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# Study of thermal conversion and patterning of a new soluble poly (*p*-phenylenevinylene) (PPV) precursor

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## Abstract

The investigation of conversion of new soluble poly(*p*-phenylenevinylene) (PPV) precursor and PPV patterns by irradiation with UV light of a film is reported. We obtained patterns by this method with well-defined edges and channel width up to 10 μm. Also, it was found that the PPV precursor polymer is a photoresist material. This allows the fabrication of PPV patterns, which can directly act as luminescent structures in organic light-emitting diodes (OLEDs). Using the atomic force microscopy (AFM) technique, investigations on the PPV thin films show that at 200 °C well-defined crystalline domains of PPV are detected, thus indicating the complete transformation of the precursor into the final polymer. The current–voltage characteristics of single and double PPV layer devices indicate that turn-on voltages around 9 and 8 V were recorded for double and single PPV layer devices, respectively. From the electroluminescence–voltage plot, an onset voltage at 10 V is detected for two PPV layers OLED. In addition, we investigate the optical, electrical and EL characteristics of pyrrolo[1,2-a][1,10]phenanthroline derivatives [Leontie L, Druta I, Danac R, Rusu GI. Synth Met 2005;155/1:138; Zugravescu I, Petrovanu M. 3 + 2 Dipolar cycloaddition. Bucharest: Roman Academic Publishing House; 1987 [in Romanian]; Druta I, Andrei M, Aburel P. Tetrahedron 1998;54:2107; Druta I, Dinica R, Bacu E, Humelnicu I. Tetrahedron 1998;54:10811; Dinica R, Druta I, Pettinari C. Synlett 2000;7:1013; Danac R, Rotaru A, Drochioiu G, Druta I. J Heterocyclic Chem 2003;40:283; Druta I, Danac R, Barbieru R, Tapu D, Andrei M. Sci Ann Al I Cuza Univ Iasi S Chem 2001;IX:149] as potential candidates for OLED applications. In this case, PPV was used as the hole-transport layer (HTL) and pyrrolo[1,2-a][1,10]phenanthroline derivatives, which were spin coated onto PPV, as the emissive layer. The structure of all PPV devices reported in this paper was fabricated using UV light for patterning.

*Keywords:* Poly(*p*-phenylenevinylene); Pyrrolo[1,2-*a*][1,10]phenanthroline derivatives; Patterning process; Organic light-emitting diode

## 1. Introduction

Polymers have attracted large interest due to their potential use as active material in electronic, optical and optoelectronic applications, such as light-emitting diodes, photodiodes, photovoltaic cells

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[1–7], field effect transistors and optically pumped lasers [8,9]. Their application, however, is inhibited at present by limitations in controlling luminescent spectra, sensitivity, efficiency and lifetime of devices. The main challenges posed by these polymers are the understanding of their electronic structure, the interplay between their chemical composition and morphology and their implementation in technological processes of device fabrication.

Poly(*p*-phenylenevinylene) (PPV) is the luminescent polymer used for the first polymer-based organic light-emitting diode (OLED), which operated successfully at low driving voltage [10,11]. Because PPV itself is not soluble, film preparation starts from a soluble precursor polymer, which is then transformed to PPV by heat treatment [12–15]. The most simple OLED structure consists of a thin organic sandwiched between two metallic or semiconducting electrodes. Such single-layer devices consist e.g. of PPV sandwiched between a transparent indium–tin-oxide (ITO) anode and a cathode made from evaporated aluminium, magnesium or calcium. The performance of PPV single-layer OLEDs is rather poor [16–23]. The reason for this is on the one hand unbalanced charge transport, which reduces the probability of exciton formation, and on the other hand exciton quenching near the electrode. To improve the performances of PPV-based OLEDs, the main idea is to use a host of electrically and/or optically active materials, usually either blended into the polymer film (blend structure) [23] or as an additional layer (heterostructure) [24–28]. Our work is focused on the direct photolithographic patterning of PPV by using a new precursor after the Brabec [36] and Vanderzende [12] route and on the investigation of single- and two-layer devices made of this type of PPV.

## 2. Results and discussions

### 2.1. Synthesis and thermal stability of PPV

### 2.1.1. Synthesis of PPV

The route of chemical synthesis of the PPV precursor according to Van Bremen et al. [12] and Brabec et al. [36] and the process of thermal conversion to PPV are schematically represented in Scheme 1. The synthesis was carried out by the method described by Vanderzende et al. [12] and Brabec et al. [36].

The PPV alkylsulphinyl precursor polymer was synthesised by polymerisation of 1-(chloromethyl)-4-[(*n*-octylsulphinyl)methyl]benzene [8]. *Step 1*: 1,4-Dichloroxylene reacts with tetrahydrothiophene to give 1,4-bis(tetrahydrothiopheniomethyl)xylene dichloride (**I**). *Step 2*: Compound **I** reacts with *n*-octanethiol to give 1-(chloromethyl)-4-[(*n*-octylsulphanyl)methyl]benzene **(II)**. *Step 3*: The oxidation of **II** by $H_2O_2/TeO_2$ yields 1-(chloromethyl)-4-[(*n*-octylsulphinyl)methyl]benzene **(III)**. *Step 4*: The polymerisation reaction is carried out with NaOtBu as a base to give the precursor polymer poly{[1,4-phenylene]-[1-(*n*-octylsulphinyl)ethylene]}(**IV**). *Step 5*: This polymer is dissolved in toluene and chloroform (1:1, v/v) and spin coated onto a quartz glass substrate, and then converted to PPV (**V**) by heating up to high temperatures in high vacuum for a certain time.

### 2.1.2. Thermal stability

The decomposition temperature of the PPV precursor was determined by thermogravimetric analysis (TGA). These results were generated by heating the PPV sample at a constant rate of 10 °C/min. Fig. 1 shows that first weight loss starts at 87 °C and is due to the evaporation or volatilisation of the solvent. At temperatures higher than 87 °C, it is shown in the curve that there is a severe overlap in weight losses, about 9.17%. The weight loss occurring at about 174 °C is due to thermal decomposition of the material.

### 2.2. Preparation and characterization of PPV thin films

### 2.2.1. Spin coating

PPV precursor films have been prepared by spin coating onto quartz substrates. The quartz substrates were previously cleaned according to a standard process and then dried in streaming $N_2$ [9]. Spin coating was carried out at a spinning speed of 2000 rpm and a spinning time of 60 s from a solution of 50 mg/ml in analytical grade toluene and chloroform (1:1 v/v).

### 2.2.2. Ellipsometry

The mean thickness and refractive index (*n*) of the films were determined by means of ellipsometry using a Plasmos SD2000 Automatic Ellipsometer operating at a wavelength of 632.8 nm. The measured different values of thickness and refractive index are shown in Table 1.