

## Photoluminescence and electroluminescence of mono- and dialkyl-substituted soluble polythiophenes

Luigi Angiolini<sup>1</sup>, Elisabetta Salatelli<sup>1</sup>, Alberto Bolognesi<sup>2\*</sup>, Chiara Botta<sup>2</sup>

<sup>1</sup> Dipartimento di Chimica Industriale e dei Materiali, Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy; Fax +39 051 2093687; [angiolin@ms.fci.unibo.it](mailto:angiolin@ms.fci.unibo.it)

<sup>2</sup> Istituto per lo Studio delle Macromolecole CNR, Via E. Bassini 15, 20133 Milano, Italy; Fax +39 02 2362946; [LB@ismac.cnr.it](mailto:LB@ismac.cnr.it)

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**Abstract:** We report a comparison between optical properties (photoluminescence and UV-Vis absorption) and electroluminescence in a series of soluble polyalkylthiophenes with the aim of better understanding the role of different structural parameters, *viz.* length of side chains and introduction of unsubstituted thiophenes and their position in the backbone, on the electro-optical properties. The potential of these polymers as material for an active film in a single layer light emitting diode is evaluated.

### Introduction

Substituted polythiophenes are interesting materials because of their optoelectronic properties. Structural modifications in this class of polymers, such as the length of side chains or the degree of regioregularity, are extremely important because they influence the packing in the solid state which is related, through band gap modulation, to the fine tuning of the electro-optical properties of these materials. E.g., the degree of order, which can be reached in the solid state through both a proper control of film preparation conditions and of the degree of regioregularity, has allowed to achieve a mobility as high as  $0.1 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$  with a poly(3-hexylthiophene) [1]. Many works [2-4] have shown how the kind of substituent on the thiophene ring can influence the band gap and the optical properties of these materials.

In the present paper we report a comparison between the optical properties (photoluminescence and UV-Vis absorption) and the electroluminescence in a series of soluble polyalkylthiophenes with the aim of better understanding the role of different structural parameters on the electro-optical properties and the potential of their use as an active film in a single layer light emitting diode.

### Results and discussion

The structures of the polymers here investigated are reported in Fig. 1. These derivatives are characterized by inherent regioregularity coupled with minimum steric interactions between the side chain alkyl groups. The polymethylene side chain, n-hexyl or n-dodecyl, affects the interchain distance, while the presence of one or two unsubstituted thiophene rings in adjacent positions in the backbone has an influence

on the band gap. These polymers have been already described in the literature: polymer P1E was fully characterized as far as spectroscopic, thermal, electrical, optical properties and crystallinity are concerned [5], the thermochromism of polymer P2E was assessed both in the solid state [6] and in solution [7] as well as its electronic absorption and fluorescence spectra in solution [8]. Chemical synthesis and molecular characterization of polymers P1D and P2D have also been reported [9] along with their electrochemical synthesis and characterization [10-13].

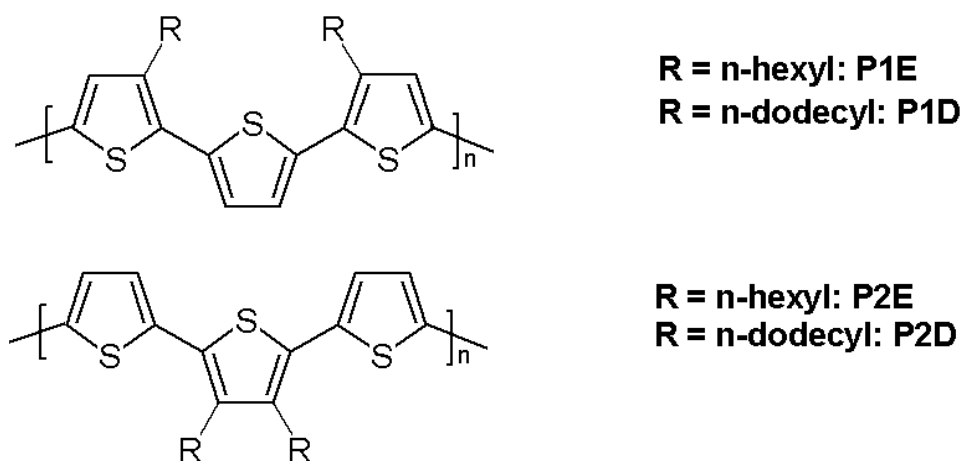


Fig. 1. Repeating units of investigated polymers

The thermal behaviour displayed by the polymeric samples, as determined by differential scanning calorimetry after one preliminary heating-cooling cycle, indicates the existence, upon heating, of several endothermic peaks related to side-chain and main-chain phase transitions. In particular, P1E exhibits a small second order signal around 53°C and multiple peaks at 159, 179, 187°C, in agreement with Zerbi's findings [5], the first one attributable to a glass transition related to side chain movements, and the others to melting followed by recrystallization of the macromolecules. No glass transition at -30°C, as reported by Zerbi, was observed. In contrast, P2E exhibits a more complicated pattern, with two glass transitions at -45 and -37°C in addition to the one at 39°C, ill defined peaks at 107, 137°C, and the melting peak at 201°C. A glass transition temperature of -46°C and a melting temperature of 250°C have been reported for this polymer [6].

Sample P1D, possessing a longer polymethylene side chain with respect to P1E, displays again a glass transition at 46°C and melting peaks at 114 and 123°C, whereas P2D exhibits only melting transitions at 165 and 174°C, and no visible glass transition.

The absorption spectra in solution of the four polymers are structureless and display maxima at about 450 nm, as reported in Tab. 1 for diluted CHCl<sub>3</sub> solutions. In Fig. 2 photoluminescence (PL) spectra of polymer solutions in tetrahydrofuran are reported. The spectra display similar maxima positions and spectral shape, showing only a small red shift for the two mono-substituted polymers with respect to the di-substituted ones. This small shift may indicate a less distorted backbone conformation in solution for the mono-substituted polymers. The PL spectra of solid state films (Fig. 3) appear red-shifted, with respect to the solutions, for all the polymers.

Tab. 1. Maxima of absorption spectra and PL spectra in diluted solutions (in nm)

	P1E	P2E	P1D	P2D
Absorption	465	446	462	459
PL	570	563	570	566

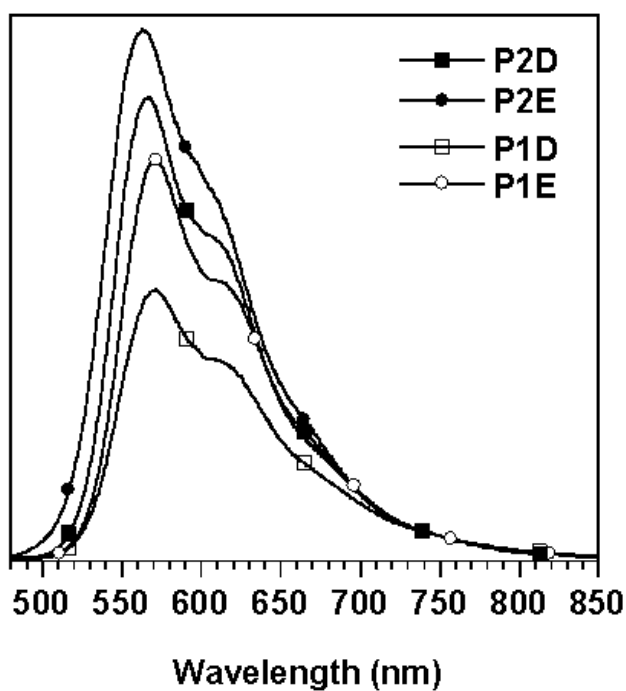


Fig. 2. PL spectra of diluted polymer solutions in tetrahydrofuran

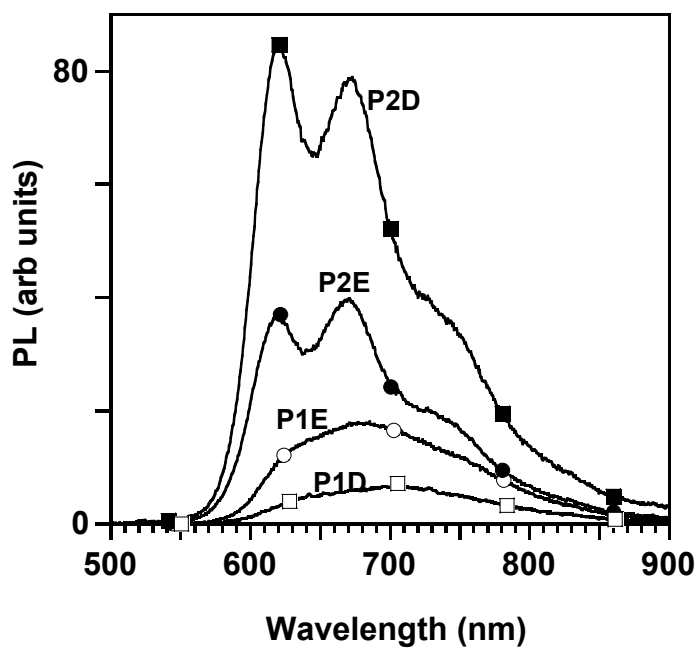


Fig. 3. PL spectra of thin films of the polymers

While for the di-substituted polymers the spectral structure typical of a vibronic progression is maintained in the solid state (probably superimposed to a weaker broad band in the longer wavelength region of the spectra), for the mono-substituted polyalkylthiophenes only a structureless band is observed. Similar low energy broad emissions have been observed for many conjugated polymers, generally displaying low PL intensity, associated to inter-chain excimer species [14].

In Tab. 2 we report the absolute photoluminescence quantum yields (PL QY) of the solutions, measured in diluted tetrahydrofuran solutions compared to quinine sulfate as a reference. The relative QY of the spin coated films are also reported, normalized to the P2D values, assumed as 1.

**Tab. 2.** PL QY in diluted solutions and spin coated films

	P1E	P2E	P1D	P2D
solution	44%	38%	35%	38%
film	0.26	0.5	0.1	1

The solid state PL intensity is higher for polymers showing minor contribution from excimer-like emission and displaying spectra with resolved vibronic progression. The different spectral shapes and PL intensities of the four polymers in the solid state suggest that the two di-substituted polymers (and in particular the one with longer alkyl chains, P2D) possess larger inter-chain distances thus reducing the related interactions in the solid state. In order to have a better understanding of the different PL behaviours of the four polymers in the solid state, we have taken into account the interchain distance as deduced from X-ray diffraction, reported in Tab. 3.

**Tab. 3.** Interchain spacing of the polymers under investigation as deduced from X-ray powder patterns

Polymer	P2D	P2E	P1D	P1E
Spacing in Å	32	19.4	20	13

For all polymers, no low-spacing peaks were found at high scattering angles, related to thiophene backbone stacking. The interchain spacing of P2D is found to be 32 Å. This polymer displays the highest PL intensity in solid state. It is worth mentioning that this distance depends on the side chain length. The interchain spacing of P2E is 19.4 Å and, accordingly, its PL QY in the solid state is half of that of P2D.

The different structural situation between P1E and P2E, as well as between P1D and P2D, can be attributed to the presence of two alkyl chains on the same monomeric unit. The steric interactions between these two chains on the same ring are strong so that the alkyl chains are forced to lay out of the thiophene plane, resulting in a more distorted situation in the backbone for the polymers with di-substituted monomers. The blue shift of the UV-Vis absorption spectra of P2E and P2D, with respect to P1E and P1D, is in agreement with these different backbone conformations. This different structural situation, with a higher degree of disorder for the di-substituted polymers

with respect to the mono-substituted ones, also fully agrees with the higher PL QY values for the former ones. In fact, while in solution the PL intensities are not very different for the four polymers, in the solid state the most distorted polymers exhibit stronger PL. We attribute this phenomenon to smaller interactions amongst the conjugated systems of adjacent polymeric chains for the di-substituted polymers, compared to the mono-substituted ones, which is, according to Cornil et al. [15], a factor increasing the PL QY.

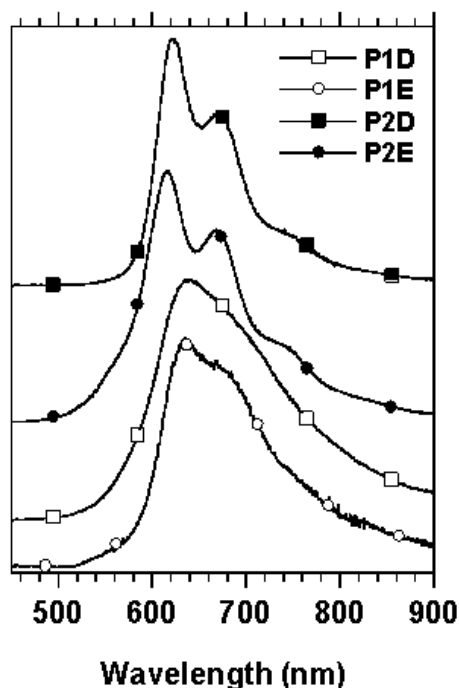


Fig. 4. EL spectra of the polymers

In Fig.4 we report the EL spectra of the four polymers, obtained with simple single layer structures. A similarity between PL and EL spectra is found only for polymers P2D and P2E, possessing very small contributions from excimer-like emission. P2D shows the highest EL external efficiency,  $10^{-2}$  % at 7 V (compared to  $10^{-3}$  % of the other ones) in agreement with its higher PL QY in the solid state.

In contrast, the EL spectra of P1E and P1D show a remarkable blue-shift with respect to PL. We think that this can be related to the fact that EL emission occurs mainly from the disordered component of the film, while PL emission has a strong excimer-like component from the better ordered component of the film. Moreover, we cannot rule out that a blue shift in the EL spectra can be induced by a disordering of these two polymers during device operation.

A typical I/V curve for a single layer device with P2D as an active film is reported in Fig. 5 together with the light intensity output. The EL efficiency measured for P2D is in the same range as that measured on LEDs having as an active layer a non-regio-regular poly(3-decylthiophene) film as deduced from ref. [16], and a poly(4,4'-decyl-2,2'-bithiophene) [17]. However, if compared to these devices the onset voltage for LEDs prepared with P2D seems to be lower, being 2.5 V for a 100 nm thick layer.

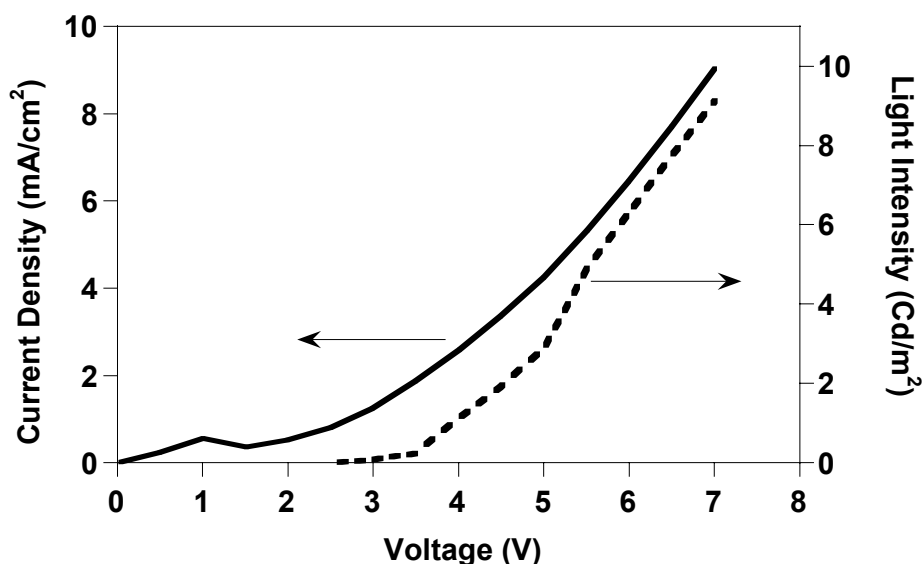


Fig. 5. I/V curve for polymer P2D; the plot of light output intensity against the voltage is also reported

### Experimental part

All the polymers were synthesized according to the method described in ref. [9], involving slight variations with respect to the previously reported procedures for P1E [18] and P2E [19]. In particular, the reaction was carried out in  $\text{CCl}_4$  solution (allowing to obtain an improved reaction yield as compared to chloroform), in the presence of anhydrous ferric chloride (4:1 mole ratio with respect to the monomer), with stirring at room temperature for 5 h and gentle nitrogen bubbling. After precipitation of the crude reaction product with methanol, followed by exhaustive (uncoloured extracts) Soxhlet extraction with methanol in order to de-dope the polymeric material and separate both the unreacted monomer and the oligomeric fraction, the residue was dried with acetone and then treated with  $\text{CHCl}_3$ . The chloroform-soluble fraction was finally used for the subsequent determinations. Yields in soluble polymeric products and average molecular weights of the products prepared are reported in ref. [9].

Differential scanning calorimetric measurements were carried out on a TA Instruments DSC 2920 Modulated apparatus at a heating rate of  $10^\circ\text{C}/\text{min}$  under nitrogen atmosphere on samples weighing 5 - 9 mg in the temperature range  $-150^\circ\text{C}$  to  $250^\circ\text{C}$ . Two heating-cooling cycles for each sample were performed.

Photoluminescence spectra were recorded with a SPEX 270M polychromator equipped with a liquid  $\text{N}_2$  cooled CCD detector. The sample was kept under inert atmosphere during EL measurements, and PL measurements were performed by exciting with an  $\text{Ar}^+$  ion laser. QY on films was obtained on spin coated films exhibiting the same optical density, and relative values are measured, while QY in solution was determined by taking quinine bisulfate solution as a reference [20]. The spectra were corrected for the spectral response of the instrument using a calibrated lamp. For electroluminescence measurements, a single layer light emitting diode was prepared. Baytron was spin coated on the top of ITO and the so obtained films were dried in a oven for 2 h at  $80^\circ\text{C}$ . The polymer film was prepared by spin coating from chloroform solution (10 mg/ml), onto the covered ITO at 2500 rpm. The aluminium cathode was evaporated in vacuum ( $3 \cdot 10^{-5}$  mm Hg) on the top of the polymer film.

The I/V plots were measured with a HP 34401A multimeter and a 6634AHP computer controlled power supply.

External EL efficiencies were evaluated by means of a calibrated silicon photodiode and a Keithley 487 Picoammeter. The external efficiency for P2D is  $10^{-2}$  Cd/A at 7 V, with a light output of 9 Cd/m<sup>2</sup> at the same voltage.

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