New Conducting Polymers Based on Poly(3,4-ethylenedioxypyrrole): Synthesis, Characterization, and Properties

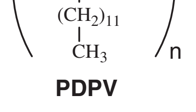
In Tae Kim,* Jung Youl Lee, and Sang Woo Lee
Department of Chemistry, Kwangwoon University, 447-1 Wolgye-Dong, Nowon-Ku, Seoul 139-701, Korea

(Received September 16, 2003; CL-030870)

Solution-processible conducting polymers **1** and **2**, based on 3,4-ethylenedioxypyrrole, were synthesized. A comparison of the polymers' optical and electrical properties showed that the introduction of a vinyl group in polymer **1** produced a decrease of bandgap. This occurrence was attributed to the enhancement of the planarity of polymer **1**.

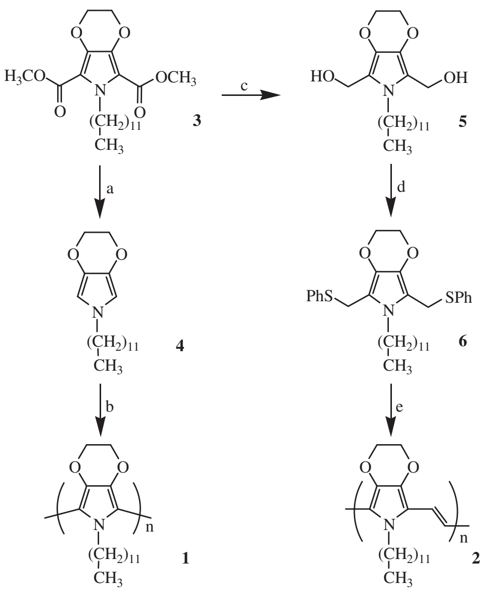
Electronically conducting polymers are known to be excellent materials for electronic devices like electrolytic capacitors, actuators, sensors, artificial muscles, and light-emitting diodes (LEDs).[1] Electron-rich conducting polymers, such as polypyrrole (PPY), poly(3,4-ethylenedioxythiophene) (PEDOT), poly(*p*-phenylenevinylene) (PPV), poly(3,4-ethylenedioxypyrrole) (PEDOP), and *N*-substituted poly(3,4-propylenedioxypyrrole) (ProDOP), are useful for the formation of stable conjugated polymer complexes that can be rapidly switched between their oxidized and neutral states.[2] In the case of PEDOT and PEDOP, ethylenedioxy substitution served to enhance their optical, electrochemical, and electronic properties.[3] The bandgap of PPV is lower by 0.3 eV than that of its parent, polyphenylene. The vinylene linkage not only reduces the bandgap of the PPV but also acts as conjugated spacer to increase the degree of coplanarity of the PPV backbones.[4] A soluble processible electron-rich low bandgap (1.67 eV) conducting poly(1-dodecyl-2,5-pyrrolylene-vinylenes) (PDPV), prepared through a new synthetic route using a monomer having a thiophenyl group as the leaving group, was recently reported.[2b]

This present study reports the preparation route and the properties of the electron-rich conjugated polypyrrole derivatives: poly(1-dodecyl-3,4-ethylenedioxy-2,5-pyrrolylene) (**1**) and poly(1-dodecyl-3,4-ethylenedioxy-2,5-pyrrolylene vinylene) (**2**) as shown in Scheme 2. Dimethyl 1-dodecyl-3,4-ethylenedioxypyrrole-2,5-dicarboxylate (**3**) was synthesized through dodecylation on the nitrogen of dimethyl-3,4-ethylenedioxypyrrole-2,5-dicarboxylate.[5] Compound **3** was hydrolyzed in NaOH aqueous solution to give 1-dodecyl-3,4-ethylenedioxypyrrole-2,5-dicarboxylic acid. Decarboxylation of 1-dodecyl-3,4-ethylenedioxypyrrole-2,5-dicarboxylic acid in triethanolamine at 180 °C yielded compound **4** as monomer. Monomer **4** was then smoothly polymerized with iron(III) chloride hexahydrate, yielding polymer **1**. The resulting oxidized polymer was washed with ethanol and reduced in concentrated hydrazine monohydrate. It was then reprecipitated in ethanol, producing a black powder completely soluble in THF, CHCI$_3$, and CH$_2$CI$_2$.[6]



PDPV

Scheme 1.



Scheme 2. a) i) NaOH, H$_2$O, 100 °C, 24 h, 85%, ii) triethanolamine, 180 °C, 15 min, 54%; b) Iron(III) chloride hexahydrate, acetonitrile, 0 °C, 12 h, hydrazine monohydrate, 82% c) LAH, THF, 0 °C, 5 h, 63%, d) benzenethiol, ZnI$_2$, CH$_2$Cl$_2$, 18 h, 32%, e) TFA, THF, −28 °C–rt, 24 h, 52%.

The reduction of compound **3** with LiAlH$_4$ generated 1-dodecyl-3,4-ethylenedioxy-2,5-dimethanol (**5**). Compound **5** was treated with benzenethiol and ZnI$_2$ in CH$_2$CI$_2$ at room temperature for 18 h. This process yielded 32% 1-dodecyl-3,4-ethylenedioxy-2,5-bis(phenylthiomethylene)pyrrole (**6**) as monomer.[7] Monomer **6** was then polymerized through treatment with trifluoroacetic acid in THF for 24 h, giving poly(1-dodecyl-3,4-ethylenedioxy-2,5-pyrrolylenevinylene) (**2**). Conversion from monomer **6** gave polymer **2** in 52% yield, which was considerably higher than what was typically obtained for poly(phenylenevinylene) prepared from bis(sulfonium) salt precursors.[8] Table 1 gives some properties of polymers **1** and **2**. The resulting deep blue-black conjugated polymer **2** was soluble in a variety of organic solvents.[9]

Gel permeation chromatography (GPC) analysis, using polystyrene standards, gave a number average molecular weight (*M*n) of 5.3×10^3 for polymer **1** and 1.3×10^4 for polymer **2**. Thermogravimetric analysis (TGA; N$_2$; 10 °C/min) of polymer **1** showed the onset of decomposition at 275 °C and 15% weight loss by 475 °C. On the other hand, polymer **2** showed the onset of

Table 1. Properties of the polymer **1** and **2**

Polymer	λ max/nm CHCl$_3$	Mn	Mw/Mn	Conductivity S cm^{-1} (dopant)	Bandgap /(eV)
Polymer **1**	312	5310	4.51	2.8×10^{-2} (I$_2$)	3.26
Polymer **2**	659	13000	1.53	0.45 (I$_2$)	1.57

decomposition at 170 °C and 15% weight loss by 240 °C. Thus, polymer **1** appeared to be more thermally stable than polymer **2**.

The electrical conductivity of polymers **1** and **2** were measured using a standard four-probe technique. The polymer **1** and **2** showed insulator properties without dopants. Table 1 shows the maximum conductivity values for polymer **1** and polymer **2** films with I$_2$ dopant. Polymer **2**, which had higher molecular weight, gave an electrical conductivity of about 0.45 Scm^{-1} with I$_2$ as dopant. Polymer **1**, on the other hand, had an electrical conductivity of 2.8×10^{-2} Scm^{-1}. The discrepancy in the electrical conductivity of polymers **1** and **2** suggested that the low conductivity of polymer **1** arises from significant steric interactions between the 1-dodecyl-3,4-ethylenedioxy pyrrole rings. These conductivity values suggested that polymer **2**, with long effective conjugation lengths, would exhibit comparable electrical conductivity of **PDPV**. On long term (1 month) exposure to air, undoped (neutral state) polymer **2** apparently became oxygen doped, showing a maximum conductivity of 1.53×10^{-7} Scm^{-1}.

The UV–vis absorption maximum was at 312 nm for polymer **1** and 659 nm for polymer **2** in THF solutions (Figure 1). These UV–vis absorption data suggested that polymer **2** has considerably longer conjugation length than that of polymer **1**. Bandgap (band edge) of 1.57 eV was obtained for polymer **2**, which was lower than that of polymer **1**, 3.26 eV. But, the bandgap of polymer **2** is compareable to that of **PDPV** (1.67 eV). This result was attributed to the vinylene linkage in polymer **2**. This linkage not only extended the electronic properties of the polymer chain but also acted as a conjugated spacer to reduce steric interactions of adjacent pyrrole rings in polymer **1**, therefore increasing the degree of coplanarity of the conjugated polymer **2** backbones.

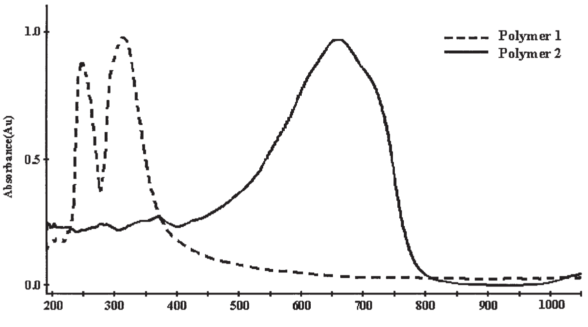


Figure 1. UV–vis spectra of polymer **1** and **2** in THF.

In summary, a new low bandgap electron-rich polymer **2** was prepared. This polymer was dark blue-black in the neutral state and became transparent light yellow-greenish when doped. According to the results obtained for polymer **2**, it was clear that the principle of inducing smaller bandgap into conducting polymers by a regular alternating of vinyl group and pyrrole ring moieties worked well.

This work was supported by research grants from the RRC program of MOST and KOSEF and Kwangwoon University (2002).

References and Notes

1 T. A. Skotheim, R. L. Elsenbumer, and J. R. Reynolds, "Handbook of Conducting Polymers," 2nd ed., Dekker, New York (1998).

2 a) C. L. Gaupp, K. Zong, P. Schottland, S. C. Thompson, C. A. Thomas, and J. R. Reynolds, *Macromolecules*, **33**, 1132 (2000). b) I. T. Kim and R. L. Elsenbaumer, *Macromolecules*, **33**, 6407 (2000). c) Y. Fu, H. Cheng, and R. L. Elsenbaumer, *Chem. Mater.*, **9**, 1720 (1997). d) G. Sönmez, I. Schwendeman, P. Schottland, K. Zong, and J. R. Reynolds, *Macromolecules*, **36**, 639 (2003).

3 H. Eckhardt, L. W. Shacklette, K. Y. Jen, and R. L. Elsenbaumer, *J. Chem. Phys.*, **91**, 1303 (1989).

4 a) G. A. Sotzing and K. Lee, *Macromolecules*, **35**, 7281 (2002). b) K. Shiraishi and T. Yammamoto, *Synth. Met.*, **130**, 139 (2002).

5 A. Merz, R. Schropp, and E. Dötterl, *Synthesis*, **1995**, 795.

6 Polymer **1**, IR: 2916, 2855, 1602, 1511, 1456, 1329, 1073, 927, 848 cm^{-1}. E_g (Band edge) = 3.26 eV. ^{1}H NMR(in Acetone-d_6), δ 4.26(s, 4H); 3.69(s, 2H); 1.28(m, 20H); 0.88(s, 3H). ^{13}C NMR(in Acetone-d_6), δ 131.97; 129.64; 66.53; 66.22; 32.76; 30.27; 30.12; 29.97; 29.81; 29.66; 29.51; 27.51; 24.16; 19.98; 14.37. Anal. Calcd for $C_{18}H_{31}NO_2$: C, 74.18; H, 10.03; N, 4.81; O, 10.98%. Found: C, 74.63; H, 9.96; N, 4.91; O, 10.40%.

7 H. Chang and R. L. Elsenbaumer, *J. Chem. Soc., Chem. Commun.*, **1995**, 1451.

8 R. W. Lenz, C. C. Han, J. S. Stenger, and F. E. Kaeasz, *J. Polym. Sci., Part A: Polym. Chem.*, **26**, 3211 (1988).

9 Polymer **2**, IR: 3068, 2922, 2849, 1694, 1535, 1402, 1262, 1110, 1049, 970 cm^{-1}. E_g (Band edge) = 1.57 eV. ^{1}H NMR(in CD_2Cl_2), δ 6.95(s, 1H); 4.43(s, 4H); 3.84(s, 2H); 2.45(s, 2H); 1.67(s, 2H); 1.26(m, 20H); 0.87(s, 3H). ^{13}C NMR(in $CDCl_3$), δ 152.22; 144.33; 136.40; 128.85; 125.95; 67.27; 66.69; 34.93; 34.66; 32.49; 30.64; 30.24; 29.93; 28.72; 28.48; 27.32; 23.25; 21.37. Anal. Calcd for $C_{40}H_{66}N_2O_4$: C, 75.43; H, 10.43; N, 4.00; O, 10.04%. Found: C, 75.30; H, 9.37; N, 4.00; O, 10.80%.

Published on the web (Advance View) December 15, 2003; DOI 10.1246/cl.2004.46