New Series of Blue-Light-Emitting Polymers Constituted of 3-Alkylthiophenes and 1,4-Di(1,3,4-oxadiazolyl)phenylene

Wei Huang,* Wang-Lin Yu, Hong Meng, Jian Pei, and Sam Fong Yau Li

Institute of Materials Research and Engineering, National University of Singapore, Singapore 119260, Republic of Singapore

Received January 30, 1998. Revised Manuscript Received July 13, 1998

A new series of conjugated polymers constituted of 3-alkylthiophenes and 1,4-di(1,3,4-oxadiazolyl)phenylene are synthesized through precursor polymers of polyhydrazides. The solubility of the precursor polymers and the corresponding target polymers is improved by increasing the length of side chains on thiophene rings, which results in a higher degree of the conversion from the precursors to the final polymers and thus results in longer effective conjugated length in the polymers bearing longer side chains. The thermal stability and electrochemical properties of the polymers are studied. The polymers emit blue light under the irradiation of UV light in their film states. The relative fluorescence yield in solutions increases with the increase in length of side chains on thiophene rings in the polymers and reaches up to 79% for the polymer bearing octyl side chains. The possibility of polymers being used as electroluminescent material in polymer light-emitting diodes (PLEDs) is demonstrated by the successful fabrication of a single-layer device of indium tin oxide (ITO)/polymer/Ca, which emits visible blue light above 8 V of forward bias.

Introduction
Conjugated polymers have attracted intensive attention in the past 20 years on account of their unique electrical and optical properties. In 1990, a spectacular advanced technology developed at Cambridge using conjugated polymers as electroluminescent materials in light-emitting diodes (LEDs) ignited a tremendous worldwide research effort on the design and synthesis of novel conjugated polymeric materials for LED application. Poly(p-phenylenevinylene) (PPV), polythiophene (PT), poly(p-phenylene) (PPP), polyfluorene (PF), and their derivatives have been widely studied as light-emitting materials in polymer LEDs. The electroluminescence (EL) from these polymers can sweep the whole range of the visible spectrum. However, all these polymers have $\pi$-excessive nature, i.e., they are typical p-dope-type polymers with much greater tendency for transporting holes than for transporting electrons. This charge imbalance is one of the key limits for increasing the EL quantum efficiency of polymer light-emitting diodes (PLEDs). Although the EL quantum efficiency of PLEDs may be increased remarkably by using low-work function metals as cathodes or adding electron injection/transporting layers between a light-emitting polymer film and a cathode, the approaches suffer from the high reactivity of the metals and the technical difficulties in fabricating multilayer structures. Therefore, the synthesis of light-emitting polymers with strong electron affinity is necessary for fabricating highly efficient and stable polymer LEDs. Unfortunately, the synthesis of soluble and stable total conjugated n-dope-type polymers with high light-emitting efficiency is still a challenge for chemists.

2-(4-Biphenylyl)-5-(tert-butylphenyl)-1,3,4-oxadiazole (PBD) is one of the most widely used electron injection/transport or hole-blocking materials. Its function is believed to result from the high electron affinity of the oxadiazole ring in the molecule. Several oxadiazole-containing polymers (copolymers and graft copolymers) have been synthesized as electron-transporting materials; a few light-emitting polymers composed of alternating phenylene and oxadiazole also have...
been synthesized in the last several years.\textsuperscript{16} To our knowledge, no effort has been devoted to the synthesis of total conjugated light-emitting polymers composed of oxadiazole and thiophene rings. In this paper we present the synthesis, characterization, and application in polymer LEDs of a new series of light-emitting polymers constituted of 3-substituted thiophenes and 1,4-di(oxadiazolyl)phenylene. The effects of the length of the substituted chains on the thiophene ring on the synthesis and optical properties of the polymers will also be discussed.

Results and Discussion

Synthesis and Characterization. The polymers were synthesized according to the route depicted in Scheme 1. The synthesis of monomer I was started with the preparation of 3-alkylthiophene from 3-bromo-thiophene by a coupling reaction with alkyl Grignard reagent in the presence of Ni(dppp)Cl\textsubscript{2}, followed by the carboxylation at the 2 and 5 positions of thiophene ring, and finally reaction with SOCl\textsubscript{2}. The reaction of Cacialli, F.; Friend, R. H. Synth. Met. 1995, 76, 153.


Figure 1. FTIR spectra of the polyhydrazide \textsuperscript{11c} before (A) and after (B) treatment with POCl\textsubscript{3}.

of LiCl and pyridine at ambient temperature gave the polyhydrazide \textsuperscript{III}. The polyhydrazide precursors are not soluble in common organic solvents and just partially dissolve in NMP. Because of the poor solubility, the purification of the polyhydrazide precursors is difficult. This should be responsible for the poor agreement of the results of elemental analysis with the calculated values (as shown in the Experimental Section). \textsuperscript{III}c was converted to the final polymer \textsuperscript{IV} by refluxing in POCl\textsubscript{3} for 4 h.

The synthesis of aromatic poly(1,3,4-oxadiazole) compounds has been reviewed recently.\textsuperscript{21} The widespread route involves the preparation of polyhydrazide precursors followed by cyclodehydration. The cyclodehydration can be achieved by heating the precursors under vacuum or by heating in dehydrating solvents. In the present work, POCl\textsubscript{3} is employed as dehydrating solvent. The degree of cyclodehydration for the polyhydrazide precursors can be estimated from Fourier transform infrared spectroscopy (FTIR). For polymer \textsuperscript{11c} (Figure 1), after the treatment with POCl\textsubscript{3}, two intensive absorption peaks around 1650 and 1543 cm\textsuperscript{-1} arising from the carbonyl groups in polyhydrazine and the absorption in the range of 3200–3300 cm\textsuperscript{-1} due to N–H stretching disappear. Meanwhile, two new peaks at 1578 and 1050 cm\textsuperscript{-1} attributed to oxadiazole ring appear. These results indicate a successful cyclodehydration. However, the completion of cyclodehydration does not happen on polymers \textsuperscript{IIIa} and \textsuperscript{IIIb}. As shown in Figure 2, the absorption around 1650 cm\textsuperscript{-1} can be identified in the FTIR spectrum of POCl\textsubscript{3}-treated polymer \textsuperscript{IIIb}, while the absorption band is still intensive in the spectrum of POCl\textsubscript{3}-treated polymer \textsuperscript{IIIa}. It is evident that the degree of cyclodehydration decreases with the decrease in length of the substituted chains on thiophene ring. This may be attributed to the lower solubility of the precursor polyhydrazides \textsuperscript{11a} and \textsuperscript{11b} and their corresponding final polymers in POCl\textsubscript{3}. The reaction mixture of \textsuperscript{IIIc} in POCl\textsubscript{3} is always clear during the whole process of cyclodehydration, while the reaction mixtures of \textsuperscript{11a} and \textsuperscript{11b} are turbid and cloudy, respectively. The chemical structures of the polymers can be further confirmed by elemental analysis and NMR. The \textsuperscript{1}H NMR spectrum of polymer \textsuperscript{IVc} is exhibited in Figure 3. The signals at 8.43 and 8.04 ppm...
are assigned to the aromatic protons on phenylene and thiophene rings, respectively. The resonance for the methylene group adjacent to the thiophene ring appears at 3.23 ppm. The weak signals below the peaks may be attributed to terminal groups, different linkage of 3-octylthiophene with oxadiazole ring, and the existence of trace amounts of noncyclodehydrated hydrazide groups. The calculated empirical formulas of the polymers from the results of elemental analysis are listed in Table 1, which show good agreement with the expected formulas. The higher contents of hydrogen can be attributed to the absorbed water, which is supported by the higher contents of oxygen, as well as the incompleteness of the cyclodehydration.

Polymer IVa is insoluble in common solvents, while polymers IVb and IVc are partially soluble in chloroform and dimethyl sulfoxide (DMSO). In mixtures of chloroform (CHCl₃) and trifluoroacetic acid (TFA), polymers IVb and IVc can dissolve readily to give clear solutions, but polymer IVa only partially dissolves. Long alkyl chains on the thiophene ring enhance the solubility of the resultant polymers. Polymers IVb and IVc are soluble up to 250 °C either in air or in nitrogen according to thermogravimetric analysis (TGA) (Figure 4). However, polymer IVa shows obvious weight-loss below 300 °C and a faster weight-loss between 300 and 350 °C with respect to the other two polymers. This may be attributed to the noncyclodehydrated hydrazide groups, which are cyclodehydrated during heating.

**Optical Properties.** Either in the solutions of CHCl₃–TFA or in film states, polymers IVb and IVc emit strong blue fluorescence under ultraviolet irradiation. The UV–visible and fluorescence spectra from the cast film of polymer IVc (from CHCl₃–TFA solutions) are given in Figure 5. The absorption spectra show a maximum at 396 nm with the onset of 445 nm, which corresponds to a band gap of 2.79 eV. The film of polymer IVb exhibits similar absorption and fluorescence spectra. However, the maximum of both absorption and fluorescence of polymer IVb appear at shorter wavelengths compared with those of polymer IVc either in solutions or in their film states. Detailed spectral data are summarized in Table 2. It can be seen clearly from the data listed in Table 2 that the maxima of absorption and fluorescence of the polymers in solutions shift to longer wavelength with the increase in length of side chains on thiophene rings, while the Ï•–Ï•* band gaps determined from the absorption onsets decrease with the increase in the length of side chains. These results indicate that the effective conjugated length of the series of polymers increases with the length of side chains on thiophene rings.

The fluorescence quantum yields of the polymers in CHCl₃–TFA solutions (ca. 10⁻⁶ M) were estimated by employing quinine sulfate (ca. 10⁻⁵ M) in 0.1 M H₂SO₄ as reference standard. The results are listed in Table 2. The relative fluorescence quantum efficiencies are 7.6%, 68%, and 79% for IVa, IVb, and IVc, respectively. The increase in fluorescence quantum...
efficiency with the increase in length of the side chain on thiophene ring can be attributed to the longer effective conjugated length in the polymers bearing longer side chains, which results from higher solubility in the synthetic process.

Cyclic Voltammetry. The electrochemical properties were studied by cyclic voltammetry (C–V). The polymer films were coated on a working platinum electrode by drying a layer of solution in CHCl₃. The cyclic voltammogram was performed in a one-compartment three-electrode cell with a Pt wire counter electrode and a Ag/AgNO₃ (0.1 M) reference at the scan rate of 50 mV/s. The electrolyte was 0.1 M Bu₄NClO₄ in acetonitrile, and the cell was purged with argon.

Figure 6 shows the cyclic voltammogram of polymer IVc. When scanning takes place in a negative direction, the n-doping (reduction) process onsets at ca. −1.17 V (vs SCE, same below) and a cathodic peak appears at ca. −1.88 V. A corresponding reoxidation (n-dedoping) peak appears at ca. −1.46 V. Accompanying the reversible n-doping and n-dedoping process, there was an obvious color change in the polymer film: yellow color in the neutral state and dark brown in the doped state. On sweeping anodically, an irreversible p-doping (oxidation) peak occurs at ca. 1.93 V with the onset at ca. 1.79 V. The band gap of the polymer thus can be estimated to be 2.96 eV from the cyclic voltammograms; it is almost the same as the optically determined one. A similar cyclic voltammogram is obtained from the film of polymer IVb (as shown in Figure 6). However, its band gap is determined to be 3.18 eV, higher than that of polymer IVc. The increase of band gap is caused mainly by the increase in n-doping onset potential, which is −1.42 V for polymer IVb. This may be attributed to the lower effective conjugated length in polymer IVc due to the incompleteness of the cyclodehydration of hydrazide groups, which has been demonstrated by FTIR. All the electrochemical data are listed in the last two columns in Table 2. The cyclic voltammogram of polymer IVa is not obtained because of the poor solubility of the polymer.

LED Device Fabrication. A polymer light-emitting diode was fabricated with polymer IVc as active material. To fabricate the device, a film of the polymer was spin-coated on an indium tin oxide (ITO) glass from its solution in CHCl₃/TFA and a layer of metal Ca was evaporated as top electrode. All the fabrication and tests were performed in a nitrogen drybox. Under a bias in the forward direction, the single-layer diode begins to emit visible blue light at about 8 V. The current–voltage (I–V) and light characteristics of the ITO/polymer IVc/Ca device are displayed in Figure 7, showing a typical diode character. With the increase of forward bias, both the current and the emitting light intensity increase rapidly after 8 V. The external quantum efficiency was determined to be ~0.0001% photons/electron. These results show the potential of these new materials as emissive material in polymer LEDs, although the optimization of chemical structure of the polymers and structure of device is necessary to improve the performance of the PLED devices based on the new series of materials.

In summary, the synthesis and characterization of a novel series of conjugated polymers constituted of 3-substituted thiophenes and 1,4-di(1,3,4-oxadiazolyl)phenylene are presented. The polymers are n-dope-type blue-light-emitting polymers and could be potential electroluminescent materials. The alkyl side chains on thiophene rings are essential for both the solubility of the resultant polymers and the successful synthesis of target polymers. A long alkyl side chain results in a higher degree of conversion from precursor polymers of polydrazides to final 1,3,4-oxadiazoyl-containing polymers and thus increases the effective conjugated length in the final polymers. Although we could not measure the molecular weights of the polymers because of their
Experimental Section

General Information. All experiments were carried out under a dry atmosphere of pure nitrogen. Diethyl ether and hexane were distilled over sodium and calcium hydride, respectively. N-Methylpyrrolidinone (NMP), N,N,N′,N′-tetramethyl-ethylenediamine (TMEDA), pyridine, and phosphorus pentoxide were used as received. Ethers were distilled before use. 

Typical synthesis of poly(3-alkyl)thiophene-2,5-hydrazide. A similar synthetic procedure was performed for the synthesis of poly(3-alkyl)thiophene-2,5-hydrazide. The reactions were carried out in a dry atmosphere of pure nitrogen. Diethyl ether and hexane were used as solvents.

3-Butylthiophene-2,5-dicarbonyl acid: MS m/z 228; 1H NMR (CDCl3) δ 7.7 (s, 1 H), 4.5 (br s, 2 H), 3.0 (t, J = 7.6 Hz, 2 H), 1.6 (m, 2 H), 1.3 (m, 2 H), and 0.9 (t, J = 7.3 Hz, 3 H) ppm; 13C NMR (CDCl3) δ 165.2, 163.7, 151.8, 142.0, 139.1, 138.3, 33.5, 29.6, 23.1, and 14.1 ppm.

3-Octylthiophene-2,5-dicarbonyl acid: MS m/z 284; 1H NMR (CDCl3) δ 7.7 (s, 1 H), 4.9 (br s, 2 H), 2.6 (t, J = 7.3 Hz, 2 H), 1.6–1.5 (m, 2 H), 1.4–1.3 (m, 2 H), and 0.9 (t, J = 7.2 Hz, 3 H) ppm; 13C NMR (CDCl3) δ 159.7, 158.6, 154.4, 142.9, 139.8, 138.9, 31.7, 30.3, 29.6, 29.3, 29.2, 29.1, 22.6, and 14.0 ppm.

3-Alkylthiophene-2,5-dicarbonyl Chloride (Ib and Ic). Excess thiol chloride and 3-alkylthiophene-2,5-dicarbonyl acid were mixed in a round-bottom flask. The mixture was refluxed for 5 h and then the excess thiol chloride was removed under reduced pressure. The residue was distilled under vacuum to give the light-yellow oil (134 °C/0.1 mbar with a yield of 89% for Ib).

3-Octylthiophene-2,5-dicarbonyl chloride (Ic): MS m/z 291; 1H NMR (CDCl3) δ 7.7 (s, 1 H), 2.9 (t, J = 7.6 Hz, 2 H), 1.6–1.3 (m, 12 H), and 0.8 (t, J = 6.5 Hz, 3 H) ppm; 13C NMR (CDCl3) δ 159.7, 158.6, 154.4, 142.9, 139.8, 138.9, 31.7, 30.3, 29.6, 29.3, 29.2, 29.1, 22.6, and 14.0 ppm. Anal. Found: C, 52.47; H, 5.78; Cl, 22.18; S, 9.03. Calcd for C21H18O2ClS: C, 52.34; H, 5.65; C, 22.07; S, 9.98.

Thiophene-2,5-dicarbonyl Chloride (Ia). Thiophene-2,5-dicarbonyl chloride was prepared from the starting material of thiophene using the same procedures in synthesizing Ib and Ic. 1H NMR (CDCl3) δ 7.93 (s, 2 H). Anal. Found: C, 34.73; H, 0.98; S, 15.90. Cl, 34.89. Calcd for C6H4Cl2O2S: C, 34.45; H, 0.97; S, 15.34; Cl, 33.97.

2,5-Terephthalic Dihydrazide (II). The compound was prepared from dimethyl 2,5-terephthalate by reaction with excess hydrazine monohydrate in methanol. 1H NMR (DMSO-d6) with little CDCl3 δ 9.9 (s, 2 H), 7.9 (s, 4 H), 4.5 (br s, 4 H). Anal. Found: C, 49.74; H, 5.33; N, 28.82. Calcd for C14H12N4O4S: C, 49.48; H, 5.02; N, 29.05.

Poly(3-alkylthiophene)-2,5-hydrazide-phenyl-2,5-hydrazide (IIIa). 3-Octylthiophene-2,5-dicarbonyl chloride (3.2 g, 0.01 mol) was added with stirring into a solution of 1.94 g (0.01 mol) of II in 20 cm3 of NMP containing 0.1 g of LiCl and 0.02 mol of pyridine at room temperature for a period of 3 h. After the reaction, the viscous solution was poured into 200 cm3 of water and the polymer was precipitated out. The polymer was isolated by filtering and was washed with water and ethanol and then dried under vacuum at 60 °C to give a white powder polymer (4.0 g, 90%). Anal. Found: C, 58.62; H, 6.15; N, 10.69; S, 7.56. Calcd for C32H28N4O4S: C, 59.72; H, 5.88, N, 12.67; S, 7.23.

A similar synthetic procedure was performed for the synthesis of IIIa and IIIb.

Poly(3-butylthiophene)-2,5-hydrazide-phenyl-2,5-hydrazide (IIId): Anal. Found: C, 53.60; H, 4.53; N, 13.00; S, 8.27. Calcd for C17H12N4O4S: C, 55.95; H, 4.66; N, 14.51; S, 8.20.


Poly(3-alkylthiophene)-2,5-oxadiazole-phenyl-2,5-oxadiazole (IVa–c). Poly(3-alkylthiophene-2,5-hydrazide-
p-phenyl-2,5-hydrazide (2.0 g) was refluxed in 25 cm³ of POCl₃ for 4 h and then the reaction mixture was poured into 200 cm³ of water. The precipitated polymer was isolated by filtering and was washed with water, ethanol, and ether successively and then was dried under vacuum at room temperature to give yellow powders.

**IVc** (90% yield): ¹H NMR (TFA-d/CDCl₃) δ 8.5 (br s, 4 H), 8.0 (br s, 1 H), 3.2 (m, 2 H), 1.9–1.3 (m, 12 H), and 0.9 (m, 3 H) ppm. Anal. Found: C, 63.53; H, 5.93; N, 13.46; S, 7.25. Calcd for C₂₂H₂₂N₄O₂S: C, 65.02; H, 5.42; N, 13.79; S, 7.88.

**IVb**: ¹H NMR (TFA-d/CDCl₃) δ 8.5 (s, with two small peaks at 8.39 and 8.26, 4 H), 8.1 (s, with two small peaks at 8.05 and 7.97, 1 H), 3.3 (m, 2 H), 1.9 (m, 2 H), 1.6 (m, 2 H), and 1.1 (m, 3 H) ppm. Anal. Found: C, 58.58; H, 4.78; N, 14.35; S, 8.85. Calcd for C₁₈H₁₄N₄O₂S: C, 61.71; H, 4.00; N, 16.00; S, 9.14.

**IVA**: Anal. Found: C, 49.91; H, 3.13; N, 15.49; S, 8.03. Calcd for C₄₄H₆₄N₄O₄S: C, 57.14; H, 2.04; N, 19.05; S, 10.88.

CM9800581