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Electrochemical preparation of an electroactive polymer poly(decyloxy dibenzothiophene) (PDBTh) 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 electro-active 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 electro-active 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 [1]. Through a combination of genetic manipulation and polymer synthesis, the organism *Pseudomonas putida* has been shown to metabolize benzene to catechol via 5,6-dihydroxycyclohex1,3-diene. The desired catechol is afforded as an extracellular product that can be isolated by solvent extraction and then converted to a monomer.

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 [2-4].

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 [5]. The hydroxyl dibenzothiophene (HDBTh) is synthesized by a biological reaction with TN399 from DBTh, and a flexible alkyl side-chain is introduced into the compound to improve the monomer solubility due to the flexible side-chain itself plays a role of solvent, 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) [6]. Therefore, a set 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

DBT was converted to hydroxy dibenzothiophene by bioconversion [6-8]. Mass spectroscopy (Fig. 1, top) and ^{1}H NMR (Fig. 1, bottom) confirm the molecular structure of the polymer. The purity of the compound was confirmed by high-pressure chromatography (Fig.1, top (inset)).

Fig. 1

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, decyloxy dibenzothiophene, thus obtained was dried under vacuum to afford the product in 67% yield (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 x 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.

Scheme 1

Fig. 2

Fig. 3

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)) (PDDBTh) 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 electrochemical polymerization 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, monomer oxidation), while on the reduction scan, a peak occurs at –0.11 to –0.13 V. The main anodic peak may be accompanied by a current shoulder. All of the peaks strengthened with the number of scans, indicative of the progressive formation of an electroactive film. The more positive voltammetric reduction signal would increase in intensity with potential cycling time. After polymerization, the polymer films were washed with electrolyte solution and acetonitrile.

Fig. 4.

2.4 IR

IR of the monomer and the polymer thin film on ITO were obtained with KBr (pellet) and Attenuated Total Reflection Transfer Infrared (ATR) method, respectively (Fig. 5). Although absorption intensity is weak, vibrations due to methylene group of the polymer is observed at the same wavelengths as absorption band of the monomer. An absorption band assigned to ν_{CH} (quinoid) of the monomer appear at cm^{-1}, while polymer shows this band at cm^{-1}. The monomer and the polymer show benzenoid ν_{CH} at cm^{-1} and cm^{-1}, respectively. The polymer exhibits weak absorption band at cm^{-1}. The IR results suggest that the monomer was polymerized by electropolymerization.

Fig. 5

2.5 Characterization

Cyclic voltammetry measurements of the PDDBTh film were performed over a range of scan rates (10, 20, 40, 60, 80, and 100 mV s^{-1}) in 0.1 M TBAP/acetonitrile solution (Fig.6). The polymer presents well defined and reversible redox process. 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. 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 [9] and well adhesion of the polymer onto the electrode [10,11].

Fig. 6.

2.5 Surface structure

Surface structure of the polymer was observed with SEM (Fig. 7). The polymer shows pebblelike structure. Observation from oblique direction reveals that polymer pebbles grows from the electrode surface via epitaxial electropolymerization process. The disordered film may be due to a less controlled polymerization reaction, resulting lower conductivity in the film obtained with four-point-probe method (< 10^{-2} S/cm). The use of planer dopant can improve the conductivity for the polymer. Furthermore, surface order control of the polymer can be achieved by using liquid crystal field [12].

3 Conclusion

The monomer was prepared by bioconversion and then polymerized by an electrochemical reaction to afford an electro-active 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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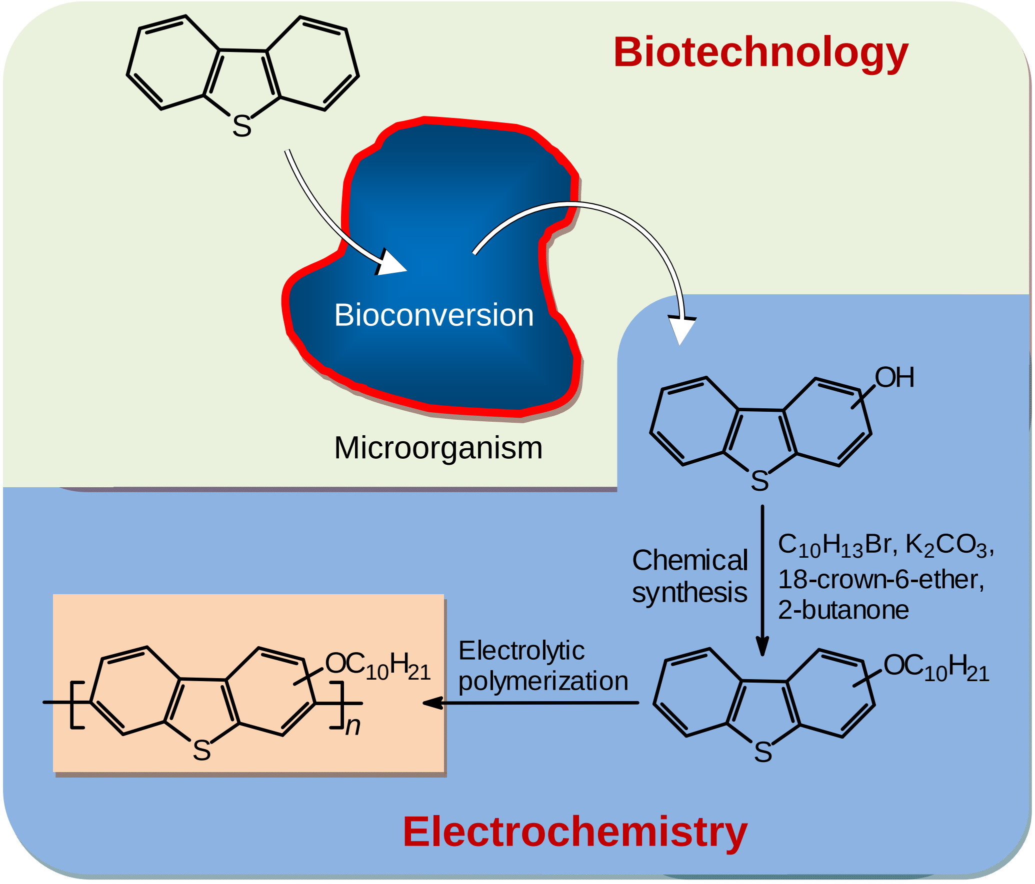

Scheme 1: Synthesis of electroactive polymer with a combination of biotechnology and electrochemical method.

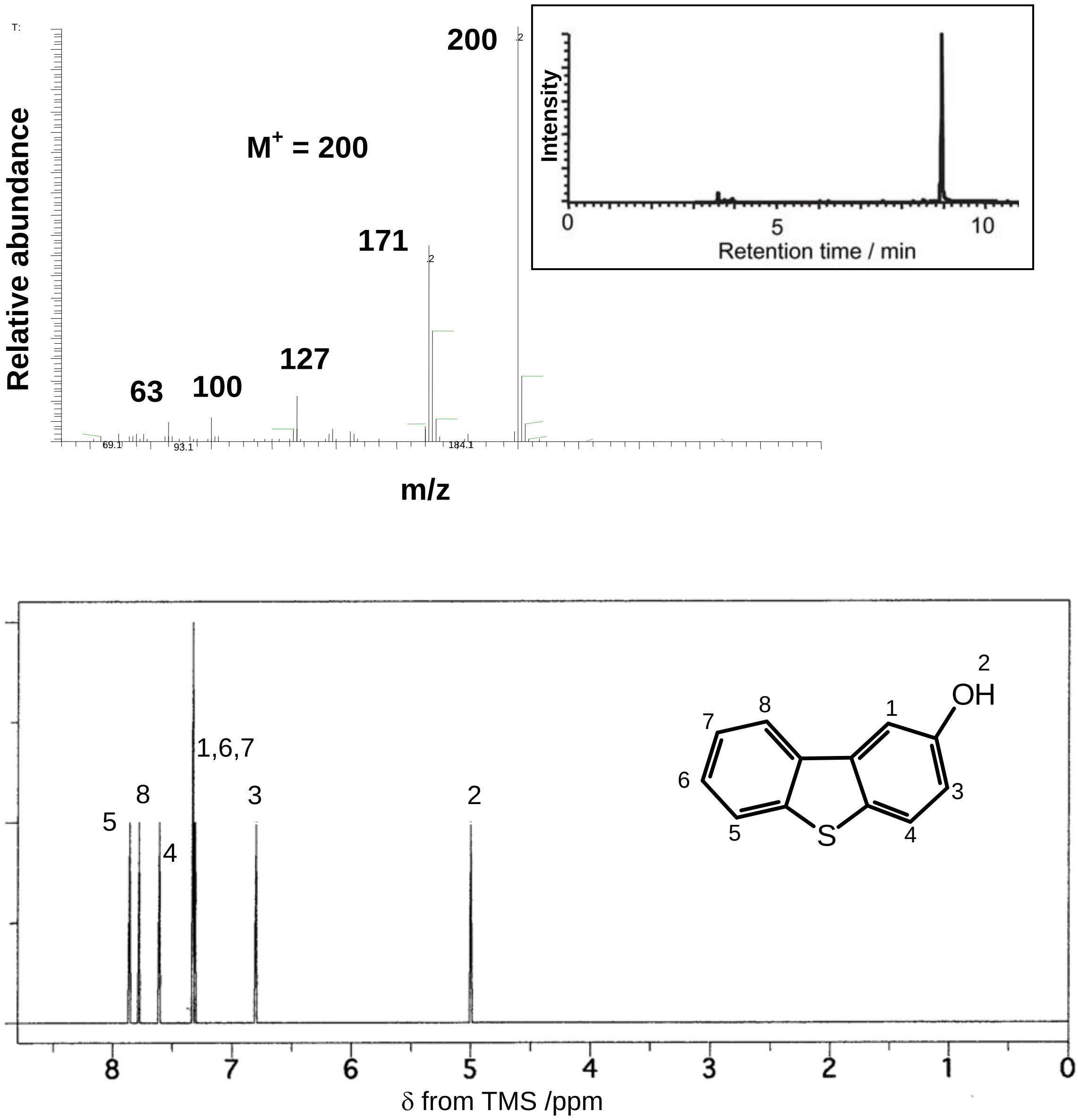

Fig. 1: (Top) Mass spectrum of precursor of the monomer (DBT). Inset shows HPLC result of the precursor. (Lower) ^{1}H NMR result of the precursor prepared with biotechnology.

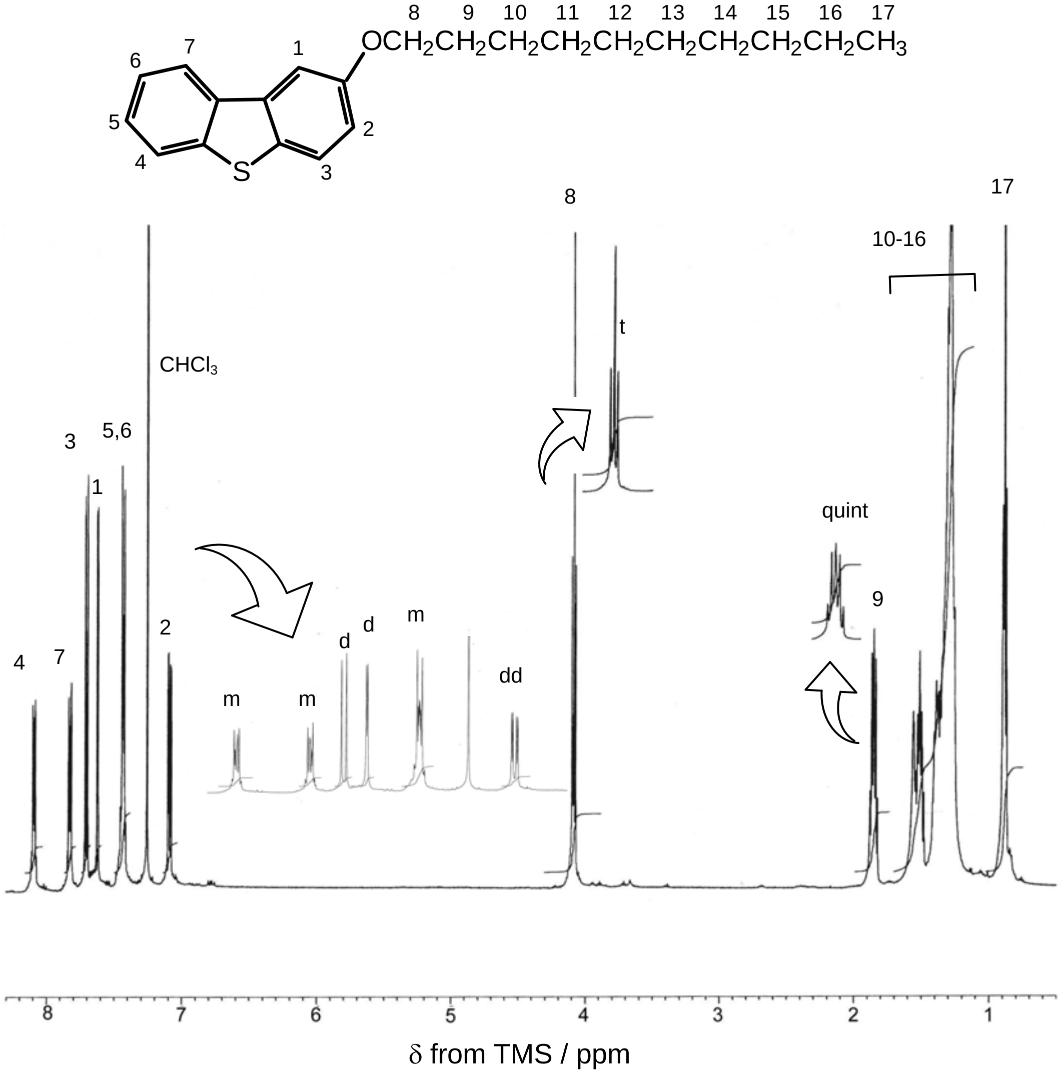

Fig. 2: ^{1}H NMR result of the monomer

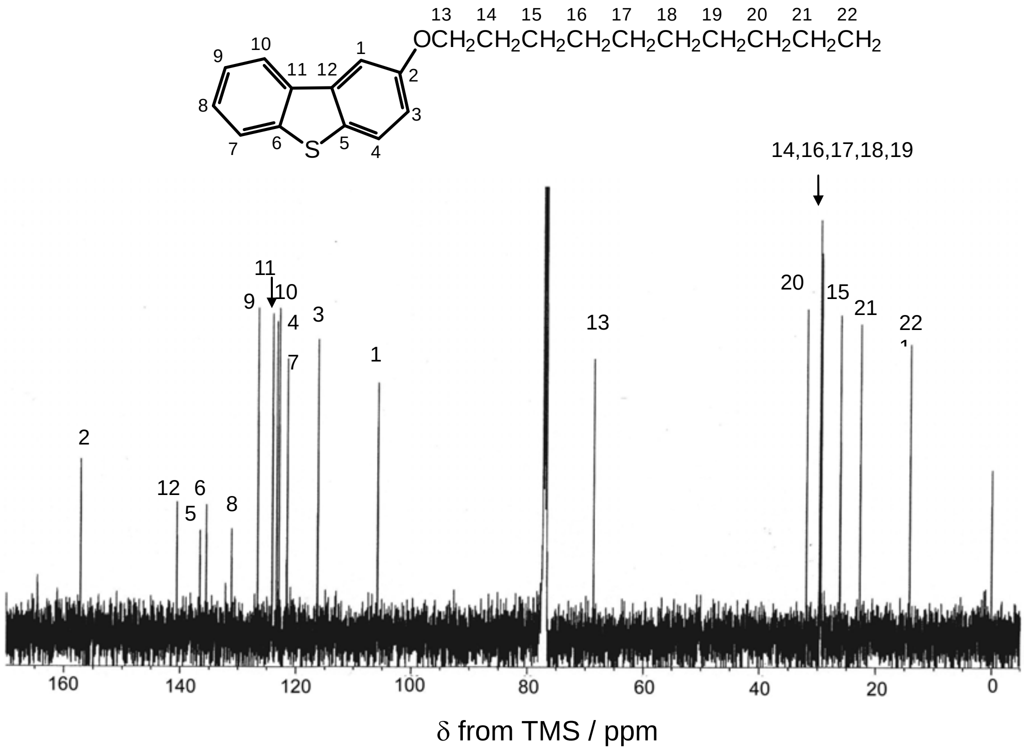

Fig. 3: ^{13}C NMR result of the monomer

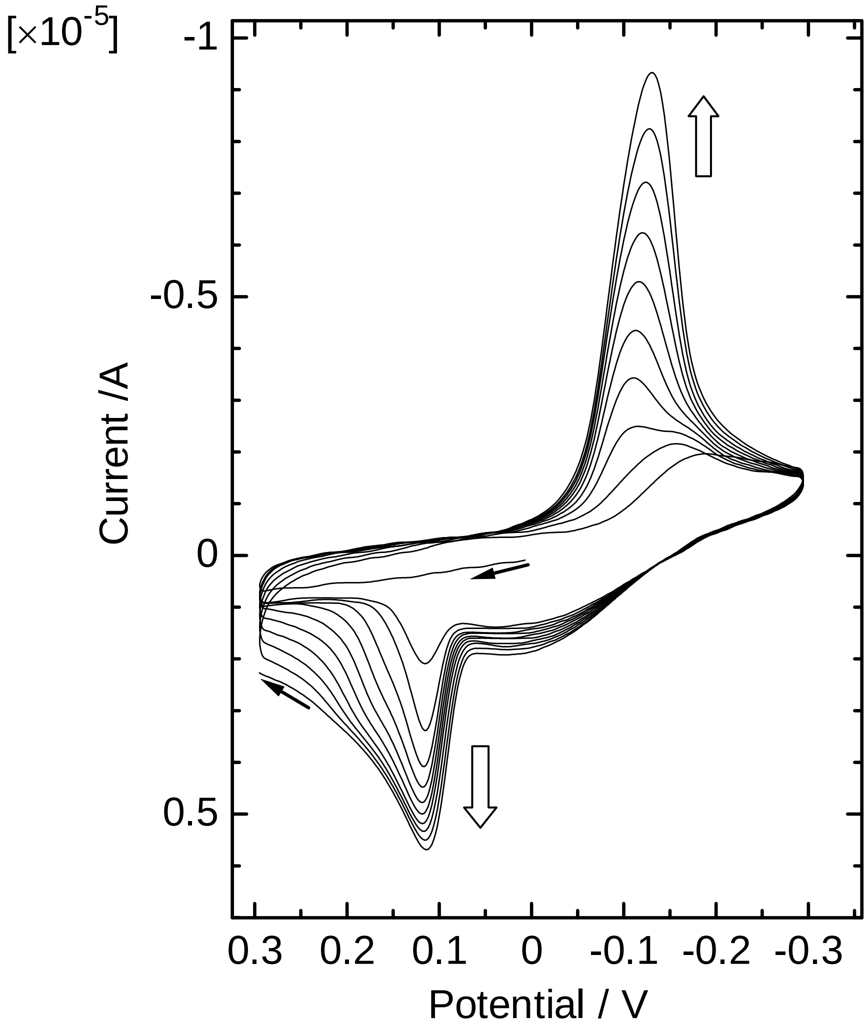

Fig. 4: Electropolymerization of decyloxydibenzothiophene (0.01 M) in 0.1 M TBAP/acetonitrile solution

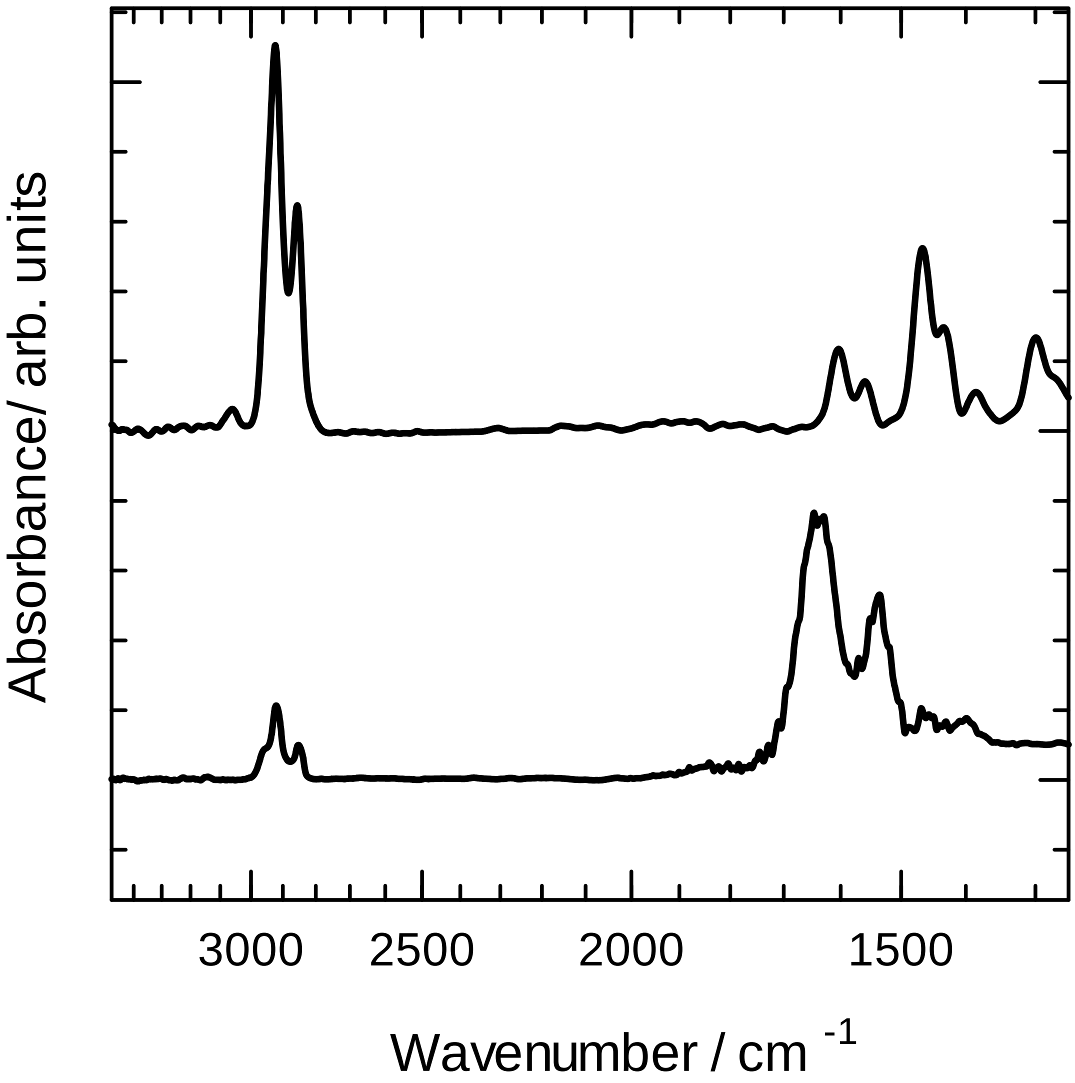

Fig. 5: IR absorption spectra of monomer (upper) and polymer (lower).

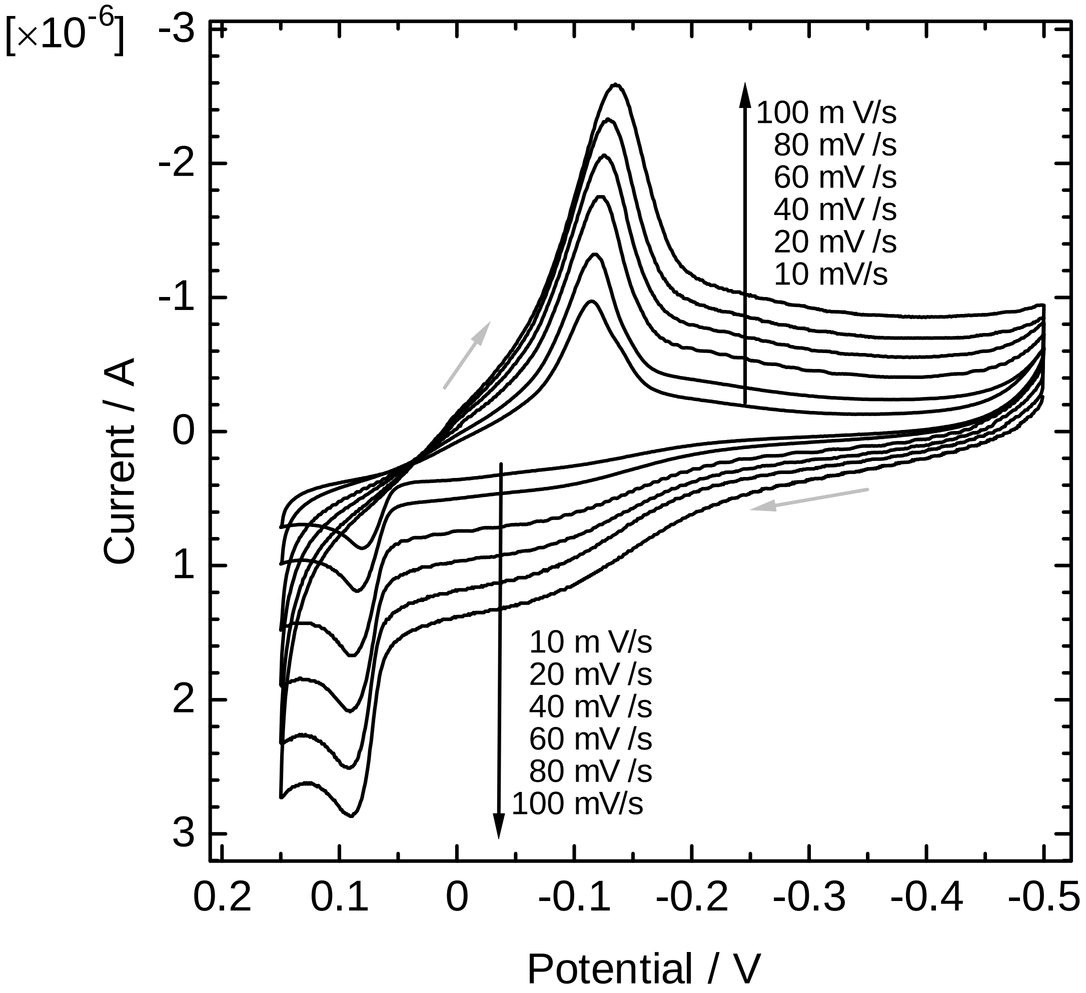

Fig.6: Cyclic voltammograms of polymer at several scan rates in 0.1 M TBAP/acetonitrile solution

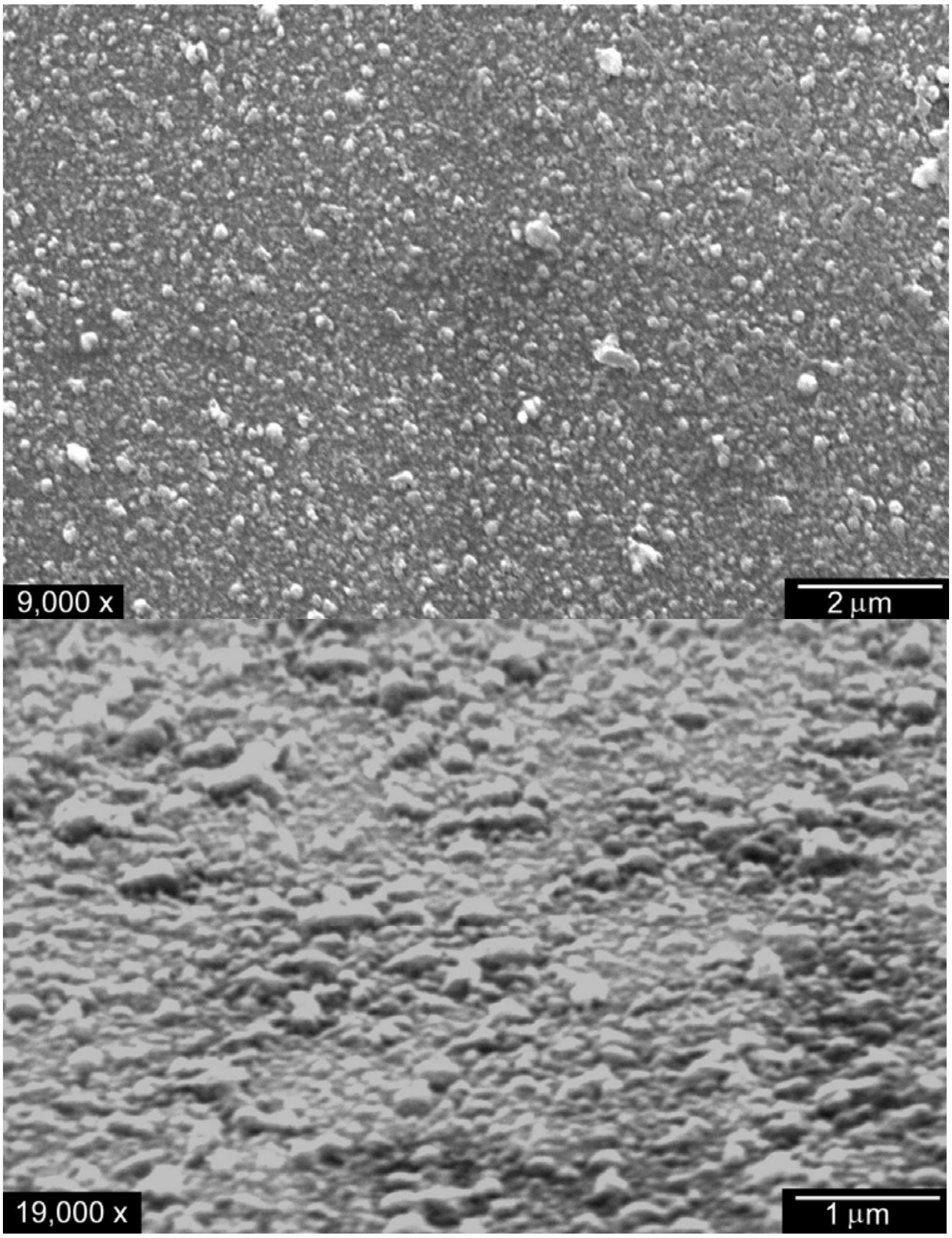

Fig.7: SEM images of polymer surface. (Top) An image from normal direction. (Lower) The image was taken from a direction oriented 30 degree from the surface