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ORIGINAL PAPER

Electrochemical preparation of an electroactive polymer poly(dodecyloxy dibenzothiophene) (polyDDBTh) from hydroxyl dibenzothiophene (HDBTh) as a bioconverted monomer

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Abstract A combination of biotechnological and electrochemical techniques is employed to synthesize an electroactive π-conjugated polymer. The monomer precursor bearing a hydroxyl group is obtained by the bioconversion of dibenzothiophene. An alkyl chain substituent is introduced by Williamson etherification with the aid of crown ether, and electrochemical polymerization is carried out by repeated potential scanning of the monomer in an electrolytic reaction solution. The polymer film thus prepared is shown to exhibit good electroactive characteristics.

Keywords Bioconversion · Electroactive polymer · Electrolytic polymerization · Petroleum pitch · π-conjugated polymer

1 Introduction

The use of micro-organisms to produce materials has contributed to progress in the pharmaceutical, chemistry, and food industries, and has recently been demonstrated to be potentially applicable to the fabrication of electrically conducting polymers for plastic electronics. Through a combination of genetic manipulation and polymer synthesis, the organism *Pseudomonas putida* has been shown to metabolize benzene to catechol via 5,6-dihydroxycyclohexl-1,3-diene. The desired catechol is afforded as an extracellular product that can be isolated by solvent extraction and then converted to a monomer [1].

Conjugated polymers, such as polypyrrole (PPy), polythiophene, polyaniline, and poly(3,4-ethylenedioxythiophene) (PEDOT), have been studied for application in electrochromic devices, transparent electrodes, electroluminescent devices, and sensors [2–5].

In the present study, a monomer synthesized using a biological route is polymerized by electrochemical polymerization to afford a conjugated polymer as an insoluble and infusible freestanding film. The hydroxyl dibenzothiophene (HDBTh) is synthesized by a biological reaction with a microorganism (*Sphingomonas strain* TN399) from DBTh [6], and a flexible alkyl side-chain is introduced into the compound to improve the monomer solubility, and the monomer is polymerized in an electrolyte to afford an electroactive polymer.

In the present method, the biological reaction and the chemical reaction followed by the electrochemical reaction yield an electroactive polymer. Specifically, DBTh can be extracted from waste oils (petroleum pitch). Therefore, some variation of this synthetic route for preparation of a conducting polymer may be a new candidate for green chemical reaction system.

2 Experimental

2.1 Preparation of hydroxy dibenzothiophene

DBTh was converted to hydroxy dibenzothiophene by bioconversion [6]. Mass spectroscopy (Fig. 1, top) and ^{1}H

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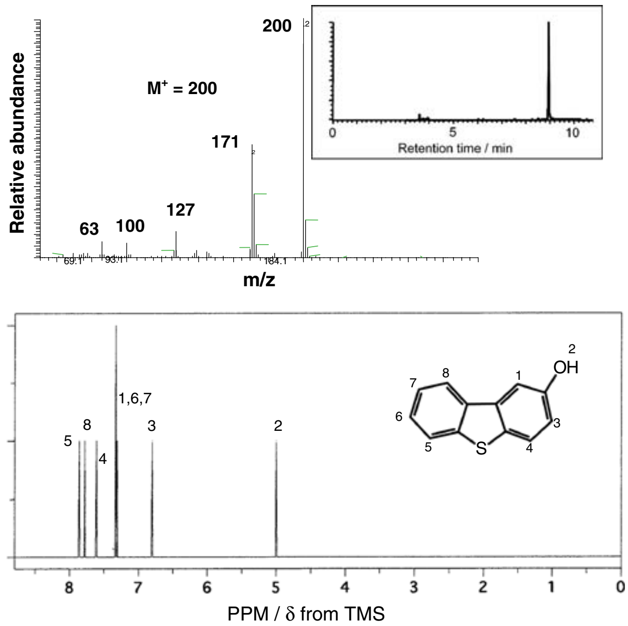
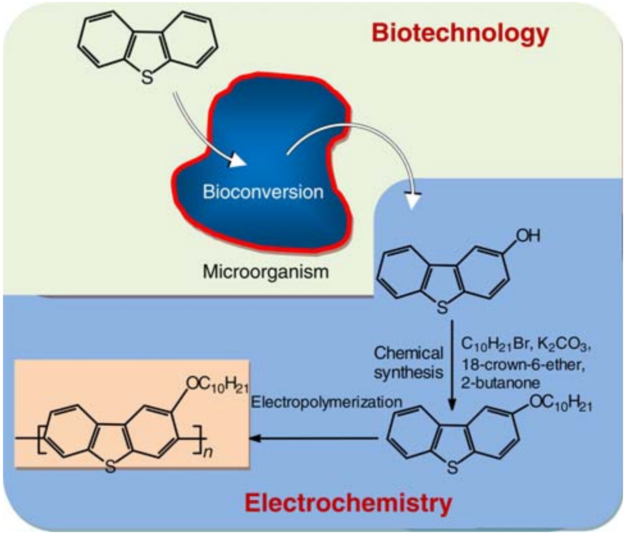


Fig. 1 *Top* Mass spectrum of the precursor of the monomer (HDBTh). *Inset* shows HPLC result of the precursor. *Lower* ^{1}H NMR of the precursor prepared using a biotechnology-base method



Scheme 1 Synthesis of electroactive polymer with a combination of biotechnology and electrochemical methods

NMR (Fig. 1, bottom) confirm the molecular structure of the polymer. The purity of the compound was checked by high-pressure liquid chromatography (HPLC) (Fig. 1, top (*inset*)).

2.2 Monomer synthesis

A monomer of hydroxy dibenzothiophene bearing a decyl group substituent was prepared by Williamson etherification with the aid of crown ether (Scheme 1). The monohydroxyl compound (hydroxyl benzothiophene, 50 mg, 0.025 mmol) was then dissolved with bromodecane (55.25 mg, 0.025 mmol) and K_2CO_3 (34.55 mg, 0.025 mmol) in 2-butanone (2 mL) in a three-necked round-bottom flask, to which a catalytic amount of 18-crown-6-ether (9 mg, 0.003 mmol) was subsequently added. The solution was then stirred and refluxed under argon at 75 °C. After 36 h, the solvent was removed by evaporation, and the mixture was washed thoroughly with water and then extracted with ether. The organic layer was collected using a separation funnel and dried with $MgSO_4$ overnight. Filtration to remove the $MgSO_4$ followed by evaporation yielded the crude product, which was finally purified by silica gel chromatography (eluent, hexane/dichloromethane = 1/1). The compound thus obtained was dried under vacuum to afford the product in 67% yield (DDBTh, pale yellow powder). The chemical structure of the compound was confirmed by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) analysis (Figs. 2 and 3). ^{1}H NMR ($CDCl_3$, δ from TMS, ppm, 500 MHz): 0.88 (t, 3H, $-CH_3$, $J = 6.9$ Hz), 1.25–1.55 (m, 18H, $-CH_2-$), 1.85 (quint, 2H, $-O-CH_2C\underline{H_2}CH_2-$, $J = 7.4$ Hz), 4.09 (t, 2H, $-OCH_2-$, $J = 6.57$ Hz), 7.10 (dd, 1H, ph–H, $J = 8.70$ Hz), 7.43 (m, 2H, ph–H × 2), 7.62 (d, 1H, ph–H, $J = 2.46$), 7.71 (d, 1H, ph–H, $J = 8.70$ Hz), 7.27 (m, ph–H), 8.10 (m, ph–H). ^{13}C NMR ($CDCl_3$, δ from TMS, ppm, 125 MHz): 14.13, 22.70, 26.12, 29.34, 29.37, 29.45, 29.59, 29.62, 31.92, 68.60, 105.86, 116.26, 121.54, 122.10, 123.37, 124.10, 126.62, 131.12, 135.52, 136.60, 140.57, 157.19.

2.3 Electropolymerization procedure

Electropolymerization of the monomer was performed by the established method for the preparation of conducting polymers. The polymer (poly(decyloxy dibenzothiophene)) (polyDDBTh) was prepared electrochemically from solutions containing 0.01 M of the monomer and 0.1 M of tetrabutylammonium perchlorate (TBAP) in anhydrous acetonitrile. The monomer was polymerized by electro-oxidation onto a platinum disc by repeated scanning with respect to an Ag/Ag$^+$ reference electrode at 50 mV s^{-1}. Figure 4 shows the repeated potential scans during electropolymerization of the monomers with the decyloxy substituent. In the oxidative scan, a wide peak and trough in current appear at −0.03 V and 0.11 V (0.112–0.115 V), while on the reduction scan, a peak occurs at −0.11 to −0.13 V. The main anodic peak often accompanied by a current shoulder. Although, clear signals due to monomer oxidation are not observed in this potential range, all of the

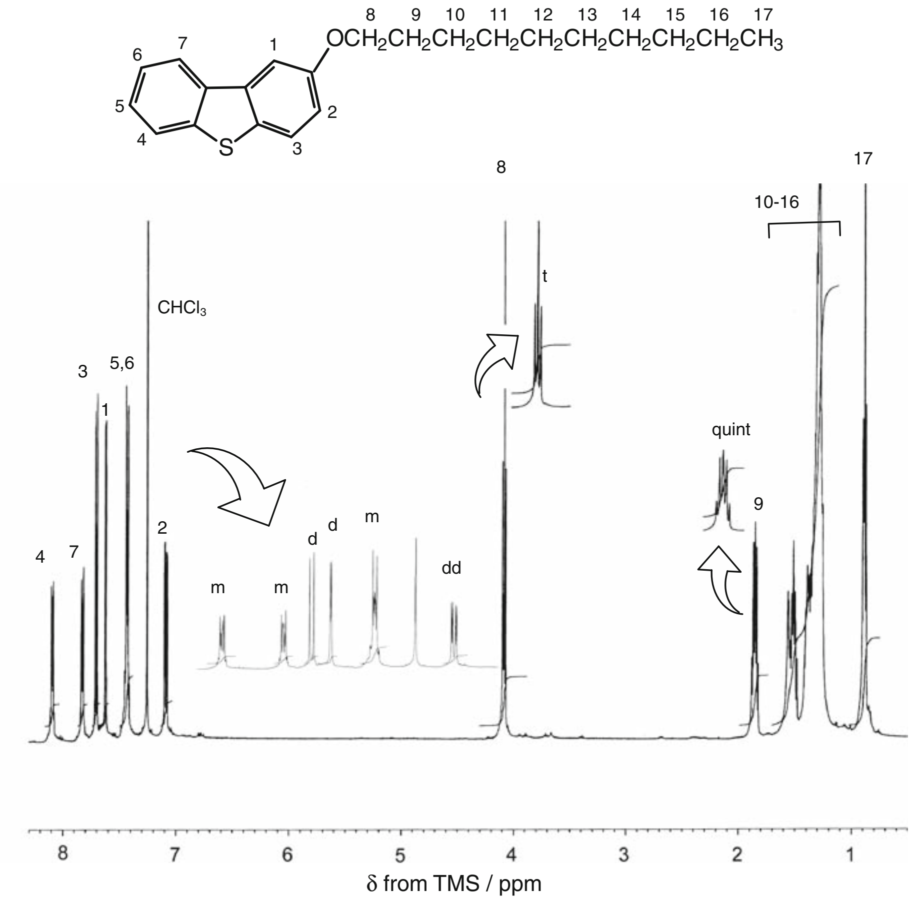


Fig. 2 ^{1}H NMR of the monomer (DDBTh)

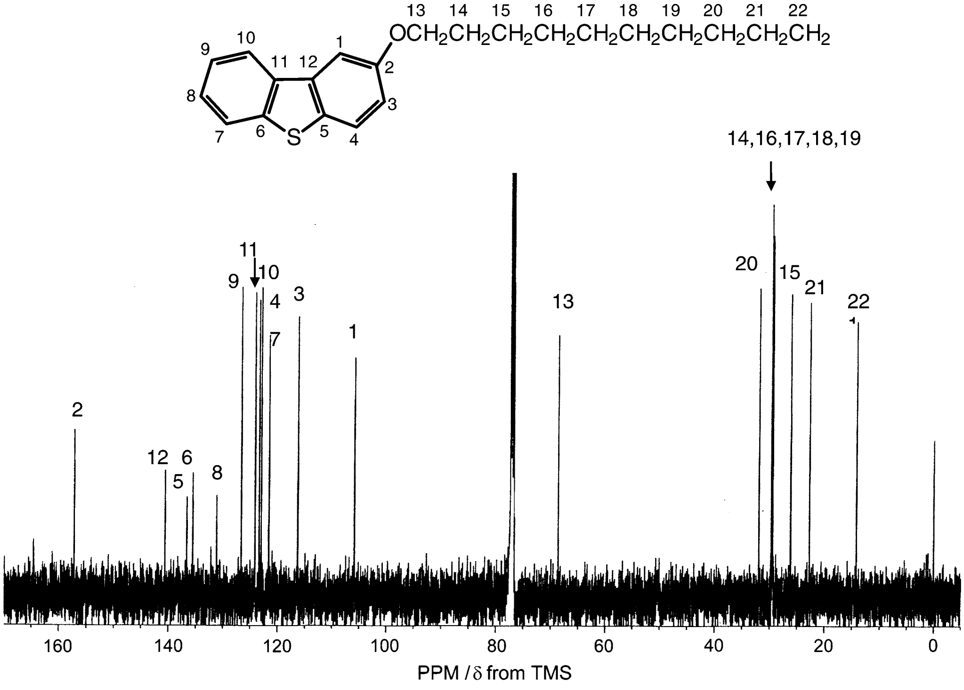


Fig. 3 ^{13}C NMR of the monomer (DDBTh)

peaks strengthened with the number of scans, indicative of the progressive formation of an electroactive film. The more positive voltammetric reduction signal should have increase in intensity with potential cycling time. After polymerization, the polymer films were washed with electrolyte solution and acetonitrile.

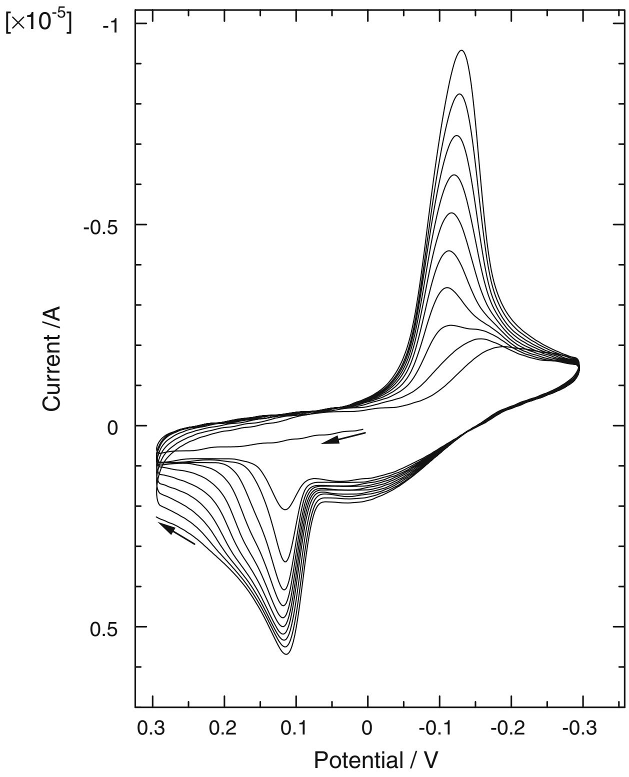


Fig. 4 Electropolymerization of decyloxydibenzothiophene (DDB Th) (0.01 M) in 0.1 M TBAP/acetonitrile solution

2.4 IR

IR spectra of the monomer and the polymer thin film prepared on indium-tin-oxide (ITO) coated glass were obtained with the KBr (pellet) method and the Attenuated Total Reflection Transfer (ATR) method (Fig. 5). Although absorption intensity is weak, C–H stretching vibrations due to methylene group of the substituent of the polymer are observed at the same wavenumbers as in the absorption band of the monomer. An absorption band assigned to $v_{\mathrm{C=C}}$ of benzene ring (quinoid) of the monomer appears at 1608 cm^{-1}, while the polymer shows this band at 1645 cm^{-1}. The monomer and the polymer show benzenoid $v_{\mathrm{C=C}}$ at 1550 and 1542 cm^{-1}, respectively. The polymer exhibits a weak absorption band at 1470 cm^{-1}. The polymer shows no absorption bands related to CH out-of-plane on the benzene ring. This may be due to the fact that the polymerization occurred at several polymerization sites on the DDBTh, resulting in cross-linking. The IR results confirm that the monomer was polymerized by electropolymerization.

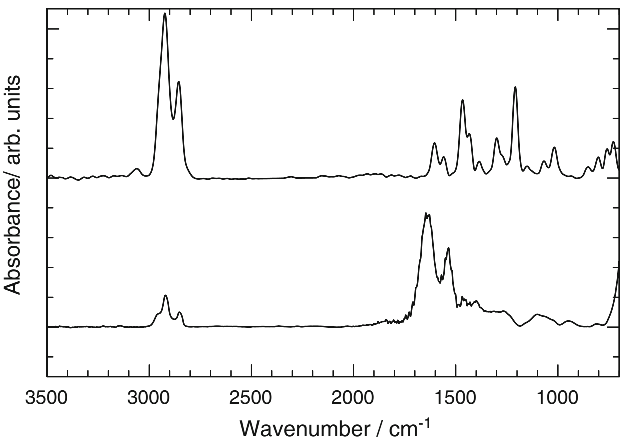


Fig. 5 IR absorption spectra of monomer (DDBTh) (*upper*) and polymer (polyDDBTh) (*lower*)

2.5 Characterization

Cyclic voltammetry measurements of the polyDDBTh film were performed over a range of scan rates (10, 20, 40, 60, 80, and 100 mV s^{-1}) in a 0.1 M TBAP/acetonitrile solution (Fig. 6). The positions of the oxidation wide peak (−0.04 V) and trough (0.08–0.09 V) and reduction peak (−0.11 V to −0.13 V) are consistent with those observed in the polymerization process. The redox switching of the films in the electrolyte solution defines a quasi-reversible redox process with relatively low oxidation potential, indicating that the polymer acts as a good electroactive material. Also, the current response is proportional to the scan rate. This suggests that the electron transfer is easily accessed and rapid with relatively high scans rate and good adhesion of the polymer onto the electrode [7–9].

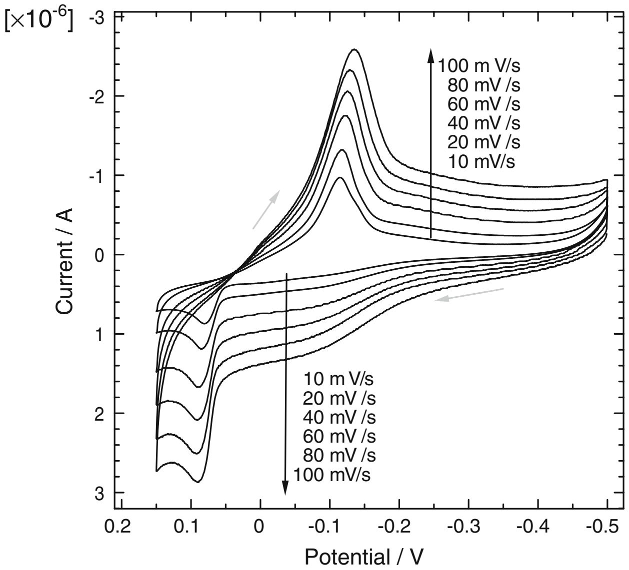


Fig. 6 Cyclic voltammograms of polymer (polyDDBTh) at several scan rates in 0.1 M TBAP/acetonitrile solution

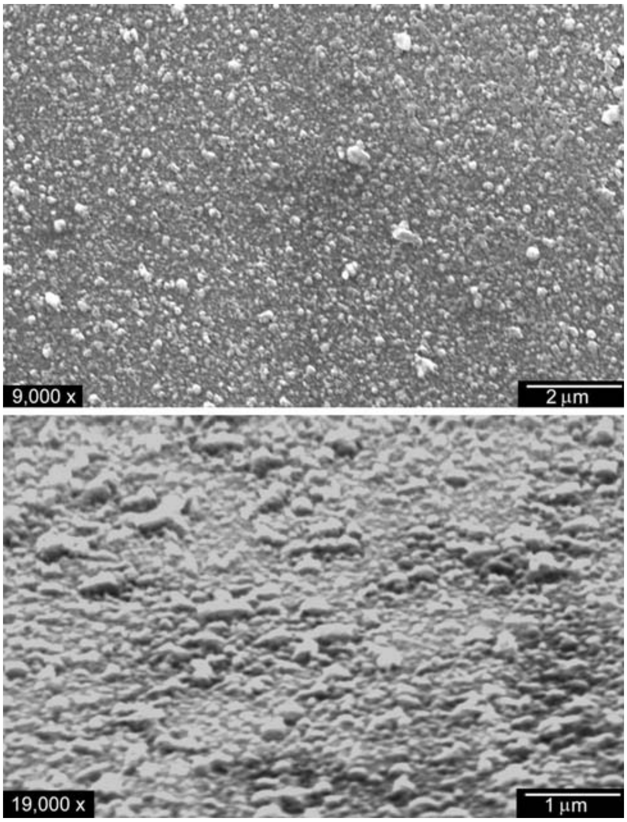


Fig. 7 Scanning electron microscopic (SEM) images of polymer (polyDDBTh) surface. *Top* A surface image from the normal direction. *Lower* The image taken 30° from the surface

2.6 Surface structure

Surface structure of the polymer prepared on ITO glass electrodes was observed with a scanning optical microscopy (SEM) (Fig. 7). The polymer shows pebble-like structure. Observation from oblique direction reveals that polymer pebbles grow from the substrate surface via an epitaxial electropolymerization process. Although pebbles of the present polymer are arranged randomly, surface-order control of the polymer may be achieved by a using liquid crystal field [10].

3 Conclusion

The monomer was prepared by bioconversion and then polymerized by an electrochemical reaction to afford the polymer film. This procedure demonstrates that electroactive polymers can be prepared by a combination of electrochemical and biotechnological techniques. The polymer films thus produced are suitable for application in plastic electronics, such as plastic electrodes in capacitors.

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