Synthesis and Characterization of Regiosymmetric Poly(3,4-propylenedioxythiophene) Derivative

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Chemical oxidative polymerization of 3,3-diheptyl-3,4-dihydro-2H-thieno[3,4-b] [1,4]dioxepine, (heptyl₂-PDOT) with iron trichloride (FeCl₃) gave the regiosymmetric poly(3,3-diheptyl-3,4-dihydro-2H-thieno[3,4-b] [1,4] dioxepine), poly-(heptyl₂-PDOT), which has a high glass transition temperature (195°C) and a good solubility behavior in most of common solvents. Electrochemically polymerized one showed higher conductivity at the positively applied potential (1.50 × 10⁻² S/cm at +1.0 V) than the negatively applied one (2.99 × 10⁻⁵ S/cm at −0.3 V).

Keywords: conductivity; electronic application; poly(propylenedioxythiophene); regiosymmetry; transmittance

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INTRODUCTION

The development of soluble and processable highly conducting polymers has opened up application possibilities that range from conductive anti-static coatings to organic light-emitting diodes and photovoltaic devices. The regioregularity of the poly(3-alkylthiophene)s (PAThs) played an important role for the enhancement of the electrical conductivity. Chen et al. reported that the regioregular PAThs exhibited a higher conductivity than the regiorandom PAThs [1]. On the other hand, polymerization of 3,4-disubstituted thiophenes is a useful way to prevent undesirable α-, β-coupling of the thiophene ring and the substitution at the 3- and 4-positions of thiophene with heteroatoms (oxygen and/or sulfur) [2,3] make the oxidized form even more stable with less steric distortion. Among those polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) has attracted much attention over the past 10 years. PEDOT exhibits many favorable properties, which include low band gap and oxidation potential for conversion to the conducting state, and high stability in the conducting form [4,5]. But the poor solubility of 3,4-alkylenedioxy PThs was the most drawbacks to their further applications in electrical and optical devices.

Generally regioregular PAThs were synthesized using Rieke zinc or nickel catalyzed cross-coupling [1,6,7]. However, the Rieke zinc or nickel catalyzed cross-coupling would need a special technique to handle for preparing the regioregular PTh derivatives, while oxidative polymerization using FeCl₃ of thiophene derivative is very simple method to get PThs derivative.

On the basis of above results, we designed 3,3-diheptyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (heptyl₁₂-PDOT, 3) as a monomer, 3,3-dihexylpropyl derivative could give the solubility to the polymer and its symmetric structure make it possible to polymerize using iron trichloride as an oxidant to give regiosymmetric polymer, poly(3,3-dihexyl-3,4-dihydro-2H-thieno[3,4-b]-[1,4]dioxepine), poly(heptyl₁₂-PDOT). Also the electrical and optical properties of poly(heptyl₁₂-PDOT) were investigated.

EXPERIMENTAL

Synthesis of 2,2-Diheptyl Malonic Acid Diethylester (1)

In a 1L three-neck flask filled with 500 mL ethanol equipped with reflux condenser, sodium metal (14.87 g, 0.65 mol) was added and stirred to resolve all of the sodium. After slow addition of diethyl malonate (31.47 g, 0.20 mol), the reaction mixture was heated to reflux. When it start to reflux, 1-bromoheptane (130.21 g, 0.73 mol) in 100 mL ethanol was added slowly and refluxed for 3 days. After removing the ethanol,
cold water was added then extracted with ether. Organic layer was
dried with anhydrous MgSO$_4$ then removed solvent at reduced
pressure. The remained organic residue was distilled at reduced
pressure to get 80\% (55.68 g) of 3,3-diheptyl malonic acid diethyl ester.
$^1$H-NMR (CDCl$_3$, $\delta$ ppm): 4.17 (q, 4H), 1.86 (m, 4H), 1.40 – 1.00 (m, 20H),
0.87 (t, 6H).

**Synthesis of 2,2-Diheptyl-1,3-Propanediol (2)**

LiAlH$_4$ (9.5 g, 0.25 mol) was placed in a 1L 3-neck flask equipped with
reflux condenser under N$_2$ atmosphere. With stirring 500 mL of dry
ether was added slowly to the reaction flask. 2,2-Diheptyl malonic acid
diethyl ester, 1 (51.4 g, 0.14 mol) was added slowly, then reflux the
reaction mixture for 24 h. After cooling the reaction mixture with
ice-bath, distilled water was slowly added until evolving hydrogen
gas was ceased. 0.1 M H$_2$SO$_4$ was added until all of the white solid pre-
cipitates were dissolved, then extracted with ether, and dried with
anhydrous MgSO$_4$ to get crude 2,2-diheptyl-1,3-propanediol (37.27 g,
95\%), which was used for next reaction without further purification.
$^1$H-NMR (CDCl$_3$, $\delta$ ppm): 3.59 (s, 4H), 2.11 (s, br, 2H), 1.40 – 1.00
(m, 20H), 0.90 (t, 6H).

**Synthesis of 3,3-Diheptyl-3,4-Dihydro-2H-Thieno[3,4-b] [1,4]
Dioxepine (3, Heptyl$_2$-PDOT)**

1.97 g (13.6 mmol) of 3,4-dimethoxythiophene, 7.45 g (27.2 mmol) of 2,
0.26 g (1.36 mmol) of $p$-toluenesulfonic acid monohydrate, and
120 mL of toluene were combined in a three-neck flask equipped with
a reflux condenser at an N$_2$ atmosphere, then reflux the solution for 3
days. The reaction mixture was cooled and washed with water. The
toluene was removed under reduced pressure, then the crude product
was purified by column chromatography on silica gel with methylene
chloride/hexane (2/3) as an eluent to yield 3.74 g (78\%) of heptyl$_2$-
PDOT (3). $^1$H-NMR (CDCl$_3$, $\delta$ ppm): 6.43 (s, 2H), 3.86 (s, 4H), 1.38
(m, 4H), 1.38 – 1.22 (m, 20H), 0.90 (t, $J = 6.8$ Hz, 6H). $^{13}$C-NMR
(CDCl$_3$, $\delta$ ppm): 151.0, 104.9, 77.8, 44.0, 32.09, 32.07, 30.7, 29.5,
23.1, 22.9, 14.4. HR-MASS: Calcd. for C$_{21}$H$_{36}$O$_2$S: 352.2436. Found:
352.2433.

**Synthesis of Poly(3,3-Diheptyl-3,4-Dihydro-2H-Thieno[3,4-b]
[1,4] Dioxepine), Poly(Heptyl$_2$-PDOT)**

A solution of heptyl$_2$-PDOT, 3 (1.00 g, 2.84 mmol) dissolved in dry
chloroform (5 mL) was added to a suspension of FeCl$_3$ (1.84 g,
11.3 mmol) in 10 mL of chloroform at room temperature under N₂ atmosphere and the reaction mixture was stirred at room temperature 48 h. The mixture was poured into 400 mL of methanol and the precipitated polymer was filtered and redissolved in chloroform and precipitated in methanol two more times. The resulting polymer was then completely dedoped by stirring the polymer, chloroform, and concentrated ammonia while the mixture was being boiled for 30 min. The water phase was separated, and fresh ammonia was added. One more time boiled for 30 min. and then the chloroform solution was washed with water two times and two times of 0.05 M ethylenediamine tetra-acetic acid (EDTA), then washed again with water three times. The amount of chloroform was reduced, and the residue was poured into methanol and the polymer precipitated. Further purification was achieved by dissolving the polymer in chloroform and precipitating in methanol, followed by filtration. After drying in a vacuum overnight at 40°C, the polymer was characterized. ¹H-NMR (CDCl₃, δ ppm): 4.0 (br, 4H), 1.8 – 1.0 (br, 24H), 1.0 – 0.7 (br, 6H). Elemental analysis: Calcd. for (C₂₁H₃₄O₂S)ₙ: C, 71.95; H, 9.78; S, 9.15. Found: C, 70.42; H, 9.46; S, 9.29.

RESULTS AND DISCUSSION

As shown in Scheme 1, heptyl₂-PDOT (3) was synthesized by a trans-esterification reaction between 3,4-dimethoxythiophene and 2,2-diheptyl-1,3-propandiol (2). The synthetic strategy of monomer is introduction of 3,4-propylenedioxy substitutent containing diheptyl solubilizing group to improve the solubility of resulting polymer. Oxidative polymerization of 3 with FeCl₃ as an oxidant gave a crude

![Scheme 1](image)

SCHEME 1 Synthesis of poly(heptyl₂-PDOT).
poly(heptyl2-PDOT) as a dark purple solid. The crude polymer was repeatedly precipitated into methanol, washed with ammonia and EDTA to completely dedoping. The polymer was further purified by Soxhlet extraction with methanol and acetone to remove low molecular weight oligomers, then extracted with chloroform to get pure polymer. The molecular weight and polydispersity of poly(heptyl2-PDOT) is 22,000 g/mol and 2.0. In accordance with the peaks broadening of 3 at 1H-NMR spectrum in Figure 1, the singlet proton peak of 6.43 ppm, which comes from 2- and 5-positon protons of thiophene ring at monomer, was disappeared during the polymerization reaction. The polymer was fully soluble in common organic solvents, such as THF, methylene chloride, chloroform, chlorobenzene, toluene, o-dichlorobenzene, 1,1,2-trichloroethylene. The glass transition temperature of poly(heptyl2-PDOT) is 195°C. The degradation temperature of 5% weight loss in N2 atmosphere was found at 323°C.

The HOMO and LUMO energy levels are 4.80 eV and 2.82 eV, respectively. The HOMO energy level of the polymer was obtained from the onset potential for the oxidation, and the LUMO was estimated by the subtraction of the optical band gap from the HOMO level. The optical band gap was determined by the absorption edge of a polymer thin film. The relatively high HOMO binding energy of poly(heptyl2-PDOT) is promising material for replacing the PEDOT as the hole injection and transport material. The absorption maximum

**FIGURE 1** 1H-NMR spectra of heptyl2-PDOT and poly(heptyl2-PDOT) in CDCl3.
peak of poly(heptyl$_2$-PDOT) showed at 507 nm in thin film, which is almost identical to the 506 nm observed in chloroform solution (Figure 2).

Even the annealing of the film at 120°C could not change the shape of absorption spectrum. The fully dedoped polymer film has a relatively transparent. The transmittance throughout the 300 nm to 2500 nm region with 100 nm thickness film has more than 60% with the lowest transmittance value 60% at the 507 nm and has more than 90% over 644 nm. Conductivity measurements for the polymer film were made from 3 in situ [8], applying the potentials from 0.0 to +1.0 V in a CH$_2$Cl$_2$ solution containing 0.1 M TBAP. The insulating gap was introduced onto the gold film electrode prepared by vacuum evaporation by cutting with a razor blade. The gap was determined to be 28 μm apart by the optical microscopic method, which was bridged by growing the polymer film. The currents were read with applied voltages across the bridge in the dichloromethane solution.
and conductivities were calculated. The conductivity changed as a function of the applied potential; $2.99 \times 10^{-5}$ S/cm at $-0.3$ V, $3.86 \times 10^{-4}$ S/cm at $0.0$ V, $8.64 \times 10^{-3}$ S/cm at $+0.3$ V, and $1.50 \times 10^{-2}$ S/cm at $+1.0$ V. In this case, the conductivity increased monotonically as the potential went to the more positive, indicating the conductivity increased even when the polymer is fully oxidized. This type of variation in conductivity was related to generation and degeneration of the conjugated structure by polaron and/or bipolaron formation until the maximum population.

CONCLUSIONS

We first synthesized high soluble and processable regiosymmetric poly(3,4-propylenedioxythiophene) derivative through oxidative polymerization with FeCl₃. The good solubility in common organic solvents and the fairly good conductivity with low optical absorption through the visible region will render many possible optoelectronic applications to this polymer.

REFERENCES

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