

### 2.3. Oxidation

The polyradical **1b** was prepared by chemical oxidation of **1a** with  $\text{PbO}_2$  under nitrogen in a glovebox as follows. A degassed benzene solution of **1a** (0.1–2 mM per phenol unit) was treated with 20 equiv of recently prepared  $\text{PbO}_2$  and was vigorously stirred for 1 h. After filtration, the solution was used for spectroscopic and magnetic measurements.

### 2.4. Measurements

IR spectra were obtained using a Shimadzu FTIR 8100 spectrometer.  $^1\text{H}$  NMR spectra were measured using a JEOL GSX-270 (270 MHz) spectrometer. Average molecular weights ( $M_n$  and  $M_w$ ) were evaluated by GPC calibrated by polystyrene standard at 25 °C on THF eluent using Jasco Liquid Chromatograph instruments with PU-2080, DG-2080-53, CO-2060, UV2070, CD-2095, and polystyrene gel columns (Shodex KF-807L). CD and UV-vis absorption spectra were recorded using a Jasco J-720WI Spectropolarimeter with a peltier controller for temperatures at  $-10$ – $50$  °C (a quartz cell of 1 mm path length; sample concentration = 0.1–1 mM

based on the monomer unit), and were analyzed using the associated J-700 software. MCD and UV-vis absorption spectra were recorded using a Jasco J-720WI Spectropolarimeter with an electromagnet MCD-317 for magnetic fields of 1 T, and were analyzed using the associated J-700 software. ESR spectra were taken on a JEOL JES-2XG ESR spectrometer with 100 kHz field modulation in the X-band frequency region. Signal positions were calibrated against an external standard of  $\text{Mn}^{2+}/\text{MgO}$  ( $g=1.981$ ). The spin concentrations of each sample were determined by careful double integration of the ESR signal calibrated with that of the 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) standard solution. Static magnetic susceptibility was measured using a Quantum Design MPMS XL1 SQUID magnetometer. The powder sample of **1b** was prepared by evaporating solvent from the solution immediately after oxidation, and was contained in a diamagnetic capsule. The static magnetic susceptibility was measured from 2 to 300 K in a field of 0.5 T.

## 3. Results and discussion

The polymerization of the monomers was carried out in the presence of  $\text{Pd}(\text{PPh}_3)_4$  catalyst. A yellow solid polymer **1a** was obtained by precipitation from the polymerization mixtures into methanol. The polymerization data for these resultant polymers are summarized in Table 1. The polymer was soluble in chloroform, dichloromethane, THF, ethyl acetate, benzene, diethyl ether and toluene, but insoluble in hexane, cyclohexane, acetone, acetonitrile, methanol, ethanol, DMSO and water. It was confirmed by IR and  $^1\text{H}$  NMR spectra of the polymers that polymerization proceeded by cross-coupling reaction between a terminal acetylene and halogeno group of monomers, i.e., the reduction of the peaks assignable to the ethynyl group of **3** at  $3308\text{ cm}^{-1}$  ( $\nu_{\text{C-H}}$ ) in IR and  $\delta$  3.08 ppm (s, 2H,  $\equiv\text{C-H}$ ) in  $^1\text{H}$  NMR, and the reduction of the peak assignable to the aromatic proton of **2a** at  $\delta$  8.10 ppm (t, 1H, ArH) in  $^1\text{H}$  NMR. The alternate structure of **2a** and **3** in the polymer was confirmed by  $^1\text{H}$  NMR.

The polyradical **1b** was obtained by oxidizing the polymer **1a** by treatment of the polymer solution in degassed benzene with fresh  $\text{PbO}_2$ . The spin concentration of **1b** reached ca. 0.8 spin/unit by selecting the oxidative conditions. The polyradicals were appropriately stable for maintaining the initial spin concentration under the CD, ESR and SQUID measurement conditions. The ESR spectrum of **1b** showed a unimodal broad signal at  $g=2.0046$  indicating the formation of the phenoxyl radical, where disappearance of hyperfine structure is attributable to the intramolecular aggregation of radical units along the main chain.

The CD spectra of enantiomeric **1a** and **1b** obtained by polymerization using (R)-**2a** and (S)-**2a** (abbreviated as (R)-**1a**, (S)-**1a**, (R)-**1b** and (S)-**1b**, respectively) were measured in various solutions such as chloroform, THF and benzene solution. Clear Cotton effects were

**Table 1**  
Polymerization of **2a** and **3** using  $\text{Pd}(\text{PPh}_3)_4$  catalyst.

No.	Monomer		Yield <sup>b</sup> (%)	$M_w^c$ ( $\times 10^4$ )	$M_w/M_n^c$	DP <sup>d</sup>
	$M_1$	$M_2$				
1 <sup>a</sup>	(R)- <b>2a</b>	<b>3</b>	100	4.6	3.0	46
2 <sup>b</sup>	(S)- <b>2a</b>	<b>3</b>	96	15	5.9	150
3	rac- <b>2a</b>	<b>3</b>	94	4.4	3.3	44

<sup>a</sup>  $[M_1]_0 = [M_2]_0 = 0.25\text{ M}$ ,  $[M_1]_0/[Pd(\text{PPh}_3)_4]_0 = 20$ ,  $[Cu]_0/[Pd(\text{PPh}_3)_4]_0 = 4$ , THF/triethylamine (1/1, v/v), r.t., 24 h.

<sup>b</sup> Methanol insoluble part. Yield is based on the repeating unit (=997.39).

<sup>c</sup> Determined by GPC calibrated with polystyrene standard (THF eluent).

<sup>d</sup> Based on the repeating unit, and estimated from  $M_w$ .

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