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Communications to the Editor

Metal-Induced Chirality Induction and Chiral Recognition of Optically Active, Regioregular Polythiophenes

Eiji Yashima,*,†,‡ Hidetoshi Goto,‡ and Yoshio Okamoto*,‡

Department of Molecular Design and Engineering and Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan

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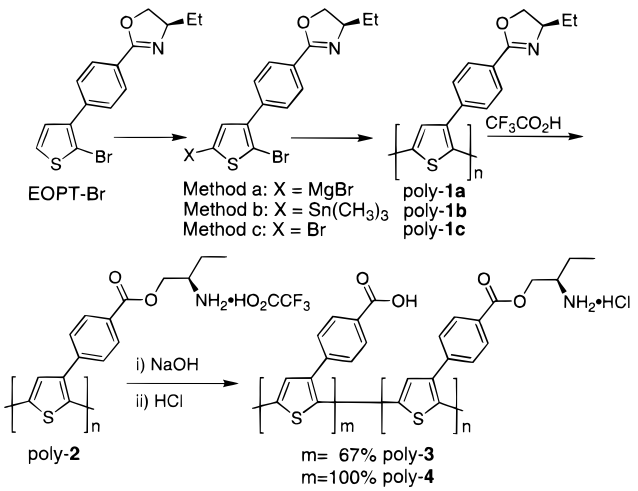
Introduction. The design and synthesis of chiral conjugated polymers with a well-defined structure have attracted considerable interest in recent years[1] in view of their potential applications not only to optoelectronic devices and batteries[2] but also to enantioselective sensors,[3] electrodes,[4] catalysts,[5] and adsorbents.[6] In particular, chiral regioregular (head-to-tail, HT) polythiophenes (PTs)[7] bearing an optically active substituent at the 3-position or 3,4-position have extensively been studied for these purposes.[8] Nevertheless, most previously studies of chiral PTs have mainly focused on their unusual chiroptical behavior depending on solvent (solvatochromism) and temperature (thermochromism).[8e−k] Chiral PTs, in sharp contrast with other optically active polymers,[9] exhibit optical activity in the $\pi-\pi^*$ transition derived from the main-chain chirality when they are aggregated to form a supramolecular, π-stacked self-assembly with intermolecular interactions in poor solvent, at low temperature, or in the film, whereas they showed no optical activity in the region in a good solvent or at high temperatures.[8e,g,h,k] A complete structural interpretation of the aggregated chiral PTs for induced optical activity still remains unclear.

In this communication, we report that a novel, optically active, regioregular PT, poly[(*R*)-3-(4-(4-ethyl-2-oxazolin-2-yl)phenyl)thiophene] (poly-**1**), exhibits a unique induced circular dichroism (ICD) in the $\pi-\pi^*$ transition region of the main chain upon coordination of the oxazoline groups to metal ions in a good solvent for poly-**1**. We also found, for the first time, that a hydrolyzed derivative of the polythiophene showed chiral recognition ability and exhibited a characteristic ICD in the UV−vis region upon complexation with chiral amines.

Experimental Section. a. Materials. Regioregular poly-**1** containing metal-ligating oxazoline residues was prepared from optically active (*R*)-2-bromo-3-(4-(4-ethyl-2-oxazolin-2-yl)phenyl)thiophene (EOPT-Br) using the McCullough (**a**)[7b,c] and a CuO-modified Stille cross-coupling (**b**)[10] methods (Scheme 1).[11] Regiorandom poly-**1** was also prepared for comparison from the 2,5-dibromo derivative using a Ni-catalyzed homocoupling method (**c**). EOPT-Br was obtained by the selective bromination of (*R*)-3-(4-(4-ethyl-2-oxazolin-2-yl)phenyl)thiophene (EOPT) at the 2-position using *N*-bromosuccinimide (NBS) in dimethylformamide (DMF). The enantiomeric excess of EOPT was determined to be nearly 100% using the chiral NMR shift reagent $Eu(tfc)_3$ which can completely discriminate the enantiomers in $CDCl_3$. Experimental details for the synthesis of the thiophene monomers including intermediates, polymerization, and spectroscopic data of the monomers and polymers are described in the Supporting Information.

Scheme 1



b. Measurements. ^1H NMR spectra were measured on a Varian VXR-500S spectrometer operating at 500 MHz using TMS as the internal standard. IR spectra were recorded using a Jasco Fourier transform IR-7000 spectrophotometer with a Jasco PTL-396 data processor. Absorption spectra were taken on a Jasco Ubest-55 spectrophotometer. CD spectra were measured in a 0.01 or 0.10 cm quartz cell unless otherwise noted using a Jasco J-720 L spectropolarimeter. The concentration of poly-**1** was calculated based on monomer units. Static light scattering experiments were performed on a DLS-700 (Otsuka Electronics Co.) equipped with a 5 mW He−Ne laser (632.8 nm) at 25 °C.

Results and Discussion. The chiroptical properties of optically active PTs were investigated with UV−vis and CD spectroscopies. As well as previously reported chiral, regioregular PTs, poly-**1a** also showed no ICD in the $\pi-\pi^*$ transition region ($\lambda_{max} = 448$ nm) over a temperature range (−40−25 °C) in a good solvent, chloroform, while the polymer exhibited an intense ICD at longer wavelengths (400−700 nm) upon the addition of a nonsolvent like methanol (55−65%, v/v) to the chloroform solution, and the solution spontaneously

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† Department of Molecular Design and Engineering.

‡ Department of Applied Chemistry.

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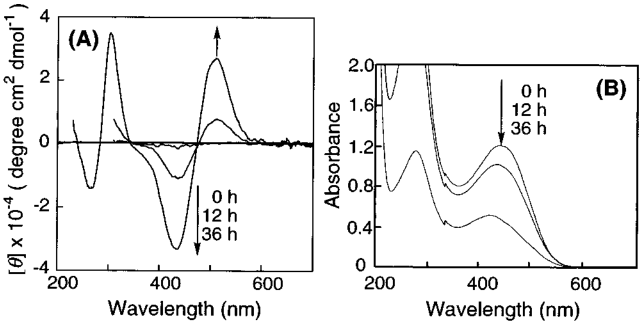

Figure 1. CD (A) and absorption (B) spectral changes of poly-**1a** in the presence of Cu(OTf)$_2$ in chloroform. The CD spectra were measured in chloroform solution in a 0.01 cm quartz cell at ambient temperature (20–22 °C) with an initial poly-**1a** concentration of 5.0 mg (20 μmol monomer units)/mL and [poly-**1a**]/[Cu(II)] = 1.0. We also measured CD and absorption spectra of the complex in dilute solution (0.05 mg/mL of poly-**1a**) in a 0.50 cm quartz cell and found no significant changes in the spectra.

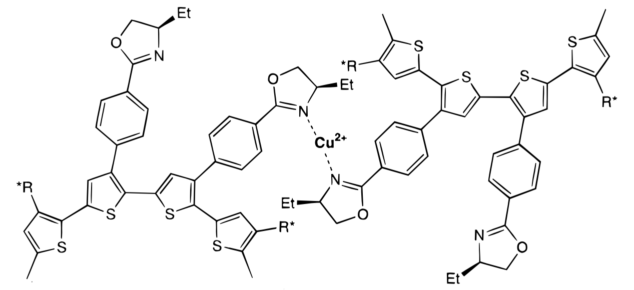

Figure 2. A possible chiral structure of the poly-**1a**–Cu(II) complex.

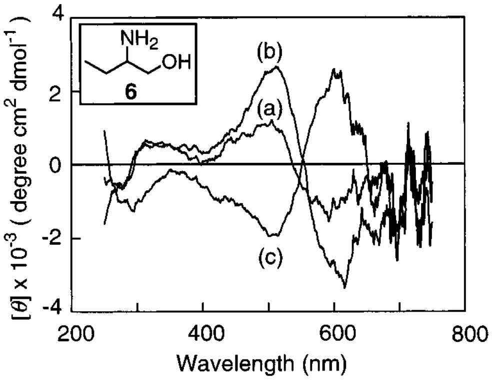

Figure 3. CD spectra of poly-**3** in DMSO (a) and in a mixture of DMSO and (*R*)- (b) and (*S*)-**6** (c); the volume ratio of **6** to DMSO is 1:1 (v/v). The CD spectra were measured in a 0.01 cm quartz cell at ambient temperature (20–22 °C) with a poly-**3** concentration of 2.5 mg (11 μmol monomer units)/mL.

changed from yellow-orange to purple. These significant changes in the ICDs were accompanied by a gradual red shift in the absorption up to 200 nm with a series of vibronic transitions at λ_{max} = 558, 590, and 650 nm and a clear isosbestic point at 492 nm (see Supporting Information). A similar solvatochromism has been reported for other regioregular chiral PTs and is considered due to a transition from a disordered, coillike form to a rodlike, π-stacked one in order to give a chiral supramolecular aggregate with interchain interactions of transoidal PTs.[8e,g,h,k] A variety of other poor solvents such as ethanol, *n*-butanol, and (*R*)- and (*S*)-2-butanol also gave rise to a chirality induction to poly-**1a**, thus showing similar ICDs. On the other hand, poly-**1c** showed almost no ICD even in the presence of 70% methanol, accompanied by only minor changes in the UV–vis spectra.

In the course of our studies, we have, incidentally, found that poly-**1b** prepared with the CuO-modified Stille method exhibited an ICD in the UV–vis region in chloroform. We anticipated that a small amount of Cu(II) ion coordinating to an oxazoline residue of the side chain induced a helix formation on the main chain of poly-**1b** even in the good solvent, since the ICD signals disappeared after removal of the Cu(II) by extraction with aqueous EDTA. To gain further evidence, poly-**1a** prepared by the McCullough method was allowed to complex with Cu(OTf)$_2$. Equimolar Cu(OTf)$_2$ was suspended in the homogeneous chloroform solution of poly-**1a**, and the changes in the UV–vis and CD spectra of the supernatant were followed at appropriate time intervals (Figure 1). Although Cu(OTf)$_2$ is scarcely soluble in chloroform, the poly-**1a** solution exhibited a split-type ICD in the π–π* transition region, and the intensity gradually increased with time.

The appearance of the ICD accompanied negligible changes in the UV–vis spectra (no color change), indicating that chirality induction may not be derived from π-stacked chiral aggregations of poly-**1a** as seen in poor solvents, but from the main-chain chirality such as a predominantly one-handed helical structure induced by Cu(II) ions.[13] Moreover, the supernatant was a nonviscous liquid, and no gel formation was observed. However, red particles precipitated during the complexation, and therefore, the UV–vis intensity gradually decreased, while the ICD intensity increased and showed a constant value after 36 h. The red particles were soluble in acetone, which is a nonsolvent for poly-**1a**, and the solution showed almost the same UV–vis and CD spectra as the poly-**1a**-Cu(OTf)$_2$ complex in chloroform. Preliminary static light scattering (SLS) analysis of the poly-**1a**–Cu(OTf)$_2$ complex in chloroform ([Cu]/[poly-**1a**] = 0.5) revealed that the complex has the radius of gyration (R_g) of ca.80 nm, while the original poly-**1a** did not show scattering from polymer molecules since the molecular weight of the polymer is low, and hence R_g is too low to be detected by SLS measurements. Figure 2 shows a possible structure of the aggregated complexes. Intermolecular coordination of the oxazoline groups to Cu(II) ion may lead to the formation of stable colloidal particles where poly-**1a** may form a one-handed helical, cisoidal conformation to exhibit an ICD. Further structural analyses of poly-**1a**–metal complexes should be necessary, for instance, NMR measurements of a poly-**1a** complex with diamagnetic Cu(I) ion together with detailed static and dynamic light scattering measurements of the metal complexes.

Similar, but relatively weak, ICDs also appeared for the complexes with Cu(I) and Fe(III) ions in chloroform (see Supporting Information). The regiorandom poly-**1c**–Cu(II) complex showed almost no ICD in chloroform.

The present polymers have a great advantage such that they have chiral oxazoline residues that can be easily converted to the corresponding chiral amino esters (poly-**2**) by acid hydrolysis and further to achiral carboxy groups (poly-**3** and poly-**4**) by the saponification of the amino esters (Scheme 1).[10,15] These derivatives are expected to be soluble in water.[16]

Poly-**2** derived from poly-**1a** was soluble in DMSO (λ_{max} = 448 nm), methanol (λ_{max} = 556, 590, and 650 (shoulder) nm), and water containing a small amount of DMSO (19/1, v/v; λ_{max} = 438 nm) and showed ICDs in these solvents (first Cotton ([θ]) = 6×10^3 (607 nm, methanol) and 1×10^3 (474 nm, H_2O/DMSO (19/1)). However, completely hydrolyzed poly-**4** was, unfortunately, not soluble in the common organic solvents, and therefore, we could not explore the possibility of whether the poly-**4** responds to chiral amines, thus showing a characteristic ICD through acid−base interactions as seen in the case of poly((4-carboxyphenyl)acetylene).[17] Partially hydrolyzed poly-**3** containing a chiral amino ester group (33 mol %) was soluble in DMSO and found to respond to the chirality of amines, thus exhibiting an ICD depending on the absolute configuration of amines in the $\pi-\pi^*$ transition region. Figure 3 shows the CD spectra of poly-**3** in the presence of optically active (*R*)- or (*S*)-2-amino-1-butanol (**6**). Poly-**3** is sensitive to the chirality of the amino alcohol and the enantiomers induced split-type ICDs of mirror images. Poly-**3** also responded to other chiral amines, for instance, 2-amino-1-propanol, and showed a characteristic ICD change depending on the chirality of the amines.

Although the first evidence of chiral recognition on chiral PTs was reported by Lemaire et al.,[8a] they investigated chiral recognition using an *achiral detector* (cyclic voltammogram) based on changes in the shapes of the voltammograms of regiorandom chiral PTs in the presence of chiral doping agents such as camphorsulfonic acid during the voltammetric cycles. The present study may be the first clear example of chiral recognition on a chiral PT detected by *chiral* CD spectroscopy. We hopefully expect that the metal complexes of poly-**1a** may be used as chiral, helical polymeric catalysts for asymmetric synthesis,[5] since some metal complexes with chiral bisoxazolines have been used as highly enantioselective catalysts.[18] This work is now in progress.

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Supporting Information Available: Experimental procedures, NMR spectra of polymers, UV−vis and CD spectral changes of poly-**1a** in chloroform−methanol mixtures, and UV−vis and CD spectra of the complexes of poly-**1a** with Cu(I) and Fe(III) ions. This material is available for free of charge via the Internet at http://pubs.acs.org.

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(11) The resulting polymers soluble in chloroform were purified and isolated as the methanol-insoluble fraction. The molecular weight (M_n) was estimated to be 5.3×10^3, 3.3×10^3, and 3.4×10^3 for poly-**1a**, poly-**1b**, and poly-**1c**, respectively, as determined by gel permeation chromatography (GPC) using chloroform as the eluent. Relatively low molecular weights of these polymers may be due to precipitation in solvents during polymerization. The ^{1}H NMR spectrum of poly-**1a** in $CDCl_3$ showed a sharp singlet centered at 6.84 ppm due to the thiophene ring proton at the 4-position, indicating that the polymer possesses a highly HT regioregular structure. On the contrary, the ^{1}H NMR spectrum of poly-**1b** prepared with the CuO-modified Stille method showed rather broad resonances due to contamination with a small amount of paramagnetic Cu(II) ion used as a cocatalyst during the polymerization. After removal of the Cu(II) ion by extraction with aqueous ethylenediaminetetraacetic acid (EDTA), the resonances became sharper. Standard titration experiments[12] using sodium diethyldithiocarbamate suggest that the poly-**1b** contains 0.2 equiv of Cu(II) ion to a monomer unit of poly-**1b**.

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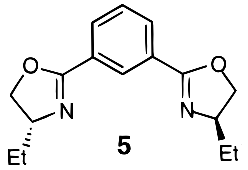
(13) There may be other possibilities to explain the appearance of the ICD of the poly-**1a**−Cu(II) complex; one is chiral induction through a metal-to-ligand charge transfer (MLCT) between the chiral oxazoline residues and Cu(II) ions.[14] However, this may be excluded since the complex of $Cu(OTf)_2$ with an optically active bisoxazoline (**5**), a model compound of the poly-**1a**, exhibited no ICD in chloroform and acetone in the 350−600 nm ranges. Moreover, the complex of poly-**1a** with a different metal ion such as Fe(III) also showed a similar ICD irrespective of the kinds of metal ions (see text). Another chirality induction possibility may be derived from the oxidation of the main chain, since $Cu(OTf)_2$ can work as a dopant. However, the doping

of HT-poly(3-hexylthiophene) with $Cu(OTf)_2$ caused a significant red shift of the $\pi-\pi^*$ transition of over 300 nm, and therefore, this possibility may also be excluded.



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