

# PPV-derivatives containing phenothiazine and alkyloxy-substituted oxadiazole/Phenyl units for OLED

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## Abstract

The heterocycle of phenothiazine unit was investigated as the backbone of organic light-emitting polymeric materials because of its strong luminescence, potential ability of anti-oxidation and p-type semiconductor properties. The dialdehyde and dibromo-substituted phenothiazines were synthesized successfully by Vilsmeier method and bromination respectively. The homo and co-polymers from phenothiazine and substituted oxadiazole were synthesized successfully. Their photo- and electroluminescent properties were investigated.

**Keywords:** Conducting polymers; Electroluminescence; Heterocycle synthesis

## 1. Introduction

Polymer light emitting diodes (PLED) have made unexpected dramatic progress in comparison to classical semiconductor light-emitting diodes over the past years<sup>[1,2]</sup>. The active layer of PLEDs is prepared using a simple coating-procedure, therefore these devices have the potential to provide an innovative low cost technology for backlighting, illumination, and display applications<sup>[3]</sup>. Conjugated polymers, with alternating single and double bonds which form a pi-pi\* extension in the molecular backbone, combine the optical and electrical properties with the mechanical advantages for preparation of optoelectronic devices. In order to have better performance, it is essential to develop novel structural polymeric materials with balanced transport of both injected electrons and holes.

In this study, new PPV-copolymers containing phenothiazine and different phenyl and/or diphenyl-1,3,4-oxadiazolyl units in the main chain were synthesized with the aim to balance the hole and electron injection. Known as fluorescent dyes, phenothiazine monomer can be easily tailored by connecting flexible groups to the N-position to improve solubility or varying the aromatic structure with functional groups for further polymerization. Diaryl-1,3,4-oxadiazolyl species are preferably and widely used as electron-transporting or hole-blocking units in polymers designed for electroluminescent devices<sup>[4]</sup>. In our previous work<sup>[5]</sup>, PPV-

type polymer containing oxadiazole units in the skeleton exhibited much better charge-injection balance than that of PPV material itself. In order to explore the

possibility of enhancing electron-injection in phenothiazine polymer more thoroughly, different functional monomers, such as phenyl, cyano-substituted phenyl, non-alkoxy-substituted 1,3,4-oxadiazolyl, and alkoxy-substituted 1,3,4-oxadiazolyl, were used to make the copolymers by multiple step reactions successfully. Finally, single layer devices with these copolymers were fabricated, and their electroluminescent properties were tested and compared.

## 2. Experimental Section

### 2.1 Reagents and Materials

All reagents were purchased from Aldrich or Fluka and used as received unless otherwise noted. Dimethyl sulfoxide was distilled from 4 Å molecular sieves.

### 2.2 Characterization

Nuclear magnetic resonance (NMR) spectra were collected on a Bruker ACF 300 spectrometer using chloroform-d as a solvent and tetramethylsilane (TMS) as an internal standard. Electron impact mass spectra were obtained from a Micromass VG7035F mass spectrometer using an ion current of 70 eV. Fourier transform infrared (FTIR) spectra were recorded on a Bio-Rad FTS 165 spectrometer by dispersing samples in KBr discs. Ultraviolet-visible (UV-

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vis) and fluorescence spectra were obtained using a Shimadzu UV 3101PC UV-vis-near infrared spectrophotometer and a Perkin-Elmer LS 50B luminescence spectrometer with a xenon lamp as light source, respectively. The HPLC system used was equipped with Phenogele MXL and MXM columns using polystyrene as standard and THF as eluant was employed.

### 2.3 Synthesis

2,5-bis(p-bromomethyl)phenyl-1,3,4-oxadiazole<sup>[6]</sup>, 2,5-bis[[p-(triphenylphosphonio)methyl]phenyl]-1,3,4-oxadiazole dibromide<sup>[7]</sup>, 2-methoxy-5-(2-ethylhexyloxy)-1,4-dicyanomethylbenzene and 2-methoxy-5-(2-ethylhexyloxy)-1,4-bis(diethyl ester phosphonato methyl)benzene<sup>[8]</sup> were prepared according to the procedures reported in the literature. Polymers of Poly[N-(2-ethylhexyl)-2,7(8)-phenothianinylenevinylene-co-alt-2-methoxyl-5-(2'-ethylhexyloxy)-(p-phenylenevinylene)] (**PH-P**), Poly[N-(2-ethylhexyl)-2,7(8)-phenothianinylenevinylene-co-alt-2-methoxyl-5-(2'-ethylhexyloxy)-(p-phenylene-1,1'-dicyanovinylene)] (**PH-P-CN**), and Poly{N-(2-ethylhexyl)-2,7(8)-phenothianinylenevinylene-co-alt-2,5-bis[2-octyloxy-(p-phenylenevinylene)-1,3,4-oxadiazole]} (**PH-OXA-C<sub>8</sub>**) were prepared according to the Wittig-Horner polycondensation. The detailed synthetic routes are illustrated in Figure 1.

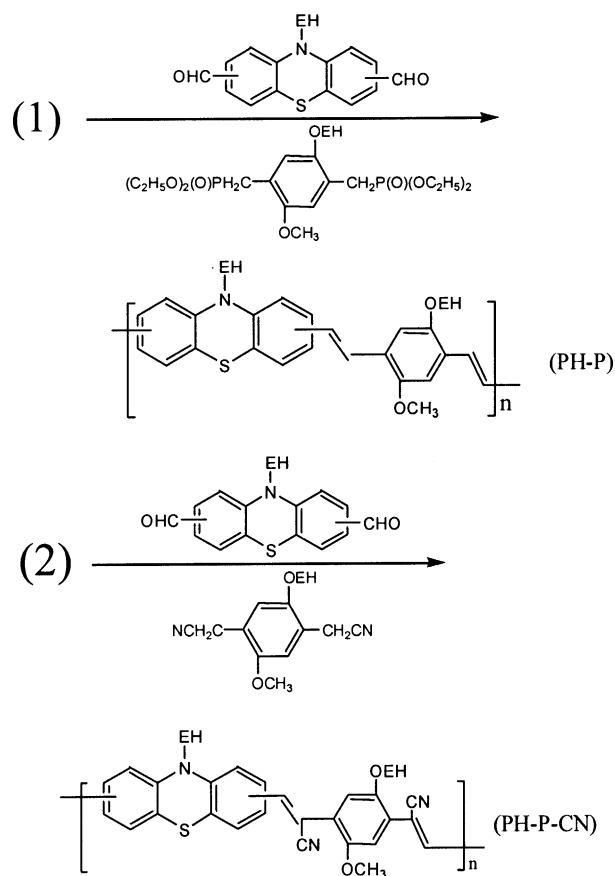
## 3. Results and Discussion

### 3.1 Synthesis of Monomers and Polymers

Phenothiazine is a fused six-membered heterocyclic ring exhibiting excellent antioxidant activities<sup>[9]</sup>. To render solubility of the phenothiazine containing polymers in common organic solvents, the branched and flexible group of 2-ethylhexyl was attached at the N-position. Then it was modified into dialdehyde by a Vilsmeier reaction. Experimental results showed that the Vilsmeier reagents (herein referred to as  $\text{Me}_2\text{N}=\text{CHCl}^+$ ) were readily deactivated after the monocarbonyl group was introduced into the phenothiazine ring due to its electron-withdrawing character under normal stoichiometry of  $\text{POCl}_3/\text{DMF}$ . With a large excess of  $\text{POCl}_3/\text{DMF}$  (~25 times) reagent and high reaction temperature (up to 160 °C), the diformylated product was synthesized successfully in a comparatively short reaction time (6h) and a good yield (~54 %). However, the proton resonance signals appearing at 7.02, 7.64 and 7.74 ppm from the heterocyclic ring made it very difficult to confirm the substitution position exactly, and the diformylated product is a mixture of 2,7- and 2,8-position substitution. Fortunately, this kind of unlocalized diformylation has little side effect on the later polycondensation because the linkage of copolymers was connected by condensing reaction with aldehyde groups directly.

The polymerization process was fast and straightforward under basic conditions. Polymers of PH-P, PH-P-CN, and PH-OXA-C<sub>8</sub> had excellent solubility in common organic

solvents, such as tetrahydrofuran, chloroform, and toluene. Gel permeation chromatography measurements (using polystyrene standards) gave molecular weight for PH-P ( $M_w = 17,549$ , PDI: 2.3), PH-P-CN ( $M_w = 5,480$ , PDI: 1.9), and PH-OXA-C<sub>8</sub> ( $M_w = 38,420$ , PDI: 3.0). All polymers showed excellent film-forming properties from chloroform solution. Measurement of thermal gravimetric analysis (TGA) showed that polymers of PH-P, PH-P-CN, and PH-OXA-C<sub>8</sub> are stable up to 350 °C, which is essential for improving performance of EL devices. The chemical shifts of the polymers at  $\delta$  6.80-6.90 ppm in the <sup>1</sup>HNMR spectra showed the vinylene protons with the exception of polymer PH-P-CN, in which the resonance peaks of the vinylene protons shifted to 9.80 ppm due to the strong electron-withdrawing effect of the cyano group. Moreover, the strong bend vibration (out of the plane) of C-H at about 957-960  $\text{cm}^{-1}$  (nearly no absorption at 690  $\text{cm}^{-1}$ ) showed totally *trans*-vinylene conformation in the polymers, as expected from a Wittig-Horner type condensation. Additionally, the elemental analysis data of the polymers are in good agreement with the expected polymeric structures.



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