Synthesis and characterization of aromatic polyoxadiazoles containing 3,4-alkylenedioxythiophenes

Uma P. Ojha, K. Krishnamoorthy, Anil Kumar

Department of Chemistry, Indian Institute of Technology, Bombay, Mumbai 400076, India

Abstract

In this work, we report the synthesis and characterization of wholly aromatic polyoxadiazoles containing 3,4-alkylenedioxythiophenes. The polymers are synthesized using the precursor polyhydrazide route. The polymers have well-defined structures and exhibit good thermal stability with the onset decomposition temperature in nitrogen at around 330 °C. These polymers are characterized by FTIR, 1H NMR, UV-Vis and fluorescence spectroscopy. Electrochemical properties of these polymers are studied using cyclic voltammetry. Polyoxadiazoles based on 3,4-alkylenedioxythiophenes exhibit good hole-blocking properties.

Keywords: Poly(aromatic oxadiazoles); Poly(3,4-ethylenedioxythiophene); Poly(3,4-propylenedioxythiophene); Hole-blocking polymers

1. Introduction

Conducting polymers have been found to be the promising candidates for wide range of applications like electrochromic devices, sensors and light emitting diodes (LEDs), etc. [1]. Several reports are available on polymeric light emitting diodes using poly(p-phenylenevinylene) [2,3], poly(thiophene) [4], poly(p-phenylene) [5] and their derivatives. However, all these polymers are π excessive in nature and hence have greater tendency to transport holes than electrons. On the other hand, polymers having π deficient heterocycles like pyridine, oxadiazoles have greater tendency to transport electrons than holes [6]. The balance of the injection of electrons and holes in LEDs is crucial for its performance. Different approaches have been developed to achieve this. The first is the design of multilayer devices, in which a charge injection layer is sandwiched between cathode and the emissive polymer [7]. This layer serves three purposes: (a) charge carrier injection is enhanced, (b) quenching of radiative recombination near the metal interface is avoided, and (c) balanced electron and hole injection is achieved. Yang and Pei [8] have reported the increase in the quantum efficiency of a device containing the emissive polymer poly(2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylenevinylene) by a factor of 40 using poly(phenylene-1,3,4-oxadiazole-phenylene-hexafluoro-isopropylidine) as an electron injection layer. Strukelj et al. [6] have also observed an increase in the efficiency of the devices using similar approach. Second approach employs a metal with low work function like calcium as cathode [9]. The disadvantage of this approach is that calcium is unstable in air, and also reaction may occur at the interface with the active luminescent layer. Though problems have been reduced by the approaches mentioned above, better polymer LEDs were developed by intrinsically balancing the hole and electron injecting ability of the electroluminescent polymers. Polymers of this kind contain alternating p- and n-dopable segments in its backbone to adjust the energy of HOMOLUMO of the resulting polymers [10,11]. In this direction, Yu et al. [12,13] and Huang et al. [14] have synthesized polymers having oligothiophene as p-dopable blocks and di(1,3,4-oxadiazole) phenylene as n-dopable blocks. Reynolds and coworkers have used 3,4-ethylenedioxythiophene as an electron rich block and pyridine as an electron poor block [15]. 3,4-Ethylenedioxythiophene (EDOT) has low oxidation potential and the corresponding polymer (PEDOT) is thermally stable with low band gap and can be easily p-doped [16]. Therefore, PEDOT is an ideal candidate for p-dopable block. In this paper, we report on the synthesis and characterization of p- and n-dopable polymers where EDOT has been used as an electron rich
p-dope type segment and 1,3,4-oxadiazole as electron deficient n-type segment (Scheme 1).

2. Experimental

3,4-Alkylenedioxy-2,5-dicarbomethoxythiophene, 1 and 2, were synthesized as reported earlier [17]. Acetonitrile was dried and distilled over calcium hydride. N-methylpyrrolidone (NMP), tetrahydrofuran (THF), chloroform, and trifluoroacetic acid (TFA) were purchased from Aldrich and were used as received. Tetraethyl ammonium hexafluorophosphate (TEAHFP) was purchased from Fluka and was used without further purification. The electrochemical studies were carried out using EG&G PAR model M273 potentiostat/galvanostat. Cyclic voltamograms were recorded using glassy carbon button as working electrode, Pt wire as counter electrode. All potentials are reported with respect to Ag/AgCl reference electrode. UV-Vis spectra were recorded in Shimadzu UV 2100 spectrophotometer. Fluorescence spectra were recorded using JASCO V-530 spectrophotometer. Molecular weight of the polymers was determined by Merck LaChrom GPC instrument. Polystyrene standards were used with THF as eluant with polymer labs (PLGel 3 μ) mixed-bed column. Infrared spectra were recorded on Nicolet Impact 400 FTIR spectrometer. Solid compounds were recorded as thin KBr pellets. The 300 MHz 1H NMR spectra were recorded on VXR 300 NMR spectrometer using the TMS/solvent signal as internal reference. Analytical thin layer chromatography (TLC) was performed on glass plates coated with silica gel GF 254.

2.1. Synthesis of 3,4-alkylenedioxythiophene-2,5-dicarbonylhydrazone (3,4)

3,4-Alkylenedioxy-2,5-dicarbomethoxythiophene (0.5 g) was stirred at room temperature in 10 ml of hydrazine hydrate for 1 h. The reaction mixture was poured into excess of methanol and was refluxed for an additional 30 min to get product as white precipitate. The precipitates were filtered and washed with excess of petroleum ether. The product obtained was dried in oven to get white solid.

3,4-Ethylendioxythiophene-2,5-dicarbonylhydrazone (3): yield: 90%, mp: 228 °C (dec.). IR: 3289 and 1648 cm⁻¹.

3,4-Propylenedioxythiophene-2,5-dicarbonylhydrazone (4): yield: 92%, mp: 224 °C (dec.). IR: 3288 and 1646 cm⁻¹.

Elemental calculated for C₉H₁₃N₂O₃S (3): C, 37.21; H, 3.9; N, 21.69; S, 12.42. Found: C, 38.31; H, 3.77; N, 22.57; S, 12.29.

Elemental calculated for C₉H₁₃N₂O₃S (4): C, 39.7; H, 4.44; N, 20.58; S, 11.78. Found: C, 39.67; H, 4.22; N, 20.34; S, 11.73.

2.2. Synthesis of 3,4-ethylendioxythiophene-2,5-dicarboxylic acid (5)

A mixture of 3,4-ethylendioxy-2,5-dicarbomethoxythiophene (500 mg, 1.93 mmol) and 20 ml of 5% sodium hydroxide was refluxed for 8 h to get a clear solution. The solution was then cooled to room temperature and was acidified with concentrated H₂SO₄ (pH = 2), to get white precipitates. The precipitates were filtered, washed with water and dried in oven to get 0.267 g (yield 60%) of pure product. mp: 217 °C, 1H NMR (DMSO-d⁶) 4.2 (s, 4H), 13 (s, broad), IR: 2848.3 and 1680 cm⁻¹.

2.3. Synthesis of 3,4-ethylendioxythiophene-2,5-dicarboxylic acid chloride (6)

0.5 g of 3,4-ethylendioxythiophene-2,5-dicarboxylic acid (2.17 mmol) was refluxed with excess (15 ml) of thionyl
chloride for 4 h. Excess of thionyl chloride was distilled out from the reaction mixture and the residual green solid was dissolved in methylene chloride and was washed with water. The organic layer was passed through anhydrous sodium sulphate and the solvent was evaporated to get 0.522 g (yield 90%) of the product. $^1$H NMR (CDCl$_3$): 4.5 (s, 4H), IR: 1745 cm$^{-1}$.

2.4. Synthesis of terephthaloyl chloride (7)

Terephthalic acid (0.5 g, 3.01 mmol) was refluxed with excess (15 ml) of thionyl chloride until it formed a clear solution. The excess thionyl chloride was distilled out and the green mass obtained was dissolved in methylene chloride and was washed with water till it became neutral. The organic layer was passed through anhydrous sodium sulphate and then the solvent was evaporated to get 0.55 g (yield 90%) of pure compound. $^1$H NMR (CDCl$_3$): 8.0 (s, 4H).

2.5. General procedure for synthesis of polyhydrazides (8,9,10)

The mixture of appropriate dihydrazide (1 eq.), AlCl$_3$ (2 eq.), and pyridine (3 drops) were taken in NMP and to it 1 eq. of the appropriate diacid chloride was added at room temperature with stirring. The resulting mixture was further stirred at room temperature for 14–24 h. The yellowish mixture formed was heated at 80 °C for 24 h. The mixture was poured in water, centrifuged and washed repeatedly with water and finally with acetone before drying in oven to get the corresponding polyhydrazides in 60–80% yield.

8: Yield: 80%, IR: 1640, 1570, 1490, 1090 cm$^{-1}$. 9: Yield: 75%, IR: 1640, 1575 cm$^{-1}$. 10: Yield: 60%, IR: 1640, 1600, 1570, 1480 cm$^{-1}$.

2.6. General procedure for the preparation of polyoxadiazoles (11,12,13)

The mixture of polyhydrazides and excess of POCI$_3$ was stirred at room temperature for half an hour. After the polyhydrazide got dispersed, the mixture was refluxed for 24 h and progress of the reaction was monitored by IR spectroscopy. After the completion of the reaction, the mixture was cooled to room temperature and was poured into excess of water. The resulting precipitates were centrifuged and washed with sufficient water followed by acetone to get the polymers in 70–80% yields after drying in vacuum oven.

11: $^1$H NMR: 4.6 (s), IR: 1700, 1640, 1500, 1460, 1085 cm$^{-1}$. 12: $^1$H NMR: 4.56 (s, 4H), 4.6 (s, 4H), 2.5 (s, 2H), IR: 1680, 1625, 1090, 1500, 1460 cm$^{-1}$. 13: $^1$H NMR: 8.1 (s, 4H), 4 (s, 4H), IR: 1700, 1600, 1630, 1090 cm$^{-1}$.

Mixture of CDCl$_3$ and trifluoroacetic acid was used as solvent to record NMR.

3. Results and discussion

3.1. Synthesis and characterization of polymers

The polymers were synthesized through precursor polymers of polyhydrazides, which were prepared by poly-condensation of dicarboxylchloride of 3,4-ethylene-dioxythiophene (EDOT) with EDOT dihydrazide and propylenedioxythiophene (ProDOT)-2,5-dihydrazone in NMP in presence of AlCl$_3$ and pyridine. Polyhydrazide 10 was prepared by condensation of terephthaloyl dichloride and EDOT dihydrazide. The dicarboxylchlorides and the dihydrazides were synthesized following the routes depicted in Scheme 1. For synthesis of EDOT-2,5-dicarboxylchloride, the diesters of EDOT and ProDOT were synthesized first, [17] and then were hydrolysed using 5% NaOH followed by reaction with SOCl$_2$. 1,4-Terphthaloylchloride was prepared by refluxing terphthalic acid with SOCl$_2$. The dihydrazides were obtained by the reactions of EDOT 2,5-diester and ProDOT 2,5-diester with excess of hydrazine monohydrate (Scheme 1). The polyhydrazides 8–10 were obtained as light-yellow powders. As observed for other polyhydrazides, these polyhydrazides are also insoluble in all organic solvents at ambient and at elevated temperatures [14]. As shown in Scheme 1, the polyhydrazides were converted to the final polymers 11–13 via a cyclodehydration reaction by refluxing in POCI$_3$, which was used both as a dehydrating reagent and as a solvent. The successful dehydrination was confirmed by FTIR spectra, in which absorption bands around 1570 cm$^{-1}$ (due to polyhydrazide linkage) disappeared and new peak around 1685 cm$^{-1}$ (due to the exocyclic double bond of the oxidized structure of polyoxadiazole) was observed. The FTIR characteristics of our polyhydrazides and polyoxadiazoles are different because the nature of the ring is different. We have the dialkoxythiophene rings in the backbone compared to that of the phenylene or the alklythiophene rings reported by other groups [13,14]. Since the dialkoxythiophene ring is more electron rich compared to the alklythiophene or phenylene ring, the IR frequencies will shift to the lower values for the acyl hydrazides and hence for the oxadiazoles also. Polymers 11, 12 and 13 were obtained as yellow, brown, and pale-yellow powders, respectively. All the polymers were partially soluble in both chloroform and THF. However, all the three polymers readily dissolved in chloroform with a little amount of trifluoroacetic acid (TFA) to give clear solutions. The chemical structure of the polymers was confirmed by $^1$H NMR. In the $^1$H NMR of 11, only one singlet peak was observed at 4.55 due to the $-OCH_2^-$ group on the EDOT ring. In case of 12, there were two signals, which are assigned to $-OCH_2^-$ proton on ProDOT ring (4.55 ppm) and the middle methylene of the $-OCH_2CH_2O^-$ group (2.6 ppm). Because the polymers are partially soluble in THF, only the molecular weight of the THF-soluble part of the polymers was measured by means of GPC using THF as eluant against polystyrene standards. The
molecular weights of the THF-soluble parts were measured as $M_n = 26,333$ (PD = 1.88) for 11, 53,561 (PD = 1.18) for 12 and 48,863 (PD = 1.27) for 13. The actual molecular weights of the polymers should be higher than these measured values because of the insolubility of the parts with higher molecular weights. Although the results cannot give accurate information on molecular weights of the polymers, they convince us of the polymeric structure of the obtained products. The elemental analysis results for the polymers were not within the acceptable range. This is because the polymers are insoluble and hence purification to remove the impurities or the trapped solvent was impossible even after vacuum drying. Thermogravimetric analysis (TGA) reveals good thermal stability of the polymer with starting temperature of decomposition of $\sim 330^\circ$C under nitrogen atmosphere. In order to observe glass transition temperature ($T_g$) of the polymers, thermal studies were done under nitrogen using DSC. The samples were heated up to 300 °C at a heating rate of 10 °C/min. No $T_g$ or melting point was observed. This indicates that the polymers are either having very high $T_g$ or are highly crystalline in nature and decompose before melting.

### 3.2. Optical properties

The absorption and fluorescence spectra of polymers 11–13 in chloroform and TFA mixture are shown in Fig. 1. The absorption maximum for 11 and 12 was observed at 339 nm whereas for 13, it was observed at 358 nm. It is worth noticing that the resolutions of a well-defined structure in the spectra are minimum in all the three polymers. This phenomenon implies that the polymers have a regular structure. As shown in Fig. 1, the emissive maxima are 476 nm for 11, 483 nm for 12 and 433 nm for 13 with well-defined sub peaks at 438 and 545 nm for 13. The Stokes shift determined to be 137 nm for 11, 144 nm for 12 and 75 nm for 13. The large difference between the spectral behaviors of two types of polymers (11, 12, based on alkynedioxythiophene and polymer 13, which is based on EDOT and 1,4-phenylene) may be attributed to the internal charge transfer along the backbone of polymers in the excited state. The overlapping of emission and absorption spectra of these polymers is very little, which indicates the reabsorption of the emitted light by the polymer is negligible. These results indicate that the polymers can be good light emitting materials. While our work was in progress, Ng et al. [18] have reported polymers having oxadiazoles and dialkoxymiophenes in the backbone. The stokes shift of the polymer reported here are comparable to their results.

### 3.3. Electrochemical properties

Thin films of the polymers were prepared by evaporating the THF solution of the polymers on glassy carbon (GC) button electrode to study the electrochemical behavior. Cyclic voltammograms were recorded after purging argon for 15 min in 0.1 M tetraethyl ammonium hexafluorophosphate (TEAHFP) in acetonitrile (Fig. 2). The polymers coated on GC button electrode were scanned anodically and cathodically in 0.1 M TEAHFP in acetonitrile. While sweeping anodically, polymer 11 showed an irreversible oxidation peak at $+1.75$ V, and in the cathodic sweep, it showed a reduction peak at $-1.5$ V and a reoxidation peak at $-1.5$ V. Polymer 12 showed an irreversible oxidation peak at $+1.5$ V on the anodic sweep. In cathodic sweep, two reduction peaks, at $-1.3$ and $-1.8$ V, and a reoxidation peak at $-1.5$ V were observed. Polymers 11 and 12 showed higher oxidation potentials compared to some of the other oxadizole polymers [11]. However, in the reverse sweep both the polymers showed reduction waves at lower potentials. The n-doping potential was even lower than that of 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadizole (PBD), the widely used electron-transporting material in PLEDs [11]. These results suggest that these polymers have a low LUMO and excellent hole-blocking properties [19]. Polymer 13 showed an oxidation peak at $+1.1$ V in the anodic sweep and a corresponding reduction peak at $+1$ V in the reverse sweep. There was a small reduction peak at $-1.95$ V. The lower oxidation potential and the corresponding reduction potential compared to some of the oxadizole polymers suggest that it can be a good hole transport layer in LEDs [20]. Band gap of these polymers, calculated both from the optical spectra as well as from the cyclic voltammograms,
Polymers 11 and 12 showed reversible n-doping at lower potential and 13 showed reversible p-doping at lower potential than other oxadiazole based conjugated polymers reported till date. Optical and electrochemical measurements revealed that the polymers 11 and 12 have low band gap and high stokes shift which indicates that these polymers are good electroluminescent materials. Work is in progress to improve the solubility of these polymers by connecting alkyl spacer on the EDOT rings.

Acknowledgements

We would like to thank MHRD India for financial help and RSIC Mumbai for instrumental facilities. Ojha thanks CSIR India for the research fellowship. We also thank Prof. P. Manisankar for electrochemical studies.

References


Table 1

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Absorption $\lambda_{\text{max}}$ (nm)</th>
<th>Emission $\lambda_{\text{max}}$ (nm)</th>
<th>Electrochemical band gap (eV)</th>
<th>Optical band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>339</td>
<td>476</td>
<td>2.6</td>
<td>2.6</td>
</tr>
<tr>
<td>12</td>
<td>339</td>
<td>483</td>
<td>2.4</td>
<td>2.7</td>
</tr>
<tr>
<td>13</td>
<td>258</td>
<td>433, 468, 545</td>
<td>2.9</td>
<td>2.9</td>
</tr>
</tbody>
</table>

were found to be comparable and the values are reported in Table 1.

4. Conclusions

We have synthesized p- and n-dopable copolymers consisting of 3,4-alkylenedioxythiophenes and oxadiazoles.