Transactions of the Materials Research Society of Japan 30[3] 743-746 (2005)

Chiral BEDOT-based Copolymers Prepared by Chemical and Electrochemical Polymerization

Y. S. Jeong[1], H. Goto[1], S. Iimura[2], T. Asano[2], and K. Akagi[1,*]
[1]Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), Institute of Material Science, University of Tsukuba, Ibaraki, 305-8573
Fax: 81-29-855-7440, e-mail: akagi@ims.tsukuba.ac.jp
[2]Ibaraki Prefectural Government Industrial Technology Institute, Ibaraki, 311-3195

Abstract

Optically active conjugated copolymers, *poly*[1,4-bis[2-(3,4-ethylenedioxy)thienyl]-2,5-benzoic acid-1-methylheptyl ester] [*poly*(BEDOT-B(OCT*)], were synthesized by chemical and electrochemical oxidative polymerizations. *Poly*[BEDOT-B(OCT*)] of both (*R*) and (*S*) configuration were synthesized by introducing chiral octyloxycarbonyl group in the side chain. The dibromo compounds, (*R*)-1 and (*S*)-1, were prepared by Mitsunobu reaction by an esterification of (*R*) or (*S*)-octanol and 2,5-dibromobenzoic acid with an aid of diethyl azodicarboxylate (DEAD) and triphenylphosphine (TPP) in tetrahydrofuran. The monomers were then prepared with Stille coupling technique using $Pd(PPh_3)_4Cl_2$ as a catalyst to produce (*R*)-1 and (*S*)-1. The monomer was electrochemical polymerized onto platinum button and ITO glass electrodes by repeated scanning from - 1.0 V to + 1.0 V versus Ag/Ag^+ at 20 mV/s. The polymer was electrochromic and reversibly switching from purple to green upon oxidation. The chemical polymerization was also carried out in dimethylformamide with a $Ni(cod)_2$ catalyst. Optical absorption and circular dichroism (CD) measurements were examined. The polymers showed Cotton effects in CD spectra. This method therefore represents a new technique for the preparation of chiral polymer with helicity, which can disclose a possibility toward "chiralelectrochemistry".

*Keywords:*PEDOT, circular dichroism, electrochromism, electrochemical polymerization

1. INTRODUCTION

Circulary dichroism (CD) is one of the most rewarding properties of aromatic conjugated polymers, as well as the linearly polarized dichloism. The CD of conjugated polymers originating from their chiral structure requires no macroscopic alignment of the polymers. Helical conjugated polymer can be obtained by polymerization of monomer under chiral nematic liquid crystal reaction field [1]. Introduction of chiral moiety into the side chain of the conjugated polymer is another approach to induce the helicity of the main chain. Many approaches to produce stable optically active polymers with chiral structures have been proposed, such as the introduction of an optically active substituent to the polymer side chain, and induction of chiroptical properties. It is important for the introduction of helicity to locate the chiral center of the side chain as close as to the conjugated backbone. In this study, *poly*(BEDOT-phenylene) of both (*R*) and (*S*) configuration were synthesized by introducing chiral octyloxy carbonyl group in the side chain [BEDOT: bis(3,4-ethylenedioxy)thiophene derivative]. Synthesis of conjugated polymer involves chemical and electrochemical polymerization [2]. Many chiral polymers were synthesized by chemical polymerization with metal catalyst such as nickel and palladium complexes to carry out polycondensation reaction [3]. We have developed new electrochemical polymerization method under chiral nematic liquid crystal (N*-LC) to produce poly(3,4-ethylene dioxythiophene) (PEDOT) and polypyrrole [4]. We confirmed macroscopic spiral structure of the polymers in optical microscope and scanning electron microscope [5]. Although there have been reports on production of chiral thiophene derivateves by electrochemical polymerization method in isotropic electrolyte such as water or acetonitrile, there has been no report of electrochemical polymerization of chiral PEDOT [6]. In this study we report the synthesis and characterization of chiral BEDOT-based copolymers, obtained by the chemical and electrochemical polymerization of (*R*), (*S*)-1,4-bis[2-(3,4-ethylenedioxy)thienyl]-2,5-benzoic acid octyl ester [BEDOT-B(OCT*)].

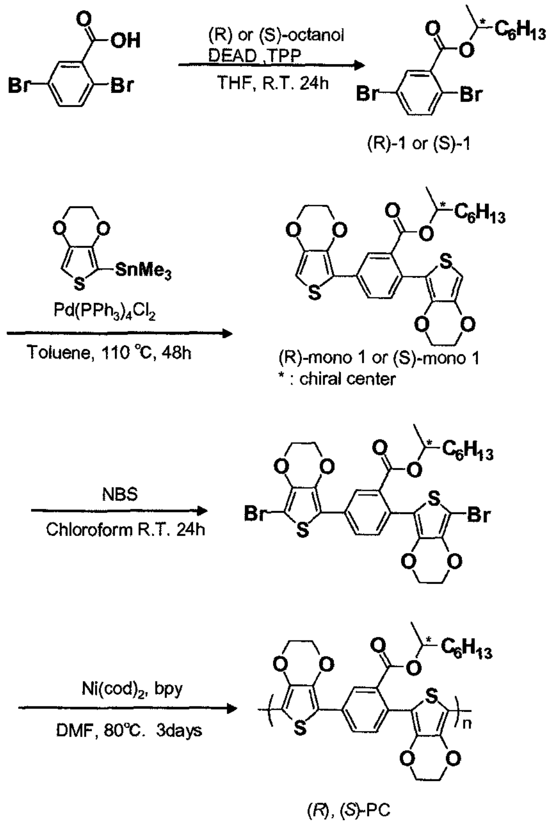
2. EXPERIMENTAL

2.1 Synthesis of 2,5-dibromo-benzoic acid 2-(S)-octyl ester

To a solution of triphenylphosphine (4.77 g, 18 mmol) and 2,5-dibromobenzoic acid (3.0 g, 18 mmol) in THF (40 mL), a mixture consisting of DEAD (8.0 g, 40 wt % in toluene, 18 mmol), and (*S*)-2-octanol (2.22 g, 15 mmol) in THF (45 mL) was very slowly added using a pressure equalized dropping funnel. The reaction mixture was stirred at room temperature overnight under an argon atmosphere. Thin layer chromatography (TLC) indicated completion of the reaction. The precipitate was filtered. The filtrate was evaporated to remove the solvent. The residue was purified by column chromatography (silica gel, hexane and ethyl acetate 2:1). The product was recrystallized from a mixture of *n*-hexane and dried under vacuum to give 4.0 g as colorless liquid.

2.2 Synthesis of [BEDOT-B(OCT)]*

The synthesis was carried out as outlined in Scheme 1, where Stille reaction was employed to accomplish coupling reaction between EDOT and 5-dibromo-benzoic acid 2-(S)-octyl ester to give [BEDOT-B(OCT*)] [4].



Scheme 1 Synthesis of poly[BEDOT-B(OCT*)]

A solution of (*S*)-1(1.52 g, 11.6 mmol) in dry toluene (25 ml) was added dropwise (30min) at 110 ℃ to 2-tributylstannyl-3,4-ethylenedioxythiophene (5 g, 11.6 mmol). A catalyst of $Pd(PPh_3)_4Cl_2$ was added. Compound was stirred at overnight under an argon atmosphere. After evaporation of the solvent, the residue was thoroughly washed with water and extracted with chloroform. The chloroform layer was dried over anhydrous $MgSO_4$ overnight. The solution was evaporated and purified by column chromatography with a mixure of hexane and ethyl acetate (2:1). After removing the solvent, the light green liquid was collected.

2.3 Chemical polymerization of poly(S)-[BEDOT-B(OCT)]*

(*S*)-[BEDOT-B(OCT*)] was brominated using N-bromosuccinimide to give (*S*)-dibromo[BEDOT -B(OCT*)]. The polymerization of the (*S*)-dibromo[BEDOT -B(OCT*)] was reacted with 1 equivalent of $Ni(cod)_2$ and 2,2-biphyridyl in dimethylformamide as shown Scheme 1. The crude product was poured into a large amount of methanol, collected by filtration, and dried in vacuum to give a dark green powder of *poly*(*S*)-[BEDOT-B(OCT*)].

2.4 Electrochemical polymerization of poly(S)-[BEDOT-B(OCT)]*

Electrochemical polymerizations were performed to prepare PEDOT derivative. Copolymers were prepared electrochemically from solutions containing 0.01 M of monomer and 0.1M tetrabutylammonium perchlorate (TBAP) in anhydrous acetonitrile for *poly*[(*R*) or (*S*)-BEDOT-B(OCT*)]. Both monomers were electro-oxidatively polymerized onto platinum disk and indium tin oxide (ITO)-coated glass by repeated scanning versus Ag/Ag$^+$ at 10 mV/s.

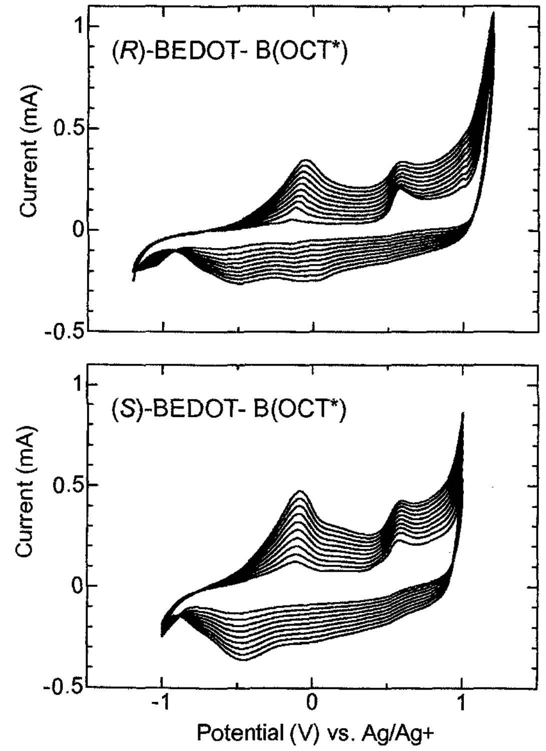


Fig. 1 Repeated potential scanning electro chemical polymerization of (*R*), (*S*) - BEDOT-B(OCT*) (0.01 M) carried out 0.1 M TBAP in acetonitrile at 10 mV/s.

3. RESULT AND DISCUSSION

3.1 Electrochemistry.

Both monomers were electro-oxidatively polymerized onto platinum disk by repeated scanning versus Ag/Ag$^+$ at 10 mV/s. Fig. 1 shows the first nine scans for a repeated potential scanning electrochemical polymerization of the monomers with chiral substituents of (*R*) or (*S*)-configuration. The repeat scanning graph for the electrochemical polymerization of (*R*) and (*S*)-BEDOT-B(OCT*) are similar. During the oxidative scanning for both monomer solutions, monomer oxidation peaks and $E_{p,m}$ are observed at −0.08 V and +0.59 V. On the reserve scanning, polymer reduction is seen. A growing polymer redox process can be seen with subsequent scans. All peaks exhibit an increased current response, indicating the formation of electroactive films. After the polymerization, polymer thin films were washed with an electrolyte solution, and acetonitrile. Their redox switching in monomer-free electrolyte solution showed a well-defined redox process. The films of *poly*[BEDOT-B(OCT*)]s were deposited on ITO-coated glass substrates using electrochemical deposition from a 0.01 M monomer solution of 0.1M TBAP in acetonitrile.

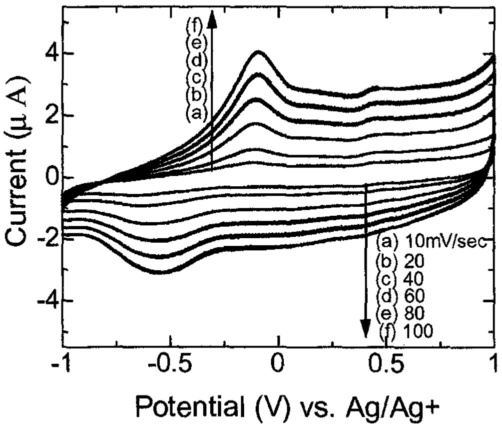


Fig. 2 Cyclic voltammetry of *poly*[(*S*)-BEDOT-B(OCT*)]

Fig. 2 shows the cyclic voltamogram of (*S*)-*poly*[BEDOT- B(OCT*)] film at scan rates of 10, 20, 30, 60, 80 and 100 mV/s in 0.1 M TBAP in acetonitrile. The polymer presents a relatively low half oxidation potential and very well defined and reversible redox process.

3.2 UV-vis and CD spectroscopy

Fig. 3 shows UV-Vis absorption spectra of *poly*[(*R*), (*S*)-BEDOT-B(OCT*)] in oxidized and reduced states. Upon oxidization, the π - π* transition of the reduced state at 536 nm decreased in intensity, and extended absorption to near-infrared region appeared. The films in oxidized and reduced states are purple and green, respectively. Fig. 4 presents CD spectra of the polymer thin films. The signs in Cotton effect of the monomer and corresponding polymer are identical in the short wavelength region. The reduced polymer films exhibit a mirror image of bisignate Cotton effect in longer wavelength region. This result suggests that the polymer main chain itself is chiral in the film state.

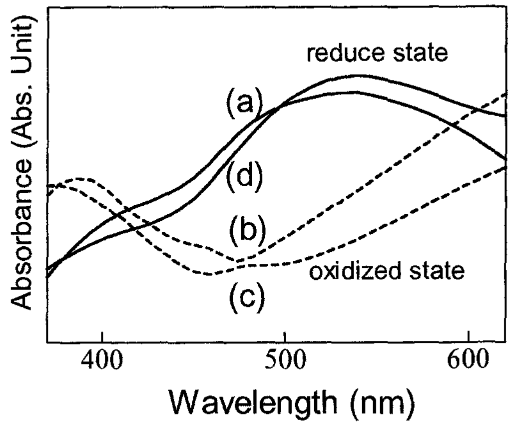


Fig. 3 UV-Vis absorption spectra of polymer on ITO glass (a), (b): *poly*[(*S*)-BEDOT-B(OCT*)], (c), (d): *poly*[(*R*)-BEDOT-B(OCT*)].

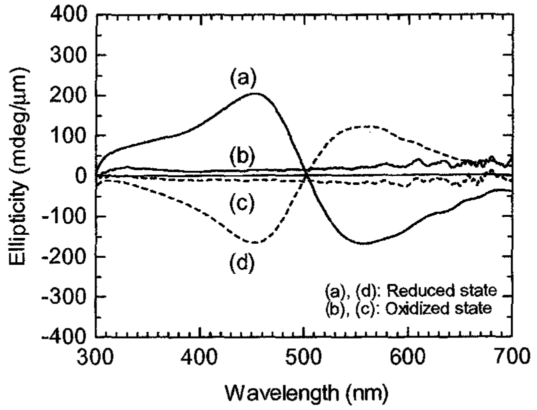
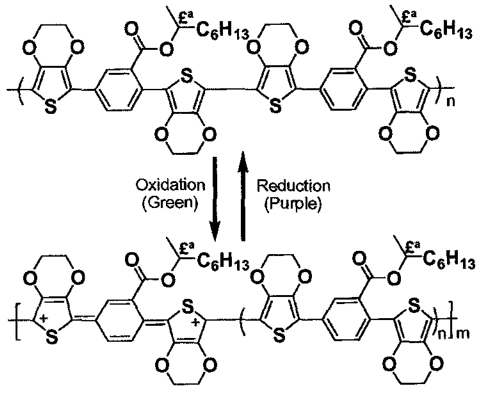


Fig. 4 CD spectra of polymer thin films. (a), (b): poly[(R)-BEDOT-B(OCT*)], (c), (d): *poly*[(*S*)-BEDOT-B(OCT*)].



Scheme 2 The change of molecular structure upon oxidation and reduction.

As shown in Scheme 2, the polymer in the oxidation state forms a quinoid structure, where the planarity of the main chain increases to give rise to a decrease or disappearance of chirality. The polymer in the reduction state, on the other hand, forms a benzonoid structure of less planarity, compared with that of the quinoid one. Thus, the polymer chirality induced by the chiral substituent in restored. This sort of structural change should give negligibly small and sufficiently large Cotton effects in CD spectra for the oxidized and reduced polymers, respectively. The redox process allows a reversible change in CD intensity.

4. CONCLUSIONS

The electrochemical polymerization of chiral monomer affords the chiral polymer film through the oxidative polymerization. The optical activity of the deposited film on ITO can be tuned by electrochemical method according to the change of electronic state of the polymer. This method may give an advantage for preparation of electrochromic device with durability, since the chiral polymer generally shows good film-forming property. This method therefore represents a new technique for the preparation of chiral polymer with helicity, and proposes a new field of "chiralelectro chemistry".

ACKNOWLEDGMENT

The present study was supported by Grant-in-Aid for Scientific Research from Ministry of Education, Culture and Science of Japan.

REFERENCES

[1] K. Akagi, G. Piao, S. Kaneko, K. Sakamaki, H. Shirakawa and M. Kyotani *Science,* 282 (1998) 1683.

[2] I. Dierking, *Adv. Mater.* 3 (2000) 12.

[3] J. A. Irvin, I. Schwendeman, Y. Lee, K. Abboud, J. R. Reynolds, *J. Polym. Sci., Part A: Polym. Chem.,* 2001, 39, 2164; B.C. Thompson, P. Schottland, K. Zong, J. R. Reynolds, *Chem. Mater.* 12 (2000) 1563.

[4] H. Goto, K. Akagi *Macromol. Rapid Commun.,* 16 (2004) 1437.

[5] S.K. Deb, Appl. Opt. Suppl. 3 (1969) 192.

[6] D. Iarossi, A. Mucci, F. Prenti, L. Schenetti, R. Seeber, C. Zanardi, A. Formi and M. Tonelli *Chem. Eur. J.* 3 (2001) 676.

(Received December 23, 2004; Accepted June 15, 2005)